MATHEMATICAL METHODS FOR MOLECULAR SCIENCE
Mathematical Methods for Molecular Science

Version 2.0

John E. Straub

This work is licensed under a Creative Commons “Attribution-NonCommercial-ShareAlike 4.0 International” license.
To my parents, Jack and Maurine, and my family, Mary, Philip, and Joshua.
## CONTENTS

Introduction  xi  

1  Functions and coordinate systems  15  
   1.1  Survey of common functions of continuous variables  15  
   1.2  Exploring coordinate systems and their utility  22  
       A1  End-of-chapter problems  29  

2  Complex numbers and logarithms  31  
   2.1  Complex numbers and the complex plane  31  
   2.2  Special properties of logarithms  36  
       A2  Application of logarithms and the logarithmic scale  39  
       B2  Logarithms and Stirling’s approximation  40  
       C2  Connecting complex numbers and logarithms  41  
       D2  Visualizing complex functions of complex variables  42  
       E2  End-of-chapter problems  44  

3  Differentiation in one and many dimensions  47  
   3.1  Differentiating functions of one variable  47  
   3.2  Partial derivatives of functions of many variables  53  
   3.3  Infinitesimal change and the total differential  56  
       A3  Euler’s theorem for homogeneous functions  60  
       B3  Geometric interpretation of the total differential  61  
       C3  End-of-chapter problems  62  

4  Scalars, vectors, and vector algebra  67  
   4.1  Fundamental properties of scalars and vectors  67  
   4.2  Multiplication of vectors  71  
       A4  End-of-chapter problems  77  

5  Scalar and vector operators  81  
   5.1  Scalar operators  81  
   5.2  Differentiation of vector functions  84  
       A5  The force and the potential energy  90  
       B5  A survey of potential energy landscapes  91  
       C5  Explicit forms of vector operations  93  
       D5  Deriving explicit forms for vector operations  95  
       E5  End-of-chapter problems  103  

6  Extremizing functions of many variables  107  
   6.1  Extremizing functions of one and many variables  107  
   6.2  The method of Lagrange undetermined multipliers  109  
       A6  Variational calculation of the energy of a one electron atom  112  
       B6  Extremizing the multiplicity subject to constraints  115  
       C6  End-of-chapter problems  116  

7  Sequences, series, and expansions  121  
   7.1  Series, convergence, and limits  121  
   7.2  Power series  124  
   7.3  Expanding functions as Maclaurin and Taylor series  126  
       A7  Taylor series expansions of potential energy functions  132  
       B7  Useful approximations to functions based on power series  134  
       C7  Self-similarity and fractal structures  136  
       D7  End-of-chapter problems  139
## 8 Integration in one and many dimensions 145

### 8.1 Integrating functions of one variable 145

### 8.2 Integrating functions of many variables 155

- **A** An alternative to integration by parts for exponential integrals 160
- **B** Evaluating the definite integral of a gaussian function 162
- **C** An alternative to integration by parts for gaussian integrals 163
- **D** Properties of delta functions 163
- **E** End-of-chapter problems 166

## 9 Fundamentals of probability and statistics 171

### 9.1 Probability distributions of discrete variables 171

### 9.2 Probability distributions of continuous variables 178

### 9.3 Probability distributions in the physical sciences 187

- **A** Connecting the gaussian and binomial probability distributions 192
- **B** Uniform distributions of independent random variables 193
- **C** Gaussian distributions of independent random variables 195
- **D** Three definitions of Pythagorean means 196
- **E** Propagation of error through total differentials and Taylor series 196
- **F** End-of-chapter problems 199

## 10 Ordinary differential equations 205

### 10.1 First order ordinary differential equations 205

### 10.2 Applications of first order differential equations 209

- **A** Functions derived from exact differentials and integrating factors 215
- **B** End-of-chapter problems 217

## 11 More ordinary differential equations 221

### 11.1 Second order ordinary differential equations 221

### 11.2 Applications of second order differential equations 223

### 11.3 Power series solutions to differential equations 229

- **A** Quantum theory of a particle in a box 233
- **B** Classical theory of motion of a harmonic oscillator 235
- **C** Classical theory of a damped harmonic oscillator 238
- **D** Power series solutions to special equations in quantum theory 242
- **E** End-of-chapter problems 249

## 12 Partial differential equations 253

### 12.1 The classical heat equation 253

### 12.2 The classical diffusion equation 256

### 12.3 The classical wave equation 261

- **A** Survey of partial differential equations in the physical sciences 266
- **B** End-of-chapter problems 269

## 13 Fourier series, Fourier transforms, and harmonic analysis 275

### 13.1 Fourier series 275

### 13.2 Fourier transforms 291

- **A** Orthogonal vectors and orthogonal functions 300
- **B** End-of-chapter problems 305
14 Matrices and matrix algebra 313
   14.1 Vectors, matrices, and determinants 313
   14.2 Basic properties of matrix algebra 320
   14.3 Solving coupled linear equations using Cramer’s rule 332
       A14 Applications of determinants in Hückel theory 335
       B14 End-of-chapter problems 336
15 Eigenvalues and eigenvectors 343
   15.1 Matrix eigenvalues and eigenvectors 343
   15.2 Matrix methods for coupled differential equations 349
   15.3 Scalar operators and eigenfunctions 358
       A15 End-of-chapter problems 360
16 Geometric transforms and molecular symmetry 369
   16.1 Eigenvectors, geometric transforms, and symmetry 369
   16.2 Matrix transformations and molecular symmetry 375
   16.3 Point groups and the symmetry decision tree 381
       A16 End-of-chapter problems 388
Supplements 395
   S1 Notes on notation 395
   S2 Formulas from geometry 397
   S3 Formulas from trigonometry 399
   S4 Table of power series 401
   S5 Table of definite integrals 402
   S6 Table of indefinite integrals 403
   S7 Error function table 410
   S8 Complementary error function table 411
   S9 Table of Fourier transform pairs 412
Bibliography 413
Index 415
Colophon 419
Introduction

It is widely acknowledged that the traditional calculus sequence required of most molecular science majors, consisting of a year of differential and integral calculus and possibly a semester of multivariate calculus, does not provide the mathematical background needed for success in the quantum mechanics and statistical thermodynamics courses that follow. Mastery of key ideas in quantum mechanics requires knowledge of operators, differential equations, multidimensional integration, vector algebra, and functions of complex numbers. Statistical thermodynamics and kinetics require facility with partial differentiation, extremizing functions subject to constraints, and knowledge of differential equations. However, a treatment of these topics through specialized courses offered by mathematics departments is prohibitively time consuming for many molecular science majors in the fields of chemistry, biochemistry, biophysics, and materials science.

Mathematical Methods for Molecular Science is designed to support a one semester course that builds on the introductory calculus sequence and covers critical topics in multivariate calculus, ordinary and partial differential equations, and linear algebra.

Philosophy

Mathematicians are justly fond of abstract mathematical problems involving rather simple functions. In the physical sciences our challenges are typically quite different. We face concrete mathematical problems involving complicated functions with multiple variables and many physical constants. Solutions are found using standard algebraic operations that must be carefully applied. And without careful calculation, we are doomed!

These observations inform the approach taken by this text. The narrative and exercises in this text are focused solely on the mathematical functions and methods most relevant to physical science.

Examples demonstrate how complicated functions can be made manageable through the proper substitution of variables, simplifying expressions and facilitating problem solving.

The only way to develop mastery of mathematical methods is through devoted practice. Many exercises are provided so that we can practice, practice, and practice some more.

The text is designed to provide a concise narrative, examples worked in full detail, ample visualizations, and plenty of homework problems for practice-to-mastery of course concepts.

How to use this book

This text is written to serve a third semester course in calculus. While it assumes the student has had a thorough introduction to differential and integral calculus of functions of one-variable, it also provides a summary of key ideas from that subject with examples and exercises to test and consolidate the student’s knowledge.

CHAPTER NARRATIVES include qualitative conceptual discussions and quantitative exercises that are worked in full detail. The chapters are concise and should be read before lecture. Completely. The student should review each example and then repeat the exercise to verify that the example is well understood before moving on to the end-of-chapter exercises.
END-OF-CHAPTER EXERCISES are the heart of the text. They are divided into three classes.

Warm-ups explore the key ideas presented in each Chapter at a basic level. All warm-ups should be completed by all students.

Homework exercises can be assigned in part or in whole depending on the topics emphasized by the instructor.

Bonus problems explore advanced concepts introduced in the Complements and are highlighted by an *.

Sitting in front of a problem you cannot solve is psychologically challenging. Even painful. However, finding a solution to the problem brings both relief and reward. Learn to love the process and it will serve you well.8

VISUALIZATIONS are used throughout the text. More than 300 original figures explore mathematical concepts that can be challenging to learn through equations alone. A variety of graphics are offered, from line drawings to surfaces and volumes, vectors and vector fields, and even atoms and molecules (click this interactive 3D figure using Adobe Acrobat Reader).

The visualizations offer examples of how quantitative information can be effectively displayed and analyzed.9

CHAPTER COMPLEMENTS are used to introduce advanced topics. The main body of each Chapter presents the foundation of information on a particular topic. At the end of each Chapter, a set of Complements exploring advanced topics is included.10 Each complement is self-contained and understandable given the information provided in the main body of the Chapter. Complements may be assigned at the discretion of the instructor.

---

8 "I have really struggled through this course, but I have learned a ton."

9 "Explains concepts very well and draws out diagrams which helped me as a visual learner."

10 "Thank you for creating a text that I can trust to be succinct and teach me lessons beyond the scope of the course."
NARRATIVE ENRICHMENTS are included through two principal means. The main narrative is to be read and understood by all students. When there is brief additional detail that can enrich a discussion, it is included as a margin note that may be read or not depending on the interest of the student. In addition, historical notes are included to highlight the chronological development of the topic as well as the diverse backgrounds and interests of the individuals who have made seminal contributions to the subject.

SUPPLEMENTS at the end of the text include a compilation of mathematical symbols and constants, collections of geometric and trigonometric formulas, lists of power series, definite integrals, and indefinite integrals, and tables of error functions. Students will benefit from printing this material and using it as a valuable study resource.

Coauthors

I am grateful for the advice provided by a number of individuals who are effectively coauthors of this text. Joshua Straub contributed to the content and narrative of every topic. His advice helped establish the tone of the work and the emphasis on providing simple explanations and fully worked examples. Wei-Lun “Amy” Tsai 蔡瑋倫 reviewed the text and provided invaluable advice from the perspective of a former student of the course. Mi Kyung Lee 芮敏姬 assisted with typesetting and typography. In addition, I am indebted to the students I have had the pleasure to teach at Boston University from whom I have learned so much.

The selection of topics was informed by my experience with Applied Mathematics for Physical Chemistry by James Barrante as well as the advice and feedback of students and teaching fellows of CH225 Mathematical Methods for Chemists at Boston University. Certain end-of-chapter exercises were adapted from problems appearing in Barrante’s text as well as Mathematics for Physical Chemistry by Donald McQuarrie. Amy Hendrickson of TEXnology, Inc. served as a consultant and developed customized extensions that enhanced the processing of the \LaTeX source code.

I am grateful to the teachers and students that use this text. Suggestions for improvements are welcome. In addition, a reward of $3.14 will gratefully be paid to the first person to note any error, whether mathematical, historical, or typographical.

January 2019

Cambridge, Massachusetts

---

11 “The text is also VERY helpful and provides excellent supplemental material for homework and general curiosity.”

12 “This class has helped me actually enjoy math again!”


1 Functions and coordinate systems

1.1 Survey of common functions of continuous variables

There is a small set of functions that are commonly used to describe physical systems and their properties. These include polynomial functions (such as a line or parabola), exponential and logarithmic functions, trigonometric functions (such as sine and cosine), and the gaussian (a special case of the exponential function). In this section, we explore the general properties of the most commonly used functions of a single variable.

1.1.1 Linear functions and slope

A great deal of information is summarized in even the simplest graph. Consider the example of a linear equation

\[ y(x) = mx + b \]

where the function \( y(x) \) depends on the single variable \( x \) and two constants \( m \) and \( b \). We can plot the function \( y(x) \) as a function of \( x \) using the cartesian coordinate system.\(^1\) The value of the variable \( x \) is measured by the \( x \)-axis (the \( \text{abscissa} \)) and the value of the function \( y(x) \) is measured by the \( y \)-axis (the \( \text{ordinate} \)) as shown in Figure 1.1.

What can we learn from this graph? Each point on the \( xy \)-plane is defined by an \( \text{ordered pair} \ (x, y) \). At the point \( (x, y) = (0, -2) \) the red line crosses the \( y \)-axis. We call that point the \( y \)-\( \text{intercept} \). It defines the parameter \( b \) in Equation 1.1 since \( y(0) = b = -2 \). The point at which the red line crosses the \( x \)-axis is called the \( x \)-\( \text{intercept} \). At that point \( y(x) = 0 \) so that \( x = -b/m = -2 \). Since \( b = -2 \) we find the slope of the line \( m = -(-2)/1 = 2 \). Combining these results, the equation for the red line is

\[ y(x) = 2x - 2 \]

We can also determine the slope of the red line by calculating the \( \text{rise} \) of the function \( \Delta y = y(x_2) - y(x_1) \) divided by the \( \text{run} \) of the function \( \Delta x = x_2 - x_1 \). For the red line in Figure 1.1 we can use the two points \( (2, 2) \) and \( (3, 4) \) to find the slope as

\[ \text{slope} = \frac{\Delta y}{\Delta x} = \frac{y(x_2) - y(x_1)}{x_2 - x_1} = \frac{4 - 2}{3 - 2} = 2 \]

This definition of the slope is called a \( \text{finite difference} \) equation. It defines the slope in terms of a finite difference in the function \( \Delta y \) divided by a finite difference in the variable \( \Delta x \).

1.1.2 Quadratic functions and the quadratic formula

Now consider a quadratic equation

\[ y(x) = ax^2 + bx + c \]

where \( a, b \) and \( c \) are constants. Several examples are plotted in Figure 1.2. In each case, the curve takes the form of a \( \text{parabola} \), which may point upward or downward intercepting the \( x \)-axis twice (red curve), once (black curve) or not at all (blue curve).

\(^1\) As a plot can be worth a thousand words. And an equation can be worth a thousand plots.

\(^2\) Named for the French philosopher and mathematician René Descartes (1596-1650) who developed analytical geometry as a bridge between algebra and geometry.
By setting the equation equal to zero we have the quadratic equation
\[ y(x) = ax^2 + bx + c = 0 \]  
(1.3)
The values of \( x \) that satisfy the equation are defined by the quadratic formula\(^3\)
\[ x_{\pm} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]  
(1.4)
At the points \( x = x_+ \) and \( x = x_- \), the function \( y(x_{\pm}) = 0 \). As such, we call \( x_{\pm} \) the roots of the quadratic equation.

The argument of the square root \( b^2 - 4ac \) is known as the discriminant. Depending on the value of the discriminant the equation can yield two distinct real roots \( (b^2 - 4ac > 0, \text{red curve}) \), one real root \( (b^2 - 4ac = 0, \text{black curve}) \), or two complex roots \( (b^2 - 4ac < 0, \text{blue curve}) \).\(^4\) We will return to the quadratic formula again and again. Take it to heart.

### 1.1.3 Application of the quadratic formula

Solutions to the quadratic equation are important in the study of chemical equilibrium. Consider the unimolecular decomposition reaction

\[ \text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g) \]

with the equilibrium constant

\[ K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5} P_{\text{ref}}} \]

If there is an initial pressure of \( P_{\text{PCl}_5} \) of 1.0 atm and no \( P_{\text{PCl}_3} \) or \( P_{\text{Cl}_2} \), we can assign \( x = P_{\text{Cl}_2} = P_{\text{PCl}_3} \) and \( P_{\text{PCl}_5} = 1.0 - x \) so that

\[ K_p = \frac{(x)(x)}{1.0 - x} \]

This is a quadratic equation that can also be expressed in the form

\[ x^2 + K_p x - K_p = 0 \]

The roots of this equation provide the pressures of the gases at equilibrium

\[ x = P_{\text{Cl}_2} = P_{\text{PCl}_3} = \frac{1}{2} K_p \left[ 1 + \sqrt{1 + 4/K_p} \right] \]

and \( P_{\text{PCl}_5} = 1.0 - x \).
Note that while the quadratic equation has two solutions, only one is physically meaningful. We ignore the second root of the quadratic equation as the predicted pressures would be negative and therefore would not represent a physically meaningful solution.

### 1.1.4 Polynomial functions of varying degrees

We have examined linear and quadratic functions. They are special cases of a more general function called a polynomial and written

$$y(x) = a_n x^n + a_{n-1} x^{n-1} + \ldots + a_2 x^2 + a_1 x + a_0$$  \hspace{1em} (1.5)

where the $a_n, a_{n-1}, \ldots, a_1, a_0$ are constant coefficients. The highest power $n$ is called the degree of the polynomial. So a linear function is degree 1 polynomial, a quadratic function is a degree 2 polynomial and so on. A few examples are shown in Figure 1.3.

![Figure 1.3: Polynomial functions of varying orders, including linear (black), quadratic (red), cubic (gray) and quartic double well (blue) functions. Function zeros are marked with dots.](image)

Let’s derive an equation for the linear function plotted in Figure 1.3 in the form of Equation 1.1. The $y$-intercept is found at $y(0) = 2$. The slope can be determined from the points $(3, 8)$ and the $x$-intercept $(-1, 0)$ using the finite difference equation

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{y(x + \Delta x) - y(x)}{\Delta x} = \frac{8 - 0}{3 - (-1)} = 2$$

From that information, we know that the equation describing the line is given by

$$y(x) = 2x + 2$$

The parabola in Figure 1.3 is described by the quadratic function having a minimum at $x = 1$. As such, we can express the quadratic function as

$$y(x) = a_2 (x - 1)^2 = a_2 \left(x^2 - 2x + 1\right)$$

where the minimum occurs at $x = 1$. We can determine the constant coefficient $a_2$ by noting that the parabola passes though the points $(0, 4)$ and $(2, 4)$ where $y(0) = y(2) = a_2 = 4$. Our final equation for the parabola is

$$y(x) = 4(x - 1)^2$$

with its minimum at $x = 1$ where $y'(1) = 0$ and curvature $y''(1) = 8$.  

\footnote{This compact form of the quadratic equation is called completing the square.}
1.1.5 Odd and even symmetry of polynomial and sinusoidal functions

Consider the cubic polynomial function

\[ y(x) = -x^3 \]

shown in Figure 1.3 (gray line). This cubic equation is an odd function of \( x \) since \( y(-x) = -y(x) \). Another odd function of \( x \) is \( \sin(-x) = -\sin(x) \). Also note that the cubic equation is unbounded.

The final polynomial shown in Figure 1.3 (in blue) is a quartic double well function that is very useful in modeling various physical processes. The form of the function is

\[ y(x) = x^4 - 2x^2 + 1 = (x^2 - 1)^2 \]  \hspace{1cm} (1.6)

The curvature of the function at its minimum located at \( x = 1 \) is 8. That fact explains the close agreement between the quartic double well function (blue line) and inverted parabolic function (red line) near the zero located at \( x = 1 \) (black dot). Note that the quartic double well is an even function of \( x \) since \( y(-x) = y(x) \). Another even function of \( x \) is \( \cos(-x) = \cos(x) \).

1.1.6 Tips for drawing functions by hand... and its value

If you want to become familiar with the form and properties of a function, draw it by hand. To plot a function \( y(x) \) you must consciously consider the range of the variable \( x \) and the associated range of the function \( y(x) \). Is the function defined over a limited domain of values of \( x \) or over the whole real line? Is the function bounded from above or below by a finite constant or it is unbounded diverging to infinity? Is the function continuous or does it have discontinuities?

Even for a rough plot, it is helpful to know the exact value of the function for at least one point. You also need to know how the function behaves near that point, if it is increasing or decreasing, or if its curvature is positive or negative. It is also helpful to know how the function behaves asymptotically as it may converge to a constant, oscillate, or diverge to infinity.

With relatively little information about the function, you can develop a graphical representation that captures essential properties of the function's behavior that can be of real value in problem solving. Make it a habit to sketch your functions when you are solving a problem. Ask if your function captures the most essential properties qualitatively, such as the number of zeros, slope and curvature, in terms of the function's general behavior, and quantitatively, in terms of specific values of the function. We will find that as problems become increasingly complicated being able to define the qualitative features of the solution can be an essential step in finding the quantitative solution to the problem.

1.1.7 Exponential functions describing growth and decay

A function widely used in describing physical processes is the exponential function

\[ y(x) = e^x = \exp(x) \]  \hspace{1cm} (1.7)

where the constant \( e \) is approximately \( e = 2.718 \). In modeling physical processes, the exponential function can represent exponential growth. Since \( e > 1 \), the function \( y(x) = e^x \) increases with increasing \( x \). The exponential function can also be used to represent exponential decay as

\[ y(x) = e^{-x} = \frac{1}{e^x} = \exp(-x) \]

Figure 1.4: Lines define functions \( y(x) = \exp(x) \) (black) and \( y(x) = \exp(-x) \) (red) over a range of \( x \). Note that \( e^x \) is the image of \( e^{-x} \) reflected across the vertical line \( x = 0 \) (gray line).

The mathematical constant \( e \) was first estimated to be \( 2 < e < 3 \) by Swiss mathematician Jacob Bernoulli (1655-1705). Today \( e \) is commonly known as Euler’s constant.
Since \( e^x \) is an increasing function of \( x \), \( e^{-x} \) decreases as \( x \) increases (see Figure 1.4).

Consider what we need to know to draw \( y(x) = e^x \). When \( x = 0 \) the function \( y(0) = e^0 = 1 \). That gives us one point to draw at \((x, y) = (0, 1)\).\(^7\) As \( x \) increases the function grows and as \( x \to \infty \) the function approaches \( \infty \). As \( x \) becomes more negative the function diminishes and as \( x \to -\infty \) the function decreases to 0. That is enough information to draw a rough graph of \( y(x) = e^x \). In addition, once we can draw \( y(x) = e^x \) we can draw \( y(x) = e^{-x} \) by symmetry (see Figure 1.4).

1.1.8 Logarithm as the anti-exponential

Another function commonly used to model physical systems is the logarithmic function. Let’s explore the natural logarithm \( y(x) = \ln(x) \) defined as the inverse of the exponential function

\[
\ln(\exp(x)) = \exp(\ln(x)) = x
\]

This property of the logarithm as the anti-exponential is shown in Figure 1.5. The natural logarithm \( \ln(x) \) is the reflection of the exponential \( e^x \) across the diagonal defined by \( y(x) = x \).

If a function \( y(x) = \exp(-1/x) \) then the natural logarithm of the function is

\[
\ln(y(x)) = \ln\left(e^{-1/x}\right) = -\frac{1}{x}
\]

Using the logarithm, we can convert an exponential function into an algebraic function. We will explore many useful properties of logarithms in Chapter 2.

1.1.9 Application of logarithms in visualizing exponential functions

Consider the exponential function used to model dependence of the vapor pressure above a liquid on the temperature \( T \)

\[
p(T) = A \exp\left(-\frac{\Delta H}{RT}\right)
\]

where the argument of the exponential function, \( \Delta H/RT \), must be a dimensionless number. A plot of \( p(T) \) as a function of \( T \) is shown as the black line in Figure 1.6. Note that \( p(T) \) remains very small for small values of \( T \) and then rapidly increases.

As \( p(T) \) is an exponential function of \( 1/T \), the logarithm of \( p(T) \) will be an
algebraic function of $T$ where

$$\ln[p(T)] = \ln A - \frac{\Delta H}{RT}$$  \hspace{1cm} (1.9)

where we have used the property of the natural logarithm that $\ln(xy) = \ln x + \ln y$. The result is also shown in Figure 1.6 (red line). Note that we can observe the behavior of $\ln[p(T)]$ (red line) over a much broader range of $T$.

The $x$-intercept of the function is located at the point $(T_0, 0)$ where

$$\ln[p(T_0)] = \ln A - \frac{\Delta H}{RT_0} = 0$$

Solving for $T_0$ we find

$$T_0 = \frac{\Delta H}{R \ln A}$$

as shown in Figure 1.7 (black dot).

Let’s explore one more way to plot $p(T)$. Suppose we plot $\ln[p(T)]$ as a function of $1/T$ rather than $T$. We find that $\ln[p(T)]$ is a linear function of $1/T$. The result is shown in Figure 1.7.

While $p(T)$ increases with increasing $T$, it decreases with increasing values of $1/T$. The same is true for the logarithm $\ln[p(T)]$ that decreases linearly as $1/T$ increases. We say that the function $p(T)$ is a log-linear function of the variable $1/T$ as it is a linear function on a semi-log plot (see Figure 1.7).

### 1.1.10 Sinusoidal functions have maxima, minima and zeros

Let’s explore plotting the trigonometric sine and cosine functions $\sin(2\pi x)$ and $\cos(\theta)$. Both functions are defined over the whole real line, oscillate with a fixed period, and are bounded between 1 and $-1$. We begin by plotting $\sin(2\pi x)$ as $x$ varies from 0 to 1. The sine function is periodic, repeating every $2\pi$ units of its argument. The argument of the function is $2\pi x$ so the period of oscillation is 1 as shown in Figure 1.8.

The plot identifies a local maximum and local minimum, shows the function’s initial slope, and marks and the function’s zeros that appear at values of $x$ satisfying

$$\sin(2\pi x) = 0$$

at $x = 0, \frac{1}{2}, 1$. These general properties can be easily read off of a plot of the function. Alternatively, those properties can helpful when drawing the function by hand.
Let’s use what we learned about the sine function to draw the cosine function over one period of oscillation. In the last example, we plotted \( \sin(2\pi x) \) over one period, which was the range \( x \in [0, 1] \). In this case we will plot \( \cos(\theta) \), where one period of oscillation will occur over the range \( \theta \in [0, 2\pi] \).

To get a rough idea of how the function \( \sin(2\pi x) \) will vary as a function of \( x \) we mark five points that include the initial and final values that are local maxima at \( (\theta, y(\theta)) = (0, 1) \) and \((2\pi, 1)\), the local minimum \((\pi, -1))\), and two zeros \((\pi/2, 0)\) and \((3\pi/2, 0)\). We can make a rough sketch of the function by connecting the five points by straight lines (red line).

For some approximations, the red line would be good enough. It exactly captures the function’s maxima, minima, zeros, and period of oscillation. For a more accurate representation, we can further improve this plot by adding information about the slope of the function. For example, at the minima and maxima the slope is zero. That means we should round off the sharp corners where the line passes through minima and maxima. The result is the gray line in Figure 1.9 representing a good approximation to the function \( \cos(\theta) \).

1.1.11 Compound functions and the exponentially damped sinusoid

Many physical processes are described mathematically in terms of a product of common functions referred to as a \textit{compound function}. An example is a cosine function multiplied by a decaying exponential that is called a \textit{damped cosine}

\[
f(t) = \exp(-t/\tau) \cos(2\pi vt) \tag{1.10}
\]

where the argument of the sinusoidal function, \(2\pi vt\), must be a dimensionless number. The behavior of this compound function \( f(t) \) is depicted in Figure 1.10.

To interpret the behavior of this function, it is helpful to think of the variable \( t \) as time. The cosine function oscillates with a frequency \( \nu \) and corresponding period

\[
T = \frac{1}{\nu}
\]

In a time \( t \) the cosine undergoes \( t/T = vt \) oscillations. The higher the frequency \( \nu \) the shorter the period \( T \). The oscillations of the cosine are bounded by a maximum of 1 and a minimum of -1. The exponential has a decay time \( \tau \).

After a time \( \tau \) the exponential is \( 1/e \) of its initial value. Since the compound function \( f(t) \) is a product of the cosine and the exponential, it oscillates with a frequency \( \nu \) and an amplitude that decays exponentially in time.

When \( T/\tau \ll 1 \) the exponential will change very little during a period of oscillation. We say the oscillation is \textit{underdamped}. When \( T/\tau \gg 1 \) the

\[\text{overdamped}\]

\[\text{underdamped}\]

\[\text{min}\]

\[\text{max}\]

\[\text{slope}\]

\[\min\]

\[\max\]

\[\cos(\theta)\]

\[\cos(2\pi vt)\]

\[f(t)\]

\[e^{-t/\tau}\]

\[\cos(\theta)\]

\[f(t)\]

\[\cos(\theta)\]

\[\cos(2\pi vt)\]

\[\cos(\theta)\]

\[\cos(2\pi vt)\]

\[\cos(\theta)\]

\[\cos(2\pi vt)\]

\[\cos(\theta)\]

\[\cos(2\pi vt)\]
function oscillates little if at all. We say the oscillation is overdamped. Examples of underdamped and overdamped behavior are shown in Figure 1.11.

1.1.12 Gaussian functions and the bell curve

Another useful function in the physical sciences is the gaussian function\footnote{Named for the German mathematician Carl Friedrich Gauss (1777-1855).}, an exponential function with a quadratic argument

\[ p(x) = \exp \left( -\frac{1}{2\sigma^2} x^2 \right) \]  

(1.11)

The gaussian function has the shape of a bell curve and is used to form the normal distribution that appears throughout the physical and social sciences and can be used to describe everything from a distribution of course grades to the distribution of speeds of molecules in a gas.

Consider the gaussian function

\[ p(x) = \exp \left( -\frac{1}{4} (x - 3)^2 \right) = \exp \left( -\frac{1}{2\sigma^2} (x - x_0)^2 \right) \]

where the parameters \( x_0 = 3 \) and \( \sigma^2 = 2 \) (see Figure 1.12).

![Figure 1.12: The gaussian function \( p(x) = \exp(- (x - 3)^2/2\sigma^2) \) where \( \sigma = \sqrt{2} \) (red) is compared with the inverted parabola \( y(x) = 1 - (x - 3)^2/4 \) (black).](image)

This function has a single global maximum at \( x = x_0 = 3 \). The width is associated with the parameter \( \sigma = \sqrt{2} = 1.414 \). Asymptotically, the function approaches zero for large and small values of \( x \)

\[ \lim_{x \to \pm \infty} p(x) = 0 \]

We will return to the gaussian function again and again in modeling a variety of physical processes.

1.2 Exploring coordinate systems and their utility

A variety of coordinate systems may be used to represent and visualize the mathematical functions. A function that may be complicated in one set of coordinates appears simple in another. In this section, we explore the basic properties of commonly used coordinate systems including cartesian coordinates, plane polar coordinates, spherical polar coordinates, and cylindrical coordinates.

1.2.1 Two-dimensional cartesian coordinates

A point on the \( xy \)-plane can be represented as an ordered pair of cartesian coordinates \((x, y)\). We used the two-dimensional cartesian coordinate system
functions and coordinate systems

To represent a function \( y(x) \) where the abscissa defines the variable \( x \) and the ordinate the function \( y(x) \).

![Function Representation](image)

For functions of one variable, we represent an increment of length on the one-dimensional \( x \)-axis as \( dx \). In the same way, we can represent a two-dimensional increment of area corresponding to a small increment \( dx \) along the \( x \)-axis and a small increment \( dy \) along the \( y \)-axis. That area increment is represented as the small square \( dA = dx dy \) in Figure 1.13, reflecting the square symmetry of cartesian coordinates.

To get a better feeling for the square symmetry of the cartesian coordinate system, let’s draw a round circle on the two-dimensional cartesian plane. The equation for a circle can be written

\[ x^2 + y^2 = a^2 \]  

where \( a \) is a constant defining the radius of the circle. To plot this function, we can solve for \( y \) as a function of \( x \) as

\[ y(x) = \pm \sqrt{a^2 - x^2} \text{ for } x \in [-a,a] \]

Note that we need to restrict the range of \( x \) as it cannot be greater than the radius of our circle in the positive or negative direction. In addition, \( y(x) \) is not a single-valued function of \( x \). For every value of \( x \in (-a,a) \) there are two corresponding values of \( y \). For example, when \( x = 0 \) the equation can be satisfied by \( y = \pm a \). For that reason, there is a \( \pm \) in front of the radical.

The example of the unit circle where \( a = 1 \) is shown in Figure 1.14. In cartesian coordinates, the circle is defined by \( y(x) = \sqrt{a^2 - x^2} \) in quadrants I and II and \( y(x) = -\sqrt{a^2 - x^2} \) in quadrants III and IV. There is no single equation that describes the full unit circle in cartesian coordinates. The take home message is that a circle with round symmetry is not easy to describe using square cartesian coordinates.

### 1.2.2 Two-dimensional plane polar coordinates

Fortunately, there is a coordinate system in which round functions are easily expressed known as plane polar coordinates. In plane polar coordinates a point in the two-dimensional plane is defined in terms of its radial distance from the origin, \( r \), and the angle, \( \theta \), measured counter-clockwise from the \( x \)-axis to the line connecting the point to the origin (see Figure 1.15).
We can translate between the two representations using the equations

\[ x = r \cos \theta \]
\[ y = r \sin \theta \]  \hspace{1cm} (1.13)

or conversely

\[ r = \sqrt{x^2 + y^2} \]
\[ \theta = \arctan \left( \frac{y}{x} \right) = \tan^{-1} \left( \frac{y}{x} \right) \]  \hspace{1cm} (1.14)

The point \( x = r \cos \theta \) is the projection of \( r \) on the \( x \)-axis and \( y = r \sin \theta \) is the projection of \( r \) on the \( y \)-axis. A right triangle is formed by the triples \((0,0) - (r,\theta) - (x,0)\) or \((0,0) - (r,\theta) - (0,y)\) and by Pythagoras' theorem\(^\text{11}\)

\[ x^2 + y^2 = r^2 \cos^2 \theta + r^2 \sin^2 \theta = r^2 \]

By varying the radial distance \( r \in [0,\infty) \) and the angle \( \theta \in [0,2\pi) \), we can reach any point on the infinite two-dimensional plane. Just as we could identify a unique address for any point on the two-dimensional plane in cartesian coordinates as \( (x,y) \), we can represent any point uniquely in plane polar coordinates as the ordered pair \((r,\theta)\).

Note that some care needs to be taken in determining the angle \( \theta \) from the cartesian coordinates \( x \) and \( y \) since \( \tan^{-1}(y/x) \) is a multivalued function. Recall that \( \theta \in [0,2\pi) \). For the point \((x,y) = (1,1)\) we find \( \theta = \tan^{-1}(1) = \pi/4 \) as we expect. However, for \((x,y) = (-1,1)\) we expect \( \theta = 3\pi/4 \) but find that \( \tan^{-1}(-1) = -\pi/4 \). What gives?

It turns out it is not enough to determine the ratio \( y/x \) and its inverse tangent, we also need to consider the quadrant of the point \((x,y)\) on the \( xy \)-plane (see Figure 1.14). Take the point \((-1,1)\) in quadrant II for which \( \tan^{-1}(y/x) = \tan^{-1}(-1) = -\pi/4 \). We say \( \theta = \pi + \tan^{-1}(-1) = 3\pi/4 \). For the point \((-1,-1)\) in quadrant III we say \( \theta = \pi + \tan^{-1}(y/x) = 5\pi/4 \). And for the point \((1,-1)\) in quadrant IV we say \( \theta = 2\pi + \tan^{-1}(y/x) = 7\pi/4 \). The identities used to map the \( y/x \) to \( \theta \) for the four quadrants forming the \( xy \)-plain are summarized in Figure 1.16.

![Figure 1.16](image-url)

Figure 1.16: The value of \( \theta \) as a function of the ratio \( y/x \) (red line). The identity relating the coordinates \( x \) and \( y \) to the variable \( \theta \in [0,2\pi) \) depends on the multivalued inverse tangent \( \tan^{-1}(y/x) \).

What is the area element created by taking a small radial increment \( dr \) and small angular increment \( d\theta \)? The circumference of a circle of radius \( r \) is the length of an arc created by a change in angle of \( 2\pi \) equal to

\[ C = 2\pi r \]
The length of an arc created by a small change in angle $d\theta$ is $r d\theta$. It follows that the area element is the length of the arc $r d\theta$ times the increment in the radius $dr$ or

$$dA = r dr d\theta$$

(1.15)

That volume is shown as the small box in Figure 1.17.

You might say, "Wait a minute! You can’t just multiply the arc length $r d\theta$ by $dr$. The arc is not a straight line!" It turns out that we can as long as our increments $dr$ and $d\theta$ are infinitesimal increments in $r$ and $\theta$. An infinitesimal arc is essentially a straight line. As such, our estimate of the area element $dA = r dr d\theta$ will be accurate for infinitesimal $dr$ and $d\theta$.

Now let’s repeat the exercise of drawing a unit circle on the two-dimensional plane, but this time we will use plane polar coordinates. The equation for the circle of radius $a$ is simply

$$r = a$$

(1.16)

Since $\theta$ does not appear in this equation, the relation holds for all values of $\theta \in [0, 2\pi)$. The result is shown in Figure 1.18 (red circle). Shown for comparison is the unit circle with origin displaced along the $x$-axis (black circle). In cartesian coordinates this can be written

$$y(x) = \pm \sqrt{1 - (x - 1)^2} \text{ for } x \in [0, 2]$$

but in plane polar coordinates it is simply written $r = 2 \cos \theta$.

Note that we can also have a function of two variables $f(r, \theta)$ in two-dimensional plane polar coordinates. In general, plotting this function requires two dimensions to define the point $(r, \theta)$ and a third dimension to represent the value of the function $f(r, \theta)$ at that point.

### 1.2.3 Three-dimensional cartesian coordinates

Moving from two to three dimensions is a simple exercise in cartesian coordinates. Points in three-dimensional space are represented as an ordered triplet $(x, y, z)$. The corresponding volume element is a cube of volume

$$dV = dx dy dz$$

(1.17)

These definitions are represented in Figure 1.19.

A function of one variable $y(x)$ is conveniently plotted in two-dimensional cartesian coordinates. At each point $x$ the value of the function $y(x)$ is repre-
where \( z \) is the magnitude of the function as shown in Figure 1.20. Just as a function \( y(x) \) is represented as a one-dimensional line, a function \( z(x, y) \) is represented as a two-dimensional surface.

Note that we can also have a function of three variables \( f(x, y, z) \) in three-dimensional cartesian coordinates. In general, plotting this function requires three dimensions to define the point \( (x, y, z) \) and a fourth dimension to represent the value of the function \( f(x, y, z) \) at that point. As such, in graphically representing functions of three variables, we often constrain one variable to a constant or represent the surface defined by \( f(x, y, z) = \) constant.

### 1.2.4 Three-dimensional spherical polar coordinates

Some functions in three dimensions are most easily represented using spherical polar coordinates, an extension of plane polar coordinates to three dimensions. Any point in the infinite three-dimensional space can be uniquely defined in terms of the ordered triplet \((r, \theta, \varphi)\) where \( r \in [0, \infty) \) is the radial distance from the origin, \( \theta \in [0, \pi] \) is the angle between a line connecting the point to the origin and the \( z \)-axis, and \( \varphi \in [0, 2\pi] \) is the angle between the \( x \)-axis and a line connecting the origin to the projection of the point onto the \( xy \)-plane (see Figure 1.21).

We can translate between points in cartesian coordinates \((x, y, z)\) and spherical polar coordinates \((r, \theta, \varphi)\) using

\[
\begin{align*}
  x &= r \sin \theta \cos \varphi \\
  y &= r \sin \theta \sin \varphi \\
  z &= r \cos \theta 
\end{align*}
\]

or conversely

\[
\begin{align*}
  r &= \sqrt{x^2 + y^2 + z^2} \\
  \theta &= \arccos \left( \frac{z}{r} \right) = \cos^{-1} \left( \frac{z}{r} \right) \\
  \varphi &= \tan^{-1} \left( \frac{y}{x} \right)
\end{align*}
\]

Considering the right triangle formed by points \((0, 0, 0) - (r, \theta, \varphi) - (0, 0, z)\) we see that \( z = r \cos \theta \). The opposite side of that right triangle has length \( r \sin \theta \).

On the \( xy \)-plane we find two right triangles formed by the origin, the projection of the point \((r, \theta, \varphi)\) on the \( xy \)-plane, and the point \((x, 0, 0)\) or \((0, y, 0)\). From these two triangles, we recognize that \( x = r \sin \theta \cos \varphi \) and \( y = r \sin \theta \sin \varphi \) (see Figure 1.21).

What is the volume element created by taking a small radial increment \( dr \) and small angular increments \( d\theta \) and \( d\varphi \)? We note that as we increase \( r \), the length of an arc created by a change in \( \theta \) increases linearly with growing \( r \) as \( r d\theta \). Similarly, the length of an arc created by a change in \( \varphi \) is the arc’s radius \( r \sin \theta \) times the increment \( d\varphi \). The volume element is then given by the length
of the two angular arcs times the radial increment $dr$ or

$$dV = r^2 \sin \theta dr d\theta d\phi$$  \hfill (1.20)$$

That volume is shown as the small box in Figure 1.22.

Note that there is more than one convention for defining the angles $\theta$ and $\phi$. What we call $\theta$ mathematicians call $\phi$ and what we call $\phi$ mathematicians reasonably call $\theta$ as an extension of the definition of $\theta$ in two-dimensional plane polar coordinates (see Figure 1.15). For some reason, physical scientists use the opposite convention. We will use the physical scientist’s convention for $\theta$ and $\phi$ defined in Figure 1.21.

Just as a circle was simply represented in plane polar coordinates, a spherical surface is simply represented in spherical polar coordinates. A spherical shell of radius $a$ defined in cartesian coordinates is

$$x^2 + y^2 + z^2 = a^2$$  \hfill (1.21)$$

while in spherical polar coordinates the relation is simply $r = a$ with the implication that the set of points includes $r = a$ for all values of $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi)$.

Figure 1.23 provides an example of the two-dimensional spherical surface in three-dimensional space. This is an example of a three dimensional function $f(x,y,z) = x^2 + y^2 + z^2$ graphically represented as the surface defined by the function set to a constant

$$f(x,y,z) = a^2 = \text{constant}$$

1.2.5 Three-dimensional cylindrical coordinates

Another three-dimensional coordinate system that is useful in describing physical systems is cylindrical coordinates, in which the plane polar coordinates covering the $xy$-plane are extended linearly along the $z$-axis.

In cylindrical coordinates a point in space is uniquely defined in terms of the ordered triplet $(r, \theta, z)$ where $r \in [0, \infty)$, $\theta \in [0, 2\pi]$, and $z \in (-\infty, \infty)$ (see Figure 1.24). A point expressed in cartesian coordinates $(x,y,z)$ to cylindrical coordinates $(r, \theta, z)$ is

$$x = r \cos \theta$$

$$y = r \sin \theta$$

$$z = z$$  \hfill (1.22)$$
or conversely expressing \((r, \theta, z)\) in terms of \((x, y, z)\) we find

\[
\begin{align*}
  r & = \sqrt{x^2 + y^2} \\
  \theta & = \arctan \left( \frac{y}{x} \right) = \tan^{-1} \left( \frac{y}{x} \right) \\
  z & = z
\end{align*}
\]

As in plane polar coordinates, right triangles are formed by the triples \((0,0,0) - (r,\theta,0) - (x,0,0)\) and \((0,0,0) - (r,\theta,0) - (0,y,0)\). The point \(x = r \sin \theta\) is the projection of \(r\) on the \(x\)-axis and \(y = r \cos \theta\) is the projection of \(r\) on the \(y\)-axis (see Figure 1.24).

The volume element defined by a small radial increment \(dr\), small angular increment \(d\theta\), and small increment in height \(dz\) is simply the area increment \(rdrd\theta\) in the \(xy\)-plane times the height \(dz\) or

\[
\begin{align*}
  dV & = rdrd\theta dz
\end{align*}
\]

That volume element is shown as the small box in Figure 1.25.

Let’s consider a helical curve represented in cylindrical coordinates. For a helical curve of radius \(a\) and pitch \(1.0\) (so that one helical turn occurs every increment of \(1.0\) in \(z\)) we write

\[
\begin{align*}
  r & = a \\
  \theta & = 2\pi z
\end{align*}
\]

as shown in Figure 1.26.

Note that a parametric function can be used to define the unit circle. Defining a parameter \(t \in [0,1)\) the equations

\[
\begin{align*}
  x(t) & = \cos(2\pi t) \\
  y(t) & = \sin(2\pi t)
\end{align*}
\]

define a unit circle as shown in Figure 1.14. Using this parametric equation to define the unit circle, as \(t\) increases the unit circle is repeated with a frequency of 1.

Note that we can also express this helical curve in cartesian coordinates as

\[
\begin{align*}
  x & = x(z) = a \cos(2\pi z) \\
  y & = y(z) = a \sin(2\pi z)
\end{align*}
\]

In these equations, \(z\) is treated as a parameter. As \(z\) is varied the values of \(x\)
and \( y \) will also change. We say that the cartesian coordinates \( x \) and \( y \) depend \textit{parametrically} on the parameter \( z \). As \( z \in (-\infty, \infty) \) the equations describe an infinite helix traced on the surface of an infinitely tall cylinder of radius \( a \).

**A.1 End-of-chapter problems**

If I were again beginning my studies, I would follow the advice of Plato and start with mathematics.

---

**Warm-ups**

1.1 Determine the values of the cartesian coordinates \((x, y)\) for the following points expressed in terms of plane polar coordinates \((r, \theta)\).

(a) \( r = 4.65, \theta = 225^\circ \)  
(b) \( r = 4.00, \theta = 130^\circ \)  
(c) \( r = 3.00, \theta = 0^\circ \)

1.2 Determine the values of the plane polar coordinates \((r, \theta)\) for the following points expressed as \((x, y)\).

(a) \((0, 2)\)  
(b) \((-2, -2)\)  
(c) \((3, 0)\)

1.3 Determine the values of the spherical polar coordinates \((r, \theta, \varphi)\) for the following points expressed in three-dimensional cartesian coordinates \((x, y, z)\).

(a) \((0, 0, 2)\)  
(b) \((-2, 0, 1)\)  
(c) \((1, -2, -3)\)

1.4 We constructed the cylindrical coordinate system by extending a \( z \)-axis from the origin of a plane polar coordinate system perpendicular to the \( xy \)-plane. A point in this system is expressed as \((r, \theta, z)\). Derive the differential volume element \(dV\) for the cylindrical coordinate system.

1.5 Identify the roots of the following equations.

(a) \( 2(y - 2) = -6x \)  
(b) \( y = x^2 + x - 12 \)  
(c) \( y = \cos x \)

1.6 Plot the following functions in plane polar coordinates for \( \theta \in [0, 2\pi] \), noting that \( r \geq 0 \).

(a) \( r = 2 \)  
(b) \( r = \theta/36^\circ \)  
(c) \( r = 2 \cos \theta \)

1.7 Plot the following functions using the two-dimensional cartesian coordinate system. Select a range of the variable such that your plot displays the essential features of the function.

(a) \( y(x) = x^2 - x + 3 \)  
(b) \( p(V) = 8/V \)  
(c) \( C(t) = 3e^{-t} \)

1.8 Draw by hand the following functions over the specified range of \( x \).

(a) \( y(x) = -1 + 3x, -2 \leq x \leq 2 \)  
(b) \( y(x) = 2x^2 - 4x + 2, -1 \leq x \leq 3 \)  
(c) \( y(x) = x^3, -2 \leq x \leq 2 \)  
(d) \( y(x) = 3e^{-\frac{x}{3}}, 0 \leq x \leq 6 \)  
(e) \( y(x) = \ln(2x + 1), 0 < x \leq 10 \)  
(f) \( y(x) = 2e^{-\frac{x}{3}}, 0 < x \leq 10 \)  
(g) \( y(x) = \sin(x), -4\pi \leq x \leq 4\pi \)  
(h) \( y(x) = e^{-x} \cos(2\pi x), 0 \leq x \leq 3 \)  
(i) \( y(x) = e^{-(x-1)^2}, -2 \leq x \leq 4 \)

**Homework exercises**

1.9 Plot the following functions using the two-dimensional cartesian coordinate system. Select a range of the variable...
such that your plot displays the essential features of the function.

(a) \( V(r) = -2/r, r > 0 \)
(b) \( E(v) = \frac{1}{2}v^2, v \geq 0 \)
(c) \( F(r) = 1/r^2, r > 0 \)
(d) \( k_r(T) = e^{-1/T}, T \geq 0 \)
(e) \( A(t) = e^{-t}, t \geq 0 \)
(f) \( A(t) = \frac{1}{1+t}, t \geq 0 \)

1.10 Plot the functions in the previous problem, choosing the coordinates so that the resulting plot is a straight line. For example, plotting the function \( y = 1 - x^2 \) as a function of \( x^2 \) for \( x > 0 \) results in a straight line with an \( x \)-intercept at \( x = 1 \).

1.11 Plot the function \( f(x) = |x| - x \) over a range \(-4 \leq x \leq 4\). Determine if \( f(x) \) is a continuous function of \( x \).

1.12 Prove that the hyperbolic sine function

\[
\sinh(x) = \frac{e^x - e^{-x}}{2}
\]

is an odd function of \( x \) by demonstrating that \( \sinh(-x) = -\sinh(x) \). Further show that the hyperbolic cosine function

\[
\cosh(x) = \frac{e^x + e^{-x}}{2}
\]

is an even function of \( x \) by demonstrating that \( \cosh(-x) = \cosh(x) \).

1.13 Characterize each function as being an odd function of \( x \), an even function of \( x \), or neither even or odd.

(a) \( \tanh(x) \)
(b) \( e^x \sin(x) \)
(c) \( \frac{e^x}{(e^x + 1)^2} \)
(d) \( \cos(x) + \sin(x) \)

1.14* Consider the function

\[
f(x) = \frac{1}{1 - e^{-x}}
\]

Evaluate \( f(x) \) in the following one-sided limits (a) \( \lim_{x \to 0^+} f(x) \), in which \( x \) approaches 0 from above, and (b) \( \lim_{x \to 0^-} f(x) \), in which \( x \) approaches 0 from below.

1.15* The Heaviside step function is defined

\[
\theta(x) = \begin{cases} 
0 & x < 0 \\
1 & x \geq 0 
\end{cases}
\]

and shown in the figure below.

The function is characterized by the one-sided limits \( \lim_{x \to 0^+} \theta(x) = 1 \), in which \( x \) approaches 0 from above, and \( \lim_{x \to 0^-} \theta(x) = 0 \), in which \( x \) approaches 0 from below. Plot \( f(x) = \theta(x) - \theta(x - 1) \) over \(-1 < x < 2\).
2 Complex numbers and logarithms

2.1 Complex numbers and the complex plane

While complex numbers have imaginary components their occurrence and usefulness in modeling properties of physical systems are quite real. We encounter complex numbers in the classical mechanical theory of an oscillating mass on a spring and throughout the quantum mechanical theory of atoms and molecules. This section explores the properties of complex numbers, their algebra, and how they can be graphically represented on the complex plane.

2.1.1 Imaginary numbers, complex numbers and the complex plane

Consider the quadratic equation

\[ x^2 + 1 = 0 \]

with two roots at \( x_\pm = \pm \sqrt{-1} \). This equation confused mathematicians for hundreds of years, because no one could think of a number that could be squared to equal the negative number \(-1\). Solving this problem required the discovery of imaginary numbers.\(^1\)

Imaginary numbers are defined using the definition

\[ i = \sqrt{-1} \]  (2.1)

It follows that \( i^2 = -1 \) and that \((-i)(i) = (i)(-i) = 1\). If we multiply two real numbers, the result is real. If we multiply two imaginary numbers, the result is also real as \( i^2 = -1 \) is a real number. However, if we multiply a real number by an imaginary number, such as \( 3 \times 2i = 6i \), the result is imaginary.

Imaginary numbers can be combined with real numbers to create complex numbers, a number with a real part and an imaginary part.\(^2\) Any complex number can be written as

\[ z = x + iy \]  (2.2)

where the real part of the complex number \( z \) is \( \text{Re}(z) = x \) and the imaginary part of the complex number \( z \) is \( \text{Im}(z) = y \). In other words

\[ z = \text{Re}(z) + i \text{Im}(z) \]  (2.3)

We need two dimensions to represent a complex number graphically, one dimension to represent the real component and a second dimension to represent the imaginary component. This can be done on the complex plane (see Figure 2.1). The ordinate \( y \)-axis is used to represent the imaginary component of the complex number and the abscissa \( x \)-axis is used to represent the real part of the complex number.

\[ \begin{align*}
0 & \quad \text{Re}(z) \\
x & \quad \text{Im}(z)
\end{align*} \]

Figure 2.1: On the complex plane the \( x \)-axis is the real number line and the \( y \)-axis is the imaginary number line. A point on the two-dimensional complex plane \( z = x + iy \) has real \( (x) \) and imaginary \( (y) \) components.

\(^1\) We say discovery rather than invention. Just as no one invented gravity, mathematical truths exist in the space of possible ideas, waiting to be discovered.

\(^2\) Complex numbers were discovered by Italian mathematician, physicist, chemist, biologist, physician, philosopher and gambler Gerolamo Cardano (1501-1576) in his attempts to solve the cubic equation.
2.1.2 The magnitude of a complex number and the complex conjugate

What is the magnitude of a complex number? For a real number, the magnitude is the absolute value of the number computed as $|x| = \sqrt{x^2}$. The magnitude $|x|$ is the distance of the point $x$ from the origin $x = 0$ on the real axis. That definition works well if the number is positive, negative or zero.

Let’s apply that definition to a complex number $z = x + iy$. We find

$$\sqrt{z^2} = \sqrt{(x + iy)^2} = \sqrt{x^2 - y^2 + 2ixy}$$

but that is not the magnitude of $z$. The magnitude $|z|$ must be a real number as it is the distance of the point $z = x + iy$ from the origin on the complex plane defined $|z| = \sqrt{x^2 + y^2}$.

With this insight, we can define a general formula to compute the magnitude $|z|$. To do that, we introduce the complex conjugate of $z = x + iy$ written $z^* = x - iy$. To create the complex conjugate of $z$ we simply change the sign of the imaginary component. Why is this useful? Consider the product $(z^*)z = z^*z$ computed as

$$z^*z = (x - iy)(x + iy) = x^2 + y^2$$

We see that $z^*z$ is a real number equal to the square of the distance of the point $z$ from the origin on the complex plane (the length of the red arrow in Figure 2.1). We call this product the absolute value of $z$ written

$$|z| = \sqrt{z^*z} = \sqrt{x^2 + y^2} \quad (2.4)$$

Note that the complex conjugate has other interesting properties. For example, $z + z^* = 2x = 2\text{Re}(z)$ and $z - z^* = 2iy = 2i\text{Im}(z)$. These relationships are represented graphically in Figure 2.2.

2.1.3 An alternate view of the complex plane and Euler’s formula

We can use our definition of the magnitude of $z$ and knowledge of coordinate systems explored in Chapter 1 to find an alternative way to represent complex numbers. Suppose we think of the complex plane in terms of plane polar coordinates. The radial distance of the point $z$ from the origin is $r = |z| = \sqrt{x^2 + y^2}$ and the angle between the $x$-axis and the arrow connecting $z$ to the origin is $\theta$. Any complex number $z = x + iy$ can be represented as a point on the complex plane $(r, \theta)$ where $r \in [0, \infty)$ and $\theta \in [0, 2\pi)$ (see Figure 2.3).

Using our knowledge of the plane polar coordinate system and Equa-
With these definitions, we can express any complex number as

\[ x = \text{Re}(z) = r \cos \theta \]
\[ y = \text{Im}(z) = r \sin \theta \]

or conversely\(^3\)

\[ r = \sqrt{x^2 + y^2} \]
\[ \theta = \tan^{-1} \left( \frac{y}{x} \right) \]

With these definitions, we can express any complex number as

\[ z = x + iy = r \cos \theta + ir \sin \theta \quad (2.5) \]

Recall the power series representations of \( \cos \theta \)

\[ \cos \theta = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} + \ldots \]

and \( \sin \theta \)

\[ \sin \theta = \frac{\theta}{1!} - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} + \ldots \]

where \( n \text{ factorial} \) is defined \( n! = 1 \times 2 \times 3 \times \ldots \times (n - 1) \times n \).\(^4\) Using the properties of \( i \) we can rewrite these equations as

\[ \cos \theta = 1 + (i \theta)^2 \frac{\theta^2}{2!} + (i \theta)^4 \frac{\theta^4}{4!} + \ldots \]

and

\[ i \sin \theta = i \theta + (i \theta)^3 \frac{\theta^3}{3!} + (i \theta)^5 \frac{\theta^5}{5!} + \ldots \]

where we have used the fact that \( i^2 = -1, i^3 = -i, i^4 = 1 \) and so on. If we sum the two series we find

\[ \cos \theta + i \sin \theta = 1 + i \theta + \frac{(i \theta)^2}{2!} + \frac{(i \theta)^4}{4!} + \ldots \]

which is the power series of the exponential function \( \exp(i \theta) \).\(^5\) The result is the remarkable relation

\[ e^{i \theta} = \cos \theta + i \sin \theta \]

known as Euler’s formula.\(^6\)

What does this have to do with complex numbers? Returning to Equation 2.5 we find

\[ z = r \cos \theta + ir \sin \theta = r(\cos \theta + i \sin \theta) = re^{i \theta} \]

This result has great utility in the algebra of complex numbers.

2.1.4 Properties of Euler’s formula and Euler’s identity

The complex conjugate of \( z \) can be written using Euler’s formula as

\[ z^* = r \cos \theta - ir \sin \theta = re^{-i \theta} \]

Here we have used the fact that \( \cos \theta = \cos(-\theta) \) is an even function of \( \theta \) and \( \sin \theta = -\sin(-\theta) \) is an odd function of \( \theta \). Combining the last two relations we find the satisfying result that the magnitude of \( z \)\(^8\)

\[ |z| = \sqrt{z^* z} = \sqrt{(re^{-i \theta})(re^{i \theta})} = \sqrt{r^2} = r \]

3 The exact relation used to map the ratio \( y/x \) to \( \theta \) depends on the quadrant containing the point \((x, y)\). See the discussion surrounding Figure 1.16.

4 These power series representations of cosine and sine may be more readily recognized when written as \( \cos x = 1 - x^2/2! + x^4/4! - \ldots \) and \( \sin x = x - x^3/3! + x^5/5! - \ldots \).

5 The power series of \( \exp(x) = 1 + x + x^2/2! + x^3/3! + \ldots \).

6 Discovered by the Swiss mathematician, logician, physicist, astronomer and engineer Leonhard Euler (1707-1783).

7 An alternative proof of Euler’s formula goes as follows. Define a function \( f(t) = e^{-it} \). The derivative \( df(t)/dt = e^{-it}(-\sin t + i \cos t) - ie^{-it}(\cos t + i \sin t) = 0 \) demonstrating that \( f(t) \) is constant. Since \( f(0) = 1 \) it must be that \( f(t) = 1 \). Therefore \( e^{it} = \cos t + i \sin t \).

8 Here we make use of the identity \( \exp(x) \exp(y) = \exp(x + y) \).
Let’s explore other properties of Euler’s formula (see Figure 2.4). For the point \((x, y) = (1, 0)\) we find \(r = 1\) and \(\theta = 0\) so that
\[
z = 1 = \cos (0) + i \sin (0) = e^0
\]
for the point \((x, y) = (0, 1)\) we find \(r = 1\) and \(\theta = \pi/2\) so that
\[
z = i = \cos \left(\frac{\pi}{2}\right) + i \sin \left(\frac{\pi}{2}\right) = e^{i\pi/2}
\]
for the point \((x, y) = (-1, 0)\) we find \(r = 1\) and \(\theta = \pi\) so that
\[
z = -1 = \cos (\pi) + i \sin (\pi) = e^{i\pi}
\]
and for the point \((x, y) = (0, -1)\) we find \(r = 1\) and \(\theta = 3\pi/2\) so that
\[
z = -i = \cos \left(\frac{3\pi}{2}\right) + i \sin \left(\frac{3\pi}{2}\right) = e^{i3\pi/2}
\]
The result is the set of identities \(1 = e^0, i = e^{i\pi/2}, -1 = e^{i\pi}, -i = e^{i3\pi/2}\), and back to \(1 = e^{i2\pi}\).

Suppose we sum two complex numbers using the identity \(z = x + iy\) as
\[
z_1 + z_2 = (x_1 + iy_1) + (x_2 + iy_2) = (x_1 + x_2) + i(y_1 + y_2)
\]
The magnitude of the sum is \(|z_1 + z_2| = [(x_1 + x_2)^2 + (y_1 + y_2)^2]^{1/2}\). Now let’s repeat that sum using Euler’s formula \(z = re^{i\theta}\). We find
\[
z_1 + z_2 = r_1 e^{i\theta_1} + r_2 e^{i\theta_2}
\]
which is difficult to reduce to the simple form \(z_1 + z_2 = re^{i\theta}\). This demonstrates that Euler’s formula is not helpful when adding or subtracting complex numbers.

On the other hand, multiplying two complex numbers is easily performed using Euler’s formula where
\[
z_1z_2 = r_1e^{i\theta_1} \times r_2e^{i\theta_2} = (r_1r_2) \ e^{i(\theta_1+\theta_2)} = re^{i\theta}
\]
The point on the complex plane representing the product will be found a distance \(r = \sqrt{r_1r_2}\) from the origin, rotated through an angle \(\theta = \theta_1 + \theta_2\) counterclockwise from the \(x\)-axis.

Powers of complex numbers are also readily represented using Euler’s formula. Consider the square root of the complex number \(z = x + iy = re^{i\theta}\) written
\[
z^{1/2} = \left(re^{i\theta}\right)^{1/2} = r^{1/2}e^{i\theta/2}
\]
This idea can be extended to any power \( n \) using the identity
\[
    z^n = r^n e^{i n \theta}
\] (2.6)

Finally, let’s further consider the point \( z = -1 \) that can be represented by
\[ r = 1 \quad \text{and} \quad \theta = \pi \]
\[ e^{i \pi} = -1 \] (2.7)
This remarkable relation can also be written\(^9\)
\[ e^{i \pi} + 1 = 0 \] (2.8)
which is known as Euler’s identity.

2.1.5 *The origin of complex roots of polynomial equations*

In exploring polynomial equations and their zeros, we discussed how the quadratic formula, Equation 1.4, can yield roots that are real, imaginary or complex numbers depending on the particular values of the coefficients. Real zeros of a polynomial can be identified graphically as those points where \( y(x) = 0 \) and the quadratic function intersects the \( x \)-axis (see Figure 1.2). However, when the roots are complex numbers it is possible to satisfy the equation \( y(x) = 0 \), even though the function never intersects the \( x \)-axis on a plot of \( y(x) \) versus \( x \).

How can we visualize complex roots of polynomial equations? Let’s return to the quadratic equation
\[
y(x) = x^2 - 2x + 2 = 0
\] (2.9)
represented in Figure 1.2 (in blue). This parabola never intersects the \( x \)-axis, but the quadratic equation has two roots \( x_{\pm} = 1 \pm i \). These roots are complex numbers with real and imaginary parts (see Figure 2.5).

While we think of the variable \( x \) in this quadratic equation as a real number, the fact that we accept complex numbers as solutions to the equation \( y(x) = 0 \) reveals that \( x \) is actually complex. Let’s make this explicit by writing the same quadratic equation as \( f(z) = 0 \) where we substitute \( z = x + iy \) for \( x \). We find
\[
f(z) = z^2 - 2z + 2 = 0
\] (2.10)

If we expand this equation we see that
\[
f(z) = (x + iy)^2 - 2(x + iy) + 2
= x^2 - y^2 - 2x + 2 + i(2xy - 2y) = 0
\]
Just as the complex variable \( z \) must be plotted in two-dimensions to portray its real and imaginary parts, the complex function \( f(z) \) also has a real part
\[ \text{Re}[f(z)] = x^2 - y^2 - 2x + 2 \]
and an imaginary part
\[ \text{Im}[f(z)] = 2xy - 2y \]

If we evaluate \( f(z) \) at the complex roots \( z_{\pm} = 1 \pm i \) we find \( f(1 + i) = f(1 - i) = 0 \). This demonstrates that we can search for solutions to \( f(z) = 0 \) on the two-dimensional complex plane and those solutions will be equal to the roots provided by the quadratic formula at which \( \text{Re}[f] = \text{Im}[f] = 0 \).

The challenge of graphically representing the complex roots of a complex function is explored in the Complements.
2.2 Special properties of logarithms

The scales of physical properties including energy, length, and time vary over many orders of magnitude. The electromagnetic spectrum includes wavelengths ranging from x-rays ($10^{-10}$ meters) to visible light ($10^{-7}$ meters) to microwaves ($10^{-2}$ meters) to and radio waves ($10^0 = 1$ meter). That variation of wavelength over 10 orders of magnitude is challenging to visualize on a linear scale. The logarithmic function has special properties that are useful in analyzing and visualizing functions that vary over many orders of magnitude. The properties of logarithms are explored in this section.

2.2.1 The concept of base in logarithms

We have explored how the natural logarithm can be used to transform a rapidly varying exponential function to a slowly varying linear function (see Figure 1.5).\textsuperscript{10} That example demonstrated that the logarithm acts as the inverse of an exponential function.

Consider the exponential function

$$y(x) = a^x$$

that can be inverted using a logarithmic function as

$$\log_a[y(x)] = \log_a[a^x] = x$$

where $a$ is the base of the exponential and logarithm. The base should be greater than zero and not equal to one.

In the physical sciences, the most common bases are $a = e$ (base $e$ of the natural logarithm), $a = 10$ (base 10 of the common logarithm), and $a = 2$ (base 2 of the binary logarithm).\textsuperscript{11} Physical processes are often modeled using the exponential function making it common to use the natural logarithm (see Equation 1.9). In capturing the range of a function varying over many orders of magnitude, we often use the base 10 logarithm.\textsuperscript{12}

The binary, natural, and common logarithms are plotted in Figure 2.6. We can make a number of observations based on this plot. All logarithmic functions equal zero when $x = 1$, as $a^0 = 1$ for any base $a$. For bases $a > 1$ and $x > 1$, the logarithm increases faster when the base is smaller. However, for bases $a > 1$ and $x < 1$ the opposite is true. Finally, there is a reciprocal relationship between a logarithm of base $a$ and a logarithm of base $1/a$ as $\log_a(x) = -\log_{1/a}(x)$. This is demonstrated in Figure 2.6 for the case $a = 2$.\textsuperscript{13}

\textsuperscript{10} Logarithms were discovered by Scottish mathematician, physicist and astronomer John Napier (1550-1617).

\textsuperscript{11} Various notations are used. For natural logarithms, you might see $\ln(x) = \log_e(x)$. For common logarithms, you might see $\log_{10}(x) = \log(x)$.

\textsuperscript{12} As it is common to have 10 fingers, humans find it natural to count in base 10.

\textsuperscript{13} We note that $\log_2(x) = \log_2(x) \log_2(\frac{1}{2}) = -\log_2(x)$. We will further explore the algebra of logarithmic functions later in this section.
2.2.2 The algebra of logarithmic functions

The logarithm transforms the exponential function into a linear function of $x$ as
\[ \ln(e^x) = x \]

Suppose we have a function that is a product of exponentials
\[ 10^m10^n = 10^{m+n} \]

If we take the logarithm of this product using the common logarithm we find
\[ \log_{10}(10^m10^n) = \log_{10}(10^{m+n}) = m + n \]
\[ = \log_{10}(10^m) + \log_{10}(10^n) \]

We write this fundamental property of logarithms as
\[ \log(xy) = \log(x) + \log(y) \quad (2.11) \]

We define a similar relation for the logarithm of quotients. If we take the logarithm of a quotient using the natural logarithm we find
\[ \log_e \left( \frac{e^m}{e^n} \right) = \log_e (e^{m-n}) = m - n = \log_e (e^m) - \log_e (e^n) \]

We write this fundamental property of logarithms as
\[ \log(x/y) = \log(x) - \log(y) \quad (2.12) \]

Finally, if we take the logarithm of a number such as 2 raised to a power we find
\[ \log_2 \left( 2^{mk} \right) = \log_2 \left( 2^m \right) = mk = k \log_2 (2^n) \]

We write this fundamental property of logarithms as
\[ \log(x^k) = k \log(x) \quad (2.13) \]

Through these examples we see that logarithms can turn complicated multiplication and division into simple addition and subtraction.

2.2.3 How logarithms can be used to slow functions down

Let’s explore the numerics of the common logarithm by examining a logarithmic table (see Table 2.1). This table clearly demonstrates the power of a logarithm to slow a function down. The first two columns show that a million-fold variation in a function, from 0.001 to 1000, is captured by a change in the logarithm from -3 to 3.

<table>
<thead>
<tr>
<th>Base 10 Logarithms of Numbers and Exponentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3} = 0.001$</td>
</tr>
<tr>
<td>$10^{-2} = 0.01$</td>
</tr>
<tr>
<td>$10^{-1} = 0.1$</td>
</tr>
<tr>
<td>$10^0 = 1$</td>
</tr>
<tr>
<td>$10^1 = 10$</td>
</tr>
<tr>
<td>$10^2 = 100$</td>
</tr>
<tr>
<td>$10^3 = 1000$</td>
</tr>
<tr>
<td>$10^4 = 10000$</td>
</tr>
</tbody>
</table>

For base 10 logarithms we can express any number in terms of the mantissa, a number between 1 and 9.99, and a characteristic, a power of 10.\(^{14}\) For example,
using our table of logarithms we write
\[
\log_{10} (314) = \log_{10} \left( 3.14 \times 10^2 \right) = \log_{10} (3.14) \log_{10} \left( 10^2 \right) \\
= 0.497 + 2 = 2.497
\]

How many significant figures does the result 2.497 have? The characteristic 2 is simply the power of 10. The power is an exact integer and does not contribute to the number of significant figures. The mantissa 3.14 carries all the significant figures, which in this case is three. Those significant figures appear as \( \log_{10} (3.14) = 0.497 \).

2.2.4 The very special properties of the natural logarithm

Let’s explore the origin of the special properties of the natural logarithm. We can define the logarithm in terms of the equation

\[
\frac{\Delta \ln(x)}{\Delta x} = \frac{1}{x}
\]

(2.14)

Note that this expression can be recognized as the slope of the logarithm as

\[
\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\Delta \ln(x)}{\Delta x} = \frac{1}{x}
\]

Figure 2.7 shows the natural logarithm with the slope identified at three points \( x = \frac{1}{3}, 1, \text{and} 3 \) where \( \frac{1}{3} = 3, 1, \text{and} \frac{1}{3} \). We can rewrite Equation 2.14 as

\[
\Delta \ln(x) = \ln(x + \Delta x) - \ln(x) = \frac{\Delta x}{x}
\]

(2.15)

This is known as the finite difference estimate of the change in the function, \( \Delta \ln(x) = \ln(x + \Delta x) - \ln(x) \), resulting from a finite change in the variable, \( \Delta x \).

| Estimating Values of ln(x) Using Finite Differences |
|---------------------------------|---------|---------|---------|----|
| \( x \) | \( \Delta x = 3 \) | \( \Delta x = 1 \) | \( \Delta x = 0.5 \) | exact |
| 0.0 | -1.000 | -1.500 | -∞ | |
| 0.5 | 0.000 | -0.500 | -0.693 | |
| 1.0 | 0.000 | 0.000 | 0.000 | 0.000 |
| 1.5 | 0.500 | 0.405 | |
| 2.0 | 1.000 | 0.833 | 0.693 | |
| 2.5 | 1.083 | 0.916 | |
| 3.0 | 1.500 | 1.283 | 1.099 | |
| 3.5 | 1.450 | 1.233 | |
| 4.0 | 3.000 | 1.833 | 1.386 | |
| 4.5 | 1.718 | 1.504 | |
| 5.0 | 2.083 | 1.829 | 1.609 | |
| 5.5 | 1.929 | 1.705 | |
| 6.0 | 2.283 | 2.020 | 1.792 | |
| 6.5 | 2.103 | 1.872 | |
| 7.0 | 3.750 | 2.450 | 1.946 | |
| 7.5 | 2.252 | 2.015 | |
| 8.0 | 2.593 | 2.318 | 2.079 | |
| 8.5 | 2.381 | 2.140 | |
| 9.0 | 2.718 | 2.440 | 2.197 | |
| 9.5 | 2.495 | 2.251 | |
| 10.0 | 4.179 | 2.829 | 2.548 | 2.303 |

This estimator can be useful in plotting the function \( \ln(x) \). For example, if we know the value of \( \ln(x) \) at some point \( x \), we can estimate \( \ln(x + \Delta x) \) using
Equation 2.15 rewritten as the finite difference equation

$$\ln(x + \Delta x) = \ln(x) + \frac{\Delta x}{x} \tag{2.16}$$

As \(x\) grows larger, the incremental growth of \(\ln(x)\) diminishes as \(1/x\). This is the fundamental definition of the natural logarithm. Table 2.2 shows estimates of \(\ln(x)\) generated from an initial value of \(x = 1\) where \(\ln(1) = 0\) for three values of \(\Delta x\).

As \(\Delta x\) decreases, the estimator becomes increasingly accurate. However, as \(x\) approaches 0, the function \(\ln(x)\) approaches \(-\infty\). Our estimator does a better job of estimating \(\ln(x)\) for \(1 > x > 0\) than for \(0 > x > 0\). Figure 2.8 shows how the points generated by Equation 2.15 compare with the exact value of \(\ln(x)\).

### 2.2.5 Converting between logarithms of different bases

What is the relationship between \(\log_a(x)\) and \(\log_{10}(x)\)? For the function \(y(x) = e^x\) we know that \(\log_e y(x) = \log_e(e^x) = x\). Now consider

$$\log_{10} y(x) = \log_{10} e^x$$

We use the algebra of logarithms and Table 2.1 to find

$$\log_{10} e^x = x \log_{10} e = \ln y(x) \log_{10} e = 0.4343 \ln y(x)$$

which we can also write

$$\ln y(x) = 2.303 \log_{10} y(x)$$

This can also be written more generally as

$$\log_a(x) = \log_b(b) \log_b(x) \tag{2.17}$$

These relations demonstrate how we can convert between one base and another using logarithms.\(^{15}\)

---

A2 Application of logarithms and the logarithmic scale

For certain physical variables, the range of values varies over many orders of magnitude. Examples include the acidity of a solution, the strength of an earthquake, and the wavelength or frequency of light. In those cases, it is convenient to work with the logarithm of the variable and the logarithmic scales.

Consider the acidity of an aqueous solution measured in terms of the hydrogen ion concentration \([H^+]\) and its dimensionless activity \(a_{H^+} = [H^+] / 1\) M. An acidic solution may have \([H^+] = 10^{-2}\) M while a basic solution may have \([H^+] = 10^{-12}\) M, a difference of ten-billion-fold. To simplify the discussion of acidity, it is convenient to introduce the logarithmic \(pH\) scale defined as

$$pH = -\log_{10} (a_{H^+})$$

The acidic solution with \([H^+] = 10^{-2}\) M has \(pH = 2\) while the basic solution with \([H^+] = 10^{-12}\) M has \(pH = 12\). The exponential variation over many orders of magnitude in \([H^+]\) is reduced to a linear scale over a factor of 10 in \(pH\). The \(pH\) scale is shown graphically in Figure 2.9.

The optical transmittance, \(T\), of a solution is found to vary over many orders of magnitude. As such, it is convenient to define the optical absorbance, \(A\), of a
solution in terms of the logarithm of the transmittance

\[ A = -\log_{10} T \]

Similarly, the wavelength of light varies over many orders of magnitude (see Figure 2.10). Light of wavelength \(10^{-3}\) nm is an X-ray, light of wavelength \(10^3\) nm is in the visible spectrum, and light of wavelength \(10^{11}\) nm is a radio wave. This total variation in wavelength spans 14 orders of magnitude.

Length scales of objects are also found to vary over many orders of magnitude. Consider the variation in diameter of an atomic nucleus of \(10^{-15}\) m, an atom of \(10^{-10}\) m, a cell of \(10^{-6}\) m, an apple of \(10^{-1}\) m, the Earth of \(10^7\) m, the Milky Way galaxy of \(10^{21}\) m, and the known Universe of \(10^{26}\) m. There are 41 orders-of-magnitude variation in the size of these objects defining the shape and composition of our World.

**B2 Logarithms and Stirling’s approximation**

Consider the Boltzmann entropy formula

\[ S = k_B \ln W \]

where \(k_B\) is the Boltzmann constant and \(W\) is the number of states available to a system.\(^{16}\) Think of the number of states of the system as the number of ways to order the system. For example, suppose we have a deck of 52 unique cards. There are \(W = 52! = 52 \times 51 \times 50 \times \ldots \times 2 \times 1\) ways of arranging the deck of cards.\(^{17}\) In another example, suppose we lay \(N\) coins on a table. Each coin can show a head or a tail. There are \(W = 2^N\) ways of ordering the \(N\) coins. These simple examples demonstrate that the number of ways of ordering \(N\) objects in a system grows exponentially as \(N\) increases.

It can be very challenging to represent numbers as large as \(W = 52! \approx 8 \times 10^{67}\). When we consider the number of ways we can order \(N\) atoms and molecules with \(N = 6 \times 10^{23}\) we can forget about determining \(N!\) since it is much too large! Instead, we work directly with the logarithm \(\ln(N!)\).

\(^{16}\) Named for the Austrian physicist and philosopher Ludwig Boltzmann (1844-1906).

\(^{17}\) Here \(n!\) is defined \(n! = n \times (n-1) \times (n-2) \times \ldots \times 1\) and pronounced \(n\) factorial.
Let’s consider \( \ln(N!) \) where \( N \) is very large. We write
\[
\ln N! = \ln [1 \times 2 \times \ldots \times (N-1) \times N] = \ln 1 + \ln 2 + \ldots + \ln(N-1) + \ln N
\]
which we can express as the sum
\[
\ln N! = \sum_{n=1}^{N} \ln(n) \Delta n
\]
where \( \Delta n = 1 \). For very large \( N \), we can approximate this sum as an integral
\[
\ln N! \approx \int_{1}^{N} \ln(n) \, dn = [n \ln n - n]_{1}^{N} = N \ln N - N + 1
\]
(2.18)
This result is known as Stirling’s approximation. It provides a useful way to estimate logarithms of very large numbers such as those that appear in the physical sciences.

Let’s compute \( \ln(N!) \) where \( N = 6.02 \times 10^{23} \). If we first try to determine \( N! \), we will fail. It’s just too big! But if we directly estimate \( \ln(N!) \) we find
\[
\ln(6.02 \times 10^{23}) \approx (6.02 \times 10^{23}) \ln(6.02 \times 10^{23}) - 6.02 \times 10^{23} + 1
\]
\[
= 3.30 \times 10^{25} - 6.02 \times 10^{25} + 1
\]
\[
= 3.24 \times 10^{25}
\]
The dominant term is \( N \ln N \), with a small correction from \( -N \), and a negligible contribution from 1.

Note that we can alternatively write Stirling’s approximation as
\[
N! = e^{\ln N!} \approx e^{(N \ln N - N)} = e^{N \ln N} e^{-N}
\]
(2.19)
Using the properties of the exponential function we find
\[
e^{N \ln N} = \left(e^{\ln N}\right)^N = N^N
\]
Returning to Equation 2.19 we find
\[
N! = e^{\ln N!} \approx N^N e^{-N} = \left(\frac{N}{e}\right)^N
\]
This is another useful form of Stirling’s approximation.

C2 Connecting complex numbers and logarithms

Recall Euler’s formula for expressing a complex number
\[
z(r, \theta) = re^{i\theta}
\]
It follows that the logarithm of a complex number can be written
\[
\ln(z) = \ln(re^{i\theta}) = \ln(r) + i\theta
\]
Constant values of \( \ln(r) \) are circles on the \( xy \)-plane, while constant values of \( i\theta \) are radial lines (see Figure 2.11). This result demonstrates the intimate connection between the exponential Euler relation, logarithms and complex numbers.

Due to the fact that \( e^{i\theta} = e^{i(\theta + 2\pi n)} \) where \( n \) is an integer, \( \ln(z) \) is a periodic
function of $\theta$. As such, the logarithm of a complex number

$$w = \ln(r) + i\theta = \ln(r) + i\theta + i2\pi n$$

where $n$ is any integer. The complex logarithm is a multivalued function of $r$ and $\theta$. This property is shown graphically through the Riemann surface in Figure 2.11. To remove this ambiguity, in practice we restrict the value of $\theta$ to be $-\pi < \theta \leq \pi$.

Consider the following examples of $z$ and $\ln(z)$ pairings where each point is also marked in Figures 2.11 and 2.12. The logarithm of $z = 1$ where $r = 1$ and $\theta = 0$ is $\ln(1) = 0$, just as $e^0 = 1$ (black dot). For $z = -1$ where $r = 1$ and $\theta = \pi$ we find $\ln(-1) = i\pi$, just as $e^{i\pi} = -1$ (blue dot), while for $z = -0.1$ where $r = 0.1$ and $\theta = \pi$ we find $\ln(-0.1) = -2.30 + i\pi$ (green dot). Finally, for $z = -1 - i$ where $r = \sqrt{2}$ and $\theta = \frac{5\pi}{4}$ we find $\ln(-1 - i) = \ln(\sqrt{2}) + i\frac{5\pi}{4} = 0.346 - i\frac{3\pi}{4}$ as $-\pi < \theta \leq \pi$ (red dot). These examples demonstrate the fundamental properties of the complex logarithm.

**D2 Visualizing complex functions of complex variables**

How can we graphically represent the behavior of $f(z)$ as a function of $z = x + iy$? This is challenging because the complex function $f(z)$ is two dimensional, having independent real and imaginary components. So is the complex variable $z$. To plot the dependence of $x = \text{Re}(z)$, $y = \text{Im}(z)$, $\text{Re}[f(z)]$ and $\text{Im}[f(z)]$
requires a four-dimensional coordinate system, something beyond our ability to visualize.

While we can’t visualize \( f(z) \) as function of \( z \), we can visualize the square of its magnitude

\[
|f(z)|^2 = f^* f = f(z^*) f(z)
\]

where the second equality is true for a polynomial function where \( f(0) = f^*(0) \). This function has the nice property that it is everywhere positive as \( |f(z)|^2 \geq 0 \). Therefore, we can identify the roots of the equation \( f(z) = 0 \) as local minima of the function \( |f(z)|^2 \).

Let’s return to the problem of visualizing the roots of Equation 2.10 by plotting \( |f(z)|^2 \) and identifying the zeros on the complex plane. The result is shown in Figure 2.13. The roots appear as two points on the complex plane \( z_\pm = 1 \pm i \) at which \( f(z) = 0 \) and therefore \( |f(z)|^2 = 0 \). Note that the original quadratic equation \( x^2 - 2x + 2 \) does not intersect the complex plane.

Our graphical approach to identifying roots of quadratic functions is general and also applies to quadratic functions with real roots. Consider the quadratic equation

\[
f(x) = x^2 - 1 = (x - 1)(x + 1) = 0
\]

This function has two real roots at \( x_\pm = \pm 1 \) where \( f(x) \) intersects the x-axis and \( f(\pm 1) = 0 \). Suppose we interpret this quadratic equation as a complex function

\[
f(z) = (z - 1)(z + 1)
\]

where we have substituted \( z = x + iy \) for \( x \). The square of the magnitude of this function \( |f|^2 = f(z^*) f(z) \) is shown in Figure 2.14. The two roots of the quadratic equation appear as local minima of \( |f|^2 \) located at \((1,0)\) and \((-1,0)\) on the complex plane.

Interestingly, along the imaginary \( y \)-axis, \( |f|^2 \) is a monotonically increasing function of \( y \). For example, if we set \( x = 0 \) we find \( |f(0,y)|^2 = 1 + 2y^2 + y^4 \), which increases steeply as a function of \( y \). Along the real \( x \)-axis, \( |f|^2 \) is a quartic double well function of \( x \). For example, if we set \( y = 0 \) we find \( |f(x,0)|^2 = 1 - 2x^2 + x^4 = (1 - x^2)^2 \). This is the same quartic double well function we encountered earlier in our exploration of polynomial functions with minima located at \( x = \pm 1 \) (see Equation 1.6). Note that the original quadratic equation intersects the two local minima of \( |f(x,y)|^2 = 0 \) at the roots \( x = \pm 1 \).
E2 End-of-chapter problems

To those who do not know mathematics
it is difficult to get across a real feeling
as to the beauty, the deepest beauty, of
nature.

Richard Feynman

Warm-ups

2.1 Consider the following complex numbers $z = x + iy$. By Euler’s formula we can also write $z$ in polar form as $z = re^{i\theta}$. Determine the modulus, $r$, and phase angle, $\theta$ for each complex number.

(a) 1   (b) $4i$   (c) $1 - i$
(d) $3 - 4i$   (e) $-2 + 3i$   (f) $-3 - 3i$

2.2 Demonstrate that $e^{-i\theta} = \cos \theta - i \sin \theta$.

2.3 Show that $\cos \theta = \frac{1}{2} \left( e^{i\theta} + e^{-i\theta} \right)$ and $\sin \theta = \frac{1}{2i} \left( e^{i\theta} - e^{-i\theta} \right)$.

2.4 Show for $z = x + iy$ that

$$\frac{1}{z} = \frac{x}{x^2 + y^2} - \frac{iy}{x^2 + y^2}$$

2.5 Plot the function $|z - 1| = 3$ on the complex plane.

2.6 The pH of an aqueous solution is defined $\text{pH} = -\log_{10} a_{H^+}$ where the activity of the hydrogen ion $a_{H^+} = [H^+] / 1 \text{M}$. Find the pH of the following solutions defined in terms of $a_{H^+}$.

(a) $a_{H^+} = 1.00 \times 10^{-7}$   (b) $a_{H^+} = 8.54 \times 10^{-10}$   (c) $a_{H^+} = 0.13$   (d) $a_{H^+} = 1.15$

2.7 Given the following values for the pH, find $[H^+]$ for each solution.

(a) pH = 0   (b) pH = 2.156   (c) pH = 0.234   (d) pH = 7.876

Homework exercises

2.8 Evaluate $z^* z$ and $z^2$ for each of the following complex numbers $z$.

(a) 1   (b) $1 + i$   (c) $2i$
(d) $-2 + 2i$   (e) $-4$   (f) $-4 - 4i$

2.9 Express the following complex numbers in polar form using Euler’s formula (a) $z = 1 + i$ and (b) $z = -1 - i$.

2.10 Using Euler’s formula, derive de Moivre’s identity

$$\cos(n\theta) + i\sin(n\theta) = (\cos(\theta) + i\sin(\theta))^n$$

2.11 Prove the following identities by reexpressing the functions using Euler’s formula.

(a) $\cos(ix) = \cosh(x)$   (b) $\sinh(ix) = i\sin(x)$
(c) $\sin(ix) = i\sinh(x)$   (d) $\cosh(ix) = \cos(x)$
2.12 Use Euler’s formula to evaluate \((i)^i\) as a real number.

2.13 Use Euler’s formula to derive the identities (a) \(\cos \alpha \cos \beta = \frac{1}{2} \cos(\alpha + \beta) + \frac{1}{2} \cos(\alpha - \beta)\) and (b) \(\sin \alpha \sin \beta = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)\).

2.14 For the isothermal, reversible expansion or compression of an ideal gas, the pressure-volume work done on the gas is given by

\[
w = -nRT \ln \left( \frac{V_2}{V_1} \right)
\]

where \(V_1\) and \(V_2\) are the initial and final volumes of the gas. Here \(n\) is the number of moles of gas, \(R\) is the gas constant \(= 8.314 \text{ J/mol K}\), and \(T\) is the absolute temperature. Find the work done on the gas in the isothermal, reversible expansion of 1.00 mole of ideal gas at 298.15K from a volume of 3.00 liters to a volume of 7.00 liters.

2.15 Radioactive decay is observed to follow the integrated rate law

\[
\ln \left( \frac{[A](t)}{[A]_0} \right) = -kt
\]

where \([A](t)\) is the concentration of \(A\) at time \(t\), \([A]_0\) is the initial concentration \([A](t = 0) = [A]_0\), and \(k\) is the rate constant. The predominant isotope of carbon, \(^{12}\text{C}\), is stable, while \(^{14}\text{C}\) is radioactive. The fraction of \(^{14}\text{C}\) in a sample of wood ash from an archaeological dig was found to be 0.249. How old is the wood ash, given that \(k = 1.21 \times 10^{-4} \text{ yr}^{-1}\) for the radioisotope \(^{14}\text{C}\)?

2.16 The change in entropy associated with the expansion or compression of an ideal gas is given by

\[
\Delta S = nC_V \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)
\]

where \(n\) is the number of moles of gas, \(C_V\) is the molar heat capacity of the gas at constant volume, \(V\) is the volume of the gas, and \(T\) is the absolute temperature. The subscripts indicate the initial (1) and final (2) states. In the expansion of 1.00 mole of an ideal gas from 1.00 liter to 3.00 liters, the temperature falls from 300K to 284K. Determine the change in entropy, \(\Delta S\), for the ideal gas in this process. Take \(C_V = \frac{3}{2}R\) and \(R = 8.314 \text{ J/mol K}\).

2.17\(^*\) Evaluate the logarithm \(\ln(z)\) for each of the following complex numbers \(z\).

(a) 1  
(b) \(1 + i\)  
(c) \(2i\)  
(d) \(-2 + 2i\)  
(e) \(-4\)  
(f) \(-4 - 4i\)

Recall that the logarithm of a complex number is a multivalued function. Restrict the value of the imaginary component to be between \(-\pi i\) and \(\pi i\).
2.18 The Soviet mathematical physicist Lev Landau (1908-1968) proposed a base-10 logarithmic scale to measure ability in theoretical physics. He placed Isaac Newton at 0, Albert Einstein at 0.5, and Paul Dirac at 1. Landau eventually ranked himself at 2. By Landau’s own estimate, how many times better a theoretical physicist was Einstein than Landau?
3 Differentiation in One and Many Dimensions

3.1 Differentiating functions of one variable

A foundation idea in the calculus is the concept of the derivative. The derivative provides a measure of how much a function changes as a result of a change in its variable. In modeling physical processes, we are often interested in understanding how one property (a function) varies when another property (the variable) is changed. This might involve the change in concentration (the function) after a change in time (the variable). Or the change in pressure (the function) due to a change in volume (the variable). In this section, we explore the definition of the derivative and review the principal methods of differentiation of a function of one variable.

3.1.1 The concept of the limit and the definition of the derivative

In Chapter 1 we defined the slope of a function \( f(x) \) in terms of the change in the value of the function, \( \Delta f \), resulting from an incremental change in the variable, \( \Delta x \), as

\[
\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\Delta f}{\Delta x} = \frac{f(x + \Delta x) - f(x)}{\Delta x} \quad (3.1)
\]

This is a finite difference estimate of the slope defined in terms of a difference in the function, \( \Delta f \), divided by a finite change in the variable, \( \Delta x \).

Figure 3.1 graphically depicts the measure of the slope (black line) resulting from the calculation of the rise of the function \( \Delta f = f(x_2) - f(x_1) \) divided by the run of the variable \( \Delta x = (x_2 - x_1) \) between two points \((x_1, f(x_1))\) and \((x_2, f(x_2))\). The line connecting the two points is known as the secant line. For a linear function \( f(x) = mx + b \), the slope is defined by the constant \( m \) and is independent of the position \( x \). However, when a function is non-linear the slope will vary as \( x \) varies. For example, in Figure 3.1 the function is steeper at \( x_1 \) than at \( x_2 \). As such, our estimate of the slope will depend on the value of \( \Delta x \).

To get a precise estimate of the slope at a single point using Equation 3.1, we need to know the rise of the function, \( \Delta f \), for a run in the variable, \( \Delta x \), that is as small as we like. Even zero! This is the concept of the derivative.

Figure 3.2 shows a series of secant lines defined over an interval \( x = a \) to \( x = a + \Delta x \) for varying values of \( \Delta x \). As \( \Delta x \) decreases the slope of the secant line increases. Taking the limit that \( \Delta x \) approaches 0 leads to the definition of the derivative

\[
\lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} = \frac{df}{dx} \quad (3.2)
\]

The derivative of \( f(x) \) with respect to \( x \) defines the slope of the function at a single point \( x \) represented by the heavy black tangent line in Figure 3.2. The definition of the derivative is an essential foundation of the calculus.

The derivative of \( f(x) \) can be written using a variety of notations including the

\[
\frac{df}{dx} = f'(x)
\]

\[1\] This concept of \( \Delta x \) becoming so small that it cannot be measured is related to the theory of infinitesimals explored by Greek mathematician, physicist, engineer and philosopher Archimedes (circa 287-212 BCE).

\[2\] While the tangent line is an ancient concept considered by Archimedes and Euclid, its modern development owes much to the French lawyer and mathematician Pierre de Fermat (1607-1665).
We call this the first derivative of $f(x)$. Taking the derivative of the first derivative leads to the second derivative

$$\frac{d^2 f}{dx^2} = \frac{d}{dx} f'(x) = f''(x)$$

While the first derivative defines the rate of change in $f(x)$ as $x$ varies, the second derivative defines the rate of change in $f'(x)$. This idea can be generalized to form the third derivative

$$\frac{d^3 f}{dx^3} = f'''(x)$$

and derivatives of arbitrary order.

There is a small set of rules for differentiating functions of one variable that can be used to determine the derivatives we need in modeling physical processes. The next section provides a concise summary of those rules.

### 3.1.2 Rules for differentiating functions of one variable

Let’s review the rules for differentiating functions of one variable. It is important to practice and master these rules as they form the foundation for applying calculus in the physical sciences.

1. $f(x) = c$. As the constant $c$ does not vary with $x$ the slope of $f(x)$ and its derivative are zero

$$\frac{df}{dx} = \frac{dc}{dx} = 0 \quad (3.3)$$

2. $f(x) = cx$. The first derivative of a linear function has a constant slope

$$\frac{df}{dx} = \frac{d}{dx} (cx) = c \frac{dx}{dx} = c \quad (3.4)$$

3. $f(x) = x^n$. The power rule can be applied to differentiate functions of arbitrary powers of $x$ (see Figure 3.3)

$$\frac{df}{dx} = \frac{d}{dx} x^n = nx^{n-1} \quad (3.5)$$

The power rule can also be applied to negative powers of $x$

$$\frac{df}{dx} = \frac{d}{dx} x^{-n} = -nx^{-n-1}$$

---

Figure 3.2: A series of secant lines providing a measure of the slope of $f(x)$ at $x = a$ for decreasing values of $\Delta x$ (light gray to heavy gray). The thick black line shows the tangent line representing the exact slope at $x = a$.

3 Discovery of the calculus is typically attributed to German philosopher and mathematician Gottfried Leibniz (1646-1716) and British physicist, mathematician, astronomer and theologian Isaac Newton (1642-1727).

4 The derivative may be written using a variety of equivalent derivative notations, including $df(x)/dx$ (Leibniz’s notation), $f'$ (Newton’s notation), $f'$' (Lagrange’s notation), and $D_x f(x)$ (Euler’s notation).

5 Most functions of interest in the physical sciences are continuous and smooth with derivatives of arbitrary order. A function $f(x)$ is continuous if arbitrarily small changes in $x$ result in arbitrarily small changes in $f(x)$. A function $f(x)$ is smooth if its derivatives of all orders are continuous.
As an example, consider the derivative of \( p(V) = nRT/V \) as a function of \( V \)
\[
\frac{d}{dV} p(V) = \frac{d}{dV} \left( \frac{nRT}{V} \right) = nRT \cdot \frac{1}{V^2} = -nRT \cdot \frac{1}{V^2}
\]

4. \( f(x) + g(x) \). The derivative of a sum of two functions is the sum of the derivatives
\[
\frac{d}{dx} [f(x) + g(x)] = \frac{df}{dx} + \frac{dg}{dx}
\]

Consider the derivative of the function \( f(T) = A - \frac{\Delta H}{RT} \) as a function of \( T \)
where \( A \) and \( \Delta H \) are constants
\[
\frac{df}{dT} = \frac{dA}{dT} - \frac{d}{dT} \left( \frac{\Delta H}{RT} \right) = \frac{\Delta H}{RT^2}
\]

5. \( \sin(ax) \). The derivative of \( \sin(ax) \) where \( a \) is a constant proportional to \( \cos(ax) \) (see Figure 3.4)
\[
\frac{d}{dx} \sin(ax) = a \cos(ax)
\]

Consider the derivative of
\[
\phi(x) = \left( \frac{2}{L} \right) \frac{n}{\pi} \sin \left( \frac{n\pi x}{L} \right)
\]
where \( L \) and \( n \) are constants written
\[
\frac{d}{dx} \phi(x) = \left( \frac{2}{L} \right) \left( \frac{n\pi}{L} \right) \cos \left( \frac{n\pi x}{L} \right)
\]

6. \( \cos(ax) \). The derivative of \( \cos(ax) \) is proportional to \( -\sin(ax) \)
\[
\frac{d}{dx} \cos(ax) = -a \sin(ax)
\]

Consider the derivative of \( \phi(t) = A \cos(2\pi vt) \) where \( A \) and \( v \) are constant
\[
\frac{d}{dt} \phi(t) = -A(2\pi v) \sin(2\pi vt)
\]

Returning to the prior example, we can combine the rules for differentiating sine and cosine to write the second derivative of
\[
\phi(x) = \left( \frac{2}{L} \right) \frac{n}{\pi} \sin \left( \frac{n\pi x}{L} \right)
\]
as
\[
\frac{d^2}{dx^2} \phi(x) = -\left( \frac{2}{L} \right) \left( \frac{n\pi}{L} \right)^2 \sin \left( \frac{n\pi x}{L} \right)
\]
The property that sine and cosine functions are proportional to their own second derivatives is profound. The sine and cosine functions appear in the solution of many fundamental problems in the physical sciences, particularly those involving waves.

7. \( \exp(ax) \). The derivative of a real or complex exponential function is proportional to the exponential function itself
\[
\frac{d}{dx} e^{ax} = ae^{ax}
\]

Figure 3.3: The function \( f(x) = x^3 \) (red) and its first derivative \( f'(x) = 3x^2 \) (black). At \( x = a \) the function \( f(x) \) is negative (red dot) while the corresponding derivative \( f'(a) \) is positive (black dot).

Figure 3.4: The function \( f(x) = \sin(2x) \) (red), its first derivative \( f'(x) = 2\cos(2x) \) (black) and second derivative \( f''(x) = -4\sin(2x) \) (blue). At the minimum of the function (red dot) the first derivative is zero (black dot) and the second derivative is positive (blue dot).

You can remember that \( \frac{d}{dx} \sin(x) = \cos(x) \) and \( \frac{d}{dx} \cos(x) = -\sin(x) \) by thinking graphically of the sign of the slope of the function that is being differentiated. Near \( x = 0 \) the slope of \( \sin(x) > 0 \) so \( \frac{d}{dx} \sin(x) = +\cos(x) \). Near \( x = \pi/2 \) the slope of \( \cos(x) < 0 \) so \( \frac{d}{dx} \cos(x) = -\sin(x) \) (see Figure 3.4).

One example is the particle in a box model in quantum mechanics where we encounter the equation
\[
\frac{h^2}{2m} \frac{d^2}{dx^2} \phi(x) = E \phi(x)
\]
where \( h, m \) and \( E \) are constants. Since \( \phi''(x) \) is proportional to \( \phi(x), \phi(x) \) must be a sinusoidal function of \( x \).
An example is shown in Figure 3.5. Consider the complex exponential function \( \Phi(\varphi) = Ae^{im\varphi} \) for which

\[
\frac{d}{d\varphi} \Phi(\varphi) = imAe^{im\varphi}
\]

and

\[
\frac{d^2}{d\varphi^2} \Phi(\varphi) = (im)^2 Ae^{im\varphi} = -m^2 Ae^{im\varphi}
\]

We often find that the rate of change in a property is proportional to the property itself. For example, suppose the rate of birth in a population is proportional to the population itself. In that case, the population will be an exponential function of time. This explains why the exponential function is often used to model processes in the physical processes.

8. \( f(x)g(x) \). The derivative of the product of two functions \( f(x)g(x) \) is defined by the product rule to be

\[
\frac{d}{dx} [f(x)g(x)] = f(x) \frac{dg}{dx} + g(x) \frac{df}{dx}
\]

(3.10)

Consider the compound function

\[ \varphi(x) = e^{-ax}\cos(bx) \]

where \( a \) and \( b \) are constants. We find

\[
\frac{d\varphi}{dx} = -ae^{-ax}\cos(bx) + \cos(bx) \frac{d}{dx}e^{-ax} = -e^{-ax}b \sin(bx) - a \cos(bx) e^{-ax} = -e^{-ax} [b \sin(bx) + a \cos(bx)]
\]

This result is shown for the case \( a = 1 \) and \( b = 2 \) in Figure 3.6.

One common mistake is to use the false relation

\[
\frac{d}{dx} [f(x)g(x)] = f'g'
\]

as if it were the true product rule. If you are unsure whether you have remembered the product rule correctly, take a simple example such as \( f(x) = x \) and \( g(x) = x \) for which

\[
\frac{d}{dx} [f(x)g(x)] = \frac{d}{dx}x^2 = 2x
\]

You will find that the true product rule gives the correct result

\[
\frac{d}{dx} [f(x)g(x)] = f'g' + g'f' = x + x = 2x
\]

while the false product rule

\[
\frac{d}{dx} [f(x)g(x)] = f'g' = 1
\]

does not.

9. \( \ln(x) \). The derivative of the natural logarithm is

\[
\frac{d}{dx} \ln(x) = \frac{1}{x}
\]

(3.11)

This property of the natural logarithm, introduced through Figure 2.7 and the surrounding discussion, is intimately related to the fundamental
definition of the natural logarithm
\[ d \ln(x) = \frac{dx}{x} \]

The fractional change in the function, \( \ln(x) \), resulting from a change in the variable, \( dx \), is proportional to \( \frac{1}{x} \). This result is shown in Figure 3.7.

10. \( f(g(x)) \). The derivative of a composite function is defined by the chain rule
\[ \frac{d}{dx} f(g(x)) = \frac{df}{dg} \cdot \frac{dg}{dx} \] (3.12)

Take the function \( \Phi(\theta) = 3 \cos^2(\theta) - 1 \). We define \( g(\theta) = \cos(\theta) \) so that \( \Phi(g(\theta)) = 3(\cos(\theta))^2 - 1 \). By the chain rule the derivative of \( \Phi(g(\theta)) \) with respect to \( \theta \) is
\[ \frac{d}{d\theta} \Phi(g(\theta)) = \frac{d\Phi}{dg} \times \frac{dg}{d\theta} = 6g(\theta) \times (-\sin(\theta)) = -6 \cos(\theta) \sin(\theta) \]

Consider the function
\[ U(T) = \frac{\epsilon}{2} + \frac{\epsilon}{e^{\beta \epsilon} - 1} \]

where \( \beta = 1/T \) is a function of the variable \( T \) and \( \epsilon \) is a constant. Applying the chain rule for differentiation of composite functions
\[ \frac{dU}{dT} = \frac{dU}{d\beta} \cdot \frac{d\beta}{dT} \]

The first part of this relation is
\[ \frac{dU}{d\beta} = \frac{d}{d\beta} \left[ \frac{\epsilon}{2} + \frac{\epsilon}{e^{\beta \epsilon} - 1} \right] = \frac{-\epsilon}{(e^{\beta \epsilon} - 1)^2} \cdot \frac{d}{d\beta} (e^{\beta \epsilon} - 1) = \frac{-\epsilon^2 \epsilon^{\beta \epsilon}}{(e^{\beta \epsilon} - 1)^2} \]

where we have used the power rule
\[ \frac{d}{dx} \frac{1}{f(x)} = -\frac{1}{f(x)^2} \frac{df}{dx} \]

The second part of this relation is
\[ \frac{d\beta}{dT} = \frac{d}{dT} \left( \frac{1}{T} \right) = -\frac{1}{T^2} = -\beta^2 \]
Combining these results we find
\[ \frac{dU}{dT} = \frac{dU}{d\beta} \frac{d\beta}{dT} = (\epsilon\beta)^2 \frac{e^{\beta \epsilon}}{(e^{\beta \epsilon} - 1)^2} \]

The equivalent function \( f(x) = 1/(\exp(1/x) - 1) \) and its derivative \( f'(x) \) are shown Figure 3.8.

11. \( a^x \). The derivative of a constant \( a \) raised to the power of \( x \) is
\[ \frac{d}{dx} a^x = a^x \ln a \quad (3.13) \]

The previous result for the derivative of \( e^x \) is a special case of this formula where \( a = e \) and \( \ln e = 1 \). Consider a function \( \theta^x \) where \( \theta \) is a constant. The first derivative is
\[ \frac{d}{d\theta} \theta^x = \theta^x \ln \theta \]

and the second derivative is
\[ \frac{d^2}{d\theta^2} \theta^x = \frac{d}{d\theta} \left( \frac{d}{d\theta} \theta^x \right) = \ln \theta \frac{d}{d\theta} \theta^x \]

Since \( \ln \theta \) is a constant we can pull it in front of the derivative and
\[ \frac{d}{d\theta} \theta^x \ln \theta = \ln \theta \left( \frac{d}{d\theta} \theta^x \right) = \ln \theta \left( \theta^x \ln \theta \right) = \theta^x (\ln \theta)^2 \]

This process can be generalized to the \( n \)th order derivative to find
\[ \frac{d^n}{d\theta^n} \theta^x = \theta^x (\ln \theta)^n \]

12. \( f(x)/g(x) \). The derivative of a compound function \( f(x)/g(x) \) involving a quotient can be evaluated using the product rule and the chain rule
\[
\frac{d}{dx} \left[ \frac{f(x)}{g(x)} \right] = \frac{1}{g(x)} \frac{df}{dx} + f(x) \frac{d}{dx} \left[ \frac{1}{g(x)} \right] \\
= \frac{1}{g^2(x)} g(x) \frac{df}{dx} + f(x) \left[ -\frac{1}{g^2(x)} \frac{dg}{dx} \right] \\
= \frac{1}{g^2(x)} g(x) \frac{df}{dx} - f(x) \frac{dg}{dx} \\
= \frac{df}{dx} - f(x) \frac{dg}{dx} \\
= \frac{df}{dx} - f(x) \frac{dg}{dx} 
\]

We can perform this derivative as an application of the product rule and power rule.\(^\text{10}\)

Consider the function
\[ p(\beta) = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \]
shown in Figure 3.9, which we recognize to be \( f(x)/g(x) \) where \( f(x) = e^{-\beta \epsilon} \) and \( g(x) = 1 + e^{-\beta \epsilon} \). Applying our rules for differentiating compound functions we have
\[ \frac{dp}{d\beta} = -\epsilon e^{-\beta \epsilon} \frac{1}{1 + e^{-\beta \epsilon}} - e^{-\beta \epsilon} \frac{-\epsilon e^{-\beta \epsilon}}{(1 + e^{-\beta \epsilon})^2} \\
= \frac{1}{(1 + e^{-\beta \epsilon})^2} \left[ -\epsilon e^{-\beta \epsilon} (1 - e^{-\beta \epsilon}) + \epsilon e^{-2\beta \epsilon} \right] \\
= \frac{-\epsilon e^{-\beta \epsilon}}{(1 + e^{-\beta \epsilon})^2} 
\]

The function and its derivative are shown Figure 3.9.

Further consider the compound function \( \tan(x) = \sin(x)/\cos(x) \). To \(^8\)These functions appear in Einstein’s theory of the heat capacity of solids. The thermodynamic energy is \( U(T) \) and the heat capacity \( C_V(T) = dU/dT \).
execute the derivative of \( \tan(x) \) with respect to \( x \) we first apply the product rule

\[
\frac{d}{dx} \tan(x) = \frac{d}{dx} \left( \frac{\sin(x)}{\cos(x)} \right) = 1 + \tan^2(x) = \sec^2(x)
\]

The derivative of \( \cos^{-1}(x) \) can be evaluated using the chain rule as

\[
\frac{d}{dx} \cos^{-1}(x) = \frac{1}{\cos(x)} \times \frac{d}{dx} \cos(x) = -\frac{1}{\cos^2(x)} \times (-\sin(x))
\]

Combining these results we find

\[
\frac{d}{dx} \tan(x) = \frac{\cos(x)}{\cos(x)} + \sin(x) \left( \frac{\sin(x)}{\cos^2(x)} \right) = 1 + \frac{\sin^2(x)}{\cos^2(x)}
\]

The result is shown graphically in Figure 3.10.

The rules above provide the foundation of knowledge needed to carry out differential calculus on functions of one variable. In the next section, we will find that these rules provide the tools needed to compute derivatives of functions of many variables common to the physical sciences. These rules should be practiced on simple functions and complicated functions until mastery of each rule is achieved.

### 3.2 Partial derivatives of functions of many variables

Functions of more than one variable are common in modeling properties of physical systems. For an ideal gas, the pressure can be written as a function of three variables (the volume, temperature, and number of particles). If we want to understand how the pressure changes with volume, we hold the temperature and number of particles fixed and vary only the volume. That is the concept of a partial derivative. For a function of many variables, we hold all but one variable fixed and measure the change in the function resulting from the change in that one variable. In this section, we explore the definition of the partial derivative and survey common methods for taking partial derivatives of functions of many variables.

#### 3.2.1 The concept of the partial derivative

For a function of one variable, \( f(x) \), we defined the first derivative at a point \( x \) in terms of the limit

\[
f'(x) = \frac{df}{dx} = \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}
\]

and interpreted \( f'(x) \) as the slope of the function at the point \( x \). For a function of two variables, \( f(x, y) \), we have slopes in the \( x \)- and \( y \)-directions that must be defined. To assess the rate of change in the function \( f(x, y) \) due to a change in \( x \), we hold \( y \) constant, as indicated by the \( y \)-subscript, and define the derivative of \( f(x, y) \) with respect to \( x \) as \( \frac{\partial f}{\partial x} \) (3.15)

\[
\frac{\partial f}{\partial x} = \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}
\]

This is known as a \textit{partial derivative} as it provides partial information on the rate of change in the function with respect to the change in one of many variables.
Similarly, to know the rate of change in \( f(x, y) \) due to a change in \( y \), we hold \( x \) constant and define the derivative of the function \( f(x, y) \) with respect to \( y \) as\textsuperscript{12}

\[
\frac{\partial f}{\partial y} = \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}
\]  
\[(3.16)\]

Figure 3.11 depicts a function of two variables \( f(x, y) \) and its first order partial derivatives \( f_x(a, b) \) and \( f_y(a, b) \). The heavy lines drawn over the surface represent the one-dimensional functions \( f(x, b) \) and \( f(a, y) \). The thin straight lines are tangent lines representing the partial derivatives \( f_x(a, b) \) and \( f_y(a, b) \) taken at the point \((a, b)\).

The one-dimensional functions \( f(x, b) \) and \( f(a, y) \) and associated tangent lines defined by \( f_x(a, b) \) and \( f_y(a, b) \) at the point \((a, b)\) are compared in Figure 3.12.

We can extend this concept of the first order partial derivative to create higher-order partial derivatives of a multivariate function. For a function of \( n = 2 \) variables \( f(x, y) \) there will be \( 2 \times 1 \) first order partial derivatives, \( f_x \) and \( f_y \), and \( 2 \times 2 \) second order partial derivatives

\[
f_{xx} = \frac{\partial^2 f}{\partial x^2} \quad f_{yy} = \frac{\partial^2 f}{\partial y^2} \quad f_{xy} = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x} f_y \quad f_{yx} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y} f_x
\]

In general, for a function of \( n \) variables there will be \( n \times m \) \( m \)th-order partial derivatives.

### 3.2.2 Techniques for partial differentiation

In the expression

\[
\left( \frac{\partial f}{\partial x} \right)_y
\]  
\[(3.17)\]

the subscript is used to explicitly note that when the partial derivative of \( f(x, y) \) is taken with respect to \( x \), the variable \( y \) is held constant. For example, suppose \( f(x, y) = 3xy^2 + x + 2y^2 \). In computing

\[
\left( \frac{\partial f}{\partial x} \right)_y = \frac{\partial}{\partial x} \left( 3xy^2 + x + 2y^2 \right) = \frac{\partial}{\partial x} 3xy^2 + \frac{\partial}{\partial x} x + \frac{\partial}{\partial x} 2y^2
\]

we treat the factors \( 3y^2 \) and \( 2y^2 \) as constants that can be pulled in front of the derivative. This leads to

\[
\left( \frac{\partial f}{\partial x} \right)_y = 3y^2 \frac{\partial}{\partial x} x + \frac{\partial}{\partial x} x + 2y^2 \frac{\partial}{\partial x} 1 = 3y^2 + 1
\]
Similarly, for the partial derivative with respect to $y$

$$\left( \frac{\partial f}{\partial y} \right)_x = \frac{\partial}{\partial y} \left( 3xy^2 + x + 2y^2 \right) = \frac{\partial}{\partial y} 3xy^2 + \frac{\partial}{\partial y} x + \frac{\partial}{\partial y} 2y^2$$

$$= 3x \frac{\partial}{\partial y} y^2 + x \frac{\partial}{\partial y} 1 + 2 \frac{\partial}{\partial y} y^2 = 6xy + 4y$$

We record our final results as

$$\left( \frac{\partial f}{\partial x} \right)_y = \frac{\partial f}{\partial x} = 3y^2 + 1 \quad \left( \frac{\partial f}{\partial y} \right)_x = \frac{\partial f}{\partial y} = 6xy + 4y$$

The presence of the partial derivative notation already indicates that the derivative is taken with respect to only one variable, implying that all other variables are held constant. As such, we will typically omit the explicit subscript.

In practice, we will reserve the subscript notation for cases in which variables are held constant to specific values or in cases where we want to emphasize the fact that specific variables are held constant. For example, for the function above we write

$$\left( \frac{\partial f}{\partial x} \right)_{y=1} = 4 \quad \left( \frac{\partial f}{\partial y} \right)_{x=2} = 16y \quad \left( \frac{\partial f}{\partial y} \right)_{x=2,y=1} = 16$$

where the subscripts are used to assign specific values to one or both of the variables $x$ and $y$.

Now consider the function of two variables $p(V, T)$ where

$$p(V, T) = \frac{RT}{V}$$

for which

$$\frac{\partial p}{\partial V} = -\frac{RT}{V^2} \quad \frac{\partial p}{\partial T} = \frac{R}{V}$$

The function $p(V, T)$ and the first derivatives $p_V(V, T)$ and $p_T(V, T)$ are shown graphically in Figure 3.13 for positive values of $V$ and $T$. Note the positive upward slope of $p_T(V, T)$ and negative downward slope of $p_V(V, T)$ that increase in magnitude as $V$ decreases toward zero.

Note that the partial derivatives $p_V(V, T)$ and $p_T(V, T)$ are functions of two variables that form surfaces over the $xy$-plane, as is the function $p(V, T)$. Evaluating the partial derivative $p_T(V, T)$ at a particular value of $T$ results in a function of one variable $V$ (gray line), while evaluating $p_V(V, T)$ at a particular value of $V$ results in a function of one variable $T$ (black line). Evaluating the partial derivatives at a specific point on the $VT$-plane results in numbers (gray and black points).

The second partial derivatives of $p(V, T)$ are evaluated as

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{V^3} \quad \frac{\partial^2 p}{\partial T^2} = 0$$

and

$$\frac{\partial^2 p}{\partial T \partial V} = \frac{\partial^2 p}{\partial V \partial T} = -\frac{R}{V^2}$$

If a function $f(x, y)$ has continuous mixed partial derivatives $f_{xy}$ and $f_{yx}$ then $f_{xy} = f_{yx}$. This is referred to as Clairaut’s theorem.

This equality of mixed partial derivatives is true for most functions encountered in the physical sciences, including $p(V, T)$ that has continuous second partial derivatives so that $p_{TV} = p_{VT}$. This concept can be extended to mixed partial derivatives of any order. For example, if $f_{xxy}$, $f_{xyx}$, and $f_{yxx}$ are continuous then $f_{xxy} = f_{xyx} = f_{yxx}$. 

Figure 3.13: The function $p(V, T) = \frac{RT}{V}$ (red) shown with the first derivatives $p_V(V, T) = -\frac{RT}{V^2}$ (black) and $p_T(V, T) = \frac{R}{V}$ (gray).
3.3 Infinitesimal change and the total differential

The derivative provides a measure of the rate of change in a function resulting from a small change in a variable. In one dimension, if we multiply the first derivative of a function, $df/dx$, by a small change in the variable, $dx$, the result is an estimate of the change in the function, $df$. The extension of this idea to functions of many variables leads to the concept of the total differential. The concept of the total differential is essential in the physical sciences and plays a central role in thermodynamics.

3.3.1 The concept of the total differential

The first derivative of a function $f(x)$ with respect to $x$ written

$$
\frac{df}{dx}
$$

can be thought of as a fraction, formed by a change in the function, $df$, divided by a change in the variable, $dx$. Now consider the equality

$$
\frac{df}{dx} = \frac{df}{dx}
$$

Multiplying each side by $dx$ and canceling terms leads to

$$
\left(\frac{df}{dx}\right) dx = \left(\frac{df}{dx}\right) dx = df
$$

and the identity

$$
df = \left(\frac{df}{dx}\right) dx
$$

d$df$ is known as the differential of $f$. The first derivative is the proportionality constant relating the infinitesimal change in the function, $df$, resulting from an infinitesimal change in the variable, $dx$.

To extend this concept to a multivariate function, $f(x, y)$, we write

$$
df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy
$$

Here $df$ is known as the total differential of $f$.

The total change in the function $df$ is the sum of the change in $f$ resulting from a change in $x$, proportional to $f_x$, and the change in $f$ resulting from a change in $y$, proportional to $f_y$.

In an arbitrary number of dimensions, $N$, the total differential of a function $f(x_1, x_2, \ldots x_N)$ can be written

$$
\begin{align*}
df &= \sum_{k=1}^{N} \left(\frac{\partial f}{\partial x_k}\right) dx_k \\
&= \sum_{k=1}^{N} \left(\frac{\partial f}{\partial x_k}\right) dx_k
\end{align*}
$$

The total differential defines the infinitesimal change in the function, $df$, resulting from the infinitesimal changes in the variables $dx_1, dx_2, \ldots$ and $dx_N$.

As an example, let’s determine the total differential, $dV$, for the volume of a cylinder $V(r, h) = \pi r^2 h$ as a function of changes in its radius $r$ and height $h$. Using Equation 3.19 we write the incremental change in volume, $dV$, due to an incremental change in the cylinder’s radius, $dr$, and height, $dh$, as

$$
dV = \left(\frac{\partial V}{\partial r}\right) dr + \left(\frac{\partial V}{\partial h}\right) dh = 2\pi rh \, dr + \pi r^2 \, dh
$$

The concept of the total differential of the volume of a cylinder is explored graphically for a change in height, $dh$, in Figure 3.14, and a change in radius.
We could anticipate this result from the beginning by noting that
which can also be written
\[
\frac{dU}{dz} = \frac{\partial f}{\partial u} \frac{du}{dz} + \frac{\partial f}{\partial y} \frac{dy}{dz}
\]
which is the total differential of the composite function.

Let’s determine the differential of the composite function \( U(z(x)) = mgz \) in which \( m \) and \( g \) are constants and \( z = x^2 \) depends parametrically on the variable \( x \). We write the differential
\[
dU = \frac{dU}{dz} \frac{dz}{dx} dx = mg \times 2x \times dx = 2mgx \ dx
\]
defining the change in \( U \) resulting from a small change in \( x \).

Now consider the composite function
\[
U(x(t), y(t)) = x^2(t) + y^2(t)
\]
where the variables \( x = \sin(t) \) and \( y = \cos(t) \) depend parametrically on the variable \( t \). We write the total differential
\[
dU = \left[ \frac{\partial U}{\partial x} \frac{dx}{dt} + \frac{\partial U}{\partial y} \frac{dy}{dt} \right] dt = \left[ 2x \frac{dx}{dt} + 2y \frac{dy}{dt} \right] dt
\]
which can also be written
\[
dU = [2\sin(t) \cos(t) - 2\cos(t) \sin(t)] dt = 0
\]
We could anticipate this result from the beginning by noting that
\[
U = \sin^2(t) + \cos^2(t) = 1
\]
is a constant, so that \( dU = 0 \). This result is shown graphically in Figure 3.16.
If we divide each term by \( dt \) we find an expression for the total derivative of the function with respect to \( t \)

\[
\frac{df}{dt} = \left( \frac{\partial f}{\partial t} \right) \frac{dt}{dt} + \left( \frac{\partial f}{\partial x} \right) \frac{dx}{dt} + \left( \frac{\partial f}{\partial y} \right) \frac{dy}{dt}
\]

\[
= \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt}
\]

This total derivative of the function \( f(x, y, t) \) provides a measure of the rate of change in the function resulting from a change in \( t \), including direct dependence on \( t \) and indirect dependence on \( t \) through \( x(t) \) and \( y(t) \).

For example, consider the exponentially damped sinusoidal function

\[
f(x(t), y(t), t) = e^{-t}(x + y)
\]

where \( x(t) = \sin(at) \) and \( y(t) = \cos(bt) \) and \( a \) and \( b \) are constants. The total derivative of this composite function is

\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt}
\]

\[
= -e^{-t}(x + y) + e^{-t} \frac{dx}{dt} + e^{-t} \frac{dy}{dt}
\]

\[
= -e^{-t} [\sin(at) + \cos(bt)] + e^{-t} [a \cos(at) - b \sin(bt)]
\]

The resulting function and its total derivative are shown in Figure 3.17 for the special case of \( a = 1 \) and \( b = 2 \).

### 3.3.4 Identifying exact differentials using Euler’s test

We established that the total differential of a function \( f(x, y) \) can be written

\[
df(x, y) = \left( \frac{\partial f}{\partial x} \right) dx + \left( \frac{\partial f}{\partial y} \right) dy
\]

Suppose someone proposes a differential

\[
s(x, y) \, dx + t(x, y) \, dy
\]

and claims that there exists a function \( f(x, y) \) for which the differential above is the total differential. That is, they claim that

\[
df(x, y) = s(x, y) \, dx + t(x, y) \, dy
\]

How can we know if their claim is valid? Sometimes the answer is obvious. And sometimes it’s not.

We can answer this question using a simple procedure known as Euler’s test. If the equation

\[
\frac{\partial}{\partial y} s(x, y) = \frac{\partial}{\partial x} t(x, y)
\]

is satisfied, we say that \( s(x, y) \, dx + t(x, y) \, dy \) is an exact differential. In that case, there exists a function \( f(x, y) \) for which

\[
df = s(x, y) \, dx + t(x, y) \, dy
\]

Otherwise, we say \( s(x, y) \, dx + t(x, y) \, dy \) is an inexact differential. In that case, there exists no function with that corresponding total differential.

Let’s consider a few examples starting with the differential

\[
2x \, dx + 2y \, dy
\]

The total derivative appears in fundamental equations of classical mechanics and quantum mechanics. It is surprisingly common to see the total derivative misrepresented as a partial derivative and vice versa. Don’t let this happen to you!

15 The total derivative appears in fundamental equations of classical mechanics and quantum mechanics. It is surprisingly common to see the total derivative misrepresented as a partial derivative and vice versa. Don’t let this happen to you!

16 Any total differential of the form \( a(x)dx + b(y)dy \) satisfies Euler’s test since

\[
\frac{da(x)}{dy} = \frac{db(y)}{dx} = 0
\]

As such, there will necessarily be a function \( f(x, y) \) with total differential \( df(x, y) = a(x)dx + b(y)dy \).
where \( s(x, y) = 2x \) and \( t(x, y) = 2y \). Applying Euler’s test we find
\[
\frac{\partial}{\partial y} s(x, y) = \frac{\partial}{\partial y} 2x = 0 \quad \frac{\partial}{\partial x} t(x, y) = \frac{\partial}{\partial x} 2y = 0
\]
demonstrating that \( 2x \, dx + 2y \, dy \) is an exact differential. In this case, the corresponding function is
\[
f(x, y) = x^2 + y^2
\]
To verify this result, we evaluate the total differential
\[
d f(x, y) = \left( \frac{\partial f}{\partial x} \right) dx + \left( \frac{\partial f}{\partial y} \right) dy = 2x \, dx + 2y \, dy
\]
Now consider the differential
\[
x^2 y \, dx + y \, dy
\]
Is this an exact differential? Applying Euler’s test where \( s(x, y) = x^2 y \) and \( t(x, y) = y \) we find
\[
\frac{\partial}{\partial y} s(x, y) = \frac{\partial}{\partial y} x^2 y = x^2 \quad \frac{\partial}{\partial x} t(x, y) = \frac{\partial}{\partial x} y = 0
\]
which fails the test. Equation 3.24 is an inexact differential. There exists no corresponding function \( f(x, y) \) for which the total differential corresponds to Equation 3.24.

3.3.5 Application of Euler’s test to thermodynamics

For a function \( f(x, y) \), Euler’s test is equivalent to the condition that
\[
\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}
\]
This is a property of all functions \( f(x, y) \) that have continuous mixed second partial derivatives. All thermodynamic equations of state or state functions have this property. The change in a state function depends only on the value of the function at the initial and final points, not on the path taken between the two.

To explore this idea, let’s return to the thermodynamic state function
\[
p(V, T) = \frac{RT}{V}
\]
with total differential
\[
d p = \frac{\partial p}{\partial V} dV + \frac{\partial p}{\partial T} dT = -\frac{RT}{V^2} dV + \frac{R}{V} dT
\]
We find that
\[
\frac{\partial^2 p}{\partial V \partial T} = \frac{\partial^2 p}{\partial T \partial V} = -\frac{R}{V^2}
\]
which satisfies Euler’s test as we expect for a thermodynamic state function. The result is shown graphically in Figure 3.18.

In thermodynamics, we encounter the state functions energy \( U \) and entropy \( S \). Changes in these functions are represented by exact differentials. We also encounter functions such as work and heat that are not state functions. Changes in these functions are represented by inexact differentials. Knowledge of the properties of total differentials, as well as exact and inexact differentials, is essential to the study of thermodynamic properties of physical systems.

\[17\] Any function of the form \( f(x, y) = g(x)h(y) \) will have a total differential of the form \( df(x, y) = g'(x)h(y)dx + g(x)h'(y)dy \) that satisfies Euler’s test. If you recognize the form \( g'(x)h(y)dx + g(x)h'(y)dy \) in a differential you can conclude that \( f(x, y) = g(x)h(y) \).
A3 Euler’s theorem for homogeneous functions

We say that the function \( f(x) \) is an \( n \)th order homogeneous function if

\[
f(\lambda x) = \lambda^n f(x)
\]

where \( \lambda \) is a constant. In this case

\[
f(x) = x \left( \frac{df}{dx} \right)
\]

This is known as Euler’s theorem for homogeneous functions.

![Euler's theorem diagram](image)

As an example, consider the function \( f(x) = x^n \) where \( f(\lambda x) = (\lambda x)^n = \lambda^n x^n = \lambda^n f(x) \). For this \( n \)th order homogeneous function\(^{18}\)

\[
x \left( \frac{df}{dx} \right) = x \left( \frac{d}{dx} x^n \right) = x(nx^{n-1}) = nx^n = nf(x)
\]

We can extend this result to functions of more than one variable. If \( f(x, y) \) is an \( n \)th order homogeneous function of \( x \) and \( y \) for which

\[
f(\lambda x, \lambda y) = \lambda^n f(x, y)
\]

then

\[
f(x, y) = x \left( \frac{\partial f}{\partial x} \right) + y \left( \frac{\partial f}{\partial y} \right)
\]

(3.26)

Consider the following examples. For the function \( f(x, y) = x^2 + y^2 \) we find

\[
f(\lambda x, \lambda y) = (\lambda x)^2 + (\lambda y)^2 = \lambda^2(x^2 + y^2) = \lambda^2 f(x, y)
\]

The function \( f(x, y) \), shown Figure 3.19, is a homogeneous function of order \( n = 2 \). Now consider the function \( g(x, y) = \frac{x}{x^2 + y^2} \) for which

\[
g(\lambda x, \lambda y) = \frac{\lambda x}{(\lambda x)^2 + (\lambda y)^2} = \frac{\lambda x}{\lambda^2 x^2 + y^2} = \lambda^{-1} g(x, y)
\]

The function \( g(x, y) \) is a homogeneous function of order \( n = -1 \). Finally, the function \( h(x, y) = x^2 + y^3 \) where \( h(\lambda x, \lambda y) \neq \lambda^n h(x, y) \) is not a homogeneous function.

First order homogeneous functions are common to thermodynamics. Consider the thermodynamic energy \( U(S, V) \) that is known to be an extensive

\[\text{Figure 3.19: A second order homogeneous function } f(x, y) = x^2 + y^2 \text{ (red) shown as a surface over the } xy \text{-plane along with } f(\lambda x, \lambda y) \text{ (gray) where } \lambda = 2.\]
property of the system and a function of the extensive variables entropy, $S$, and volume, $V$. If you double $S$ and $V$, you also double $U(S, V)$. We can capture this property mathematically as

$$U(\lambda S, \lambda V) = \lambda U(S, V)$$

From Euler’s theorem and Equation 3.26 where $n = 1$, we find

$$U(S, V) = S \left( \frac{\partial U}{\partial S} \right) + V \left( \frac{\partial U}{\partial V} \right)$$

relating the thermodynamic energy $U(S, V)$ to its various first partial derivatives.

Zeroth order homogeneous functions also appear in thermodynamics. Consider the temperature $T(S, V)$ which is an intensive property of the system and a function of entropy, $S$, and volume, $V$. We find

$$T(\lambda S, \lambda V) = T(S, V) = \lambda^0 T(S, V)$$

so that $T(S, V)$ is a zeroth order homogeneous function of $S$ and $V$. Equations expressing intensive variables, such as temperature or pressure, in terms of extensive variables, such as entropy and volume, are known as equations of state.

**B3 Geometric interpretation of the total differential**

For a function of one variable, $f(x)$, following Equation 3.18 we define the differential

$$df = df \frac{dx}{dx} = df \; dx$$

This identity provides a geometric interpretation of the differential, $df$, in terms of the first derivative of $f$ and the incremental change in the variable, $dx$, defining the tangent line shown in Figure 3.2. Let’s develop a similar geometric interpretation of the total differential of a function of two variables.

![Figure 3.20: The parabolic function $f(x, y)$ shown as a red surface over the $xy$-plane. Asterisks mark the point $f(a, b)$ on the surface directly above the point $(a, b)$ on the plane. The tangent plane (gray surface) is defined by the first order partial derivatives of the function at the point $(a, b)$.](image)

Consider the parabolic function $f(x, y)$ (red surface) shown in Figure 3.20. Following the work of Tall, we write the total differential of this function of two variables as

$$df = df_x + df_y$$

Moving a distance $dx$ in the $x$-direction on the tangent plane (gray surface) leads to a displacement $df_x$. Moving a distance $dy$ in the $y$-direction on the tangent
Warm-ups

3.1 Differentiate the following functions, assuming that any parameter not noted as a variable of the function is constant.

(a) \( y(x) = x^3 + 5x^2 - 2x + 3 \)  
(b) \( f(T) = \frac{-\Delta H}{RT} + K \)  
(c) \( d(v) = \frac{M}{V} \)  
(d) \( r(\theta) = 5 \tan \theta \)  
(e) \( p(T) = A e^{-b/RT} \)  
(f) \( f(x) = x^2 \tan(2x) \)  
(g) \( y(x) = x^2 \ e^{-x} \cos(x) \)  
(h) \( p(x) = \exp[-(x^2 + a^2)^{1/2}] \)  
(i) \( u(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \)  
(j) \( y(x) = x^5 \sqrt{1 - e^{2x}} \)  
(k) \( y(x) = x^{-2} (1 - e^x) \)  
(l) \( j(x) = e^{-\sin(x)} \)  
(m) \( y(x) = x^\sin(x) \)  
(n) \( W(n) = N \ln N - n \ln n \)  
(o) \( s(t) = e^{-3t} \ln t \)  
(p) \( g(p) = \frac{A}{p} + p \ln p \)  
(q) \( e(z) = \frac{E^2}{A} \left(z^2 - \frac{22}{3}z\right) \)  
(r) \( \varphi(x) = 2A \cos \left(\frac{n\pi x}{L}\right) \)

3.2 Determine the slope of each of the following functions for the value of the variable indicated.

(a) \( y(x) = 3 \ln x \) at \( x = 3 \)  
(b) \( y(x) = x^3 \) at \( x = 3 \)  
(c) \( y(x) = x^3 - 5x^2 + 2x - 3 \) at \( x = -1 \)  
(d) \( y(x) = (x^2 - 6)^{1/2} \) at \( x = 4 \)  
(e) \( r(\theta) = 5 \cos \theta \) at \( \theta = \pi \)  
(f) \( r(\theta) = 3 \sin \theta \cos \theta \) at \( \theta = \pi/2 \)

3.3 Twice differentiate the following functions with respect to \( x \).

(a) \( x^2 \cos(x) \)  
(b) \( e^{-x} \sin(x) \)  
(c) \( x^2 \ln(x) \)  
(d) \( y(x) = \ln(1 - e^x) \)  
(e) \( y(x) = \sqrt{1 - x^2} \)  
(f) \( (2 + x)e^{-x^2} \)

3.4 Evaluate the following partial derivatives.

(a) \( p(V, T) = nRT/V \); \( \partial p/\partial V \)  
(b) \( \left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \); \( \partial p/\partial V \)  
(c) \( \rho(p, T) = \frac{pM}{RT} \); \( \partial \rho/\partial T \)  
(d) \( H = a + bT + cT^2 + \frac{d}{T} \); \( \partial H/\partial T \)

C3 End-of-chapter problems

This equality can be reformed as

\[
\frac{df}{dx} = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy
\]

Combining this result with the definition of the total differential

\[
df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy
\]

leads to the identities

\[
df_x = \frac{\partial f}{\partial x} \quad df_y = \frac{\partial f}{\partial y}
\]

completing this geometrically intuitive definition of the total differential, \( df \).

Mathematics knows no races or geographic boundaries; for mathematics, the cultural world is one country.

David Hilbert
(e) \( r(x, y, z) = \sqrt{x^2 + y^2 + z^2} \); \( \frac{\partial r}{\partial y} \)

(f) \( y(r, \theta, \varphi) = r \sin \theta \cos \varphi \); \( \frac{\partial y}{\partial \varphi} \)

3.5 Use Euler’s test to demonstrate that the total differential of the volume of a cylinder of radius \( r \) and height \( h \) written

\[ dV(r, h) = \pi r^2 dh + 2\pi rh \, dr \]

is an exact differential.

**Homework exercises**

3.6 Determine the slope of each of the following functions for the value of the variable indicated.

(a) \( x(t) = \frac{1}{2}a t^2 \) at \( t = 30 \) seconds with \( a = 9.8 \) m/s\(^2\) is constant

(b) \( C_p(T) = 25.9 \text{ Jmol}^{-1} \text{ K}^{-1} + 33.0 \times 10^{-3} T \text{ Jmol}^{-1} \text{ K}^{-2} - 30.4 \times 10^{-7} T^2 \text{ Jmol}^{-1} \text{ K}^{-3} \) at \( T = 298. \text{ K} \)

(c) \( \ln \left[ \frac{p(T)}{p_0} \right] = -\Delta H / RT + B \) at \( T = 298. \text{ K} \) with \( \Delta H = 30,820. \text{ J/mol} \), \( R = 8.314 \text{ J/mol K} \), and \( B = 2.83 \)

(d) \( A(t) = A_0 e^{-kt} \) at \( t = 10.0 \) minutes with \( A_0 = 0.050 \) M and \( k = 0.021 \text{ min}^{-1} \)

3.7 The rate constant \( k(T) \) for a chemical reaction is found to vary with temperature according to the Arrhenius equation

\[ k(T) = A e^{-E^\ddagger / RT} \]

where \( A, E^\ddagger \) and \( R \) are constants. Find an expression for the change in \( k(T) \) with respect to \( T \).

3.8 The density of an ideal gas is found to vary with respect to temperature according to the equation

\[ \rho(T) = \frac{pM}{RT} \]

where \( p, M \) and \( R \) are constants. Find an expression for the slope of \( \rho \) versus \( T \).

3.9 Consider the van der Waals equation of state for a real gas

\[ \left( p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \]

where \( a \) and \( b \) are constants. The figure below shows the compressibility factor \( Z = pV / nRT \) as a function of \( V \) and \( 1/V \) for the real gas (red line) and ideal gas (black line).

Find the partial derivative of \( Z \) with respect to \( V \) and with respect to \( 1/V \).
3.10 A certain gas obeys the equation of state

\[ p(V - nb) = nRT \]

where \( n \) and \( R \) are constants. Determine the coefficient of thermal expansion

\[ \alpha = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_p \]

3.11 For the function \( f(\theta) = \ln[\cos(\theta) + i \sin(\theta)] \) show that \( \frac{df}{d\theta} = i \).

3.12* Determine the derivative of \( h(x) = x^2 \) with respect to \( x \). HINT: Take the derivative of \( d\ln[h(x)]/dx \).

3.13 Consider the van der Waals equation for one mole of gas

\[ p = \frac{RT}{(V-b)} - \frac{a}{V^2} \]

Find \( \left( \frac{\partial p}{\partial T} \right)_V \) and \( \left( \frac{\partial p}{\partial V} \right)_T \).

3.14 Show that \( V(x, y, z) = 1/\sqrt{x^2 + y^2 + z^2} \) satisfies

\[ \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \]

which is known as Laplace’s equation.

3.15* Consider an ideal gas for which \( pV = nRT \). Determine the change in pressure, \( p \), for \( n = 1.0 \) mole of an ideal gas when the temperature, \( T \), is changed from 273.15 K to 274.00 K and the volume, \( V \), is changed from 10.00 L to 9.90 L. The gas constant is \( R = 8.314 \text{ J/(mol K)} \). Express your answer in atmospheres. HINT: Use an expression for the total differential \( dp(T, V) \). Evaluate your partial derivatives at the point \((V_1, T_1)\) with the increments in volume \( dV = (V_2 - V_1) \) and \( dT = (T_2 - T_1) \).

3.16 Suppose \( u(x, y) = x^2 + y + xy^2 \) with \( x(t) = te^{-t} \) and \( y(t) = e^{-t} \). Evaluate

\[ \frac{du}{dt} = \frac{\partial u}{\partial x} \frac{dx}{dt} + \frac{\partial u}{\partial y} \frac{dy}{dt} \]

for the composite function \( u(x(t), y(t)) \).

3.17 Suppose \( u(x, y) = ye^{-x} + xy \) with \( x(s, t) = s^2t \) and \( y(s, t) = e^{-s} + t \). Find \( \frac{\partial u}{\partial s} \) and \( \frac{\partial u}{\partial t} \) where \( u \) is a function of the variables \( s \) and \( t \). HINT: Note that

\[ \frac{\partial u}{\partial s} = \frac{\partial u}{\partial x} \frac{\partial x}{\partial s} + \frac{\partial u}{\partial y} \frac{\partial y}{\partial s} \]

\[ \frac{\partial u}{\partial t} = \frac{\partial u}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial u}{\partial y} \frac{\partial y}{\partial t} \]

3.18 Suppose \( u(x, y) = e^{x+y} \) with \( x(s, t) = t e^s \) and \( y(s, t) = \sin(s) \). Find \( \frac{\partial u}{\partial s} \) and \( \frac{\partial u}{\partial t} \) where \( u \) is a function of \( s \) and \( t \).

3.19 Show that for an ideal gas

\[ \left( \frac{\partial V}{\partial T} \right)_{n,p} = \frac{1}{\left( \frac{\partial T}{\partial V} \right)_{n,p}} \]

3.20 Verify that the following relation is true for an ideal gas

\[ \left( \frac{\partial T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V = -1 \]

This is known as the cyclic rule.
3.21 Use Euler’s test to determine if the following differentials are exact differentials or inexact differentials

(a) \((x^3 + y) \, dx + (y^3 + x) \, dy\)

(b) \(e^{-s} \cosh(t) \, ds - e^{-s} \sinh(t) \, dt\)

(c) \(e^x \cos(y) \, dx - e^y \sin(x) \, dy\)

(d) \(\frac{1}{y} \, dx - \frac{1}{y} \, dy\)

(e) \(\frac{1}{V-b} \, dT + \frac{T}{(V-b)^2} \, dV\)

(f) \(-\frac{2T}{V-b} \, dT + \frac{2}{(V-b)} \, dV\)

3.22 For the exact differential

\(df(x, y) = a(x, y) \, dx + b(x, y) \, dy\)

the following identity follows from Euler’s test

\[
\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y
\]

Now consider the thermodynamic relation

\(dU(S, V) = T \, dS - pdV\)

For this the exact differential, it follows from Euler’s test that

\[
\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V
\]

This identity is known as a **Maxwell relation**.

(a) Starting from \(dH(S, p) = T \, dS + V \, dp\) complete the Maxwell relation

\[
\left(\frac{\partial V}{\partial S}\right)_p =
\]

(b) Starting from \(dA(S, V) = -S \, dT - pdV\) complete the Maxwell relation

\[
\left(\frac{\partial S}{\partial V}\right)_T =
\]

(c) Starting from \(dG(T, p) = -S \, dT + V \, dp\) complete the Maxwell relation

\[
\left(\frac{\partial V}{\partial T}\right)_p =
\]

3.23 For the exact differential

\(df(x, y, z) = a(x, y, z) \, dx + b(x, y, z) \, dy + c(x, y, z) \, dz\)

the following identities follow from Euler’s test

\[
\left(\frac{\partial a}{\partial y}\right)_{x,z} = \left(\frac{\partial b}{\partial x}\right)_{y,z} \quad \left(\frac{\partial b}{\partial z}\right)_{x,y} = \left(\frac{\partial c}{\partial y}\right)_{x,z} \quad \left(\frac{\partial c}{\partial x}\right)_{y,z} = \left(\frac{\partial a}{\partial z}\right)_{x,y}
\]

Now consider the thermodynamic relation

\(dU(S, V, N) = T \, dS - pdV + \mu \, dN\)

For this the exact differential, it follows from Euler’s test that

\[
\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \quad \left(\frac{\partial p}{\partial N}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,N} \quad \left(\frac{\partial \mu}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial N}\right)_{S,V}
\]

These identities are known as **Maxwell relations**.

(a) Starting from \(dH(S, p, N) = T \, dS + V \, dp + \mu \, dN\) complete the Maxwell relation

\[
\left(\frac{\partial V}{\partial S}\right)_{p,N} =
\]
(b) Starting from \( dA(T, V, N) = -SdT - pdV + \mu dN \) complete the Maxwell relation

\[
\left( \frac{\partial S}{\partial N} \right)_{T,V} =
\]

(c) Starting from \( dG(T, p, N) = -SdT + Vdp + \mu dN \) complete the Maxwell relation

\[
\left( \frac{\partial \mu}{\partial T} \right)_{p,N} =
\]

3.24* Consider that the total differential

\[ dU(S, V, N) = TdS - pdV + \mu dN \]

Further consider the function \( G = \mu N = U - TS + pV \). Using your knowledge of exact differentials, derive an expression for \( dG \) and substitute the result for \( dU \) to prove that

\[-SdT + Vdp - Nd\mu = 0\]

This result is known as the Gibbs-Duhem equation.
4 Scalars, vectors, and vector algebra

4.1 Fundamental properties of scalars and vectors

Some physical properties are described by a scalar number with the properties of magnitude and dimension (units). Examples include mass, charge, and energy. Other physical properties must be described by a vector with the properties of magnitude, dimension, and the additional property of direction. Examples include velocity and momentum, and electric and magnetic fields. In this chapter, we explore the basic properties of vectors and vector algebra.

4.1.1 Scalars and vectors in cartesian coordinates

Scalars are numbers that have magnitude and sign. For example, the mass of an electron can be described by the scalar number $m_e = 9.109 \times 10^{-31}$ kg, where the magnitude is $9.109 \times 10^{-31}$ and the dimension is kg. Another example is the charge of an electron expressed by the scalar number $-e = -1.609 \times 10^{-19}$ C, where the magnitude of the charge is the absolute value $| -e | = 1.609 \times 10^{-19}$ C which must be a positive real number.

Vectors are numbers that have magnitude but also direction. Consider the two-dimensional cartesian plane in Figure 4.1. The arrow with its tail at the origin $(0, 0)$ and its head at the point $(v_x, v_y)$ is a vector $v$. It has both magnitude and direction. The magnitude of the vector $|v|$ is the distance between the tail of the vector at the origin $(0, 0)$ and the head of the vector at $(v_x, v_y)$ given by

$$|v| = \sqrt{v_x^2 + v_y^2}$$

as $|v|$ is the length of the hypotenuse of the right triangle with sides $v_x, v_y,$ and $|v|$. The orientation of $v$ is defined in terms of its magnitude in the $x$-direction, $v_x$, and its magnitude in the $y$-direction, $v_y$. To express this mathematically, we define unit vectors in the $x$-direction, $\hat{x}$, and $y$-direction, $\hat{y}$ (see Figure 4.1). The unit vector $\hat{x}$ has its tail at the origin and its head at $(1, 0)$ and the unit vector $\hat{y}$ has its tail at the origin and its head at $(0, 1)$. Vectors with unit magnitude are said to be normalized. Using the unit vectors, we write $v$ in vector notation as

$$v = v_x \hat{x} + v_y \hat{y}$$

where we are literally adding the point $v_x \hat{x} = (v_x, 0)$ to $v_y \hat{y} = (0, v_y)$ to obtain the ordered pair $(v_x, v_y)$.

To represent a vector in a three-dimensional space, we define unit vectors $\hat{x}, \hat{y},$ and $\hat{z}$ oriented along the positive $x$-axis, $y$-axis, and $z$-axis, respectively. An arbitrary vector in three dimensional space with its tail at the origin $(0, 0, 0)$ and its head at a point $(w_x, w_y, w_z)$ can be defined in vector notation as

$$w = w_x \hat{x} + w_y \hat{y} + w_z \hat{z}$$

The magnitude of the vector is defined

$$|w| = \sqrt{w_x^2 + w_y^2 + w_z^2}$$

1 For any vector $a$ with magnitude $|a|$ there is a unit vector $\hat{a} = \frac{1}{|a|}a$ oriented in the direction of $a$ with unit magnitude.

2 There is a variety of notations used for vectors, including $\mathbf{v}$ and $\vec{v}$. The latter notation is commonly used when working with vectors on pen and paper.

3 This algebra should remind you of adding the complex numbers $z_1 = x$ and $z_2 = iy$, represented by the ordered pairs as $z_1 = (x, 0)$ and $z_2 = (0, y)$. Just as $v_x \hat{x} + v_y \hat{y} = (v_x, v_y)$ we have $z_1 + z_2 = (x, y)$. 
An example is shown in Figure 4.2.

Another popular notation for unit vectors along the cartesian axes is \( \hat{x}, \hat{y}, \) and \( \hat{z} \). Using this notation, the vector \( \mathbf{w} \) is written

\[
\mathbf{w} = w_x \hat{x} + w_y \hat{y} + w_z \hat{z}
\]

Physical properties described using vectors include a particle’s position in space, which can be represented as \( \mathbf{r} = x \hat{x} + y \hat{y} + z \hat{z} \). A particle’s linear momentum can be represented as \( \mathbf{p} = p_x \hat{x} + p_y \hat{y} + p_z \hat{z} \). The scalar variables \( x, y, z \) and \( p_x, p_y, p_z \) define the components of position or momentum in the \( x, y, \) and \( z \) directions, respectively. Other physical properties described using vectors include the electric field, \( \mathbf{E} = E_x \hat{x} + E_y \hat{y} + E_z \hat{z} \), and magnetic field, \( \mathbf{B} = B_x \hat{x} + B_y \hat{y} + B_z \hat{z} \). Force is a physical property that has both magnitude and direction that can be written in vector notation as \( \mathbf{F} = F_x \hat{x} + F_y \hat{y} + F_z \hat{z} \). For example, an electric field pointing in the \( z \)-direction with magnitude \( |\mathbf{E}| = E_0 \) can be written \( \mathbf{E} = E_0 \hat{z} \) and a force pointing in the \( x \)-direction with magnitude \( |\mathbf{F}| = F_0 \) can be written \( \mathbf{F} = F_0 \hat{x} \).

### 4.1.2 Addition and subtraction of vectors

Consider two vectors \( \mathbf{v}_1 = x_1 \hat{x} + y_1 \hat{y} \) and \( \mathbf{v}_2 = x_2 \hat{x} + y_2 \hat{y} \) in two-dimensional cartesian space. We add the two vectors by separately adding the \( x \)-components and \( y \)-components, respectively, as

\[
\mathbf{v}_1 + \mathbf{v}_2 = (x_1 + x_2) \hat{x} + (y_1 + y_2) \hat{y}
\]

As shown in Figure 4.3, adding \( \mathbf{v}_1 \) and \( \mathbf{v}_2 \) is equivalent to placing the tail of \( \mathbf{v}_2 \) at the head of \( \mathbf{v}_1 \), or vice versa. The sum does not depend on the order of addition

\[
\mathbf{v}_1 + \mathbf{v}_2 = \mathbf{v}_2 + \mathbf{v}_1 = (x_1 + x_2) \hat{x} + (y_1 + y_2) \hat{y}
\]

which is demonstrated graphically in Figure 4.3.

Considering the subtraction of the vectors \( \mathbf{v}_1 \) and \( \mathbf{v}_2 \), we find the results

\[
\mathbf{v}_1 - \mathbf{v}_2 = (x_1 - x_2) \hat{x} + (y_1 - y_2) \hat{y}
\]

which are represented in Figure 4.4. The difference of two vectors depends on the order of subtraction. Similar rules are followed for adding or subtracting vectors in any dimension. The addition of two vectors \( \mathbf{w}_1 = x_1 \hat{x} + y_1 \hat{y} + z_1 \hat{z} \) and \( \mathbf{w}_2 = x_2 \hat{x} + y_2 \hat{y} + z_2 \hat{z} \) in the three-dimensional cartesian space results in

\[
\mathbf{w}_1 + \mathbf{w}_2 = \mathbf{w}_2 + \mathbf{w}_1 = (x_1 + x_2) \hat{x} + (y_1 + y_2) \hat{y} + (z_1 + z_2) \hat{z}
\]
The process of the addition of the two vectors is represented graphically in Figure 4.5.

4.1.3 Scalar multiplication of vectors

When a vector is multiplied by a scalar number, each component of the vector is multiplied by the same scalar number. Consider the vector

\[ \mathbf{b} = b_x \hat{x} + b_y \hat{y} + b_z \hat{z} \]

If we multiply the vector by the scalar constant \( c \), all of the components of the vector are scaled by the same constant as

\[ c\mathbf{b} = cb_x \hat{x} + cb_y \hat{y} + cb_z \hat{z} \]

The result of scalar multiplication of a vector is shown graphically in Figure 4.6.

Note that the magnitude of the vector \( |\mathbf{b}| = (b_x^2 + b_y^2 + b_z^2)^{1/2} \) is scaled by the absolute value of the scalar constant as

\[ |c\mathbf{b}| = |c| \left( (b_x^2 + b_y^2 + b_z^2)^{1/2} \right) = |c||\mathbf{b}| \]

When the scalar constant is negative, the orientation of the vector is reversed as shown in Figure 4.6.

4.1.4 Representing vectors in other coordinate systems

We found in Chapter 1 that certain functions are most naturally represented in a coordinate system other than cartesian coordinates. For example, the radially dependent coulomb potential energy is most conveniently represented in spherical polar coordinates (see Figure 1.20), while the helical curve is most conveniently represented in cylindrical coordinates (see Figure 1.23). How can we best represent a vector in spherical polar coordinates or cylindrical coordinates?

We can represent any vector in three-dimensional space using the cartesian unit vectors \( \hat{i} \), \( \hat{j} \), and \( \hat{k} \). Suppose we have a vector beginning at the origin and ending at a point \((r, \theta, \phi)\) expressed in spherical polar coordinates. We write

\[ \mathbf{a} = a_x \hat{i} + a_y \hat{j} + a_z \hat{k} \]

where

\[ a_x = r \sin \theta \cos \phi \]
\[ a_y = r \sin \theta \sin \phi \]
\[ a_z = r \cos \theta \]

and conversely

\[ r = \sqrt{a_x^2 + a_y^2 + a_z^2} \]
\[ \theta = \arccos \left( \frac{a_z}{r} \right) = \cos^{-1} \left( \frac{a_z}{r} \right) \]
\[ \phi = \tan^{-1} \left( \frac{a_y}{a_x} \right) \]

For spherical polar coordinates, it is possible to define unit vectors centered at a point \((r, \theta, \phi)\) defining the directions of displacements in the radial distance \((dr)\), inclination \((d\theta)\), and azimuth \((d\phi)\) between points \((r, \theta, \phi)\) to \((r + dr, \theta + \)

---

Figure 4.5: The addition of vectors \( \mathbf{w}_1 \) and \( \mathbf{w}_2 \) leading to vector \( \mathbf{w}_1 + \mathbf{w}_2 \) in the three-dimensional cartesian coordinate system.

Figure 4.6: The multiplication of a vector \( \mathbf{b} \) (red) by a scalar number \( c \) results in a scaled vector \( c\mathbf{b} \), shown for scalar constants \( c = 2 \) (gray) and \( c = -1 \) (black).
70  FUNDAMENTAL PROPERTIES OF SCALARS AND VECTORS

Figure 4.7: A vector \( \mathbf{a} \) represented in the spherical polar coordinate system. The unit vectors \( \hat{r}, \hat{\theta} \) and \( \hat{\phi} \) depend on the coordinates \( \theta \) and \( \varphi \).

\[
\begin{align*}
\hat{r} &= \sin \theta \cos \varphi \hat{x} + \sin \theta \sin \varphi \hat{y} + \cos \theta \hat{z} \\
\hat{\theta} &= \cos \theta \cos \varphi \hat{x} + \cos \theta \sin \varphi \hat{y} - \sin \theta \hat{z} \\
\hat{\phi} &= -\sin \varphi \hat{x} + \cos \varphi \hat{y}
\end{align*}
\]

(4.1) (4.2) (4.3)

as shown in Figure 4.7.

Unlike the cartesian unit vectors that are independent of the magnitude and orientation of the vector \( \mathbf{a} \), the unit vectors \( \hat{r}, \hat{\theta}, \) and \( \hat{\phi} \) depend on the position \( (r, \theta, \varphi) \). As the magnitude or orientation of the vector \( \mathbf{a} \) changes, so will the orientation of the unit vectors. For this reason, when we describe a vector in three-dimensional space in spherical polar coordinates we do so using the cartesian unit vectors as

\[
\begin{align*}
\mathbf{a} &= a_x \hat{i} + a_y \hat{j} + a_z \hat{k} \\
&= r \sin \theta \cos \varphi \hat{i} + r \sin \theta \sin \varphi \hat{j} + r \cos \theta \hat{k}
\end{align*}
\]

We define the unit vectors describing the direction of displacements in the

\[
\begin{align*}
a_x &= r \cos \theta \\
a_y &= r \sin \theta \\
a_z &= z
\end{align*}
\]

or conversely

\[
\begin{align*}
r &= \sqrt{a_x^2 + a_y^2} \\
\theta &= \arctan \left( \frac{a_y}{a_x} \right) = \tan^{-1} \left( \frac{a_y}{a_x} \right) \\
z &= a_z
\end{align*}
\]

We draw the same conclusions for a vector \( \mathbf{a} \) expressed in cylindrical coordinates \( (r, \theta, z) \). Using the cartesian unit vectors \( \hat{i}, \hat{j}, \) and \( \hat{k} \) we write

\[
\begin{align*}
\mathbf{a} &= a_x \hat{i} + a_y \hat{j} + a_z \hat{k}
\end{align*}
\]

We define the unit vectors describing the direction of displacements in the

\[
\begin{align*}
\hat{r} &= \sin \theta \cos \varphi \hat{x} + \sin \theta \sin \varphi \hat{y} + \cos \theta \hat{z} \\
\hat{\theta} &= \cos \theta \cos \varphi \hat{x} + \cos \theta \sin \varphi \hat{y} - \sin \theta \hat{z} \\
\hat{\phi} &= -\sin \varphi \hat{x} + \cos \varphi \hat{y}
\end{align*}
\]

(4.1) (4.2) (4.3)
radial distance $r$, azimuth, $\theta$, and elevation $z$ as

$$\hat{r} = \cos \theta \hat{x} + \sin \theta \hat{y}$$
$$\hat{\theta} = -\sin \theta \hat{x} + \cos \theta \hat{y}$$
$$\hat{z} = \hat{z}$$  \hspace{1cm} (4.4)

as shown in Figure 4.8. As in the case of the unit vectors $\hat{r}$, $\hat{\theta}$, and $\hat{\phi}$ in spherical polar coordinates, the unit vectors $\hat{r}$ and $\hat{\theta}$ depend on the coordinates $(r, \theta, z)$. However, the unit vector $\hat{z}$ is independent of the position $(r, \theta, z)$.

### 4.2 Multiplication of vectors

There are two ways to multiply two vectors, one resulting in a scalar number and the other resulting in a vector. Both methods of vector multiplication are widely used in the physical sciences. We convert the momentum (a vector) into kinetic energy (a scalar) using the scalar product. For a mass moving in a circular orbit, we convert its velocity (a vector) and radial position (a vector) into its angular momentum (a vector) using the vector product. The properties of the scalar and vector products are explored in this section.

#### 4.2.1 Multiplying vectors and the scalar dot product

The multiplication of the two vectors $v = v_x \hat{i} + v_y \hat{j} + v_z \hat{k}$ and $w = w_x \hat{i} + w_y \hat{j} + w_z \hat{k}$ by the scalar product is defined

$$v \cdot w = v_x w_x + v_y w_y + v_z w_z$$  \hspace{1cm} (4.5)

formed by a sum of products of each vector’s scalar coefficients. This is referred to as a dot product and pronounced $v$ dot $w$. The dot product is commutative as $v \cdot w = w \cdot v$. Taking the dot product of a vector with itself leads to

$$v \cdot v = v_x^2 + v_y^2 + v_z^2 = |v|^2$$

which is the square of the magnitude of the vector. Furthermore, if we multiply the vector $v$ by a scalar constant $c$ and take the dot product of $cv$ and $w$ we find

$$(cv) \cdot w = (cv_x)w_x + (cv_y)w_y + (cv_z)w_z = c (v \cdot w)$$

demonstrating that scalar constants can be pulled out of dot products.

The dot product can also be written

$$v \cdot w = |v||w| \cos \theta$$  \hspace{1cm} (4.6)

where $\theta$ is the angle between the two vectors (see Figure 4.9). Note that if the two vectors are perpendicular the angle $\theta = \pi/2$ and $v \cdot w = 0$. In the later case, we say that the vectors are orthogonal. If the two vectors are parallel the angle $\theta = 0$ and $v \cdot w = |v||w|$. That is the case for the dot product of a vector and itself as $v \cdot v = |v|^2$.

#### 4.2.2 Geometric interpretation of the dot product

Let’s explore graphically the dot product between two vectors $v$ and $w$ (see Figure 4.10). We can interpret $v \cdot w = |v||w| \cos \theta$ in two ways. We can write

$$v \cdot w = (|v| \cos \theta) |w| = v_w |w|$$

where $v_w = |v| \cos \theta$ is the magnitude of the vector $v$ projected onto the unit vector $\hat{w} = w/|w|$ as shown in the Figure 4.10. We can write this vector projection...
of $\mathbf{v}$ onto $\hat{w}$ as

$$v_w = \mathbf{v} \cdot \hat{w} = \mathbf{v} \cdot \left( \frac{1}{|\mathbf{w}|} \mathbf{w} \right) = \frac{1}{|\mathbf{w}|} (\mathbf{v} \cdot \mathbf{w}) = \frac{1}{|\mathbf{w}|} |\mathbf{v}| |\mathbf{w}| \cos \theta = |\mathbf{v}| \cos \theta$$

Equivalently, we can write

$$\mathbf{v} \cdot \mathbf{w} = |\mathbf{v}| (|\mathbf{w}| \cos \theta) = |\mathbf{v}| \mathbf{w}_p$$

where $w_p = |\mathbf{w}| \cos \theta$ is the magnitude of the vector $\mathbf{w}$ projected onto the unit vector $\hat{w} = \mathbf{v}/|\mathbf{v}|$.

$$\mathbf{w}_p = \mathbf{w} \cdot \hat{w} = \mathbf{w} \cdot \left( \frac{1}{|\mathbf{v}|} \mathbf{v} \right) = \frac{1}{|\mathbf{v}|} (\mathbf{w} \cdot \mathbf{v}) = \frac{1}{|\mathbf{v}|} |\mathbf{w}| |\mathbf{v}| \cos \theta = |\mathbf{v}| \cos \theta$$

The dot product $\mathbf{v} \cdot \mathbf{w}$ can be considered the projection of $\mathbf{v}$ onto $\mathbf{w}$ or equivalently the projection of $\mathbf{w}$ onto $\mathbf{v}$. The dot product $\mathbf{v} \cdot \mathbf{w} = |\mathbf{v}|w_p = v_w |\mathbf{w}|$ varies from a maximum of $|\mathbf{v}| |\mathbf{w}|$, when the vectors are parallel ($v_w = |\mathbf{v}|$ and $w_p = |\mathbf{w}|$), to a minimum of $-|\mathbf{v}| |\mathbf{w}|$ when the vectors are antiparallel ($v_w = -|\mathbf{v}|$ and $w_p = -|\mathbf{w}|$). When the vectors are perpendicular $|\mathbf{v}| |\mathbf{w}| = 0$ as $v_w = w_p = 0$. This interpretation of the dot product as a vector projection is valuable when applying the dot product to model physical processes.\(^4\)

### 4.2.3 Vector projection in general

The vector projection is valuable in expressing arbitrary vectors in terms of the $x$, $y$, and $z$-components. Consider the unit vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$. Each unit vector is parallel to itself so that $\hat{x} \cdot \hat{x} = \hat{y} \cdot \hat{y} = \hat{z} \cdot \hat{z} = 1$. Each unit vector is orthogonal to the other two unit vectors so that $\hat{x} \cdot \hat{y} = \hat{y} \cdot \hat{z} = \hat{z} \cdot \hat{x} = 0$.

We can define the $x$-component of an arbitrary vector $\mathbf{v}$ as $v_x = \mathbf{v} \cdot \hat{x}$ with similar relations for the $y$-component, $v_y = \mathbf{v} \cdot \hat{y}$, and $z$-component, $v_z = \mathbf{v} \cdot \hat{z}$. As such, we can express any vector $\mathbf{v}$ as

$$\mathbf{v} = (\mathbf{v} \cdot \hat{x}) \hat{x} + (\mathbf{v} \cdot \hat{y}) \hat{y} + (\mathbf{v} \cdot \hat{z}) \hat{z}$$

$$= v_x \hat{x} + v_y \hat{y} + v_z \hat{z}$$

This identity is valuable when we are given an arbitrary vector that we wish to express in the cartesian coordinate system. An example of the decomposition of a vector into its cartesian components is shown in Figure 4.11.

Similar relations can be used to decompose the vector $\mathbf{v}$ in spherical polar coordinates

$$\mathbf{v} = (\mathbf{v} \cdot \hat{r}) \hat{r} + (\mathbf{v} \cdot \hat{\theta}) \hat{\theta} + (\mathbf{v} \cdot \hat{\phi}) \hat{\phi}$$

$$= v_r \hat{r} + v_\theta \hat{\theta} + v_\phi \hat{\phi}$$

and in cylindrical coordinates

$$\mathbf{v} = (\mathbf{v} \cdot \hat{r}) \hat{r} + (\mathbf{v} \cdot \hat{\theta}) \hat{\theta} + (\mathbf{v} \cdot \hat{z}) \hat{z}$$

$$= v_r \hat{r} + v_\theta \hat{\theta} + v_z \hat{z}$$

We must keep in mind, however, that the unit vectors $\hat{r}$, $\hat{\theta}$, and $\hat{\phi}$ are coordinate dependent.

### 4.2.4 Application of the dot product

As an example of the utility of the dot product in the physical sciences, consider the mechanical work done when a force acts over a distance. The work is a scalar $w$. The force has magnitude and direction and is expressed as a vector $\mathbf{f} = f_x \hat{x} + f_y \hat{y} + f_z \hat{z}$ as is the distance $\mathbf{d} = d_x \hat{x} + d_y \hat{y} + d_z \hat{z}$. The work is
defined as the dot product of the force and distance
\[ w = f \cdot d = f_x d_x + f_y d_y + f_z d_z = |f| |d| \cos \theta \]
where \( \theta \) is the angle between the force \( f \) and displacement \( d \). When the displacement is perfectly in line with the force, \( \theta = 0 \), and \( w = |f| |d| \) and the maximum work is done. When the displacement is perpendicular to the force, \( \theta = \pi/2 \), \( w = 0 \) and no work is done.\(^5\)

Now consider the energy of an electric dipole \( \mu \) interacting with an electric field \( E \), each characterized by a magnitude and orientation as shown in Figure 4.12. The energy is a scalar \( V = -\mu \cdot E \). Suppose that the electric field is oriented in the \( z \)-direction with magnitude \( E_0 \). The electric field vector is written \( E = E_0 \hat{z} \). If the electric dipole is \( \mu = \mu_y \hat{y} + \mu_z \hat{z} \) the energy of interaction is
\[ V = -E \cdot \mu = -E_0 \mu_z \]. In general for an electric field \( E = E_x \hat{x} + E_y \hat{y} + E_z \hat{z} \) and electric dipole \( \mu = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z} \) the interaction energy is
\[ V(\theta) = -E \cdot \mu = -|E||\mu| \cos \theta \]
where \( \theta \) is the angle between the electric field and the electric dipole as shown in Figure 4.12.

The variation in the potential energy described by the dot product over a range of \( \theta \) is shown in Figure 4.13. When the vectors \( \mu \) and \( E \) are parallel \( (\theta = 0, 2\pi) \), \( V = -|E||\mu| \) is a minimum. When the vectors \( \mu \) and \( E \) are antiparallel \( (\theta = \pi) \), \( V = |E||\mu| \) is a maximum. When the vectors are perpendicular \( (\theta = \pi/2, 3\pi/2) \) we find \( V = 0 \).

### 4.2.5 Multiplying vectors and the vector cross product

Consider the vectors \( \mathbf{v} = v_x \hat{i} + v_y \hat{j} + v_z \hat{k} \) and \( \mathbf{w} = w_x \hat{i} + w_y \hat{j} + w_z \hat{k} \). We can multiply \( \mathbf{v} \) and \( \mathbf{w} \) by taking the product of the magnitude of each vector as \( |\mathbf{v}||\mathbf{w}| \). We can also multiply \( \mathbf{v} \) and \( \mathbf{w} \) using the dot product \( \mathbf{v} \cdot \mathbf{w} = |\mathbf{v}||\mathbf{w}| \cos \theta \)
resulting in a scalar. A third way to multiply \( \mathbf{v} \) and \( \mathbf{w} \) is the vector product written \( \mathbf{v} \times \mathbf{w} \) and defined as\(^6\)
\[ \mathbf{v} \times \mathbf{w} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ v_x & v_y & v_z \\ w_x & w_y & w_z \end{vmatrix} \]
and resulting in a vector. This is also referred to as a cross product and pronounced \( \mathbf{v} \) cross \( \mathbf{w} \). An example of a cross product between two vectors \( \mathbf{v} \) and \( \mathbf{w} \) is shown in Figure 4.14. In this example, the vectors \( \mathbf{v} \) and \( \mathbf{w} \) are found in the \( xy \)-plane and the cross product \( \mathbf{v} \times \mathbf{w} \) is in the direction of the positive \( z \)-axis.

A bit of algebra can be used to demonstrate that the magnitude of the vector cross product is related to the alternative scalar products \( |\mathbf{v}||\mathbf{w}| \) and \( \mathbf{v} \cdot \mathbf{w} \) by
\[ |\mathbf{v} \times \mathbf{w}|^2 = |\mathbf{v}|^2 |\mathbf{w}|^2 - (\mathbf{v} \cdot \mathbf{w})^2 \]
Since \( |\mathbf{v} \cdot \mathbf{w}| = |\mathbf{v}||\mathbf{w}| \cos \theta \) it follows from the identity \( 1 - \cos^2 \theta = \sin^2 \theta \) that
\[ |\mathbf{v} \times \mathbf{w}| = |\mathbf{v}||\mathbf{w}| \sin \theta \]
which is the magnitude of the shaded area in Figure 4.14. The magnitude of the cross product is equal to the area of the parallelogram defined by the two vectors in the plane containing those vectors.

Note that if the two vectors are parallel the angle \( \theta = 0 \) and \( |\mathbf{v} \times \mathbf{w}| = 0 \). That is the case for the cross product of a vector and itself as \( |\mathbf{v} \times \mathbf{v}| = 0 \). If the two vectors are orthogonal the angle \( \theta = \pi/2 \) and \( |\mathbf{v} \times \mathbf{w}| = |\mathbf{v}||\mathbf{w}| \), which is the largest possible magnitude of the cross product. In practice, the dot product and Equation 4.6 provide the most convenient way to determine the angle between two vectors.

\(^5\) For example, in circular motion the inward pointing centripetal force is perpendicular to the direction of motion. The centripetal force changes the direction of motion but does no work.

\(^6\) Vector multiplication was discovered independently by American physicist, chemist, and mathematician Josiah Willard Gibbs (1839–1903) and English physicist and engineer Oliver Heaviside (1850–1925). Gibbs developed the modern field of statistical mechanics and is often considered, along with Benjamin Franklin (1706–1790), to be one of the two greatest American scientists.
4.2.6 Getting the direction of the cross product right

The cross product defined in Equation 4.7 can also be written as
\[ \mathbf{v} \times \mathbf{w} = |\mathbf{v}| |\mathbf{w}| \hat{n} \sin \theta \]
where \( \theta \) is the angle between the two vectors and \( \hat{n} \) is a unit vector that is normal to the plane containing the vectors \( \mathbf{v} \) and \( \mathbf{w} \) (see Figure 4.14).

It is standard convention to restrict \( \theta \in [0, \pi] \) so that \( 0 \leq \sin \theta \leq 1 \) with the direction of the unit vector \( \hat{n} \) being determined by the right hand rule stated:

1. point the index finger of your right hand along vector \( \mathbf{v} \)
2. point the middle finger of your right hand along vector \( \mathbf{w} \)
3. your thumb points in the direction of the cross product \( \mathbf{v} \times \mathbf{w} \)

Apply the right hand rule to determine the direction of the cross product taken between the vectors \( \mathbf{v} \) and \( \mathbf{w} \) in Figure 4.14. The vectors are found in the \( xy \)-plane so that the cross product \( \mathbf{v} \times \mathbf{w} \) will be orthogonal to the \( xy \)-plane directed along the positive or negative \( z \)-axis. You should find that the right hand rule dictates that the unit vector \( \hat{n} = \hat{z} \) is in the direction of the positive \( z \)-axis.\(^7\)

After you succeed, try your hand at determining the direction of the cross product \( \mathbf{a} \times \mathbf{b} \) shown in Figure 4.15. In this case, the relative orientation of the two vectors leads to a direction of the cross product defined by \( \hat{n} = -\hat{z} \). Finally, apply the right hand rule to the vector product shown in Figure 4.16. These examples should prepare you well for the application of the right hand rule in the calculation of vector products.

4.2.7 Properties of the cross product and its efficient calculation

The cross product is anticommutative as
\[ \mathbf{v} \times \mathbf{w} = (v_yw_z - v_zw_y) \mathbf{i} + (v_zw_x - v_xw_z) \mathbf{j} + (v_xw_y - v_yw_x) \mathbf{k} \]
\[ = -(w_yv_z - w_zv_y) \mathbf{i} - (w_zv_x - w_xv_z) \mathbf{j} - (w_xv_y - w_yv_x) \mathbf{k} \]
\[ = -\mathbf{w} \times \mathbf{v} \]

Furthermore, if we multiply the vector \( \mathbf{v} \) by a scalar constant \( c \) and take the cross product of \( c\mathbf{v} \) and \( \mathbf{w} \) we find
\[ (c\mathbf{v}) \times \mathbf{w} = ((cv_y)w_z - (cv_z)w_y) \mathbf{i} + ((cv_z)w_x - (cv_x)w_z) \mathbf{j} + ((cv_x)w_y - (cv_y)w_x) \mathbf{k} \]
\[ = c(v_yw_z - v_zw_y) \mathbf{i} + c(v_zw_x - v_xw_z) \mathbf{j} + c(v_xw_y - v_yw_x) \mathbf{k} = c(\mathbf{v} \times \mathbf{w}) \]

demonstrating that scalar constants can be pulled out of cross products.

The expression Equation 4.7 defining the cross product is rather long. In calculating a cross product, it is easy to get vector indices confused or the order of operations wrong. To avoid these difficulties, it is convenient to represent the cross product as a determinant. First consider the definition of the \( 2 \times 2 \) determinant
\[ \begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} = a_1b_2 - a_2b_1 \]

A \( 3 \times 3 \) determinant can be evaluated in terms of three \( 2 \times 2 \) determinants as
\[ \begin{vmatrix} c_1 & c_2 & c_3 \\ a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \end{vmatrix} = c_1 \begin{vmatrix} a_2 & a_3 \\ b_2 & b_3 \end{vmatrix} - c_2 \begin{vmatrix} a_1 & a_3 \\ b_1 & b_3 \end{vmatrix} + c_3 \begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} \]
With this result we can express our cross product conveniently using the determinant

$$
v \times w = \begin{vmatrix}
\hat{i} & \hat{j} & \hat{k} \\
v_x & v_y & v_z \\
w_x & w_y & w_z
\end{vmatrix}
$$

Evaluating the three $2 \times 2$ determinants leads to our original result in Equation 4.7

$$v \times w = \left( v_y w_z - v_z w_y \right) \hat{i} + \left( v_z w_x - v_x w_z \right) \hat{j} + \left( v_x w_y - v_y w_x \right) \hat{k}$$

We will return to the use of determinants in the future. It is good to gain practice now evaluating determinants in the calculation of vector products.

### 4.2.8 Geometric interpretation of the cross product

Let’s explore the magnitude of the vector product $v \times w$ and its dependence on the relative orientation of the vectors $v$ and $w$ graphically (see Figure 4.17). In the case of the scalar product we found

$$v \cdot w = v_{\parallel} w_{\parallel} = |v| |w|$$

where $v_{\parallel}$ is the component of $v$ that is parallel to $w$ and $w_{\parallel}$ is the component of $w$ that is parallel to $v$. In the case of the cross product we find the complementary result

$$|v \times w| = v_{\perp} |w| = |v| w_{\perp}$$

where $v_{\perp}$ is the component of $v$ that is perpendicular to $w$ and $w_{\perp}$ is the component of $w$ that is perpendicular to $v$.

From these relations we see that the magnitude of the vector product is the area of the parallelogram defined by the vectors $v$ and $w$. This is shown as the shaded region in Figure 4.17. This geometric interpretation of the magnitude of the cross product is useful in considering the magnitude of cross products representing physical processes. The area of the parallelogram is greatest when $v$ is orthogonal to $w$ (the vectors form a rectangle of area $|v||w|$) and a minimum when the two vectors are parallel (the area is zero).

Let’s end our discussion of vector projection by considering the unit vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$. Each unit vector is parallel to itself so that

$$\hat{x} \times \hat{x} = \hat{y} \times \hat{y} = \hat{z} \times \hat{z} = 0$$

Each unit vector is orthogonal to the other two unit vectors leading to the identities

$$\hat{x} \times \hat{y} = \hat{z} \quad \hat{y} \times \hat{z} = \hat{x} \quad \hat{z} \times \hat{x} = \hat{y}$$

By the anticommutation relation $v \times w = -w \times v$ we find $\hat{y} \times \hat{x} = -\hat{z}$, $\hat{z} \times \hat{y} = -\hat{x}$ and $\hat{x} \times \hat{z} = -\hat{y}$.

### 4.2.9 Application of the cross product

The cross product is used to express a number of fundamental physical properties. Consider the angular momentum defined in terms of the radial distance from the center of motion $r$ and the linear momentum $p = mv$ as

$$L = r \times p$$
where \( m \) is the particle mass and \( \mathbf{v} \) is the velocity. Writing the radial position as \( \mathbf{r} = x \mathbf{i} + y \mathbf{j} + z \mathbf{k} \) and the linear momentum \( \mathbf{p} = p_x \mathbf{i} + p_y \mathbf{j} + p_z \mathbf{k} \) the resulting angular momentum is

\[
\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix}
\mathbf{i} & \mathbf{j} & \mathbf{k} \\
x & y & z \\
p_x & p_y & p_z
\end{vmatrix}
= (yp_z - zp_y) \mathbf{i} + (zp_x - xp_z) \mathbf{j} + (xp_y - yp_x) \mathbf{k}
\]

As an example, consider clockwise circular motion of a mass, \( m \), in the \( xy \)-plane. The velocity \( \mathbf{v} \) of the mass is tangent to the circular trajectory and orthogonal to the radial vector \( \mathbf{r} \) with \( \theta = \pi/2 \). This creates a maximum magnitude of the angular momentum oriented in the negative \( z \)-direction \( \mathbf{l} = m (\mathbf{r} \times \mathbf{v}) = -m |\mathbf{r}| |\mathbf{v}| \mathbf{\hat z} \). This result is depicted in Figure 4.18 where the area of the shaded region is the magnitude of the vector product.

Now consider a particle of mass \( m \) with charge \( q \) moving with a velocity \( \mathbf{v} = v_x \mathbf{i} + v_y \mathbf{j} + v_z \mathbf{k} \) in an external magnetic field \( \mathbf{B} = B_x \mathbf{i} + B_y \mathbf{j} + B_z \mathbf{k} \). A force \( \mathbf{F} \) acts on the particle with magnitude and orientation defined by

\[
\mathbf{F} = q (\mathbf{v} \times \mathbf{B})
\]

This force appears almost mysteriously as it is oriented perpendicular to both the direction of motion and the magnetic field. Consider a charge \( q \) that is moving in the \( x \)-direction with a velocity \( \mathbf{v} = v_x \mathbf{\hat x} \) in the presence of a magnetic field \( \mathbf{B} = B_0 \mathbf{\hat z} \) oriented along the \( z \)-axis. The force acting on the charge will be

\[
\mathbf{F} = q (\mathbf{v} \times \mathbf{B}) = q [(v_x \mathbf{\hat x}) \times (B_0 \mathbf{\hat z})] = q \begin{vmatrix}
\mathbf{\hat x} & \mathbf{\hat y} & \mathbf{\hat z} \\
v_x & 0 & 0 \\
0 & 0 & B_0
\end{vmatrix}
= -qv_x B_0 \mathbf{\hat y}
\]

where the direction is determined by \( \mathbf{\hat x} \times \mathbf{\hat z} = -\mathbf{\hat y} \).

In general, when the motion of the charge is parallel to the magnetic field the force is zero. The greatest force occurs when the motion of the charge is perpendicular to the magnetic field. The direction of the force is determined by the angle between the two vectors and can be determined qualitatively by application of the right hand rule. The variation in the cross product over a range of \( \theta \) is shown in Figure 4.19.
Warm-ups

4.1 Determine the magnitude, |\( \mathbf{a} \)|, and direction, in terms of \( \theta \) in two dimensions and \( \theta \) and \( \varphi \) in three dimensions, of the following vectors.

- (a) \( \mathbf{a} = \hat{x} + 3\hat{y} \)
- (b) \( \mathbf{a} = 2\hat{x} - 2\hat{y} \)
- (c) \( \mathbf{a} = -3\hat{x} + 2\hat{y} \)
- (d) \( \mathbf{a} = -2\hat{x} + 2\hat{z} \)
- (e) \( \mathbf{a} = -\hat{x} - 5\hat{y} + 3\hat{z} \)
- (f) \( \mathbf{a} = \hat{x} + \hat{y} + 3\hat{z} \)

4.2 For each of the following sums \( \mathbf{c} = \mathbf{a} + \mathbf{b} \) determine the magnitude, |\( \mathbf{c} \)|, and direction, in terms of \( \theta \) in two dimensions and \( \theta \) and \( \varphi \) in three dimensions, of the resulting vector.

- (a) \( \mathbf{a} = \hat{x} + 3\hat{y} \quad \mathbf{b} = 3\hat{x} + \hat{y} \)
- (b) \( \mathbf{a} = -\hat{x} + 2\hat{y} \quad \mathbf{b} = 2\hat{x} + 2\hat{y} \)
- (c) \( \mathbf{a} = -2\hat{x} + 3\hat{y} \quad \mathbf{b} = -\hat{x} - 4\hat{y} - 6\hat{z} \)
- (d) \( \mathbf{a} = 2\hat{x} + 3\hat{z} \quad \mathbf{b} = -3\hat{x} + 6\hat{y} - 9\hat{z} \)

4.3 Determine the scalar number resulting from the following dot products \( \mathbf{a} \cdot \mathbf{b} \).

- (a) \( \mathbf{a} = \hat{x} + 4\hat{y} \quad \mathbf{b} = 4\hat{x} + \hat{y} \)
- (b) \( \mathbf{a} = -\hat{x} + 2\hat{y} \quad \mathbf{b} = 2\hat{x} + 2\hat{y} \)
- (c) \( \mathbf{a} = 3\hat{y} + 2\hat{z} \quad \mathbf{b} = -\hat{x} - 4\hat{y} - 6\hat{z} \)
- (d) \( \mathbf{a} = -2\hat{x} + 3\hat{z} \quad \mathbf{b} = -3\hat{x} + 6\hat{y} - 9\hat{z} \)

4.4 For each of the following vector products \( \mathbf{c} = \mathbf{a} \times \mathbf{b} \) determine the magnitude, |\( \mathbf{c} \)|, and direction, in terms of \( \theta \) in two dimensions and \( \theta \) and \( \varphi \) in three dimensions, of the resulting vector.

- (a) \( \mathbf{a} = 2\hat{x} + 3\hat{y} \quad \mathbf{b} = 3\hat{x} + 2\hat{y} \)
- (b) \( \mathbf{a} = -\hat{x} + 2\hat{y} \quad \mathbf{b} = 2\hat{x} - 2\hat{y} \)
- (c) \( \mathbf{a} = -2\hat{x} + 4\hat{z} \quad \mathbf{b} = \hat{x} - 4\hat{y} - 5\hat{z} \)
- (d) \( \mathbf{a} = 2\hat{x} + 3\hat{z} \quad \mathbf{b} = -3\hat{x} + 6\hat{y} \)

Homework exercises

4.5 Use the dot product relation \( \mathbf{a} \cdot \mathbf{b} = |\mathbf{a}| |\mathbf{b}| \cos \theta \) to determine the angle \( \theta \) between the following vectors.

- (a) \( \mathbf{a} = 3\hat{x} - \hat{y} \quad \mathbf{b} = 4\hat{y} \)
- (b) \( \mathbf{a} = \hat{x} + \hat{y} + \hat{z} \quad \mathbf{b} = 2\hat{x} + 3\hat{y} + 4\hat{z} \)

4.6 Use the cross product relation \( |\mathbf{a} \times \mathbf{b}| = |\mathbf{a}| |\mathbf{b}| \sin \theta \) to determine the angle \( \theta \) between the following vectors.

- (a) \( \mathbf{a} = 3\hat{x} - \hat{y} \quad \mathbf{b} = 4\hat{y} \)
- (b) \( \mathbf{a} = \hat{x} + \hat{y} + \hat{z} \quad \mathbf{b} = 2\hat{x} + 3\hat{y} + 4\hat{z} \)

4.7 Show that scalar multiplication is commutative and vector multiplication is not. That is, show for \( \mathbf{a} = a_x\hat{x} + a_y\hat{y} + a_z\hat{z} \) and \( \mathbf{b} = b_x\hat{x} + b_y\hat{y} + b_z\hat{z} \) that

\[
\mathbf{a} \cdot \mathbf{b} = \mathbf{b} \cdot \mathbf{a}
\]

but

\[
\mathbf{a} \times \mathbf{b} \neq \mathbf{b} \times \mathbf{a}
\]

4.8 Show that \( \mathbf{a} \cdot \mathbf{a} = |\mathbf{a}|^2 \)

4.9 Show that

\[
\mathbf{a} + (\mathbf{b} + \mathbf{c}) = (\mathbf{a} + \mathbf{b}) + \mathbf{c}
\]
4.10* Show that
\[ a \cdot (b \times c) = b \cdot (c \times a) = c \cdot (a \times b) \]

4.11* Show that
\[ a \times (b \times c) = (a \cdot c)b - (a \cdot b)c \]

4.12* Show that
\[ (a \times b) \cdot (c \times d) = (a \cdot c)(b \cdot d) - (a \cdot d)(b \cdot c) \]

4.13 Angular momentum is given by the equation \( l = r \times p \), where \( r = x \mathbf{i} + y \mathbf{j} + z \mathbf{k} \) is the radius of curvature of the motion and \( p = p_x \mathbf{i} + p_y \mathbf{j} + p_z \mathbf{k} \) is the linear momentum of the body in motion. Assuming that \( l = l_x \mathbf{i} + l_y \mathbf{j} + l_z \mathbf{k} \)
find the components of the angular momentum in the \( x \), \( y \), and \( z \) directions.

4.14 Consider the three vectors \( a = 2\mathbf{i} + \mathbf{j}, b = -\mathbf{i} + \mathbf{j} \) and \( c = \mathbf{i} + \mathbf{j} + 3\mathbf{k} \) shown in the figure below.

The volume of the shaded parallelepiped is given by the *scalar triple product*
\[ V = a \times b \cdot c \]
where \(|a \times b|\) is the area of the base of the parallelepiped (shaded blue) in the \( xy \)-plane and \(|c| \cos \varphi\) is the parallelepiped’s altitude. Determine the volume \( V \).

4.15 Show that the vectors \( a = \frac{1}{2}q_1 + \frac{1}{2}q_2 + \frac{1}{2}q_3 + \frac{1}{2}q_4 \) and \( b = \frac{1}{2}q_1 - \frac{1}{2}q_2 + \frac{1}{2}q_3 - \frac{1}{2}q_4 \), where \( q_1, q_2, q_3, \) and \( q_4 \) are orthogonal unit vectors, are orthogonal and normalized.

4.16 For a particle of charge, \( q \), moving with velocity, \( v \), in an external electric field, \( E \), and magnetic field, \( B \), the force acting on the particle is the Lorentz force defined
\[ F = q (E + v \times B) \]
Suppose a particle of mass, \( m \), and charge, \( q \), is moving with velocity \( v = v_z \mathbf{k} \) in the presence of an electric field \( E = E_x \mathbf{i} + E_y \mathbf{j} \) and magnetic field \( B = B_x \mathbf{i} \). Determine the total Lorentz force, \( F \), acting on the particle.

4.17 Consider a particle of mass, \( m \), moving on a circle of radius, \( r_0 \), with velocity
\[ v = v_x \mathbf{i} + v_y \mathbf{j} \]
at a position $r = r_x \hat{i} + r_y \hat{j}$ where $r_0 = \sqrt{r_x^2 + r_y^2}$. Determine the angular momentum of the particle

$$l = r \times p$$

where the momentum, $p = mv$.

4.18 For an electric dipole, $\mu = \mu_E \hat{j}$, in an external electric field, $E = E_x \hat{i} + E_y \hat{j}$, determine the energy defined

$$V = -\mu \cdot E$$

4.19 For a magnetic dipole, $\mu = \mu_B \hat{i}$, in an external magnetic field, $B = B_z \hat{k}$, determine the torque on the magnetic dipole defined

$$T = -\mu \times B$$
5 Scalar and vector operators

5.1 Scalar operators

Mathematical operations transform one function into another. Examples of mathematical operations include multiplying a function by a constant or taking the derivative of a function. The mathematical symbol or function that carries out the operation is known as an operator. In this section, we explore a variety of types of operators in action so that we understand the concept and its utility.

5.1.1 Operators transform one function into another

An operator transforms one mathematical function into another. Consider the scalar operator $\hat{A}$ acting on a function $f(x)$ as

$$\hat{A}f(x) = 2f(x)$$

The operator $\hat{A}$ acts on the function $f(x)$ multiplying the function by the scalar number 2. Alternatively, we might define an operator $\hat{B}$ that acts to square the function it operates on as

$$\hat{B}f(x, y) = (f(x, y))^2$$

The operator $\hat{A}$ is called a linear operator as (1) its action is distributed over the sum of two functions as

$$\hat{A}(f(x) + g(x)) = \hat{A}f(x) + \hat{A}g(x)$$

and (2) it acts on a scalar $c$ times a function as

$$\hat{A}(cf(x))) = c\hat{A}f(x)$$

The operator $\hat{B}$ is not a linear operator since

$$\hat{B}(f(x) + g(x)) = f^2(x) + 2f(x)g(x) + g^2(x)$$

$$\neq \hat{B}f(x) + \hat{B}g(x) = f^2(x) + g^2(x)$$

and

$$\hat{B}(cf(x))) = c^2f^2(x) \neq c\hat{B}f(x) = cf^2(x)$$

The majority of operators of importance in modeling physical processes are linear operators. The concept of the operator may seem abstract when we consider the operator on its own. However, the operator only has value when acting on a function. As such, it is often best to view the operator in action, acting on a function, so that its nature and practical significance are clear.
orientation in space. In applications to physical systems, the most commonly used operators are differential operators and rotational operators. Differential and rotational operators are fundamental to quantum theory and the evaluation of symmetry.

5.1.2 Algebra of differential operators

Let’s explore how the derivative can be expressed using the idea of the operator. Consider the partial derivative of a function

$$\frac{\partial}{\partial x}f(x,y) = f_x(x,y)$$

We can identify

$$\hat{d}_x = \frac{\partial}{\partial x}$$

as a differential operator acting on the function $f(x,y)$ as

$$\hat{d}_x f(x,y) = \frac{\partial}{\partial x}(f(x,y)) = f_x(x,y)$$

We can similarly define the operator $\hat{d}_y$ as

$$\hat{d}_y f(x,y) = \frac{\partial}{\partial y}(f(x,y)) = f_y(x,y)$$

This differential operator is a linear operator as

$$\hat{d}_x (f(x,y) + g(x,y)) = \frac{\partial}{\partial x}(f(x,y) + g(x,y)) = \frac{\partial}{\partial x}f(x,y) + \frac{\partial}{\partial x}g(x,y)$$

$$= \hat{d}_x f(x,y) + \hat{d}_x g(x,y)$$

and

$$\hat{d}_x (c f(x,y)) = \frac{\partial}{\partial x}(c f(x,y)) = c \frac{\partial}{\partial x}f(x,y) = c\hat{d}_x f(x,y)$$

Operators can act sequentially on a function as

$$\hat{d}_y \hat{d}_x f(x,y) = \frac{\partial}{\partial y} \left( \frac{\partial}{\partial x} f(x,y) \right) = \frac{\partial^2}{\partial y \partial x} f(x,y) = f_{yx}(x,y)$$

or

$$\hat{d}_x \hat{d}_y f(x,y) = \frac{\partial}{\partial x} \left( \frac{\partial}{\partial y} f(x,y) \right) = \frac{\partial^2}{\partial x \partial y} f(x,y) = f_{xy}(x,y)$$

Note that the action of the operators can depend on the order of operation as $\hat{d}_x \hat{d}_y f(x,y)$ is not necessarily equal to $\hat{d}_y \hat{d}_x f(x,y)$. Taking the difference between the two results above results in a compact representation of Euler’s test

$$\left( \hat{d}_x \hat{d}_y - \hat{d}_y \hat{d}_x \right) f(x,y) = \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} = f_{xy}(x,y) - f_{yx}(x,y) = 0$$

When this relation is satisfied we say that the operators $\hat{d}_x$ and $\hat{d}_y$ commute.

It is common to use the compact notation

$$\left[ \hat{d}_x, \hat{d}_y \right] = \left( \hat{d}_x \hat{d}_y - \hat{d}_y \hat{d}_x \right)$$ (5.1)

where $\left[ \hat{d}_x, \hat{d}_y \right]$ is known as the commutator. Using the commutator notation $[\hat{A}, \hat{B}] f(x) = \hat{A} (\hat{B} f(x)) - \hat{B} (\hat{A} f(x))$. When this is true, the order of operation is not important.
5.1.3 More complicated operators

Let’s apply the rules of operator algebra to more complicated differential operators. Extending the idea of a product of operators, we can take powers of operators. Consider the total differential operator

\[ \hat{D}_x \equiv \frac{d}{dx} \]

raised to the third power as

\[ (\hat{D}_x)^3 f(x) = \left( \frac{d}{dx} \right)^3 f(x) = \frac{d^3}{dx^3} f(x) \]

We can also consider more complicated linear differential operators

\[ \hat{C} f(x) = \left( \hat{D}_x^2 + 2 \hat{D}_x + 3 \right) f(x) \]

Linear differential operators play an important role in quantum theory where they are used to measure physical properties including the linear momentum and energy. Examples include the linear momentum operator

\[ \hat{p} \psi(x) = -i\hbar \frac{d\psi(x)}{dx} \]

where

\[ \hat{p} \equiv -i\hbar \frac{d}{dx} \]

and the energy operator

\[ \hat{H} \psi(x) = -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x) \psi(x) \]

The energy operator can be written as a sum of the kinetic energy operator and potential energy operator

\[ \hat{H} \equiv \hat{T} + \hat{V} = \frac{1}{2m} \hat{p}^2 + V(x) \]

where \( \hat{V} = V(x) \) is a function of \( x \).

Consider the commutation of the operators \( \hat{p} \) and \( \hat{p}^2 \) where

\[ \left( \hat{p} \hat{p}^2 - \hat{p}^2 \hat{p} \right) \psi(x) = \hat{p} \left( \hat{p}^2 \psi(x) \right) - \hat{p}^2 \left( \hat{p} \psi(x) \right) \]

\[ = \hat{p}^3 \psi(x) - \hat{p}^3 \psi(x) = 0 \]

The operators \( \hat{p} \) and \( \hat{p}^2 \) commute. This result may be generalized to show that a linear operator will always commute with itself, multiples of itself, or arbitrary powers of itself.

Finally, consider the commutation of the operators \( \hat{\rho} \) and \( \hat{H} \) where

\[ (\hat{\rho} \hat{H} - \hat{H} \hat{\rho}) \psi(x) \]

Expanding the operator \( \hat{H} \) we find

\[ (\hat{\rho} \hat{H} - \hat{H} \hat{\rho}) \psi(x) = \left[ \hat{\rho} \left( \frac{1}{2m} \hat{p}^2 + V(x) \right) - \left( \frac{1}{2m} \hat{p}^2 + V(x) \right) \hat{\rho} \right] \psi(x) \]

\[ = \left[ \frac{1}{2m} \hat{p}^3 + \hat{\rho} V(x) - \frac{1}{2m} \hat{p}^3 - V(x) \hat{\rho} \right] \psi(x) \]
Canceling the two terms containing $\hat{p}^3$ leaves

$$ (\hat{p}\hat{H} - \hat{H}\hat{p}) \psi(x) = [\hat{p}V(x) - V(x)\hat{p}] \psi(x) $$

Noting that the differential operator $\hat{p}$ acts on $V(x)$ as well as $\psi(x)$, we expand the expression above and find

$$ [\hat{p}V(x) - V(x)\hat{p}] \psi(x) = -i\hbar \psi(x) \frac{dV}{dx} - i\hbar V(x) \frac{d\psi}{dx} + i\hbar V(x) \frac{d\psi}{dx} $$

Noting that the second and third terms cancel, we arrive at the final result

$$ (\hat{p}\hat{H} - \hat{H}\hat{p}) \psi(x) = -i\hbar \psi(x) \frac{d}{dx} V(x) $$

If $dV(x)/dx = 0$ the operators $\hat{p}$ and $\hat{H}$ commute. Otherwise, they do not commute.

### 5.2 Differentiation of vector functions

Physical properties including position, momentum, and force have magnitude and orientation and are described as vectors. The concept of differentiation of scalar functions can be generalized when combined with the concept of vectors. We can describe the slope of a scalar function of two variables $f(x,y)$ at a point in space in terms of a vector defining the slopes in the $x$- and $y$-directions. Alternatively, we can define the scalar magnitude of the rate of change of a vector function by summing the rate of change of the function in each of its dimensions. In this section, we explore the differentiation of vector-valued functions and vector fields commonly used to describe physical processes.

#### 5.2.1 Vector-valued functions

A scalar function $f(x,y)$ associates a scalar number with every point $(x,y)$ on the $xy$-plane. That number has a magnitude $|f(x,y)|$ and sign. In contrast, a vector-valued function $\mathbf{f}(t)$ is a vector function that associates with every point $(x,y)$ a vector with magnitude and orientation that may depend on the parameter $t$.

![Figure 5.1: The vector-valued functions $x(t) = \sin(2\pi t)$ $\hat{x}$ (blue) and $y(t) = \sin(2\pi t)$ $\hat{y}$ (red). Also shown are $x(t) + y(t)$ (light gray) and $x(t) - y(t)$ (light red).](image)

Consider the equation for the plane waves

$$ x(t) = \sin(2\pi t) \hat{x} \quad y(t) = \sin(2\pi t) \hat{y} $$

oscillating in the $\hat{x}$ or $\hat{y}$ direction as a function of the parameter $t$. Using vector notation, we can present both functions in a single three-dimensional plot as depicted in Figure 5.1. Oscillations in the $x$-direction are shown in red and those
in the $y$ direction are shown in blue. The linear combinations $x(t) + y(t)$ (light gray) and $x(t) - y(t)$ (light red) appear on the $x = y$ plane and $x = -y$ plane, respectively.

Recall the helical curve written in cartesian coordinates in Equation 1.26 as

$$
\begin{align*}
  x &= x(z) = a \cos(2\pi z) \\
  y &= y(z) = a \sin(2\pi z)
\end{align*}
$$

That same function can be written as a vector-valued function

$$
\mathbf{r}(t) = a \cos(2\pi t) \hat{\mathbf{i}} + a \sin(2\pi t) \hat{\mathbf{j}} + t \hat{\mathbf{k}}
$$

where we have introduced the parameter $t$ and $z = t$. The result is shown in Figure 5.2.

### 5.2.2 Vector functions and vector fields

Consider the vector function

$$
f(x, y) = 2x\hat{\mathbf{x}} + 2y\hat{\mathbf{y}}
$$

shown in Figure 5.3. This vector function assigns a vector to each point in space $(x, y)$. This assignment of a vector to each point in space forms a vector field. All vector fields are vector-valued functions, but not all vector-valued functions are vector fields. For example, the helical curve $\mathbf{r}(t)$ defined by Equation 5.2 is a vector-valued function that is not a vector field as it assigns vectors given the value of a parameter $t$ rather than to each point in space $(x, y)$.

At the point $(1, 1)$ the value of the function is

$$
f(1, 1) = 2\hat{\mathbf{x}} + 2\hat{\mathbf{y}}
$$

which is a vector of magnitude $2\sqrt{2}$ oriented outward from the origin along the line $x = y$. At the point $(0, -1)$ the value of the function is

$$
f(0, -1) = -2\hat{\mathbf{y}}
$$

which is a vector of magnitude 2 oriented outward along the negative $y$-axis. At the point $(-2, 2)$ the value of the function is

$$
f(-2, 2) = -4\hat{\mathbf{x}} + 4\hat{\mathbf{y}}
$$

which is a vector of magnitude $4\sqrt{2}$ oriented outward along the line $x = -y$. The value of $f(x, y)$ at these three points is displayed in Figure 5.3.

If we add to the number of points presented, we can depict the variation of the vector field $f(x, y)$ over a region of the $xy$-plane (see Figure 5.4). At each point the vector function is defined in terms of a magnitude and orientation depicted by small arrows. The collection of arrows provides a sense of the changing magnitude and direction of the vector function over the $xy$-plane.

A vector field is used to model the force acting on a charge in an electric field. At each point in space, the force acting on the charge will have a specific magnitude and a direction. Vector fields are also used to model fluids for which each element of the fluid at some point in space has a given speed and direction of flow. Points from which vectors flow outward are sources and points to which vectors flow inward are sinks. Points with no net inward or outward flow are saddle points.

Now consider the periodic two-dimensional vector function

$$
f(x, y) = \cos x \hat{\mathbf{x}} + \cos y \hat{\mathbf{y}}
$$

Figure 5.2: A helical curve $\mathbf{r}(t)$ (red) expressed in vector notation as a vector-valued function of the parameter $t$. The gray arrows mark the point $\mathbf{r}(t)$ for five values of $t$.

Figure 5.3: The vector function $f(x, y) = 2x\hat{\mathbf{x}} + 2y\hat{\mathbf{y}}$ evaluated at three points on the $xy$-plane. Arrow length and orientation indicate magnitude and direction of the vector function.

Figure 5.4: The vector field $f(x, y) = 2x\hat{\mathbf{x}} + 2y\hat{\mathbf{y}}$ shown as an array of arrows on the $xy$-plane. The center of the graph is a source as vectors are directed outward from that point.
shown in Figure 5.5. In the upper right quadrant the vector field points inward toward a sink (black dot), while in the lower left quadrant the vectors point outward from a source (red dot). In the remaining quadrants, there are saddle points (crosses) with no net inward or outward flow. Overall, the collection of arrows represent the vector field \( f(x, y) \) over this region of the \( xy \)-plane.

5.2.3 Vector differentiation of a scalar function and the gradient

Consider the vector function

\[
f(x, y) = \frac{\partial V}{\partial x} \hat{x} + \frac{\partial V}{\partial y} \hat{y} = V_x \hat{x} + V_y \hat{y}
\]

where \( V(x, y) \) is a differentiable scalar function of \( x \) and \( y \). The vector \( f(x, y) \) describes the slope of the scalar function \( V(x, y) \) at the point \((x, y)\) in the \( \hat{x} \) and \( \hat{y} \) directions. We say that \( f \) is the gradient of \( V(x, y) \).

This expression can be written in the compact notation

\[
f(x, y) = \left( \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) V(x, y) = \nabla V(x, y)
\]

where

\[

\nabla \equiv \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y}
\]

is the gradient operator in two-dimensions. The gradient operator is a vector operator that acts on a scalar function and returns a vector function.

An example is shown in Figure 5.6 for the gradient \( \nabla V(x, y) \) of the function \( V(x, y) = -(x^2 + y^2) \). The resulting vector field \( \nabla V(x, y) = V_x \hat{x} + V_y \hat{y} = f(x, y) = -2x \hat{x} - 2y \hat{y} \)

is shown as an array of arrows on the \( xy \)-plane. The partial derivatives \( V_x \) and \( V_y \) determine the magnitude of the \( x \)- and \( y \)-components of the gradient as shown by the vectors at two points on the surface defined by \( V(x, y) \). The magnitude of the gradient \( |\nabla V(x, y)| = (V_x^2 + V_y^2)^{\frac{1}{2}} = (4x^2 + 4y^2)^{\frac{1}{2}} \) in plane polar coordinates \( V = -r^2 \) so that \( \nabla V = -2r \hat{r} \) and \( |\nabla V| = 2r \).

The direction of the gradient is the direction of fastest increase of the function at a given point in the \( xy \)-plane. The magnitude of the gradient provides a measure of the rate of increase of the function.
Another example is shown in Figure 5.7 for the gradient of the function

\[ V(r, \theta) = \ln(r) \]

The gradient can be determined in cartesian coordinates

\[ \nabla V(x, y) = V_x \hat{x} + V_y \hat{y} = f(x, y) = \frac{x}{r^2} \hat{x} + \frac{y}{r^2} \hat{y} \]

However, it is most naturally determined using the gradient operator in plane polar coordinates provided in the Complements

\[ \nabla V(r, \theta) = \hat{r} \frac{\partial V}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial V}{\partial \theta} = f(r, \theta) = \frac{1}{r} \hat{r} \]

The resulting vector field is shown as an array of arrows on the xy-plane. The partial derivatives \( V_x \) and \( V_y \) determine the magnitude of the x- and y-components of the gradient as shown by the vectors at a point on the surface.

The gradient operator in three-dimensions is the natural extension of the gradient operator in two-dimensions\(^6\)

\[ \nabla = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \]

The forms of the gradient operator in plane polar coordinates, spherical polar coordinates, and cylindrical coordinates are provided in the Complements.

As an example, let’s see how the gradient operator acts on a function

\[ V(x, y, z) = x^2 + y^2 + z^2 + 2xyz \]

in three-dimensional cartesian space. The gradient of \( V(x, y, z) \) is

\[
\begin{align*}
\nabla V(x, y, z) &= \left( \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y} + \hat{z} \frac{\partial V}{\partial z} \right) V(x, y, z) \\
&= \left( \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y} + \hat{z} \frac{\partial V}{\partial z} \right) \\
&= (2x + 2yz)\hat{x} + (2y + 2xz)\hat{y} + (2z + 2xy)\hat{z}
\end{align*}
\]

which is a vector function \( f(x, y, z) = \nabla V(x, y, z) \). These examples demonstrate the mechanics of calculating gradients and should provide a sense of how to interpret the gradient as the direction and rate of fastest increase of a function.
5.2.4 Vector differentiation of a vector function and the divergence

As we saw previously, a scalar function \( V(x, y) \) can be transformed into a vector function \( f(x, y) \) using the gradient operator

\[
\nabla V(x, y) \equiv \mathbf{\hat{x}} \frac{\partial V}{\partial x} + \mathbf{\hat{y}} \frac{\partial V}{\partial y}
\]

which is a vector function. Earlier we explored the dot product between two vectors \( \mathbf{v} \) and \( \mathbf{w} \) defined by

\[
\mathbf{v} \cdot \mathbf{w} = v_x w_x + v_y w_y + v_z w_z
\]

In the same way, we can take a dot product between two vector functions \( f(x, y) = a(x, y) \mathbf{\hat{x}} + b(x, y) \mathbf{\hat{y}} \) and \( g(x, y) = c(x, y) \mathbf{\hat{x}} + d(x, y) \mathbf{\hat{y}} \) leading to a scalar function

\[
f(x, y) \cdot g(x, y) = a(x, y)c(x, y) + b(x, y)d(x, y)
\]

These examples show how we can use the dot product to multiply vectors and vector functions.

Suppose we take the dot product of the gradient operator \( \nabla \) with the vector function \( \nabla V(x, y) \) leading to

\[
\nabla \cdot (\nabla V) = \left( \mathbf{\hat{x}} \frac{\partial}{\partial x} + \mathbf{\hat{y}} \frac{\partial}{\partial y} \right) \cdot \left( \mathbf{\hat{x}} \frac{\partial V}{\partial x} + \mathbf{\hat{y}} \frac{\partial V}{\partial y} \right)
\]

\[
= (\mathbf{\hat{x}} \cdot \mathbf{\hat{x}}) \frac{\partial^2 V}{\partial x^2} + (\mathbf{\hat{y}} \cdot \mathbf{\hat{y}}) \frac{\partial^2 V}{\partial y^2}
\]

Writing the gradient of the scalar function \( V(x, y) \) in terms of the vector function \( \nabla V(x, y) \) we see that\(^7\)

\[
\nabla \cdot (\nabla V) = \nabla \cdot f(x, y)
\]

where \( \nabla \cdot f(x, y) \) is called the divergence of \( f(x, y) \) and \( \nabla \cdot \) is the divergence operator.\(^8\) The divergence operator acts on a vector function and returns a scalar function.

For a general vector field in two-dimensions

\[
f(x, y) = a(x, y) \mathbf{\hat{x}} + b(x, y) \mathbf{\hat{y}}
\]

the divergence can be written

\[
\nabla \cdot f(x, y) = \frac{\partial a}{\partial x} + \frac{\partial b}{\partial y}
\]

The divergence operator provides a scalar measure of the total rate of change of a vector function in all directions at a specific point in space.

Consider the vector function

\[
f(x, y) = \cos x \mathbf{\hat{x}} + \cos y \mathbf{\hat{y}}
\]

examined previously and shown in Figure 5.5. The divergence of \( f(x, y) \) is the scalar function

\[
\nabla \cdot f(x, y) = \left( \mathbf{\hat{x}} \frac{\partial}{\partial x} + \mathbf{\hat{y}} \frac{\partial}{\partial y} \right) \cdot (\cos x \mathbf{\hat{x}} + \cos y \mathbf{\hat{y}})
\]

\[
= \frac{\partial}{\partial x} \cos x + \frac{\partial}{\partial y} \cos y = - (\sin x + \sin y)
\]
Figure 5.8: The divergence of the vector function $f(x,y) = \cos x \hat{x} + \cos y \hat{y}$. The divergence is a scalar function $\nabla \cdot f(x,y) = - (\sin x + \sin y)$ shown as a red surface. The vector field of $f(x,y)$ is depicted as an array of arrows on the $xy$-plane. The surface includes a source (red dot) representing a maximum in the divergence, a sink (black dot) representing a minimum in the divergence, and two saddle points (crosses).

Let’s consider one last example of the divergence of the vector function

$$f(x,y) = \frac{x}{r^2} \hat{x} + \frac{y}{r^2} \hat{y}$$

where $r^2 = x^2 + y^2$. The divergence is computed

$$\nabla \cdot f(x,y) = \left( \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) \cdot \left( \frac{x}{r^2} \hat{x} + \frac{y}{r^2} \hat{y} \right) = \frac{\partial}{\partial x} \left( \frac{x}{r^2} \right) + \frac{\partial}{\partial y} \left( \frac{y}{r^2} \right)$$

We can compute the derivative

$$\frac{\partial}{\partial x} \left( \frac{x}{r^2} \right) = \frac{1}{r^2} - \frac{2x^2}{r^4}$$

A similar result can be found for the derivative

$$\frac{\partial}{\partial y} \left( \frac{x}{r^2} \right) = \frac{1}{r^2} - \frac{2y^2}{r^4}$$

Combining these terms leads to the final result for the divergence

$$\nabla \cdot f(x,y) = \left( \frac{1}{r^2} - \frac{2x^2}{r^4} \right) + \left( \frac{1}{r^2} - \frac{2y^2}{r^4} \right) = \frac{2}{r^2} \left( 1 - \frac{x^2}{r^2} - \frac{y^2}{r^2} \right) = 0$$

The vector field $f(x,y)$ and its divergence $\nabla \cdot f(x,y)$ are shown in Figure 5.9. Note that the origin has properties of both a source (arrows pointing outward) and a sink (arrows pointing inward). Summing those contributions results in the divergence being zero.

### 5.2.5 Combining the gradient and the divergence to form the Laplacian

Consider the mathematical function

$$g(x,y) = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2}$$

Figure 5.9: The divergence of the vector field $f(x,y) = \frac{x}{r^2} \hat{x} + \frac{y}{r^2} \hat{y}$ where $r^2 = x^2 + y^2$ is depicted as an array of arrows on the $xy$-plane. The divergence of the vector field is a scalar constant $\nabla \cdot f(x,y) = 0$. 
where both \( V(x, y) \) and \( g(x, y) \) are scalar functions of \((x, y)\). Alternatively, this equation can be written

\[
g(x, y) = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) V(x, y) = \nabla^2 V(x, y)
\]

where

\[
\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}
\]

is called the Laplace operator. The Laplace operator acts on a scalar function and returns a scalar function.\(^9\)

Now consider again the vector function

\[
f(x, y) = \frac{x}{r^2} \hat{x} + \frac{y}{r^2} \hat{y}
\]

where \( r = \sqrt{x^2 + y^2} \). We showed that the divergence

\[
\nabla \cdot f(x, y) = 0
\]

The vector field \( f(x, y) \) can be generated from the gradient of the scalar function \( V(x, y) = \ln r \) as\(^{10}\)

\[
\nabla V(x, y) = \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y} = \hat{x} \frac{\partial}{\partial x} \ln r + \hat{y} \frac{\partial}{\partial y} \ln r = \hat{x} \frac{x}{r^2} + \hat{y} \frac{y}{r^2}
\]

Combining these two results we find

\[
\nabla \cdot f(x, y) = \nabla \cdot (\nabla V(x, y)) = \nabla^2 V(x, y) = 0
\]

which we can rewrite as

\[
\nabla^2 V(x, y) \equiv \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0
\]

which is known as Laplace’s equation.\(^{11}\) This demonstrates that \( V(x, y) = \ln r \) satisfies Laplace’s equation in two-dimensions.

The three-dimensional version of Laplace’s equation in cartesian coordinates is written

\[
\nabla^2 V(x, y, z) \equiv \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0
\]

It can be shown that the scalar function \( V(x, y, z) = 1/r \) where \( r = \sqrt{x^2 + y^2 + z^2} \) satisfies Laplace’s equation in three-dimensions. The forms of Laplace’s operator in plane polar coordinates, spherical polar coordinates, and cylindrical coordinates are provided in the Complements.

---

**A5 The force and the potential energy**

Force is something we experience directly. When Newton considered the response of a particle of mass \( m \) to a force \( \mathbf{F} \), he reasoned that the force is equal to the mass times the acceleration.

\[
\mathbf{F} = m \frac{d^2 \mathbf{x}}{dt^2} = m \frac{d \mathbf{v}}{dt} = ma
\]

where \( \mathbf{x} \) is the position and the acceleration, \( \mathbf{a} \), is the rate of change in the velocity \( \mathbf{v} \).

Newton discovered that the gravitational force between an object of mass \( m \)
and another of mass $M$ separated by a distance $r$ follows an inverse square law:

$$F(r) = -\frac{GmM}{r^2} \hat{r}$$

where $G$ is the gravitational constant. In doing so, he provided a fundamental explanation of Kepler’s laws for planetary motion around the Sun. However, he never imagined the gravitational potential energy:

$$V(r) = -\frac{GmM}{r}$$

that is related to the force through the equation:

$$F(r) = -\frac{dV(r)}{dr} \hat{r}$$

The gravitational potential energy and force are shown in Figure 5.10. The force is a vector that points in the direction of lower potential energy. If the slope of the potential energy is positive, the force is negative (pointing inward).

Suppose we have a force that depends only on the coordinates of the system. We can express the force in three-dimensions using cartesian coordinates as:

$$F = \hat{x} f_x + \hat{y} f_y + \hat{z} f_z = -\left[ \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y} + \hat{z} \frac{\partial V}{\partial z} \right]$$

where the cartesian components of the force are defined in terms of the respective partial derivatives of the potential energy:

$$f_x = -\frac{\partial V}{\partial x} \quad f_y = -\frac{\partial V}{\partial y} \quad f_z = -\frac{\partial V}{\partial z}$$

We can also express the force as:

$$F = -\left[ \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \right] V(x, y, z) = -\nabla V(x, y, z)$$

which is the negative gradient of the potential energy. The later result

$$F = -\nabla V$$

is general. One simply employs the appropriate form of the gradient operator for the particular coordinate system. The forms of the gradient operator in plane polar coordinates, spherical polar coordinates, or cylindrical coordinates are provided in the Complements.

**B5 A survey of potential energy landscapes**

Potential energy is an abstract concept. We do not experience potential energy in the same way we experience force. The most direct experience we have with potential energy is derived from moving in a hilly landscape. We know that we must do work to climb to the top of a hill. Doing this work we are storing potential energy that has the potential to do work in the future. From the top of a hill, we coast downward without doing work. We convert our stored potential energy into the kinetic energy of motion. When we consider potential energy in physical science, it can be useful to think in terms of a potential energy landscape that describes the potential energy as a function of position in space. We can then use our intuition developed by moving over hills, valleys, and planes to inform how we interpret the ups and downs of energy functions.
Consider a mass connected by a spring (see Figure 5.11). The resting point for the mass is \( x = x_0 \). For \( x < x_0 \) the spring is compressed and a force pushes outward to lengthen the spring. For \( x > x_0 \) the spring is stretched and a force pushes inward to shorten the spring. The force acting on the mass is described mathematically by Hooke’s law\(^{14}\)

\[
F(x) = -\kappa (x - x_0)
\]

where \( \kappa \) is the spring’s force constant. Hooke’s law says the restoring force varies linearly with the displacement \( (x - x_0) \) of the spring. For the same displacement \( (x - x_0) \), a stiffer spring with a larger value of \( \kappa \) will result in a greater restoring force than a softer spring with a smaller value of \( \kappa \). The corresponding potential energy

\[
V(x) = \frac{1}{2} \kappa (x - x_0)^2
\]

is quadratic in the displacement of the spring and related to the force as

\[
F(x) = -\frac{dV(x)}{dx} = -\kappa (x - x_0)
\]

The potential energy function and corresponding force vectors, that vary in magnitude and direction, are shown in Figure 5.11. This quadratic potential energy function is used to model vibrations of bonds in molecules and small displacements of atoms in solids.

The interaction of two neutral atoms can be modeled by the Lennard-Jones potential energy function

\[
V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]

which depends on the radial distance \( r \) between the two atoms. The parameter \( \sigma \) represents the atomic diameter for which \( V(r) = 0 \). The potential energy function has a minimum value at \( r_{min} = \sqrt[6]{2} \sigma \) of \( V(r_{min}) = -\varepsilon \) as shown in Figure 5.12. The force acting between the atoms is

\[
F(r) = -\frac{dV(r)}{dr} \hat{r} = 4\varepsilon \left[ 12 \left( \frac{\sigma}{r} \right)^{12} - 6 \left( \frac{\sigma}{r} \right)^6 \right] \frac{\hat{r}}{r}
\]

When \( r < r_{min} \) the repulsive force proportional to \( 1/r^{12} \) dominates the total force, while at distances \( r > r_{min} \) the attractive force proportional to \( 1/r^6 \) is dominant.

Another important force in physical science is the coulomb force acting between charges \( q_1 \) and \( q_2 \) separated by a distance \( r \). Coulomb’s law states that the force is proportional to the product of the charges divided by the square of the radial distance \( r \) between the charges\(^{15}\)

\[
F(r) = \frac{C q_1 q_2}{r^2} \hat{r}
\]

where \( C = 1/4\pi\varepsilon_0 \) is a constant and \( \varepsilon_0 \) is the permittivity of a vacuum. This force can be related to the coulombic potential energy function

\[
V(r) = \frac{C q_1 q_2}{r}
\]

For two opposite charges \( q_1 = e \) and \( q_2 = -e \), the force is attractive and pointing inward as

\[
F(r) = -\frac{Ce^2}{r^2} \hat{r}
\]

\(^{14}\) Named for English natural philosopher Robert Hooke (1635-1703). He published a popular book Micrographia, describing his seminal contributions to microscopy, and coined the word cell.

\(^{15}\) Named for French military engineer and physicist Charles-Augustin de Coulomb (1736-1806).
while for two like charges $q_1 = q_2 = -e$ the force is repulsive and pointing outward

$$F(r) = \frac{C e^2}{r^2} \mathbf{\hat{r}}$$

The attractive and repulsive coulomb potentials are shown in Figure 5.13 along with vectors indicating the varying magnitude and direction of the force acting between the charges. Just as in the case of the gravitational potential energy, the $1/r$ dependence of the potential energy leads to a $1/r^2$ dependence of the force.

The coulomb interaction is the essential force determining the properties of atoms and molecules. Negatively charged electrons are repelled by other negatively charged electrons but attracted to positively charged nuclei. This balance of forces gives rise to the rich variety of atoms and molecules that compose our world.

---

C5 Explicit forms of vector operations

In this Chapter, we explored the form of the gradient and divergence in two dimensions and three dimensions in cartesian coordinates. It is also possible to express the gradient and divergence in two dimensions in terms of plane polar coordinates and the gradient, divergence, and curl in three dimensions in spherical polar coordinates and cylindrical coordinates. Useful expressions for the gradient, divergence, curl, and Laplace operator are provided below.

Included for completeness are the differential line element $d\mathbf{l}$, the line segment associated with an infinitesimal displacement, the differential area element $dA$, the change in surface area associated with an infinitesimal displacement in two dimensions, or volume element $dV$, the change in volume associated with an infinitesimal displacement in three dimensions. In the Complement that follows, a concise derivation of each vector operator is presented.

**Cartesian coordinates (two dimensions)**

Consider the two-dimensional scalar function $V(x, y)$ and vector function $\mathbf{f}(x, y) = \mathbf{\hat{x}} f_x + \mathbf{\hat{y}} f_y$ expressed in cartesian coordinates $(x, y)$. The differential line and area elements are defined

$$d\mathbf{l} = \mathbf{\hat{x}} dx + \mathbf{\hat{y}} dy = \mathbf{\hat{x}} l_x + \mathbf{\hat{y}} l_y$$

$$dA = l_x l_y = dx dy$$
while the operator relations for gradient, divergence, and Laplace operator are
\[
\nabla V = \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y}
\]
\[
\nabla \cdot \mathbf{f} = \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y}
\]
\[
\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2}
\]
in two-dimensional Cartesian coordinates.

**Plane polar coordinates (two dimensions)**

Consider the two-dimensional scalar function \( V(r, \theta) \) and vector function \( \mathbf{f}(r, \theta) = \hat{r} f_r + \hat{\theta} f_\theta \) expressed in plane polar coordinates \((r, \theta)\) (see Figure 5.14). The differential line and area elements are defined
\[
dl = \hat{r} \, dr + \hat{\theta} \, r \, d\theta = \hat{r} \, dl_r + \hat{\theta} \, dl_\theta
\]
while the operator relations for gradient, divergence, and Laplace operator are
\[
\nabla V = \hat{r} \frac{\partial V}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial V}{\partial \theta}
\]
\[
\nabla \cdot \mathbf{f} = \frac{1}{r} \frac{\partial}{\partial r} (rf_r) + \frac{1}{r} \frac{\partial f_\theta}{\partial \theta}
\]
\[
\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial V}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2}
\]
in two-dimensional plane polar coordinates.

**Cartesian coordinates (three dimensions)**

Consider the three-dimensional scalar function \( V(x, y, z) \) and vector function \( \mathbf{f}(x, y, z) = \hat{x} f_x + \hat{y} f_y + \hat{z} f_z \) expressed in cartesian coordinates \((x, y, z)\) (see Figure 5.15). The differential line and volume elements are defined
\[
dl = \hat{x} \, dx + \hat{y} \, dy + \hat{z} \, dz = \hat{x} \, dl_x + \hat{y} \, dl_y + \hat{z} \, dl_z
\]
\[
dV = \, dl_x \, dl_y \, dl_z = dx \, dy \, dz
\]
while the operator relations for gradient, divergence, curl, and Laplace operator are
\[
\nabla V = \hat{x} \frac{\partial V}{\partial x} + \hat{y} \frac{\partial V}{\partial y} + \hat{z} \frac{\partial V}{\partial z}
\]
\[
\nabla \cdot \mathbf{f} = \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}
\]
\[
\nabla \times \mathbf{f} = \hat{x} \left( \frac{\partial f_y}{\partial z} - \frac{\partial f_z}{\partial y} \right) + \hat{y} \left( \frac{\partial f_z}{\partial x} - \frac{\partial f_x}{\partial z} \right) + \hat{z} \left( \frac{\partial f_x}{\partial y} - \frac{\partial f_y}{\partial x} \right)
\]
\[
\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2}
\]
in three-dimensional Cartesian coordinates. Note that we have added the definition of the curl operator that we did not define in two-dimensions.

**Spherical polar coordinates (three dimensions)**

Consider the three-dimensional scalar function \( V(r, \theta, \phi) \) and vector function \( \mathbf{f}(r, \theta, \phi) = \hat{r} f_r + \hat{\theta} f_\theta + \hat{\phi} f_\phi \) expressed in spherical polar coordinates \((r, \theta, \phi)\)
The differential line and volume elements are defined as

\[dl = \hat{t} \, dr + \hat{\theta} \, r \, d\theta + \hat{\varphi} \, r \sin \theta \, d\varphi = \hat{t} \, dl_t + \hat{\theta} \, dl_\theta + \hat{\varphi} \, dl_\varphi\]
\[dV = dl_t \, dl_\theta \, dl_\varphi = r^2 \sin \theta \, dr \, d\theta \, d\varphi\]

while the operator relations for gradient, divergence, curl, and Laplace operator are

\[\nabla V = \frac{1}{r} \frac{\partial V}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial V}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial V}{\partial \varphi}\]

\[\nabla \cdot \mathbf{f} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 f_r \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta f_\theta \right) + \frac{1}{r \sin \theta} \frac{\partial f_\varphi}{\partial \varphi}\]

\[\nabla \times \mathbf{f} = \frac{1}{r \sin \theta} \left( \frac{\partial}{\partial \theta} \left( \sin \theta f_\varphi \right) - \frac{\partial f_\theta}{\partial \varphi} \right) + \frac{1}{r} \left( \frac{1}{\sin \theta} \frac{\partial f_r}{\partial \varphi} - \frac{\partial f_\varphi}{\partial \theta} \right)\]

\[\nabla^2 V = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 V}{\partial \varphi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \frac{\sin \theta \frac{\partial V}{\partial \theta}}{\sin \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 V}{\partial \varphi^2}\]

in three-dimensional spherical polar coordinates.

**Cylindrical coordinates (three dimensions)**

Consider the three-dimensional scalar function \(V(r, \theta, z)\) and vector function \(\mathbf{f}(r, \theta, z) = \hat{r} f_r + \hat{\theta} f_\theta + \hat{z} f_z\) expressed in cylindrical coordinates \((r, \theta, z)\) (see Figure 5.17). The differential line and volume elements are defined as

\[dl = \hat{r} \, dr + \hat{\theta} \, r \, d\theta + \hat{z} \, dz = \hat{r} \, dl_r + \hat{\theta} \, dl_\theta + \hat{z} \, dl_z\]
\[dV = dl_r \, dl_\theta \, dl_z = r \, dr \, d\theta \, dz\]

while the operator relations for gradient, divergence, curl, and Laplace operator are

\[\nabla V = \frac{1}{r} \frac{\partial V}{\partial r} + \frac{1}{r} \frac{\partial V}{\partial \theta} + \frac{\partial V}{\partial z}\]

\[\nabla \cdot \mathbf{f} = \frac{1}{r} \frac{\partial f_r}{\partial r} + \frac{1}{r} \frac{\partial f_\theta}{\partial \theta} + \frac{\partial f_z}{\partial z}\]

\[\nabla \times \mathbf{f} = \hat{r} \left( \frac{1}{r} \frac{\partial f_z}{\partial \theta} - \frac{\partial f_\theta}{\partial z} \right) + \hat{\theta} \left( \frac{\partial f_z}{\partial r} - \frac{\partial f_r}{\partial \theta} \right) + \hat{z} \left( \frac{\partial f_\theta}{\partial r} - \frac{\partial f_r}{\partial \theta} \right)\]

\[\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2} + \frac{\partial^2 V}{\partial z^2}\]

in three-dimensional cylindrical coordinates.

We have explored vector operators in two orthogonal coordinate systems in two-dimensions and three orthogonal coordinate systems in three-dimensions. All five coordinate systems are commonly used in the physical sciences.

---

**D5 Deriving explicit forms for vector operations**

The explicit forms of vector operators including the gradient, divergence, curl, and laplacian were presented in a Complement in Chapter 5. In this Complement, we derive the explicit form of the gradient, divergence, and...
deriving explicit forms for vector operations in two-dimensional cartesian and plane polar coordinates, as well as three-dimensional cartesian, spherical polar and cylindrical coordinates.

An intuitive approach based on the line element is used to derive the gradient operator, which is subsequently used to derive the divergence and laplacian. This approach is more economical and significantly less complicated than direct approaches using partial differentiation.

**Cartesian coordinates (two dimensions)**

Consider a curve in two-dimensional cartesian coordinates where a displacement along the curve can be written in terms of the line element

\[ d\mathbf{l} = dx \hat{x} + dy \hat{y} = dl_x \hat{x} + dl_y \hat{y} \]

We can express the gradient of a function \( V(x, y) \) in terms of its \( x \) and \( y \) components as

\[ \nabla V = (\nabla V \cdot \hat{x}) \hat{x} + (\nabla V \cdot \hat{y}) \hat{y} = (\nabla V)_x \hat{x} + (\nabla V)_y \hat{y} \]

Our goal is to derive an expression for the gradient operator by finding explicit expressions for \((\nabla V)_x \) and \((\nabla V)_y \) (see Figure 5.18).

![Figure 5.18: The line element \( d\mathbf{l} \) (red) with the gradient \( \nabla V \) (black) and components of its projection onto the unit vectors \( \hat{x} \) and \( \hat{y} \) (gray).](image)

The total differential of \( V(x, y) \) can be written

\[ dV = \frac{\partial V}{\partial x} dx + \frac{\partial V}{\partial y} dy \]

It can also be expressed as the scalar product of the gradient \( \nabla V \) and the line element \( d\mathbf{l} \) as

\[ dV = \nabla V \cdot d\mathbf{l} = (\nabla V)_x dx + (\nabla V)_y dy \]

Comparing terms in the two expressions for \( dV \) we find

\[ (\nabla V)_x = \frac{\partial V}{\partial x} \quad (\nabla V)_y = \frac{\partial V}{\partial y} \]

so that the gradient and gradient operator in two-dimensional cartesian coordinates are

\[ \nabla V = \frac{\partial V}{\partial x} \hat{x} + \frac{\partial V}{\partial y} \hat{y} \quad \nabla \equiv \left( \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) \quad (5.5) \]

The divergence of a vector function \( \mathbf{f} = f_x \hat{x} + f_y \hat{y} \) is defined as the scalar product of the gradient operator and the vector function

\[ \nabla \cdot \mathbf{f} = \left( \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) \cdot (f_x \hat{x} + f_y \hat{y}) \]
In Cartesian coordinates, the unit vectors are independent of the coordinates. As such, the divergence is simply

$$\nabla \cdot \mathbf{f} = \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} \quad (5.6)$$

From this result, we can evaluate the Laplacian of \( V \) defined as

$$\nabla^2 V = \nabla \cdot \nabla V = \left( \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) \cdot \left( \frac{\partial V}{\partial x} \hat{x} + \frac{\partial V}{\partial y} \hat{y} \right)$$

Once again, as the unit vectors are independent of the coordinates we find

$$\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} \quad (5.7)$$

**Plane polar coordinates (two dimensions)**

Let's repeat that process in two-dimensional plane polar coordinates. We define a displacement along a curve in terms of the line element

$$\text{dl} = dr \hat{r} + r \, d\theta \hat{\theta} = \text{dl}_r \hat{r} + \text{dl}_\theta \hat{\theta}$$

We can express the gradient of a function \( V(r, \theta) \) in terms of its \( r \) and \( \theta \) components as

$$\nabla V = (\nabla V)_r \hat{r} + (\nabla V)_\theta \hat{\theta} = (\nabla V)_r \hat{r} + (\nabla V)_\theta \hat{\theta}$$

Our goal is to derive an expression for the gradient operator by finding explicit expressions for \((\nabla V)_r\) and \((\nabla V)_\theta\) (see Figure 5.19).

The total differential of \( V(r, \theta) \) can be written

$$dV = \frac{\partial V}{\partial r} dr + \frac{\partial V}{\partial \theta} d\theta$$

It can also be expressed as the scalar product of the gradient \( \nabla V \) and the line element \( \text{dl} \) as

$$dV = \nabla V \cdot \text{dl} = (\nabla V)_r dr + (\nabla V)_\theta r \, d\theta$$

Comparing terms in the two expressions for \( dV \) we find

$$(\nabla V)_r = \frac{\partial V}{\partial r} \quad (\nabla V)_\theta = \frac{1}{r} \frac{\partial V}{\partial \theta}$$

so that the gradient and gradient operator in two-dimensional plane polar coordinates are

$$\nabla V = \frac{\partial V}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial V}{\partial \theta} \hat{\theta} \quad \nabla \equiv \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} \quad (5.8)$$

The divergence of a vector function \( \mathbf{f} = f_r \hat{r} + f_\theta \hat{\theta} \) is defined as the scalar product of the gradient operator and the vector function

$$\nabla \cdot \mathbf{f} = \left( \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} \right) \cdot (f_r \hat{r} + f_\theta \hat{\theta})$$

In plane polar coordinates, the unit vectors are dependent on the coordinates as

$$\hat{r} = \cos \theta \hat{x} + \sin \theta \hat{y} \quad \hat{\theta} = -\sin \theta \hat{x} + \cos \theta \hat{y}$$

leading to the relations

$$\frac{\partial \hat{r}}{\partial r} = 0 \quad \frac{\partial \hat{\theta}}{\partial r} = 0 \quad \frac{\partial \hat{r}}{\partial \theta} = \hat{\theta} \quad \frac{\partial \hat{\theta}}{\partial \theta} = -\hat{r}$$
As such, in evaluating $\nabla \cdot \mathbf{f}$ we must consider derivatives of the unit vectors as well as the coefficients leading to $2 \times (2 \times 2) = 8$ terms

$$
\nabla \cdot \mathbf{f} = \mathbf{\hat{r}} \cdot \left( \frac{\partial f_r}{\partial r} + f_r \frac{\partial \mathbf{\hat{r}}}{\partial r} + \frac{\partial f_\theta}{\partial \theta} \mathbf{\hat{\theta}} + f_\theta \frac{\partial \mathbf{\hat{r}}}{\partial \theta} + f_\phi \mathbf{\hat{\phi}} \right) + \frac{1}{r} \mathbf{\hat{\theta}} \cdot \left( \frac{\partial f_r}{\partial r} + f_r \frac{\partial \mathbf{\hat{\theta}}}{\partial r} + \frac{\partial f_\theta}{\partial \theta} \mathbf{\hat{r}} + f_\theta \frac{\partial \mathbf{\hat{\theta}}}{\partial \theta} + f_\phi \mathbf{\hat{\phi}} \right) + \frac{1}{r} \mathbf{\hat{\phi}} \cdot \left( \frac{\partial f_r}{\partial r} + f_r \frac{\partial \mathbf{\hat{\phi}}}{\partial r} + \frac{\partial f_\theta}{\partial \theta} \mathbf{\hat{\theta}} + f_\theta \frac{\partial \mathbf{\hat{\phi}}}{\partial \theta} - \frac{1}{r} f_\phi \mathbf{\hat{r}} \right)
$$

As the unit vectors are orthonormal we have $\mathbf{\hat{r}} \cdot \mathbf{\hat{\theta}} = 1$ and $\mathbf{\hat{r}} \cdot \mathbf{\hat{\phi}} = 0$ leading to our final expression for the divergence in plane polar coordinates

$$
\nabla \cdot \mathbf{f} = \frac{\partial f_r}{\partial r} + \frac{1}{r} \left( f_r + \frac{\partial f_\theta}{\partial \theta} \right) \tag{5.9}
$$

From this result, we can evaluate the laplacian of $V$ defined as

$$
\nabla^2 V = \nabla \cdot \nabla V = \nabla \cdot \mathbf{f}
$$

where

$$
f = \frac{\partial V}{\partial r} \mathbf{\hat{r}} + \frac{1}{r} \frac{\partial V}{\partial \theta} \mathbf{\hat{\theta}} = f_r \mathbf{\hat{r}} + f_\theta \mathbf{\hat{\theta}}
$$

Inserting the forms for $f_r$ and $f_\theta$ into Equation 5.9 leads to

$$
\nabla^2 V = \frac{\partial}{\partial r} \left( \frac{\partial V}{\partial r} \right) + \frac{1}{r} \left[ \frac{\partial V}{\partial r} + \frac{\partial}{\partial \theta} \left( \frac{1}{r} \frac{\partial V}{\partial \theta} \right) \right] = \frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2}
$$

where the first two terms can be cleverly combined to form the final compact expression

$$
\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2} \tag{5.10}
$$

**Cartesian coordinates (three dimensions)**

Let’s repeat that process for three-dimensional cartesian coordinates. We define a displacement along a curve in terms of the line element

$$
dl = dx \mathbf{\hat{x}} + dy \mathbf{\hat{y}} + dz \mathbf{\hat{z}} = dl_x \mathbf{\hat{x}} + dl_y \mathbf{\hat{y}} + dl_z \mathbf{\hat{z}}
$$

We can express the gradient of a function $V(x, y, z)$ in terms of its $x$, $y$ and $z$ components as

$$
\nabla V = (\nabla V \cdot \mathbf{\hat{x}}) \mathbf{\hat{x}} + (\nabla V \cdot \mathbf{\hat{y}}) \mathbf{\hat{y}} + (\nabla V \cdot \mathbf{\hat{z}}) \mathbf{\hat{z}} = (\nabla V)_x \mathbf{\hat{x}} + (\nabla V)_y \mathbf{\hat{y}} + (\nabla V)_z \mathbf{\hat{z}}
$$

Our goal is to derive an expression for the gradient operator by finding explicit expressions for $(\nabla V)_x$, $(\nabla V)_y$ and $(\nabla V)_z$ (see Figure 5.20).

The total differential of $V(x, y, z)$ can be written

$$
dV = \frac{\partial V}{\partial x} dx + \frac{\partial V}{\partial y} dy + \frac{\partial V}{\partial z} dz
$$

it can also be expressed as the scalar product of the gradient $\nabla V$ and the line element $dl$ as

$$
dV = \nabla V \cdot dl = (\nabla V)_x dx + (\nabla V)_y dy + (\nabla V)_z dz
$$

Comparing terms in the two expressions for $dV$ we find

$$
(\nabla V)_x = \frac{\partial V}{\partial x} \quad (\nabla V)_y = \frac{\partial V}{\partial y} \quad (\nabla V)_z = \frac{\partial V}{\partial z}
$$

so that the gradient and gradient operator in three-dimensional cartesian
coordinates are
\[ \nabla V = \frac{\partial V}{\partial x} \hat{x} + \frac{\partial V}{\partial y} \hat{y} + \frac{\partial V}{\partial z} \hat{z} \]

The gradient of a scalar function \( V \) results in a vector field.

The divergence of a vector function \( \mathbf{f} = f_x \hat{x} + f_y \hat{y} + f_z \hat{z} \) is defined as the scalar product of the gradient operator and the vector function
\[ \nabla \cdot \mathbf{f} = \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) \cdot \left( f_x \hat{x} + f_y \hat{y} + f_z \hat{z} \right) \]

In cartesian coordinates, the unit vectors are independent of the coordinates. As such, the divergence is simply
\[ \nabla \cdot \mathbf{f} = \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z} \]

The divergence of a vector field \( \mathbf{f} \) results in a scalar function.

From this result, we can evaluate the laplacian of \( V \) defined as
\[ \nabla^2 V = \nabla \cdot \nabla V = \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)^2 \]

Once again, as the unit vectors are independent of the coordinates we find
\[ \nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} \]

The laplacian of a scalar function \( V \) results in a scalar function.

Finally, the curl in three-dimensional cartesian coordinates can be expressed using the determinant as
\[ \nabla \times \mathbf{f} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ f_x & f_y & f_z \end{vmatrix} = \hat{x} \left( \frac{\partial f_z}{\partial y} - \frac{\partial f_y}{\partial z} \right) + \hat{y} \left( \frac{\partial f_x}{\partial z} - \frac{\partial f_z}{\partial x} \right) + \hat{z} \left( \frac{\partial f_y}{\partial x} - \frac{\partial f_x}{\partial y} \right) \]

The curl of a vector field \( \mathbf{f} \) results in a vector field.

**Spherical polar coordinates (three dimensions)**

Let’s repeat that process for three-dimensional spherical polar coordinates. We define a displacement along a curve in terms of the line element
\[ ds = dr \hat{r} + r d\theta \hat{\theta} + r \sin \theta d\varphi \hat{\varphi} = dl, \hat{r} + dl \hat{\theta} + dl \varphi \hat{\varphi} \]

We can express the gradient of a function \( V(r, \theta, \varphi) \) in terms of its \( r, \theta \) and \( \varphi \) components as
\[ \nabla V = (\nabla V \cdot \hat{r}) \hat{r} + (\nabla V \cdot \hat{\theta}) \hat{\theta} + (\nabla V \cdot \hat{\varphi}) \hat{\varphi} = (\nabla V)_r \hat{r} + (\nabla V)_\theta \hat{\theta} + (\nabla V)_\varphi \hat{\varphi} \]

Our goal is to derive an expression for the gradient operator by finding explicit expressions for \((\nabla V)_r\), \((\nabla V)_\theta\) and \((\nabla V)_\varphi\) (see Figure 5.21).

The total differential of \( V(r, \theta, \varphi) \) can be written
\[ dV = \frac{\partial V}{\partial r} dr + \frac{\partial V}{\partial \theta} d\theta + \frac{\partial V}{\partial \varphi} d\varphi \]

it can also be expressed as the scalar product of the gradient \( \nabla V \) and the line
element $dV$ as

$$dV = \nabla V \cdot dl = (\nabla V)_{r} dr + (\nabla V)_{\theta} r d\theta + (\nabla V)_{\phi} r \sin \theta d\phi$$

Comparing terms in the two expressions for $dV$ we find

$$(\nabla V)_{r} = \frac{\partial V}{\partial r}, \quad (\nabla V)_{\theta} = \frac{1}{r} \frac{\partial V}{\partial \theta}, \quad (\nabla V)_{\phi} = \frac{1}{r \sin \theta} \frac{\partial V}{\partial \phi}$$

so that the gradient and gradient operator in three-dimensional spherical polar coordinates are

$$\nabla V = \frac{\partial V}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial V}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial V}{\partial \phi} \hat{\phi} \quad \nabla \equiv \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad (5.15)$$

The gradient of a scalar function $V$ results in a vector field.

The divergence of a vector function $\mathbf{f} = f_{r} \hat{r} + f_{\theta} \hat{\theta} + f_{\phi} \hat{\phi}$ is defined as the scalar product of the gradient operator and the vector function

$$\nabla \cdot \mathbf{f} = \left( \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right) \cdot (f_{r} \hat{r} + f_{\theta} \hat{\theta} + f_{\phi} \hat{\phi})$$

In spherical polar coordinates, the unit vectors are dependent on the coordinates as in Equation 4.3

$$\hat{r} = \sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z}$$
$$\hat{\theta} = \cos \theta \cos \phi \hat{x} + \cos \theta \sin \phi \hat{y} - \sin \theta \hat{z}$$
$$\hat{\phi} = -\sin \phi \hat{x} + \cos \phi \hat{y}$$

As such, in evaluating $\nabla \cdot \mathbf{f}$ we must consider derivatives of the unit vectors as well as the coefficients leading to $2 \times (3 \times 3) = 18$ terms. Evaluating the derivatives

$$\frac{\partial \hat{r}}{\partial r} = 0, \quad \frac{\partial \hat{\theta}}{\partial r} = 0, \quad \frac{\partial \hat{\phi}}{\partial r} = 0$$
$$\frac{\partial \hat{r}}{\partial \theta} = \hat{\theta}, \quad \frac{\partial \hat{\theta}}{\partial \theta} = -\hat{r}, \quad \frac{\partial \hat{\phi}}{\partial \theta} = 0$$
$$\frac{\partial \hat{r}}{\partial \phi} = \sin \theta \hat{\phi}, \quad \frac{\partial \hat{\theta}}{\partial \phi} = \cos \theta \hat{\phi}, \quad \frac{\partial \hat{\phi}}{\partial \phi} = -\cos \theta \hat{\theta} - \sin \theta \hat{r}$$

and noting that the unit vectors are orthonormal, such that $\hat{r} \cdot \hat{r} = \hat{\theta} \cdot \hat{\theta} = \hat{\phi} \cdot \hat{\phi} = 1$ and $\hat{r} \cdot \hat{\theta} = \hat{r} \cdot \hat{\phi} = \hat{\theta} \cdot \hat{\phi} = 0$, we find that 10 of the 18 terms are zero. The remaining terms are

$$\nabla \cdot \mathbf{f} = \left( \hat{r} \frac{\partial f_{r}}{\partial r} + \hat{\theta} \frac{\partial f_{r}}{\partial \theta} + \hat{\phi} \frac{\partial f_{r}}{\partial \phi} - f_{r} \right) \cdot \hat{r}$$

$$+ \frac{1}{r \sin \theta} \hat{\theta} \left( f_{\theta} \sin \theta + \hat{\theta} f_{\phi} \cos \theta + \hat{\phi} \frac{\partial f_{\phi}}{\partial \phi} + f_{\phi} (-\hat{\theta} \cos \theta - \hat{r} \sin \theta) \right)$$

$$= \frac{\partial f_{r}}{\partial r} + \frac{1}{r} \frac{\partial f_{r}}{\partial \theta} \left( f_{r} \sin \theta + f_{\theta} \cos \theta + \frac{\partial f_{\phi}}{\partial \phi} \right)$$

A clever combination of terms leads to the final compact expression for the divergence in spherical polar coordinates

$$\nabla \cdot \mathbf{f} = \frac{1}{r} \frac{\partial f_{r}}{\partial r} \left( r^{2} f_{r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( f_{\theta} \sin \theta \right) + \frac{1}{r \sin \theta} \frac{\partial f_{\phi}}{\partial \phi} \quad (5.16)$$

The divergence of a vector field $\mathbf{f}$ results in a scalar function.
We can express the gradient of a function $f$ in cylindrical coordinates (three dimensions) as

$$\nabla f = \frac{\partial f}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial f}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial f}{\partial \phi} \hat{\phi}$$

Inserting the forms for $f_r$, $f_\theta$ and $f_\phi$ into Equation 5.16 leads to

$$\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 V}{\partial \phi^2}$$

and our final expression for the laplacian in spherical polar coordinates

$$\nabla^2 V = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial V}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 V}{\partial \phi^2}$$

The laplacian of a scalar function $V$ results in a scalar function.

Finally, the curl in three-dimensional spherical polar coordinates can be defined

$$\nabla \times f = \frac{1}{r^2 \sin \theta} \begin{vmatrix} \hat{r} & r \hat{\theta} & r \sin \theta \hat{\phi} \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \\ \frac{f_r}{r} & \frac{f_\theta}{r} & \frac{f_\phi}{\sin \theta} \end{vmatrix} = \frac{\hat{r}}{r \sin \theta} \left( \frac{\partial}{\partial \theta} (\sin \theta f_\phi) - \frac{\partial f_\theta}{\partial \phi} \right)$$

The curl of a vector field $f$ results in a vector field.

**Cylindrical coordinates (three dimensions)**

Let’s repeat that process for three-dimensional cylindrical coordinates. We define a displacement along a curve in terms of the line element

$$dl = dr \hat{r} + r d\theta \hat{\theta} + dz \hat{z} = dl_r \hat{r} + dl_\theta \hat{\theta} + dl_z \hat{z}$$

We can express the gradient of a function $V(r, \theta, z)$ in terms of its $r$, $\theta$ and $z$ components as

$$\nabla V = (\nabla V \cdot \hat{r}) \hat{r} + (\nabla V \cdot \hat{\theta}) \hat{\theta} + (\nabla V \cdot \hat{z}) \hat{z} = (\nabla V)_r \hat{r} + (\nabla V)_\theta \hat{\theta} + (\nabla V)_z \hat{z}$$

Our goal is to derive an expression for the gradient operator by finding explicit expressions for $(\nabla V)_r$, $(\nabla V)_\theta$ and $(\nabla V)_z$, (see Figure 5.22).

The total differential of $V(r, \theta, z)$ can be written

$$dV = \frac{\partial V}{\partial r} dr + \frac{\partial V}{\partial \theta} d\theta + \frac{\partial V}{\partial z} dz$$

It can also be expressed as the scalar product of the gradient $\nabla V$ and the line element $dl$ as

$$dV = \nabla V \cdot dl = (\nabla V)_r dr + (\nabla V)_\theta d\theta + (\nabla V)_z dz$$

Comparing terms in the two expressions for $dV$ we find

$$(\nabla V)_r = \frac{\partial V}{\partial r} \quad (\nabla V)_\theta = \frac{1}{r} \frac{\partial V}{\partial \theta} \quad (\nabla V)_z = \frac{\partial V}{\partial z}$$

so that the gradient and gradient operator in three-dimensional cylindrical coordinates are

$$\nabla V = \frac{\partial V}{\partial r} \hat{r} + \frac{\partial V}{\partial \theta} \hat{\theta} + \frac{\partial V}{\partial z} \hat{z} \quad \nabla \equiv \frac{\partial}{\partial r} \hat{r} + \frac{\partial}{\partial \theta} \hat{\theta} + \hat{z} \frac{\partial}{\partial z}$$

(5.19)
The gradient of a scalar function $V$ results in a vector field.

The divergence of a vector function $f = f_r \hat{\mathbf{r}} + f_\theta \hat{\mathbf{\theta}} + f_z \hat{\mathbf{z}}$ is defined as the scalar product of the gradient operator and the vector function

$$\nabla \cdot f = \left( \frac{\partial V}{\partial r} \hat{\mathbf{r}} + \frac{1}{r} \frac{\partial V}{\partial \theta} \hat{\mathbf{\theta}} + \frac{\partial V}{\partial z} \hat{\mathbf{z}} \right) \cdot \left( f_r \hat{\mathbf{r}} + f_\theta \hat{\mathbf{\theta}} + f_z \hat{\mathbf{z}} \right)$$

In cylindrical coordinates, the unit vectors are dependent on the coordinates as in Equation 4.4

$$\hat{\mathbf{r}} = \cos \theta \hat{\mathbf{x}} + \sin \theta \hat{\mathbf{y}} \quad \hat{\mathbf{\theta}} = -\sin \theta \hat{\mathbf{x}} + \cos \theta \hat{\mathbf{y}} \quad \hat{\mathbf{z}} = \hat{\mathbf{z}}$$

As such, in evaluating $\nabla \cdot f$ we must consider derivatives of the unit vectors as well as the coefficients leading to $2 \times (3 \times 3) = 18$ terms. Evaluating the derivatives

$$\begin{align*}
\frac{\partial \hat{\mathbf{r}}}{\partial r} &= 0 \\
\frac{\partial \hat{\mathbf{r}}}{\partial \theta} &= \hat{\mathbf{\theta}} \\
\frac{\partial \hat{\mathbf{r}}}{\partial z} &= 0 \\
\frac{\partial \hat{\mathbf{\theta}}}{\partial r} &= 0 \\
\frac{\partial \hat{\mathbf{\theta}}}{\partial \theta} &= \hat{\mathbf{r}} \\
\frac{\partial \hat{\mathbf{\theta}}}{\partial z} &= 0 \\
\frac{\partial \hat{\mathbf{z}}}{\partial r} &= 0 \\
\frac{\partial \hat{\mathbf{z}}}{\partial \theta} &= 0 \\
\frac{\partial \hat{\mathbf{z}}}{\partial z} &= 0
\end{align*}$$

and noting that the unit vectors are orthonormal, such that $\hat{\mathbf{r}} \cdot \hat{\mathbf{\theta}} = \hat{\mathbf{\theta}} \cdot \hat{\mathbf{z}} = 1$ and $\hat{\mathbf{r}} \cdot \hat{\mathbf{\theta}} = \hat{\mathbf{\theta}} \cdot \hat{\mathbf{z}} = \hat{\mathbf{\theta}} \cdot \hat{\mathbf{\theta}} = 0$, we find that 14 of the 18 terms are zero. The remaining terms form the final expression for the divergence in cylindrical coordinates

$$\nabla \cdot f = \frac{\partial f_r}{\partial r} + \frac{1}{r} \left( f_\theta + \frac{\partial f_\theta}{\partial \theta} \right) + \frac{\partial f_z}{\partial z}$$  \hspace{1cm} (5.20)$$

The divergence of a vector field $f$ results in a scalar function.

From this result, we can evaluate the laplacian of $V$ defined as

$$\nabla^2 V = \nabla \cdot \nabla V = \nabla \cdot f$$

where

$$f = \frac{\partial V}{\partial r} \hat{\mathbf{r}} + \frac{1}{r} \frac{\partial V}{\partial \theta} \hat{\mathbf{\theta}} + \frac{\partial V}{\partial z} \hat{\mathbf{z}} = f_r \hat{\mathbf{r}} + f_\theta \hat{\mathbf{\theta}} + f_z \hat{\mathbf{z}}$$

Inserting the forms for $f_r, f_\theta$ and $f_z$ into Equation 5.20 leads to

$$\nabla^2 V = \frac{\partial}{\partial r} \left( \frac{\partial V}{\partial r} \right) + \frac{1}{r} \left[ \frac{\partial V}{\partial \theta} + \frac{\partial}{\partial \theta} \left( \frac{1}{r} \frac{\partial V}{\partial \theta} \right) \right] + \frac{\partial}{\partial z} \left( \frac{\partial V}{\partial z} \right)$$

where the first two terms can be cleverly combined to form the final expression

$$\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 V}{\partial \theta^2} + \frac{\partial^2 V}{\partial z^2}$$  \hspace{1cm} (5.21)$$

The laplacian of a scalar function $V$ results in a scalar function.

Finally, the curl in three-dimensional cylindrical coordinates can be written

$$\nabla \times f = \begin{vmatrix}
\hat{\mathbf{r}} & r \hat{\mathbf{\theta}} & \hat{\mathbf{z}} \\
\frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial z} \\
f_r & f_\theta & f_z
\end{vmatrix}
= \hat{\mathbf{r}} \left( \frac{\partial f_z}{\partial \theta} - \frac{\partial f_\theta}{\partial z} \right) + \hat{\mathbf{\theta}} \left( \frac{\partial f_r}{\partial z} - \frac{\partial f_z}{\partial r} \right) + \hat{\mathbf{z}} \left( \frac{\partial f_\theta}{\partial r} - \frac{\partial f_r}{\partial \theta} \right)$$  \hspace{1cm} (5.22)$$

The curl of a vector field $f$ results in a vector field. These expressions define the gradient, divergence, laplacian, and curl operators in coordinate systems having square, cubic, circular, spherical, or cylindrical symmetry.
E5 End-of-chapter problems

In mathematics you don’t understand things. You just get used to them.
John von Neumann

Warm-ups

5.1 Consider the scalar total differential operator

\[ \hat{D}_x \equiv \frac{d}{dx} \]

For the function \( f(x) = ax^2 + bx + c \), determine \((\hat{D}_x)^2 f(x)\).

5.2 Consider the scalar partial differential operators

\[ \hat{d}_x \equiv \frac{\partial}{\partial x} \quad \hat{d}_y \equiv \frac{\partial}{\partial y} \]

For the function \( g(x, y) = x^2y + xy + 3 \), show that the commutator \([\hat{d}_x, \hat{d}_y]g(x, y) = 0\).

5.3 Consider the scalar differential operator

\[ \hat{p} \equiv -i\hbar \frac{d}{dx} \]

where \( \hbar \) is a constant. For the function \( \psi(x) = e^{ikx} \), show that \( \hat{p}\psi(x) = \hbar k \psi(x) \).

5.4 Consider the scalar differential operator

\[ \hat{H} \equiv -\frac{\hbar^2}{8\pi^2m} \frac{d^2}{dx^2} \]

For the function \( \psi(x) = \sin \left( \frac{\pi x}{L} \right) \), show that \( \hat{H}\psi(x) = \frac{\hbar^2}{8mL^2} \psi(x) \).

5.5 Prove the following commutator relations where \([\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}\) and \(a\) and \(b\) are constants.

(a) \[ [\hat{A}, \hat{A}] = 0 \]
(b) \[ [\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \]
(c) \[ [\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \]
(d) \[ [a + \hat{A}, b + \hat{B}] = [\hat{A}, \hat{B}] \]
(e) \[ [\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \]
(f) \[ [\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \]

5.6 Show that \( \nabla \cdot \nabla \varphi = \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} \).

5.7 Show that \( \nabla (\varphi \psi) = \varphi \nabla \psi + \psi \nabla \varphi \).

5.8 For a scalar potential energy, \( V(x, y, z) = x^2 + y^2 + z^2 \), derive the force

\[ \mathbf{F} = -\nabla V \]

defined as the negative gradient of the potential energy.

Homework exercises

5.9 Perform the following operations involving differential operators
5.10 An interpretation of the Heisenberg uncertainty principle is that the operator for linear momentum in the \(x\)-direction does not commute with the operator for position along the \(x\)-axis. Let
\[
\hat{p} = -i\hbar \frac{d}{dx} \quad \text{and} \quad \hat{x} = x
\]
where \(i = \sqrt{-1}\) and \(\hbar\) is a constant. Evaluate the commutator
\[
[\hat{p}, \hat{x}] = \hat{p}\hat{x} - \hat{x}\hat{p}
\]
and show that it does not equal zero. HINT: Apply the operators \(\hat{x}\) and \(\hat{p}\) to an arbitrary function \(\varphi(x)\) and appreciate that \(x\varphi(x)\) must be differentiated as a product.

5.11* The differential operator for angular momentum is given by the expression
\[
\hat{\mathbf{M}} = -i\hbar (\mathbf{r} \times \nabla)
\]
where \(\hbar\) is a constant, \(\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z}\), and
\[
\nabla = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z}
\]
Assuming that \(\hat{\mathbf{M}} = \hat{x}\hat{M}_x + \hat{y}\hat{M}_y + \hat{z}\hat{M}_z\), find the components \(\hat{M}_x, \hat{M}_y,\) and \(\hat{M}_z\) of \(\hat{\mathbf{M}}\).

5.12* The electric potential, \(V\), produced by a point electric dipole is
\[
V(\mathbf{r}) = \frac{\mu \cdot \mathbf{r}}{r^3}
\]
where the dipole moment is written \(\mu = \mu_x \hat{i} + \mu_y \hat{j} + \mu_z \hat{k}\), the components \(\mu_x, \mu_y, \mu_z\) are constants, and the vector \(\mathbf{r} = x\hat{i} + y\hat{j} + z\hat{k}\). Shown below is the electric dipole potential produced by a point dipole located at the origin and oriented along the positive \(x\)-axis, with contours denoting \(V > 0\) (solid lines) and \(V < 0\) (dashed lines).

![Electric Dipole Potential](image)

The electric field, \(\mathbf{E}\), is defined as the negative gradient of the electric potential
\[
\mathbf{E} = -\nabla V = \frac{3(\mu \cdot \mathbf{r}) \mathbf{r}}{r^5} - \frac{\mu}{r^3}
\]

Derive the equation above using cartesian coordinates in which the electric potential can be written
\[
V = \frac{\mu \cdot \mathbf{r}}{r^3} = \frac{\mu_x x + \mu_y y + \mu_z z}{(x^2 + y^2 + z^2)^{3/2}}
\]
Note that
\[
\nabla V = \left( \hat{i} \frac{\partial V}{\partial x} + \hat{j} \frac{\partial V}{\partial y} + \hat{k} \frac{\partial V}{\partial z} \right)
\]

5.13 Show that the two-dimensional scalar function \( V(x, y) = \ln \left( \sqrt{x^2 + y^2} \right) \) satisfies Laplace’s equation
\[
\nabla^2 V(x, y) = 0
\]
First determine the gradient \( \nabla V(x, y) = f(x, y) \). Further determine the divergence \( \nabla \cdot f(x, y) = \nabla^2 V(x, y) \). Show that your result \( \nabla^2 V = 0 \).

5.14 Show that the two-dimensional scalar function \( V(r, \theta) = \ln r \) satisfies Laplace’s equation
\[
\nabla^2 V(r, \theta) = 0
\]
First determine the gradient \( \nabla V(r, \theta) = f(r, \theta) \). Further determine the divergence \( \nabla \cdot f(r, \theta) = \nabla^2 V(r, \theta) \). Show that your result \( \nabla^2 V = 0 \).

5.15 Show that the three-dimensional scalar function \( V(x, y, z) = (x^2 + y^2 + z^2)^{-1/2} \) satisfies Laplace’s equation
\[
\nabla^2 V(x, y, z) = 0
\]
First determine the gradient \( \nabla V(x, y, z) = f(x, y, z) \). Further determine the divergence \( \nabla \cdot f(x, y, z) = \nabla^2 V(x, y, z) \). Show that your result \( \nabla^2 V = 0 \).

5.16 Show that the three-dimensional scalar function \( V(r, \theta, \phi) = \frac{1}{r} \) satisfies Laplace’s equation
\[
\nabla^2 V(r, \theta, \phi) = 0
\]
First determine the gradient \( \nabla V(r, \theta, \phi) = f(r, \theta, \phi) \). Further determine the divergence \( \nabla \cdot f(r, \theta, \phi) = \nabla^2 V(r, \theta, \phi) \). Show that your result \( \nabla^2 V = 0 \).
6 Extremizing functions of many variables

6.1 Extremizing functions of one and many variables

In modeling physical systems, we often want to determine the maximum or minimum value of a function of one or many variables. Examples include characterizing the minima, maxima, and saddle points on a potential energy surface or achieving the best fit of a function to a set of data. This section explores the general problem of determining the extrema of functions of one and many variables.

6.1.1 Extremizing functions of one variable and the max/min problem

Derivatives can be used to identify extrema (maxima or minima) of functions. Consider the function $f(x)$ shown in Figure 6.1. This function has local and global maxima and minima. A local extremum is a maximum or minimum. A global extremum is the highest maximum or lowest minimum for that function over the allowed range of $x$.

At an extremum located at $x = x^*$ the slope of the function is zero and

$$\frac{df}{dx} \bigg|_{x=x^*} = 0 \quad (6.1)$$

The type of extremum at $x = x^*$ is determined uniquely by the second derivative of the function

$$\frac{d^2 f(x)}{dx^2} \bigg|_{x=x^*} = \begin{cases} < 0, & \text{maximum} \\ = 0, & \text{inflection point} \\ > 0, & \text{minimum} \end{cases}$$

When the second derivative is negative, the function’s curvature is downward and at $x = x^*$ the function is a maximum. When the second derivative is positive, the function’s curvature is upward and at $x = x^*$ the function is a minimum. When the second derivative is zero, $x = x^*$ is an inflection point where the second derivative changes sign while passing through zero.

6.1.2 Extremizing functions of many variables

Derivatives can also be used in a similar way to identify extrema of functions of many variables. For a function $f(x, y)$ of two variables $x$ and $y$, we expect that at an extremum

$$df = \frac{\partial f}{\partial x} \, dx + \frac{\partial f}{\partial y} \, dy = 0$$

for small variations in $x$ and $y$ written $dx$ and $dy$. Since $dx$ and $dy$ are independent, we can consider varying one or both at a time. As such, for $df = 0$ it must be that

$$\frac{\partial f}{\partial x} = 0 \quad \frac{\partial f}{\partial y} = 0$$
What type of extremum do we have at the critical point \((x^*, y^*)\) at which this condition is satisfied? This is determined using the hessian \(D\) written in terms of the second derivatives of \(f(x, y)\) as

\[
D = \begin{pmatrix}
\frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\
\frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2}
\end{pmatrix}
\]  

(6.2)

The type of extremum at the critical point \((x^*, y^*)\) is determined by

\[
\frac{\partial^2 f}{\partial x^2} \bigg|_{(x^*, y^*)} = \begin{cases} < 0 & D > 0 \text{ maximum} \\ > 0 & D > 0 \text{ minimum} \end{cases}
\]

For the case \(D < 0\), we expect a saddle point for which the curvature is positive in some directions and negative in others. When \(D = 0\), the test is inconclusive.

For example, consider the function

\[
f(x, y) = f_0 - \frac{1}{2}(x - a)^2 - \frac{1}{2}(y - b)^2
\]

shown in Figure 6.2 where

\[
\frac{\partial f}{\partial x} = -(x - a) = 0 \quad \frac{\partial f}{\partial y} = -(y - b) = 0
\]

Solving the two linear equations we find an extremum located at the critical point \((x^*, y^*) = (a, b)\) at which \(f_x = f_y = 0\). Evaluating the hessian where \(f_{xx} = -1\), \(f_{xy} = -1\), and \(f_{yx} = 0\) we find

\[
D = \left| \begin{array}{cc}
\frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\
\frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2}
\end{array} \right| = 1
\]

for all \(x\) and \(y\). As \(D > 0\) the extremum at \((x^*, y^*) = (a, b)\) is a maximum as shown in Figure 6.2.

An important application in the physical sciences of this method for locating extrema is identifying minima, maxima, and saddle points on potential energy surfaces. Consider the model potential energy function

\[
V(x, y) = (x^2 - 1)^2 + y^2
\]

shown in Figure 6.3. This is an example of a double well potential used to model chemical reactions and phase transitions.

\[1\] Named for German mathematician Ludwig Otto Hesse (1811-1874). For the functions of interest in this Chapter we can assume \(df\) is an exact differential and \(f_{xy} = f_{yx}\).

\[2\] The test is formulated more generally in terms of the hessian matrix of second derivatives. For a function of two variables \(f(x, y)\) the hessian matrix is

\[
\begin{bmatrix}
f_{xx} & f_{xy} \\
f_{yx} & f_{yy}
\end{bmatrix}
\]

The hessian

\[
D = f_{xx}f_{yy} - f_{xy}f_{yx}
\]

is the determinant of the hessian matrix.

Figure 6.2: The inverted parabolic function \(f(x, y)\) shown as a red surface over the \(xy\)-plane. The black point on the surface \((a, b)\) marks the maximum of the function \(f(a, b)\). Thick black lines represent one-dimensional curves \(f(a, y)\) and \(f(x, b)\). The slopes of the tangent lines at the point \((a, b)\) are zero.

Figure 6.3: The function \(V(x, y) = (x^2 - 1)^2 + y^2\). The thick horizontal lines show the derivatives \(f_x = 0\) and \(f_y = 0\) at a minimum (green dot) and saddle point (blue dot). The second derivatives and hessian are noted at each of these points.
We recognize two local minima on the potential energy surface. The locations of the minima are defined by
\[
\begin{align*}
\frac{\partial V}{\partial x} &= 0 = 4x^3 - 4x \\
\frac{\partial V}{\partial y} &= 0 = 2y
\end{align*}
\]
There are three solutions located at the critical point \((x^*, y^*) = (1, 0), (0, 0),\) and \((-1, 0)\). We can use the hessian to determine the type of extremum at each point. Recognizing that
\[
\frac{\partial^2 V}{\partial x^2} = 12x^2 - 4 \quad \frac{\partial^2 V}{\partial y^2} = 2 \quad \frac{\partial^2 V}{\partial x \partial y} = 0
\]
we find that
\[
D = \left( \frac{\partial^2 f}{\partial x^2} \right) \left( \frac{\partial^2 f}{\partial y^2} \right) - \left( \frac{\partial^2 f}{\partial x \partial y} \right)^2 = 24x^2 - 8
\]
where the value of \(D(x, y)\) depends on the position of the extremum. We find \(D(-1, 0) = D(1, 0) = 16\). Given that
\[
\frac{\partial^2 V}{\partial x^2} = 8 > 0 \quad D = 16 > 0
\]
the positions represent potential energy minima. We also find that \(D(0, 0) = -8\) and as
\[
\frac{\partial^2 V}{\partial x^2} = -4 < 0 \quad D = -8 < 0
\]
the position \((0, 0)\) is a saddle point as shown in Figure 6.3. This demonstrates how the method to identify and characterize extrema can be applied to characterize potential energy surfaces.

### 6.2 The method of Lagrange undetermined multipliers

The search for extrema of a function of many variables often occurs in the presence of constraints. For example, we might want to know the lowest possible total energy of a negative charge orbiting a positive charge subject to the constraint that the angular moment of the system is a constant. To solve such problems, Lagrange developed the method of undetermined multipliers. This section presents the general theory of undetermined multipliers and explores applications to a number of systems.

#### 6.2.1 The method of undetermined multipliers

We have an effective approach for extremizing functions of multiple variables in the absence of constraints. What do we do in the case of constrained optimization of a function of multiple variables, a situation that often arises in the physical sciences? Lagrange proposed one approach known as the method of undetermined multipliers.3

Suppose we have a function \(f(x, y)\) and constraint equation
\[
g(x, y) = 0
\]
At an extremum of the function we know that \(df = 0\) so that
\[
df = \frac{\partial f}{\partial x} \, dx + \frac{\partial f}{\partial y} \, dy = 0
\]

---

3 The method of undetermined multipliers was developed by the Italian mathematician and astronomer Joseph-Louis Lagrange (1736-1813). Born Giuseppe Lodovico Lagrangia, Lagrange’s treatise Mécanique Analytique (1788) provided the foundation for the development of mathematical physics in the 19th century.
As \( g(x, y) = 0 \) it follows that \( dg = 0 \) so that

\[
dg = \frac{\partial g}{\partial x} \, dx + \frac{\partial g}{\partial y} \, dy = 0
\]

From the constraint equation we can express \( dy \) in terms of \( dx \) as

\[
dy = -\left( \frac{\partial g}{\partial x} \frac{\partial}{\partial y} \right) dx
\]

so that

\[
df = \left[ \frac{\partial f}{\partial x} - \left( \frac{\partial g}{\partial x} \right) \frac{\partial f}{\partial y} \right] dx = 0
\]

Given this result, we recognize that an extremum will be found at a point where the total derivative

\[
\frac{df}{dx} = 0
\]

which is satisfied when

\[
\frac{\partial f}{\partial x} \left( \frac{\partial g}{\partial x} \right)^{-1} = \frac{\partial f}{\partial y} \left( \frac{\partial g}{\partial y} \right)^{-1} = \lambda
\]

where \( \lambda \) is a constant.

This result can be written as set of simultaneous equations

\[
\begin{align*}
\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} &= 0 \\
\frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} &= 0
\end{align*}
\]

that can be solved to define the location of the extremum. In practice, we determine the derivatives of the functions \( f(x, y) \) and \( g(x, y) \), set up the simultaneous equations, and solve for the undetermined multiplier \( \lambda \). We then return to the constraint equations \( g(x, y) = 0 \) and substitute for \( \lambda \) to determine the position of the extremum in terms of \( x = x^* \) and \( y = y^* \).

In the next section we explore an alternative derivation of the key equations of the method of undetermined multipliers. We will then practice the application of this powerful method of constrained optimization on a few classic examples from geometry and the physical sciences.

6.2.2 An alternative derivation

Consider the function \( f(x, y) \) presented in Figure 6.4 as a red parabolic surface. The constraint \( g(x, y) = 0 \) is represented by a gray plane. We seek the extremum of the function \( f(x, y) \) on the line defined by the intersection of the red surface defined by \( f(x, y) \) and the gray plane defined by the constraint \( g(x, y) = 0 \).

The gradient of the constraint \( g(x, y) \) is confined to the plane as is the gradient of the function \( f(x, y) \) consistent with the constraint. This means the gradient of \( f(x, y) \) and \( g(x, y) \) must be parallel, differing only in magnitude. We can express this as

\[
\nabla f(x, y) = \lambda \nabla g(x, y)
\]

where \( \lambda \) is a constant. This observation provides an intuitive and elegant proof of the method of Lagrange multipliers.

We can demonstrate equivalence of Equation 6.3 and Equation 6.4. We write the gradient of \( f(x, y) \) as

\[
\nabla f(x, y) = \frac{\partial f}{\partial x} \hat{x} + \frac{\partial f}{\partial y} \hat{y}
\]
and the gradient of $g(x,y)$ as

$$\nabla g(x,y) = \frac{\partial g}{\partial x} \hat{x} + \frac{\partial g}{\partial y} \hat{y}$$

It follows that Equation 6.3 can be rewritten

$$\left( \frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} \right) \hat{x} + \left( \frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} \right) \hat{y} = 0$$

Since the terms in the $x$-direction and $y$-direction are independent, each term in parentheses must be zero. It follows that

$$\nabla f(x,y) - \lambda \nabla g(x,y) = 0$$

### 6.2.3 Application to optimizing geometric functions with constraints

To practice the application of the method of undetermined multipliers, we consider the rectangular area in Figure 6.5 with sides of length $x$ and $y$. The rectangle’s perimeter has a fixed length $C = 2x + 2y$. For a rectangle of fixed perimeter $C$, what are the length $x = x^*$ and width $y = y^*$ that maximize the rectangle’s area $A(x,y) = xy$?

We can answer this question by extremizing the area subject to a constraint on the circumference imposed using the Lagrange multiplier. The function to be maximized is the area

$$A(x,y) = xy$$

and the constraint is expressed as

$$g(x,y) = C - (2x + 2y) = 0$$

where the circumference has been set to a constant $C$. Following the procedure defined by Equation 6.3 we have

$$\frac{\partial A}{\partial x} - \lambda \frac{\partial g}{\partial x} = y + 2\lambda = 0$$
$$\frac{\partial A}{\partial y} - \lambda \frac{\partial g}{\partial y} = x + 2\lambda = 0$$

Therefore, the largest possible rectangle is a square with sides $x = -2\lambda$ and $y = 2\lambda$. 

---

**Figure 6.4:** The inverted parabolic function $f(x,y)$ shown as a red surface over the $xy$-plane. The constraint function $g(x,y) = 0$ is represented by the gray surface. The black point on the surface is $f(a,b)$ and the thick black line is the one-dimensional curve $f(a,y)$ where $x$ is constrained by $g(x,y) = x - a = 0$ to be $x = a$. The slope of the tangent line at the point $(a,b)$ is $f_y(a,b)$.

**Figure 6.5:** A rectangle of circumference $C = 2x + 2y$ and area $A = xy$. 

---
y = −2λ. Since
\[ C = (2x + 2y) = −8λ \]
we find \( \lambda = \frac{C}{8} \) and
\[ x^* = y^* = \frac{C}{4} \]
The rectangle with the largest possible area for a given circumference is a square. Inserting back into our original equations, we find that the constraint is satisfied and the area of the rectangle is \( A = \frac{C^2}{16} \).

Let’s explore another constrained extremization problem using Lagrange multipliers. Consider a cylinder of height \( z \) with circular base of radius \( r \) shown in Figure 6.6. The volume of the cylinder is
\[ V(r, z) = \pi r^2 z \]
and the surface area of the cylinder is
\[ A(r, z) = 2\pi r (z + r) \]
which is the sum of the area of the side of the cylinder, \( 2\pi rz \), and the areas of the top and bottom circular caps each having area \( \pi r^2 \). Suppose we hold the surface area to be a constant \( A_0 \). For a cylinder of fixed surface area \( A_0 \), what are the values of \( r = r^* \) and \( z = z^* \) that maximize the cylinder’s volume?

Following the procedure defined by Equation 6.3 we extremize the volume \( V(r, z) \) subject to the constraint
\[ g(r, z) = A_0 - [2\pi r (z + r)] = 0 \]
so that
\[
\begin{align*}
\frac{\partial V}{\partial r} - \lambda \frac{\partial g}{\partial r} &= 2\pi rz + \lambda (2\pi z + 4\pi r) = 0 \\
\frac{\partial V}{\partial z} - \lambda \frac{\partial g}{\partial z} &= \pi r^2 + \lambda 2\pi r = 0
\end{align*}
\]
The second equation yields \( \lambda = -\frac{r}{2} \). Substituting into the first equation yields
\[ 2\pi rz - \frac{r}{2} (2\pi z + 4\pi r) = 0 \]
or \( \pi rz = 2\pi r^2 \) so that \( z = 2r \). Substituting into the constraint defined by Equation 6.5 results in \( A_0 = 6\pi r^2 \) or equivalently \( z^* = 2r^* = 2\sqrt{\frac{A_0}{6\pi}} \). As our final result, we find the maximum volume of a cylinder of surface area \( A_0 \) is
\[ V(r^*, z^*) = \pi r^{*2} z^* = \frac{1}{3} A_0 \sqrt{\frac{A_0}{6\pi}} \]

Conversely, for a cylinder of fixed volume \( V_0 \) we can use the method of undetermined multipliers to determine the dimensions of height and radius that minimize the surface area of the cylinder.

A6 Variational calculation of the energy of a one electron atom

One interesting application of Lagrange’s method of undetermined multipliers involves Bohr’s model of a one electron atom. In the Bohr model, an electron of charge \( -e \) and mass \( m_e \) moves in a circular orbit around a central charge \( Ze \)
centered at the origin (see Figure 6.7).\footnote{The Danish physicist and philosopher Niels Bohr (1885-1962) developed a \textit{semiclassical} model of the one-electron atom using elements of both classical and quantum theory.}

The total energy of the orbiting electron, given by the sum of the kinetic energy and potential energy, will be a function of the radius of the orbit $r$ and the velocity of the electron $v$

$$E(r, v) = \frac{1}{2} m_e v^2 - \frac{Ze^2}{r}$$

where the first term is the kinetic energy of the electron and the second term is the potential energy between the negatively charged electron and the central positive charge. Bohr assumed only certain orbits were allowed where the electron’s angular momentum was constrained to be\footnote{As the angular momentum may assume only certain discrete values we say that the angular momentum is quantized.}

$$l = m_e vr = \frac{nh}{2\pi} = n\hbar$$

where $n$ is a positive integer, $\hbar$ is Planck’s constant, and $\hbar = \frac{h}{2\pi}$.

If we consider that the electron can be modeled as a wave with de Broglie wavelength\footnote{Named for French physicist Louis de Broglie (1892-1987) who proposed that electrons and all matter have properties of a wave.}

$$\lambda = \frac{h}{m_e v}$$

we see that the constraint on the angular momentum is equivalent to the assumption that there are a fixed number of de Broglie wavelengths $\lambda$ in the circumference of the orbit $2\pi r$ or

$$n\lambda = 2\pi r = \frac{nh}{m_e v}$$

This constraint is demonstrated in Figure 6.7 that shows a wave with $n = 4$.

We can find the allowed orbits using the \textit{variational principle} where we minimize the total energy $E(r, v)$ as a function of $r$ and $v$ subject to the constraint on the angular momentum written

$$g(r, v) = m_e vr - n\hbar = 0 \quad (6.6)$$

We follow the procedure defined by Equation 6.3 taking our undetermined multiplier to be a constant $\alpha$ so that

$$\frac{\partial E}{\partial r} - \alpha \frac{\partial g}{\partial r} = 0$$
$$\frac{\partial E}{\partial v} - \alpha \frac{\partial g}{\partial v} = 0$$
Computing the necessary derivatives we find
\[ \frac{\partial E}{\partial r} = \frac{Ze^2}{r^2} \quad \frac{\partial E}{\partial v} = m_e v \]
and
\[ \frac{\partial g}{\partial r} = m_e v \quad \frac{\partial g}{\partial v} = m_e r \]
Combining these results we find
\[ \frac{\partial E}{\partial r} - \alpha \frac{\partial g}{\partial r} = \frac{Ze^2}{r^2} - \alpha m_e v = 0 \]
\[ \frac{\partial E}{\partial v} - \alpha \frac{\partial g}{\partial v} = m_e v - \alpha m_e r = 0 \]
The second equation yields
\[ \alpha = \frac{v}{r} \]
so that the first equation can be written
\[ \frac{Ze^2}{r^2} = \alpha m_e v = \frac{m_e v^2}{r} \tag{6.7} \]
This is the condition to form a stable orbit. The inward pointing centripetal force due to the coulomb attraction is exactly balanced by the outward pointing centrifugal force.

Given the constraint on the angular moment given by Equation 6.6, the velocity
\[ v = \frac{\hbar}{m_e r} \]
Substituting into Equation 6.7 we find that the allowed values of the radius and velocity are
\[ r^* = \frac{n^2 \hbar^2}{Z m_e e^2} \quad v^* = \frac{Ze^2}{n \hbar} \quad n = 1, 2, 3, \ldots \]
With these results for the radius and velocity we can solve for the total energy
\[ E(r^*, v^*) = \frac{1}{2} m_e v^*^2 - \frac{Ze^2}{r^*} \]
\[ = \frac{1}{2} m_e \left( \frac{Z^2 e^4}{n^2 \hbar^2} \right) - Ze^2 \left( \frac{Z m_e e^2}{n^2 \hbar^2} \right) \]
\[ = \frac{1}{2} m_e \frac{Z^2 e^4}{n^2 \hbar^2} \quad n = 1, 2, 3, \ldots \]
which we find to be a function of counting number \( n \). This equation defines the infinity of allowed energies for the electron orbiting the central nuclear charge.

We can write the potential energy, \( V(r) \) in the alternative units
\[ V(r) = -\frac{Ze^2}{4 \pi \epsilon_0 r} \]
where \( \epsilon_0 \) is the permittivity of a vacuum. In this system of units, we find the allowed total energies
\[ E(r, v) = -\frac{Z^2}{n^2} \left( \frac{m_e e^4}{8 \epsilon_0^2 \hbar^2} \right) \quad n = 1, 2, 3, \ldots \]
where the complicated ratio of fundamental physical constants including the mass and charge of the electron, the permittivity of a vacuum, Planck’s constant,
We assume that \( N \) where \( n^2 \) we can use Stirling’s approximation defined by Equation 2.18 so that

\[
\frac{n!e^d}{\sqrt{2\pi n}} = hR = \mathcal{H}
\]

that defines the Rydberg constant, \( R = 3.29 \times 10^{15} \) Hz, and the Hartree constant, \( \mathcal{H} = 2.18 \times 10^{-18} \) Joules.\(^7\)

\[ \text{B}_6 \text{ Extremizing the multiplicity subject to constraints} \]

Let’s consider a system with \( N \) observations each of which has \( k = 2 \) distinguishable and equally probable outcomes. For example, this could be a series of \( N \) coin flips, each of which might be a head or tail. In a given series of \( N \) observations there will be \( n_1 \) outcomes of the first type and \( n_2 \) outcomes of the second type where \( n_1 + n_2 = N \). The total number of outcomes is given by the binomial coefficient

\[
W(n_1, n_2; N) = \frac{N!}{n_1!n_2!} = \frac{N!}{n_1!(N-n_1)!}
\]

where \( n! \) is pronounced \( n \text{ factorial} \) and defined

\[
n! = n \times (n-1) \times (n-2) \times \ldots \times 1
\]

Suppose we want to know the most probable outcome \( \{n^*_1, n^*_2\} \) that corresponds to the maximum multiplicity \( W(n^*_1, n^*_2; N) \) subject to the constraint that \( N = n^*_1 + n^*_2 \). The numerator is fixed to be \( N! \) so we can maximize the multiplicity by making the denominator \( n_1!n_2! = n_1!(N-n_1)! \) as small as possible. That will occur when we have an even distribution with an equal number of each type of object\(^8\) so that \( n^*_1 = n^*_2 = N/2 \) and

\[
W(n^*_1, n^*_2; N) = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}
\]

Now let’s consider the slightly more complicated example of a system with \( N \) total objects of \( k = 3 \) distinguishable types. Suppose we want to know the most probable outcome \( \{n^*_1, n^*_2, n^*_3\} \) corresponding to the maximum multiplicity \( W(n^*_1, n^*_2, n^*_3; N) \) subject to the constraint that \( N = n^*_1 + n^*_2 + n^*_3 \). To do this, we will use the method of Lagrange multipliers. The multiplicity is given by the multinomial coefficient

\[
W(n_1, n_2, n_3; N) = \frac{N!}{n_1!n_2!n_3!}
\]

Since the multiplicity can be a very large number, it is convenient to work with the logarithm of the multiplicity\(^9\)

\[
f(n_1, n_2, n_3) = \ln \left[ W(n_1, n_2, n_3; N) \right]
\]

Let’s maximize the function \( f(n_1, n_2, n_3) \) subject to the constraint

\[
g(n_1, n_2, n_3) = N - (n_1 + n_2 + n_3) = 0
\]

We assume that \( N \) as well as \( n_1, n_2, \) and \( n_3 \) are much greater than 1. As such, we can use Stirling’s approximation defined by Equation 2.18 so that

\[
f(n_1, n_2, n_3) \approx N \ln N - (n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln n_3)
\]

\(^7\) The lowest allowed total energy of the Bohr model for \( Z = 1 \) is coincidently the ground state energy of the hydrogen atom. These fundamental constants are named for Swedish physicist Johannes Rydberg (1854-1919) and English mathematician and physicist Douglas Hartree (1897-1958).
Following the procedure defined by Equation 6.3 we find
\[
\frac{\partial f}{\partial n_1} - \lambda \frac{\partial g}{\partial n_1} = -\ln n_1 - 1 + \lambda = 0 \\
\frac{\partial f}{\partial n_2} - \lambda \frac{\partial g}{\partial n_2} = -\ln n_2 - 1 + \lambda = 0 \\
\frac{\partial f}{\partial n_3} - \lambda \frac{\partial g}{\partial n_3} = -\ln n_3 - 1 + \lambda = 0
\]
This leaves
\[n_1 = n_2 = n_3 = e^{\lambda - 1} = \text{constant}\]
which is a uniform distribution. Returning to our constraint equation we find
\[N = n_1 + n_2 + n_3 = \text{constant}\]
so that \(n_1^* = n_2^* = n_3^* = N/3\) and the maximum multiplicity is\(^8\)
\[W(n_1^*, n_2^*, n_3^*; N) = \frac{N!}{(N/3)! (N/3)! (N/3)!}\]

\section*{C6 End-of-chapter problems}

Nothing takes place in the world whose meaning is not that of some maximum or minimum. 

\begin{flushright}
Leonhard Euler
\end{flushright}

\textbf{Warm-ups}

6.1 For each function determine whether it reaches a maximum value, a minimum value, or both. Evaluate each function that does reach a maximum or minimum value at each extremum. NOTE: The parameters \(A, \epsilon, \sigma, \epsilon, \pi, m, k, \) and \(T\) are positive constants.

(a) \(y(x) = 3x^2 - 5x + 2 \quad x \in (-\infty, \infty)\) \hspace{1cm} (b) \(p(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}} \quad v \in [0, \infty)\)

(c) \(V(r) = 4e \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \quad r \in [0, \infty)\) \hspace{1cm} (d) \(P(E) = 2\pi^{-1/2}(kT)^{-3/2}e^{-E/kT} E^{1/2} \quad E \in [0, \infty)\)

6.2 The electron density distribution function for an electron in a one-dimensional box in its ground state is
\[p(x) = \left(\frac{2}{L}\right) \sin^2 \frac{\pi x}{L} \quad x \in [0, L]\]
where \(L\) is the length of the box. Find the value of \(x = x^*\) for which \(p(x)\) is a maximum.

6.3 The electron density distribution function for an electron in the ground state of the hydrogen atom is
\[p(r) = 4 \left(\frac{1}{a_0}\right)^3 r^2 e^{-\frac{r}{\alpha}}\]
Find the value of \(r = r^*\) for which \(p(r)\) is a maximum.

6.4 Consider a rectangular box of dimensions \(x, y,\) and \(z\). The volume of the rectangular box is
\[V(x, y, z) = xyz\]
and the surface area of the rectangular box is

\[ A(x, y, z) = 2(x^2 + y^2 + z^2). \]

The volume of the box is constrained to be a constant \( V_0 \). Using the method of undetermined multipliers, find the dimensions \( x = x^*, y = y^* \), and \( z = z^* \) that minimize the surface area of the box. Determine the value of \( A(x^*, y^*, z^*) \) in terms of \( V_0 \).

6.5 Consider the function

\[ f(x, y) = x^2 - y^2 \]

Find the critical point at which \( f_x = 0 \) and \( f_y = 0 \). Evaluate the hessian \( D = f_{xx}f_{yy} - f_{xy}f_{yx} \) at the critical point. If the second derivative test is conclusive (\( D \neq 0 \)), classify the critical point as a minimum, maximum, or saddle point.

**Homework exercises**

6.6 The potential energy, \( V(r) \), of a diatomic molecule as a function of its bond length, \( r \), can be approximated by the Morse function

\[ V(r) = A(1 - e^{-B(r-r_0)})^2 \]

where \( A \), \( B \), and \( r_0 \) are positive constants. Find the bond length \( r = r^* \) for which \( V(r) \) is a minimum.

6.7 Consider the function

\[ f(x, y) = xy \]

defining a hyperbolic saddle in three-dimensional cartesian space depicted in the figure below as the red surface. Suppose you impose the constraint

\[ g(x, y) = x^2 + y^2 - 2 = 0 \]

Using the method of undetermined multipliers determine the four critical points \( (x^*, y^*) \). Evaluate the function \( f(x^*, y^*) \) at each critical point and determine if that point represents a maximum or a minimum of the constrained function.

6.8 Consider the function

\[ f(x, y, z) = x + y + 2z \]

three-dimensional cartesian space. Suppose you impose the constraint

\[ g(x, y, z) = x^2 + y^2 + z^2 - 3 = 0 \]

Using undetermined multipliers determine the two critical points \( (x^*, y^*, z^*) \). Evaluate the function \( f(x^*, y^*, z^*) \) at each critical point and determine if that point represents a maximum or a minimum.
6.9 Consider a cone of height, \( h \), and circular base of radius, \( r \). The volume of the cone is

\[
V(r, h) = \frac{1}{3}\pi r^2 h
\]

and the lateral surface area of the cone (the surface area of the top of the cone, excluding the base) is

\[
A(r, h) = \pi r \sqrt{r^2 + h^2}
\]

where \( \sqrt{r^2 + h^2} \) is the length of the side of the cone. The volume of the cone is constrained to be a constant \( V_0 \). Using the method of undetermined multipliers, find the radius \( r = r^∗ \) and height \( h = h^∗ \) that minimize the lateral surface area of the cone. Determine the minimal area \( A(r^∗, h^∗) \) in terms of the fixed volume \( V_0 \).

6.10* Consider the butterfly potential energy function

\[
V(x, y) = ((x - y)^2 - 1)^2 + 10x^2 y^2
\]

shown in the figure below. There are seven critical points at which \( V_x = 0 \) and \( V_y = 0 \). Evaluate the hessian

\[
D = V_{xx}V_{yy} - V_{xy}V_{yx}
\]

at the critical points \((1, 0)\), \((0, 0)\), and \((1/3, -1/3)\). If the second derivative test is conclusive \((D \neq 0)\), classify the critical point as a minimum, maximum, or saddle point.

6.11* Consider the function

\[
W(n_1, n_2, \ldots, n_M) = \frac{N!}{n_1! n_2! \ldots n_M!}
\]

where

\[
N = \sum_{k=1}^{M} n_k
\]

(a) Using Stirling’s approximation, derive an approximate form of \( \ln W(n) \) that has no factorials and is valid for large values of \( N \) and \( n_k \) for all \( k \).

(b) Using the method of undetermined multipliers, find the values of all \( n_k \) for which the function

\[
S(n_1, n_2, \ldots, n_M) = \ln W(n_1, n_2, \ldots, n_M)
\]

is a maximum subject to the constraint that \( \sum_{k=1}^{M} n_k - N = 0 \).

6.12* Find the value of \( \lambda \) for which the function \( \rho(\lambda) \) is a maximum where

\[
\rho(\lambda) = \frac{8\pi h c}{\lambda^5} \left[ \frac{1}{\exp(\beta h c / \lambda) - 1} \right]
\]

HINT: Introduce the variable \( x = \beta h c / \lambda \). Substitute \( \lambda \) in terms of \( x \) to find the simplified function \( \rho(x) \). Determine the
maximum of the function by solving the equation

\[ \frac{d\rho(x)}{dx} \bigg|_{x=x_{\text{max}}} = 0 \]

The maximum of \( \rho(\lambda) \) will occur at \( \lambda_{\text{max}} = \beta \hbar c / x_{\text{max}} \).

6.13* The variational method in quantum mechanics provides a means of finding the lowest energy configuration of nuclei and electrons. A trial wave function is assumed, depending on one or more parameters, and the values of the parameters are varied to find the lowest energy possible. In this problem, you will apply the variational method to find the allowed energies of the one electron atom or ion given by the Bohr model.

Consider the classical Bohr model of the one electron hydrogen atom that assumes the electron moves in a circular orbit about the nucleus (see Figure 6.7). The energy of the hydrogen atom in this model is

\[ E(r, v) = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi \varepsilon_0 r} \]

where \( \varepsilon_0 \) is the permittivity of a vacuum. The nucleus of charge \( +e \) is centered at the origin. The electron of charge \( -e \) and mass \( m_e \) moves in a circular orbit of radius, \( r \), and linear velocity, \( v \).

Bohr assumed only certain orbits were possible and that those orbits had values of the angular momentum

\[ L = m_e v r = \frac{nh}{2\pi} \quad n = 1, 2, 3, \ldots \]

where \( h \) is Planck's constant and \( n \) is the quantum number. Use the method of undetermined multipliers to minimize the energy of the atom, \( E(r, v) \), subject to the constraint that

\[ \frac{nh}{2\pi} - m_e v r = 0 \]

(a) Show that the radius of an allowed orbits is given by

\[ r = \left( \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} \right) n^2 = a_0 n^2 \quad n = 1, 2, 3, \ldots \]

where the constant \( h = h/2\pi \) and \( a_0 = 0.529 \times 10^{-10} \text{m} \) is known as the Bohr radius.

(b) Show that the allowed energies for the orbits are given by

\[ E = -\frac{1}{n^2} \left( \frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} \right) \quad n = 1, 2, 3, \ldots \]
7 Sequences, series, and expansions

7.1 Series, convergence, and limits 121
7.2 Power series 124
7.3 Expanding functions as Maclaurin and Taylor series 126
   A7 Taylor series expansions of potential energy functions 132
   B7 Useful approximations to functions based on power series 134
   C7 Self-similarity and fractal structures 136
   D7 End-of-chapter problems 139

7.1 Series, convergence, and limits

Many physical processes are conveniently modeled mathematically using a finite or infinite series. For example, the divergent harmonic series captures overtones of a vibrating string and harmonics in music. The convergent geometric series appears in Einstein’s theory of the heat capacity of solids. In this section, we explore basic definitions of sequences and series and examine how we can determine their limits.

7.1.1 Infinite series and partial sums

Consider the infinite series

$$\sum_{n=0}^{\infty} u_n = u_0 + u_1 + u_2 + \ldots$$

where \( n \) is a counting number that serves as an index.\(^1\) The characters \( i, j, k, l, m \) or \( n \) are most commonly used to represent discrete variables.\(^2\) Now consider the partial sum formed by the first \( N + 1 \) terms in the infinite series

$$S_N = \sum_{n=0}^{N} u_n = u_0 + u_1 + \ldots + u_N$$

The infinite series will be convergent if

$$\lim_{N \to \infty} S_N = S$$

where \( S \) is finite.\(^3\)

Let’s examine the geometric series

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \ldots$$

which is important in the physical sciences and arises in many problems in thermodynamic equilibria and quantum molecular science.\(^4\) The partial sum is

$$S_N = \sum_{n=0}^{N} x^n = 1 + x + x^2 + x^3 + \ldots + x^N$$

We make the clever observation that

$$S_N - xS_N = 1 + x + \ldots + x^N - \left(x + x^2 + \ldots + x^{N+1}\right)$$

$$= 1 - x^{N+1}$$

\(^1\) The choice of the initial value of the index is arbitrary. However, a specific value typically appears to be most natural for a given series.

\(^2\) Characters most commonly used to represent continuous variables include \( r, s, t, u, v, w, x, y, \) and \( z.\)

\(^3\) The question of how a sum of an infinite series of numbers can be finite is known as Zeno’s paradox after Zeno of Elea (circa 490-430 BCE).

\(^4\) The geometric series is defined as a series with a constant ratio between terms. It was mentioned by Euclid (circa 300 BCE) who employed partial sums to explore its properties.
Solving for $S_N$ we find

$$S_N = \frac{1 - x^{N+1}}{1 - x}$$

This partial sum $S_N$ is shown in Figure 7.1 for the specific value of $x = \frac{1}{2}$ and $N = 0$ to 10. As $N$ increases the partial sum approaches the limit $S = 2$.

Let’s consider the convergence of the geometric series more generally as a function of $x$. Since $\lim_{N \to \infty} x^N = 0$ for $|x| < 1$ we find

$$\lim_{N \to \infty} S_N = \frac{1}{1 - x} \quad |x| < 1$$

leading to the result that the geometric series

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \ldots = \frac{1}{1 - x} \quad |x| < 1 \quad (7.1)$$

converges for $-1 < x < 1$. For $|x| \geq 1$ the geometric series diverges.

As an example application of the geometric series, consider the unit square of area one as shown in Figure 7.2. We start by shading one quarter of the unit square, and then one quarter of a quarter, and then one quarter of a quarter of a quarter, and so on. Each new shaded area is a $\frac{1}{4}$ the previous shaded area. After an infinite number of steps, what is the total shaded area?

This series representing the shaded area can be written

$$S = \frac{1}{4} + \frac{1}{16} + \frac{1}{64} + \ldots = \sum_{n=1}^{\infty} \left(\frac{1}{4}\right)^n$$

This series can be transformed into a geometric series by adding one since

$$1 + S = 1 + \frac{1}{4} + \frac{1}{16} + \frac{1}{64} + \ldots = \sum_{n=0}^{\infty} x^n$$

where $x = 1/4$. The series sums to

$$1 + S = \frac{1}{1 - \frac{1}{4}} = \frac{4}{3}$$

leading to the final result that the total shaded area $S = \frac{1}{3}$.

7.1.2 Checking for convergence with the ratio test

Every infinite series will converge to a finite number or diverge. In general, how can we tell if a specific infinite series

$$\sum_{n=0}^{\infty} u^n = u_1 + u_2 + u_3 + \ldots$$

will converge or diverge? One approach is the ratio test that assesses the relative magnitude or ratio of neighboring terms $u_n$ and $u_{n+1}$ as $n$ approaches $\infty$. We write the limit of this ratio as

$$r = \lim_{n \to \infty} \left| \frac{u_{n+1}}{u_n} \right|$$

If $r < 1$ the series converges, if $r > 1$ the series diverges, and if $r = 1$ the test is inconclusive.

Let’s apply the ratio test to the geometric series where $u_n = x^n$ and $u_{n+1} = x^{n+1}$ so that

$$r = \lim_{n \to \infty} \left| \frac{u_{n+1}}{u_n} \right| = \lim_{n \to \infty} \left| \frac{x^{n+1}}{x^n} \right| = |x|$$

The shaded area covers $\frac{1}{3}$ the total area of the bounding square.

The ratio test was proposed by French mathematician, physicist, philosopher, and music theorist Jean le Rond d’Alembert (1717-1783).
According to the ratio test, if $|x| < 1$ the series converges and if $|x| > 1$ the series diverges. This result agrees with our prior conclusion drawn from an analysis of the partial sum (see Equation 7.1).

Let’s look at another example. Consider the exponential function

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2!} x^2 + \frac{1}{3!} x^3 + \ldots$$

We can define the partial sum

$$S_N(x) = \sum_{n=0}^{N} \frac{1}{n!} x^n$$

so that $S_0(x) = 1$, $S_1(x) = 1 + x$, $S_2(x) = 1 + x + \frac{1}{2} x^2$ and so on. As $N$ increases, the approximation of the partial sum to the exact exponential function becomes increasingly accurate. This behavior is shown in Figure 7.3 for partial sums from $N = 0$ to 4. The partial sum is most accurate near $x = 0$. As the magnitude of $x$ increases, an increasingly large value of $N$ is required to accurately approximate the exponential function.

Applying the ratio test to our infinite series where $u_n = \frac{1}{n!} x^n$ and $u_{n+1} = \frac{1}{(n+1)!} x^{n+1}$ we find

$$r = \left| \frac{u_{n+1}}{u_n} \right| = \lim_{n \to \infty} \left| \frac{n! x^{n+1}}{(n+1)! x^n} \right|$$

which can be simplified to

$$r = \lim_{n \to \infty} \left| \frac{x}{n+1} \right| = 0$$

This demonstrates that the series converges for all values of $x$. This is what we expect for the exponential function as $e^x$ is finite for any finite value of $x$.

As a final example, let’s consider the convergence of the harmonic series

$$\sum_{n=1}^{\infty} \frac{1}{n} = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \ldots$$

which is depicted graphically in Figure 7.4. Applying the ratio test we find $u_n = \frac{1}{n}$ and $u_{n+1} = \frac{1}{n+1}$ so that

$$r = \left| \frac{u_{n+1}}{u_n} \right| = \lim_{n \to \infty} \left| \frac{n}{n+1} \right| = 1$$

For the harmonic series the ratio test is inconclusive. To further test the convergence of the harmonic series, let’s compare the it with the series

$$S = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{4} + \frac{1}{8} + \frac{1}{8} + \frac{1}{8} + \frac{1}{8} + \ldots$$

which is divergent as

$$S = 1 + \frac{1}{2} + \left( \frac{1}{4} + \frac{1}{4} \right) + \left( \frac{1}{8} + \frac{1}{8} + \frac{1}{8} + \frac{1}{8} \right) \ldots$$

$$= 1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \ldots = \infty$$

Noting that every term in the divergent series $S$ is less than or equal to the corresponding term in the harmonic series, we conclude that the harmonic series also diverges.

The comparison test employed in this proof provides a powerful method for determining convergence properties of series. Suppose we have two series $\sum a_n$ and $\sum b_n$.

Figure 7.3: The exponential function (black) shown with partial sums $S_N(x)$ for $N = 0$ to 4 in increasingly dark shades of red.

Figure 7.4: The shaded rectangles vary in area as $\frac{1}{n}$ where the total shared area is defined by $1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \ldots = \infty$ known as the harmonic series.

6 Harmonic sequences are often associated with the Greek mathematician Pythagoras (570–495 BCE) and his followers. The concept of the harmonic series has inspired theories of mathematics, music, art, and architecture.

7 This elegant proof of the divergence of the harmonic series was presented by French philosopher Nicole Oresme (circa 1320–1382). It is considered by many to be the high point of mathematical reasoning in medieval Europe.
and $\sum b_n$. If $a_n > b_n$ for all $n$ then if $\sum a_n$ converges so does $\sum b_n$. Similarly, if $\sum b_n$ diverges so does $\sum d_n$.

### 7.2 Power series

Power series may be used to represent special mathematical constants such as $e$ and $\pi$ and functions commonly used in modeling physical processes such as $e^x$ and $\ln x$. In this section, we explore the definition of a power series and how we can determine its limits.

#### 7.2.1 Testing convergence of infinite power series

Many functions $S(x)$ of interest in the physical sciences can be represented as an infinite series of powers of $x$ known as a **power series**

$$S(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + \ldots$$

known as a *power series*. We have already seen one example in the exponential function

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2!} x^2 + \frac{1}{3!} x^3 + \ldots$$

where the coefficients $a_n = 1/n!$. Applying the ratio test to the general case, we see that the power series will converge if

$$r = \lim_{n \to \infty} \left| \frac{a_{n+1}}{a_n} \right| = \lim_{n \to \infty} \left| \frac{a_{n+1} x^{n+1}}{a_n x^n} \right| = |x| \lim_{n \to \infty} \left| \frac{a_{n+1}}{a_n} \right| < 1$$

This can be expressed as a condition on the magnitude of $x$ as

$$|x| < \lim_{n \to \infty} \left| \frac{a_{n+1}}{a_n} \right| = \lim_{n \to \infty} \left| \frac{a_n}{a_{n+1}} \right| = R$$

where $R$ is the **radius of convergence**. In general, the power series converges in the interval $-R < x < R$.

Let’s consider the example

$$S(x) = \sum_{n=1}^{\infty} \frac{1}{n} \left( \frac{x}{2} \right)^n$$

where the partial sum can be written

$$S_N(x) = \sum_{n=1}^{N} \frac{1}{n} \left( \frac{x}{2} \right)^n$$

For this series $a_n = \frac{1}{n2^n}$ and the radius of convergence is

$$R = \lim_{n \to \infty} \left| \frac{a_n}{a_{n+1}} \right| = \lim_{n \to \infty} \frac{(n+1)2^{n+1}}{n2^n} = 2$$

We conclude that the power series converges in the interval $-2 < x < 2$. Figure 7.5 shows the partial sum $S_N(x)$ as a function of $x$ for $N = 1, 5,$ and 10. The infinite series $S(x = 2)$ is the harmonic series that we found to be divergent. However, the infinite series $S(x = -2)$ is the alternating harmonic series that converges to $\ln(2)$ as we will demonstrate in the next section. Therefore, we can refine our interval of convergence to be $-2 < x < 2$.

---

$^8$ The radius of convergence was formulated by French mathematician and physicist Augustin-Louis Cauchy (1789-1857).

---

**Figure 7.5**: The partial sum $S_N(x)$ of the infinite power series with coefficients $a_n = \frac{1}{n2^n}$ shown for $N = 1, 5,$ and 10 in increasingly dark shades of red.
7.2.2 Differentiating and integrating power series

If a power series converges over an interval $-R < x < R$ it is also a continuous function of $x$ over that interval. Moreover, if the power series

$$f(t) = \sum_{n=0}^{\infty} a_n t^n$$

converges, so does its integral\(^9\)

$$S(x) = \int_0^x f(t) \, dt = \int_0^x \left( \sum_{n=0}^{\infty} a_n t^n \right) \, dt = \sum_{n=0}^{\infty} \left( \int_0^x a_n t^n \, dt \right)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n+1} a_n x^{n+1}$$

since the radius of convergence of $S(x)$

$$R = \lim_{n \to \infty} \left| \frac{(n+2) a_n}{(n+1) a_{n+1}} \right| = \lim_{n \to \infty} \left| \frac{a_n}{a_{n+1}} \right|$$

is the same as for the power series itself. Similarly, the derivative of a convergent power series\(^10\)

$$S(x) = \frac{d}{dt} f(t) \bigg|_{t=x} = \frac{d}{dt} \sum_{n=0}^{\infty} a_n t^n \bigg|_{t=x} = \sum_{n=0}^{\infty} \left( \frac{d}{dt} a_n t^n \right) \bigg|_{t=x}$$

$$= \sum_{n=0}^{\infty} a_n nx^{n-1}$$

is convergent since the radius of convergence of $S(x)$ is the same as for the power series itself

$$R = \lim_{n \to \infty} \left| \frac{(n+1) a_n}{n a_{n+1}} \right| = \lim_{n \to \infty} \left| \frac{a_n}{a_{n+1}} \right|$$

Let’s explore these properties of convergent power series for the geometric series

$$f(t) = \sum_{n=0}^{\infty} t^n = 1 + t + t^2 + \ldots = \frac{1}{1-t} \quad |t| < 1$$

Figure 7.6 shows the geometric series along with its derivative and integral as a function of $x$.

Integrating the geometric series we find

$$S(x) = \int_0^x f(t) \, dt = \sum_{n=0}^{\infty} \left( \int_0^x t^n \, dt \right)$$

Using the identity

$$\int_0^x t^n \, dt = \frac{1}{n+1} x^{n+1} \bigg|_0^x = \frac{1}{n+1} x^{n+1}$$

leads to the result

$$S(x) = \sum_{n=0}^{\infty} \frac{1}{n+1} x^{n+1} = x + \frac{1}{2} x^2 + \frac{1}{3} x^3 + \ldots$$

However, since $f(t) = \frac{1}{1-t}$ we can also write\(^11\)

$$S(x) = \int_0^x f(t) \, dt = \int_0^x \frac{1}{1-t} \, dt = -\ln(1-x)$$

Combining these results leads to an expression for the power series of the

\(^9\) Note that order of integration and summation may be reversed as

$$\int \left( \sum_{n=0}^{\infty} f_n(x) \right) \, dx$$

can be written

$$\int f_0(x) \, dx + \int f_1(x) \, dx + \ldots$$

which is equal to

$$\sum_{n=0}^{\infty} \int f_n(x) \, dx$$

\(^10\) Note that order of differentiation and summation may be reversed as

$$\frac{d}{dx} \left( \sum_{n=0}^{\infty} f_n(x) \right)$$

can be written

$$\frac{d}{dx} f_0(x) + \frac{d}{dx} f_1(x) + \ldots$$

which is equal to

$$\sum_{n=0}^{\infty} \frac{d}{dx} f_n(x)$$

\(^11\) Here we use the identity

$$\int_0^x \frac{1}{1-t} \, dt = -\ln(1-t) \bigg|_0^x = -\ln(1-x)$$

as $\ln(1) = 0.$
natural logarithm

\[ S(x) = \ln(1 - x) = -\sum_{n=0}^{\infty} \frac{1}{n+1} x^{n+1} \]

with a radius of convergence \( R = 1 \), which is the radius of convergence of the original geometric series.

Differentiating the geometric series we find

\[ S(x) = \left. \frac{d}{dt} f(t) \right|_{t=x} = \sum_{n=0}^{\infty} \left( \left. \frac{d}{dt} t^n \right|_{t=x} \right) = \sum_{n=0}^{\infty} n x^{n-1} = 1 + 2x + 3x^2 + \ldots \]

However, we can also write

\[ S(x) = \left. \frac{d}{dt} f(t) \right|_{t=x} = \frac{d}{dt} \left. \frac{1}{1-t} \right|_{t=x} = \frac{1}{(1-x)^2} \]

Combining these results leads to the identity

\[ S(x) = \frac{1}{(1-x)^2} = \sum_{n=1}^{\infty} n x^{n-1} \]

with a radius of convergence \( R = 1 \).

These examples demonstrate how differentiating or integrating a known convergent power series, such as the geometric series, can lead to novel identities for useful convergent power series of functions, such as \( \ln(1 - x) \) and \( \frac{1}{1-x^2} \). In the next section, we explore a more general approach to defining power series of functions commonly encountered in the physical sciences.

### 7.3 Expanding functions as Maclaurin and Taylor series

**Mathematical functions that are continuous and infinitely differentiable** may be systematically represented in terms of the function’s derivatives at a single point. The Maclaurin series represents a function as power series in \( x \) with coefficients depending on the derivatives of the function at \( x = 0 \). The Maclaurin series is a special case of the Taylor series, which represents a function in terms of derivatives of the function at an arbitrary point \( x_0 \) and powers of the displacement \( x - x_0 \). In this section, we explore the basic properties of Maclaurin and Taylor series and their application to problems in the physical sciences.

#### 7.3.1 Maclaurin power series expansion

In our explorations of power series, we have examined power series representations of basic functions and used the ratio test to determine their associated radii of convergence. We can also ask the complementary question, for a given function \( f(x) \) what is its power series representation

\[ f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + \ldots \]

We want to know the identity of all coefficients \( a_n \). We note that the value of the function at \( x = 0 \) is

\[ f(0) = a_0 \]

We further note that the first derivative of the function

\[ \frac{d}{dx} f(x) = a_1 + 2a_2 x + 3a_3 x^2 + \ldots \]
evaluated at $x = 0$ results in an identity for the coefficient $a_1$

$$\left. \frac{d}{dx} f(x) \right|_{x=0} = a_1$$

Repeating this process for the second derivative of the function we find

$$\left. \frac{d^2}{dx^2} f(x) \right|_{x=0} = 2 a_2 + 2 \cdot 3 a_3 x + 3 \cdot 4 a_4 x^2 + \ldots$$

evaluated at $x = 0$ results in an identity for $a_2$

$$\left. \frac{d^2}{dx^2} f(x) \right|_{x=0} = 2 a_2$$

Evaluating the third derivative of the function at $x = 0$ we find

$$\left. \frac{d^3}{dx^3} f(x) \right|_{x=0} = 2 \cdot 3 a_3$$

In general, we can show that

$$\left. \frac{d^n}{dx^n} f(x) \right|_{x=0} = 1 \cdot 2 \cdot 3 \cdot \ldots \cdot n a_n = n! a_n$$

providing a general result for the identity of the coefficients

$$a_n = \frac{1}{n!} \left. \frac{d^n}{dx^n} f(x) \right|_{x=0}$$

Returning to our original power series for $f(x)$ we can write

$$f(x) = f(0) + \left. \frac{d}{dx} f(x) \right|_{x=0} x + \frac{1}{2!} \left. \frac{d^2}{dx^2} f(x) \right|_{x=0} x^2 + \ldots$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n}{dx^n} f(x) \right|_{x=0} x^n$$

known as the Maclaurin series.\(^{12}\)

Expressing a function $f(x)$ as a Maclaurin series may at first seem complex. However, we will find that the power series expansion of common functions has great utility in the physical sciences.

### 7.3.2 Applications of Maclaurin power series

Let’s look at a few examples of how Maclaurin series can be used to derive power series representations of functions that commonly occur in the physical sciences. Take the exponential function

$$f(x) = e^x$$

for which

$$\frac{d}{dx} e^x = e^x$$

and

$$\left. \frac{d^n}{dx^n} e^x \right|_{x=0} = e^x \left. \frac{d^n}{dx^n} e^x \right|_{x=0} = e^x \left. \frac{d^n}{dx^n} e^x \right|_{x=0} = 1$$

As a result

$$a_n = \frac{1}{n!} \left. \frac{d^n}{dx^n} f(x) \right|_{x=0} = \frac{1}{n!}$$

and the Maclaurin series of the exponential function is\(^{13}\)

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2} x^2 + \ldots$$

\(^{12}\) Named for Scottish mathematician Colin Maclaurin (1698-1746).

\(^{13}\) Evaluating this expression at $x = 1$ we find an identity for the constant $e = \sum_{n=0}^{\infty} \frac{1}{n!}$. 
This example demonstrates how Maclaurin series can be used to derive power series representations of functions commonly used in the physical sciences.

Now let’s use a Maclaurin series to derive a power series representation of

\[ f(x) = \sin x \]

Taking the first few derivatives of \( \sin x \)

\[
\begin{align*}
\frac{d}{dx} \sin(x) \bigg|_{x=0} &= \cos(0) = 1 \\
\frac{d^2}{dx^2} \sin(x) \bigg|_{x=0} &= -\sin(0) = 0 \\
\frac{d^3}{dx^3} \sin(x) \bigg|_{x=0} &= -\cos(0) = -1 \\
\frac{d^4}{dx^4} \sin(x) \bigg|_{x=0} &= \sin(0) = 0
\end{align*}
\]

we recognize that when \( n \) is odd

\[
\frac{d^n}{dx^n} f(x) \bigg|_{x=0} = (-1)^{\frac{n-1}{2}} \cos x \bigg|_{x=0} = (-1)^{\frac{n-1}{2}}
\]

while when \( n \) is even

\[
\frac{d^n}{dx^n} f(x) \bigg|_{x=0} = (-1)^{\frac{n}{2}} \sin x \bigg|_{x=0} = 0
\]

As a result, the Maclaurin series of \( \sin(x) \) contains only odd powers of \( x \).

Writing the first few terms we find

\[
\sin x = x - \frac{1}{3!} x^3 + \frac{1}{5!} x^5 - \ldots
\]

Recalling that

\[
\sin x = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + \ldots
\]

this means that \( a_0 = 0, a_1 = -1, a_2 = 0, a_3 = \frac{1}{3}, \) and so on.

To simplify our expression, let’s define a new counter \( k = \frac{n-1}{2} \) so that \( n = 2k + 1 \). Then we can write

\[
\sin x = x - \frac{1}{3!} x^3 + \frac{1}{5!} x^5 - \ldots = \sum_{k=0}^{\infty} (-1)^k \frac{1}{(2k+1)!} x^{2k+1}
\]

We can derive the same result more deliberately by evaluating the expressions term by term

\[
\begin{align*}
\sin x &= f(0) + \frac{df}{dx} \bigg|_{x=0} x + \frac{1}{2!} \frac{d^2 f}{dx^2} \bigg|_{x=0} x^2 + \frac{1}{3!} \frac{d^3 f}{dx^3} \bigg|_{x=0} x^3 + \ldots \\
&= \sin(0) + \cos(0)x + \frac{1}{2!} (-\sin(0)) x^2 + \frac{1}{3!} (-\cos(0)) x^3 + \ldots \\
&= x - \frac{1}{3!} x^3 + \ldots \quad (7.2)
\end{align*}
\]

The partial sum for the Maclaurin series of \( \sin(x) \) is

\[
S_N(x) = \sum_{k=0}^{N} (-1)^k \frac{1}{(2k+1)!} x^{2k+1}
\]

which is shown in Figure 7.7 for values of \( N = 0 \) to 4. For a given value of \( N \), the partial sum \( S_N(x) \) most accurately represents the function \( \sin(x) \) for values of \( x \) near \( x = 0 \). As \( N \) increases the partial sum provides an increasingly accurate approximation to \( \sin x \) over a growing range of \( x \). Remarkably, in the limit \( N \to \infty \) the Maclaurin series provides an exact representation of the infinity of oscillations of this periodic function over \( -\infty < x < \infty \).
In the same way we can derive the Maclaurin series expansion of $\cos x$ as

$$\cos x = f(0) + \frac{d f}{dx}{|}_{x=0} x + \frac{1}{2!} \frac{d^2 f}{dx^2}{|}_{x=0} x^2 + \frac{1}{3!} \frac{d^3 f}{dx^3}{|}_{x=0} x^3 + \ldots$$

$$= \cos(0) - \sin(0) x + \frac{1}{2!} (-\cos(0)) x^2 + \frac{1}{3!} \sin(0) x^3 + \ldots$$

$$= 1 - \frac{1}{2!} x^2 + \ldots \quad (7.3)$$

It follows that the partial sum for the Maclaurin series of $\cos(x)$ is

$$S_N(x) = \sum_{k=0}^{N} (-1)^k \frac{1}{(2k)!} x^{2k}$$

Only even powers of $x$ appear in this Maclaurin series expansion reflecting that $\cos(x)$ is an even function of $x$.

We can use our power series expansions of $\sin(x)$ and $\cos(x)$ to derive approximate expressions for these functions that are valid for small values of $x$. Note that for small $x$ we find

$$\sin(x) \approx x$$

and

$$\cos(x) \approx 1 - \frac{1}{2} x^2$$

as shown in Figure 7.8. Graphical comparison of the approximation and the exact function demonstrates the substantial range of $x$ over which the approximation is valid. Truncated power series are commonly applied when seeking approximate solutions to problems in the physical sciences.

### 7.3.3 Taylor power series expansion

The Maclaurin series provides a general expression for the function $f(x)$ in terms of its derivatives evaluated at $x = 0$. We observed that for a finite number of terms the Maclaurin series provided the most accurate representation of the function near $x = 0$. However, at times we may be interested in representing a function most accurately near an arbitrary point $x = x_0$. For that purpose, we appeal to the Taylor series.

Suppose we want to express the function in terms of its derivatives evaluated...
at an arbitrary point \( x = x_0 \) as
\[
f(x) = \sum_{n=0}^{\infty} a_n (x - x_0)^n = a_0 + a_1 (x - x_0) + a_2 (x - x_0)^2 + \ldots
\]
Evaluating the function at \( x = x_0 \) we find
\[
f(x_0) = a_0
\]
The first derivative of the function evaluated at \( x = x_0 \) is
\[
\left. \frac{d}{dx} f(x) \right|_{x=x_0} = a_1
\]
and the second derivative of the function evaluated at \( x = x_0 \) is
\[
\left. \frac{d^2}{dx^2} f(x) \right|_{x=x_0} = 2a_2
\]
In general we can show that
\[
\left. \frac{d^n}{dx^n} f(x) \right|_{x=x_0} = 1 \cdot 2 \cdot 3 \cdots n \ a_n = n! \ a_n
\]
so that
\[
a_n = \frac{1}{n!} \left. \frac{d^n}{dx^n} f(x) \right|_{x=x_0}
\]
With this set of coefficients we can express the function \( f(x) \) in the power series
\[
f(x) = f(x_0) + \left. \frac{d}{dx} f(x) \right|_{x=x_0} (x - x_0) + \frac{1}{2!} \left. \frac{d^2}{dx^2} f(x) \right|_{x=x_0} (x - x_0)^2 + \ldots
\]
\[
= \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n}{dx^n} f(x) \right|_{x=x_0} (x - x_0)^n
\]
known as the Taylor series.\(^1^6\) Note that the Maclaurin series is a special case of the Taylor series for \( x_0 = 0 \).

### 7.3.4 Applications of Taylor power series

Let’s look at a few examples of how Taylor series can be used to derive power series representations of functions that commonly occur in the physical sciences. Take the natural logarithm
\[
f(x) = \ln x
\]
that we wish to expand around the point \( x_0 = 1 \) where the function \( f(1) = \ln(1) = 0 \). We write
\[
\ln(x) = \ln(1) + \left. \frac{d}{dx} \ln(x) \right|_{x=1} (x - 1) + \frac{1}{2!} \left. \frac{d^2}{dx^2} \ln(x) \right|_{x=1} (x - 1)^2 + \ldots
\]
\[
= 0 + \sum_{n=1}^{\infty} \frac{1}{n!} \left. \frac{d^n}{dx^n} \ln(x) \right|_{x=1} (x - 1)^n
\]
with derivatives evaluated at \( x_0 = 1 \) resulting in
\[
\ln(x) = (x - 1) - \frac{1}{2!} (x - 1)^2 + \frac{2}{3!} (x - 1)^3 - \frac{2 \cdot 3}{4!} (x - 1)^4 + \ldots
\]
\[
= (x - 1) - \frac{1}{2} (x - 1)^2 + \frac{1}{3} (x - 1)^3 - \frac{1}{4} (x - 1)^4 + \ldots
\]
(7.4)

Now suppose we write this series in terms of \( \ln(1 + x) \) where we are interested in values of \( x \) near \( x_0 = 1 \) or small values of the deviation \( (x - 1) \). Substituting

---

\(^1^6\) Named for English mathematician Brook Taylor (1685-1731).
\[ 1 + x \text{ for } x \text{ in Equation 7.4 we find} \]
\[ \ln(1 + x) = x - \frac{1}{2} x^2 + \frac{1}{3} x^3 - \frac{1}{4} x^4 + \ldots = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{n} x^n \]

We can write the partial sum for this infinite series
\[ S_N(x) = \sum_{n=1}^{N} (-1)^{n+1} \frac{1}{n} x^n \]

The convergence of the partial sum \( S_N(x) \) for increasing \( N = 1 \) to 4 is shown in Figure 7.9 along with the exact function \( \ln(1 + x) \). Note that for small \( x \) we find
\[ \ln(1 + x) \approx x \]

which is equivalent to our previous result that near \( x = 0 \)
\[ \exp(x) \approx 1 + x \]

These approximations are useful tools in our box that will allow us to determine limiting forms of complicated functions in an efficient and intuitive manner. Now consider the gaussian function
\[ f(x) = \exp \left[ -\frac{(x - \bar{x})^2}{2\sigma^2} \right] \]

which we encounter in the kinetic theory of gases, quantum mechanics of a vibrating bond. Let’s expand this function in a Taylor series about the point \( x = \bar{x} \) as
\[ f(x) = \exp \left[ -\frac{(x - \bar{x})^2}{2\sigma^2} \right] = f(\bar{x}) + \frac{df}{dx} \bigg|_{x=\bar{x}} (x - \bar{x}) + \frac{1}{2!} \frac{d^2f}{dx^2} \bigg|_{x=\bar{x}} (x - \bar{x})^2 + \ldots \]

The function evaluated at \( x = \bar{x} \) is
\[ f(\bar{x}) = 1 \]

the first derivative evaluated at \( x = \bar{x} \) is
\[ \frac{df}{dx} \bigg|_{x=\bar{x}} = -\frac{(x - \bar{x})}{\sigma^2} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} \bigg|_{x=\bar{x}} = 0 \]

and the second derivative evaluated at \( x = \bar{x} \) is
\[ \frac{d^2f}{dx^2} \bigg|_{x=\bar{x}} = \left[ -\frac{1}{\sigma^2} + \frac{(x - \bar{x})^2}{\sigma^4} \right] e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} \bigg|_{x=\bar{x}} = \frac{1}{\sigma^2} \]

while the third derivative evaluated at \( x = \bar{x} \) is
\[ \frac{d^3f}{dx^3} \bigg|_{x=\bar{x}} = \left[ 3(x - \bar{x}) \frac{1}{\sigma^4} - \frac{(x - \bar{x})^3}{\sigma^6} \right] e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} \bigg|_{x=\bar{x}} = 0 \]

and so on.

The final result for the Taylor series representing the gaussian function is\(^\text{17}\)
\[ e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} = 1 - \frac{1}{2\sigma^2} (x - \bar{x})^2 + \frac{1}{8\sigma^4} (x - \bar{x})^4 - \frac{1}{48\sigma^6} (x - \bar{x})^6 + \ldots \]
\[ = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} \left( \frac{(x - \bar{x})^2}{2\sigma^2} \right)^n \]

Only even powers of \( (x - x_0) \) appear in the power series representation reflecting

\(^\text{17}\) Note that we can also find this result directly from our Maclaurin series expansion of the exponential function
\[ e^{-a} = \sum_{n=0}^{\infty} (-1)^n \frac{a^n}{n!} = 1 - a + \frac{a^2}{2} - \ldots \]

where \( a = (x - \bar{x})^2/2\sigma^2 \).
the fact that the gaussian function is an even function of \((x - x_0)\). With this result, we can define the partial sum known as the Taylor polynomial

\[
S_N(x) = \sum_{n=0}^{N} (-1)^n \frac{1}{n!} \left( \frac{(x - x_0)^2}{2\sigma^2} \right)^n
\]

which is shown in Figure 7.10 for \(N = 0\) to \(4\).

Our Taylor series expansion of the gaussian function provides us with a practically useful approximation to the gaussian function near its maximum value

\[
\exp \left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \approx 1 - \frac{1}{2}(x - x_0)^2
\]

The expansion of the gaussian function in powers of \((x - x_0)\) has great utility in addressing problems in quantum theory and thermodynamics.

## A7 Taylor series expansions of potential energy functions

Recall that we were able to identify minima (stable points) and saddle points (transition states) of potential energy functions by looking for those points at which the first derivatives of the potential energy were zero. For example, consider the Morse oscillator potential energy function

\[
V(r) = \epsilon \left[ 1 - e^{-\beta(r-r_0)} \right]^2 = \epsilon \left[ 1 - 2e^{-\beta(r-r_0)} + e^{-2\beta(r-r_0)} \right]
\]

that can be used to model a bond between two atoms that can fluctuate at low energy and dissociate for energy greater than \(\epsilon\). This function has an extremum at \(r = r_0\) since

\[
\frac{dV}{dr} \bigg|_{r=r_0} = \epsilon \left[ 2\beta e^{-\beta(r-r_0)} - 2\beta e^{-2\beta(r-r_0)} \right]_{r=r_0} = 0
\]

as shown in Figure 7.11. The second derivative of the potential energy function evaluated at \(r = r_0\) is

\[
\frac{d^2V}{dr^2} \bigg|_{r=r_0} = \epsilon \left[ -2\beta^2 e^{-\beta(r-r_0)} + 4\beta^2 e^{-2\beta(r-r_0)} \right]_{r=r_0} = 2\epsilon \beta^2
\]

which is positive indicating that the extremum at \(r = r_0\) is a potential energy minimum.

Using a Taylor series we can expand the Morse oscillator potential function about \(r = r_0\) as

\[
V(r) = V(r_0) + \frac{dV}{dr} \bigg|_{r=r_0} (r - r_0) + \frac{1}{2!} \frac{d^2V}{dr^2} \bigg|_{r=r_0} (r - r_0)^2 + \ldots
\]

where

\[
V(r_0) = 0, \quad \frac{dV}{dr} \bigg|_{r=r_0} = 0, \quad \frac{d^2V}{dr^2} \bigg|_{r=r_0} = 2\epsilon \beta^2
\]

so that

\[
V(r) = \frac{1}{2!} 2\epsilon \beta^2 (r - r_0)^2 + O \left[ \beta^3 (r - r_0)^3 \right]
\]

where \(O[x]\) means on the order of \(x\).

For small deviations of \(r\) from \(r_0\), so that \(\beta (r - r_0)\) is close to zero, we expect

\[
\beta^2 (r - r_0)^2 \gg \beta^3 (r - r_0)^3
\]

so that we can ignore the higher order terms and employ a harmonic approxima-
tion to the potential energy function

\[ V(r) \approx \frac{1}{2} \kappa (r - r_0)^2 \]

where \( \kappa \) is the harmonic oscillator force constant.\(^{18}\)

Many chemical bonds are modeled using the Morse potential. At low energies, vibrations consist of small harmonic oscillations near the potential energy minimum. At larger energies, vibrations are anharmonic. When the energy exceeds the well depth \( \epsilon \) the bond length \( r \) can increase toward infinity and the bond can break.

Let’s consider another potential energy function that is useful for modeling chemical reactions and thermodynamic phase transitions

\[ V(x) = V_0 (x^2 - 2x^2 + 1) \]

which is a quartic double well potential with minima at \( x = \pm 1 \) and a transition state at \( x = 0 \).

We can expand the function \( V(x) \) near the potential energy minimum at \( x_0 = 1 \) using a Taylor series for the special case \( V_0 = 1 \). We find

\[
\begin{align*}
V(x) &= V(x = 1) + \frac{dV}{dx} \bigg|_{x=1} (x - 1) + \frac{1}{2!} \frac{d^2V}{dx^2} \bigg|_{x=1} (x - 1)^2 + \ldots \\
&= (4x^3 - 4x) \bigg|_{x=1} (x - 1) + \frac{1}{2} (12x^2 - 4) \bigg|_{x=1} (x - 1)^2 + \ldots \\
&= 4(x - 1)^2 + O \left( (x - 1)^3 \right)
\end{align*}
\]

This truncated Taylor series takes the form of a quadratic equation approximation to the full potential energy function\(^{19}\)

\[ V(x) \approx 4(x - 1)^2 \]

We expect this approximation to be accurate for small displacements from the minimum near \( x_0 = 1 \). Locally, the potential energy is an upward facing parabolic potential well.\(^{20}\) This quadratic approximation to the potential energy function takes the form of the harmonic oscillator potential energy function

\[ V(x) = \frac{1}{2} \kappa (x - x_0)^2 \]

where the minimum is \( x_0 = 1 \) and the force constant \( \kappa = 8 \) (see Figure 7.12).

What is the nature of \( V(x) \) near the transition state at \( x = 0 \)? In that case

\[
\begin{align*}
V(x) &= V(x = 0) + \frac{dV}{dx} \bigg|_{x=0} x + \frac{1}{2!} \frac{d^2V}{dx^2} \bigg|_{x=0} x^2 + \ldots \\
&= 1 + (4x^3 - 4x) \bigg|_{x=0} x + \frac{1}{2} (12x^2 - 4) \bigg|_{x=0} x^2 + \ldots \\
&= 1 - 2x^2 + O \left[ x^4 \right]
\end{align*}
\]

Fitting the truncated Taylor series to the harmonic oscillator potential energy function we find

\[ V(x) = 1 + \frac{1}{2} \kappa x^2 + O \left[ x^4 \right] \]

with force constant \( \kappa = -4 \). Near the transition state between the two energy minima, the potential energy function is a downward facing parabola (see Figure 7.12).

Finally, let’s explore the convergence of the Taylor series expansion of the quartic double well potential energy function in Equation 7.5. As the potential

\[ \text{Figure 7.12: The quartic double well potential energy function } V(r) \text{ (red) shown with the harmonic approximation to the barrier (black) and to the well (blue).} \]
function is a polynomial, the Taylor series consists of a finite number of terms. For \( x_0 = 0 \) the series expansion can be written

\[
V(x) = 1 + \frac{1}{2!}(12x^2 - 4)\bigg|_{x=0} x^2 + \frac{1}{4!}24\bigg|_{x=0} x^4 = 1 - 2x^2 + x^4
\]

Note that the odd power terms in \( x \) are zero reflecting the fact that \( V(x) \) is an even function of \( x \). Furthermore, for this fourth order polynomial function the Taylor series has a finite number of terms as derivatives higher than the fifth order in \( x \) are equal to zero.

Now consider the Taylor expansion about \( x_0 = 1 \)

\[
V(x) = (4x^3 - 4x)|_{x=1} (x - 1) + \frac{1}{2}(12x^2 - 4)|_{x=1} (x - 1)^2 + \frac{1}{6}24|x=1| (x - 1)^3 + \frac{1}{24}|x=1| (x - 1)^4
= 4(x - 1)^2 + 4(x - 1)^3 + (x - 1)^4
\]

which sums to the exact potential energy function \( V(x) = x^4 - 2x^2 + 1 \).

Figure 7.13 shows the convergence of the partial sums \( S_2(x) = 4(x - 1)^2 \), \( S_3(x) = S_2(x) + 4(x - 1)^3 \), and \( S_4(x) = S_3(x) + (x - 1)^4 \) to the exact function.

B7 Useful approximations to functions based on power series

There are many examples of physical processes in which an extreme condition justifies the use of a simpler, limiting form of a more complicated, general result. In considering those problems, the use of series solutions and truncated series is a powerful tool.

**Partial dissociation of a weak acid at equilibrium**

Consider the chemical equilibrium for the dissociation of a weak acid

\[
\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)
\]

where the concentration dependent equilibrium constant is

\[
K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]

Suppose the initial concentration of acid is \([\text{HA}]_0\). Further suppose that a small amount of acid dissociates creating the concentrations \( [\text{A}^-] = [\text{H}_3\text{O}^+] = x \). It follows that the amount of undissociated acid remaining is \([\text{HA}] = [\text{HA}]_0 - x\).

Substituting back into our expression for the equilibrium constant we find

\[
K_c = \frac{x^2}{[\text{HA}]_0 - x}
\]

that can be written as a quadratic equation in \( x \)

\[
x^2 + K_c x = K_c [\text{HA}]_0
\]

The roots of this equation can be solved exactly using the quadratic formula (see Equation 1.4). The result is shown in Figure 7.14 where \( x^2 + K_c x \) is plotted as a function of \( x \) for \([\text{HA}]_0 = 1.0 \) and \( K_c = 0.001 \). The intersection of \( x^2 + K_c x \) with the line at \( K_c [\text{HA}]_0 \) marks the equilibrium concentration.

Suppose a small fraction of the initial concentration of weak acid has dissociated. This means that \([\text{HA}]_0 \gg x\). As such, we can make the approximation
that
\[ K_c = \frac{x^2}{[HA]_0 - x} \approx \frac{x^2}{[HA]_0} \]

With this equation, we can immediately solve for
\[ x = A^- = H_2O^+ = \sqrt{K_c[HA]_0} \quad (7.6) \]

This approximation is plotted in Figure 7.14 as a red line. For \([HA]_0 = 1.0\) and \(K_c = 0.001\) the approximation is almost indistinguishable from the exact result.\(^\text{21}\)

If we want to know the next order correction we can write
\[ K_c = \frac{x^2}{[HA]_0 - x} = \frac{x^2}{[HA]_0 \left( 1 - \frac{x}{[HA]_0} \right)} \approx \frac{x^2}{[HA]_0} \left( 1 + \frac{x}{[HA]_0} \right) \]

where we have used the property of the geometric series that
\[ \frac{1}{1-x} = 1 + x + O \left[ x^2 \right] \]

This expression provides us with a way to evaluate the goodness of our original approximation that led to Equation 7.6. For the approximation to be valid, it must be that
\[ \frac{x}{[HA]_0} \ll 1 \]

which is identical to the physical assumption that motivated our initial approximation that little of the weak acid dissociates and \([HA]_0 \gg x\).

**Statistical probability distributions in the high temperature limit**

The truncated expansion is also useful in problems involving the Boltzmann probability
\[ p(T) \propto \exp \left[-\frac{\epsilon}{k_B T}\right] \]

where for sufficiently high temperatures such that
\[ \frac{\epsilon}{k_B T} \ll 1 \quad \text{or} \quad T \gg \frac{\epsilon}{k_B} \]

we can approximate \(p(T)\) as
\[ p(T) \propto \exp \left[-\frac{\epsilon}{k_B T}\right] \approx 1 - \frac{\epsilon}{k_B T} \]

where we have used the property of an exponential series expansion
\[ e^{-x} = 1 - x + O \left[ x^2 \right] \]

and the observation that higher order terms in the small parameter \(\frac{\epsilon}{k_B T}\) do not contribute significantly to the sum.

Let’s apply this result to an expression appearing in Planck’s theory of blackbody radiation
\[ f(v) = \frac{1}{1 - \exp(-\beta hv)} \]

where \(\beta \equiv \frac{1}{k_B T}\) and \(hv\) is the energy of a photon of light of frequency \(v\). When the temperature is high enough that
\[ T \gg \frac{hv}{k_B} \quad \text{or} \quad \beta hv \ll 1 \]

we can approximate the exponential using a Maclaurin series truncated at first
order in the small parameter $\beta h \nu$ where $\exp(-\beta h \nu) \approx 1 - \beta h \nu$. We find
\[ f(\nu) = \frac{1}{1 - \exp(-\beta h \nu)} \approx \frac{1}{1 - (1 - \beta h \nu)} = \frac{1}{\beta h \nu} \]

Now consider an expression taken from Einstein’s theory of the heat capacity of solids
\[ p(\beta) = (\beta h \nu)^2 e^{-\beta h \nu} \left(1 - e^{-\beta h \nu}\right)^2 \] (7.7)
shown in Figure 7.15. We wish to evaluate this expression in the limit as $T \to \infty$ or equivalently $\beta \to 0$. Unfortunately, both the numerator and denominator go to zero as $\beta$ goes to zero!

There are two ways to address this. We can apply l’Hôpital’s rule by differentiating the numerator and denominator and retaking the limit. First we simplify the expression by substituting $x = \beta h \nu$ and noting that the limit as $\beta \to 0$ becomes $x \to 0$. Further noting that in the limit that $x \to 0$ the exponential in the numerator is unity, our limit becomes
\[ \lim_{x \to 0} \frac{x^2}{(1 - e^{-x})^2} \]

Finally, we apply l’Hôpital’s rule three times to find
\[ \lim_{x \to 0} \frac{x^2}{(1 - e^{-x})^2} = \lim_{x \to 0} \left[ \frac{2x}{2e^{-x}(1 - e^{-x})} \right] = \lim_{x \to 0} \left[ \frac{x}{e^{-x} - e^{-2x}} \right] = 1 \]

A second and more efficient approach is to use our high temperature expansion of the Boltzmann probability
\[ e^{-\beta h \nu} \approx 1 - \beta h \nu + O \left[ (\beta h \nu)^2 \right] \]
Taking the limit of Equation 7.7 we find
\[ \lim_{\beta \to 0} (\beta h \nu)^2 \frac{e^{-\beta h \nu}}{(1 - e^{-\beta h \nu})^2} = \lim_{\beta \to 0} (\beta h \nu)^2 \left[ \frac{1}{1 - (1 - \beta h \nu)} \right]^2 = \lim_{\beta \to 0} (\beta h \nu)^2 \left( \frac{1}{\beta h \nu} \right)^2 = 1 \]

This demonstrates how truncated series expansions can be used to make controlled approximations that simply expressions and facilitate the identification of limits of complicated expressions common to the physical sciences.

C7 Self-similarity and fractal structures

Many objects in nature have a self-similar structure. The shape of part of the object is similar to the shape of the object as a whole. For example, trees display a self-similar structure on many length scales. Thick branches divide into many thin branches that divide into many still thinner branches. Consider the Pythagoras tree depicted in Figure 7.16. The pattern of growth repeats itself on many length scales.

Self-similar structure is also observed in the dendritic arms of snowflakes. When a portion of a snowflake is magnified again and again, the branching of arms is found to repeat itself on many length scales. Consider the Koch snowflake
Figure 7.16: This Pythagorean cherry tree is a self-similar object formed from squares arranged such that the area enclosed by contact between three squares forms a right triangle.

Figure 7.17: The construction of the Koch snowflake begins with a single equilateral triangle. An equilateral triangle with side $\frac{1}{3}$ that of the original triangle is added to each face. This process is repeated $ad infinitum$. The outer perimeter of this Koch snowflake formed from triangles on 5 length scales is shown in red.

Objects possessing self-similar structure are called fractals. Fractal objects are important to the physical sciences as self-similarity occurs throughout nature. Fractal objects are found in the structure of growing crystals, agglomerated soot particles, and dendritic molecular assemblies.

Consider the construction of a fractal object known as the Sierpiński carpet. One starts from a solid unit square, with sides of length 1, that we call our carpet. Initially, a single square hole with side $\frac{1}{3}$ and area $\frac{1}{9}$ is added to the center of the carpet. Afterwards, in each of the surrounding 8 squares of area $\frac{1}{9}$, the same process is repeated $ad infinitum$.

---

22 Discovered by Swedish mathematician Helge von Koch (1870-1924).

23 The term fractal was introduced by Polish-born mathematician Benoît Mandelbrot (1924-2010).

\[ \frac{1}{9} \], one forms additional holes of side \( \frac{1}{3} \) and area \( \frac{1}{9} \). This process is repeated once again to add 64 holes with sides of length \( \frac{1}{9} \) and area \( \frac{1}{81} \). An example of a Sierpiński carpet is shown in Figure 7.18.

Rather than thinking of the area of the holes, we can equivalently consider the area of carpet remaining after \( n \) iterations of the process of forming holes. Initially, the carpet has area \( A_0 = 1 \). After \( n = 1 \) iteration, the first square hole is formed with side of length \( L_1 = \frac{1}{3} \) and area \( L_1^2 = \frac{1}{9} \). The area of the remaining carpet is

\[
A_1 = 1 - \frac{1}{9} = \frac{8}{9}
\]

We can think of the area of the remaining carpet being \( N_1 L_1^2 = \frac{8}{9} \) where \( N_1 = 8 \) is the number of squares of carpet with area equal to that of the smallest hole \( L_1^2 \).

After \( n = 2 \) iterations, 8 new square holes of side \( L_2 = \frac{1}{9} \) and area \( L_2^2 = \frac{1}{81} \) are added. The area of the remaining carpet is

\[
A_2 = 1 - \frac{1}{9} - \frac{8}{81} = \frac{64}{81} = \left( \frac{8}{9} \right)^2
\]

This area can be thought of as consisting of \( N_2 = 64 \) squares of carpet each of area \( \frac{1}{81} \). After \( n \) iterations, the area of carpet remaining will be

\[
A_n = N_n L_n^2
\]

The total area replaced by holes is \( 1 - A_n \).

Repeating this process starting from an equilateral triangle as opposed to a square results in a Sierpiński gasket shown in Figure 7.19. The Sierpiński carpet and Sierpiński gasket have self-similar fractal structures. A small square of carpet repeats the structure of the carpet as a whole. The pattern of holes in the gasket is repeated at every length scale.

We can define the fractal dimension in terms of the limit\(^{25}\)

\[
d \equiv - \lim_{n \to \infty} \frac{\ln N_n}{\ln L_n}
\]

where \( N_n \) is the number of elements of area \( L_n^2 \) needed to cover the fractal surface. The fractal dimension can be thought of as the capacity of a particular pattern to fill space. For this reason, the fractal dimension is also referred to as the capacity dimension.

For example, suppose we completely cover a unit square surface with \( N = n^2 \) solid elements of area \( L_n^2 = 1/n^2 \). The fractal dimension is calculated as

\[
d = - \lim_{n \to \infty} \frac{\ln N_n}{\ln L_n} = - \lim_{n \to \infty} \frac{\ln (n^2)}{\ln (n^{-1})} = \lim_{n \to \infty} \frac{2 \ln n}{\ln n} = 2
\]

The repeating pattern of the solid square has the capacity to cover the surface completely. As such, the fractal dimension of the solid two-dimensional square is \( d = 2 \).

Now let’s consider the Sierpiński carpet where \( N_n = 8^n \) and \( L_n = 3^{-n} \). Returning to our definition of the fractal dimension we find

\[
d = - \lim_{n \to \infty} \frac{\ln 8^n}{\ln 3^{-n}} = \frac{\ln 8}{\ln 3} = \log_3(8) = 1.8927 \ldots
\]

The repeating pattern of the porous Sierpiński carpet lacks the capacity to completely fill the two-dimensional space. As a result, the fractal dimension is something less than 2.

\(^{25}\) The definition of the fractal dimension suggests the scaling relation

\[ N \propto L^{-d} \]

where the number of elements, \( N \), required to cover the fractal surface grows exponentially as the length scale of the elements, \( L \), diminishes.
End-of-chapter problems

All things are number.
Pythagoras

Warm-ups

7.1 Determine whether the following series are convergent or divergent. If the series is convergent, determine the sum.

(a) 1 + 3 + 5 + 7 + 9 + … (b) $\frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + …$
(d) $\frac{3}{2} + \frac{3}{4} + \frac{3}{6} + \frac{3}{8} + …$
(e) $\frac{1}{3} + \frac{4}{9} + \frac{4}{27} + \frac{4}{81} + …$
(f) $\frac{1}{4} + \frac{2}{7} + \frac{3}{10} + \frac{4}{13} + …$

7.2 Use the ratio test to determine whether the following series are convergent, divergent, or if your evaluation is inconclusive.

(a) $\frac{1}{2} + \frac{1}{2^2} + \frac{1}{2^3} + \frac{1}{2^4} + …$
(b) $3 + \frac{3^2}{2} + \frac{3^3}{2^2} + \frac{3^4}{2^3} + …$
(d) $2 + \frac{2^2}{2!} + \frac{2^3}{3!} + \frac{2^4}{4!} + …$
(e) $\frac{1}{2} + \frac{2^2}{2^2} + \frac{3^2}{3^2} + \frac{4^2}{4^2} + …$
(f) $3 + \frac{3^2}{2} + \frac{3^3}{3!} + \frac{3^4}{4!} + …$

7.3 Determine the interval of convergence for the following power series.

(a) $1 + x + x^2 + x^3 + …$
(b) $1 - x^2 + \frac{x^4}{2!} - \frac{x^6}{3!} + …$
(d) $x - \frac{x^2}{2!} + \frac{x^3}{3!} - \frac{x^4}{4!} + …$
(e) $-1 + 2x + 3x^2 - 4x^3 + …$
(f) $x - \frac{1}{3}x^3 + \frac{1}{5}x^5 - …$

7.4 Expand the following functions in a Maclaurin series.

(a) $\frac{1}{1 + x}$ (b) $\frac{1}{(1 + x)^2}$ (c) $(1 + x)^{1/2}$ (d) $\ln(1 - x)$
(e) $e^{-x^2}$ (f) $\frac{a^x}{a^x}$ (g) $\cos x$ (h) $(1 + x)^3$

7.5 Show that for small values of $X_B$ the function $\ln(1 - X_B) \approx -X_B$.

7.6 Show that for small values of $\theta$ the function $\sin \theta \approx \theta$.

Homework exercises

7.7 Use your knowledge of power series to derive the following expressions for fundamental mathematical constants defined in terms of infinite series

(a) $e = \sum_{n=0}^{\infty} \frac{1}{n!}$  (b) $\ln 2 = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{n}$  (c) $\frac{\pi}{4} = \sum_{n=0}^{\infty} (-1)^n \frac{1}{2n+1}$

This infinite series representation of the mathematical constant $e$ was used by Leonhard Euler (1707-1783) to provide an approximate value of $e = 2.718281828459045235$ to 18 decimal places.

7.8 Consider the power series

$$\sum_{n=0}^{\infty} nx^n$$
(a) Show that the interval of convergence of this series is $|x| < 1$.

(b) Find the function, $f(x)$, that corresponds to the above power series. To do so, differentiate the geometric series

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$$

with respect to $x$ and then multiply by $x$. Use your result to show that

$$f(x) = \sum_{n=1}^{\infty} nx^n = \frac{x}{(1-x)^2} \quad |x| < 1$$

7.9 Find the function, $f(x)$, that corresponds to the series

$$\sum_{n=1}^{\infty} n^2 x^n$$

HINT: Start from the fact that

$$\frac{x}{(1-x)^2} = \sum_{n=1}^{\infty} nx^n$$

7.10 Show that the Maclaurin series of the hyperbolic sine function

$$\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \ldots$$

for all $x$ where

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

7.11 Expand the function $\sin x$ in powers of $(x-a)$ using a Taylor series including terms to the fourth order in $(x-a)$.

7.12 Consider the integral below where the upper limit of integration is a variable

$$I(x) = \int_{0}^{x} e^{-t^2} \, dt$$

and the function $I(x)$ is related to the error function as $\text{erf}(x) = \frac{2}{\sqrt{\pi}} I(x)$.

(a) Derive a formula for $I(x)$ by expanding the integrand in a Maclaurin series, keeping only the first four terms.

(b) Determine the numerical value of $I(\frac{1}{2})$. Compare your result to the value derived using the error function tabulated in Supplement S7.

(c) Determine the numerical value of $I(\frac{1}{2})$. Compare your result to the value derived using the error function tabulated in Supplement S7.

7.13 Consider the expansion of $\ln(x)$ near $x = 1$.

(a) Show that the Maclaurin series of $\ln(1+x)$ expanded about $x = 0$ is

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - + \ldots$$

(b) Show that the Taylor series of $\ln(x)$ expanded about $x = 1$ is

$$\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - + \ldots$$

(c) Show that the series derived in (a) and (b) have equivalent intervals of convergence $|x| < 1$ and $|x-1| < 1$, respectively.
Consider the quartic double well potential energy function

\[ V(x) = (x^2 - 1)^2 \]

with minima at \( x = \pm 1 \) and local maximum at \( x = 0 \) (see Figure 7.12).

(a) What is the height of the barrier separating the two minima?

(b) For small displacements around \( x = 1 \), the potential energy can be approximated as the harmonic oscillator potential energy function

\[ V(x) = \frac{1}{2} \kappa (x - 1)^2 \]

Expand the potential in a Taylor series about the point \( x = 1 \) to second order in the displacement \( (x - 1) \) to determine the value of \( \kappa \).

(c) For small displacements near \( x = 0 \), the potential can be approximated as a downward facing parabola

\[ V(x) = 1 - \frac{1}{2} \kappa x^2 \]

Expand the potential in a Taylor series about the point \( x = 0 \) to second order in the displacement \( x \) to determine the value of \( \kappa \).

7.15 The distribution of frequencies, \( \nu \), for blackbody radiation was derived by Planck and found to be

\[ \rho(\nu, T) \approx \frac{8 \pi h}{c^3} \frac{\nu^3}{e^{\beta \hbar \nu} - 1} \]

where \( \rho(\nu, T) \) is the intensity of radiation from the blackbody at frequency \( \nu \) and temperature \( T \) where \( \beta = \frac{1}{k_B T} \) (see below). Show that for low frequencies or high temperatures, such that \( \beta \nu \hbar \ll 1 \), the distribution can be written

\[ \rho(\nu, T) \approx \frac{8 \pi k_B T}{c^3} \frac{\nu^2}{e^{\beta \hbar \nu} - 1} \]

In the figure on the right below, the exact distribution \( \rho(\nu) \) is shown in black. The approximation good at low frequencies or high temperatures appears in red.

7.16 The Einstein model for the temperature dependence of the constant volume heat capacity of a crystal can be written

\[ C_V(T) = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{-\Theta_E/T}}{(1 - e^{-\Theta_E/T})^2} \]

where \( \Theta_E \) is a constant known as the Einstein temperature. The temperature dependence of \( C_V(T) \) is shown below. Show that for high temperatures \( T >> \Theta_E \) that

\[ C_V(T) \approx 3R \]
which is the classic law of Dulong and Petit.

7.17* According to one theory of electrolyte (salt) solutions the thermodynamic energy of the solution can be written

\[ U(\kappa, a) = \frac{(\kappa a)^2 + (\kappa a) - \kappa a(1 + 2\kappa a)^{1/2}}{4\pi\beta a^3} \]

where \( \kappa \) is related to the concentration of the salt solution, \( \beta = \frac{1}{k_B T} \), and \( a \) is the average radius of a positive or negative ion found in the solution.

Show that as \( \kappa a \to 0 \), \( U(\kappa, a) \) varies as

\[ U(\kappa, a) \approx \frac{\kappa^3}{8\pi\beta} + \mathcal{O}(\kappa a) \]

7.18 A chemical bond modeled as a harmonic oscillator has quantum mechanically allowed vibrational energies given by

\[ \varepsilon_n = \left( n + \frac{1}{2} \right) \hbar \nu \quad n = 0, 1, 2, 3, \ldots \]

where \( \nu \) is the frequency of the bond oscillation. The average energy of the bond is defined

\[ \langle \varepsilon \rangle = \frac{1}{\theta} \sum_{n=0}^{\infty} \left( n + \frac{1}{2} \right) \hbar \nu \ e^{-\beta(n+\frac{1}{2})\hbar \nu} \]

where

\[ q = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar \nu} \]

(a) Show that

\[ q = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar \nu} = \frac{e^{-\frac{\beta\hbar \nu}{2}}}{1 - e^{-\beta\hbar \nu}} \]

HINT: Pull out a factor of \( e^{-\frac{\beta\hbar \nu}{2}} \) and substitute \( x = e^{-\beta\hbar \nu} \). You will recognize a familiar series.

(b) Return to the definition of the average energy, \( \langle \varepsilon \rangle \). Use the result in (a) to show that

\[ \langle \varepsilon \rangle = \frac{\hbar \nu}{2} + \frac{\hbar \nu e^{-\beta\hbar \nu}}{1 - e^{-\beta\hbar \nu}} \]

7.19* Consider the Koch snowflake shown in Figure 7.17. The initial area of the equilateral triangle at the center of the snowflake is \( A_0 = 1 \).
(a) In the $n = 1$ iteration, three new triangles of area $\frac{1}{9}A_0$ are added. The overall area of the snowflake becomes

$$A_1 = A_0 \left( 1 + 3 \frac{1}{9} \right)$$

Use your knowledge of the geometric sequence to derive a formula for the area of the snowflake $A_n$ after $n$ iterations.

(b) Use your knowledge of the geometric series to show that in the limit that the number of iterations $n \to \infty$ the area of the snowflake is

$$\lim_{n \to \infty} A_n = A_0 \frac{8}{5}$$

c) Consider the initial equilateral triangle at center of the snowflake. The length of a side of the triangle is $S_0$. There are $N_0 = 3$ faces so that the perimeter of the triangle is $P_0 = N_0 S_0 = 3 S_0$. After $n = 1$ iteration of adding additional triangles there are $N_1 = 12$ faces of the snowflake of equal length $S_1 = \frac{1}{3} S_0$. As such, the length of the perimeter of the snowflake is

$$P_1 = N_1 S_1 = \frac{12}{3} S_0$$

Derive a formula for the perimeter of the snowflake $P_n = N_n S_n$ after $n$ iterations.

(d) Take the limit that the number of iterations $n \to \infty$ to determine

$$\lim_{n \to \infty} P_n = P_\infty$$

7.20* Consider the Sierpiński carpet, shown in Figure 7.18, formed from a square of area $A_0 = 1$ in the absence of holes. A square hole of area $H_1 = 1/9$ is formed in the center of the carpet. The remaining area of the carpet is $A_1 = 1 - H_1 = 1 - 1/9 = 8/9$.

(a) Derive the geometric sequence that equals the total area of the carpet occupied by holes $H_n = 1 - A_n$ after $n$ iterations.

(b) Use your knowledge of the geometric series to determine

$$\lim_{n \to \infty} H_n = H_\infty$$

where $H_\infty$ is total area occupied by holes once the number of iterations $n \to \infty$.

7.21* Consider the Sierpiński gasket, shown in Figure 7.19, formed from an equilateral triangle with area $A_0 = 1$ in the absence of holes. A triangular hole of area $H_1 = 1/4$ is formed in the center of the gasket. The remaining area of the gasket is

$$A_1 = 1 - H_1 = 1 - \frac{1}{4} = \frac{3}{4}$$

After $n = 2$ iterations the remaining area of the gasket is

$$A_2 = 1 - \frac{1}{4} - 3 \left( \frac{1}{4} \right)^2 = 1 - \frac{1}{4} - \frac{3}{16} = 1 - H_2$$

(a) Show that the total area of the gasket remaining after $n$ iterations is

$$A_n = \left( \frac{3}{4} \right)^n$$

(b) The total area of the gasket remaining after $n$ iterations derived in (a) can be interpreted as $A_n = N_n L_n^2$ where $N_n$ is the number of triangles of area $L_n^2$. Determine $N_n$ and $L_n$ for the Sierpiński gasket.

(c) The fractal dimension is defined in terms of $N_n$ and $L_n$ as

$$d = - \lim_{n \to \infty} \frac{\ln N_n}{\ln L_n}$$

Show that the fractal dimension of the Sierpiński gasket is $\log_2(3) = 1.5849\ldots$ which is a number greater than the dimension of a line, $d = 1$, and less than the dimension of a filled triangle, $d = 2$. 
7.22* Consider the Menger sponge, shown below. It is formed from a volume \( V_0 = 1 \) in the absence of holes. Each face of the cube is divided into nine squares, subdividing the cube into 27 smaller cubes (as for a Rubik's cube). The central cube of each face and the cube at the center of the larger cube (7 smaller cubes in all) are removed. This creates a sponge with a hole of volume \( H_1 = 7/27 \). The remaining volume of the sponge is \( V_1 = 1 - H_1 = 1 - \frac{7}{27} = \frac{20}{27} \). The process is then repeated ad infinitum for each of the remaining cubes.

(a) Show that the total volume of the sponge remaining after \( n \) iterations is

\[
V_n = \left( \frac{20}{27} \right)^n
\]

(b) The total volume of the sponge remaining after \( n \) iterations derived in (a) can be interpreted as \( V_n = N_n L_n^3 \) where \( N_n \) is the number of cubes of volume \( L_n^3 \). Determine \( N_n \) and \( L_n \) for the Menger sponge.

(c) The fractal dimension is defined in terms of \( N_n \) and \( L_n \) as

\[
d \equiv -\lim_{n \to \infty} \frac{\ln N_n}{\ln L_n}
\]

Show that the fractal dimension of the Menger sponge is \( \log_3(20) = 2.7268 \ldots \) which is a number greater than the dimension of a square, \( d = 2 \), and less than the dimension of a filled cube, \( d = 3 \).
8 Integration in One and Many Dimensions

8.1 Integrating functions of one variable

A foundation idea in the calculus is the concept of integration. The integral measures the area under a curve described by a function over a range of its variable. In modeling physical processes, we are often interested in summing the value of one property (the function) times the change in another property (the variable). Pressure-volume work done by a gas is calculated by summing the pressure (the function) times the volume (the variable) as the volume is varied. In NMR spectroscopy, the amount of energy absorbed or released by nuclei undergoing spin flips is measured by summing the signal intensity (the function) multiplied by the chemical shift frequency (the variable). In this section, we explore the definition of the integral and review the principal methods of integrating a function of one variable.

8.1.1 The concept of the antiderivative and definition of the integral

We can think of an integral as an antiderivative. Consider the derivative of a function \( f(x) \) with respect to the variable \( x \) defined

\[
\frac{d}{dx} f(x) = f'(x)
\]

Rearranging this result, we find an expression for the total differential

\[
df(x) = f'(x)dx
\]

relating the change in the function \( f(x) \) resulting from an incremental change in the variable \( dx \). We can then define the integral as the operation that transforms the incremental change \( df(x) \) into the function \( f(x) \) itself

\[
f(x) = \int df(x) = \int f'(x)dx
\]

The integral is the antiderivative as it transforms the derivative of a function into the function itself.

We developed a good working knowledge of differentiation in Chapter 3. That means we already know something about integrals as antiderivatives. For example, for \( x \) raised to a power \( n \) we know that

\[
f(x) = \frac{1}{n}x^n \quad f'(x) = x^{n-1}
\]

which implies that\(^1\)

\[
\int f'(x)dx = \int x^{n-1}dx = \frac{1}{n}x^n = f(x)
\]

Similarly, for the exponential function

\[
f(x) = \frac{1}{a}e^{ax} \quad f'(x) = e^{ax}
\]

\(^1\) This form of integral, for which the range of \( x \) is unspecified, is known as an indefinite integral.
so that
\[ f(x) = \int f'(x) \, dx = \int e^{ax} \, dx = \frac{1}{a} e^{ax} \]

For the natural logarithm we find
\[ f(x) = \ln(x) \quad f'(x) = \frac{1}{x} \]
so that
\[ f(x) = \int f'(x) \, dx = \int \frac{1}{x} \, dx = \ln(x) \]

Finally, for the sine and cosine functions
\[ f(x) = \frac{1}{a} \cos(ax) \quad f'(x) = \sin(ax) \]
so that
\[ f(x) = \int f'(x) \, dx = \int \sin(ax) \, dx = -\frac{1}{a} \cos(ax) \]
and
\[ f(x) = \frac{1}{a} \sin(ax) \quad f'(x) = \cos(ax) \]
so that
\[ f(x) = \int f'(x) \, dx = \int \cos(ax) \, dx = \frac{1}{a} \sin(ax) \]

These results demonstrate that our knowledge of differentiation translates into a knowledge of integration as antidifferentiation.

### 8.1.2 Interpretation of the integral

The derivative is interpreted as the rate of change in a function for a given value of its variable. The integral sign \( \int \) is an elongated \( S \) standing for summation. The process of integration is the process of summing the area under the curve of the function being integrated.\(^2\)

Let’s explore the interpretation of the integral through the example of determining the pressure-volume work done by an ideal gas at constant temperature defined
\[ w = \int_{V_A}^{V_B} p(V) \, dV = \int_{V_A}^{V_B} \frac{nRT}{V} \, dV \]
where we have used the ideal gas equation of state \( pV = nRT \) to define \( p(V) = \frac{nRT}{V} \).\(^3\) The function to be integrated, in this case \( p(V) \), is known as the integrand. The factor \( nRT \) is a constant independent of \( V \) and can be pulled out of the integral leaving
\[ w = nRT \int_{V_A}^{V_B} \frac{1}{V} \, dV \]

From our antiderivative relations in the previous section we know that
\[ \int \frac{1}{x} \, dx = \ln(x) \]
so that\(^4\)
\[ w = nRT \left. \int_{V_A}^{V_B} \frac{1}{V} \, dV \right|_{V_A}^{V_B} = nRT \ln \left( \frac{V_B}{V_A} \right) \]
where we have used the fact that \( \ln(V_B) - \ln(V_A) = \ln \left( \frac{V_B}{V_A} \right) \).

What is the physical interpretation of this result? We interpret the integral as the antiderivative. As such, the integral represents the summing up of many small changes in the work \( dw = p(V) \, dV \) that take place over many small

---

\(^2\) The fact that the definite integral of a function over an interval is equal to the difference between the antiderivatives of the function evaluated at the endpoints of the interval is known as the fundamental theorem of calculus.

\(^3\) This form of integral, for which the range of \( x \) is specified, is known as a definite integral.

\(^4\) Note that \( f(x) \bigg|_{x_1}^{x_2} = f(x_2) - f(x_1) \).
changes in volume
\[ w = \int dw = \int p(V) \, dV \]

Each increment of the work \( dw \) is the area formed by the height of the function \( p(V) \) times the width resulting from a change in volume \( dV \).

Figure 8.1 shows \( p(V) \) as a function of volume \( V \) between the volumes \( V_A \) and \( V_B \). Suppose we divide the interval \([V_A, V_B]\) into \( N \) subintervals \([V_1, V_2], [V_2, V_3], ..., [V_N, V_{N+1}]\) where \( V_1 = V_A, V_{N+1} = V_B \) and \( V_n = V_A + (n-1)\Delta V \). The width of each interval is \( \Delta V = (V_B - V_A)/N \). We can approximate the integral defined as the area under the curve by the sum
\[ w \approx p(V_1)\Delta V + p(V_2)\Delta V + \ldots + p(V_N)\Delta V \]
\[ = \sum_{n=1}^{N} p(V_n)\Delta V \]
which is the sum of the areas of \( N \) rectangles each of width \( \Delta V \) and height \( p(V_n) \). Each shaded area is an increment of work \( dw \). The integral is the sum of many of these areas adding up to the total change \( w \).

As \( N \) increases, the number of rectangles increases and the accuracy of the estimate to the area under the curve improves. In the limit \( N \to \infty \) the sum converges to the exact result
\[ w = \lim_{N \to \infty} \sum_{n=1}^{N} p(V_n)\Delta V = \int_{V_A}^{V_B} p(V) \, dV \]  \hfill (8.2)

The area under the curve between the lower limit of integration \( V_A \) and the upper limit of integration \( V_B \) represents the definite integral of \( p(V) \) taken between \( V_A \) and \( V_B \).

Our choice of the height of each rectangle as the leftmost point in the interval was arbitrary. We could just as well take the rightmost point in the interval to be the height of the rectangle. In that case, the sum approximating the integral is
\[ w = \lim_{N \to \infty} \sum_{n=1}^{N} p(V_{n+1})\Delta V = \int_{V_A}^{V_B} p(V) \, dV \]  \hfill (8.3)
which represents the shaded area in Figure 8.2. Note that for finite \( \Delta V > 0 \), the first approximation using the leftmost point in the interval leads to an overestimate of the area under the curve. In contrast, using the rightmost point in the interval leads to an underestimate of the area under the curve. Nevertheless, in the limit \( \Delta V \to 0 \) both approximations lead to the same exact result.

With these insights, we can develop a general definition of the integral in terms of the Riemann sum. Suppose we partition the interval \([V_A, V_B]\) into \( N \) subintervals \([V_1, V_2], [V_2, V_3], ..., [V_N, V_{N+1}]\) where \( V_A = V_1 < V_2 < \ldots < V_N < V_{N+1} = V_B \). The integral of \( p(V) \) between \( V_A \) and \( V_B \) can be approximated by the sum
\[ w = \lim_{N \to \infty} \sum_{n=1}^{N} p(V_n^*)\Delta V_n = \int_{V_A}^{V_B} p(V) \, dV \]  \hfill (8.4)
where \( V_n^* \in [V_n, V_{n+1}] \) and \( \Delta V_n = V_{n+1} - V_n \). In our previous sums, the subintervals \( \Delta V_n \) were of uniform width. In this Riemann sum, the intervals \( V_n \) may be of varying width. Moreover, in our previous sums the height of each rectangle was taken to be the value of \( p(V) \) for the leftmost or rightmost point in the interval. In the Riemann sum, the height of the rectangle is taken to be \( p(V_n^*) \) where \( V_n^* \) is any point in the interval \([V_n, V_{n+1}]\). An example of a
Riemann sum having subintervals of varying width $\Delta V_n$ and randomly chosen points $V_n^*$ within each subinterval is shown in Figure 8.3.$^5$

We can now combine our definition of the derivative given by Equation 3.2

$$\lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} = \frac{df}{dx}$$

with our equivalent definition of the integral

$$\lim_{N \to \infty} \sum_{n=1}^{N} f(x_n) \Delta x = \int f(x) dx \quad (8.5)$$

These geometric interpretations of the derivative and integral in terms of finite differences $\Delta x$ in the variable $x$ are useful in numerically estimating derivatives and integrals when the indefinite integrals or exact derivatives are not known. By performing the sum for increasing values of $N$ and decreasing values of $\Delta x$, we realize an increasingly accurate approximation to the integral.

8.1.3 Revisiting the rules for integrating functions of one variable

There are a number of useful rules for integrating functions of one variable. We introduce these rules by exploring the integration of a variety of commonly appearing functional forms. It is important to practice and master these rules. They are essential to our successful application of the calculus to problems in the physical sciences.

1. $df(x)$. Integration of the exact differential of a function leads to the function itself plus $C$, an integration constant $^6$

$$\int df(x) = f(x) + C$$

2. $a$. Integration of a constant produces a linear function plus a constant

$$\int a \, dx = a \int dx = ax + C$$

Differentiation of the result produces $a$. Note that when we have a constant times a function of $x$, we can pull the constant out of the integral as shown above. Pulling the constant out in front of the integral can be helpful in simplifying the integration of complicated expressions.

$^5$ The results in Equations 8.2 and 8.3 are known as left method and right method Riemann sums, respectively. Alternative definitions include the maximum method and minimum method for which the height of each rectangle is defined by the endpoint with the larger or smaller value, respectively.

$^6$ The derivative of a function is equal to the derivative of the same function plus a constant

$$\frac{d}{dx} f(x) = \frac{d}{dx} (f(x) + C)$$

As such, the antiderivative of a function equals the integral of that function plus a constant

$$\int df(x) = f(x) + C$$

The integration constant $C$ is undetermined for an indefinite integral. It can be evaluated once the limits of integration are imposed.
3. $x^n$. Using our knowledge of the power rule for derivatives of powers of $x$ we find
\[ \int x^n \, dx = \frac{1}{n+1} x^{n+1} + C \quad n \neq -1 \]
Consider the integral
\[ \int v_0 \, t \, dt = v_0 \int t \, dt = \frac{1}{2} v_0 \, t^2 + C \]
Further consider the integral
\[ \int \frac{\Delta H}{RT^2} \, dT = \frac{\Delta H}{R} \int \frac{1}{T^2} \, dT = -\frac{\Delta H}{R} \frac{1}{T} + C \]

4. $x^{-1}$. Using our knowledge of the derivative of the natural logarithm we find the indefinite integral
\[ \int \frac{1}{x} \, dx = \ln x + C \]
The definite integral of $\frac{1}{x}$ over the range $x \in [a, b]$ can be written
\[ \int_a^b \frac{1}{x} \, dx = [\ln x]^b_a = \ln(b) - \ln(a) = \ln \left( \frac{b}{a} \right) \]
This result is shown graphically in Figure 8.4. The integral is equal to shaded area under the curve. The black line shows the accumulating area under the curve, which increases as $\ln \left( \frac{x}{a} \right)$ from 0 at $x = a$ to the final result $\ln \left( \frac{b}{a} \right)$. In the kinetics of certain reactions, the rate of change in the concentration $c(t)$ is proportional to the concentration itself. As the rate of change in $c(t)$ is $\frac{dc}{dt}$, this proportional relationship can be written
\[ \frac{dc}{dt} = -kc \quad \text{or} \quad \frac{1}{c} \, dc = -k \, dt \]
where $k$ is a constant.\(^7\) We can solve this equation for $c(t)$. Using our knowledge of integrals, we can transform the result
\[ \int \frac{1}{c} \, dc = -\int k \, dt \]
into a relation for the concentration, $c(t)$, as a function of time
\[ \ln c(t) = -kt + C \]
By exponentiating each side of this equation, the result can also be expressed as
\[ c(t) = Ae^{\frac{-kt}{C}} \]
where $A = e^C$.

As another example, consider the following fundamental relation in thermodynamics\(^8\)
\[ \frac{dp}{dT} = \frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{1}{p} \, dp = \frac{\Delta H}{RT^2} \, dT \]
We can solve the latter equation for $p(T)$ using our knowledge of integrals as
\[ \int \frac{1}{p} \, dp = \frac{\Delta H}{R} \int \frac{1}{T^2} \, dT \]
and
\[ \ln p = -\frac{\Delta H}{RT} + C \]

\(^7\) Known as the Clausius-Clapeyron equation, this relation describes the dependence of vapor pressure on temperature. Note that we treat $\frac{dp}{dT}$ as an algebraic ratio, which allows us to separate the incremental changes $dp$ and $dT$.\(^8\)
This can be rewritten in the familiar form

\[ p(T) = A \exp \left( -\frac{\Delta H}{kT} \right) \]

where \( \ln A = C \).

5. \( f(x) + g(x) \). Integration is a linear operation, like multiplication or differentiation. As such, the integral of the sum of two functions is the sum of two integrals

\[ \int [f(x) + g(x)] \, dx = \int f(x) \, dx + \int g(x) \, dx \]

For example, consider the integral of the function \( C_p(T) = a + bT + cT^2 \) over \( T \), where \( a \), \( b \), and \( c \) are constants. We find

\[ \int C_p(T) \, dT = \int \left( a + bT + cT^2 \right) \, dT = a \int dT + b \int T \, dT + c \int T^2 \, dT = aT + \frac{1}{2} bT^2 + \frac{1}{3} cT^3 + C \]

6. \( e^{ax} \). Using our knowledge of the derivative of the exponential function we find

\[ \int e^{ax} \, dx = \frac{1}{a} e^{ax} + C \]

For example, consider the indefinite integral over a function \( c(t) \) with respect to \( t \), where \( c(t) = C_0 e^{-t/\tau} \) and \( C_0 \) and \( \tau \) are constants. We find

\[ \int C_0 e^{-t/\tau} \, dt = C_0 \int e^{-t/\tau} \, dt = -C_0 \tau e^{-t/\tau} + C \]

Further consider the definite integral of \( e^{-x} \) over the range \( x \in [a, b] \). We find

\[ \int_a^b e^{-x} \, dx = - \left[ e^{-x} \right]_a^b = e^{-a} - e^{-b} \]

This result is shown graphically in Figure 8.5.

7. \( \sin(ax) \) and \( \cos(ax) \). Using our knowledge of derivatives of sine and cosine functions we find

\[ \int \sin(ax) \, dx = -\frac{1}{a} \cos(ax) + C \]
\[ \int \cos(ax) \, dx = \frac{1}{a} \sin(ax) + C \]

For example, consider the integral over a sinusoidal function

\[ \int_0^\pi \sin(x) \, dx = -\cos(x) \bigg|_0^\pi = \cos(a) - \cos(b) \]

This result is shown graphically in Figure 8.6. The sinusoidal function takes on positive and negative values which add and subtract from the total area under the curve. The result is an accumulating area that oscillates as the contributions from positive and negative regions of the sine are summed.

8. \( \delta(x - x_0) \). The Dirac delta function (or \( \delta \) function) was discovered by Paul Dirac and plays an important role in the mathematics of quantum mechanics. While the function may seem strange, in some ways, the integral over the \( \delta \) function could not be simpler. The function \( \delta(x - x_0) \) is zero everywhere
except at the point $x = x_0$ where it is infinite

$$\delta(x - x_0) = \begin{cases} \infty & x = x_0 \\ 0 & x \neq x_0 \end{cases}$$

The area under the function when integrated over a range of $x$ containing $x_0$ is unity as

$$\int_{-\infty}^{\infty} \delta(x - x_0) \, dx = 1$$

An attempt to graphically depict the Dirac delta function is shown in Figure 8.7.

Consider the integration over all space of the delta function multiplying a function $f(x)$. The product of $f(x)\delta(x - x_0)$ is zero everywhere except at $x = x_0$ so that

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0) \, dx = f(x_0) \int_{-\infty}^{\infty} \delta(x - x_0) \, dx = f(x_0)$$

Note that we can pull the term $f(x_0)$ out of the integral as it is a constant. We will explore the utility of the $\delta$ function later in this chapter.

9. $e^{-ax^2}$. The gaussian function has many important applications in the physical sciences. There is a simple closed form solution for the definite integral of the gaussian function over all space

$$\int_{-\infty}^{\infty} e^{-ax^2} \, dx = \sqrt{\frac{\pi}{a}}$$

This fundamentally important result is widely used in applications of integration in the physical sciences. The identity is proven in the Complements.

The integral over a gaussian function occurs frequently in the physical sciences. It is called the $\text{error function}$ and defined

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} \, dt \quad (8.6)$$

The error function is positive for positive values of $x$, representing the area under the gaussian function over the range $[0, x]$ (see Figure 8.8). The
complementary error function is defined

\[
erfc(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} \, dt = 1 - \text{erf}(x) \quad (8.7)
\]

and represents the area under the gaussian function not included in the error function. As such, \( \text{erf}(x) + \text{erfc}(x) = 1 \) (see Figure 8.8). Numerical values of the error function and complementary error function are tabulated in Supplement S7.

The rules of integration above provide us with the foundation of knowledge we need to address problems in the physical sciences involving the integration of functions.

### 8.1.4 Useful tricks for integrating functions of one variable

In addition to the fundamental rules previously introduced, we can use the fundamental rules of integration with a few basic tricks that will prove useful in performing integrals on more complicated functions.

1. **Algebraic substitution.** In differentiation we encountered complicated expressions that were simplified using an algebraic substitution of variables. For example, consider the function

\[
f(x) = e^{-\frac{1}{x}}
\]

Taking the derivative of this function with respect to \( x \) can be simplified by introducing the variable

\[
y = \frac{1}{x} \quad \text{where} \quad \frac{dy}{dx} = -\frac{1}{x^2}
\]

Using the chain rule where

\[
\frac{df}{dx} = \frac{df}{dy} \frac{dy}{dx}
\]

the derivative of \( f(x) \) with respect to \( x \) can be simplified as

\[
\frac{d}{dx} \left( e^{-\frac{1}{x}} \right) = \frac{d}{dy} e^{-y} \frac{dy}{dx} = -e^{-y} \left( -\frac{1}{x^2} \right) = \frac{1}{x^2} e^{-1/x}
\]

We can use a similar trick in integration as follows. Suppose we want to integrate the function

\[
f(x) = \frac{1}{x^2} e^{-\frac{1}{x}}
\]

This looks hard! We first simplify the function with the substitution\(^{10}\)

\[
y = \frac{1}{x} \quad \text{and} \quad dy = -\frac{1}{x^2} \, dx
\]

This allows us to write

\[
\int \frac{1}{x^2} e^{-\frac{1}{x}} \, dx = \int e^{-y} \, dy = -e^{-y} + C = e^{-\frac{1}{x}} + C
\]

where as a final step we have convert back to the original variable \( x \). This example demonstrates how a clever substitution of variables turns an apparently challenging integral into a problem with a familiar solution.\(^{11}\)

Further consider the example

\[
\int \frac{1}{V - nb} \, dV \quad (8.8)
\]
where we make the algebraic substitution often referred to as $u$-substitution
\[ u = V - nb \quad du = \frac{dV}{1} \quad du = dV \]
so that
\[ \int \frac{1}{V - nb} \, dV = \int \frac{1}{u} \, du = \ln u + C = \ln (V - nb) + C \]
While the proper substitution may be apparent in this example, in other cases careful consideration of the problem is required to identify the optimal substitution.
Finally, consider the example
\[ \int \cos^2 x \sin x \, dx \]
where we make the algebraic substitution
\[ u = \cos x \quad du = -\sin x \, dx \]
so that
\[ \int \cos^2 x \sin x \, dx = -\int u^2 \, du = -\frac{1}{3}u^3 + C = -\frac{1}{3}\cos^3 x + C \]
A wide range of integrals can be solved using algebraic substitution, including integrals involving polynomial, exponential, and sinusoidal integrands. Algebraic substitution is particularly valuable in the physical sciences as the proper substitution of variables can convert a complicated integrand into a simplified and manageable function.

2. Trigonometric transformation. Consider the integral
\[ \int \sin^2 x \, dx \]
We know how to integrate $\sin x$ but not $\sin^2 x$. Fortunately, we can get rid of the square by transforming the expression using the trigonometric transformation
\[ \sin^2 x = \frac{1}{2} (1 - \cos(2x)) \]
so that
\[ \int \sin^2 x \, dx = \frac{1}{2} \int (1 - \cos(2x)) \, dx = \frac{1}{2} \left[ dx - \frac{1}{2} \int \cos(2x) \, dx \right] = \frac{1}{2}x - \frac{1}{4} \sin(2x) + C \]
When you encounter an integral over a trigonometric function that you don’t recognize, consider trigonometric identities that might transform the integral into a solvable form.

3. Partial fractions. For an integral like Equation 8.8, the numerator $dV$ is a derivative of the denominator $(V - nb)$. In that case, the integral can be solved using algebraic substitution. However, for the integral
\[ \int \frac{1}{(a - x)(b - x)} \, dx \]
the numerator $dx$ is not the derivative of the denominator $(a - x)(b - x)$. In this case, we can reform our integral using partial fractions.$^{12}$

We can make use of a clever identity relating the product of the reciprocal differences to the difference of the reciprocal differences$^{13}$

$^{12}$ The method of partial fractions is a special case of the more general Heaviside cover-up method named for English physicist and engineer Oliver Heaviside (1850-1925).

$^{13}$ We can prove this
\[ \frac{1}{(b - a)} \left[ \frac{1}{a - x} \right] = \frac{1}{(b - a)} \left[ \frac{b - x}{(a - x)(b - x)} - \frac{a - x}{(a - x)(b - x)} \right] \]
that can be simplified as
\[ \frac{1}{(b - a)} \left[ \frac{b - x - (a - x)}{(a - x)(b - x)} \right] = \frac{1}{(a - x)(b - x)} \]
Integrating functions of one variable. Integration by parts. A final trick that is valuable in evaluating integrals

We can evaluate these integrals using our knowledge of the integral identity

The transformation of

This is a very useful result.

Integrating both sides of this equation leads to

resulting in

The transformation of \( \frac{1}{(a-x)(b-x)} \) using partial fractions is graphically depicted in Figure 8.9. It is somewhat remarkable that the product of the reciprocal functions \( (a-x)^{-1} \) and \( (b-x)^{-1} \) is proportional the difference of the two functions.

4. Integration by parts. A final trick that is valuable in evaluating integrals found in the physical sciences is known as integration by parts. Recall the product rule

Multiplying both sides of the equation by \( dx \) results in

that can be reformed as

Integrating both sides of this equation leads to

This is a very useful result. Consider the integral

We decompose \( xe^{-ax}dx \) as \( udv \) as

Combining these results and Equation 8.9 we find

14 Integration by parts was first introduced by English mathematician Brook Taylor (1685-1731).

15 We have used the identity

16 To find \( v \) we integrate \( dv \) as

17 We use the result

At the lower limit \( xe^{-ax} \) is zero when \( x = 0 \). For the upper limit we find

that can be shown using l’Hôpital’s rule as
As a final example of integration by parts, consider the indefinite integral
\[ \int x \sin x \, dx = \int udv \]
We decompose \( x \sin x \, dx = u \, dv \) as
\[
\begin{align*}
  u &= x \\
  dv &= \sin x \, dx \\
  du &= dx \\
  v &= -\cos x
\end{align*}
\]
Combining these results and Equation 8.9 we find
\[ \int x \sin x \, dx = \int udv = uv - \int vdu = -x \cos x + \int \cos x \, dx \]
\[ = -x \cos x + \sin x \, dx + C \]
where \( C \) is an undetermined integration constant.

This concludes our review of rules for integrating functions of one variable. In the next section, we apply the rules for integrating functions of one variable to the integration of functions of many variables.

8.2 Integrating functions of many variables

Functions of more than one variable are commonly encountered in modeling the properties of physical systems. The concentration of a substance in three-dimensions is a function of the position in space defined by the values of three cartesian coordinates. The total amount of substance in a given volume of solution is the multiple integral of the concentration taken over all three coordinates. In this section, we explore the definition of multiple integrals and survey common methods for evaluating multiple integrals over functions of many variables.

8.2.1 Double integrals

We interpret the integral of a function of one variable \( f(x) \) between points \( x = a \) and \( x = b \) written
\[ \int_a^b f(x) \, dx \]
to be the area under the curve formed by \( f(x) \) over \( x \in [a, b] \). An example is shown in Figure 8.10 where the shaded area is the value of the integral. This concept can be generalized to integrals of functions of many variables.

In two dimensions, we define the double integral over a function of two variables \( f(x, y) \) taken over a rectangular area of the \( xy \)-plane defined by the limits \( x \in [a, b] \) and \( y \in [c, d] \) as
\[ \int_c^d \int_a^b f(x, y) \, dxdy \]
We interpret the double integral to be the volume under the surface formed by \( f(x, y) \) taken over the rectangular area. An example is shown in Figure 8.11 where the shaded volume is the value of the integral.

It is important to understand the notation used for a double integral. For the double integral written
\[ \int_c^d \int_a^b f(x, y) \, dxdy = \int_c^d \left[ \int_a^b f(x, y) \, dx \right] dy \]
the order of integration is implied to be integration over \( x \) first, followed by integration over \( y \).18

\[ f(x) \]

Figure 8.10: The function \( f(x) \) shown over a range of \( x \) from \([a, b]\). The integral \( \int_a^b f(x) \, dx \) equals the shaded area under the curve.

18 The concept of the antiderivative is defined strictly for functions of one variable (see Equation 8.1). As such, the definition of the indefinite integral does not immediately extend to functions of many variables.
Let’s consider a simple example to see how the double integral works. Suppose we wish to integrate the constant function \( f(x, y) = c \) over an area defined by \( x \in [0, a] \) and \( y \in [0, b] \) (see Figure 8.12). Since the function is a constant we can write

\[
\int_0^b \int_0^a f(x, y) \, dx \, dy = c \int_0^b \int_0^a dx \, dy
\]

Since the limits of integration over \( x \) do not depend on \( y \) we can separate the integral over \( x \) from the integral over \( y \) as

\[
c \int_0^b \int_0^a dx \, dy = c \int_0^b dy \times \int_0^a dx
\]

We have now reduced our two-dimensional integral to two one-dimensional integrals that we can readily perform to find

\[
c \int_0^b dy \times \int_0^a dx = cb \int_0^a dx = cba
\]

The value of the double integral is the height of the function, \( c \), times the area over which the integral is performed on the \( xy \)-plane, \( ab \), which is the volume \( abc \).

### 8.2.2 Double integrals and the order of integration

Not all integrals on the \( xy \)-plane are as simple as our previous example. Consider the challenge of finding the area between a straight line and intersecting parabola shown in Figure 8.13. We define the area as the double integral over the \( xy \)-plane restricted to the area between the curves.

Suppose we wish to first integrate over \( x \). As the integral is restricted to the area between the curves, the lower and upper bounds of the integral in \( x \) will depend on the particular value of \( y \). The lower bound for integration over \( x \) is defined by the straight line so that \( x = \frac{y}{2} \) while the upper bound for integration over \( x \) is defined by the parabola so that \( x = \sqrt{y} \). Integration over \( y \) follows integration over \( x \) with the lower and upper bounds of \( y = 0 \) and \( y = 4 \), respectively.

With this understanding we can write a formula for the area between the curves in terms of the double integral\(^{19}\)

\[
\int_0^2 \int_0^{\sqrt{y}} dx \, dy
\]
\[ \int_0^4 \left( \sqrt{\frac{y}{2}} \right) \, dx = \int_0^4 \left[ \int_0^x \sqrt{\frac{y}{2}} \, dy \right] \, dx = \int_0^4 \left( \sqrt{\frac{y}{2}} \right) \, dy \]

Evaluating the inner integral
\[ \int_0^4 \left( \sqrt{\frac{y}{2}} \right) \, dy = \left[ \frac{2}{3} \left( \frac{y^{3/2}}{2} - \frac{y^2}{4} \right) \right]_0^4 = \frac{2}{3} \left( \frac{4^{3/2}}{2} - \frac{4^2}{4} \right) = \frac{4}{3} \]

We now have two definite integrals to complete as
\[ \int_0^4 \int_0^x \sqrt{\frac{y}{2}} \, dy \, dx = \int_0^4 \left( x \sqrt{\frac{y}{2}} \right) \, dx = \int_0^4 \left( x - x^2 \right) \, dx = \frac{4}{3} \]

So we see that the order of integration does not matter. This will be true for most of the integrals of interest to us.

### 8.2.3 Double integrals of separable functions

The examples above demonstrate that integration over \( x \) and \( y \) can be coupled by integrating over areas that make the limits of integration over \( x \) dependent on \( y \) (and vice versa). However, integration over \( x \) and \( y \) can also be coupled when \( f(x, y) \) is a non-separable function of \( x \) and \( y \) and \( f(x, y) \neq g(x)h(y) \).

Fortunately, most of the integrals of interest in the physical sciences are taken over separable functions. When \( f(x, y) = g(x)h(y) \) we can write
\[
\int_a^b \int_c^d f(x, y) \, dx \, dy = \int_a^b \int_c^d g(x)h(y) \, dx \, dy
\]
\[
= \int_c^d h(y) \, dy \times \int_a^b g(x) \, dx
\]

This reduces the two-dimensional integral over the \( xy \)-plane to a product of two one-dimensional integrals. Separability will often depend on the right choice of coordinate systems. To better understand this critical idea, we will explore a variety of examples in detail.

### 8.2.4 Double integrals and the Tables of Integrals

A valuable application of integration in many dimensions involves determination of the area or volume of a geometric object by integration of a constant over the area or volume of the object. Consider the evaluation of the area of a circle shown in Figure 8.14. We can divide and conquer this integral by first performing the integration over one quadrant. We then multiply that result by four. In that case, we wish to determine the shaded area of the quarter circle.

The range of integration of \( x \) depends on the value of \( y \) as along the perimeter of the circle \( x = \sqrt{1 - y^2} \). As such, the range of integration in \( x \) will have a lower bound of 0 and upper bound of \( x = \sqrt{1 - y^2} \). The range of integration of \( y \) is from 0 to 1. With this understanding we can write the integral over the quadrant as
\[
\int_0^1 \int_0^{\sqrt{1 - y^2}} \, dx \, dy = \int_0^1 \sqrt{1 - y^2} \, dy
\]

What do we do now? While we have reviewed methods for performing integrals

Figure 8.14: One quadrant of the unit circle with area equal to \( \frac{\pi}{4} \).
of a single variable, nothing in our survey prepared us for this integral.

We will find that for many integrals of interest, the best way to solve them is to look up the result in a table of integrals.\textsuperscript{20} Tables of definite and indefinite integrals sufficient to perform the problems in this text are included in Supplements S_5 and S_6. This table includes the result

\[
\int_0^a \sqrt{a^2 - x^2} \, dx = \left[ \frac{1}{2} \left( x \sqrt{a^2 - x^2} + a^2 \sin^{-1} \left( \frac{x}{a} \right) \right) \right]_0^a
\]

Using this result from the table of integrals for our case of \( a = 1 \) we find

\[
\int_0^1 \sqrt{1 - x^2} \, dx = \frac{1}{2} \sin^{-1} (1) = \frac{1}{4} \pi
\]

for the area over one quadrant of the unit circle. Four times this result is our answer to the original problem to determine the area of the unit circle. The area of the unit circle is \( \pi \).

8.2.5 Double integrals and the choice of coordinate system

The evaluation of the integral representing the area within the unit circle was somewhat complicated in cartesian coordinates. Cartesian coordinates have a natural square symmetry while the unit circle has round symmetry. Let’s evaluate the integral again in plane polar coordinates, which better reflect the round symmetry of the unit circle.

Using the coordinate transformations explored in Chapter 1 and depicted in Figure 8.15, we can transform the integral over a quarter of the unit circle in two-dimensional cartesian coordinates to plane polar coordinates as

\[
\int_0^{\pi/2} \int_0^1 r \, dr \, d\theta = \int_0^{\pi/2} \frac{\pi}{2} \times \frac{1}{2} = \frac{\pi}{4}
\]

Multiplying this answer by 4 leads to the result that the area of the unit circle is \( \pi \). However, in evaluating the integral in plane polar coordinates there is no need to break the integral into integrals over quarter circles as was required in cartesian coordinates. We can perform the integral at once over the whole unit circle as

\[
\int_0^{2\pi} \int_0^1 r \, dr \, d\theta = \int_0^{2\pi} \frac{\pi}{2} \times \frac{1}{2} = \frac{\pi}{4}
\]

Much simpler! Note that in cartesian coordinates, the integrals over \( x \) and \( y \) were coupled through the limits of integration. In plane polar coordinates the integrals over \( r \) and \( \theta \) are separable. The take home lesson is that the right choice of coordinate system, in which the variables reflect the natural symmetry of the function, can make the work of integration much easier.

8.2.6 Double integrals and the delta function

Suppose we want to determine the length of the circumference of a circle using an integral along the line forming the circle. We can accomplish this using the delta function. Let’s start with the double integral over the \( xy \)-plane expressed in plane polar coordinates

\[
\int_0^{2\pi} \int_0^\infty r \, dr \, d\theta
\]
Now suppose we insert in the integrand \( \delta(r - a) \). This makes the integrand zero unless \( r = a \), which defines the perimeter of a circle. In that case the integral over the \( xy \)-plane will be reduced to an integral over the perimeter of the circle only. This gives us a formula for the circumference of the circle

\[
C = \int_0^{2\pi} \int_0^\infty \delta(r - a) r \, dr \, d\theta
\]

Performing the integral over \( r \) first\(^{21} \) followed by the integral over \( \theta \) we find

\[
\int_0^{2\pi} \int_0^\infty \delta(r - a) r \, dr \, d\theta = 2\pi \int_0^\infty \delta(r - a) r \, dr = 2\pi a
\]

which is the circumference of a circle of radius \( a \). Inserting the delta function reduces the two-dimensional integral over the \( xy \)-plane to a one-dimensional integral over the perimeter of the circle.

### 8.2.7 Triple integrals

The evaluation of the volume of a solid is a fundamental importance in the physical sciences.\(^{22} \) In order to extend our understanding of multiple integrals, let’s consider the evaluation of the volume of a cylinder of radius \( a \) and height \( h \) (see Figure 8.16). Defining the volume of a cylinder in cartesian coordinates is complicated. The limits of integration in \( x \) and \( y \) are coupled just as we found in the integration over the unit circle. However, the integral over the volume of a cylinder can be naturally and simply expressed in using cylindrical coordinates.

The triple integral representing the volume of the cylinder can be written

\[
V = \int_0^h \int_0^{2\pi} \int_0^a r \, dr \, d\theta \, dz = \int_0^h dz \times \int_0^{2\pi} d\theta \times \int_0^a r \, dr
\]

\[= h \times 2\pi \times \frac{a^2}{2} = \pi a^2 h\]

which is the intuitive result that the volume of the cylinder is equal to the circular area of the cylinder, \( \pi a^2 \), times the height \( h \).

Now suppose we want to determine the volume of a sphere. We want to select a coordinate system that shares the natural symmetry of a sphere. In cartesian coordinates, the limits of integration over \( x, y, \) and \( z \) are coupled. However, the spherical polar coordinate system depicted in Figure 8.17 has the

\[
dA = r^2 \sin \theta \, dr \, d\theta \, d\phi
\]

where the Dirac delta function is zero everywhere other than the perimeter of the circle where \( r = a \).

\[^{21}\] Here we use the identity

\[
\int_0^\infty \delta(r - a) r \, dr = a
\]

\[^{22}\] Archimedes (circa 287-212 BCE) determined geometric volumes using the theory of infinitesimals before the concept of the integral was developed. The theory of infinitesimals was further applied to the calculation of areas and volumes by Johannes Kepler (1571-1630) in his 1615 treatise New Solid Geometry of Wine Barrels.
natural symmetry of a sphere. If we transform our function into spherical polar
coordinates we find the integral is separable in \( r \), \( \theta \), and \( \phi \) as
\[
V = \int_0^{2\pi} \int_0^\pi \int_0^a r^2 \sin \theta \, dr \, d\theta \, d\phi
= \int_0^{2\pi} d\phi \times \int_0^\pi \sin \theta \, d\theta \times \int_0^a r^2 \, dr
= 2\pi \times 2 \times \frac{a^3}{3} = \frac{4}{3} \pi a^3
\]
This is the well-known result for the volume of a sphere of radius \( a \).\(^{23}\)

These examples show how integration in three-dimensions can be used
to derive important identities for volumes of shapes such as cylinders and
spheres. Moreover, the examples show how the proper choice of coordinate
system can convert a many dimensional integral into a series of independent
one-dimensional integrations. For the integrals of greatest interest to us in the
physical sciences, we will often find that multiple integrals can be simplified in
this way.\(^{24}\)

### 8.2.8 Triple integrals and the delta function

Suppose we want to determine the surface area of a sphere of radius \( a \). We can
accomplish this using the delta function. Let’s start with the triple integral over
all space in spherical polar coordinates
\[
\int_0^{2\pi} \int_0^\pi \int_0^\infty f(r, \theta, \phi) r^2 \sin \theta \, dr \, d\theta \, d\phi
\]
We insert in the integrand a function \( f(r, \theta, \phi) \) that is zero everywhere in three-
dimensional space other than on the surface of the sphere. We do that using the
delta function
\[
f(r, \theta, \phi) = \delta(r - a)
\]
which is zero everywhere other than on the spherical surface defined by \( r = a \).
As result we find the area of the surface of a sphere defined by the separable integral
\[
A = \int_0^{2\pi} \int_0^\pi \int_0^\infty \delta(r - a) r^2 \sin \theta \, dr \, d\theta \, d\phi
= \int_0^{2\pi} d\phi \times \int_0^\pi \sin \theta \, d\theta \times \int_0^\infty \delta(r - a) r^2 \, dr
\]
Performing the integral over \( r \) first followed by the integrals over \( \theta \) and \( \phi \) we
find
\[
A = a^2 \times \int_0^{2\pi} d\phi \times \int_0^\pi \sin \theta \, d\theta = a^2 \times 2\pi \times 2 = 4\pi a^2
\]
which is the area of the surface of a sphere of radius \( a \). Inserting the delta function
reduces the three-dimensional integral over all space to a two-dimensional
integral over the surface of the sphere.

---

\(^{23}\) We used the identity
\[
\int_0^\pi \sin(x)dx = -\left[\cos x\right]_0^\pi = -(1 - 1) = 2
\]
to complete the integral over \( \theta \).

\(^{24}\) It is possible to extend the concept of the double and triple integrals
to integrals over arbitrarily large numbers of variables. As large, in fact, as
Avogadro’s number, and larger still.

---

**A8 An alternative to integration by parts for exponential integrals**

In exploring useful tricks for integrating function of one variable, we performed
integrals over an exponential function \( e^{ax} \) times a power of \( x \) such as
\[
\int x e^{ax} 
\]
using integration by parts as

\[ u = x \quad \quad dv = e^{ax} \, dx \]
\[ du = dx \quad \quad v = \frac{1}{a} e^{ax} \quad (8.12) \]

so that

\[ \int xe^{ax} \, dx = \frac{1}{a} xe^{ax} - \int \frac{1}{a} e^{ax} \, dx = \frac{1}{a} xe^{ax} - \frac{1}{a^2} e^{ax} \]
\[ = \frac{1}{a^2} (ax - 1) e^{ax} + C \]

That was not too bad. However, to perform the integral

\[ \int x^A e^{ax} \, dx \]

would require applying integration by parts four times! Let’s explore a way to improve our efficiency in performing integrals of this kind.

Consider the identity

\[ xe^{ax} = \frac{d}{da} e^{ax} \]

where we have used the derivative with respect to the constant \( a \) to pull down a power of \( x \). With this identity, we can rewrite the integral of interest as\(^{25}\)

\[ \int xe^{ax} \, dx = \frac{d}{da} \int e^{ax} \, dx \]

This integral can be evaluated using our knowledge of the exponential integral as

\[ \int xe^{ax} \, dx = \frac{d}{da} \left( \frac{1}{a} e^{ax} \right) = -\frac{1}{a^2} e^{ax} + \frac{1}{a} xe^{ax} \]
\[ = \frac{1}{a^2} (ax - 1) e^{ax} + C \quad (8.13) \]

just as we found using integration by parts.

The real power of this approach is evident in evaluating definite integrals over an exponential function \( e^{-ax} \) times a power of \( x \). For example, we can readily evaluate

\[ \int_0^\infty xe^{-ax} \, dx = -\frac{d}{da} \int_0^\infty e^{-ax} \, dx = -\frac{d}{da} \frac{1}{a} = \frac{1}{a^2} \]

which is consistent with the result derived with greater effort using integration by parts.

\[ u = x \quad \quad dv = e^{-ax} \, dx \]
\[ du = dx \quad \quad v = -\frac{1}{a} e^{ax} \quad (8.14) \]

so that

\[ \int_0^\infty xe^{-ax} \, dx = -\frac{1}{a} xe^{-ax} \bigg|_0^\infty + \int_0^\infty \left( -\frac{1}{a} e^{-ax} \right) \, dx \]
\[ = \frac{1}{a^2} e^{-ax} \bigg|_0^\infty = \frac{1}{a^2} \]

We see how our trick of differentiating with respect to \( a \) is more efficient than integration by parts for these particular definite integrals over the range \( 0 \leq x \leq \)}
This is even more true for integrals such as
\[
\int_0^\infty x^2 e^{-ax} \, dx = \frac{d^2}{da^2} \int_0^\infty e^{-ax} \, dx = \frac{d^2}{da^2} \frac{1}{a} = -\frac{d}{da} \frac{1}{a^2} = 2 \frac{1}{a^3}
\]
This integral would require two rounds of integration by parts to be solved. Using our trick we can solve the problem by simply differentiating the exponential twice with respect to \(a\).

**B8 Evaluating the definite integral of a gaussian function**

Consider the integral over the gaussian function
\[
I = \int_\infty^{-\infty} e^{-ax^2} \, dx
\]

There is no obvious way to evaluate this integral using our standard methods such as algebraic substitution or integration by parts. Consider the algebraic substitution \(y = x^2\). This leads to \(dy = 2xdx\) introducing a factor of \(x\). Similar problems arise in integration by parts where the derivative of the gaussian function introduces a factor of \(x\). To evaluate this integral we will use an inspired trick imagined by the German mathematician Carl Friedrich Gauss for whom the gaussian function is now named.

Consider the product of two equivalent one-dimensional integrals
\[
\int_\infty^{-\infty} e^{-ax^2} \, dx \times \int_\infty^{-\infty} e^{-ay^2} \, dy = I \times I = I^2
\]
This product can be thought of as one two-dimensional integral over the \(xy\)-plane
\[
I^2 = \int_\infty^{-\infty} \int_\infty^{-\infty} e^{-a(x^2+y^2)} \, dxdy
\]
This integral is most simply evaluated in plane polar coordinates where
\[
r^2 = x^2 + y^2 \quad \Rightarrow \quad \int_\infty^{-\infty} \int_\infty^{-\infty} dxdy \rightarrow \int_0^{2\pi} \int_0^\infty r \, d\theta \, dr
\]
With this transformation of variables
\[
I^2 = \int_\infty^{-\infty} \int_\infty^{-\infty} e^{-a(x^2+y^2)} \, dxdy = \int_0^{2\pi} \int_0^\infty e^{-ar^2} r \, d\theta \, dr
\]
Defining \(u = r^2\) so that \(du = 2r \, dr\) results in
\[
I^2 = 2\pi \int_0^\infty e^{-ar^2} r \, dr = \pi \int_0^\infty e^{-au} \, du = \pi \left[-\frac{1}{a} e^{-au}\right]_0^\infty = \frac{\pi}{a}
\]
leading to our final result
\[
I = \int_\infty^{-\infty} e^{-ax^2} \, dx = \sqrt{\frac{\pi}{a}}
\]
This result is recorded in the Table of Definite Integrals in Supplement S5 #2. We commonly encounter integrals over gaussian functions in the physical sciences. As such, it is worthwhile to memorize this fundamental result.
C₈ An alternative to integration by parts for gaussian integrals

We can extend our trick for efficiently integrating over integrands of the form $x^n e^{-ax^2}$ to integrands of the form $x^n e^{-ax^2}$ containing a gaussian function.

Consider the gaussian integral

$$\int_{0}^{\infty} e^{-ax^2} \, dx = \frac{1}{2} \int_{-\infty}^{\infty} e^{-ax^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

Differentiating the gaussian function with respect to the parameter $a$ pulls down a factor of $-x^2$ as

$$\frac{d}{da} \int_{0}^{\infty} e^{-ax^2} \, dx = \int_{0}^{\infty} \frac{d}{da} e^{-ax^2} \, dx = -\int_{0}^{\infty} x^2 e^{-ax^2} \, dx$$

That means that

$$\int_{0}^{\infty} x^2 e^{-ax^2} \, dx = -\frac{d}{da} \int_{0}^{\infty} e^{-ax^2} \, dx = -\frac{d}{da} \left( \frac{1}{2} \sqrt{\frac{\pi}{a}} \right)$$

$$= \frac{1}{4a^{3/2}} \sqrt{\pi}$$

For the odd powers of $x$ we can start from the integral identity\(^{26}\)

$$\int_{0}^{\infty} x e^{-ax^2} \, dx = \frac{1}{2a}$$

and use our trick to show

$$\int_{0}^{\infty} x^3 e^{-ax^2} \, dx = -\frac{d}{da} \int_{0}^{\infty} x e^{-ax^2} \, dx = -\frac{d}{da} \left( \frac{1}{2} \sqrt{\frac{\pi}{a}} \right) = \frac{1}{2a^2}$$

While integrals of this form can be evaluated using integration by parts, the effort required is significant. Using our trick we can most efficiently evaluate integrals over gaussian functions that commonly occur in the physical sciences.

D₈ Properties of delta functions

Delta functions can be used to select specific terms in a series or points in a function. Here we explore the properties of two delta functions that are commonly used in the physical sciences, the Kronecker delta function and the Dirac delta function.

Kronecker delta function

The Kronecker delta function, $\delta_{nm}$, is a function of two discrete indices $n$ and $m$. It is defined to be zero except when $n = m$

$$\delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

This function is used in sums to select those terms for which two indices are equal (see Figure 8.18).\(^ {27}\) For example, consider the sum

$$\sum_{n=-\infty}^{\infty} a_n \delta_{nm} = a_m$$

\(^{26}\) We can evaluate the integral $I = \int_{0}^{\infty} x e^{-ax^2} \, dx$ with the algebraic substitution $y = x^2$ so that $dy = 2x \, dx$ and

$$I = \frac{1}{2} \int_{0}^{\infty} e^{-ay} \, dy = \frac{1}{2a}$$

\(^{27}\) The German mathematician Leopold Kronecker (1902-1984) made important contribution to number theory and logic.
where $\delta_{nm}$ is used to select only the elements $a_n$ for which $n = m$. This is known as the sifting property.

The Kronecker delta function is normalized as

$$\sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \delta_{nm} = 1$$

A variety of other relations stem from these basic definitions including

$$\sum_{k=-\infty}^{\infty} \delta_{nk} \delta_{km} = \delta_{nm}$$

These examples demonstrate how the Kronecker delta function can be used to sift through and select specific terms in a finite or infinite series.

**Dirac delta function**

The Dirac delta function, $\delta(x - x_0)$, is zero everywhere except at the point $x = x_0$ where it is infinite

$$\delta(x - x_0) = \begin{cases} \infty & x = x_0 \\ 0 & x \neq x_0 \end{cases}$$

This function is used in integrals to select a particular value of the variable $x$ (see Figure 8.19). For example, consider the integral

$$\int_{-\infty}^{\infty} f(x) \delta(x - x_0) = f(x_0)$$

where $\delta(x - x_0)$ is used to select the single value of the function $f(x)$ for which $x = x_0$. This is the sifting property encountered earlier in our discussion of the Kronecker delta function.

The Dirac delta function is normalized as

$$\int_{-\infty}^{\infty} \delta(x - x_0) = 1$$

and can be defined in terms of the first derivative of the Heaviside step function, $\theta(x - x_0)$, which is 0 for $x < x_0$ and unity for $x \geq x_0$ (see Figure 8.5).

There is a rich variety of ways to represent the Dirac delta function. In problem solving in the physical sciences, one representation of the delta function might lead to an easier solution to a problem than another. One popular representation of the delta function is defined in terms of a normalized gaussian function in the limit that the standard deviation $\sigma$ goes to zero

$$\delta(x - x_0) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

(8.15)

The function is continuous and differentiable with a maximum at $x = x_0$. As $\sigma \to 0$, the function’s height increases as $1/\sigma$ toward infinity while its width decreases as $\sigma$ to zero, preserving the normalization

$$\int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} \, dx = 1$$

for all values of $\sigma$. This gaussian function is shown in Figure 8.19 for values of the parameter $\sigma$ ranging from 0.5 to 0.025.

These observations provide a guide to designing other representations of the Dirac delta function. We need a function that is normalized with a single parameter that controls the width and height of the function such that in some limit the function becomes infinitely tall and infinitesimally wide.
Let’s consider the **lorentzian function**

$$
\delta(x - x_0) = \frac{1}{\pi} \lim_{\sigma \to 0} \frac{\sigma}{(x - x_0)^2 + \sigma^2}
$$

(8.16)

Like the gaussian function, it is continuous and differentiable with a height proportional to $1/\sigma$ and width proportional to $\sigma$ leaving the area normalized for all values of $\sigma$ (see Supplement S5#13). This lorentzian function is shown in Figure 8.20 for values of the parameter $\sigma$ ranging from 1 to 0.05.

![Figure 8.20: Three functional forms used to represent the Dirac delta function.](image)

Less obvious functional representations of the Dirac delta function include the sinusoidal function

$$
\delta(x - x_0) = \frac{1}{\pi} \lim_{\sigma \to 0} \frac{1}{x - x_0} \sin \left( \frac{x - x_0}{\sigma} \right)
$$

(8.17)

This function is normalized since

$$
\int_{-\infty}^{\infty} \frac{1}{x - x_0} \sin \left( \frac{x - x_0}{\sigma} \right) dx = \pi
$$

independent of the parameter $\sigma$ (see the Table of Definite Integrals in Supplement S5). This is surely one of the more remarkable definitions of the mathematical constant $\pi$. The height of the function at $x = x_0$ increases as $1/\sigma$ as $\sigma$ decreases and the width of the function decreases in proportion to $\sigma$. This function is shown in Figure 8.20 for values of the parameter $\sigma$ ranging from 1 to 0.05.

Another definition of the Dirac delta function involves an infinite cosine series

$$
\delta(x - x_0) = \frac{1}{2\pi} + \lim_{N \to \infty} \frac{1}{\pi} \sum_{n=1}^{N} \cos \left( n \left( x - x_0 \right) \right)
$$

(8.18)

Note that this formulation is independent of a parameter $\sigma$ controlling the height and width of the function. The increased height and decreased width are realized through the constructive and destructive interference between terms of the cosine series. This function is shown in Figure 8.20 for values of the parameter $N$ ranging from 1 to 40.

The Dirac delta function is useful in modeling a point charge, point mass, or electron. These examples show a few of the many ways the Dirac delta function can be represented in terms of continuous and differentiable functions of one variable. Many other examples exist and some can be found in Chapter 13 that explores Fourier transforms and harmonic analysis.
E8 End-of-chapter problems

I consider that I understand an equation when I can predict the properties of its solutions, without actually solving it.

Paul Dirac

Warm-ups

8.1 Evaluate the following indefinite integrals. Consider italicized letters other than the integration variable to be constants. Include the integration constant $C$ in your result.

(a) $\int mv\,dv$  
(b) $\int \frac{1}{x^3}\,dx$  
(c) $\int \sin 3x\,dx$

(d) $\int (3x + 5)^2\,dx$  
(e) $\int e^{-\epsilon/k_B}\,d\epsilon$  
(f) $\int \cos(2\pi vt)\,dt$

(g) $\int \frac{RT}{p}\,dp$  
(h) $\int \frac{1}{2}kx^2\,dx$  
(i) $\int \frac{q^2}{4\pi \epsilon_0 r^2}\,dr$

8.2 Evaluate the following integrals, using various methods of integration and the tables of integrals found in Supplements $S_5$ and $S_6$ as needed. Consider italicized letters other than the integration variable to be constants. Include the integration constant $C$ in your result.

(a) $\int \cos(5x)\cos(3x)\,dx$  
(b) $\int x^4 e^{-ax}\,dx$  
(c) $\int \sin^2 \left(\frac{n\pi x}{L}\right)\,dx$

(d) $\int \frac{dx}{(a - x)^n}$  
(e) $\int ye^{-y^2/2a^2}\,dy$  
(f) $\int e^{-\gamma x}\sin x\,dx$

(g) $\int \frac{dx}{4 - x)(3 - x)}$  
(h) $\int \cos^2 \varphi \sin \varphi\,d\varphi$  
(i) $\int x^3 \cos 2x\,dx$

8.3 Evaluate the following definite integrals, using the tables of integrals found in Supplements $S_5$ and $S_6$ as needed. Consider italicized letters other than the integration variable to be constants.

(a) $\int_{-\infty}^{\infty} x^3 e^{-ax^2}\,dx$  
(b) $\int_{-p_1}^{p_2} \frac{RT}{p}\,dp$  
(c) $\int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{n^2 \theta}{V^2}\right)\,dV$

(d) $\int_{0}^{L} x^2 \sin^2 \left(\frac{n\pi x}{L}\right)\,dx$  
(e) $\int_{T_1}^{T_2} \frac{\Delta H}{RT^2}\,dT$  
(f) $\int_{T_1}^{T_2} (a + bT + cT^2 + \frac{d}{T})\,dT$

(g) $\int_{0}^{\infty} e^{-2r/b_0}\,r\,dr$  
(h) $\int_{0}^{\infty} e^{-\beta x^2/2kT}\,q^3\,dv$  
(i) $\int_{0}^{(2J + 1)} e^{-a(|t|^2 + f)}\,dT$

8.4 Evaluate the following multiple integrals, using the tables of integrals found in Supplements $S_5$ and $S_6$ as needed. For indefinite integrals be sure to include an integration constant.

(a) $\int \int y x^2\,dx\,dy$  
(b) $\int \int (x^2 + y^2)\,dx\,dy$

(c) $\int \int y \ln x\,dy\,dx$  
(d) $\int \int x^2 \ln ye^{2x}\,dx\,dy\,dz$

(e) $\int_{0}^{\pi/2} \int_{0}^{\sqrt{2}} r \cos \theta\,dr\,d\theta$  
(f) $\int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{V} r^2 \sin \theta\,dv\,d\theta\,d\varphi$

(g) $\int_{0}^{\infty} \int_{0}^{\infty} \left(x^2 + y^2\right) e^{-\frac{1}{2}(x^2 + y^2)}\,dx\,dy$  
(h) $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\left(m_1^2+m_2^2+m_3^2\right)}\,dx\,dy\,dz$


Homework exercises

8.5 Evaluate the following integral, which commonly appears in quantum mechanics and statistical thermodynamics

\[ I = \int_0^\pi (3 \cos^2 \theta - 1)^2 \sin \theta d\theta \]

8.6 The allowed energies of a quantum mechanical particle in a one-dimensional box of length \( L \) can be written

\[ E_n = -\frac{\hbar^2}{2mL^2} \int_0^L \sin \left( \frac{n\pi x}{L} \right) \left[ \frac{d^2}{dx^2} \sin \left( \frac{n\pi x}{L} \right) \right] dx \]

where \( n = 1, 2, 3, \ldots \) and \( \hbar = h/2\pi \) is the constant \( \hbar \). Complete the integral to show that

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

8.7 Consider the integral

\[ \iiint z^2 \, dx \, dy \, dz \]

taken over the volume of a sphere of radius \( a \). Using spherical polar coordinates where \( z = r \cos \theta \) the integral takes the form

\[ \int_0^a \int_0^{2\pi} \int_0^{\pi/2} (r \cos \theta)^2 r^2 \sin \theta \, d\phi \, d\theta \, dr \]

Evaluate this integral.

8.8 Consider the integral over all space

\[ \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} e^{-2r \cos^2 \theta} r^2 \sin \theta \, d\phi \, d\theta \, dr \]

Evaluate this integral.

8.9 Consider the integral

\[ \iiint xyz \, dx \, dy \, dz \]

taken over the volume defined by \( 0 \leq z < a \) and \( x^2 + y^2 \leq b^2 \) where \( x \geq 0 \) and \( y \geq 0 \). This integral can be expressed in cylindrical coordinates as

\[ \int_0^a \int_0^\sqrt{b^2 - x^2} \int_0^z (r^2 \cos \theta \sin \theta) z \, dr \, d\theta \, dz \]

Evaluate this integral.

8.10 Consider a gas of atoms interacting with a pairwise square well potential energy function dependent on the distance \( r \) between a pair of atoms

\[ V(r) = \begin{cases} \infty & 0 < r \leq \sigma \\ -\varepsilon & \sigma < r \leq \lambda \sigma \\ 0 & r > \lambda \sigma \end{cases} \]

where \( \lambda > 1 \) controls the width of the well of depth \( \varepsilon \). The potential function is shown below (red line) and compared with the smooth Lennard-Jones potential energy function (blue line) examined in Chapter 5 (see Figure 5.12). The compressibility factor of the gas can be written as a Taylor’s series expansion in powers of the number of density \( n/V \) as

\[ Z = \frac{PV}{nRT} = 1 + B(T) \frac{n}{V} + C(T) \left( \frac{n}{V} \right)^2 + \text{higher order terms} \]

This is known as the virial expansion where the coefficients \( B(T) \) and \( C(T) \) are the second and third virial coefficients, respectively.
The second virial coefficient is defined as

\[ B(T) = -\frac{1}{2} \int_0^\infty \int_0^{2\pi} \left[ e^{-\beta V(r)} - 1 \right] r^2 \sin \theta \, d\theta \, d\phi \, dr \]

where \( \beta = 1/k_B T \).

(a) Plot the potential energy \( V(r) \) as a function of \( r \) over the range \( 0 < r < 2\lambda \sigma \) taking \( \lambda = 2 \).

(b) Show that \( B(T) \) can be written

\[ B(T) = -2\pi \int_0^\infty \left[ e^{-\beta V(r)} - 1 \right] r^2 \, dr \]

(c) Evaluate the integral in (b) to show that

\[ B(T) = \frac{2\pi \sigma^3}{3} \left[ 1 - (\lambda^3 - 1)(e^{\delta \epsilon} - 1) \right] \]

(d) Take the limit of your result as \( \lambda \to 1 \) and provide a physical interpretation of that limit.

8.11 Prove that

\[ I_n = \int_0^\infty r^n e^{-\beta r} \, dr = \frac{n!}{\beta^{n+1}} \]

This result is recorded in the Table of Definite Integrals in Supplement S5 #1.

8.12 Starting from the result that

\[ I_0 = \int_0^\infty e^{-ax^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \]

show that

\[ I_{2n} = \int_0^\infty x^{2n} e^{-ax^2} \, dx = \frac{(2n-1)!!}{2^{n+1}a^n} \sqrt{\frac{\pi}{a}} \]

where the double factorial is defined

\[ (2n-1)!! = (2n-1)(2n-3)\ldots3\cdot1 \]

This result is recorded in the Table of Definite Integrals in Supplement S5 #4.

8.13 Starting from the result that

\[ I_1 = \int_0^\infty x e^{-ax^2} \, dx = \frac{1}{2a} \]
show that
\[ I_{2n+1} = \int_0^\infty x^{2n+1} e^{-ax^2} \, dx = \frac{n!}{2a^{n+1}} \]

This result is recorded in the Table of Definite Integrals in Supplement S5 #7.

8.14* The Dirac delta function is defined as
\[ \delta(x - x_0) = \begin{cases} 0 & \text{if } x \neq x_0 \\ \infty & \text{if } x = x_0 \end{cases} \]
such that
\[ \int_{-\infty}^{\infty} \delta(x - x_0) \, dx = 1 \]
and
\[ \int_{-\infty}^{\infty} \delta(x - x_0) f(x) \, dx = f(x_0) \]

Evaluate the following integrals involving the Dirac delta function.

(a) \( I = \int_0^{2\pi} \delta(\theta - \pi) \cos \theta \, d\theta \)
(b) \( I = \int_0^\infty \delta(t - 1) e^{-t} \, dt \)
(c) \( I = \int_0^{2\pi} \delta(r - a) \, r \, dr \, d\theta \)
(d) \( I = \int_{-2L}^{2L} \int_{-2L}^{2L} \delta(x - L) \, dx \, dy \)
(e) \( I = \int_{-2L}^{2L} \int_{-2L}^{2L} \int_{-2L}^{2L} \delta(y + L) \, dx \, dy \, dz \)
(f) \( I = \int_{-\infty}^{\infty} \delta(x - 1)(x^2 - 1)^2 \, dx \)

8.15* In Chapter 1, we considered the transformation of a volume element from one coordinate system to another. For example, using geometric arguments we found the volume element in two-dimensional cartesian coordinates, \( dA = dx \, dy \) in Figure 1.13, is transformed to \( dA = r \, dr \, d\theta \) in two-dimensional plane polar coordinates (see Figure 1.17). This exercise explores a systematic approach for transforming a volume element between coordinate systems that draws on our knowledge of partial derivatives and the determinant.

Suppose we start from the volume element \( dA = dx \, dy \) in two-dimensional cartesian coordinates. That volume element can be transformed to plane polar coordinates using the formula
\[ dx \, dy = |J| \, dr \, d\theta \]
where \(|J|\) is the determinant of the jacobian matrix defined
\[ J = \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{pmatrix} = \begin{pmatrix} \frac{\partial (x, y)}{\partial (r, \theta)} \end{pmatrix} \]
The mapping between \((x, y)\) and \((r, \theta)\) is defined by
\[ x = r \cos \theta \quad y = r \sin \theta \]
so that the determinant of the jacobian matrix is
\[ |J| = \begin{vmatrix} \cos \theta & -r \sin \theta \\ \sin \theta & r \cos \theta \end{vmatrix} = r \cos^2 \theta + r \sin^2 \theta = r \]
resulting in
\[ dx \, dy = |J| \, dr \, d\theta = r \, dr \, d\theta \]
So you see how it works.

(a) Write the jacobian matrix for the transformation from three-dimensional cartesian coordinates \((x, y, z)\) to spherical
polar coordinates \((r, \theta, \varphi)\) defined by

\[
dxdydz = |J| drd\theta d\varphi = \left| \frac{\partial(x, y, z)}{\partial(r, \theta, \varphi)} \right| drd\theta d\varphi
\]

Evaluate the determinant of the jacobian matrix to show that the volume element \(dV = r^2 \sin \theta \, drd\theta d\varphi\).

(b) Write the jacobian matrix for the transformation from three-dimensional cartesian coordinates \((x, y, z)\) to cylindrical coordinates \((r, \theta, z)\) defined by

\[
dxdydz = |J| drd\theta dz = \left| \frac{\partial(x, y, z)}{\partial(r, \theta, z)} \right| drd\theta dz
\]

Evaluate the determinant of the jacobian matrix to show that the volume element \(dV = r \, drd\theta dz\).
9 Fundamentals of probability and statistics

9.1 Probability distributions of discrete variables 171
9.2 Probability distributions of continuous variables 178
9.3 Probability distributions in the physical sciences 187
   A Connecting the gaussian and binomial probability distributions 192
   B Uniform distributions of independent random variables 193
   C Gaussian distributions of independent random variables 195
   D Three definitions of Pythagorean means 196
   E Propagation of error through total differentials and Taylor series 196
   F End-of-chapter problems 199

9.1 Probability distributions of discrete variables

Functions of discrete variables arise in problems in which a number of observations are made of a property of the system consisting of individually separate and distinct states. Matter at the atomic level is discrete. Energy levels in quantum mechanical systems are discrete. Simple models of classical phenomena such as gases, liquids, and solids often assume a discrete set of possible states of the system. This section explores functions of discrete variables commonly used in the physical sciences.

9.1.1 Factorials

Consider the set of numbers \{1, 2, 3, 4\}. The number of ways to order the four numbers is

\[4 \times 3 \times 2 \times 1\]

since there are four possible choices for the first number in the sequence, leaving three choices for the second number, two choices for the third number, and one choice for the fourth number. Introducing the factorial defined

\[n! = n \times (n-1) \times (n-2) \times \ldots \times 1\]

where we pronounce \(n!\) as \(n\) factorial. We say that there are \(4! = 4 \times 3 \times 2 \times 1 = 24\) ways to order the four numbers.\(^1\) The dependence of \(n!\) on \(n\) is displayed in Figure 9.1 on a semi-log plot.

Let’s explore a few examples to appreciate the size of factorials. Suppose we have a peptide consisting of a sequence of 10 unique amino acids. There are \(10! = 3.6 \times 10^6\) possible unique peptide sequences. Consider a deck of 52 playing cards. There are \(52! \approx 8.1 \times 10^{67}\) ways of ordering the deck of cards. To appreciate how large this number is, consider that there may be \(10^{22}\) stars in the observable Universe and \(10^{50}\) atoms composing the Earth. If we shuffled our deck of cards once every four seconds, we would explore a meager \(10^{17}\) shuffles over the age of the Universe. Now consider a crystal consisting of \(N_0 = 6 \times 10^{23}\) indistinguishable atoms. There are \(N_0!\) ways of arranging the atoms in the crystal, a number that seems too large to imagine.

9.1.2 The binomial probability distribution

Consider an event with two possible outcomes, such as the flip of a coin. Further consider the probability of observing an outcome of interest, referred to as a favorable outcome, such as observing two heads in two tosses of a coin.\(^2\)

\[^1\] Note that as \(n! = n \times (n-1)!\) it must be that \(1! = 1 \times 0! = 1\) so that \(0! = 1\).

\[^2\] The probability of an event is a measure of the likelihood of the event happening. Mathematically, the probability of a favorable event is the ratio of the number of favorable outcomes to the total number of possible outcomes. As such, the probability is expressed as a number between 0 and 1, with 0 representing impossibility and 1 representing certainty. The larger the probability of an event, the more likely the event is to occur.
For a fair coin, for each coin flip the probability of observing a head is $\frac{1}{2}$ and the probability of observing a tail is $\frac{1}{2}$.

We assume that the probability of observing a head or tail is independent of whether a head or tail was observed the prior flip. The outcome of the coin toss is treated as an independent random variable. When an independent random variable is sampled (say by observing the flip of a coin), the result of the next observation (a second flip of the coin) is independent of all prior observations.

It follows that if we have two coin flips, the probability of a specific outcome such as a head followed by a tail (written HT) is the joint probability of flipping a head first followed by a tail

$$\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$$

In general, for $N$ coin flips each with one of two possible outcomes the total number of possible outcomes is $2^N$ and the probability of observing any one specific outcome is

$$\frac{1}{2^N}$$

Now suppose that we don’t care about the order of outcomes. We only care how many heads and how many tails occur in $N$ coin flips. Note that for two coin flips there is a total of $2^2 = 4$ possible outcomes

$$HH \quad HT \quad TH \quad TT$$

If we ignore the order, there are three unique outcomes, one with two heads, one with a head and a tail, and one with two tails. There is one way of observing two heads (HH), two ways of observing one head and one tail (HT, TH), and one way of observing two tails (TT). The results are distributed according to a binomial distribution.

The number of ways to order $N$ outcomes is $N!$. For $N = 2$ coin flips there will be $N! = 2! = 2$ ways of ordering any outcome. However, if we flip $n_1 = 2$ heads, there is really only one unique sequence. So we must divide $2!$ by the number of ways of permuting the 2 heads, which is $n_1! = 2! = 2$, times the number of ways of permuting $0$ tails, which is $n_2! = 0! = 1$. We say there is one way

$$\frac{N!}{(n_1!n_2!)} = \frac{2!}{2!0!} = 1$$

of flipping two heads. Similarly, if we flip two tails there are $n_1 = 0$ heads, $n_2 = 2$ tails, and $\frac{N!}{(n_1!n_2!)} = \frac{2!}{0!2!} = 1$ way of flipping two tails. The number of ways to flip one head and one tail is the total number of ways $N!$ divided by the number of ways of permuting one head, $n_1! = 1$, times the number of ways of permuting $0$ tails, $n_2! = 1$, or $\frac{N!}{n_1n_2!} = \frac{2!}{1!1!} = 2$ ways to flip a head and a tail.

If we have three coin flips, there are $2^3 = 8$ possible outcomes

$$HHH \quad HHT \quad HTH \quad HTT \quad THH \quad THT \quad TTH \quad TTT$$

The number of ways of flipping three heads is $\frac{N!}{n_1n_2!} = \frac{3!}{3!1!} = 1$, the number of ways of flipping two heads and one tail is $\frac{N!}{n_1n_2!} = \frac{3!}{2!1!} = 3$, the number of ways of flipping one head and two tails is $\frac{N!}{n_1n_2!} = \frac{3!}{1!2!} = 3$, and the number of ways of flipping three tails is $\frac{N!}{n_2!} = \frac{3!}{3!} = 1$. The resulting distribution is shown in Figure 9.2.

In general, for $N$ coin flips each having two possible outcomes, the number of ways of having a specific outcome with $n_1$ heads and $n_2$ tails is

$$W(n_1, n_2; N) = \frac{N!}{n_1!n_2!} = \frac{N!}{n_1!(N-n_1)!} \quad (9.1)$$

Figure 9.2: The binomial distribution for the relative probability of the four possible outcomes of $N = 3$ flips of a coin. Here we assume the order of events does not matter. As such, TTH, THT, and HTT are identical outcomes as each has $n = 1$ head and 2 tails. The same holds for THH, THT, and HHT, which are three identical outcomes each having $n = 2$ heads and 1 tail.

3 A random process is a series of actions having no defined method and leading to no discernable pattern of outcomes.
where we recognize that \( N = n_1 + n_2 \). The factor \( W(n_1, n_2; N) \) is known as the binomial coefficient.

We can now consider the probability of observing a given outcome of interest in a series of coin flips. Recall that for \( N \) coin flips there are \( 2^N \) possible outcomes with each individual outcome occurring with a probability of \( \frac{1}{2^N} \). As such, the probability of having \( N \) coin flips with \( n_1 \) heads and \( n_2 = N - n_1 \) tails is the probability \( \frac{1}{2^N} \) times the number of outcomes having \( n_1 \) heads and \( n_2 \) tails of flipping \( n_1 \) heads and \( n_2 \) tails or

\[
p(n_1, n_2; N) = \frac{1}{2^N} \cdot W(n_1, n_2; N) = \frac{1}{2^N} \cdot \frac{N!}{n_1!(N - n_1)!} \quad (9.2)
\]

In the final form of the equation we have set \( n = n_1 \). This result is known as the binomial probability distribution.\(^4\)

The resulting distribution of probabilities for the case \( N = 6 \) is shown in Figure 9.3. Note that the mean value of the distribution is \( \frac{N}{2} = 3 \). Further note that in comparison to the distribution for \( N = 3 \) (see Figure 9.2) the distribution for \( N = 6 \) is somewhat more sharply peaked.

Let’s evaluate the probabilities defined by Equation 9.2 for a few specific cases. For \( N = 2 \) events, the probabilities for the three possible outcomes (HH), (HT or TH), and (TT) are

\[
\begin{align*}
&1 \quad 2 \quad 1 \\
&\frac{1}{4} \quad \frac{1}{2} \quad \frac{1}{4}
\end{align*}
\]

Each probability is equal to \( \frac{1}{3} \) times the binomial coefficient, 1, 2 or 1, expressing the number of ways of observing a given outcome (HH), (HT or TH), or (TT). The binomial coefficients form a series 1, 2, 1.

For \( N = 3 \) events, the probabilities for the four possible outcomes (HHH), (HHT or HTH or THH), (THT or THT or HTT), and (TTT) are

\[
\begin{align*}
&1 \quad 3 \quad 3 \quad 1 \\
&\frac{1}{8} \quad \frac{3}{8} \quad \frac{3}{8} \quad \frac{1}{8}
\end{align*}
\]

where the binomial coefficients form a series 1, 3, 3, 1. For \( N = 4 \) events, the probabilities for the five possible outcomes are

\[
\begin{align*}
&1 \quad 4 \quad 6 \quad 4 \quad 1 \\
&\frac{1}{16} \quad \frac{1}{16} \quad \frac{1}{16} \quad \frac{1}{16} \quad \frac{1}{16}
\end{align*}
\]

where the binomial coefficients form a series 1, 4, 6, 4, 1. And so on.

The pattern of binomial coefficients can be captured graphically in the form of Pascal’s triangle shown in Figure 9.4.\(^5\) The pattern starts with 1 at the top. We then form the next line by summing the number above to the left and the number above to the right. Almost magically, each row in Pascal’s triangle forms a series of numbers equal to the binomial coefficients for a value of \( N \).

### 9.1.3 Applications of the binomial probability distribution

Let’s use the binomial distribution to analyze the outcome of a coin flipped six times resulting in four heads and two tails. The number of ways to flip a coin \( N = 6 \) times with a total of \( n_1 = 2 \) heads and \( n_2 = 4 \) tails is

\[
W(2, 4; 6) = \frac{6!}{2!4!} = 15
\]

The total number of possible outcomes for \( N = 6 \) coin flips is \( 2^6 = 64 \). The probability of flipping the coin \( N = 6 \) times with a total of \( n_1 = 2 \) heads and \( n_2 = 4 \) tails is

\[
p(2, 4; 6) = \frac{1}{2^6} W(2, 4; 6) = \frac{15}{64} \approx 0.234
\]

---

\(^4\) The binomial theorem was first mentioned by Greek mathematician Euclid (circa 300 BCE).

\(^5\) Named for French mathematician, physicist, and inventor Blaise Pascal (1623-1662). A child prodigy, as a teenager he carried out fundamental work on the properties of computing machines and the properties of fluids. He is known beyond the sciences for proposing Pascal’s wager.
The computed probability at \( n = 2 \) is \( p(n = 2) \approx 0.234 \) as shown in Figure 9.3.\(^6\)

Now suppose we have \( N = 10 \) electrons, each with the property of spin that can take on one of two states said to be up or down. If each spin is distinguishable, there are \( 2^N = 2^{10} = 1024 \) possible ways of ordering the spins. Now suppose the spins are indistinguishable. If nine spins are up and one spin is down, the one down spin could be any of the ten spins. In that case the total number of ways of ordering \( n_1 = 9 \) up spins and \( n_2 = 1 \) down spin is \( \frac{N!}{n_1!n_2!} = \frac{10!}{9!1!} = 10 \). It follows that the total probability of observing nine up spins and one down spin is \( p(9, 1; 10) = \frac{10}{1024} = 0.00976 \) or just less than 1%.\(^7\)

### 9.1.4 The multinomial probability distribution

Suppose we randomly draw a number from a set \{1, 2, 3, 4\}. There are \( k = 4 \) numbers in the set and the probability of drawing any one number is \( \frac{1}{4} \), which is 1 specific outcome divided by 4 possible outcomes. If we return to the full set \{1, 2, 3, 4\} and again draw a number at random, the probability of drawing any one number is again \( \frac{1}{4} \). For the two draws, there are \( 4^2 \) possible outcomes so the probability of observing 1 specific outcome will be \( \frac{1}{4^2} = \frac{1}{16} \approx 6.2\% \).

If we return to the full set \{1, 2, 3, 4\} a third time, the probability of drawing any one number is \( \frac{1}{4} \). It follows that the probability of drawing any particular sequence of three numbers such as 2, 3, 4 or 1, 4, 2 or 3, 1, 1 will be \( \frac{1}{4^3} = \frac{1}{64} \approx 1.5\% \).

In general, the probability of observing a particular sequence of \( N \) draws each with \( k \) possible outcomes is

\[
\frac{1}{k^N}
\]

Now let’s ask what the probability of drawing a sequence of \( N \) numbers will be if we ignore the order in which the numbers are drawn. For example, for \( N = 3 \) draws of \( k = 4 \) numbers from the set \{1, 2, 3, 4\} the outcomes 2, 3, 4 and 1, 3, 4 are unique but 2, 3, 4 and 3, 2, 4 are taken to be the same. The probability of drawing a unique sequence of numbers will be the probability of drawing that sequence times the multiplicity of ways that the sequence can be drawn.

For example, there is one way a sequence with 3 twos can be drawn (2, 2, 2), but there are three ways a sequence with 1 one and 2 twos can be drawn

\[1, 2, 2 \quad 2, 1, 2 \quad 2, 2, 1\]

For a sequence in which each number is different such as 3, 2, 4 there are six
unique ways the numbers can be ordered

\[
3, 2, 4 \quad 3, 4, 2 \quad 2, 3, 4 \quad 2, 4, 3 \quad 4, 3, 2 \quad 4, 2, 3
\]

Let’s generalize these observations. For a sequence of \( N \) draws from a set \{1, 2, 3, 4\} having \( n_1 \) ones, \( n_2 \) twos, \( n_3 \) threes, and \( n_4 \) fours there will be

\[
n_1!n_2!n_3!n_4!
\]

ways of ordering the sequence where \( n_1 + n_2 + n_3 + n_4 = N \). It follows that the number of unique sequences that can be drawn, having \( n_1 \) ones, \( n_2 \) twos, \( n_3 \) threes, and \( n_4 \) fours, is the total number of possible sequences, \( N! \), divided by the number of non-unique ways of ordering the sequence, \( n_1!n_2!n_3!n_4! \), or

\[
\frac{N!}{n_1!n_2!n_3!n_4!}
\]

In general, for \( N \) draws from \( k \) distinguishable outcomes with \( n_j \) draws of the \( j \)th specific outcome, the number of ways a unique sequence can be drawn is

\[
W(n_1, n_2, n_3, \ldots, n_k; N) = \frac{N!}{n_1!n_2!n_3!\ldots n_k!} \quad (9.3)
\]

where \( N = n_1 + n_2 + n_3 + \ldots + n_k \). The function \( W(n_1, n_2, n_3, \ldots, n_k; N) \) is known as the multinomial coefficient.

The probability of observing \( N \) draws leading to an outcome defined by \( n_1, n_2, n_3, \ldots, n_k \) will be the probability \( \frac{1}{k^N} \) of a draw times the multiplicity of ways the sequence can be drawn \( W(n_1, n_2, n_3, \ldots, n_k; N) \) or

\[
p(n_1, n_2, n_3, \ldots, n_k; N) = \frac{1}{k^N} W(n_1, n_2, n_3, \ldots, n_k; N)
\]

### 9.1.5 Applications of the multinomial probability distribution

The multinomial coefficient can be used to determine the number of ways one can roll a six-sided die \( N \) times with the outcome \( n_1 \) ones, \( n_2 \) twos, \( n_3 \) threes, \( n_4 \) fours, \( n_5 \) fives, and \( n_6 \) sixes. For example, the number of ways to roll the die \( N = 5 \) times resulting in \( n_1 = 2 \) ones and \( n_6 = 3 \) sixes is

\[
W(2, 0, 0, 0, 3; 5) = \frac{5!}{2!0!0!0!3!} = 10
\]

The total number of possible outcomes rolling the die \( N = 5 \) times is \( k^N = 6^5 = 7,776 \). Therefore, the probability of rolling the die \( N = 5 \) times and having \( n_1 = 2 \) ones and \( n_6 = 3 \) sixes is

\[
p(2, 0, 0, 0, 3; 5) = \frac{1}{6^5} W(2, 0, 0, 0, 3; 5)
\]

\[
= \frac{10}{7,776} \approx 1.28 \times 10^{-3}
\]

For another example, consider \( k = 6 \) different levels of varying energy, \( \varepsilon \), that can be occupied by \( N = 24 \) indistinguishable particles. The total number of ways the particles can be arranged over the six energy levels is given by the multinomial coefficient

\[
W(n_1, n_2, n_3, \ldots, n_6; N) = \frac{N!}{n_1!n_2!n_3!\ldots n_6!}
\]

where \( n_j \) is the number of particles occupying the \( j \)th energy level. Consider the distribution shown in Figure 9.5. For this case, \( n_1 = 10, n_2 = 7, n_3 = 4, n_4 = 2, n_5 = 1, n_6 = 0 \). There are \( 6 \times 5 = 30 \) different pairs that can be formed from the numbers \{1, 2, 3, 4, 5, 6\}. As such, the probability of rolling a full house of 2 of one kind and 3 of another in five rolls is \( 30 \times \left(\frac{1.28 \times 10^{-3}}{6^5}\right) = 3.85\% \).

Figure 9.5: An arrangement of \( N = 24 \) particles (red balls) occupying \( k = 6 \) energy levels of varying energy \( \varepsilon \). \( n(\varepsilon) \) represents the number of particles occupying a level of energy \( \varepsilon \).
\( n_5 = 1 \), and \( n_6 = 0 \). The number of ways the \( N \) indistinguishable particles can be arranged is

\[
W(10, 7, 4, 2, 1, 0; 24) = \frac{24!}{10!7!4!2!1!0!} \approx 7.0 \times 10^{11} \quad (9.4)
\]

### 9.1.6 Moments of the binomial and multinomial distributions

Suppose there is a measurement on an observed property of a system. There are \( n \) possible outcomes sampled over \( N \) trials. The probability of observing a specific outcome is

\[
p_k = \frac{N_k}{N} \quad k = 1, 2, \ldots, n
\]

where \( N_k \) is the number of times that the \( k \)th possible outcome is observed in \( N \) trials. We know that the total number of observations must equal the number of trials

\[
\sum_{k=1}^{n} N_k = N
\]

so that

\[
\sum_{k=1}^{n} p_k = \sum_{k=1}^{n} \left( \frac{N_k}{N} \right) = \frac{1}{N} \sum_{k=1}^{n} N_k = \frac{1}{N} N = 1
\]

Now suppose there is a property \( x \) that has a specific value \( x_k \) for each of the \( n \) possible outcomes. We can write the average or the mean value of \( x \) as the probability of a specific outcome \( p_k \) times the measured value of \( x \) for that outcome \( x_k \) summed over all possible outcomes. This can be written

\[
\bar{x} = \sum_{k=1}^{n} x_k p_k
\]

where \( \bar{x} \) is the mean value of \( x \).

We can also define the average of the square of the observable \( x \) known as the mean square value of \( x \) and written

\[
\bar{x}^2 = \sum_{k=1}^{n} (x_k)^2 p_k
\]

Now consider the mean square deviation of \( x \) from its average value \( \bar{x} \)

\[
(x - \bar{x})^2 = \sum_{k=1}^{n} (x_k - \bar{x})^2 p_k
\]

This is known as the variance and often written

\[
\sigma_x^2 \equiv (x - \bar{x})^2
\]

The variance provides a measure of the size of fluctuations in observations of \( x \) around its mean value \( \bar{x} \).

If we expand the square we find

\[
(x - \bar{x})^2 = \sum_{k=1}^{n} \left( (x_k)^2 - 2\bar{x} x_k + \bar{x}^2 \right) p_k
\]

\[
= \sum_{k=1}^{n} (x_k)^2 p_k - 2\bar{x} \sum_{k=1}^{n} x_k p_k + \bar{x}^2 \sum_{k=1}^{n} p_k
\]

\[
= \bar{x}^2 - 2\bar{x}^2 + \bar{x}^2 = \bar{x}^2 - \bar{x}^2 \geq 0
\]

relating the mean-square difference to the averages \( \bar{x}^2 \) and \( \bar{x} \). The resulting
identity for the variance is
\[ \sigma_x^2 = \frac{(x - \bar{x})^2}{n} = \frac{x^2 - \bar{x}^2}{n} \] (9.5)

This is a fundamental result that we will return to in many contexts in the physical sciences, including quantum theory and thermodynamics.

An interesting quantity is the square root of the variance, \( \sigma_x \), known as the **standard deviation**. The ratio of the standard deviation to the mean value of the distribution
\[ \frac{\sigma_x}{n} = \frac{\sqrt{(x - \bar{x})^2}}{n} \]
provides a useful measure of the size of the fluctuations about the mean value relative to the mean value itself.

Consider the binomial probability distribution. There are two outcomes each assumed to have probability \( \frac{1}{2} \) so that
\[ p(n; N) = \frac{1}{2N} \frac{N!}{n!(N-n)!} \]
where
\[ \sum_{n=0}^{N} p(n; N) = \frac{1}{2N} \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = \frac{1}{2N}2^N = 1 \] (9.6)
The mean value of \( n \) for the binomial distribution is
\[ \bar{n} = \sum_{n=0}^{N} n p(n; N) = \frac{1}{2N} \sum_{n=0}^{N} n \frac{N!}{n!(N-n)!} \]
\[ = \frac{1}{2N} \sum_{n=1}^{N} n \frac{N!}{n!(N-n)!} \] (9.7)
where we note that the \( n = 0 \) term in the sum is zero. Rewriting the coefficient
\[ \frac{n}{n!(N-n)!} = \frac{N!}{(n-1)!(N-n)!} \]
\[ = \frac{(N-1)!}{(n-1)!(N-1-(n-1))!} \]
and substituting \( r = n - 1 \) we find
\[ \bar{n} = \sum_{n=0}^{N} n p(n; N) = \frac{1}{2N} \sum_{r=0}^{N-1} N \frac{(N-1)!}{r!(N-1-r)!} \] (9.8)
In a final step, we note that the sum appearing in Equation 9.6 can alternatively be written in terms of the index \( r \) with the sum extending from \( r = 0 \) to \( r = N - 1 \) as
\[ \sum_{r=0}^{N-1} \frac{(N-1)!}{r!(N-1-r)!} = 2^{N-1} \]
Substituting this relation in Equation 9.8, we arrive at our final result
\[ \bar{n} = \frac{N}{2N} \sum_{r=0}^{N-1} \frac{(N-1)!}{r!(N-1-r)!} = \frac{N}{2N}2^{N-1} = \frac{N}{2} \] (9.9)
This result makes sense. The binomial distribution is a symmetric function with a single peak and the average \( \bar{n} \) is the maximum value and midpoint \( N/2 \).
With additional effort we can also prove that the mean square value of \( n \) is

\[
\overline{n^2} = \sum_{n=0}^{N} n^2 p(n; N) = \frac{1}{2} \sum_{n=0}^{N} n^2 \frac{N!}{n!(N-n)!} = \frac{N^2}{4} + \frac{N}{4}
\]

so that the variance is

\[
\sigma_n^2 = \overline{(n - \overline{n})^2} = \left( \frac{N^2}{4} + \frac{N}{4} \right) - \left( \frac{N}{2} \right)^2 = \frac{N}{4} \tag{9.10}
\]

As a result, the standard deviation is

\[
\sigma_n = \frac{1}{2} \sqrt{N}
\]

and the ratio of the standard deviation to the mean is\(^\text{10}\)

\[
\frac{\sigma_n}{\overline{n}} = \frac{\sqrt{N}}{\overline{n}} = \frac{1}{\sqrt{N}}
\]

The mean and standard deviation are depicted for a binomial distribution with \( N = 10 \) in Figure 9.6.

This final result states that as the number of observations \( N \) increases, the magnitude of fluctuations in the average value of \( n \) from the mean value \( \overline{n} \) will decrease as \( N^{-1/2} \). This is a fundamental property of the binomial probability distribution that has important implications in the kinetic theory of matter.

Finally, consider the multinomial distribution in which there are \( k \) possible outcomes each with probability \( p_k \). When there are \( N \) observations the average value of the \( k \)th outcome is \( n_k = Np_k \). The variance, defined as the mean square fluctuation in the \( k \)th outcome relative to the average, is \( \sigma_k^2 = Np_k(1 - p_k) \).

Let’s consider the binomial distribution as a special case of the multinomial distribution. We take the probability of one outcome to be \( p_1 = p \) and that of the second outcome to be \( p_2 = 1 - p = q \). In that case, the mean value of observing the first outcome is \( Np_1 = Np \) and the associated variance is \( \sigma_1^2 = Np_1(1 - p_1) = Np(1 - p) = Npq \). These results agree with our prior results in Equation 9.9 and Equation 9.10 for the binomial distribution assuming equal probabilities \( p_1 = p_2 = \frac{1}{2} \) where the mean was shown to be \( \frac{N}{2} \) with a variance of \( \frac{N}{4} \).

9.2 Probability distributions of continuous variables

Functions of continuous variables arise in problems in which a number of observations are made of a property of the system consisting of a continuity of states. The position of atoms in space is defined in terms of continuous variables. The kinetic energy of atoms modeled as classical particles is taken to be continuous. The variables defining the pressure and temperature of a system are taken to be continuous. This section introduces probability distributions for continuous variables and explores a few functions of continuous variables commonly encountered in the physical sciences.

9.2.1 Properties of probability distributions of a continuous variable

For discrete variables such as a number of coin flips, the probability of a favorable event is the ratio of the number of favorable outcomes to the total number of possible outcomes. A sum over all possible outcomes must equal unity, the probability of any event happening. For a continuous variable such as the position, we need to generalize our concept of probability. The probability of observing a discrete state, \( p_k \), is replaced by the probability of finding the variable within a range of values, \( x \in [x, x + dx] \), as\(^\text{11}\)
\[ p_k \rightarrow p(x)dx \]

where \( p(x) \) is a probability distribution function. The sum over the probabilities of all discrete states is replaced by an integral

\[ \sum_k p_k \rightarrow \int p(x)dx \]

Let’s see how this works for the specific case of the uniform probability distribution.

Consider a random variable \( x \). There is a constant probability \( C \) of observing a value of \( x \) between \( x = a \) and \( x = b \) and zero probability of observing \( x \) outside of that region. We define the corresponding uniform probability distribution function

\[ p(x) = \begin{cases} 
0 & x < a \\
\frac{1}{b-a} & x \in [a,b] \\
0 & x > b 
\end{cases} \]

The probability of selecting a value of \( x \) in the region \([x, x+dx]\) at random is

\[ \text{probability of finding } x \in [x, x+dx] = p(x) \, dx \]

where \( dx \) represents a small increment of \( x \).\(^{12}\) The probability of randomly choosing a value of \( x \) somewhere between \( x = a \) and \( x = b \) must be unity. To reflect this, we say that the probability distribution is a normalized distribution meaning that

\[ \text{probability of finding } x \in [a,b] = \int_a^b p(x) \, dx = 1 \]

This constraint allows us to determine the value of the constant \( C \) as

\[ \int_a^b p(x) \, dx = \int_a^b C \, dx = C \int_a^b dx = C(b-a) = 1 \]

so that \( C = 1/(b-a) \). We call \( C \) the normalization constant. The resulting normalized uniform probability distribution function is

\[ p(x) = \begin{cases} 
0 & x < a \\
\frac{1}{b-a} & x \in [a,b] \\
0 & x > b 
\end{cases} \]

This function is depicted in Figure 9.7.\(^{12}\)

The general definition of the mean value or average of \( x \) is

\[ \bar{x} = \int_a^b xp(x) \, dx \]

which we evaluate for the uniform distribution as

\[ \bar{x} = \frac{1}{(b-a)} \int_a^b x \, dx = \frac{1}{(b-a)} \left[ \frac{1}{2}x^2 \right]_a^b = \frac{1}{2} \frac{1}{(b-a)} (b^2 - a^2) = \frac{1}{2} (b + a) \]

which we can reform as

\[ \bar{x} = a + \frac{1}{2} (b - a) \]

This is a very intuitive result. The average value of \( x \) is the midpoint of the
range \([a, b]\). For example, for the specific values \(a = 0\) and \(b = 1\) the mean
\(\bar{x} = 1/2\).

The average value of \(x^2\) is defined
\[
\bar{x^2} = \int_a^b x^2 p(x) \, dx
\]
which we evaluate for the uniform distribution as
\[
\bar{x^2} = \frac{1}{(b-a)} \int_a^b x^2 \, dx = \frac{1}{(b-a)} \left[ \frac{1}{3} x^3 \right]_a^b = \frac{1}{3} (b^3 - a^3)
\]
\[
= \frac{1}{3} (b^2 + ab + a^2)
\]
For the specific values \(a = 0\) and \(b = 1\) we find \(\bar{x^2} = 1/3\).

With this result we can evaluate the variance of \(x\) as
\[
\sigma^2_x = (\bar{x} - \bar{x})^2 = \bar{x^2} - \bar{x}^2 = \frac{1}{3} (b^2 + ab + a^2) - \left( \frac{1}{2} (b + a) \right)^2
\]
\[
= \frac{1}{12} (b - a)^2
\]
For the specific values \(a = 0\) and \(b = 1\) we find \(\sigma^2_x = 1/12\). Finally, the
ratio of the root-mean square value of \((x - \bar{x})\) and the mean \(\bar{x}\) is
\[
\frac{\sigma_x}{\bar{x}} = \frac{\sqrt{\bar{x^2} - \bar{x}^2}}{\bar{x}} = \frac{1}{\sqrt{3}} \left( \frac{b - a}{b + a} \right)
\]
For the specific values \(a = 0\) and \(b = 1\) we find the ratio \(1/\sqrt{3}\).

### 9.2.2 Properties of exponential probability distributions

Many measured observables in the physical sciences are well described by
an exponential probability distribution function. Consider the exponential
distribution function \(p(x)\) characterized by a maximum value at \(x = 0\) and an
exponential decrease with increasing \(x\)
\[
p(x) = C \, \exp \left( -\gamma x \right)
\]
where \(\gamma > 0\). The probability distribution function is normalized
\[
\int_0^\infty p(x) \, dx = 1
\]
which means that
\[
C \int_0^\infty \exp \left( -\gamma x \right) \, dx = C \left[ -\frac{1}{\gamma} e^{-\gamma x} \right]_0^\infty = \frac{1}{\gamma} C = 1
\]
so that the normalization constant \(C = \gamma\). With this result we find the normal-
ized exponential probability distribution function
\[
p(x) \, dx = \gamma \, \exp \left( -\gamma x \right) \, dx
\]
which is shown in Figure 9.8. Note that the probability of randomly selecting a
value of \(x\) between \(x = a\) and \(x = b\) is
\[
\text{probability of finding } x \in [a, b] = \int_a^b p(x) \, dx
\]
depicted as the shaded area in Figure 9.8.
The general definition of the mean value or average of $x$ is
\[ \bar{x} = \int_{0}^{\infty} x p(x) \, dx \]
and for the exponential probability distribution
\[ \bar{x} = \gamma \int_{0}^{\infty} x \exp(-\gamma x) \, dx \]
We can evaluate this integral using integration by parts or our trick exploiting differentiation with respect to the constant $\gamma$. In either case we find
\[ \bar{x} = \gamma \int_{0}^{\infty} x \exp(-\gamma x) \, dx = \gamma \frac{1}{\gamma^2} = \frac{1}{\gamma} \]
The average value of $x^2$ is defined
\[ \bar{x^2} = \int_{0}^{\infty} x^2 p(x) \, dx \]
and for the exponential probability distribution function
\[ \bar{x^2} = \gamma \int_{0}^{\infty} x^2 \exp(-\gamma x) \, dx \]
We can evaluate this integral using integration by parts or our trick exploiting differentiation with respect to the constant $\gamma$ leading to
\[ \bar{x^2} = \gamma \int_{0}^{\infty} x^2 \exp(-\gamma x) \, dx = \gamma \frac{2}{\gamma^3} = \frac{2}{\gamma^2} \]
With this result we can evaluate the variance
\[ \sigma_x^2 = (\bar{x} - \bar{x^2})^2 = \bar{x^2} - \bar{x}^2 = \frac{2}{\gamma^2} - \left( \frac{1}{\gamma} \right)^2 = \frac{1}{\gamma^2} \]
The ratio of the root-mean square value of $x$ and the mean of $x$ is
\[ \frac{\sigma_x}{\bar{x}} = \frac{\sqrt{\bar{x^2} - \bar{x}^2}}{\bar{x}} = \sqrt{\frac{1}{\gamma^2}} = 1 \]
The exponential probability distribution has the special property that the root-mean square width of the distribution is equal to the mean.

### 9.2.3 Applications of the exponential probability distribution

Consider the case of a sample of $N_0$ radioactive atomic nuclei. Observations of the system demonstrate that the rate of radioactive decay of the nuclei varies with time as $\frac{dN}{dt} = \frac{N_0}{\tau} \exp(-t/\tau)$,
\[ N(t) \, dt = \frac{N_0}{\tau} \exp(-t/\tau) \, dt \]
where $N(t = 0) = N_0/\tau$ is the initial rate of decay at $t = 0$ and $N(t)\,dt$ is the number of nuclei that decay between times $t$ and $t + dt$. Over all time, the number of nuclei that will decay is
\[ \int_{0}^{\infty} N(t) \, dt = \frac{N_0}{\tau} \int_{0}^{\infty} \exp(-t/\tau) \, dt = N_0 \]
the total number of nuclei in the sample. The form of $N(t)$ is shown in Figure 9.9.

Suppose we would like to know how many nuclei decay between a time $t_d$.
and $t_b$. We can calculate this as
\[ \int_{t_a}^{t_b} N(t) \, dt = \frac{N_0}{\tau} \int_{t_a}^{t_b} \exp(-t/\tau) \, dt = N_0 \left[ e^{-t_a/\tau} - e^{-t_b/\tau} \right] \]
If we set $t_a = 0$ and $t_b = t$ we find
\[
\text{number of nuclei decayed} = N_0 \left[ 1 - e^{-t/\tau} \right]
\]
It follows that the survival probability, which is the probability that a nucleus has not decayed after time $t$, is
\[
\text{survival probability} = \frac{N_0 - N(t)}{N_0} = e^{-t/\tau}
\]
For example, after a time $t = \ln(2) \tau = 0.693 \tau$ the survival probability is $1/2$. We call this time $\tau_{1/2} = \ln(2) \tau$ the half-life of the exponential distribution. After a time $\tau_{1/2}$ one-half of the nuclei have decayed and one-half have survived.

Let’s consider another application involving an exponential distribution of energy\[ p(E) = C \exp(-E/k_B T) \]
To normalize this probability distribution we demand that
\[ \int_{-\infty}^{\infty} p(E) \, dE = C \int_{-\infty}^{\infty} \exp(-E/k_B T) \, dE = Ck_B T = 1 \]
so that $C = 1/k_B T$ and
\[ p(E) \, dE = \frac{1}{k_B T} \exp(-E/k_B T) \, dE \]
What is probability of having energy less than or equal to the thermal energy $k_B T$? We can evaluate this as
\[ \frac{1}{k_B T} \int_{0}^{k_B T} \exp(-E/k_B T) \, dE = \frac{1}{k_B T} k_B T \left[ \exp(-E/k_B T) \right]_0^{k_B T} = 1 - \frac{1}{e} = 0.632 \]
We can further ask for the fraction having energy less than $2k_B T$, which is
\[ \frac{1}{k_B T} \int_{0}^{2k_B T} \exp(-E/k_B T) \, dE = 1 - \frac{1}{e^2} = 0.865 \]
or less than $3k_B T$, which is $1 - \frac{1}{e^3} = 0.950$. This result is shown graphically in Figure 9.10.

\[ Figure 9.10: \text{The exponential probability distribution function } p(E) = \frac{1}{k_B T} \exp(-E/k_B T) \text{ as a function of energy } E. \text{ The shaded areas represent the fraction of atoms having energy } E \text{ less than } k_B T, 2k_B T, \text{ or } 3k_B T. \]

\[ 9.2.4 \text{ Properties of gaussian probability distributions} \]
In the physical sciences, we commonly employ the gaussian function to represent a probability distribution function that is centered at $x = x_0$ with mean square width $\sigma^2$
\[ p(x) = C \exp \left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \]
where the distribution function is normalized as
\[ \int_{-\infty}^{\infty} p(x) \, dx = 1 \]
Imposing the normalization condition we find
\[ \int_{-\infty}^{\infty} p(x) \, dx = C \int_{-\infty}^{\infty} \exp\left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \, dx = 1 \]

With the algebraic substitution \( y = (x - x_0) \) so that \( dy = dx \) we find
\[ C \int_{-\infty}^{\infty} \exp\left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \, dx = C \int_{-\infty}^{\infty} \exp\left[ -\frac{y^2}{2\sigma^2} \right] \, dy \]

Using the identity
\[ \int_{-\infty}^{\infty} e^{-\alpha y^2} \, dy = \sqrt{\frac{\pi}{\alpha}} \]
we find
\[ C \int_{-\infty}^{\infty} \exp\left[ -\frac{y^2}{2\sigma^2} \right] \, dy = C \sqrt{2\pi\sigma^2} = 1 \]

so that the normalization constant \( C = 1/\sqrt{2\pi\sigma^2} \). The resulting normalized gaussian probability distribution function
\[ p(x) \, dx = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \, dx \]
is shown in Figure 9.11.

Note that the probability of randomly selecting a value of \( x \) between \( x_0 - \sigma \) and \( x_0 + \sigma \) is
\[ \text{probability of finding } x \in [x_0 - \sigma, x_0 + \sigma] = \int_{x_0-\sigma}^{x_0+\sigma} p(x) \, dx \approx 0.6827 \]
depicted as the shaded area in Figure 9.11. The probability of randomly selecting a value of \( x \) within two standard deviations of the mean \( x \in [x_0 - 2\sigma, x_0 + 2\sigma] \) is roughly 0.9545, and within three standard deviations of the mean \( x \in [x_0 - 3\sigma, x_0 + 3\sigma] \) is approximately 0.9973. This is the origin of the 68-95-99.7 rule.

The mean of \( x \) is defined
\[ \bar{x} = \int_{-\infty}^{\infty} x p(x) \, dx \]
and for the gaussian distribution centered at \( x = x_0 \) with variance \( \sigma^2 \)
\[ \bar{x} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x \exp\left[ -\frac{(x - x_0)^2}{2\sigma^2} \right] \, dx \]

With the algebraic substitution \( y = (x - x_0) \) so that \( x = y + x_0 \) and \( dy = dx \) we find
\[ \bar{x} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} (y + x_0) \exp\left[ -\frac{y^2}{2\sigma^2} \right] \, dy \]
\[ = \frac{1}{\sqrt{2\pi\sigma^2}} \left[ \int_{-\infty}^{\infty} y \exp\left[ -\frac{y^2}{2\sigma^2} \right] \, dy + x_0 \int_{-\infty}^{\infty} \exp\left[ -\frac{y^2}{2\sigma^2} \right] \, dy \right] \]
\[ = x_0 \]
where the first integral is zero
\[ \int_{-\infty}^{\infty} y \exp(-ay^2) \, dy = 0 \]
as the integrand is an odd function of \( y \), being the product of a gaussian function centered at the origin, that is an even function of \( y \), and the linear function \( y \), that is an odd function of \( y \).
The average value of $x^2$ is defined

$$\bar{x^2} = \int_{-\infty}^{\infty} x^2 p(x) \, dx$$

and for the gaussian distribution centered at $x = x_0$ with variance $\sigma^2$

$$\bar{x^2} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x^2 \exp\left[-\frac{(x - x_0)^2}{2\sigma^2}\right] \, dx$$

With the algebraic substitution $y = (x - x_0)$ so that $x^2 = y^2 + 2yx_0 + x_0^2$ and $dy = dx$ we find

$$\bar{x^2} = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} (y^2 + 2yx_0 + x_0^2) \exp\left[-\frac{y^2}{2\sigma^2}\right] \, dy$$

The first integral is

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} y^2 \exp\left[-\frac{y^2}{2\sigma^2}\right] \, dy = \sigma^2$$

The second integral is zero by symmetry since the integrand is an odd function of $y$. The third integral is equal to $x_0^2$. This leads to the final result

$$\bar{x^2} = x_0^2 + \sigma^2$$

Using this result we can determine the average of the square of the deviation in $x$ from the mean value $\bar{x} = x_0$ as

$$\frac{(x - x_0)^2}{\int_{-\infty}^{\infty} (x - x_0)^2 p(x) \, dx} = \bar{x^2} - 2x_0\bar{x} + x_0^2$$

This demonstrates that $\sigma^2$ is the variance of the gaussian distribution.

### 9.2.5 Applications of the gaussian probability distribution

Consider the kinetic energy of an ideal gas of atoms. In one-dimension the kinetic energy of an atom is

$$E = \frac{1}{2}mv^2$$

where $m$ is the mass of the atom and $v$ is the velocity. The distribution of kinetic energy is given by the Boltzmann exponential probability distribution

$$p(E) \, dE = \frac{1}{k_BT} \exp\left(-\frac{E}{k_BT}\right) \, dE$$

Since the energy varies as the square of the velocity the distribution of velocities is a gaussian probability distribution function

$$p(v) \, dv = \sqrt{\frac{m}{2\pi k_BT}} \exp\left(-\frac{mv^2}{2k_BT}\right) \, dv$$

shown graphically in Figure 9.12. The mean velocity is $\bar{v} = 0$ and the variance in the distribution of velocities is

$$\sigma^2 = \frac{k_BT}{m}$$

Suppose we want to know the fraction of atoms with kinetic energy less than or equal to $\frac{k_BT}{2}$ so that

$$\frac{1}{2}mv^2 \leq \frac{k_BT}{2}$$

Figure 9.12: The function $p(v)$ as a function of $v$ where $\sigma_v = \sqrt{\frac{k_BT}{m}}$. The integral over $v$ between $-\sigma_v$ and $\sigma_v$, representing the fraction of atoms with kinetic energy $E \leq \frac{k_BT}{2}$, is the shaded area under the curve.
or \( v \in [-\sigma_v, \sigma_v] \) where \( \sigma_v = \sqrt{\frac{kaT}{m}} \). That fraction is represented by the integral

\[
\sqrt{\frac{1}{2\pi\sigma_v^2}} \int_{-\sigma_v}^{\sigma_v} \exp\left( -\frac{v^2}{2\sigma_v^2} \right) dv = \text{erf}\left( \frac{1}{\sqrt{2}} \right) = 0.683
\]

where \( \text{erf}(x) \) is the error function introduced in Chapter 8 through Equation 8.7 and Figure 8.6. It follows that the fraction of atoms having kinetic energy greater than \( \frac{kaT}{2} \) is \( 1 - \text{erf}\left( \frac{1}{\sqrt{2}} \right) \) where \( \text{erf}(x) \) is the error function and \( \text{erfc}(x) \) is the complementary error function.

### 9.2.6 Probability distributions in many dimensions

The concept of the probability distribution can be extended to many dimensions. Consider two random variables, \( x \) and \( y \), where the probability of measuring a value of \( x \in [x, x + dx] \) and \( y \in [y, y + dy] \) is written

\[
p(x, y) \, dx \, dy
\]

where \( p(x, y) \) is a two-dimensional probability distribution function. An example is shown graphically in Figure 9.13. The probability of measuring \( x \in [x, x + dx] \) and \( y \in [y, y + dy] \) is the volume of the column over the area \( dx \, dy \) under the surface defined by \( p(x, y) \).

The integral over all \( x \) and \( y \) is the total probability of observing an outcome \((x, y)\) somewhere on the \( xy \)-plane which must equal unity

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(x, y) \, dx \, dy = 1
\]

which is our normalization condition. We can further define the mean values of the \( x \) and \( y \) as

\[
\bar{x} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x \, p(x, y) \, dx \, dy \quad \bar{y} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} y \, p(x, y) \, dx \, dy
\]

In defining the variances of this two-dimensional probability distribution function, we encounter a new concept. We define the variances \( \sigma_x^2 \) and \( \sigma_y^2 \) as

\[
\sigma_x^2 = \bar{x}^2 - \bar{x}^2 \\
\sigma_y^2 = \bar{y}^2 - \bar{y}^2
\]
where the mean square values of \(x\) and \(y\) are defined

\[
\bar{x}^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x^2 \ p(x,y) \ dx dy \quad \bar{y}^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} y^2 \ p(x,y) \ dx dy
\]

We can also define a measure of the cross correlation between a deviation from the mean in \(x\), \((x - \bar{x})\), and a deviation from the mean in \(y\), \((y - \bar{y})\), as

\[
\sigma_{xy} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x - \bar{x})(y - \bar{y}) \ p(x,y) \ dx dy
\]

This is known as the covariance.

The value of \(\sigma_{xy}\) provides a measure of the correlation between observations of the two variables. We can define a useful measure of the magnitude of the correlation as

\[
\rho_{xy} = \frac{\sigma_{xy}}{\sigma_x \sigma_y}
\]

where \(\rho_{xy}\) is the correlation coefficient. When measurements of \(x\) and \(y\) are uncorrelated, the probability distribution \(p(x,y)\) is separable and can be written as a product of the probability of observing a value of \(x\) times the independent probability of observing a value of \(y\)

\[
p(x,y) \ dx \ dy = p_x(x) \ dx \times p_y(y) \ dy
\]

In that case

\[
\sigma_{xy} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x - \bar{x})(y - \bar{y}) \ p(x,y) \ dx dy
\]

\[
= \int_{-\infty}^{\infty} (x - \bar{x})p_x(x) \ dx \times \int_{-\infty}^{\infty} (y - \bar{y})p_y(y) \ dy = 0
\]

and the correlation coefficient \(\rho_{xy} = 0\). An example of a distribution with \(\rho_{xy} = 0\) is shown in Figure 9.14. In this case, we say that the observations of \(x\) and \(y\) are uncorrelated. In general, the correlation coefficient will vary as

\[-1 \leq \rho_{xy} \leq 1\]

where positive values of \(\rho_{xy}\) indicate positive correlation and negative values of \(\rho_{xy}\) indicate negative correlation. When \(\rho_{xy} = 0\) the variables \(x\) and \(y\) are independent. Examples of distributions with positive and negative values of \(\rho_{xy}\) are provided in Figure 9.15.

Consider the case of two fair coins. We expect the outcome of the flip of the first coin to be independent of the outcome of a flip of the second coin. In that case, the value of \(\rho_{xy} = 0\) and the observations are uncorrelated. Now consider the case of an ideal gas for which the pressure can be written

\[
p = \frac{nRT}{V}
\]

Suppose the gas is at constant volume. The average pressure is measured to be \(\bar{p}\) and the average temperature \(\bar{T}\). If the pressure is higher than its mean value, so that \((p - \bar{p}) > 0\), we expect the temperature to be higher than its mean value, so that \((T - \bar{T}) > 0\). In this case we expect \(\sigma_{pT} > 0\) and \(\rho_{pT} > 0\). We say that the pressure and temperature are positively correlated.

Now suppose the gas is at constant temperature. The average pressure is measured to be \(\bar{p}\) and the average volume \(\bar{V}\). If the pressure is higher than its mean value, then \((p - \bar{p}) > 0\). Given the inverse dependence of volume on pressure, if the pressure is greater than its mean value, the volume will be lower than its mean value and \((V - \bar{V}) < 0\). In this case we expect \(\sigma_{pV} < 0\) and \(\rho_{pV} < 0\). We say that the pressure and volume are negatively correlated.
9.3 Probability distributions in the physical sciences

The most commonly encountered multiple integrals in the physical sciences involve integration over multivariate probability distributions. Examples include the Maxwell-Boltzmann probability distribution in kinetic theory, the Boltzmann probability distribution in thermodynamics, and square of the modulus of the wave function in quantum theory. The functions are typically complicated by the presence of many physical constants. However, careful simplification of the expressions by algebraic substitution followed by the right choice of coordinate system can convert an intimidating multiple integral into a readily evaluated expression. This section will explore some of the more common functional forms encountered in the physical sciences.

9.3.1 Properties of the Maxwell-Boltzmann probability distribution

Probability distributions are common in the physical sciences. We are often challenged to describe the properties of a very large number of particles, so large that it is hopeless to track the energy or velocity of each particle. Instead, we hope to describe the average properties of the system using statistical assumptions and statistical probability distributions.

The probability of observing a state of given energy can be written in terms of the Boltzmann exponential probability distribution

\[ \exp \left( -\frac{E}{k_B T} \right) \]

Suppose \( E \) is the kinetic energy of a particle with velocity \( \mathbf{v} = u_x \hat{x} + u_y \hat{y} + u_z \hat{z} \) written in vector notation

\[ E = \frac{1}{2} m \mathbf{v} \cdot \mathbf{v} = \frac{1}{2} m (u_x^2 + u_y^2 + u_z^2) \]

Inserting this energy into the Boltzmann probability distribution leads to the Maxwell-Boltzmann distribution

\[ p(u_x, u_y, u_z) = C \exp \left[ -\frac{m}{2k_B T} (u_x^2 + u_y^2 + u_z^2) \right] \]

If we demand that the distribution is normalized

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(u_x, u_y, u_z) du_x du_y du_z = 1 \]

then

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C \exp \left[ -\frac{m}{2k_B T} (u_x^2 + u_y^2 + u_z^2) \right] du_x du_y du_z = 1 \]

We note that this triple integral is separable and can be represented as a product of three one-dimensional integrals\(^\text{16}\):

\[ C \int_{-\infty}^{\infty} e^{-\frac{\pi}{m} u_x^2} du_x \times \int_{-\infty}^{\infty} e^{-\frac{\pi}{m} u_y^2} du_y \times \int_{-\infty}^{\infty} e^{-\frac{\pi}{m} u_z^2} du_z = C \left( \frac{2\pi k_B T}{m} \right)^{\frac{3}{2}} = 1 \]

As a result, the normalization constant \( C = \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \). The final result for the statistical distribution of velocities is

\[ p(u_x, u_y, u_z) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left[ -\frac{m}{2k_B T} (u_x^2 + u_y^2 + u_z^2) \right] \]

\( ^{\text{16}} \) We use the identity

\[ \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \]

where \( x = u_x \) and \( a = \frac{m}{2\pi k_B T} \).
where
\[
p(x, u_y, u_z) \, du_x du_y du_z
\]
expresses the probability of finding a particle with velocity components in the range
\[
[u_x, u_x + du_x] \times [u_y, u_y + du_y] \times [u_z, u_z + du_z]
\]
which is a small increment of volume \(du_x du_y du_z\) in the space of all possible velocities.

### 9.3.2 Mean and variance of the Maxwell-Boltzmann distribution

We can compute the mean and variance of the Maxwell-Boltzmann distribution using a similar approach. Consider first the mean of the velocity defined as
\[
\mathbf{v} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathbf{v} p(x, u_y, u_z) \, du_x du_y du_z
\]
where integration is carried out in cartesian coordinates defined in Figure 9.16. We note that this integral is a sum of three triple integrals, each corresponding to the average of the velocity in one of the three principal directions \(x, y,\) and \(z\) depicted in Figure 9.17. As such, we express the average velocity as
\[
\mathbf{v} = \overline{u}_x \mathbf{\hat{k}} + \overline{u}_y \mathbf{\hat{y}} + \overline{u}_z \mathbf{\hat{z}}
\]
where the averages are defined
\[
\overline{u}_x = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_x p(x, u_y, u_z) \, du_x du_y du_z
\]
\[
\overline{u}_y = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_y p(x, u_y, u_z) \, du_x du_y du_z
\]
\[
\overline{u}_z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_z p(x, u_y, u_z) \, du_x du_y du_z
\]
Each of the averages is a three-dimensional integral that we recognize is separable and can be evaluated as a product of three one-dimensional integrals. Consider
\[
\overline{u}_x = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_x p(x, u_y, u_z) \, du_x du_y du_z
\]
\[
= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} u_x e^{-\frac{m u_x^2}{2 k_B T}} \, du_x \times \int_{-\infty}^{\infty} e^{-\frac{m u_y^2}{2 k_B T}} \, du_y \times \int_{-\infty}^{\infty} e^{-\frac{m u_z^2}{2 k_B T}} \, du_z
\]
\[
= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} u_x e^{-\frac{m u_x^2}{m k_B T}} \, du_x \times \sqrt{\frac{2\pi k_B T}{m}} \times \sqrt{\frac{2\pi k_B T}{m}}
\]
\[
= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} u_x e^{-\frac{u_x^2 m k_B T}{m}} \, du_x
\]
where we have evaluated the integrals over \(u_y\) and \(u_z\) as we did in normalizing the distribution.

We are left with an integral over \(u_x\) in which the integrand is an odd function of \(u_x\). As such
\[
\overline{u}_x = \int_{-\infty}^{\infty} u_x e^{-\frac{u_x^2 m k_B T}{m}} \, du_x = 0
\]
Repeating the process for the averages of \(u_y\) and \(u_z\) leads to \(\overline{u}_y = \overline{u}_z = 0\).
The state of an electron in a one-electron atom is described in terms of a wave function. The square of the modulus of that function describes the electron’s spatial distribution (or shape) in three-dimensional space.

Consider the form of the wave function for four possible states of an electron in a one-electron atom. These functions are most naturally expressed in spherical polar coordinates. For the electron in the lowest energy 1s ground state the wave function is

$$\psi_{1s}(r, \theta, \varphi) = N_1 e^{-r/a_0}$$

The remaining integral can be performed by integration by parts or using our differentiation with respect to a parameter trick explored in the Complements to Chapter 8. The result is

$$\overline{u_x^2} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u_x^2 \rho(u_x, u_y, u_z) \, du_x du_y du_z$$

Grouping terms we find

$$\overline{u_x^2} = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} u_x^2 e^{-\frac{m u_x^2}{2k_B T}} \, du_x \times \int_{-\infty}^{\infty} e^{-\frac{m u_y^2}{2k_B T}} \, du_y \times \int_{-\infty}^{\infty} e^{-\frac{m u_z^2}{2k_B T}} \, du_z$$

$$\overline{u_x^2} = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} u_x^2 e^{-\frac{m u_x^2}{2k_B T}} \, du_x \times \sqrt{\frac{2\pi k_B T}{m}} \times \frac{2\pi k_B T}{m}$$

$$\overline{u_x^2} = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} u_x^2 e^{-\frac{m u_x^2}{2k_B T}} \, du_x$$

The remaining integral can be performed by integration by parts or using our differentiation with respect to a parameter trick explored in the Complements to Chapter 8. The result is

$$\overline{u_x^2} = \frac{k_B T}{m} \sqrt{\frac{2\pi k_B T}{m}} \frac{m}{2\pi k_B T} = \frac{k_B T}{m}$$

By symmetry we recognize the result will be the same for \(\overline{u_y^2}\) and \(\overline{u_z^2}\). With this result we can write

$$\sigma_v^2 = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} = \frac{k_B T}{m} + \frac{k_B T}{m} + \frac{k_B T}{m} = \frac{3k_B T}{m}$$

for the variance in the velocity in three-dimensions. These examples demonstrate the challenge of multiple integration over complicated functions resulting from models in the physical sciences. It is not that the integrals require great invention. The integral identities used in the derivation are familiar. The principal challenge comes from managing the complicated algebraic expressions without error.

### 9.3.3 Properties of the electron density probability distribution

The state of an electron in a one-electron atom is described in terms of a wave function. The square of the modulus of that function describes the electron’s spatial distribution (or shape) in three-dimensional space.

Consider the form of the wave function for four possible states of an electron in a one-electron atom. These functions are most naturally expressed in spherical polar coordinates. For the electron in the lowest energy 1s ground state the wave function is

$$\psi_{1s}(r, \theta, \varphi) = N_1 e^{-r/a_0}$$

This result makes physical sense. It is equally likely that the velocity will be oriented in the positive or negative direction in a given cartesian dimension. This makes the average velocity in each cartesian dimension zero.
where $N_1$ is a normalization constant, $r$ is the distance of the electron from the nucleus, and $a_0$ is known as the Bohr radius.

The wave functions for the electron in the four excited states are

$$
\psi_{2s}(r, \theta, \varphi) = N_2 \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}
$$
$$
\psi_{2p_1}(r, \theta, \varphi) = N_2 \left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin \theta \cos \varphi
$$
$$
\psi_{2p_2}(r, \theta, \varphi) = N_2 \left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin \theta \sin \varphi
$$
$$
\psi_{2p_3}(r, \theta, \varphi) = N_2 \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos \theta
$$

where $N_2$ is a normalization constant. Figure 9.18 depicts the radial dependence of the $\psi_{1s}(r, \theta, \varphi)$ and $\psi_{2s}(r, \theta, \varphi)$ wave functions.

We can determine the normalization constants $N_1$ and $N_2$ by taking the square of the wave function and integrating the resulting electron distribution over all space. Consider the $\psi_{1s}$ wave function where the square of the wave function is

$$
|\psi_{1s}(r, \theta, \varphi)|^2 = \left(N_1 e^{-r/a_0}\right)^2 = N_1^2 e^{-2r/a_0}
$$

The normalization constant can be determined from the definition

$$
\int_0^\infty \int_0^{2\pi} \int_0^\pi \psi_{1s}(r, \theta, \varphi)^2 r^2 \sin \theta \, d\varphi \, d\theta \, dr = 1
$$

where we chose to work in spherical polar coordinates reflecting the fact that the wave functions are natural functions of $r$, $\theta$, and $\varphi$. It follows that

$$
\int_0^\infty \int_0^{2\pi} \int_0^\pi N_1^2 e^{-2r/a_0} r^2 \sin \theta \, d\varphi \, d\theta \, dr = 1
$$

The volume element for integration in spherical polar coordinates $dV = r^2 \sin \theta \, dr \, d\theta \, d\varphi$ contributes a factor of $r^2$ to the radial dependence of the integrand (see Figure 9.19).

This three-dimensional integral is separable in spherical polar coordinates and can be expressed in terms of the product of three one-dimensional integrals

$$
N_1^2 \int_0^\infty e^{-2r/a_0} \, r^2 \, dr \times \int_0^{\pi} \sin \theta \, d\theta \times \int_0^{2\pi} d\varphi = 1
$$

We have encountered each of these integrals before. Integration over $\theta$ and $\varphi$ results in a familiar factor of $4\pi$

$$
\int_0^{\pi} \sin \theta \, d\theta \times \int_0^{2\pi} d\varphi = 2 \times 2\pi = 4\pi
$$

so that the original triple integral is simplified to

$$
4\pi N_1^2 \int_0^\infty e^{-2r/a_0} \, r^2 \, dr = 1
$$

where the $r^2$ term scales $|\psi(r)|^2$ in proportion to the growing area to be integrated over with increasing $r$ (see Figure 9.19). The final integral over an exponential function can be evaluated using integration by parts or differentiation with respect to a parameter explored in the Complements to Chapter 8. The result is

$$
\int_0^\infty x^2 e^{-ax} \, dx = \frac{2}{a^3}
$$
where \( x = r \) and \( a = 2/a_0 \). The final result is

\[
4\pi N_1^2 \left( \frac{a_0^3}{4} \right) = N_1^2 \pi a_0^3 = 1
\]

so that \( N_1 = \frac{1}{\sqrt{\pi a_0}} \). A similar calculation can be used to show that \( N_2 = \frac{1}{\sqrt{3}} \pi a_0^3 \) for each of these four excited states. Examples of the three-dimensional forms of the wave functions noted above are provided in Figure 9.20 and Figure 9.21.

### 9.3.4 Mean and variance of the electron density probability distribution

Let’s compute the mean and variance of the position of the electron in the 1s ground state. The mean position of the electron is defined as the position \( r \) averaged over the electron density distribution \( \left| \psi_{1s}(r, \theta, \phi) \right|^2 \) as

\[
\overline{r} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \left| \psi_{1s}(r, \theta, \phi) \right|^2 r^2 \sin \theta \ d\phi \ d\theta \ dr
\]

This three-dimensional integral over all space is separable and can be written as a product of three one-dimensional integrals

\[
\overline{r} = \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^3 e^{-2r/a_0} \sin \theta \ d\phi \ d\theta \ dr
\]

The integral over \( r \) can be performed using integration by parts, but only with many steps. The most straightforward way to determine the integral is to use the identity

\[
\int_0^\infty x^3 e^{-ax} \ dx = - \frac{d^3}{da^3} \int_0^\infty e^{-ax} \ dx = - \frac{d^3}{da^3} \frac{1}{a} = \frac{6}{a^4}
\]

Applied to our integral of interest with \( x = r \) and \( a = 2/a_0 \) results in

\[
\overline{r} = 4\pi \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^3 e^{-2r/a_0} \ dr = 4 \frac{1}{a_0^3} \left( \frac{6a_0^4}{16} \right) = \frac{3}{2} a_0
\]

We can use the same approach to determine the variance in the position of the electron defined

\[
\sigma_r^2 = \overline{r^2} - \overline{r}^2
\]

We can determine \( \overline{r^2} \) defined as

\[
\overline{r^2} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \left| \psi_{1s}(r, \theta, \phi) \right|^2 r^2 \sin \theta \ d\phi \ d\theta \ dr
\]

Using the integral identity

\[
\int_0^\infty x^4 e^{-ax} \ dx = \frac{d^4}{da^4} \int_0^\infty e^{-ax} \ dx = \frac{d^4}{da^4} \frac{1}{a} = \frac{24}{a^5}
\]
where \( x = r \) and \( a = 2/a_0 \) leads to
\[
\bar{r}^2 = 4\pi \frac{1}{\pi a_0^3} \int_0^\infty r^4 e^{-2r/a_0} dr = 4 \frac{1}{a_0^3} \left( \frac{24a_0^5}{32} \right) = 3a_0^2
\]

The final result for the variance in the position of the electron is
\[
\sigma_r^2 = \bar{r}^2 - \bar{r}^2 = 3a_0^2 - \left( \frac{3a_0}{2} \right)^2 = \frac{3}{4}a_0^2
\]

We find that an apparently complicated set of three-dimensional integrals can be reduced to a series of one-dimensional integrations of familiar functions.

\[A_9\] Connecting the gaussian and binomial probability distributions

Let’s examine the binomial probability distribution when the number of outcomes \( N = 20 \). The distribution of probabilities is shown in Figure 9.22. Note the mean of the distribution is \( \bar{n} = \frac{N}{2} = 10 \) and the variance \( \sigma_n^2 = \frac{N}{4} = 5 \). Suppose we use these values of the mean and variance to parameterize a gaussian distribution. We find
\[
p(n; N) = \frac{1}{\sqrt{2\pi \sigma_n^2}} \exp \left[ -\frac{(n - \bar{n})^2}{2\sigma_n^2} \right]
\]
so that
\[
p(n; N) = \frac{1}{\sqrt{\pi N/2}} \exp \left[ -\frac{(n - N/2)^2}{N/2} \right] \tag{9.11}
\]

The result is shown in Figure 9.22 where the continuous gaussian probability distribution function is compared with the discrete binomial probability distribution.

For the binomial distribution we found that the ratio of the width of the distribution \( \sigma_n \) relative to the mean \( \bar{n} \) varies as
\[
\frac{\sigma_n}{\bar{n}} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}
\]
As \( N \) increases the mean increases as \( \bar{n} = \frac{N}{2} \) and standard deviation increases as \( \sigma_n = \frac{\sqrt{N}}{2} \). As \( N \) increases the distribution appears to be more and more narrow. Another way to interpret this is to think of \( \sigma_n \) as the uncertainty in the measurement of the mean \( \bar{n} \), where we might report our measurement as
\[
\bar{n} \pm \sigma_n
\]
The relative uncertainty, \( \sigma_n/\bar{n} \), in the measurement of the mean, \( \bar{n} \), decreases with increasing \( N \) as \( N^{-1/2} \). For the distribution in Figure 9.2 with \( N = 3 \) we find \( \frac{\sigma_n}{\bar{n}} = 0.577 \), for the distribution in Figure 9.3 with \( N = 6 \) we find \( \frac{\sigma_n}{\bar{n}} = 0.408 \), and for the distribution in Figure 9.13 with \( N = 20 \) we find \( \frac{\sigma_n}{\bar{n}} = 0.224 \). As \( N \) increases the ratio \( \frac{\sigma_n}{\bar{n}} \) decreases, making the variance a smaller and smaller fraction of the mean. This demonstrates the increasing certainty in our measurement of the mean with increasing \( N \).

This point is made more clearly in Figure 9.23 in which the gaussian approximation to the binomial distribution provided by Equation 9.11 is used to compare \( Np(n; N) \) for varying \( N = 10, 50, \) and 150. Both the mean and standard deviation increase with \( N \), but the mean increases as \( N \) while the standard deviation increases only as \( \sqrt{N} \).
This relative narrowing is best exposed in Figure 9.24 in which the distributions are plotted as a function of the normalized index \( \frac{n}{N} \) for \( N = 10, 50, \) and 150. As \( N \) increases the mean increases as \( \pi = \frac{N}{2} \) and standard deviation increases as \( \sigma_n = \frac{\sqrt{N}}{2} \).

Finally, let’s consider the random sampling of an independent random variable. We assume that when we sample the variable once, the outcome of the next sampling is independent of the prior result. We make a series of \( N \) observations from which we compute the mean. As \( N \) is increased the normalized sum of the measured averages tends to a gaussian distribution. Remarkably this is true even if the variables themselves (such as the coin flips) are not distributed according to a gaussian distribution. This important result is known as the central limit theorem. Let’s return to the coin flip. Suppose we flip a coin many times. As the number of flips is increased, the probability of observing a certain number of heads in a series of flips will approach a gaussian probability distribution also referred to as the normal distribution. This remarkable result explains the ubiquitous use of the normal distribution in modeling phenomena in the physical and social sciences.

**B.9 Uniform distributions of independent random variables**

Flipping a coin provides a means of generating independent random numbers. For example, suppose we take a head to be 0 and a tail to be 1. The outcome of \( N = 20 \) random coin flips can be written

\[
00110 \ 11110 \ 11101 \ 00101
\]

forming a series of independent random variables. In this case there are 8 heads and 12 tails, an outcome with probability \( p(n; N) = p(8; 20) = 0.120 \) or 12 percent. Other physical methods for generating random variables include drawing numbered balls from a bin or measuring decay events from a source of radioactive matter.

Now suppose we want to generate 10,000 independent random variables. We won’t want to do that by flipping a coin! The challenge of generating independent random variables using mathematics alone is not at all trivial and has captured the imagination of mathematicians for decades. Consider the middle square method. One takes a large odd integer, squares it, and then selects the middle set of numbers as the random variable.

\[\text{(This observation and its application to the study of coin flips was first reported by French mathematician } \text{Abraham de Moivre (1667-1754).)}\]

\[\text{(This method was developed by Hungarian-American mathematician and physicist John von Neumann (1903-1957). Von Neumann invented and built the first modern computer, developed game theory into a power tool in the social sciences, and made critical contributions to the development of the first atomic bomb.)}\]
For example, we start with the *random seed* 579, 203, square it to form 335, 476, 115, 209, and select the middle digits to arrive at 476, 115. Repeating the process leads to 685, 493. Repeating again yields 900, 653 and 175, 826 and 914, 782. And so on. We can visualize this process as

\[(579, 203)^2, 335, 476, 115, 209, (476, 115)^2, 226, 685, 493, 225, (685, 493)^2, 469, 900, 653, 049, (900, 653)^2, 811, 175, 826, 409, (175, 826)^2, 030, 914, 782, 276, 914, 782\]

Note that the last operation produced an 11-digit number. We created a 12-digit number by padding the left side with a 0.

This method is not perfect. It has a relatively short *recurrence time* after which the series repeats itself. It can also converge to zero. As such, we say that the series is formed of *pseudorandom numbers*. If we wish to have the generated series of pseudorandom numbers occur over the interval \([0, 1]\) we simply divide by one million.

\[\begin{align*}
    (579, 203)^2 & \Rightarrow 335, 476, 115, 209 \\
    (476, 115)^2 & \Rightarrow 226, 685, 493, 225 \\
    (685, 493)^2 & \Rightarrow 469, 900, 653, 049 \\
    (900, 653)^2 & \Rightarrow 811, 175, 826, 409 \\
    (175, 826)^2 & \Rightarrow 030, 914, 782, 276 \\
    914, 782
\end{align*}\]

Suppose we have a process for generating random numbers \(x \in [0, 1]\) from a *uniform probability distribution*. The result of sampling 10,000 independent random numbers \(x \in [0, 1]\) is shown in Figure 9.25 and compared with a uniform distribution. The randomly sampled numbers approximate the uniform distribution over the range of \(x \in [0, 1]\). The computed mean value \(\bar{x} = 0.497\) is slightly smaller than the exact value \(\bar{x} = 0.5\), and the computed standard deviation \(\sigma_x = 0.2883\) is slightly smaller than the exact value \(\sigma_x = 12^{-\frac{1}{2}} = 0.2887\ldots\) for \(N = 10,000\).

We can use the same method to generate a two-dimensional uniform probability distribution of independent random variables \(x \in [0, 1]\) and \(y \in [0, 1]\). To do this we can use the middle square method to generate \(x\) and repeat the process to generate \(y\). The result for sampling 10,000 independent random variables from a uniform distribution in \(x\) and \(y\) is shown in Figure 9.26.\(^{21}\) As the number of dimensions increases, the number of samples must increase to achieve the same level of convergence. These examples convey the challenges associated with generating random samples, and the substantial data set required to represent an adequately converged random distribution.

\(^{21}\) Note the significant variation in the number of observations in a given increment \(dx\ dy\) across the distribution, even for a sampling of 10,000 numbers.
C9 Gaussian distributions of independent random variables

The middle square method provides a way to generate independent random variables corresponding to a uniform probability distribution. How can we sample independent random variables from a gaussian distribution? It turns out that there is a clever method for transforming independent random variables sampled from a uniform distribution to independent random variables sampled from a gaussian distribution.

Suppose we generate independent random numbers uniformly over the interval \( x \in [0,1] \). We generate two such numbers \( x_1 \) and \( x_2 \). We can transform these to two independent random variables sampled from a uniform distribution, \( x_1 \) and \( x_2 \), into two independent random variables sampled from a gaussian distribution, \( z_1 \) and \( z_2 \), as

\[
  z_1 = \sqrt{-2 \ln x_1} \cos(2\pi x_2)
\]
\[
  z_2 = \sqrt{-2 \ln x_1} \sin(2\pi x_2)
\]

This is known as the Box-Mueller method.\(^{22}\)

Take two independent pseudorandom variables sampled from a uniform distribution in the interval [0,1]

\[
  x_1 = 0.579203 \quad x_2 = 0.476115
\]

Using the Box-Mueller method they can be transformed to two independent random variables sampled from a gaussian distribution

\[
  z_1 = \sqrt{-2 \ln(0.579203)} \cos[2\pi(0.476115)] = -0.680981
\]
\[
  z_2 = \sqrt{-2 \ln(0.579203)} \sin[2\pi(0.476115)] = 0.102972
\]

Figure 9.27 shows the result of a sampling of 10,000 independent random variables compared with a gaussian probability distribution. We see that the Box-Mueller method provides a simple and effective way to generate independent random gaussian variables.

It is also possible to extend this method to sample a two-dimensional gaussian probability distribution in the variables \( x \) and \( y \). Figure 9.28 shows a two-dimensional histogram over the xy-plane depicting the frequency of sampling two independent gaussian random variables, \( x \) and \( y \), for a sample of 50,000

\(^{22}\) This method was originally presented by American mathematician and philosopher Norbert Wiener (1894-1964). Wiener was a famous child prodigy who made seminal contributions to the fields of cybernetics, robotics, and control systems.
points. For a large sampling of points the distribution will be well approximated by a two-dimensional gaussian probability distribution function.

The ability to sample independent random variables from a gaussian distribution is useful to model physical processes such as the random motion of atoms in an ideal gas or the molecular diffusion of molecules in a liquid. It also provides a means of modeling statistical error. Ultimately, our success in generate independent gaussian random variables relies on our ability to effectively generate uniform random numbers.

D9 Three definitions of Pythagorean means

There are several ways to define the mean value of a series of numbers. The most familiar is the arithmetic mean defined

\[ A_M = \frac{1}{n} (x_1 + \ldots + x_n) \]

for averaging reaction times. The arithmetic mean of \( a \) and \( b \) is \( A_M = \frac{1}{2} (a + b) \).

However, we can also consider the geometric mean defined

\[ G_M = \sqrt[n]{x_1 \times \ldots \times x_n} \]

not quite clear for the physical sciences. The geometric mean of \( a \) and \( b \) is \( G_M = \sqrt{ab} \). Or the harmonic mean defined

\[ H_M = \frac{1}{n} \left( \frac{1}{x_1} + \ldots + \frac{1}{x_n} \right)^{-1} \]

for averaging rates. The harmonic mean of \( a \) and \( b \) is \( H_M = \frac{2}{\frac{1}{a} + \frac{1}{b}}^{-1} = 2 \frac{ab}{a+b} \). These three means are known as Pythagorean means.

In addition, we can define the quadratic mean also known as the root mean square value

\[ Q_M = \frac{1}{n} \sqrt{x_1^2 + \ldots + x_n^2} \]

It is useful in computing the root mean square speed. The quadratic mean of \( a \) and \( b \) is \( Q_M = \frac{1}{2} \sqrt{a^2 + b^2} \).

The geometric relationships between these four definitions of the mean are displayed in Figure 9.29 for the case of \( a = 0.8 \) and \( b = 1 - a = 0.2 \) for which \( A_M = 0.5 \), \( G_M = 0.4 \), \( H_M = 0.32 \), and \( Q_M = 0.41 \). Note that only the case \( a = b \) leads to the same mean value \( A_M = G_M = H_M = Q_M \) for all four definitions of the mean.

E9 Propagation of error through total differentials and Taylor series

Suppose we have a function \( f(x, y) \) of two independent variables \( x \) and \( y \). We would like to know how the error in our estimate of the function \( f \) is related to the known error in the averages of the variables \( x \) and \( y \).

We define the mean value of the function, \( \bar{f} \), and the mean values of the variables, \( \bar{x} \) and \( \bar{y} \). We further define the deviation of the observed values from the mean values as the errors

\[ \varepsilon_x = x - \bar{x} \quad \varepsilon_y = y - \bar{y} \quad \varepsilon_f = f - \bar{f} \]
Since \( f(x,y) \) is a function of \( x \) and \( y \), we can ask how the error in our estimate of the function, \( \epsilon_f \), is related to the error in our measurements of the variables, \( \epsilon_x \) and \( \epsilon_y \). We start from the Taylor series

\[
f(x,y) = \bar{f} + \frac{\partial f}{\partial x} \left|_{\bar{x}, \bar{y}} \right. (x - \bar{x}) + \frac{\partial f}{\partial y} \left|_{\bar{x}, \bar{y}} \right. (y - \bar{y}) + \frac{1}{2} \frac{\partial^2 f}{\partial x^2} \left|_{\bar{x}, \bar{y}} \right. (x - \bar{x})^2 + \frac{\partial^2 f}{\partial y^2} \left|_{\bar{x}, \bar{y}} \right. (y - \bar{y})^2 + \ldots
\]

which we can rewrite as

\[
\epsilon_f = f(x,y) - \bar{f} = \frac{\partial f}{\partial x} \left|_{\bar{x}, \bar{y}} \right. \epsilon_x + \frac{\partial f}{\partial y} \left|_{\bar{x}, \bar{y}} \right. \epsilon_y + \frac{1}{2} \frac{\partial^2 f}{\partial x^2} \left|_{\bar{x}, \bar{y}} \right. \epsilon_x^2 + \frac{\partial^2 f}{\partial y^2} \left|_{\bar{x}, \bar{y}} \right. \epsilon_y^2 + \frac{\partial^2 f}{\partial x \partial y} \left|_{\bar{x}, \bar{y}} \right. \epsilon_x \epsilon_y + \ldots
\]

If the errors \( \epsilon_x \) and \( \epsilon_y \) are small enough, we can truncate the series and ignore higher order terms to find

\[
\epsilon_f \approx \frac{\partial f}{\partial x} \left|_{\bar{x}, \bar{y}} \right. \epsilon_x + \frac{\partial f}{\partial y} \left|_{\bar{x}, \bar{y}} \right. \epsilon_y
\]

If the errors \( \epsilon_x \) and \( \epsilon_y \) are large, we need to retain higher order terms in the Taylor series.

We want to relate the mean square error in our estimate of the function \( f(x,y) \) defined\(^2\)

\[
\overline{\epsilon_f}^2 = (f - \bar{f})^2
\]

to the mean square error in our measurements of the variables, \( x \) and \( y \), defined \( \overline{\epsilon_x}^2 \) and \( \overline{\epsilon_y}^2 \). Using the Taylor series approximation above we find

\[
\overline{\epsilon_f}^2 \approx \left( \frac{\partial f}{\partial x} \left|_{\bar{x}, \bar{y}} \right. \epsilon_x + \frac{\partial f}{\partial y} \left|_{\bar{x}, \bar{y}} \right. \epsilon_y \right)^2
\]

\[
= \left( \frac{\partial f}{\partial x} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \epsilon_x^2 + \left( \frac{\partial f}{\partial y} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \epsilon_y^2 + 2 \left( \frac{\partial f}{\partial x} \right) \left( \frac{\partial f}{\partial y} \right) \left|_{\bar{x}, \bar{y}} \right. \epsilon_x \epsilon_y
\]

Averaging and noting that since \( x \) and \( y \) are independent variables \( \overline{\epsilon_x \epsilon_y} = 0 \) leads to\(^3\)

\[
\overline{\epsilon_f}^2 \approx \left( \frac{\partial f}{\partial x} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \epsilon_x^2 + \left( \frac{\partial f}{\partial y} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \epsilon_y^2
\]

We interpret the mean square error in our estimate of \( f \) as the variance

\[
\sigma_f^2 = \overline{\epsilon_f}^2 = (f - \bar{f})^2
\]

and similarly \( \sigma_x^2 = \overline{\epsilon_x}^2 \) and \( \sigma_y^2 = \overline{\epsilon_y}^2 \). We can now write our final result relating the mean square error in our measurement of the variables \( x \) and \( y \) to the mean square error in our estimate of the function \( f \) as

\[
\sigma_f^2 \approx \left( \frac{\partial f}{\partial x} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \sigma_x^2 + \left( \frac{\partial f}{\partial y} \right)^2 \left|_{\bar{x}, \bar{y}} \right. \sigma_y^2
\]

(9.12)

Let’s apply this result to the measurement of the pressure of a gas. Suppose we measure the temperature, \( T \), and volume, \( V \), of the gas. Using the ideal gas law, the pressure of the gas can be written as a function of the temperature and volume as

\[
p(T,V) = \frac{RT}{V}
\]

\(^2\) Note that \( \overline{\epsilon_f} = (f - \bar{f}) = \bar{f} - \bar{f} = 0 \). To measure the error \( \epsilon_f \) we must average the square of the error and take the square root

\[
\sigma_f = \sqrt{\overline{\epsilon_f}^2} = \sqrt{(f - \bar{f})^2}
\]

\(^3\) Suppose we have a function of one variable \( f(x) \). We define the mean values \( \bar{f} \) and \( \bar{x} \) and associated errors \( \epsilon_f = f - \bar{f} \) and \( \epsilon_x = x - \bar{x} \). Suppose we take \( N \) measurements, each uncorrelated in error. We expect that

\[
\overline{\epsilon_f} = N \epsilon_f
\]

which we can also write as

\[
\sigma_f^2 = N \epsilon_f^2
\]

As such

\[
\epsilon_f \propto \sqrt{N} \epsilon_x
\]
We would like to know the error in our estimate of \( p \) is related to our error in the measurements of \( T \) and \( V \). Taking \( p \equiv f \), \( T \equiv x \), and \( V \equiv y \), the resulting expression for the mean square error in our estimate of the pressure \( \sigma^2_p \) is

\[
\sigma^2_p \approx \left( \frac{\partial p}{\partial T} \right)_{T,V}^2 \sigma^2_T + \left( \frac{\partial p}{\partial V} \right)_{T,V}^2 \sigma^2_V \tag{9.13}
\]

in terms of the mean square errors in the temperature, \( \sigma^2_T \), and volume, \( \sigma^2_V \). This distribution is depicted in Figure 9.30.

![Figure 9.30: A two-dimensional probability distribution for the variables \( T \) and \( V \). The distribution is centered around the average \( (\bar{T}, \bar{V}) \). The width of the distribution represents the standard deviations \( \sigma_T \) and \( \sigma_V \) in the \( T \) and \( V \) dimensions, respectively. The probability of observing a value of \( T \in [T, T + dT] \) and \( V \in [V, V + dV] \) is given by the volume of the vertical column over the area \( dT \, dV \).](image)

Suppose there is 20% random error in \( T \) and \( V \). Interpreting the random error as the root-mean square error or standard deviation we can write

\[
\sigma_T = 0.2 \bar{T} \quad \sigma_V = 0.2 \bar{V}
\]

so that \( \sigma^2_T = (0.2\bar{T})^2 \) and \( \sigma^2_V = (0.2\bar{V})^2 \). We further know that

\[
\frac{\partial p}{\partial T} = \frac{R}{V} \quad \frac{\partial p}{\partial V} = -\frac{RT}{V^2}
\]

Combining these results with Equation 9.13 we find

\[
\sigma^2_p \approx \left( \frac{R}{\bar{V}} \right)^2 \times (0.2\bar{T})^2 + \left( \frac{RT}{\bar{V}^2} \right)^2 \times (0.2\bar{V})^2
\]

\[
= 0.08 \left( \frac{RT}{\bar{V}^2} \right)^2 = 0.08 \, p^2
\]

Let’s look at one more example involving the average of small differences between large numbers. Consider the function

\[
f(x, y) = x - y
\]

where \( \overline{x} \pm \sigma_x = 30 \pm 1 \) and \( \overline{y} + \sigma_y = 29 \pm 1 \). We can return to our earlier result for the mean square error defined

\[
\sigma^2_f \approx \left( \frac{\partial f}{\partial x} \right)_{x,y}^2 \sigma^2_x + \left( \frac{\partial f}{\partial y} \right)_{x,y}^2 \sigma^2_y
\]

where

\[
\frac{\partial f}{\partial x} = 1 \quad \frac{\partial f}{\partial y} = -1
\]
so that $\sigma_f^2 \approx \sigma_x^2 + \sigma_y^2 = 1 + 1 = 2$. It follows that

$$\sigma_f = \sqrt{2} = 1.41$$

so that

$$\bar{f} = x - y = 30 - 29 = 1$$

and

$$\bar{f} \pm \sigma_f = 1 \pm 1.41$$

The error is larger than the difference itself. This examples demonstrates the importance of considering not only the relative error in variables but the total error in the function itself.

---

### F9 End-of-chapter problems

Life’s most important questions are, for the most part, nothing but probability problems.

Pierre-Simon Laplace

---

### Warm-ups

9.1 Calculate the probability of getting (a) exactly five heads in ten tosses of a fair coin, (b) exactly 1 head in five tosses of a fair coin, and (c) 5 heads in the order of THHTTHTHH.

HINT: A coin toss has two possible outcomes, head or tail. The binomial distribution gives the probability of observing $n$ heads and $N - n$ tails in $N$ flips of a fair coin as

$$p(n; N) = \frac{N!}{(N-n)!n!} \left(\frac{1}{2}\right)^N$$

where the binomial coefficient

$$\binom{N}{n} = \frac{N!}{(N-n)!n!}$$

is the number of ways that $n$ heads and $N - n$ tails can be observed in $N$ flips out of $2^N$ possible outcomes.

9.2 Determine the relative error in Stirling’s approximation

$$\ln N! \approx \ln N - N$$

in calculations of $\ln N!$ for $N=10, 50$, and $100$. The relative error is defined as the difference between the estimated value and the exact value, divided by the exact value.

9.3 In the card game bridge you can distribute 52 cards having 4 suits (hearts, diamonds, clubs, and spades) of thirteen cards each. A bridge hand consists of 13 cards. What is the total number of possible bridge hands?

9.4 Find the number of different permutations for the letters in the words Euler, Laplace, and Lagrange.

HINT: An event has $k$ possible outcomes. The multinomial coefficient gives the number of ways of observing $k$ possible outcomes, defined as a set of $\{n_1, n_2, n_3, \ldots, n_k\}$ where $n_i$ is the number of times the $i^{th}$ outcome was observed in $N$ trials

$$\binom{N}{n_1, n_2, n_3, \ldots, n_k} = \frac{(n_1 + n_2 + n_3 + \cdots n_k)!}{n_1!n_2!n_3!\cdots n_k!} = \frac{N!}{n_1!n_2!n_3!\cdots n_k!}$$
where
\[ \sum_{i=1}^{k} n_i = N \]

9.5 Consider the simple uniform distribution

\[ p(x) = \begin{cases} 
C & 0 \leq x \leq 5 \\
0 & \text{otherwise} 
\end{cases} \]

(a) If \( p(x) \) is normalized, what is the normalization constant \( C \)?
(b) What is the mean \( \bar{x} \)?
(c) What is the standard deviation \( \sigma_x \) defined in terms of the variance \( \sigma_x^2 = (x - \bar{x})^2 \)?

9.6 Consider the exponential distribution

\[ p(r) \, dr = C e^{-\lambda r} \, dr \quad 0 \leq r \leq \infty \]

(a) If \( p(r) \) is normalized, what is the normalization constant \( C \)?
(b) What is the mean \( \bar{r} \)?
(c) What is the standard deviation \( \sigma_r \) defined in terms of the variance \( \sigma_r^2 = (r - \bar{r})^2 \)?

**Homework exercises**

9.7 Consider the probability distribution of the one-dimensional particle in a box

\[ p(x) \, dx = |\psi_n(x)|^2 \, dx = \frac{2}{L} \sin^2 \left( \frac{n\pi x}{L} \right) \, dx \quad n = 1, 2, 3, \ldots \]

where \( 0 \leq x \leq L \).

(a) Show that \( p(x) \) is normalized.
(b) Show that the mean is \( \bar{x} = \frac{L}{2} \)
(c) Show that the variance is

\[ (x - \bar{x})^2 = \frac{L^2}{12} \left( 1 - \frac{6}{n^2 \pi^2} \right) \]

9.8 Consider the distribution of energies of an ideal gas

\[ p(\varepsilon) \, d\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} \exp \left[ -\frac{\varepsilon}{k_B T} \right] \, d\varepsilon \]

where \( 0 \leq \varepsilon < \infty \).

(a) Show that \( p(\varepsilon) \) is normalized.
(b) Determine the mean \( \bar{\varepsilon} \). Compare your result to the average kinetic energy of an ideal gas particle

\[ \frac{1}{2} \frac{m v^2}{m} = \frac{3}{2} k_B T \]
(c) Show that the variance is

\[ \sigma_{\varepsilon}^2 = (\varepsilon - \bar{\varepsilon})^2 = \frac{3}{2} (k_B T)^2 \]

9.9 The mean value \( \pi \) and variance \( \sigma_{\pi}^2 = (\pi - \bar{\pi})^2 \) of a binomial distribution are defined by Equations 9.9 and 9.10 to be

\[ \pi = \frac{N}{2} \quad \sigma_{\pi}^2 = (\pi - \bar{\pi})^2 = \frac{N}{4} \]
when each outcome is assumed to have probability 1/2. Consider the general case in which one outcome has probability \( p \) and the other outcome has probability \( 1 - p = q \). The binomial probability of observing \( n \) events each having probability \( p \) and \( N - n \) events each having probability \( 1 - p = q \) takes the form

\[
p(n; N) = \frac{N!}{n!(N-n)!} p^n (1 - p)^{N-n} = \frac{N!}{n!(N-n)!} p^n q^{N-n}
\]

(a) Show that the mean value is given by

\[
\pi = \sum_{n=0}^{N} np(n; N) = Np
\]

which reduces to the result \( \pi = N/2 \) for the case \( p = q = 1/2 \).

(b) Show that the variance is given by

\[
\sigma_n^2 = (n - \pi)^2 = Np(1 - p) = Npq
\]

which reduces to the result \( \sigma_n^2 = (n - \pi)^2 = N/4 \) for the case \( p = q = 1/2 \).

9.10 Find the mean value

\[
r = 4 \left( \frac{1}{a_0} \right)^3 \int_{0}^{\infty} e^{-2r/a_0} r^3 \, dr
\]

for an electron in the 1s state of the hydrogen atom.

9.11 The probability distribution of a quantum mechanical particle in a three-dimensional rectangular box of volume \( V = L_x L_y L_z \) can be written as

\[
I = \iiint |\psi(x, y, z)|^2 \, dx \, dy \, dz
\]

\[
= \left[ \int_{0}^{L_x} \int_{0}^{L_y} \int_{0}^{L_z} \right] C \sin^2 \left( \frac{n_x \pi x}{L_x} \right) \sin^2 \left( \frac{n_y \pi y}{L_y} \right) \sin^2 \left( \frac{n_z \pi z}{L_z} \right) \, dx \, dy \, dz = 1
\]

where \( n_x = 1, 2, 3, \cdots \), \( n_y = 1, 2, 3, \cdots \), and \( n_z = 1, 2, 3, \cdots \).

(a) Carry out the multiple integral to determine the normalization constant \( C \).

(b) Determine the average position of the particle in the box

\[
\bar{r} = \iiint r |\psi(x, y, z)|^2 \, dx \, dy \, dz
\]

where \( \bar{r} = x \hat{x} + y \hat{y} + z \hat{z} \).

9.12 Consider the Maxwell distribution of velocities defined as

\[
p(v) dv = C \exp \left[ -\frac{\beta m}{2} \left( u_x^2 + u_y^2 + u_z^2 \right) \right] du_x \, du_y \, du_z
\]

where \( \beta = \frac{1}{k_B T} \), the velocity \( v = u_x \hat{i} + u_y \hat{j} + u_z \hat{k} \), and the speed \( u \) is defined as the magnitude of the velocity

\[
u = |v| = \sqrt{u_x^2 + u_y^2 + u_z^2}
\]

(a) Carry out the following integral

\[
I = \iiint p(v) dv = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(u_x, u_y, u_z) \, du_x \, du_y \, du_z = 1
\]

to determine the normalization constant \( C \).
(b) Show that the distribution in (a) may be written in spherical polar coordinates as

\[
p(v)dv = C \exp \left[ -\frac{\beta m}{2}u^2 \right] u^2 \sin \theta \, du \, d\theta \, d\phi
\]

where \( u^2 = u_x^2 + u_y^2 + u_z^2 \).

(c) Determine the average speed defined by the integral

\[
I = \int \int \int u \, p(v) \, dv = \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} C \, u \exp \left[ -\frac{\beta m}{2}u^2 \right] u^2 \sin \theta \, d\phi \, d\theta \, du
\]

(d) Determine the mean square speed defined by the integral

\[
I = \int \int \int u^2 \, p(v) \, dv = \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} C \, u^2 \exp \left[ -\frac{\beta m}{2}u^2 \right] u^2 \sin \theta \, d\phi \, d\theta \, du
\]

9.13 Consider a bivariate (two variable) probability distribution \( p(x, y) \) with variances \( \sigma_x^2 = (x - \bar{x})^2 \) and \( \sigma_y^2 = (y - \bar{y})^2 \).

The cross correlation between \( x \) and \( y \) can be measured using

\[
\rho_{xy} = \frac{1}{\sigma_x \sigma_y} (x - \bar{x})(y - \bar{y})
\]

where \( \rho_{xy} \) is defined as the correlation coefficient. The distribution is shown in the figure below for three values of the correlation coefficient \( \rho_{xy} \).

Assume that \( x \) and \( y \) are independent random variables with probability distribution given by

\[
p(x, y) \, dx \, dy = \frac{\alpha}{\pi} e^{-\alpha[(x-\bar{x})^2 + (y-\bar{y})^2]} \, dx \, dy
\]

Show that \( \rho_{xy} = 0 \).

9.14 Consider the bivariate normal probability distribution

\[
p(x, y) \, dx \, dy = \frac{1}{2\pi\sqrt{1 - \rho_{xy}^2}} \exp \left[ -\frac{1}{2(1 - \rho_{xy}^2)} (x^2 + y^2 - 2\rho_{xy} xy) \right] \, dx \, dy
\]

The distribution is shown in the figure above for three values of the correlation coefficient \( \rho_{xy} \).

(a) Show that the marginal probability distributions take the form

\[
p(x) = \int_{-\infty}^{\infty} p(x, y) \, dy = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}
\]

and

\[
p(y) = \int_{-\infty}^{\infty} p(x, y) \, dx = \frac{1}{\sqrt{2\pi}} e^{-y^2/2}
\]
by integrating over \( x \) (or \( y \)) leading to a normal distribution in \( y \) (or \( x \)).

(b) Perform the integral

\[
I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(x, y) \, dx \, dy
\]

and demonstrate that the distribution is normalized.

9.15* The volume of a cylindrical capillary tube is given by the expression \( V = \pi r^2 h \), where \( r \) is the radius of the tube and \( h \) is the length of the tube. If the radius of the capillary tube is found to be 0.030 cm with an error of \( \pm 0.002 \) cm and the length of the tube is found to be 4.0 cm with a error of \( \pm 0.1 \) cm, what is the volume of the capillary tube and its error? What measurement must be made to a higher precision to decrease the error in the volume?

9.16* The molar mass of a vapor is determined by filling a bulb of known volume with the vapor at a known temperature and pressure and measuring the mass of the bulb. The vapor is assumed to be an ideal gas so that molar mass, \( M \), is given by

\[
M = \frac{mRT}{pV}
\]

where \( m \) is the mass of the vapor, \( R \) is the gas constant, \( T \) is the absolute temperature, \( p \) is the pressure, and \( V \) is the volume. Measurements are summarized as \( m = 1.0339 \pm 0.0007 \) g, \( T = 274.0 \pm 0.5 \) K, \( p = 1.050 \pm 0.001 \) bar, \( V = 0.1993 \pm 0.0001 \) liters, and \( R = 0.08314 \) L \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \) (no error as the value is taken to be exact). Determine the error in the molar mass \( M \).

9.17* Suppose you measure independent variables \( x \) and \( y \). You have a function \( f(x, y) \) that depends on those variables. Average quantities are defined \( \bar{x}, \bar{y}, \) and \( \bar{f} \). We can further define the error in \( x, y, \) and \( f(x, y) \) as

\[
\epsilon_x = x - \bar{x} \quad \epsilon_y = y - \bar{y} \quad \epsilon_f = f - \bar{f}
\]

(a) Use a Taylor series expansion to express the measured error in \( f(x, y), \epsilon_f \), as a function of errors \( \epsilon_x \) and \( \epsilon_y \) in \( x \) and \( y \). HINT: Expand \( f(x, y) \) about the point \( (\bar{x}, \bar{y}) \) to first order in \( x - \bar{x} \) and \( y - \bar{y} \).

(b) Derive a formula for the mean square error \( \epsilon_f^2 \) as a function of \( \epsilon_x^2 \) and \( \epsilon_y^2 \).

(c) Consider the ideal gas law with \( f \equiv p = \frac{RT}{V}, x \equiv T, \) and \( y \equiv V \). If \( T \) and \( V \) have 10% errors, how large is the error in \( p \)?

(d) You add \( N \) measurements with uncorrelated error in \( x, \epsilon_x \). How will the error in \( \epsilon_f \) increase with increasing \( N \)?
10 ORDINARY DIFFERENTIAL EQUATIONS

10.1 First order ordinary differential equations

10.2 Applications of first order differential equations

A10 Functions derived from exact differentials and integrating factors

B10 End-of-chapter problems

10.1 First order ordinary differential equations

The fundamental equations of thermodynamics, kinetics, and quantum theory are expressed in the form of differential equations. Differential equations are used to relate the change in a property, such as pressure, concentration, or position, resulting from the change in a variable, such as temperature, position, or time. This section explores the general form and properties of first order ordinary differential equations.

10.1.1 General features of first order ordinary differential equations

In order to become familiar with the general features of differential equations, we will begin by looking at a few specific examples. We will then generalize our observations and discuss approaches to analyzing and solving differential equations.

Consider the concentration of some species, $c(t)$, that varies as a function of time, $t$. The initial concentration is $c(t = 0) = c_0$ and the rate of change in the concentration with changing time is defined by the derivative

$$\frac{dc}{dt}$$

written in terms of the change in concentration, $dc$, divided by the change in time, $dt$. Suppose the concentration is observed to decrease with time at a rate proportional to the concentration itself. We can record all of this information in the simple equation

$$\frac{d}{dt} c(t) = -k c(t)$$

(10.1)

where $k$ is a positive proportionality constant known as the rate constant with units of inverse time. The negative sign captures the fact that $dc < 0$ and the concentration is decreasing. This is known as a linear ordinary first order differential equation. It is linear as the rate of change in $c(t)$ is a linear function of $c(t)$. It is ordinary as it involves a function $c(t)$ of a single variable $t$. It is first order as the highest order derivative in the equation is a first derivative.

We seek a function $c(t)$ that is proportional to its own derivative, which must be the exponential function $\exp(\alpha t)$. With this insight, we can guess the functional form for $c(t)$ to be

$$c(t) = Ae^{\alpha t}$$

(10.2)

where $A$ is a proportionality constant. We call this guess our ansatz. Inserting Equation 10.2 into Equation 10.1 we find

$$\frac{d}{dt} c(t) = \frac{d}{dt} Ae^{\alpha t} = A \frac{d}{dt} e^{\alpha t} = A \alpha e^{\alpha t} = \alpha c(t) = -k c(t)$$

so that $\alpha = -k$. We can determine the value of the constant $A$ using the initial condition for the concentration $c(t = 0) = c_0$ as

$$c(t = 0) = Ae^{\alpha t} \bigg|_{t = 0} = A = c_0$$

1 This educated guess is often called an ansatz, the German word for approach or attempt.
so that the final form for the concentration as a function of time is
\[ c(t) = c_0 e^{-kt} \]  \hspace{1cm} (10.3)

This result is plotted in Figure 10.1.

As another example, suppose we seek to model the population of some species, \( p(t) \), as it changes in time, \( t \). One simple model is that each unit in the population reproduces itself at a constant rate

\[ \text{birth rate } = b \]

and dies at a constant rate

\[ \text{death rate } = d \]

We model this birth-death process mathematically as a linear first order ordinary differential equation

\[ \frac{d}{dt} p(t) = bp(t) - dp(t) = (b - d)p(t) \]

When the birth rate exceeds the death rate \( (b - d) > 0 \) and the population increases. When the death rate exceeds the birth rate \( (b - d) < 0 \) and the population decreases. When \( b = d \), the population is constant. The behavior of \( p(t) \) in the regimes of growth, decline, and stasis is shown in Figure 10.2.

Consider a slightly different model for the birth-death process. In this model, each species has a birth rate \( b \), but as the population increases the birth rate decreases in proportion to the population as a result of competition for limited resources. This can be written

\[ \text{birth rate } = b - cp(t) \]

where \( c \) is a constant. The birth rate leads to a rate of change in the population defined by the differential equation

\[ \frac{d}{dt} p(t) = (b - cp(t)) p(t) - dp(t) = (b - d)p(t) - cp(t)^2 \]

This is a non-linear first order ordinary differential equation as the rate of change in \( p(t) \) depends on both \( p(t) \) and \( p(t)^2 \). Non-linear differential equations can be very challenging to solve. Fortunately, most of the physical processes of interest to us can be modeled using linear differential equations.

\[ \text{Figure 10.1: The concentration } c(t) \text{ as a function of time for } k = 1 \text{ and three initial conditions } c_0 = 5, 2, \text{ and } 1. \]

\[ \text{Figure 10.2: The population } p(t) \text{ as a function of time for the conditions of growth } b > d, \text{ stasis } b = d, \text{ and decline } b < d. \]

\[ \text{Note if there are two solutions, } p_1(t) \text{ and } p_2(t), \text{ each satisfying the differential equation, than the sum or superposition of the solutions } p_1(t) + p_2(t) \text{ is also a solution to the differential equation. Suppose } \]
\[ \frac{dp}{dt} = ap = 0 \]
\[ \text{then} \]
\[ \frac{d}{dt} (p_1 + p_2) = \frac{dp_1}{dt} + \frac{dp_2}{dt} = a(p_1 + p_2) \]
\[ \text{Since} \]
\[ \frac{dp_1}{dt} = ap_1 = 0 \quad \frac{dp_2}{dt} = ap_2 = 0 \]
\[ \text{it follows that } p_1 + p_2 \text{ is also a solution.} \]
10.1.2 General approach to solve linear first order differential equations

Consider the linear first order ordinary differential equation

\[ \frac{dy(x)}{dx} + q(x)y(x) = r(x) \]  \hspace{1cm} (10.4)

where the goal is to solve for \( y(x) \). Both \( q(x) \) and \( r(x) \) are coefficients that may depend on \( x \). We start by solving the reduced equation

\[ \frac{dy(x)}{dx} + q(x)y(x) = 0 \]  \hspace{1cm} (10.5)

in which \( r(x) \) is taken to be zero. This is known as a homogeneous equation as each term is proportional to \( y(x) \).\(^3\)

To solve this equation, we employ a trick familiar from solving elementary kinetic equations such as

\[ \frac{dc(t)}{dt} = -k c(t) \]

with the initial condition \( c(t = 0) = c_0 \). We separate the numerator and denominator of the derivative and rearrange the equation

\[ \frac{1}{c(t)} \frac{dc(t)}{dt} = -k \]

so that the dependence on \( c(t) \) is on the left hand side and the explicit dependence on \( t \) is on the right hand side. Integrating each side of the equation from the initial time (or concentration) to the final time (or concentration) leads to\(^4\)

\[ \int_{c(0)}^{c(t)} \frac{1}{c} \, dc = \ln(c(t)) - \ln(c(0)) = - \int_0^t k \, dt = -kt \]

with the solution for \( c(t) \)

\[ \ln(c(t)) - \ln(c(0)) = \ln\left(\frac{c(t)}{c(0)}\right) = -kt \]

We can use this approach to solve our original reduced equation, Equation 10.5, as

\[ \int \frac{1}{y} \, dy = -q(x) \]

so that

\[ \int \frac{1}{y} \, dy = -\int q(x) \]

leaving

\[ \ln y(x) = -\int q(x) + C \]

where \( C \) is an integration constant that will be defined by the boundary condition.\(^5\) Exponentiating each side results in

\[ y(x) = \exp\left[-\int q(x) + C\right] = A \exp\left[-\int q(x)\right] \]

where \( A = e^C \). This is a general solution of our reduced equation for \( y(x) \).

The form of this equation may be unfamiliar and appear quite complex. There is an exponential in which the argument is an integral. To better understand this expression, let’s apply it to the solution of Equation 10.1. We recognize that

\[ \frac{d}{dx}y(x) = -q(x)y(x) \rightarrow \frac{d}{dt}c(t) = -k c(t) \]
so that \( y(x) \equiv c(t), \quad x \equiv t, \) and \( q(x) \equiv k. \) According to our general solution
\[
y(x) = A \exp \left[ - \int q(x) dx \right] \rightarrow c(t) = A \exp \left[ - \int k dt \right]
\]
The integral in the exponential is evaluated as \( \int k dt = kt \) leading to our final result
\[
c(t) = A \exp \left[ - \int k dt \right] = A \exp [-kt]
\]
To evaluate the undetermined constant \( A \) we exploit the initial condition \( c(t = 0) = c_0 \) so that
\[
c(t = 0) = A = c_0
\]
leading to the final result
\[
c(t) = c_0 \exp [-kt]
\]
which agrees with our earlier solution (see Equation 10.3). This example shows how we can use the general solution to the reduced equation to address a familiar problem.

Let’s return to the original differential equation, Equation 10.4, written
\[
\frac{d}{dx} y(x) + q(x)y(x) = r(x)
\]
where we employ the ansatz
\[
y(x) = u(x) \exp \left[ - \int q(x) dx \right]
\]
This functional form might not immediately come to mind, but let’s see where it takes us.\(^6\) Inserting this form for \( y(x) \) into Equation 10.4 we find
\[
\frac{d}{dx} y(x) + q(x)y(x) = \frac{d}{dx} u(x) \times \exp \left[ - \int q(x) dx \right]
\]
\[
- u(x) \times q(x) \exp \left[ - \int q(x) dx \right] + q(x)u(x) \exp \left[ - \int q(x) dx \right]
\]
\[
= r(x)
\]
or simply that
\[
\frac{d}{dx} u(x) \times \exp \left[ - \int q(x) dx \right] = r(x)
\]
Using our trick of separating the numerator and denominator of the derivative and the fact that
\[
\exp \left[ - \int q(x) dx \right] = \frac{1}{\exp \left[ \int q(x) dx \right]}
\]
leads to
\[
du(x) = r(x) \exp \left[ \int q(x) dx \right] dx
\]
Integrating each side of this relation as
\[
\int du(x) = \int r(x) \exp \left[ \int q(x) dx \right] dx
\]
results in
\[
u(x) = \int r(x) \exp \left[ \int q(x) dx \right] dx + C
\]
Substituting this expression for $u(x)$ into our ansatz for $y(x)$ leads to a general solution to Equation 10.4

$$y(x) = e^{-\int q(x)dx} \left[ r(x)e^{\int q(x)dx}dx + C \right]$$

(10.6)

where the integration constant, $C$, is determined by specifying an initial or boundary condition.

10.2 Applications of first order differential equations

The principal application of first order ordinary differential equations in physical science is physical kinetics. The rate of change in time in the amount or concentration of a species is modeled as the first derivative of the concentration set equal to a function of concentration. In this section we explore the application of our general method for solving first order differential equations to two important models of physical kinetics.

10.2.1 Application to reversible first order kinetic equations

Let’s explore the application of our general solution to linear first order ordinary differential equations for the case of reversible kinetics

$$A \xrightleftharpoons{\k_f}{\k_b} B$$

where $A$ is the reactant, $B$ is the product, and $\k_f$ and $\k_b$ are the forward and backward reaction rate constants, respectively. The initial conditions of the concentrations of each species at time $t = 0$ are defined as $A(0) = A_0$ and $B(0) = 0$. Moreover, the sum $A(t) + B(t)$ is a constant since when one $A$ is lost one $B$ is gained and vice versa.

We interpret this kinetic scheme in the form of two coupled linear first order differential equations

$$\frac{dA}{dt} = -\k_f A + \k_b B \quad \frac{dB}{dt} = \k_f A - \k_b B$$

(10.7)

While there are two variables $A(t)$ and $B(t)$ there is really only one independent variable since

$$A(t) + B(t) = A(0) + B(0) = A_0$$

and so $B(t) = A_0 - A(t)$. Inserting this result in our equation for the rate of change in $A$ we find

$$\frac{dA}{dt} = -\k_f A + \k_b (A_0 - A(t)) = -(\k_f + \k_b)A(t) + \k_b A_0$$

Comparing this specific equation with the general form of our linear first order ordinary differential equation defined by Equation 10.4 we find

$$\frac{d}{dx}y(x) + q(x)y(x) = r(x) \rightarrow \frac{dA}{dt} + (\k_f + \k_b)A(t) = \k_b A_0$$

where $y \equiv A$, $x \equiv t$, $q(x) \equiv (\k_f + \k_b)$ and $r(x) \equiv \k_b A_0$. It follows that the solution for $A(t)$ can be written

$$A(t) = e^{-\int (\k_f + \k_b)dt} \left\{ \k_b A_0 e^{\int (\k_f + \k_b)dt}dt + C \right\}$$

Since $\int (\k_f + \k_b)dt = (\k_f + \k_b)t$ we find

$$A(t) = e^{-(\k_f + \k_b)t} \left\{ \k_b A_0 e^{(\k_f + \k_b)t}dt + C \right\}$$
Performing the final integral leads to

\[ A(t) = e^{-(k_f + k_b)t} \left( \frac{k_b}{k_f + k_b} e^{(k_f + k_b)t} + C \right) = \frac{k_b}{k_f + k_b} + Ce^{-(k_f + k_b)t} \]

Applying the initial condition \( A(0) = A_0 \) results in

\[ A(0) = \left[ A_0 \frac{k_b}{k_f + k_b} + C \right] = A_0 \]

so that \( C = A_0 \frac{k_f}{k_f + k_b} \). We arrive at the final result

\[ A(t) = A_0 \frac{k_b}{k_f + k_b} \left( 1 + \frac{k_f}{k_b} e^{-(k_f + k_b)t} \right) \]

(10.8)

We know that \( A(t) + B(t) = A_0 \) for all time. As such, we can say that \( B(t) = A_0 - A(t) \) so that

\[ B(t) = A_0 \frac{k_f}{k_f + k_b} \left( 1 - e^{-(k_f + k_b)t} \right) \]

The behavior of \( A(t) \) and \( B(t) \) as a function of \( t \) is shown in Figure 10.3.

The rate of change in the populations of \( A \) and \( B \) is defined by the sum of the elementary forward and backward rate constants \( k_f \) and \( k_b \). Note that as \( t \to \infty \) we find the equilibrium populations

\[ A_{eq} = A_0 \frac{k_b}{k_f + k_b} \quad B_{eq} = A_0 \frac{k_f}{k_f + k_b} \]

where the ratio of the equilibrium populations defines the equilibrium constant

\[ K_{eq} = \frac{B_{eq}}{A_{eq}} = \frac{k_f}{k_b} \]

reflecting the underlying condition of detailed balance

\[ k_f A_{eq} = k_b B_{eq} \]

This condition states that the forward rate of reaction is equal to the backward rate of reaction. While reactions continue to occur, the populations of reactant and product are kept constant in a state of dynamic equilibrium.

### 10.2.2 Application to coupled first order kinetic equations

Let’s explore the application of our general solution to linear first order ordinary differential equations for the kinetic scheme

\[ \text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C} \]

The initial conditions define the concentration of each species at time \( t = 0 \) as \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \). We interpret this kinetic scheme in the form of three coupled linear first order ordinary differential equations

\[ \frac{dA}{dt} = -k_1 A \quad \frac{dB}{dt} = k_1 A - k_2 B \quad \frac{dC}{dt} = k_2 B \]

(10.9)

These equations will be solved one at a time using our general approach to the solution of first order ordinary differential equations.

Comparing the general linear first order ordinary differential equation with
the specific form of our differential equation for the rate of change in $A$ we find
\[
\frac{d}{dx} y(x) + q(x)y(x) = r(x) \rightarrow \frac{dA}{dt} + k_1 A = 0
\]
where $y \equiv A$, $x \equiv t$, $q(x) \equiv k_1$, and $r(x) \equiv 0$. It follows that the solution for $A(t)$
can be expressed
\[
y(x) = A \exp \left[ - \int q(x) dx \right] \rightarrow A(t) = A_0 \exp \left[ - \int k_1 dt \right]
\]
Since $\int k_1 dt = k_1 t$ we arrive at the result
\[
A(t) = A_0 e^{-k_1 t} \quad \text{(10.10)}
\]

Returning to our equation for the rate of change in $B(t)$, we insert our result for $A(t)$ to find
\[
\frac{dB}{dt} = k_1 A - k_2 B = k_1 A_0 e^{-k_1 t} - k_2 B
\]
Comparing this equation with the general form of a first linear first order ordinary differential equation
\[
\frac{d}{dx} y(x) + q(x)y(x) = r(x) \rightarrow \frac{dB}{dt} + k_2 B = k_1 A_0 e^{-k_1 t}
\]
we find $y \equiv B$, $x \equiv t$, $q(x) \equiv k_2$, and $r(x) \equiv k_1 A_0 \exp(-k_1 t)$. As the solution for
$y(x)$ is
\[
y(x) = e^{-\int q(x) dx} \left[ \int r(x) e^{\int q(x) dx} dx + C \right]
\]
it follows that the solution for $B(t)$ is
\[
B(t) = e^{-\int k_2 dt} \left[ k_1 A_0 e^{-k_1 t} e^{\int k_2 dt} dt + C \right]
\]
Since $\int k_2 dt = k_2 t$ we arrive at the result
\[
B(t) = e^{-k_2 t} \left[ k_1 A_0 e^{-k_1 t} e^{k_2 t} dt + C \right]
\]
We are left with an integral over an exponential function
\[
\int k_1 A_0 e^{-k_1 t} e^{k_2 t} dt = k_1 A_0 \int e^{-(k_1 - k_2) t} dt = - \frac{k_1 A_0}{k_1 - k_2} e^{-(k_1 - k_2) t}
\]
so that
\[
B(t) = e^{-k_2 t} \left[ - \frac{k_1 A_0}{k_1 - k_2} e^{-(k_1 - k_2) t} + C \right] = - \frac{k_1 A_0}{k_1 - k_2} e^{-k_2 t} + Ce^{-k_2 t}
\]
Applying our initial condition at $t = 0$ we find
\[
B(0) = 0 = - \frac{k_1 A_0}{k_1 - k_2} + C
\]
so that
\[
C = \frac{k_1 A_0}{k_1 - k_2}
\]
leading to the solution
\[
B(t) = \frac{k_1 A_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right] = \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} \left[ 1 - e^{-(k_2 - k_1) t} \right] \quad \text{(10.11)}
\]
With general solutions for $A(t)$ and $B(t)$, we are left to solve for $C(t)$. We
could approach this using our general solution for linear first order ordinary
differential equations defined by Equation 10.6. However, we can also note that
the total amount of \( A(t) + B(t) + C(t) = \) constant. From the initial conditions
\( A(0) = A_0 \) and \( B(0) = C(0) = 0 \) we can say that
\[
C(t) = A_0 - (A(t) + B(t))
\]
or that
\[
C(t) = A_0 \left( 1 - e^{-k_1 t} \right) - \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} \left[ 1 - e^{-(k_2-k_1)t} \right] = A_0 \left[ 1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_1 t} \right] \tag{10.12}
\]

\( A(t), B(t), \) and \( C(t) \) as a function of \( t \) for three sets of elementary rate constants
\((k_1, k_2)\) are shown in Figure 10.4.

10.2.3 Analyzing solutions using limiting laws and approximations

Let’s explore our solution in three regimes
\[ k_1 \ll k_2 \quad k_1 = k_2 \quad k_1 \gg k_2 \]

We will find that in each regime our general solution takes on a specific form
that provides insight into the underlying kinetics.

Case #1 \( k_1 \gg k_2 \)

In the regime \( k_1 \gg k_2 \), we expect the rapid production of \( B \) from \( A \) with slower
conversion of \( B \) to \( C \). In this case starting from the general solution
\[
B(t) = \frac{k_1 A_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right]
\]
we can approximate
\[
\frac{k_1 A_0}{k_2 - k_1} \approx -\frac{k_1 A_0}{k_1} = -A_0
\]
and
\[
\left[ e^{-k_1 t} - e^{-k_2 t} \right] \approx -e^{-k_2 t}
\]
so that

\[ B(t) \approx A_0 e^{-k_2 t} \]

This result is identical to the result found in Equation 10.3 and for the reaction \( A \rightarrow B \) in Equation 10.8 for the case that \( k_f = k_2 \) and \( k_b = 0 \). Our result reflects the fact that A is rapidly converted to B which is subsequently converted to C at a rate \( k_2 \). This behavior is depicted in Figure 10.5. Note that while the approximate solution (black) deviates from the exact result at short times, it provides an accurate representation of the exact result (red) for longer times \( t \gg \frac{1}{k_1} \).

**Case #2 \( k_1 \ll k_2 \)**

In the regime \( k_1 \ll k_2 \), we expect that once B is made it is rapidly converted to C. Starting from the general solution

\[ B(t) = \frac{k_1 A_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right] \]

we can approximate

\[ \frac{k_1 A_0}{k_2 - k_1} \approx \frac{k_1 A_0}{k_2} \]

and

\[ \left[ e^{-k_1 t} - e^{-k_2 t} \right] \approx e^{-k_1 t} \]

so that

\[ B(t) \approx \frac{k_1 A_0}{k_2} e^{-k_1 t} \]

This result reflects the fact that the rate of production of B is governed by the slow conversion of A at a rate \( k_1 \). The prefactor is an effective initial condition for the amount of B created after a time \( t = \frac{1}{k_2} \) (see Figure 10.6).

Returning to the original kinetic scheme, taking \( k_1 \ll k_2 \) we find the approximate expression

\[ \frac{dB}{dt} + k_2 B = k_1 A_0 e^{-k_1 t} \rightarrow \frac{dB}{dt} + k_2 B = k_1 A_0 \]

For times \( \frac{1}{k_2} < t < \frac{1}{k_1} \), B will be converted to C at a rate much faster than it is created from A. As a result, the concentration of B will be small and relatively constant for times \( t < \frac{1}{k_1} \) shorter than the time scale for conversion of A to B. As such, we can say that

\[ \frac{dB}{dt} = 0 \]

as if the system was in a steady state condition and \( B(t) \approx A_0 \frac{k_1}{k_2} \). This is an effective initial condition for the amount of B. In this limit, the amount of B diminishes slowly in time at a rate \( k_1 \) from an effective initial amount given by \( B(0) \approx A_0 \frac{k_1}{k_2} \). This behavior is depicted in Figure 10.6. Note that the rate of decay of B is determined by the slow step of creating B from A with a time scale set by \( k_1 \).

**Case #3 \( k_1 = k_2 \)**

For the special case of \( k_1 = k_2 \) we note that

\[ B(t) = \frac{k_1 A_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right] \]
which can also be written
\[ B(t) = \frac{k_1A_0}{k_2 - k_1} e^{-k_1 t} \left[ 1 - e^{-(k_2 - k_1) t} \right] \]

As \( k_1 \to k_2 \) the difference
\[ 1 - e^{-(k_2 - k_1) t} \]
in the numerator goes to zero and the difference \((k_2 - k_1)\) in the denominator also goes to zero! We need to take care in evaluating \( B(t) \) when \( k_1 = k_2 \).

We can evaluate this limit using l'Hôpital’s rule or alternatively use the trick of expanding the exponential as a Taylor series
\[ e^{-(k_2 - k_1) t} = 1 - (k_2 - k_1) t + \ldots \]
Retaining only the leading order term \((k_2 - k_1) t\) we find
\[ B(t) = \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} \{ 1 - [1 - (k_2 - k_1) t] \} = k_1 A_0 t e^{-k_1 t} \quad (10.13) \]

Evaluating this solution, we see that initially \( B \) is produced from \( A \) at a rate \( k_1 \). This leads to a linear increase in \( B(t) \approx k_1 A_0 t \) at short times where \( t \ll 1/k_1 \) and the exponential term is near unity. As \( B \) is produced it is converted to \( C \). At longer times, the conversion of \( B \) to \( C \) exceeds the production of \( A \) from \( B \) and the overall amount of \( B \) decreases. The amount of \( B \) reaches a maximum value when
\[ \frac{d}{dt} B(t) = 0 \]
which is determined by
\[ \frac{d}{dt} B(t) = \frac{d}{dt} k_1 A_0 t e^{-k_1 t} = k_1 A_0 (1 - k_1 t) e^{-k_1 t} = 0 \]
with the solution \( t = 1/k_1 \). This behavior is depicted in Figure 10.7.

Let’s return to the original equation kinetic scheme where we set \( k_2 = k_1 \) at the beginning
\[ A \xrightarrow{k_1} B \xrightarrow{k_1} C \]
With the initial conditions \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \) we find
\[ \frac{dB}{dt} + k_1 B = k_1 A_0 e^{-k_1 t} \]
with the solution
\[ B(t) = e^{-\int k_1 dt} \left[ k_1 A_0 e^{-k_1 t} e^{\int k_1 dt} dt + C \right] = e^{-k_1 t} [k_1 A_0 t + C] \]
Evaluating this expression at \( t = 0 \) we find \( B(0) = C = 0 \) and the final result
\[ B(t) = k_1 A_0 t e^{-k_1 t} \]
As expected, this agrees with our result in Equation 10.13 found by evaluating the general solution in the limit \( k_1 \to k_2 \).

First order ordinary differential equations describing physical kinetics can be used to model population dynamics, the spread of infectious disease, predator-prey relations, and the reactions of atoms and molecules. These applications involving first order physical kinetics demonstrate the power of our general method for the solution of first order ordinary differential equations.
A10 Functions derived from exact differentials and integrating factors

Consider the exact differential of an unknown function \( f(x, y) \)
\[
df = a(x, y) \, dx + b(x, y) \, dy
\]
which satisfies Euler’s test
\[
\frac{\partial}{\partial y} a(x, y) = \frac{\partial}{\partial x} b(x, y)
\]
How can we determine the function \( f(x, y) \) for this exact differential? We approach this problem by first noting that
\[
\frac{\partial f}{\partial x} = a(x, y)
\]
so that
\[
f(x, y) = \int df = \int a(x, y) \, dx + c(y) \quad (10.14)
\]
Equation 10.14 provides an expression for \( f(x, y) \). If we can determine \( c(y) \) we can define \( f(x, y) \).

Let’s differentiate the proposed function \( f(x, y) \) with respect to \( y \) as
\[
\frac{\partial f}{\partial y} = \frac{\partial}{\partial y} \left[ \int a(x, y) \, dx + c(y) \right] = b(x, y)
\]
Rearranging this expression we find
\[
\frac{\partial}{\partial y} c(y) = b(x, y) - \frac{\partial}{\partial y} \left[ \int a(x, y) \, dx \right]
\]
We can integrate this expression to determine \( c(y) \) as
\[
c(y) = \int \left[ b(x, y) - \frac{\partial}{\partial y} \left[ a(x, y) \, dx \right] \right] \, dy
\]
This results in the final expression for \( f(x, y) \) as
\[
f(x, y) = \int a(x, y) \, dx + \int \left[ b(x, y) - \frac{\partial}{\partial y} \left[ a(x, y) \, dx \right] \right] \, dy \quad (10.15)
\]
While this form appears to be complicated, a few examples will demonstrate how to apply this method.

Suppose we have the total differential
\[
dV = \left( \frac{\partial V}{\partial r} \right) \, dr + \left( \frac{\partial V}{\partial h} \right) \, dh = 2\pi rh \, dr + \pi r^2 \, dh
\]
and want to determine the function \( V(r, h) \). Using our general result in Equation 10.15 we find
\[
V(r, h) = \int 2\pi rh \, dr + \int \left[ \pi r^2 - \frac{\partial}{\partial h} \left( 2\pi rh \right) \right] \, dh
\]
\[
= \pi r^2 h + \int \left[ \pi r^2 - \frac{\partial}{\partial h} \left( \pi r^2 h \right) \right] \, dh + C
\]
\[
= \pi r^2 h + \int \left[ \pi r^2 - \pi r^2 \right] \, dh + C = \pi r^2 h + C
\]
providing a form for the function \( V(r, h) \). To determine the integration constant
Now suppose we have an inexact differential
\[ q = nC_T dT + \frac{nRT}{V} dV \]
that fails Euler’s test
\[ \frac{\partial}{\partial V} (nC_T) = 0 \quad \frac{\partial}{\partial T} \left( \frac{nRT}{V} \right) = \frac{nR}{V} \]
It is possible to turn this inexact differential into an exact differential by applying an integrating factor. If we divide by \( T \) we have a new total differential
\[ \frac{q}{T} = \frac{nC_V}{T} dT + \frac{nR}{V} dV \]
which passes Euler’s test
\[ \frac{\partial}{\partial V} \left( \frac{nC_V}{T} \right) = 0 \quad \frac{\partial}{\partial T} \left( \frac{nR}{V} \right) = 0 \]
and is an exact differential. We can integrate this exact differential to determine a function that we will call
\[ S(T, V) = \frac{q}{T} \]

We find that
\[
S(T, V) = \int \frac{nC_V}{T} dT + \int \left[ \frac{nR}{V} - \frac{\partial}{\partial V} \left( \frac{nC_V}{T} \right) \right] dV \\
= nC_V \ln(T) + \int nR dV + \int \left( \frac{nR}{V} - \frac{\partial}{\partial V} nC_V \ln(T) \right) dV + C \\
= nC_V \ln(T) + nR \ln(V) + C \\
\]
To determine the integration constant \( C \) we note that when \( n = 0 \) the function \( S = 0 \), therefore \( C = 0 \). Finally, we can prove our result by taking the total differential of \( S(T, V) \) to find
\[ dS(T, V) = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV = \frac{nC_V}{T} dT + \frac{nR}{V} dV \]
as desired. The function \( S(V, T) \) and its first derivatives \( S_T(V, T) \) (gray) and \( S_V(T, V) \) are shown graphically in Figure 10.8.

\[ \text{Figure 10.8: The function } S(V, T) = nC_V \ln(T) + nR \ln(V) \text{ (red) plotted with the first derivatives } S_T(V, T) \text{ (black) and } S_V(T, V) \text{ (gray).} \]
B10 End-of-chapter problems

It is still an unending source of surprise for me to see how a few scribbles on a blackboard or on a sheet of paper could change the course of human affairs
Stanislaw Ulam

Warm-ups

10.1 Determine the general solution, \( y(x) \), for the following first order linear differential equations. Take \( k_1, k_2, \) and \( a \) to be constants.

(a) \( \frac{dy(x)}{dx} + 3y(x) = 0 \)
(b) \( x \frac{dy(x)}{dx} + y(x) = x^2 + 1 \)
(c) \( \frac{dx(t)}{dt} = k_1(a - x(t)) - k_2x(t) \)
(d) \( \frac{df(r)}{dr} + 4rf(r) = r \)

10.2 Consider the differential equation
\( \frac{dy(x)}{dx} = x^2 - 3xy(x) \)

(a) Find the general solution, \( y(x) \).
(b) Prove that your solution is correct by inserting your result for \( y(x) \) into the differential equation and confirming the equality.

10.3 Consider the differential equation
\( \frac{dy(x)}{dx} + 2x^2y(x) = x^2 + 2 \)

(a) Find the general solution, \( y(x) \).
(b) Prove that your solution is correct by inserting your result for \( y(x) \) into the differential equation and confirming the equality.

10.4 Find the general solution, \( f(r) \), to the following differential equation
\( r \frac{df(r)}{dr} + f(r) = 2r \)

with boundary condition \( f(2) = 2 \).

10.5 Find the general solution, \( s(t) \), to the following differential equation
\( t \frac{ds(t)}{dt} = (3t + 1)s(t) + t^3 e^{3t} \)

with boundary condition \( \left. \frac{ds}{dt} \right|_{t=0} = 1 \).

Homework exercises

10.6 Find the general solution, \( m(t) \), to the differential equation
\( \frac{dm(t)}{dt} + \frac{4m(t)}{20 + t} = 2 \)

with initial condition \( m(0) = 20 \).
10.7 Consider the Clapeyron equation, a first order differential equation describing the change in pressure, $p(T)$, with changing temperature, $T$

$$\frac{dp(T)}{dT} = \frac{\Delta H}{T(V_g - V_l)}$$

where $\Delta H$ is the enthalpy of vaporization and $V_g$ and $V_l$ are the volumes of the bulk substance in the gas and liquid phases, respectively. Since $V_g \gg V_l$, we find that

$$\frac{dp(T)}{dT} = \frac{\Delta H}{T V_g} \approx \frac{\Delta H}{T}$$

Using the ideal gas equation of state, we arrive at the differential equation

$$\frac{dp(T)}{dT} = \frac{\Delta H}{R T^2} p(T)\]$$

(a) Solve this equation for $p(T)$. Your solution will include an undetermined constant $C$.

(b) Consider the log-lin plot below where $p(T_0) = p_0$ is the reference pressure at the reference temperature $T_0$ (red dot). Express the constant $C$ in terms of $p_0$ and $T_0$.

10.8 In physical kinetics, we frequently encounter the reaction

$$A \xrightarrow{k_f \quad k_b} B$$

The corresponding rate equation is

$$\frac{dA}{dt} = -k_f A + k_b B$$

where $k_f$ and $k_b$ are the forward and backward rate constants. By conservation of mass, we know that $A(t) + B(t) = A_0 + B_0$ with the initial conditions $A(0) = A_0$ and $B(0) = B_0$.

(a) Solve for $A(t)$ and $B(t)$.

(b) The reaction quotient $Q(t) = B(t)/A(t)$. At sufficiently long times we find

$$\lim_{t \to \infty} Q(t) = \frac{B(\infty)}{A(\infty)} = K_{eq}$$

Show that $K_{eq} = k_f/k_b$.

10.9 A container holds 50.0 L of a 1.00 mol/L solution. Pure water is added to the container at a rate of 1.00 L/s. The resulting solution is pumped out of the container at a rate of 0.50 L/s. How long will it take for the solution to reach a concentration of 0.05 mol/L?
10.10 Consider the following two total differentials for the pressure, \( p \), as a function of temperature, \( T \), and volume, \( V \).

\[
(a) \quad \frac{2RT}{(V - b)^2} \, dV + \frac{R(V - b)}{b^2} \, dT \quad \quad (b) \quad - \frac{RT}{(V - b)^2} \, dV + \frac{R}{(V - b)} \, dT
\]

Determine if either or both are exact differentials.

10.11* Consider the exact differential for a function of two variables

\[
dp(T, V) = \frac{nR}{V} \, dT - \frac{nRT}{V^2} \, dV
\]

Use the method of integrating factors and Equation 10.15 to find the function \( p(T, V) \). To validate your result, show that the function \( p(V, T) \) has the correct total differential.

10.12* Consider the exact differential for a function of two variables

\[
dE(T, V) = nCV \, dT + \frac{n^2a}{V^2} \, dV
\]

Use the method of integrating factors and Equation 10.15 to find the function \( E(T, V) \). To validate your result, show that the function \( E(T, V) \) has the correct total differential.

10.13* Use Euler’s test to prove that the total differential \( f'(x)g(y)dx + f(x)g'(y)dy \) is an exact differential. Use the method of integrating factors and Equation 10.15 to find the corresponding function \( h(x, y) \).

10.14* Consider the two coupled first order differential equations

\[
\frac{dx(t)}{dt} = \frac{p(t)}{m} \quad \quad \frac{dp(t)}{dt} = -kx(t)
\]

where \( k \) and \( m \) are constants. The functions \( x(t) \) and \( p(t) \) are related by the equation

\[
2E = kx(t)^2 + \frac{1}{m}p(t)^2 = \text{constant}
\]

which forms an ellipse in the \( xp \)-plane (see figure).

(a) Define the complex variable

\[
\rho(t) = \sqrt{k}x(t) + \frac{1}{\sqrt{m}}p(t)
\]

where \( x(t) = \frac{1}{\sqrt{k}} \text{Re}[\rho(t)] \) and \( p(t) = \sqrt{m} \text{Im}[\rho(t)] \). Show that \( |\rho|^2 = \rho^*\rho = 2E \).

(b) Show that the first order differential equation for the complex variable \( \rho(t) \) written

\[
\frac{d\rho(t)}{dt} = -i\omega \rho(t) \quad \quad \omega^2 = \frac{k}{m}
\]
is equivalent to the two first order differential equations above for the real variables $x(t)$ and $p(t)$.

(c) Solve this equation to find

$$\rho(t) = \left(\sqrt{k}x_0 + i \frac{1}{\sqrt{m}}p_0\right) e^{-i \omega t}$$

where $x(0) = x_0$ and $p(0) = p_0$.

(d) Show that

$$x(t) = \frac{1}{\sqrt{k}} \text{Re}[\rho(t)] = x_0 \cos(\omega t) + \frac{p_0}{m\omega} \sin(\omega t)$$

$$p(t) = \sqrt{m} \text{Im}[\rho(t)] = p_0 \cos(\omega t) - m\omega x_0 \sin(\omega t)$$
Since \( y_1(x) = c_1 e^{\alpha x} \) and \( y_2(x) = c_2 e^{-\alpha x} \) are each solutions to the linear second order differential equation, it follows that the linear superposition \( y(x) = y_1(x) + y_2(x) \) is also a solution.

We could equivalently propose solutions of the from \( c_1' \cos(ax) \) and \( c_2' \sin(ax) \).
Now consider the homogeneous linear second order ordinary differential equation
\[ \frac{d^2}{dx^2} y(x) + b \frac{d}{dx} y(x) + c y(x) = 0 \] (11.3)
with constant coefficients \( b \) and \( c \). We propose the ansatz
\[ y(x) = e^{\alpha x} \]
where \( \alpha \) is a complex number. Inserting this form for \( y(x) \) we find
\[ \frac{d^2}{dx^2} e^{\alpha x} + b \frac{d}{dx} e^{\alpha x} + c e^{\alpha x} = \alpha^2 e^{\alpha x} + b \alpha e^{\alpha x} + c e^{\alpha x} = 0 \]
Ignoring the trivial solution \( e^{\alpha x} = 0 \), we arrive at the result \(^3\)
\[ \alpha^2 + b\alpha + c = 0 \] (11.4)
known as the auxiliary equation. This quadratic equation in the variable \( \alpha \) has two roots, \( \alpha_{\pm} \), defined by the quadratic formula
\[ \alpha_{\pm} = \frac{-b \pm \sqrt{b^2 - 4c}}{2} \]
Returning to our ansatz, we observe that both \( c_1 e^{\alpha_{+} x} \) and \( c_2 e^{\alpha_{-} x} \) are solutions to Equation 11.3, where \( c_1 \) and \( c_2 \) are constant coefficients. As such, we write the general solution to Equation 11.3 as
\[ y(x) = c_1 e^{\alpha_{+} x} + c_2 e^{\alpha_{-} x} \] (11.5)
where the constant coefficients \( c_1 \) and \( c_2 \) are determined by the boundary conditions typically defined in terms of the value of the function, \( y(0) \), and its derivative, \( y'(0) \).

11.1.2 Qualitative theory of second order ordinary differential equations

Our observations above can be summarized as follows. For the second order differential equation
\[ \frac{d^2}{dx^2} y(x) + b \frac{d}{dx} y(x) + c y(x) = 0 \]
there is a general solution of the form
\[ y(x) = c_1 e^{\alpha_{+} x} + c_2 e^{\alpha_{-} x} \]
where the constants \( \alpha_{\pm} \) are the roots of the auxiliary equation
\[ \alpha^2 + b\alpha + c = 0 \]
defined by the quadratic formula
\[ \alpha_{\pm} = \frac{-b \pm \sqrt{b^2 - 4c}}{2} \]
The nature of the solution \( y(x) \) is determined by the roots \( \alpha_{\pm} \), which may be real, imaginary, complex, or degenerate (double) roots depending on the particular values of the parameters \( b \) and \( c \).

The nature of the roots in each range of the \( bc \)-parameter space is depicted in Figure 11.1. When \( b^2 > 4c \), the roots \( \alpha_{\pm} \) are real, resulting in a solution \( y(x) \) that is exponentially increasing or decreasing with increasing \( x \). When \( b = 0 \), the roots \( \alpha_{\pm} \) are imaginary, resulting in a solution \( y(x) \) that is a purely oscillatory function of \( x \). When \( b^2 < 4c \), the roots \( \alpha_{\pm} \) are complex, leading to a solution
More ordinary differential equations

223

\[ b^2 = 4c \]

double imaginary sinusoidal

complex complex oscillatory oscillatory
damped forced

real (+, +) exponential increase

real (−, −) exponential decrease

real (+, −) hyperbolic

real (−, +) hyperbolic

Figure 11.1: The nature of roots of the auxiliary equation as a function of the parameters \( b \) and \( c \). Double roots are found on the parabola defined by \( b^2 = 4c \) (thick green). Complex roots are found atop the parabolic curve for \( c > b^2/4 \). Purely imaginary roots occupy a surface normal to the \( bc \)-plane (thick blue). In this projection, imaginary roots are restricted to the positive \( c \)-axis. Below the parabolic curve the roots are real, forming exponential or hyperbolic functions.

\[ y(x) \]

that oscillates with an amplitude that exponentially increases or decreases with increasing \( x \). Finally, when \( b^2 = 4c \), we find the special case of double roots where \( \alpha_+ = \alpha_- \). Examples of the various kinds of solutions to Equation 11.3 are presented in Figure 11.2.

This analysis suggests that Equation 11.3

\[
\frac{d^2}{dx^2} y(x) + b \frac{d}{dx} y(x) + c y(x) = 0
\]

can be used to model a wide variety of physical phenomena. Real roots support solutions involving exponentially decaying or growing functions of the kind found in physical kinetics, capturing the behavior of populations or concentrations that grow or diminish exponentially in time. Imaginary roots support solutions involving oscillatory functions of the kind used to model waves found in the study of quantum theory as well as classical wave theory. Complex roots result in oscillating functions with amplitudes that may grow or diminish and can be used to model physical systems such as an oscillating mass on a spring in a viscous medium. In the next section, we explore the solution of Equation 11.3 for a variety of examples relevant to modeling processes in the physical sciences.

11.2 Applications of second order differential equations

Second order differential equations with constant coefficients yield solutions exhibiting a wide range of behavior, including exponential growth or decay, sinusoidal oscillation, and exponentially attenuated oscillation. This section explores applications exhibiting the variety of behavior found in solutions of second order ordinary differential equations.

11.2.1 Survey of second order ordinary differential equations

We will explore specific examples of differential equations representing each of these unique regimes, having real roots, imaginary roots, complex roots, and double roots. In doing so, we will appreciate how this variety of solutions can be used to model a remarkable diversity of physical systems.
Case #1 real roots

When the coefficients $b$ and $c$ are such that $b^2 > 4c$, the roots

$$a_{\pm} = \frac{-b \pm \sqrt{b^2 - 4c}}{2}$$

are real. For the case $c = 0$, there will be one zero root and one non-zero root equal to $-b$ leading to a solution of the form

$$y(x) = c_1 + c_2 e^{-b x}$$

For the more general case of $c \neq 0$ and $b^2 > 4c$, the roots of the auxiliary equation $a_{\pm}$ are real and the solution $y(x)$ will have exponentially divergent behavior as a function of $x$.

When the coefficients $c_1$ and $c_2$ are of the same sign, the solution $y(x)$ has the character of a hyperbolic cosine (see Figure 11.3, red line). In contrast, when the coefficients $c_1$ and $c_2$ are of opposite sign, the general solution has the character of a hyperbolic sine (see Figure 11.3, black line). In each case, the solution $y(x)$ diverges with increasing $x$. Exponential growth of this kind is observed in population growth as observed in Chapter 10.

Let’s explore the solution of the second order ordinary differential equation

$$\frac{d^2}{dx^2} y(x) + \frac{d}{dx} y(x) - 2y(x) = 0$$

(11.6)

with the boundary conditions $y(0) = 3$ and $y'(0) = 0$. We take the ansatz

$$y(x) = e^{\alpha x}$$

and insert it into Equation 11.6 as

$$\frac{d^2}{dx^2} e^{\alpha x} + \frac{d}{dx} e^{\alpha x} - 2e^{\alpha x} = \alpha^2 e^{\alpha x} + \alpha e^{\alpha x} - 2e^{\alpha x} = 0$$

leading to the auxiliary equation

$$\alpha^2 + \alpha - 2 = (\alpha - 1)(\alpha + 2) = 0$$

This quadratic equation has real roots

$$\alpha_{\pm} = \left\{ \begin{array}{ll} 1 \\ -2 \end{array} \right.$$

leading to the general solution defined by Equation 11.5

$$y(x) = c_1 e^{\alpha x} + c_2 e^{-\alpha x}$$

The coefficients $c_1$ and $c_2$ are determined by applying the boundary conditions

$$y(0) = c_1 + c_2 = 3$$

and

$$\left. \frac{dy}{dx} \right|_{x=0} = \left[ c_1 e^{\alpha x} - 2c_2 e^{-\alpha x} \right]_{x=0} = c_1 - 2c_2 = 0$$

We find $c_1 = 3 - c_2$ and $c_2 = 2c_1$ so that $c_1 = 2$ and $c_2 = 1$. The final solution to Equation 11.6 is

$$y(x) = 2e^{\alpha x} + e^{-\alpha x}$$

(11.7)

This result is plotted in Figure 11.4. Note that we can validate our solution,
Equation 11.7, by inserting it into the original differential equation, Equation 11.6, and proving the equality.

\textit{Case \#2 imaginary roots}

When the coefficients $b$ and $c$ are such that $b^2 < 4c$ and $b = 0$, the roots

$$a_\pm = \pm i \sqrt{c}$$

are purely imaginary leading to solutions of the form

$$y(x) = c_1 e^{i \sqrt{c} x} + c_2 e^{-i \sqrt{c} x}$$

(11.8)

Recall that Euler’s formula provides a connection between exponentials of imaginary arguments and the cosine and sine functions

$$e^{ix} = \cos(x) + i \sin(x)$$

Using this identity, we can reformulate Equation 11.8 as

$$y(x) = c'_1 \cos(\sqrt{c} x) + c'_2 \sin(\sqrt{c} x)$$

where $c'_1 = c_1 + i c_2$ and $c'_2 = i(c_1 - c_2)$. When the roots of the auxiliary equation are imaginary and the coefficients $c_1$ and $c_2$ are real, the resulting solution $y(x)$ is a real sinusoidal function of $x$.

Let’s apply this method to solve the second order ordinary differential equation

$$\frac{d^2}{dx^2} y(x) + 9 y(x) = 0$$

(11.9)

with the boundary conditions $y(0) = 1$ and $y'(0) = 6$. We take the ansatz

$$y(x) = e^{ax}$$

and insert it into Equation 11.9 as

$$\frac{d^2}{dx^2} e^{ax} + 9 e^{ax} = a^2 e^{ax} + 9 e^{ax} = 0$$

leading to the auxiliary equation

$$a^2 + 9 = (a - 3i)(a + 3i) = 0$$

This quadratic equation has imaginary roots

$$a_\pm = \begin{cases} 
3i \\
-3i 
\end{cases}$$

leading to the general solution defined by Equation 11.5

$$y(x) = c'_1 \cos(3x) + c'_2 \sin(3x)$$

The coefficients $c'_1$ and $c'_2$ can be determined by applying the boundary conditions

$$y(0) = c'_1 = 1$$

and

$$\left. \frac{dy}{dx} \right|_{x=0} = [-3c'_1 \sin(3x) + 3c'_2 \cos(3x)]_{x=0} = 3c'_2 = 6$$

We find $c'_1 = 1$ and $c'_2 = 2$. The final solution to Equation 11.9 is

$$y(x) = \cos(3x) + 2 \sin(3x)$$

(11.10)
This result is plotted in Figure 11.5. Note that we can validate our solution, Equation 11.10, by inserting it into the original differential equation, Equation 11.9, and proving the equality.

Case #3 complex roots

When the coefficients $b$ and $c$ are such that $b^2 < 4c$, the radical $\sqrt{b^2 - 4c}$ is imaginary. When $b \neq 0$ the roots

$$\alpha \pm \frac{\sqrt{b^2 - 4c}}{2}$$

are complex with real and imaginary parts. As a result, solutions are of the form

$$y(x) = c_1 \exp \left[ -\frac{1}{2} \left( b - i\sqrt{c'} \right) x \right] + c_2 \exp \left[ -\frac{1}{2} \left( b + i\sqrt{c'} \right) x \right]$$

where $c' = b^2 - 4c$. Pulling out the common exponential factor $e^{-bx/2}$ leads to

$$y(x) = e^{-bx/2} \left[ c_1 e^{i\sqrt{c'} x/2} + c_2 e^{-i\sqrt{c'} x/2} \right]$$

Using Euler’s formula, we can convert the sum of exponentials with imaginary arguments to sinusoidal functions as

$$y(x) = e^{-bx/2} \left[ c'_1 \cos \left( \sqrt{c'} x / 2 \right) + c'_2 \sin \left( \sqrt{c'} x / 2 \right) \right]$$

where again $c'_1 = c_1 + c_2$ and $c'_2 = i(c_1 - c_2)$. The solutions $y(x)$ are exponentially decreasing ($b > 0$) or increasing ($b < 0$) sinusoidal functions.

Let’s apply this method to solve the second order ordinary differential equation

$$\frac{d^2}{dx^2} y(x) + 2 \frac{d}{dx} y(x) + 10 y(x) = 0$$

with the boundary conditions $y(0) = 1$ and $y'(0) = 0$. We take the ansatz

$$y(x) = e^{ax}$$

and insert it into Equation 11.11 as

$$\frac{d^2}{dx^2} e^{ax} + 2 \frac{d}{dx} e^{ax} + 10 e^{ax} = a^2 e^{ax} + 2ae^{ax} + 10 e^{ax} = 0$$

leading to the auxiliary equation

$$a^2 + 2a + 10 = 0$$

This quadratic equation has complex roots

$$\alpha = \left\{ -1 + 3i, -1 - 3i \right\}$$

leading to the general solution defined by Equation 11.5

$$y(x) = e^{-x} \left[ c_1 e^{3ix} + c_2 e^{-3ix} \right]$$

more conveniently written

$$y(x) = e^{-x} \left[ c'_1 \cos(3x) + c'_2 \sin(3x) \right]$$

The coefficients $c'_1$ and $c'_2$ can be determined by applying the boundary condi-
ordinary differential equations

\[ y(x) = e^{-x} \left[ \cos(3x) + \frac{1}{3} \sin(3x) \right] \]  

This result is plotted in Figure 11.6 (black line). The solution exhibits oscillations that exponentially decay with increasing \( x \). Note that we can validate our solution, Equation 11.12, by inserting it into the original differential equation, Equation 11.11, and proving the equality.

Now consider the second order ordinary differential equation

\[
\frac{d^2}{dx^2} y(x) - 2 \frac{d}{dx} y(x) + 10 y(x) = 0 \quad (11.13)
\]

where we have changed the coefficient of the middle term from \( b = 2 \) in Equation 11.11 to \( b = -2 \). The roots of the auxiliary equation become

\[
\alpha_\pm = \left\{ \frac{1 + 3i}{2}, \frac{1 - 3i}{2} \right\}
\]

leading to the general solution

\[ y(x) = c_1 e^{\alpha x} + c_2 x e^{\alpha x} \]

The decaying exponential in Equation 11.12 has been replaced with a growing exponential. Applying the boundary conditions \( y(0) = 0 \) and \( y'(0) = 1/200 \), the final result is

\[ y(x) = \frac{1}{600} e^{x} \sin(3x) \]

shown in Figure 11.6 (red line). The solution exhibits oscillations that exponentially grow in amplitude with increasing \( x \).

**Case #4 double roots**

When the coefficients \( b \) and \( c \) are such that \( b^2 = 4c \), the radical \( \sqrt{b^2 - 4c} \) is zero and the two roots of the auxiliary equation are degenerate

\[ \alpha_\pm = \alpha = -\frac{b}{2} \]

This case is known as double roots. In the case of double roots, the solution takes the special form

\[ y(x) = c_1 e^{\alpha x} + c_2 x e^{\alpha x} \]

Let’s prove this is true for the second order ordinary differential equation

\[
\frac{d^2}{dx^2} y(x) + 2 \frac{d}{dx} y(x) + y(x) = 0 \quad (11.14)
\]

with boundary conditions \( y(0) = 1 \) and \( y'(0) = -3 \). The solution to the
corresponding auxiliary equation

\[ \alpha^2 + 2\alpha + 1 = (\alpha + 1)(\alpha + 1) = 0 \]

is the double root \( \alpha = -1 \) leading to the special solution

\[ y(x) = c_1 e^{-x} + c_2 x e^{-x} \]

Applying the boundary conditions

\[ y(0) = c_1 = 1 \]

and

\[ \left. \frac{dy}{dx} \right|_{x=0} = [-c_1 e^{-x} + c_2 (e^{-x} - x e^{-x})]_{x=0} = -c_1 + c_2 = -3 \]

so that \( c_1 = 1 \) and \( c_2 = -2 \). The final result

\[ y(x) = e^{-x} - 2x e^{-x} \quad (11.15) \]

is shown in Figure 11.7. Checking our solution, we use \( y'(x) = -3e^{-x} + 2xe^{-x} \) and \( y''(x) = 5e^{-x} - 2xe^{-x} \). Inserting these relations into our original Equation 11.14 yields

\[
\frac{d^2}{dx^2} y(x) + 2 \frac{dy}{dx} y(x) + y(x) = (5e^{-x} - 2xe^{-x}) + 2 (-3e^{-x} + 2xe^{-x}) + (e^{-x} - 2xe^{-x}) = 0
\]

validating our solution.

When we model a system using Equation 11.3 where

\[
\frac{d^2}{dx^2} y(x) + b \frac{dy}{dx} y(x) + c y(x) = 0
\]

the coefficients \( b \) and \( c \) are real numbers defined by fundamental physical constants. The coincidence of having an auxiliary equation with the exact equality \( b^2 = 4c \) is unlikely. As such, we do not expect to encounter double roots when when solving accurately parameterized models of physical systems.

In this section, we have developed a general method for the solution of linear second order ordinary differential equations with constant coefficients \( b \) and \( c \), as in Equation 11.3. In the section that follows, we explore a more general class of second order ordinary differential equations applicable to cases where the coefficients \( b(x) \) and \( c(x) \) are functions of \( x \).
11.3 Power series solutions to differential equations

Many first and second order ordinary differential equations yield solutions represented by common functions such as the exponential, sine and cosine, and hyperbolic sine and cosine. Our approach has been to make an educated guess or ansatz, plug that in, and find a set of parameters representing a solution. However, it is possible to employ a more general approach to the solution of ordinary differential equations in which our ansatz is a power series representing continuous and differentiable functions normally encountered in modeling physical systems. In this section, we will explore this general and powerful approach to the solution of first and second order ordinary differential equations.

11.3.1 Solving ordinary differential equations using power series

Let’s review our current ability to solve first and second order ordinary differential equations. We developed a general solution for homogeneous and non-homogeneous linear first order ordinary differential equations of the form

$$\frac{d}{dx}y(x) + q(x)y(x) = r(x)$$

and homogeneous linear second order ordinary differential equations with constant coefficients\(^5\)

$$\frac{d^2}{dx^2}y(x) + b \frac{d}{dx}y(x) + c y(x) = 0$$

However, we have no general solution for non-homogeneous linear second order ordinary differential equations of the form

$$\frac{d^2}{dx^2}y(x) + b(x) \frac{d}{dx}y(x) + c(x) y(x) + d(x) = 0$$

We also have no general solution for homogeneous linear second order ordinary differential equations where \(d(x) = 0\) but the coefficients \(b(x)\) and \(c(x)\) depend on \(x\).

How can we solve this more general differential equation when we cannot anticipate the specific form of our solution? We recall that most functions used to model physical properties can be expressed as a power series

$$y(x) = \sum_{n=0}^{\infty} a_n x^n$$

Depending on the specific set of coefficients \(\{a_n\}\), the function \(y(x)\) may be an exponential, sinusoid, damped sinusoid, polynomial, logarithm, or a variety of other functions. With this insight, we propose the power series as our ansatz, representing a general continuous and differentiable function. Inserting our proposed solution into the differential equation of interest, we solve for the coefficients \(\{a_n\}\) defining our solution. Let’s see how this works by solving two familiar ordinary differential equations using the power series method.

11.3.2 Power series solutions for first order differential equations

Let’s apply this approach to solve the familiar first order ordinary differential equation

$$\frac{d}{dx}y(x) + y(x) = 0 \quad (11.16)$$
with the boundary condition \( y(0) = 2 \). As our ansatz we propose the power series

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n
\]

(11.17)

Inserting this proposed solution in Equation 11.16, we must evaluate the first derivative of \( y(x) \) with respect to \( x \) as

\[
\frac{d}{dx} y(x) = \frac{d}{dx} \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} a_n \left( \frac{d}{dx} x^n \right) = \sum_{n=0}^{\infty} a_n n x^{n-1}
\]

Using this result in Equation 11.16 we find

\[
\frac{d}{dx} y(x) + y(x) = \sum_{n=0}^{\infty} a_n n x^{n-1} + \sum_{n=0}^{\infty} a_n x^n = 0
\]

To simplify this result, we must add the two power series together. To do that, we must form each series over the same range of \( n \) with terms of a given \( n \) having the same power of \( x \).

We are left to combine the two series. In the first series, the coefficient is proportional to \( n \) so that the \( n = 0 \) term is always zero. Removing the \( n = 0 \) term from the first series results in

\[
\sum_{n=0}^{\infty} a_n n x^{n-1} \rightarrow \sum_{n=1}^{\infty} a_n n x^{n-1} = a_1 + a_2 x + a_3 x^2 + \ldots
\]

where we have increased the lower end of the index \( n \) from 0 to 1. We are left to add the two series

\[
\sum_{n=1}^{\infty} a_n n x^{n-1} + \sum_{n=0}^{\infty} a_n x^n = 0
\]

This first power series starts from \( n = 1 \), but we would like this series to start from \( n = 0 \). To accomplish this, we shift the index \( n \rightarrow n + 1 \) with the result

\[
\sum_{n=1}^{\infty} a_n n x^{n-1} \rightarrow \sum_{n=0}^{\infty} a_{n+1} (n+1) x^n = a_1 + a_2 x + a_3 x^2 + \ldots
\]

Properly shifting the index in a power series can be tricky, but we will learn to do this with practice.\(^6\) Returning to our initial equation we find

\[
\frac{d}{dx} y(x) + y(x) = \sum_{n=0}^{\infty} a_{n+1} (n+1) x^n + \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} [a_{n+1} (n+1) + a_n] x^n = 0
\]

(11.18)

For Equation 11.18 to be true for all \( x \), it must be that

\[
a_{n+1} (n+1) + a_n = 0
\]

for all values of \( n = 0, 1, 2, \ldots \). This leads to the recursion relation. It tells us that

\[
a_{n+1} = -\frac{a_n}{n+1} \quad n = 0, 1, 2, \ldots
\]

and can be used to recursively generate our coefficients (see Figure 11.8).\(^7\)

We take our first coefficient to be \( a_0 \), a value we will determine later using our boundary conditions. We can generate the coefficient \( a_1 \) as

\[
a_1 = -\frac{a_0}{0+1} = -a_0
\]

where the negative sign in the recursion relation tells us that our solution for

\( \) Equivalently, you can introduce a new index \( n' = n - 1 \), substituting \( n \rightarrow n' + 1 \). You can then rewrite the new index \( n' \) as \( n \) before combining the sums. Try both approaches and see what works best for you.

\( \) The negative sign in the recursion relation signals the fact that the coefficients lead to an alternating series.

![Figure 11.8: The power series coefficients \( a_n = (-1)^n a_0 / n! \) (red dots) for \( a_0 = 1. \)](image-url)
\( y(x) \) will be an alternating series. We can continue to generate coefficients as

\[
a_2 = -\frac{a_1}{1+1} = -\frac{1}{2}a_1 = -\frac{1}{2} (-a_0) = \frac{1}{2} a_0
\]

and

\[
a_3 = -\frac{a_2}{2+1} = -\frac{1}{3}a_2 = -\frac{1}{3} \left( \frac{1}{2} a_0 \right) = -\frac{1}{3 \cdot 2} a_0
\]

and so on. In general, we recognize that

\[
a_n = (-1)^n \frac{1}{n!} a_0 \quad n = 0, 1, 2, \ldots
\]

Inserting this result for our coefficients in our original power series Equation 11.17 we find

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} a_0 x^n = a_0 \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} x^n
\]

We recognize this result as the power series of an exponential

\[
e^{-x} = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} x^n
\]

so that

\[
y(x) = a_0 e^{-x}
\]

Applying our initial condition that \( y(0) = 3 \) and \( y'(0) = 1 \). As our ansatz we propose

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n
\]

Inserting this proposed solution in Equation 11.17 we find

\[
\frac{d^2}{dx^2} y(x) + y(x) = \sum_{n=0}^{\infty} a_n x^n + \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} a_n (n+1) x^{n-2} = 0
\]

11.3.3 Power series solutions for second order differential equations

Consider the second order ordinary differential equation

\[
\frac{d^2}{dx^2} y(x) + y(x) = 0 \quad (11.19)
\]

with the initial conditions \( y(0) = 3 \) and \( y'(0) = 1 \). As our ansatz we propose

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n
\]

Inserting this proposed solution in Equation 11.19, we must evaluate the second derivative of \( y(x) \) with respect to \( x \) as

\[
\frac{d^2}{dx^2} y(x) = \frac{d^2}{dx^2} \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} a_n \left( \frac{d^2}{dx^2} x^n \right) = \sum_{n=0}^{\infty} a_n n(n-1)x^{n-2}
\]

Inserting this result in Equation 11.19 we find

\[
\frac{d^2}{dx^2} y(x) + y(x) = \sum_{n=0}^{\infty} a_n n(n-1)x^{n-2} + \sum_{n=0}^{\infty} a_n x^n = 0
\]

We are left to combine the two series. In the first series, the coefficient is
proportional to \(n(n-1)\) so that the \(n=0\) and \(n=1\) terms are always zero. Removing the \(n=0\) and \(n=1\) terms from the first series results in
\[
\sum_{n=0}^{\infty} a_n(n-1)x^{n-2} \rightarrow \sum_{n=2}^{\infty} a_n(n-1)x^{n-2}
\]
This leaves us with
\[
\sum_{n=2}^{\infty} a_n(n-1)x^{n-2} + \sum_{n=0}^{\infty} a_nx^n = 0
\]
The first power series starts from \(n=2\), but we would like this series to start from \(n=0\) as we must eventually combine the first series with the second series that starts from \(n=0\). To accomplish this, we shift the index \(n \rightarrow n+2\) by substituting \(n \rightarrow n+2\), \(n-1 \rightarrow n+1\), and \(n-2 \rightarrow n\) with the result:
\[
\sum_{n=2}^{\infty} a_n(n-1)x^{n-2} \rightarrow \sum_{n=0}^{\infty} a_{n+2}(n+2)(n+1)x^{n}
\]
Returning to our initial equation we find
\[
\frac{d^2}{dx^2}y(x) + y(x) = \sum_{n=0}^{\infty} a_{n+2}(n+2)(n+1)x^{n} + \sum_{n=0}^{\infty} a_nx^n = \sum_{n=0}^{\infty} [a_{n+2}(n+2)(n+1) + a_n]x^n = 0
\]
leading to the condition
\[
a_{n+2}(n+2)(n+1) + a_n = 0
\]
and the recursion relation
\[
a_{n+2} = -\frac{1}{(n+2)(n+1)}a_n \quad n = 0, 1, 2, \ldots
\]
that we will use to generate the set of power series coefficients (see Figure 11.9). The coefficients \(a_0\) and \(a_1\) will be determined through our boundary conditions. The coefficients with even indices are
\[
a_0 = a_2 = -\frac{a_0}{2}, \quad a_4 = -\frac{a_2}{4} = -\frac{a_0}{4}, \quad a_6 = -\frac{a_4}{6} = -\frac{a_0}{6!}
\]
and so on. As such
\[
a_{2n} = (-1)^n \frac{1}{(2n)!}a_0 \quad n = 0, 1, 2, \ldots
\]
(11.21)
The coefficients with odd indices are
\[
a_1 = a_3 = -\frac{a_1}{3}, \quad a_5 = -\frac{a_3}{5} = -\frac{a_1}{5!}, \quad a_7 = -\frac{a_5}{7} = -\frac{a_1}{7!}
\]
and so on, such that
\[
a_{2n+1} = (-1)^n \frac{1}{(2n+1)!}a_1 \quad n = 0, 1, 2, \ldots
\]
(11.22)
As we have identified the coefficients, we can form a series solution for \(y(x)\).

We will form two series, one for even powers of \(x\) and one for odd powers of \(x\), and combine those results. Inserting Equation 11.21 for even powers of \(x\) in our original power series Equation 11.20 results in\(^{10}\)
\[
a_0 \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n)!}x^{2n}
\]
\(^8\) Equivalently, you can introduce a new index \(n' = n - 2\), substituting \(n \rightarrow n' + 2\). You can then rewrite the new index \(n'\) as \(n\) before combining the sums.

\(^9\) Again, the negative sign in the recursion relation signals the fact that the coefficients lead to an alternating series.

\(^{10}\) Note that the sum
\[
\sum_{n=0}^{\infty} x^{2n}
\]
contains only even powers of \(x\).
while inserting Equation 11.22 for odd powers of $x$ in our original power series
Equation 11.20 results in

$$a_1 \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1}$$

Combining these results we arrive at the result

$$y(x) = a_0 \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n)!} x^{2n} + a_1 \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1}$$

Referring to our results for power series expansions of familiar functions explored in Chapter 7, including Equation 7.3 and Equation 7.2, we recognize that \textsuperscript{11}

$$\cos(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} x^{2n} \quad \sin(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} x^{2n+1}$$

We can reform our result as

$$y(x) = a_0 \cos(x) + a_1 \sin(x)$$

Applying the boundary condition $y(0) = 3$ leads to $y(0) = a_0 = 3$ while the boundary condition $y'(0) = 1$ leads to $a_1 = 1$. Our final solution is

$$y(x) = 3 \cos(x) + \sin(x)$$

which can be validated by inserting our result for $y(x)$ into Equation 11.19 and proving the equality.

We have used the power series method to rederive familiar solutions to first and second order ordinary differential equations. However, the power series method provides a general means to solve more complicated ordinary differential equations. Specific examples derived from the physical sciences are explored in the Complements.

\textbf{A\textsubscript{11}} Quantum theory of a particle in a box

Consider the time-independent Schrödinger equation for a particle in one-dimension

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \quad (11.23)$$

where $\hbar = h/2\pi$, $h$ is Planck’s constant, $m$ is the mass of the particle, $E$ is the particle’s energy, and $\psi(x)$ is the wave function describing the extent of the quantum particle along $x$. The particle is confined to a one-dimensional box defined by $0 \leq x \leq L$. The boundary conditions define the value of the wave function at the two ends of the box

$$\psi(0) = \psi(L) = 0$$

where we require two boundary conditions for this second order differential equation. Since we interpret the square of the wave function, $|\psi(x)|^2$, as a probability distribution, once we solve Equation 11.23 for $\psi(x)$ we will also impose the normalization condition

$$\int_{0}^{L} |\psi(x)|^2 dx = 1$$

This is a second order ordinary differential equation and we can solve it
using the methods developed in this Chapter. We start by inserting \( e^{\pm i \alpha} \) for \( \psi(x) \) in Equation 11.23 to find the auxiliary equation

\[
-\frac{\hbar^2}{2m} \psi''(x) = E
\]

As \( E \geq 0 \) we find the pure imaginary roots

\[
a_n = \pm i \sqrt{\frac{2mE}{\hbar^2}}
\]

and expect an oscillatory solution (see Figure 11.5). The general solution can be written

\[
\psi(x) = c_1 \exp \left( i \sqrt{\frac{2mE}{\hbar^2}} x \right) + c_2 \exp \left( -i \sqrt{\frac{2mE}{\hbar^2}} x \right)
\]

We can determine the values of the coefficients \( c_1 \) and \( c_2 \) by applying the boundary conditions. Knowing that \( \psi(0) = c_1 + c_2 = 0 \) tells us that \( c_1 = -c_2 \) so that\(^\text{12}\)

\[
\psi(x) = c_1 \exp \left( i \sqrt{\frac{2mE}{\hbar^2}} x \right) - c_1 \exp \left( -i \sqrt{\frac{2mE}{\hbar^2}} x \right) = 2i c_1 \sin \left( \sqrt{\frac{2mE}{\hbar^2}} x \right)
\]

Knowing that \( \psi(L) = 2i c_1 \sin \left( \sqrt{\frac{2mE}{\hbar^2}} L \right) = 0 \) so that

\[
\sqrt{\frac{2mE}{\hbar^2}} L = n\pi \quad n = 1, 2, 3, \ldots
\]

provides us with a solution for the allowed values of the energy

\[
E_n = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, 3, \ldots
\]

We know the wave function is normalized

\[
\int_0^L |\psi(x)|^2 dx = 1 = \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = -4c_1^2 \frac{L}{2}
\]

where the integral can be taken using the trigonometric half-angle identity \( \sin^2(ax) = \frac{1}{2} (1 - \cos(2ax)) \) noting that the integral over the cosine term will be zero. This allows us to solve for the coefficient

\[
c_1 = \frac{i}{2} \sqrt{\frac{2}{L}}
\]

with our final result for the solution to Equation 11.23

\[
\psi_n(x) = \begin{cases} 
\sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) & 0 \leq x \leq L \\
0 & \text{everywhere else}
\end{cases}
\]

for \( n = 1, 2, 3, \ldots \)

Examples of the wave function \( \psi_n(x) \) and the modulus squared of the wave function \( |\psi_n(x)|^2 \) are provided in Figure 11.10 and Figure 11.11 for \( n = 1, 2, \) and 3. Note that each solution \( \psi_n(x) \) has \( n \) half-oscillations in the box. As \( n \)
increases, the number of half-oscillations increases reflecting the increasing energy of the particle. Returning to Equation 11.23 we note that the second derivative of $\psi(x)$ is proportional to $E$. As $E$ increases the curvature of the wave function increases reflected in an increasing number of oscillations in the box.

Finally, inserting our result for $\psi_n(x)$ into our original differential equation we find

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n(x) = -\frac{\hbar^2}{2m} \left[ -\left( \frac{n\pi}{L} \right)^2 \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \right]$$

$$= \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2 \psi_n(x) = E_n \psi_n(x)$$

resulting in the allowed energies for our particle found above. This validates our solution.

B$_{11}$ Classical theory of motion of a harmonic oscillator

In Chapter 7 we found that a mass on a spring or a vibrating bond between two atoms can be modeled as a harmonic oscillator with potential energy

$$V(x) = \frac{1}{2} \kappa (x - x_0)^2$$

and force

$$F(x) = -\frac{dV}{dx} = -\kappa (x - x_0)$$

where $x$ is the displacement of the oscillator from its mechanically stable position at $x_0$ and $\kappa$ is the force constant. When $x > x_0$ the force acts in the negative direction to shorten the oscillator, when $x < x_0$ the force acts in the positive direction to extend the oscillator, and for $x = x_0$ the force is zero and the oscillator is in a state of mechanical equilibrium. These results are depicted in Figure 11.12.

The velocity is the rate of change in the position with time

$$v = \frac{dx}{dt}$$

and the total energy of the oscillator is the sum of the kinetic energy and potential energy

$$E = \frac{1}{2} mv^2 + \frac{1}{2} \kappa (x - x_0)^2$$

which is constant in time.

The acceleration is the rate of change in the velocity with time

$$a = \frac{dv}{dt} = \frac{d^2x}{dt^2}$$

When a force acts on the oscillator, the mass accelerates according to Newton’s equation of motion $ma = F$ or

$$m \frac{d^2x}{dt^2} = -\kappa (x - x_0)$$

where $\kappa > 0$ is the force constant. This is a linear second order ordinary differential equation. It can be solved to determine the position of the mass, $x(t)$, as a function of time.

We can reform the equation in terms of the variable $y(t) = x(t) - x_0$ represent-
ing the displacement of the oscillator from its equilibrium position\textsuperscript{13}

\[
m \frac{d^2y}{dt^2} = -\kappa y
\]

We would like to solve this equation to determine the position of the oscillator as a function of time \(y(t)\). Substituting \(e^{\alpha t}\) for \(y(t)\) leads to

\[
m \frac{d^2}{dt^2} e^{\alpha t} = m \alpha^2 e^{\alpha t} = -\kappa e^{\alpha t}
\]

and the auxiliary equation

\[
m \alpha^2 = -\kappa
\]

with purely imaginary roots

\[
\alpha \pm = \pm i \sqrt{\frac{\kappa}{m}}
\]

and the solution

\[
y(t) = c_1 \exp \left( i \sqrt{\frac{\kappa}{m}} t \right) + c_2 \exp \left( -i \sqrt{\frac{\kappa}{m}} t \right)
\]

describing undamped oscillatory motion.

The time scale for the dynamics of the oscillator is defined by the linear frequency of motion

\[
v = \frac{1}{2\pi} \sqrt{\frac{\kappa}{m}}
\]

or equivalently the angular frequency

\[
\omega = \sqrt{\frac{\kappa}{m}} = 2\pi v
\]

where the period of oscillation is

\[
T = \frac{1}{v} = \frac{2\pi}{\omega}
\]

The larger the force constant, the higher the frequency of oscillation. The heavier the mass, the lower the frequency of oscillation.

With these definitions, we can reform \(y(t) = x(t) - x_0\) as

\[
y(t) = c_1 \exp (i\omega t) + c_2 \exp (-i\omega t)
\]

We assume that at \(t = 0\) the oscillator is displaced to \(y_0\) and the velocity is zero

\[
y(0) = y_0 \quad v(0) = \frac{dy}{dt} \bigg|_{t=0} = 0
\]

As such, the initial total energy of the oscillator \(E(0) = \frac{1}{2} \kappa y_0^2\). Applying the initial condition for the velocity we find

\[
\frac{dy}{dt} \bigg|_{t=0} = \left[ i c_1 \omega e^{i\omega t} - i c_2 \omega e^{-i\omega t} \right]_{t=0} = i c_1 \omega - i c_2 \omega = 0
\]

so \(c_1 = c_2\) and

\[
y(t) = c_1 \left[ \exp (i\omega t) + \exp (-i\omega t) \right] = 2c_1 \cos (\omega t)
\]

Applying the second initial condition

\[
y(0) = 2c_1 \cos (\omega t) \bigg|_{t=0} = 2c_1 = y_0
\]
so that

\[ c_1 = \frac{1}{2} y_0 \]

Our final result for the position and velocity is

\[ y(t) = y_0 \cos(\omega t) \quad v(t) = \frac{dy}{dt} = -y_0 \omega \sin(\omega t) \]

This result is depicted in Figure 11.13 which shows the position as a function of time in terms of \( x(t) \) and \( y(t) \) over three periods of oscillation \( T = 2\pi/\omega \).

With a knowledge of the position and velocity of the oscillator as a function of time we can determine the total energy

\[ E(t) = \frac{1}{2} m v(t)^2 + \frac{1}{2} \kappa y(t)^2 \]

During the vibration of the oscillator the total energy is conserved and equals the initial energy

\[ E(t) = E(0) = \frac{1}{2} \kappa y_0^2 \]

Figure 11.14 shows the complementary oscillations in the kinetic and potential energies. Potential energy is transformed to kinetic energy, and kinetic energy is transformed to potential energy in a repeating cycle while the total energy remains constant.

It is interesting to consider the conservation of total energy

\[ \frac{dE}{dt} = 0 = \frac{d}{dt} \left( \frac{1}{2} m v^2 + \frac{1}{2} \kappa (x - x_0)^2 \right) \]

Evaluating the total time derivative leads to

\[ \frac{d}{dt} \left( \frac{1}{2} m v^2 + \frac{1}{2} \kappa (x - x_0)^2 \right) = m v \frac{dv}{dt} + \kappa (x - x_0) \frac{dx}{dt} \]

\[ = m \ddot{x} + \kappa \dot{x} = 0 \]

Canceling the common value of \( v \) we find

\[ m \ddot{x} + \kappa (x - x_0) = 0 \]

or

\[ m \ddot{x} = -\kappa (x - x_0) = F(x) \]

which is Newton’s equation of motion. In this case of energy conserving dynamics in one-dimension, the conservation of energy implies Newton’s equation of motion. This can be thought of as a special case of Noether’s theorem.\(^{14}\) The principle of conservation of energy (that the energy is constant in time) is a consequence of an underlying symmetry, the invariance under translation in time.

Finally, note that the position and velocity can also be written

\[ y(t) = \sqrt{\frac{2E}{\kappa}} \cos(\omega t) \quad v(t) = \frac{dy}{dt} = -\sqrt{\frac{2E}{m}} \sin(\omega t) \]

\(^{14}\) Named for German mathematician Emmy Noether (1882-1935) whose work illuminated the relationship between conserved quantities, such as energy and angular momentum, and underlying symmetries of the system, such as time and rotation.
A slightly different set of equations defining the oscillator’s motion are written in terms of the position and linear momentum $p(t) = mv(t)$

$$y(t) = \sqrt{\frac{2E}{k}} \cos (\omega t) \quad p(t) = m \frac{dy}{dt} = -\sqrt{2mE} \sin (\omega t)$$

These equations define a trajectory on the $yp$-plane formed by the position, $y$, and the momentum, $p$. The $yp$-plane is called phase space. All possible states of the oscillator’s dynamics are represented in this phase space of position and momentum. The constant total energy restricts the position and momentum to move in a cycle on an elliptical curve defined by

$$E = \frac{k}{2} y^2 + \frac{1}{2m} p^2$$

The elliptical curve defining the states visited in the oscillatory dynamics of the oscillator is called the phase portrait. Each total energy results in a unique phase portrait, an elliptical phase portrait that grows larger as the energy grows. This result is shown in Figure 11.15.

The total energy of our oscillator is

$$E = \frac{k}{2} y^2 + \frac{1}{2m} p^2$$

Dividing by $E$ we find

$$1 = \frac{k}{2E} y^2 + \frac{1}{2mE} p^2 = \frac{y^2}{a^2} + \frac{p^2}{b^2}$$

which is the equation of an ellipse

where $a = \sqrt{\frac{2E}{k}}$ and $b = \sqrt{2mE}$ (see Supplement S2).

**C11 Classical theory of a damped harmonic oscillator**

We found that a mass on a spring or a vibrating bond between two atoms can be modeled as a harmonic oscillator with potential energy $V(x) = \frac{1}{2}k(x - x_0)^2$ and force

$$F_{\text{spring}} = -\frac{dV}{dx} = -k(x - x_0)$$

where $x$ is the displacement of the oscillator from its mechanically stable position at $x_0$ and $k$ is the force constant. The corresponding velocity is the rate of change in the position with time

$$v = \frac{dx}{dt}$$

and the linear momentum $p = mv$.

The motion of this model oscillator is undamped in time. Once it begins to oscillate, it continues to oscillate with fixed frequency of motion and constant energy. However, physical oscillators such as a mass on a spring in the air or a vibrating molecule in a liquid lose energy to the surroundings over time, damping the motion of the oscillator. To model this phenomenon, we introduce
an additional force acting on the mass in the form of a frictional damping

\[ F_{\text{friction}} = -\gamma \frac{dx}{dt} = -\gamma v \]

where \( \gamma \geq 0 \) and the frictional force is proportional to the velocity. If the velocity is positive, the damping force is in the negative direction, slowing the oscillator. If the velocity is negative, the damping force is in the positive direction, slowing the oscillator. As such, the frictional force acts to reduce the speed, removing energy from the system and slowing the oscillator until the speed eventually reaches zero. This behavior is demonstrated in Figure 11.16 which can be compared with the motion of an undamped harmonic oscillator shown in Figure 11.13.

The acceleration is the rate of change in the velocity with time

\[ a = \frac{dv}{dt} = \frac{d^2x}{dt^2} \]

The equation of motion for the oscillator is given by Newton’s equation \( F = ma \) where \( m \) is the mass and \( a \) is the acceleration

\[ m \frac{d^2x}{dt^2} = F_{\text{spring}} + F_{\text{friction}} = -\kappa(x - x_0) - \gamma \frac{dx}{dt} \]

We can reform the equation in terms of the variable \( y = x - x_0 \) representing the displacement of the oscillator from its equilibrium position

\[ m \frac{d^2y}{dt^2} = -\kappa y - \gamma \frac{dy}{dt} \]

We would like to solve this equation to determine the position of the oscillator, \( y(t) \), as a function of time. Substituting \( e^{\alpha t} \) for \( y(t) \) leads to

\[ m \frac{d^2 e^{\alpha t}}{dt^2} = -\kappa e^{\alpha t} - \gamma \frac{d}{dt} e^{\alpha t} \]

Evaluating the derivatives we find

\[ ma^2 e^{\alpha t} = -\kappa e^{\alpha t} - a \gamma e^{\alpha t} \]

which reduces to the auxiliary equation

\[ a^2 + \frac{\gamma}{m} a + \frac{\kappa}{m} = 0 \]

with roots

\[ a_\pm = \frac{1}{2} \left[ -\frac{\gamma}{m} \pm \sqrt{\left( \frac{\gamma}{m} \right)^2 - \frac{4\kappa}{m}} \right] = -\frac{\gamma}{2m} \pm \sqrt{\left( \frac{\gamma}{2m} \right)^2 - \frac{\kappa}{m}} \]

leading to the general solution for the position as a function of time

\[ y(t) = c_1 e^{a_+ t} + c_2 e^{a_- t} \]

Let’s consider the nature of the roots, \( a_\pm \), that can be purely imaginary, complex, or real depending on the magnitude of \( \gamma \). In the case that \( \gamma = 0 \) there is no friction and we recover the pure imaginary roots

\[ a_\pm = \pm i \sqrt{\frac{\kappa}{m}} = \pm i \omega \]

associated with undamped oscillatory motion. In the case that \( 0 < \gamma < 2\kappa \) there
is low friction and the roots will be complex with real and imaginary terms

\[ \alpha_\pm = -\frac{\gamma}{2m} \pm \sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega^2} = -\frac{\gamma}{2m} \pm i\omega' \]

where

\[ \omega' = \sqrt{\omega^2 - \left(\frac{\gamma}{2m}\right)^2} = \omega \sqrt{1 - \left(\frac{\gamma}{2m}\omega}\right)^2} \]

For these complex roots, there is an exponential damping term, with rate of damping \( \gamma/2m \), and an oscillatory term, with frequency \( \omega' \) shifted relative to the frequency of undamped motion. In this regime the motion of the oscillator is underdamped (see Figure 1.11). Finally, in the case that \( \gamma \geq 2\omega \) there is high friction and the roots are purely real

\[ \alpha_\pm = -\frac{\gamma}{2m} \pm \sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega^2} \]

In this regime the motion of the oscillator is overdamped (see Figure 1.11).

In each of the three regimes, we can write

\[ \alpha_\pm = \alpha_0 \pm \Delta \alpha \]

where

\[ \alpha_0 = -\frac{\gamma}{2m} \quad \Delta \alpha = \sqrt{\left(\frac{\gamma}{2m}\right)^2 - \omega^2} \]

and \( \Delta \alpha \) may be real or imaginary.\(^\text{16}\) With this notation, our solution takes the form

\[ y(t) = c_1 e^{\alpha_0 t} + c_2 e^{-\alpha_0 t} = e^{\alpha_0 t} \left( c_1 e^{\Delta \alpha t} + c_2 e^{-\Delta \alpha t} \right) \]

Considering the initial conditions

\[ y(0) = y_0 \quad \frac{dy}{dt} \bigg|_{t=0} = 0 \]

we find

\[ y(0) = c_1 + c_2 = y_0 \]

and

\[ \frac{dy}{dt} \bigg|_{t=0} = \left[ \frac{d}{dt} \left( e^{\alpha_0 t} \left( c_1 e^{\Delta \alpha t} + c_2 e^{-\Delta \alpha t} \right) \right) \right]_{t=0} = \alpha_0 (c_1 + c_2) + \Delta \alpha (c_1 - c_2) = 0 \]

so \( c_2 = y_0 - c_1 \) and

\[ c_1 = \frac{(\alpha_0 - \Delta \alpha)y_0}{2\Delta \alpha} \quad c_2 = \frac{(\alpha_0 + \Delta \alpha)y_0}{2\Delta \alpha} \]

Note that when \( \gamma = 0, \alpha_0 = 0 \) and we recover the coefficients expected for the harmonic oscillator in the absence of friction where \( c_1 = c_2 = y_0/2 \). For the general case we find

\[ y(t) = y_0 e^{\alpha_0 t} \left[ \cosh (\Delta \alpha t) - \frac{\alpha_0}{\Delta \alpha} \sinh (\Delta \alpha t) \right] \]

\[ v(t) = y_0 e^{\alpha_0 t} \left[ -\frac{\omega^2}{\Delta \alpha} \sinh (\Delta \alpha t) \right] \]

where high friction leads to a real \( \Delta \alpha \), real roots, and exponential damping.

\[ \text{Figure 11.17: The kinetic energy, } T(t), \text{ potential energy, } U(t), \text{ and total energy } E(t) = T(t) + U(t) \text{ of the damped harmonic oscillator. The total energy is monotonically decreasing as a function of time.} \]
In contrast, low friction leads to an imaginary $\Delta \alpha$, complex roots, and an exponentially damped oscillator. We can also write the linear momentum as

$$p(t) = y_0 e^{\alpha t} \left[ -\frac{mc^2}{\Delta \alpha} \sinh (\Delta t) \right]$$

The solution is shown in Figure 11.16.

The total energy of the damped harmonic oscillator is defined

$$E(t) = \frac{1}{2} m v(t)^2 + \frac{1}{2} k y(t)$$

An example of the time-dependence of $E(t)$ is shown in Figure 11.17 for an underdamped harmonic oscillator for which $0 < \gamma < 2m\omega$. For $\gamma > 0$, the vibration of the oscillator is damped and the total energy decreases monotonically from its initial value

$$E(0) = \frac{1}{2} ky_0^2$$

When the kinetic energy reaches a maximum the velocity is maximized as is the rate of frictional damping. This is reflected in the variation in the total energy, where periods of higher kinetic energy are also periods of greater energy loss. This leads to the stepping behavior observed in the total energy as a function of time. Compare this behavior to that of the undamped harmonic oscillator shown in Figure 11.14 where the trajectory performs a repeating elliptical orbit in phase space.

Figure 11.18: The phase portrait of the damped harmonic oscillator (red). The gray ellipse is formed by the values of position and momentum consistent with the initial energy $E(0)$. The continuous energy loss of the damped oscillator is reflected in the narrowing of the inward spiral with increasing time.

All possible states of the oscillator’s dynamics are represented in this phase space of position and momentum. Our solutions for $y(t)$ and $p(t)$ define a trajectory on the $yp$-plane called the phase portrait. For an undamped harmonic oscillator, the position and momentum move in a repeating cycle restricted to an elliptical curve defined by the constant total energy

$$E(t) = \frac{k}{2} y(t)^2 + \frac{1}{2m} p(t)^2 = E(0)$$

For a damped harmonic oscillator, the total energy of the oscillator decreases with time. As a result, the breadth of the elliptical path decreases with time leading to a phase portrait with the form of an inward elliptical spiral. This behavior is depicted in Figure 11.18 for a harmonic oscillator for which $0 < \gamma < 2m\omega$ and the motion is underdamped. This behavior can be compared to that of the undamped harmonic oscillator shown in Figure 11.15.
D_{11} Power series solutions to special equations in quantum theory

A number of special ordinary differential equations arise in the quantum theory of matter when solving the Schrödinger equation for electronic energy of a one electron atom or the rotations and vibrations of a diatomic molecule. These special differential equations may be solved using power series. In each case, the resulting power series represents a type of special function that find wide use in the physical sciences.\(^\text{17}\)

**Hermite’s equation and Hermite polynomials**

In the quantum theory of the harmonic oscillator a special differential equation appears

\[
\frac{d^2}{dx^2}y(x) - 2x \frac{dy}{dx} + 2\alpha y(x) = 0
\]

where \(\alpha\) is a constant. This is known as *Hermite’s equation*.\(^\text{18}\) Proposing a power series solution of the form

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n
\]

we find that Equation 11.24 can be written

\[
\sum_{n=0}^{\infty} a_n n(n - 1)x^{n-2} - 2x \sum_{n=0}^{\infty} a_n nx^{n-1} + 2\alpha \sum_{n=0}^{\infty} a_n x^n = 0
\]

In order to identify the recurrence relation that defines the coefficients in our series, we must transform the first two series so that they can be combined with the third.

In the first series the coefficients are proportional to \(n(n - 1)\) so that the \(n = 0\) and \(n = 1\) terms are always zero. Removing the \(n = 0\) and \(n = 1\) terms from the first series results in

\[
\sum_{n=2}^{\infty} a_n n(n - 1)x^{n-2} \rightarrow \sum_{n=2}^{\infty} a_n n(n - 1)x^{n-2}
\]

Now the series starts with \(n = 2\) but we would like it to start from \(n = 0\). As such, we shift the index as \(n \rightarrow n + 2\) so that\(^\text{19}\)

\[
\sum_{n=2}^{\infty} a_n n(n - 1)x^{n-2} \rightarrow \sum_{n=0}^{\infty} a_{n+2}(n + 2)(n + 1)x^n
\]

For the second series, we simply absorb the factor of \(x\) in the sum

\[
-2x \sum_{n=0}^{\infty} a_n nx^{n-1} = -2 \sum_{n=0}^{\infty} a_n nx^n
\]

Inserting these results in Equation 11.25 leads to

\[
\sum_{n=0}^{\infty} a_{n+2}(n + 2)(n + 1)x^n - 2 \sum_{n=0}^{\infty} a_n nx^n + 2\alpha \sum_{n=0}^{\infty} a_n x^n = 0
\]

Combining the sums we find

\[
\sum_{n=0}^{\infty} [a_{n+2}(n + 2)(n + 1) - 2a_n + 2\alpha a_n] x^n = 0
\]

\(^\text{17}\) A classic reference for the properties of special functions is *Abramowitz and Stegun* or simply AS which still serves as a valuable compendium of special functions and their properties.

\(^\text{18}\) Named for French mathematician Charles Hermite (1822-1901).

\(^\text{19}\) Equivalently, you can introduce a new index \(n' = n - 2\), substituting \(n \rightarrow n' + 2\). You can then rewrite the new index \(n'\) as \(n\) before combining the sums.
and the condition
\[ a_{n+2}(n+2)(n+1) - 2a_n + 2\alpha a_n = 0 \]
consistent with the recursion relation\(^{20}\)
\[ a_{n+2} = -\frac{2(a - n)}{(n+2)(n+1)} a_n \]
The even indices can be generated from \(a_0\) as
\[ a_2 = -\frac{2\alpha}{2} a_0 \quad a_4 = -\frac{2(a - 2)}{4 \cdot 3} a_2 = \frac{2^2\alpha(a - 2)}{4!} a_0 \]
leading to the power series in even powers of \(x\)
\[ y_0(x) = a_0 \left[ 1 - \frac{2\alpha}{2!} x^2 + \frac{2^2\alpha(a - 2)}{4!} x^4 + \ldots \right] \]
The odd indices can be generated from \(a_1\) as
\[ a_3 = -\frac{2(a - 1)}{3 \cdot 2} a_1 \quad a_5 = -\frac{2(a - 3)}{5 \cdot 4} a_3 = \frac{2^2(a - 3)(a - 1)}{5!} a_1 \]
leading to the power series in odd powers of \(x\)
\[ y_1(x) = a_1 \left[ x - \frac{2(a - 1)}{3!} x^3 + \frac{2^2(a - 3)(a - 1)}{5!} x^5 + \ldots \right] \]
The overall solution is written as a linear superposition of the two independent solutions \(y_0(x)\) and \(y_1(x)\). The remaining coefficients \(a_0\) and \(a_1\) are defined by the boundary conditions.

![Graph of Hermite polynomials](image1.png)

Let’s examine the results for various values of the parameter \(\alpha\). We will find that the solutions to Hermite’s equation form a series of polynomial equations known as the Hermite polynomials.\(^{21}\) In defining the Hermite polynomials, we consider the even power series, \(y_0(x)\), and odd power series, \(y_1(x)\), separately. When \(\alpha = 0\), Hermite’s equation is
\[ \frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) = 0 \]
with a solution defined by the even power series
\[ y_0(x) = a_0 \]

\(^{20}\)The negative sign in the recursion relation signals the fact that the coefficients lead to an alternating series.

\(^{21}\)The Hermite polynomials were originally described by Pierre-Simon Laplace (1749-1827).
as all higher order terms contain a multiplicative factor of \( \alpha \) and are zero. This is the Hermite polynomial \( H_0(x) = 1 \) for \( a_0 = 1 \). For \( \alpha = 1 \), Hermite’s equation is

\[
\frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + 2y(x) = 0
\]

with a solution defined by the odd power series

\[
y_1(x) = a_1 x
\]

as all higher order terms in the series contain a multiplicative factor of \( (\alpha - 1) \) and are zero. This is the Hermite polynomial \( H_1(x) = 2x \) when \( a_1 = 2 \). When \( \alpha = 2 \), Hermite’s equation is

\[
\frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + 4y(x) = 0
\]

with a solution defined by the even power series

\[
y_0(x) = a_0 \left( 1 - 2x^2 \right)
\]

which is the Hermite polynomial \( H_2(x) = 4x - 2 \) when \( a_0 = -2 \). Repeating this process, we find that when \( \alpha = 3 \), the Hermite polynomial \( H_3(x) = 8x^3 - 12x \) when \( a_1 = -12 \). When \( \alpha = 4 \), the Hermite polynomial \( H_4(x) = 16x^4 - 48x^2 + 12 \) when \( a_0 = 12 \). The first five Hermite polynomials are presented in Figure 11.19.

**Laguerre’s equation and Laguerre polynomials**

In the quantum theory of the one electron atom a special differential equation describes the radial dependence of the electron’s wave function

\[
x \frac{d^2}{dx^2} y(x) - (1 - x) \frac{d}{dx} y(x) + xy(x) = 0 \quad (11.26)
\]

where \( \alpha \) is a constant. This is known as Laguerre’s equation.\(^{22}\) Proposing a power series solution

\[
y(x) = \sum_{n=0}^{\infty} a_n x^n
\]

we find that Equation 11.26 can be written

\[
x \sum_{n=0}^{\infty} a_n (n - 1) x^{n-2} - (1 - x) \sum_{n=0}^{\infty} a_n n x^{n-1} + \alpha \sum_{n=0}^{\infty} a_n x^n = 0 \quad (11.27)
\]

We must transform the first two series so that they can be combined with the third.

In the first series the coefficients are proportional to \( n \) so the \( n = 0 \) term is always zero. Removing the \( n = 0 \) term from the first series and absorbing the factor of \( x \) leads to

\[
x \sum_{n=0}^{\infty} a_n n (n - 1) x^{n-2} \to \sum_{n=1}^{\infty} a_n n (n - 1) x^{n-1}
\]

Shifting the index as \( n \to n + 1 \) results in\(^{23}\)

\[
\sum_{n=1}^{\infty} a_n n (n - 1) x^{n-1} \to \sum_{n=0}^{\infty} a_{n+1} (n + 1) n x^n
\]

which is in the desired form in terms of the range of the index \( n \) and the sum over \( x^n \) weighted by constant coefficients. We transform the second series by

\(^{22}\) Named for French mathematician Edmond Laguerre (1834-1886).

\(^{23}\) Equivalently, you can introduce a new index \( n' = n - 1 \), substituting \( n \to n' + 1 \). You can then rewrite the new index \( n' \) as \( n \) before combining the sums.
The negative sign in the recursion relation signals the fact that the coefficients lead to an alternating series.

\[
(1 - x) \sum_{n=0}^{\infty} a_n nx^{n-1} = \sum_{n=0}^{\infty} a_n nx^{n-1} - \sum_{n=0}^{\infty} a_n nx^{n}
\]

In the first series the coefficients are proportional to \(n\) so the \(n = 0\) term is always zero. Removing the \(n = 0\) term from the first series leads to

\[
\sum_{n=1}^{\infty} a_n nx^{n-1} \rightarrow \sum_{n=0}^{\infty} a_{n+1}(n+1)x^n
\]

Inserting these results in Equation 11.27 leads to

\[
\sum_{n=0}^{\infty} [a_{n+1}(n+1)n + a_{n+1}(n+1) - a_n n + a a_0] x^n = 0
\]

and the condition

\[
a_{n+1}(n+1)n + a_{n+1}(n+1) - a_n n + a a_0 = 0
\]

consistent with the recursion relation\(^4\)

\[
a_{n+1} = - \frac{\alpha - n}{(n+1)^2} a_n
\]

The coefficients can be generated starting from \(a_0\) as

\[
a_1 = -\alpha a_0 \quad a_2 = \frac{(\alpha - 1)\alpha}{(2!)^2} a_0 \quad a_3 = -\frac{(\alpha - 2)(\alpha - 1)\alpha}{(3!)^2} a_0
\]

leading to the power series solution

\[
y(x) = a_0 \left[1 - \alpha x + \frac{(\alpha - 1)\alpha}{(2!)^2} x^2 - \frac{(\alpha - 2)(\alpha - 1)\alpha}{(3!)^2} x^3 + \ldots\right]
\]

Figure 11.20: Variation in the first five Laguerre polynomials \(L_n(x)\) over the range \(x \in [-10, 15]\).

Let’s examine our results for various values of the parameter \(\alpha\). We will find that the solutions to Laguerre’s equation form a series of polynomial equations...
known as the Laguerre polynomials. When $\alpha = 0$, Laguerre’s equation is

$$x \frac{d^2}{dx^2} y(x) - (1 - x) \frac{d}{dx} y(x) = 0$$

with the solution

$$y(x) = a_0$$

as all higher order terms contain a multiplicative factor of $\alpha$ and are zero. This is the Laguerre polynomial $L_0(x) = 1$ for $a_0 = 1$. For $\alpha = 1$, Laguerre’s equation is

$$x \frac{d^2}{dx^2} y(x) - (1 - x) \frac{d}{dx} y(x) + y(x) = 0$$

and the solution is

$$y(x) = a_0(1 - x)$$

as all higher order terms in the series contain a multiplicative factor of $(\alpha - 1)$ and are zero. This is the Laguerre polynomial $L_1(x) = 1 - x$ when $a_0 = -1$. Repeating this process for $\alpha = 2$, we find the Laguerre polynomial $L_2(x) = \frac{1}{2} (x^2 - 4x + 2)$ when $a_0 = 1$. When $\alpha = 3$, we find the Laguerre polynomial $L_3(x) = \frac{1}{6} (-x^3 + 9x^2 - 18x + 6)$ when $a_0 = 1$. The first four Laguerre polynomials are depicted in Figure 11.20.

**Legendre’s equation and Legendre polynomials**

In the quantum theory of rotational motion of a diatomic molecule a special differential equation describes the rotational wave function

$$(1 - x^2) \frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + l(l + 1)y(x) = 0 \quad (11.28)$$

where $l$ is a constant. This is known as Legendre’s equation.\(^\text{25}\) Proposing a power series solution

$$y(x) = \sum_{n=0}^{\infty} a_n x^n$$

we find that Equation 11.28 can be written

$$(1 - x^2) \sum_{n=0}^{\infty} a_n n(n - 1) x^{n-2} - 2x \sum_{n=0}^{\infty} a_n n x^{n-1} + l(l + 1) \sum_{n=0}^{\infty} a_n x^n = 0 \quad (11.29)$$

We must transform the first two series so that they can be combined with the third.

We transform the first series by distributing the factor of $(1 - x^2)$ resulting in two series

$$(1 - x^2) \sum_{n=0}^{\infty} a_n n(n - 1) x^{n-2} \to \sum_{n=0}^{\infty} a_n n(n - 1) x^{n-2} - \sum_{n=0}^{\infty} a_n n(n - 1) x^n$$

In the first series the coefficients are proportional to $n(n - 1)$ so that the $n = 0$ and $n = 1$ terms are always zero. Removing the $n = 0$ and $n = 1$ terms from the first series results in

$$\sum_{n=0}^{\infty} a_n n(n - 1) x^{n-2} \to \sum_{n=2}^{\infty} a_n n(n - 1) x^{n-2}$$

Now the series starts with $n = 2$ but we would like it to start from $n = 0$. As such, we shift the index as $n \to n + 2$ so that\(^\text{26}\)\(^\text{25}\)

\(^{25}\) Named for French mathematician Adrien-Marie Legendre (1752-1833).

\(^{26}\) Equivalently, you can introduce a new index $n' = n - 2$, substituting $n \to n' + 2$. You can then rewrite the new index $n'$ as $n$ before combining the sums.
When the overall solution is written as a linear superposition

The odd indices can be generated from

\[ y_n = \sum_{n=2}^{\infty} a_n (n-1)x^{n-2} \rightarrow \sum_{n=0}^{\infty} a_{n+2}(n+2)(n+1)x^n \]

For the second series in Equation 11.29 we absorb the factor of \(-2x\) resulting in

\[-2x \sum_{n=0}^{\infty} a_n nx^{n-1} = -2 \sum_{n=0}^{\infty} a_n nx^n\]

Inserting these results in Equation 11.29 leads to

\[ \sum_{n=0}^{\infty} \left[ a_{n+2}(n+2)(n+1) - a_n(n-1) - 2a_n \right] x^n + l(l+1)a_n = 0 \]

and the condition

\[ a_{n+2}(n+2)(n+1) - a_n(n-1) - 2a_n + l(l+1)a_n = 0 \]

consistent with the recursion relation\(^{27}\)

\[ a_{n+2} = \frac{(n+1)n-l(l+1)}{(n+2)(n+1)} a_n = \frac{[l+(n+1)](l-n)}{2} \]

The even indices can be generated from \(a_0\) as

\[ a_2 = -\frac{(l+1)}{2}a_0 = -\frac{(l+1)}{2!}a_0 \]

\[ a_4 = -\frac{(l+3)(l-2)}{4!}a_2 = \frac{(l+3)(l-2)(l+1)}{4!}a_0 \]

and so on, leading to the power series in even powers of \(x\)

\[ y_0(x) = a_0 \left[ 1 - \frac{(l+1)}{2!}x^2 + \frac{(l+3)(l-2)(l+1)}{4!}x^4 + \ldots \right] \]

The odd indices can be generated from \(a_1\) as

\[ a_3 = -\frac{(l+2)(l-1)}{3!}a_1 = \frac{(l+2)(l-1)}{3!}a_1 \]

\[ a_5 = -\frac{(l+4)(l-3)}{5!}a_3 = \frac{(l+4)(l-3)(l+2)(l-1)}{5!}a_1 \]

and so on, leading to the power series in odd powers of \(x\)

\[ y_1(x) = a_1 \left[ x - \frac{(l+2)(l-1)}{3!}x^3 + \frac{(l+4)(l-3)(l+2)(l-1)}{5!}x^5 + \ldots \right] \]

The overall solution is written as a linear superposition of the two independent solutions \(y_0(x)\) and \(y_1(x)\). The remaining coefficients \(a_0\) and \(a_1\) are defined by the boundary conditions.

Let's examine our results for various values of the parameter \(l\). We will find that the solutions to Legendre's equation form a series of polynomial equations known as the Legendre polynomials. In defining the Legendre polynomials, we consider the even power series, \(y_0(x)\), and odd power series, \(y_1(x)\), separately. When \(l = 0\), Legendre's equation is

\[ (1 - x^2) \frac{d^2}{dx^2}y(x) - 2x \frac{d}{dx}y(x) = 0 \]
and the solution is

\[ y(x) = a_0 \]

as all higher order terms contain a multiplicative factor of \( l \) and are zero. This is the Legendre polynomial \( P_l(x) = 1 \) for \( a_0 = 1 \). For \( l = 1 \), Legendre’s equation is

\[
(1 - x^2) \frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + 2y(x) = 0
\]

and the solution is

\[ y(x) = a_1 x \]

as all higher order terms in the series contain a multiplicative factor of \((l - 1)\) and are zero. This the Legendre polynomial \( P_1(x) = x \) when \( a_1 = 1 \). When \( l = 2 \), Legendre’s equation is

\[
(1 - x^2) \frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + 6y(x) = 0
\]

and the solution is

\[ y(x) = a_0 \left(1 - 3x^2\right) \]

which is the Legendre polynomial \( P_2(x) = \frac{1}{2} \left(3x^2 - 1\right) \) when \( a_0 = -\frac{1}{2} \). When \( l = 3 \), Legendre’s equation is

\[
(1 - x^2) \frac{d^2}{dx^2} y(x) - 2x \frac{d}{dx} y(x) + 12y(x) = 0
\]

and the solution is

\[ y(x) = a_1 \left(x - \frac{5}{3}x^3\right) \]

which is the Legendre polynomial \( P_3(x) = \frac{1}{2} \left(5x^3 - 3x\right) \) when \( a_1 = -3 \). The first four Legendre polynomials are depicted in Figure 11.21.

The differential equations discussed in this Complement play a special role in the quantum theory of atoms and molecules. Normally, we have found that differential equations can be solved using one or more common functions such as the exponentials and sinusoids. The solution of these three differential equations using the power series method led to the discovery of three new special functions, the Hermite, Laguerre, and Legendre polynomials. It is worth remembering that at one time the exponential function was a special function as well.\(^{28}\) Through regular use, we come to regard special functions as common.

\(^{28}\) The constant \( e \), also known as Euler’s number or Napier’s constant, was not well defined until the late 17th century.
E11 End-of-chapter problems

How can it be that mathematics, being after all a product of human thought independent of experience, is so admirably adapted to the objects of reality?

Albert Einstein

Warm-ups

11.1 Consider the following second order ordinary differential equations.

(a) \( \frac{d^2 y(x)}{dx^2} - 4y(x) = 0 \)
(b) \( \frac{d^2 y(x)}{dx^2} + 2 \frac{dy(x)}{dx} + 4y(x) = 0 \)

(c) \( \frac{d^2 y(x)}{dx^2} + 9y(x) = 0 \)
(d) \( \frac{d^2 y(x)}{dx^2} + 6 \frac{dy(x)}{dx} + 4y(x) = 0 \)

In each case, assume the solution \( y(x) = e^{\alpha x} \). Find the auxiliary equation and determine the two roots \( \alpha \). Compose the overall solution \( y(x) = c_1 e^{\alpha_1 x} + c_2 e^{\alpha_2 x} \). Apply the boundary conditions \( y(0) = 0 \) and \( \frac{dy(x)}{dx} \bigg|_{x=0} = 1 \) to determine the coefficients \( c_1 \) and \( c_2 \).

11.2 Consider the linear second order differential equation

\( \frac{d^2 y(x)}{dx^2} + 2 \frac{dy(x)}{dx} + y(x) = 0 \)

(a) Assume the solution \( y(x) = e^{\alpha x} \). Find the auxiliary equation and determine the roots \( \alpha \). You should find double roots where \( \alpha_1 = \alpha \).

(b) Prove that \( y(x) = c_1 e^{\alpha x} + c_2 x e^{\alpha x} \) is a solution to the differential equation.

11.3 Consider the general second order ordinary differential equation

\( \frac{d^2 y(x)}{dx^2} + a(x) \frac{dy(x)}{dx} + b(x) y(x) = 0 \)

Prove that if \( y_1(x) \) and \( y_2(x) \) are each solutions to the differential equation, so is the linear superposition \( y(x) = c_1 y_1(x) + c_2 y_2(x) \).

11.4 Reform the following sums so that the first term in the sum is \( n = 0 \)

(a) \( \sum_{n=2}^{\infty} (n - 2) a_n x^n \) \hspace{1cm} (b) \( \sum_{n=2}^{\infty} n(n-1) a_n x^{n-2} \) \hspace{1cm} (c) \( \sum_{n=1}^{\infty} n a_n x^{n-1} \)

11.5 Consider the following recursion relations where \( n \geq 0 \). In each case, derive a general expression for the coefficient \( a_n \) in terms of \( a_0 \).

(a) \( a_{n+1} = \frac{a_n}{(n+1)^2} \) \hspace{1cm} (b) \( a_{n+1} = \frac{n+2}{2(n+1)} a_n \) \hspace{1cm} (c) \( a_{n+1} = \frac{2a_n}{n+1} \)
11.6 Consider the second order differential equation
\[ \frac{d^2}{dx^2}y(x) - y(x) = 0 \]
(a) Find two linearly independent power series solutions of the form
\[ \sum_{n=0}^{\infty} a_n x^n \]
Start by determining recursion relations for the coefficients \( a_n \). You should find two recursion relations, one for \( n \) odd and one for \( n \) even.
(b) In each case, derive a general expression for \( a_n \) in terms of \( a_0 \) or \( a_1 \).
(c) Identify the common functions representing each series.

Homework exercises
11.7 The general solution for a homogeneous second order ordinary differential equation of the form
\[ y(x) = c_1 e^{ibx} + c_2 e^{-ibx} \]
can be rewritten
\[ y(x) = c'_1 \cos(bx) + c'_2 \sin(bx) \]
Derive expressions for \( c'_1 \) and \( c'_2 \) in terms of \( c_1 \) and \( c_2 \).
11.8 The position of an oscillator, \( x(t) \), as a function of time, \( t \), satisfies the second order differential equation
\[ \frac{d^2 x(t)}{dt^2} + \omega^2 x(t) = 0 \]
where \( \omega \) is a constant. Solve this equation for \( x(t) \) given the following initial conditions.
   (a) \( x(0) = 0 \) and \( \frac{dx}{dt} \bigg|_{t=0} = u_0 \)
   (b) \( x(0) = x_0 \) and \( \frac{dx}{dt} \bigg|_{t=0} = u_0 \)
In each case, prove that \( x(t) \) oscillates with frequency \( \nu = \frac{\omega}{2\pi} \) and period \( T = \frac{2\pi}{\omega} = \frac{1}{\nu} \).
11.9 The second order differential equation
\[ \frac{d^2 f(x)}{dx^2} + \frac{25\pi^2}{L^2} f(x) = 0 \]
models the displacement, \( f(x) \), of a plucked string that is fixed at each end leading to the boundary conditions \( f(0) = f(L) = 0 \) and \( \frac{df}{dx} \bigg|_{x=0} = 5 \).
(a) Determine the general solution of the form
\[ f(x) = c_1 e^{\xi x} + c_2 e^{-\xi x} \]
(b) Simplify your result by expressing your solution in terms of a sinusoidal function.
11.10 Consider the second order inhomogeneous ordinary differential equation describing the height, \( z(t) \), of a mass, \( m \), falling under the force of gravity with constant rate of acceleration, \( g \), and experiencing a frictional drag force proportional to the speed, \( u(t) = \frac{dz(t)}{dt} \), written
\[ m \frac{d^2 z(t)}{dt^2} = -\gamma \frac{dz(t)}{dt} + mg \]
where \( \gamma \) is the friction constant.
(a) Show that this equation is equivalent to the first order ordinary differential equation for the speed of the particle

\[ \frac{du(t)}{dt} + \frac{\gamma}{m} u(t) = g \]

(b) Solve the differential equation for \( u(t) \) given that \( u(0) = 0 \).

(c) Show that as \( t \to \infty \), the speed of the falling mass approaches a constant terminal speed \( u_T = \frac{mg}{\gamma} \) as shown in the figure below.

\[ u(t) \]

\[ \frac{mg}{\gamma} \]

0 t

11.11 Determine the coefficients \( a_n \) for which the equation

\[ \sum_{n=1}^{\infty} n a_n x^{n-1} + 2 \sum_{n=0}^{\infty} a_n x^n = 0 \]

is satisfied. Substitute the resulting coefficients \( a_n \) in the power series

\[ \sum_{n=0}^{\infty} a_n x^n \]

and identify the corresponding function.

11.12∗ Consider the differential equation

\[ (x^2 + 1) \frac{d^2 y(x)}{dx^2} - 4x \frac{dy(x)}{dx} + 6y(x) = 0 \]

with the boundary conditions \( y(0) = 1 \) and \( y'(0) = 2 \).

(a) Propose a solution in the form of the power series

\[ y(x) = \sum_{n=0}^{\infty} a_n x^n \]

Derive the recursion relation

\[ a_{n+2} = \frac{(n-2)(n-3)}{(n+2)(n+1)} a_n \]

(b) Using the recursion relation above, determine the four coefficients \( a_n \) that are non-zero in terms of \( a_0 \) and \( a_1 \).

(c) Apply the boundary conditions to determine the solution for \( y(x) \).

11.13∗ Show that

\[ c_1 \cos(\omega t) + c_2 \sin(\omega t) = A \sin(\omega t + \phi) \]
where
\[ A = \sqrt{c_1^2 + c_2^2} \quad \varphi = \tan^{-1} \left( \frac{c_2}{c_1} \right) \]
or equivalently
\[ c_1 \cos(\omega t) + c_2 \sin(\omega t) = A \cos(\omega t + \varphi) \]
where
\[ A = \sqrt{c_1^2 + c_2^2} \quad \varphi = \tan^{-1} \left( -\frac{c_2}{c_1} \right) \]

HINT: Make use of the trigonometric identities provided in Supplement S3. Consider working backward from the identity \( \cos(\alpha + \beta) = \cos(\alpha) \cos(\beta) - \sin(\alpha) \sin(\beta) \). Also note that \( \sin \left( \tan^{-1}(x) \right) = \frac{x}{\sqrt{x^2+1}} \) and \( \cos \left( \tan^{-1}(x) \right) = \frac{1}{\sqrt{x^2+1}} \).

\[ 11.14^* \] Consider the differential equation
\[ \frac{d^2 y}{dx^2} - dy = y(x) \]
with the boundary conditions \( y(0) = 0 \) and \( y'(0) = 1 \).

(a) Derive the corresponding auxiliary equation and show that the two roots are \( \alpha_e = \varphi \) and \( \alpha_1 = 1 - \varphi \) where
\[ \varphi = \frac{1}{2} \left( 1 + \sqrt{5} \right) \]
is the golden ratio.

(b) Using the result from (a) and the boundary conditions, determine the solution for \( y(x) \).

(c) Propose a solution to the original differential equation in the form of the power series
\[ y(x) = \sum_{n=0}^{\infty} a_n x^n \]
and show that the coefficients
\[ a_n = \frac{1}{n!} f_n \]
where \( f_n \) are the Fibonacci numbers and \( f_0 = 0, f_1 = 1, f_2 = 1, f_3 = 2, f_4 = 3, f_5 = 5, f_6 = 8 \), and so on.

(d) Expand your result from (b) in a MacLaurin series. Compare that series term-by-term with the result from (c). Show that
\[ f_n = \frac{1}{\sqrt{5}} \left[ \left( \frac{1 + \sqrt{5}}{2} \right)^n - \left( \frac{1 - \sqrt{5}}{2} \right)^n \right] = \frac{1}{\sqrt{3}} \left[ \varphi^n - (1 - \varphi)^n \right] \]
This equation relating the Fibonacci numbers to the golden mean is known as Binet’s formula.

\[ 11.15^* \] Consider the second order differential equation known as Bessel’s equation
\[ x^2 \frac{d^2 y(x)}{dx^2} + x \frac{dy(x)}{dx} + (x^2 - \alpha^2) y(x) = 0 \]
where \( c \) is a constant. The method we have developed in this chapter cannot be used to solve this problem as the term \( x^2 y(x) \) leads to terms of order \( x^{n+2} \) in addition to the usual terms of order \( x^n \).

(a) Propose a solution of the form \( y(x) = x^r \sum_{n=0}^{\infty} a_n x^n \). Inserting into Bessel’s equation will lead to a sum of two power series. Assuming that \( a_0 \neq 0 \), show that a consistent solution can be found if \( (n+r)(n+r-1) + (n+r) - c^2 = 0 \) for \( n = 0 \). Solve that equation to identify the two allowed values of \( r = c \) and \( r = -c \).

(b) For \( r = c \), show that \( a_1 = 0 \) and therefore \( a_{2n+1} = 0 \) for \( n \geq 1 \).

(c) For \( r = c \), determine the recursion relation for the coefficients \( a_{2n} \) in terms of \( a_0 \). Use your coefficients to determine the solution \( y_+(x) \) to Bessel’s equation.

(d) Repeat steps (b) and (c) for \( r = -c \) to arrive at a second solution \( y_-(x) \) to Bessel’s equation.
12.1 The classical heat equation

The process of thermal transport involves energy moving from regions of high temperature to regions of low temperature. Microscopically, this occurs through the random motions of atoms and molecules. At a larger scale, the process can be modeled in terms of changes in temperature as a function of space and time described by the classical heat equation. This section explores the properties and solution of the classical heat equation in one-dimension.

12.1.1 The classical heat equation in one-dimension (finite bounds)

Variation in the temperature of an object as a function of position and time can be modeled by the classical heat equation

\[ \frac{\partial u(x,t)}{\partial t} = \kappa \frac{\partial^2 u(x,t)}{\partial x^2} \]  \hspace{1cm} (12.1)

where \( u(x,t) \geq 0 \) is the temperature profile that is dependent on position, \( x \), and time, \( t \) (see Figure 12.1).\(^1\) The classical heat equation is a partial differential equation as it describes changes in a function of many variables in terms of partial derivatives of the function.

The equation states that the rate of change in the temperature \( u(x,t) \), given by the first derivative of \( u(x,t) \) with respect to \( t \), is proportional to the second derivative of the temperature \( u(x,t) \) with respect to \( x \). The parameter \( \kappa \) is the thermal diffusivity that modulates the proportionality between the partial derivatives in time and position and has units of length squared divided by time.

Our goal is to solve this partial differential equation for the temperature, \( u(x,t) \). We assume that \( u(x,t) \) is a separable function of \( x \) and \( t \) and can be written

\[ u(x,t) = X(x)T(t) \]

Inserting this function into Equation 12.1 we find

\[ X(x) \frac{dT(t)}{dt} = \kappa T(t) \frac{d^2X(x)}{dx^2} \]

Rearranging the equation so that the time dependence is on the left and the position dependence is on the right leads to

\[ \frac{1}{\kappa T(t)} \frac{dT(t)}{dt} = \frac{1}{X(x)} \frac{d^2X(x)}{dx^2} \]

Since \( x \) and \( t \) are independent variables, for this equality to hold each side of the equation must be proportional to a constant as

\[ \frac{1}{\kappa T(t)} \frac{dT(t)}{dt} = -\alpha^2 = \frac{1}{X(x)} \frac{d^2X(x)}{dx^2} \]  \hspace{1cm} (12.2)

\(^1\) The classical heat equation may also be written \( u_t = \kappa u_{xx} \) using our compact notation for partial derivatives.

Figure 12.1: Curves representing the temperature profile, \( u(x,t) \), of a hot spot as a function of position, \( x \), taken at two points in time, \( t \). Regions of higher temperature fall while regions of lower temperature rise. The cooling in the center (shaded gray) equals the heating in the wings (shaded red).
where \( \alpha \) is a constant that can be determined using initial conditions or boundary conditions for \( u(x,t) \).

By assuming a separable solution \( u(x,t) = X(x)T(t) \), we have converted a single partial differential equation into two ordinary differential equations. We can now use techniques to solve first and second order ordinary differential equations of a single variable, developed in Chapters 10 and 11, to determine solutions for \( X(x) \) and \( T(t) \). Those solutions can then be combined to determine the overall solution for \( u(x,t) = X(x)T(t) \).

Let's determine the solution for \( X(x) \) by returning to Equation 12.2 and solving the second order ordinary differential equation\(^2\)

\[
\frac{d^2X(x)}{dx^2} = -\alpha^2 X(x)
\]

The boundary conditions can take on many forms. We will consider the case of reflecting boundary conditions at \( x = 0 \) and \( x = L \) for which the gradient of the temperature in space is zero

\[
\frac{\partial u}{\partial x}(0,t) = \frac{\partial u}{\partial x}(L,t) = 0
\]

The reflecting boundary condition models a perfectly insulating wall.

We take the constant \( \alpha^2 \geq 0 \) and draw on our experience in solving second order ordinary differential equations in Chapter 11 to propose a general solution of the form\(^3\)

\[
X(x) = a_1 \cos(\alpha x) + b_1 \sin(\alpha x)
\]

Let's apply the boundary conditions to this proposed solution.\(^4\) Since

\[
\frac{dX}{dx}(0) = b_1 \alpha = 0
\]

it must be that \( b_1 = 0 \). Furthermore, since

\[
\frac{dX}{dx}(L) = -a_1 \alpha \sin(\alpha L) = 0
\]

it must be that

\[\alpha L = n \pi \quad n = 0, 1, 2, \ldots\]

providing an infinite number of possible values of our constant

\[\alpha^2 = \frac{n^2 \pi^2}{L^2} \quad n = 0, 1, 2, \ldots \quad (12.3)\]

and an infinite number of potential solutions

\[X_n(x) = a_n \cos\left(\frac{n\pi x}{L}\right) \quad n = 0, 1, 2, \ldots\]

Here \( a_n \) are constant coefficients that must be determined by additional initial or boundary conditions. Note that we include the constant solution \( X_0(x) = a_0 \). This is a non-trivial solution that will prove to be critical to our overall solution for \( u(x,t) \). Since \( u(x,t) \) is a sum of cosines that can take on positive and negative values, the constant term \( a_0 \) is essential to maintain the condition that the temperature profile \( u(x,t) > 0 \) for all \( x \) and \( t \).

Now let's return to Equation 12.2 and determine the solution for \( T(t) \) by solving the first order ordinary differential equation\(^5\)

\[
\frac{dT(t)}{dt} = -\kappa \alpha^2 T(t)
\]

Having determined acceptable values of \( \alpha^2 \) in Equation 12.3 we can rewrite this...
first order ordinary differential equation for \( T(t) \) as
\[
\frac{dT(t)}{dt} = -\kappa \frac{n^2 \pi^2}{L^2} T(t) \quad n = 0, 1, 2, \ldots
\]

Drawing on our experience solving first order ordinary differential equations in Chapter 10, we propose an infinite number of potential solutions
\[
T_n(t) = c_n \exp \left[ -\frac{n^2 \pi^2}{L^2} kt \right]
\]

where \( c_n \) are constant coefficients that must be determined by additional initial or boundary conditions.

For a given value of \( n \) we find that the product \( X_n(x)T_n(t) \) is a solution of Equation 12.1. It follows that a sum of all possible solutions \( X_n(x)T_n(t) \) represents a general solution for the time and position dependence of \( u(x, t) \), which can be written\(^6\)

\[
u(x, t) = \sum_{n=0}^{\infty} X_n(x)T_n(t)
= \sum_{n=0}^{\infty} a_n \cos \left[ \frac{n\pi}{L} x \right] \times c_n \exp \left[ -\frac{n^2 \pi^2}{L^2} kt \right]
= u_0 + \sum_{n=1}^{\infty} u_n \cos \left[ \frac{n\pi}{L} x \right] \exp \left[ -\frac{n^2 \pi^2}{L^2} kt \right]
\] (12.4)

where the constant coefficients \( u_n = a_n c_n \).

To determine the values of the constant coefficients \( u_n \) we typically appeal to an initial condition at \( t = 0 \) for which our general solution takes the form

\[
u(x, 0) = u_0 + \sum_{n=1}^{\infty} u_n \cos \left[ \frac{n\pi}{L} x \right]
\]

Our result is a general solution for the heat equation with reflecting boundary conditions. Using this result, the parameters \( u_n \) are fit to match the given initial temperature profile, \( u(x, 0) \), providing a complete solution for \( u(x, t) \).

12.1.2 Application of the classical heat equation (reflecting boundaries)

Let’s consider the case of an initial condition for the temperature profile described by
\[
u(x, 0) = \sin^2 \left[ \frac{\pi}{L} x \right]
\] (12.5)

shown in Figure 12.2. The reflecting boundary conditions for the temperature profile are
\[
\frac{\partial u}{\partial x}(0, t) = \frac{\partial u}{\partial x}(L, t) = 0
\]

We return to our general solution for \( u(x, t) \), Equation 12.4, appropriate for reflecting boundary conditions

\[
u(x, t) = u_0 + \sum_{n=1}^{\infty} u_n \cos \left[ \frac{n\pi}{L} x \right] \exp \left[ -\frac{n^2 \pi^2}{L^2} kt \right]
\]

Taking the general solution at \( t = 0 \) and setting it equal to the initial distribution, Equation 12.5, we find

\[
u(x, 0) = u_0 + \sum_{n=1}^{\infty} u_n \cos \left[ \frac{n\pi}{L} x \right] = \sin^2 \left[ \frac{\pi}{L} x \right]
\]

\(^6\) This general solution to the classical heat equation was first presented by French mathematician and physicist Joseph Fourier (1768-1830). Fourier is also credited with the discovery of the greenhouse effect.
Using our knowledge of trigonometric identities, we recognize that \( \sin^2(x) = (1 - \cos(2x))/2 \) so that
\[
u(x, 0) = \sin^2 \left( \frac{\pi}{L} x \right) = \frac{1}{2} - \frac{1}{2} \cos \left( \frac{2\pi}{L} x \right)
\]
\[= u_0 + u_2 \cos \left( \frac{2\pi}{L} x \right)
\]
where \( u_0 = 1/2, u_2 = -1/2, \) and all other coefficients are zero. Having identified the coefficients of the series, we can write the general solution as a function of position and time
\[
u(x, t) = \frac{1}{2} - \frac{1}{2} \cos \left( \frac{2\pi}{L} x \right) \exp \left[ -\frac{4\pi^2}{L^2} \kappa t \right]
\]
\[\tag{12.6}\]
Figure 12.2 shows the time evolution of \( \nu(x, t) \) described by Equation 12.6. At initial times the distribution is peaked at a hot spot in the center of the box. Over time, the temperature in the center decreases, the temperature in the wings increases, and \( \nu(x, t) \) approaches a final uniform temperature distribution, \( \nu(x, \infty) \).

### 12.2 The classical diffusion equation

The process of diffusion is fundamental to studies of kinetics and transport in the physical sciences. At the microscopic level, diffusion occurs through the random motions of atoms and molecules. At a larger scale, the process of diffusion can be modeled in terms of changes in the concentration profile as a function of space and time described by the classical diffusion equation. This section explores the classical diffusion equation and its solution in one and many dimensions.

#### 12.2.1 The classical diffusion equation in one-dimension (free diffusion)

Variation in the concentration of particles as a function of position and time can be modeled by the classical diffusion equation\(^7\)
\[
\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \tag{12.7}
\]
where \( c(x, t) \) describes the physical density or concentration of a particles that is dependent on position, \( x \), and time, \( t \).\(^8\) The equation states that the rate of change in the distribution \( c(x, t) \), given by the first derivative of \( c(x, t) \) with respect to \( t \), is proportional to the second derivative of the distribution \( c(x, t) \) with respect to \( x \). The parameter \( D \) is the diffusion coefficient that modulates the proportionality between the partial derivatives in time and position and has units of length squared divided by time.

For free diffusion, the total amount of diffusing particles is conserved so that the integral of the distribution \( c(x, t) \) over all positions, \( x \), is constant for all time
\[
\int_{-\infty}^{\infty} c(x, t) dx = c_0
\]
An initial condition \( c(x, 0) \) describes the distribution of our particles in space at \( t = 0 \). The distribution of our particles at some time \( t > 0 \) in the future is defined by the solution of Equation 12.7.

Let’s consider the case of diffusion in one-dimension with no spatial boundary conditions. We call this free diffusion. Assume that our diffusing particles are initially concentrated at a single point in space, \( x = x_0 \), providing the initial

\(^7\) The diffusion equation was discovered by German physician and physiologist Adolf Fick (1829-1901).

\(^8\) The classical diffusion equation may also be written \( c_t = Dc_{xx} \) using our compact notation for partial derivatives.
We propose an ansatz for the dependence of the distribution on position, $x$, and time, $t$, written as a gaussian function

$$c(x, t) = \frac{c_0}{\sqrt{4\pi Dt}} \exp \left[ -\frac{(x-x_0)^2}{4Dt} \right]$$

We note several important properties of this proposed distribution. The integral of the distribution over all positions, $x$, is a constant

$$\int_{-\infty}^{\infty} c(x, t) dx = \frac{c_0}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} \exp \left[ -\frac{(x-x_0)^2}{4Dt} \right] dx = c_0$$

for all time $t$. Furthermore, at $t = 0$ the proposed distribution $c(x, t)$ is concentrated at a single point in space, $x = x_0$, as

$$c(x, 0) = \lim_{t \to 0} \frac{c_0}{\sqrt{4\pi Dt}} \exp \left[ -\frac{(x-x_0)^2}{4Dt} \right] = c_0 \delta(x - x_0)$$

Here we have used the definition of the Dirac delta function

$$\delta(x - x_0) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[ -\frac{(x-x_0)^2}{2\sigma^2} \right]$$

where $\sigma^2 = 2Dt$. The normalized gaussian distribution function approaches a Dirac delta function as the width of the distribution, $\sigma = \sqrt{2Dt}$, approaches zero. As time evolves the width of the distribution increases as $\sigma = \sqrt{2Dt}$ at a rate proportional to $t^{1/2}$. These properties of the distribution $c(x, t)$ are depicted in Figure 12.3.

Now let’s prove that our ansatz for $c(x, t)$ is a solution to the classical diffusion equation by substituting Equation 12.8 into Equation 12.7 and demonstrating the equality. We will do this in steps by evaluating the partial derivatives with respect to time and position separately before combining them in Equation 12.7.

For the partial derivative with respect to time we find

$$\frac{dc(x, t)}{dt} = \left[ \frac{(x-x_0)^2}{4Dt^2} - \frac{1}{2t} \right] c(x, t)$$

For the first partial derivative with respect to position we find

$$\frac{dc(x, t)}{dx} = -\frac{2(x-x_0)}{4Dt} c(x, t)$$

so that the second partial derivative with respect to position is

$$\frac{d^2c(x, t)}{dx^2} = \left[ \frac{4(x-x_0)^2}{(4Dt)^2} - \frac{2}{4Dt} \right] c(x, t)$$

Combining our results we find

$$\frac{dc(x, t)}{dt} = D \frac{d^2c(x, t)}{dx^2}$$

$$\left[ \frac{(x-x_0)^2}{4Dt^2} - \frac{1}{2t} \right] c(x, t) = D \left[ \frac{4(x-x_0)^2}{(4Dt)^2} - \frac{2}{4Dt} \right] c(x, t)$$

Canceling $c(x, t)$ on each side and multiplying through by $D$ in the right hand expression, we demonstrate the equality. This proves that our ansatz in the form of Equation 12.8 satisfies the diffusion equation.

$\delta(x - x_0)$ is concentrated at a single point in space, for all time, $x_0$.

$\delta(x - x_0)$ approaches $\delta(x)$ as $\sigma^2 = 2Dt$. The normalized gaussian distribution function approaches a Dirac delta function as the width of the distribution, $\sigma = \sqrt{2Dt}$, approaches zero. As time evolves the width of the distribution increases as $\sigma = \sqrt{2Dt}$ at a rate proportional to $t^{1/2}$. These properties of the distribution $c(x, t)$ are depicted in Figure 12.3.

Now let’s prove that our ansatz for $c(x, t)$ is a solution to the classical diffusion equation by substituting Equation 12.8 into Equation 12.7 and demonstrating the equality. We will do this in steps by evaluating the partial derivatives with respect to time and position separately before combining them in Equation 12.7.

For the partial derivative with respect to time we find

$$\frac{dc(x, t)}{dt} = \left[ \frac{(x-x_0)^2}{4Dt^2} - \frac{1}{2t} \right] c(x, t)$$

For the first partial derivative with respect to position we find

$$\frac{dc(x, t)}{dx} = -\frac{2(x-x_0)}{4Dt} c(x, t)$$

so that the second partial derivative with respect to position is

$$\frac{d^2c(x, t)}{dx^2} = \left[ \frac{4(x-x_0)^2}{(4Dt)^2} - \frac{2}{4Dt} \right] c(x, t)$$

Combining our results we find

$$\frac{dc(x, t)}{dt} = D \frac{d^2c(x, t)}{dx^2}$$

$$\left[ \frac{(x-x_0)^2}{4Dt^2} - \frac{1}{2t} \right] c(x, t) = D \left[ \frac{4(x-x_0)^2}{(4Dt)^2} - \frac{2}{4Dt} \right] c(x, t)$$

Canceling $c(x, t)$ on each side and multiplying through by $D$ in the right hand expression, we demonstrate the equality. This proves that our ansatz in the form of Equation 12.8 satisfies the diffusion equation.
258 THE CLASSICAL DIFFUSION EQUATION

12.2.2 Application of the classical diffusion equation (reflecting boundary)

Let’s consider the case of an initial condition for the concentration profile \( c(x,t) \) described by

\[
c(x,0) = c_0 \delta(x - x_0)
\]  

(12.9)

where \( x_0 > 0 \). Assume there is a reflecting boundary at the origin \( x = 0 \). Any particles diffusing to \( x = 0 \) is reflected back to \( x > 0 \) and maintained in the range \( 0 \leq x < \infty \). The reflecting boundary condition for the distribution is written

\[
\frac{\partial c}{\partial x}(0,t) = 0
\]

With the reflecting boundary, the total area under our distribution is constant in time and

\[
\int_0^\infty c(x,t) \, dx = c_0
\]

In this case, the solution to the diffusion equation can be written

\[
c(x,t) = \frac{c_0}{\sqrt{4\pi D t}} \exp \left[ -\frac{(x - x_0)^2}{4Dt} \right] + \frac{c_0}{\sqrt{4\pi D t}} \exp \left[ -\frac{(x + x_0)^2}{4Dt} \right]
\]

(12.10)

where we have added a gaussian centered at \( x = x_0 \) to an image of that gaussian function, a second gaussian function centered at \( x = -x_0 \). The function is shown in Figure 12.4.

How can we see that this function represents a valid solution to the diffusion equation over \( 0 \leq x < \infty \) with a reflecting boundary at \( x = 0 \)? First, we demonstrated earlier that gaussian functions of the form in Equation 12.10 satisfy the diffusion equation \( c_t(x,t) = D c_{xx}(x,t) \). As such, the sum of the two functions will also be a solution to the diffusion equation. Second, we can see that the derivative

\[
\frac{\partial c}{\partial x}(0,t) = 0
\]

since the derivative of the first gaussian at \( x = 0 \) will be equal in magnitude and opposite in sign to the derivative of the second gaussian at \( x = 0 \). Third, at \( t = 0 \) each gaussian becomes a Dirac delta function and

\[
c(x,0) = c_0 \delta(x - x_0) + c_0 \delta(x + x_0)
\]

As our solution is defined only for \( 0 \leq x < \infty \), only the first Dirac delta function contributes. As such, our solution satisfies the initial condition that

\[
c(x,0) = c_0 \delta(x - x_0).
\]
Finally, we are left to show that the total area under our distribution is constant in time. We can do this by evaluating

$$\int_0^\infty c(x,t)dx = \frac{c_0}{\sqrt{4\pi Dt}} \int_0^\infty e^{-\frac{(x-x_0)^2}{4Dt}} dx + \frac{c_0}{\sqrt{4\pi Dt}} \int_0^\infty e^{-\frac{(x+x_0)^2}{4Dt}} dx$$

Defining $u = (x-x_0)/\sqrt{4Dt}$, we note that for the first integral

$$\frac{1}{\sqrt{4\pi Dt}} \int_0^\infty e^{-\frac{(x-x_0)^2}{4Dt}} dx = \frac{1}{\sqrt{\pi}} \int_{\frac{-x_0}{\sqrt{4Dt}}}^\infty e^{-u^2} du = 1 - \frac{1}{2} \text{erfc}\left(\frac{x_0}{\sqrt{4Dt}}\right)$$

where $\text{erfc}(x)$ is the complementary error function. Defining $u = (x+x_0)/\sqrt{4Dt}$, we note that for the second integral

$$\frac{1}{\sqrt{4\pi Dt}} \int_0^\infty e^{-\frac{(x+x_0)^2}{4Dt}} dx = \frac{1}{\sqrt{\pi}} \int_{\frac{-x_0}{\sqrt{4Dt}}}^\infty e^{-u^2} du = \frac{1}{2} \text{erfc}\left(\frac{x_0}{\sqrt{4Dt}}\right)$$

with the final result that

$$\int_0^\infty c(x,t)dx = c_0 \left[ 1 - \frac{1}{2} \text{erfc}\left(\frac{x_0}{\sqrt{4Dt}}\right) + \frac{1}{2} \text{erfc}\left(\frac{-x_0}{\sqrt{4Dt}}\right) \right] = c_0$$

We’ve demonstrated that Equation 12.10 satisfies the diffusion equation, reflecting boundary condition and initial condition, and the constraint that the total area under the distribution is conserved, validating our solution for $c(x,t)$. The final result is shown in Figure 12.5.

![Figure 12.5: The distribution $c(x,t)$ evolving over $0 \leq x < \infty$ with a reflecting boundary at $x = 0$. The distribution is shown as a function of $x$ for several values of $t$. As time evolves, solutions are shown in lighter and lighter shades of red.](image)

Note the effect of the reflecting boundary condition on $c(x,t)$. Initially, near $x = 0$ there is growth in the distribution $c(x,t)$ as particles diffusing to the left are reflected back to $x > 0$. Over time, the distribution broadens as a function of $x$. Eventually, particles will diffuse to form a uniform concentration profile.

12.2.3 The classical diffusion equation in two dimensions (free diffusion)

For the classical diffusion equation in one-dimension

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

we proposed the ansatz that

$$c(x,t) = \frac{c_0}{\sqrt{4\pi Dt}} \exp\left[ -\frac{(x-x_0)^2}{4Dt} \right]$$

11 The error function is defined

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

while the complementary error function is defined

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$

or $\text{erfc}(x) = 1 - \text{erf}(x)$. 

where the variance of the distribution $\sigma^2 = 2Dt$. We proved this to be valid for free diffusion with the initial condition

$$c(x, 0) = c_0 \delta(x - x_0)$$

Now consider the classical diffusion equation in two-dimensions expressed in cartesian coordinates

$$\frac{\partial c(x, y, t)}{\partial t} = D \left[ \frac{\partial^2 c(x, y, t)}{\partial x^2} + \frac{\partial^2 c(x, y, t)}{\partial y^2} \right] \quad (12.11)$$

Here $c(x, y, t)$ is the concentration profile in position, $x$ and $y$, and time, $t$. Let’s examine the case of free diffusion where there are no boundary conditions on our concentration profile. The initial condition is

$$c(x, y, 0) = c_0 \delta(x - x_0) \delta(y - y_0)$$

As time evolves, the distribution broadens with growing variances $\sigma_x^2 = 2Dt$ and $\sigma_y^2 = 2Dt$.\(^\text{12}\)

With these observations and following our solution in one-dimension, we propose the ansatz for the concentration profile

$$c(x, y, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left( -\frac{(x-x_0)^2}{4Dt} \right) \times \frac{1}{\sqrt{4\pi Dt}} \exp \left( -\frac{(y-y_0)^2}{4Dt} \right)$$

which can be further simplified as

$$c(x, y, t) = \frac{1}{4\pi Dt} \exp \left( -\frac{1}{4Dt} \left( (x-x_0)^2 + (y-y_0)^2 \right) \right) \quad (12.12)$$

This represents the solution for free diffusion starting at a point $(x_0, y_0)$ and spreading at a rate defined by the diffusion coefficient, $D$. The concentration profile is initially defined by a delta function at $t = 0$. As time evolves, the variance of the distribution grows as $t$ and the width grows as

$$\text{distribution width } \propto t^{1/2}$$

Let’s examine the properties of our solution to the two-dimensional diffusion equation given by Equation 12.12. The concentration profile $c(x, y, t)$ is shown in Figure 12.6 at five times $t = 1, 2, 4, 8, \infty$. At $t = 1$ the distribution remains peaked about the point $(x_0, y_0)$ with a width equal to $\sqrt{2D}$. As the distribution evolves in time to $t = 2$ and then $t = 4$ the width grows by a factor of $\sqrt{4} = 2$. When time has evolved to $t = 8$ the width of the distribution has increased by a factor of $\sqrt{8} = 2\sqrt{2}$ from the distribution at $t = 1$. As time evolves still further the distribution will continue to spread as it approaches a uniform distribution over the $xy$-plane at $t = \infty$.

While we have assumed free diffusion in two-dimensions, it is also possible to impose boundary conditions that are absorbing or reflecting, as was done in the case of the classical heat equation. Moreover, while we have expressed Equation 12.13 in two-dimensional cartesian coordinates, the equation can be written more generally as

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (12.13)$$

where $\nabla^2$ is the Laplace operator (see Chapter 5). As such, we can readily express the diffusion equation in two-dimensional plane polar coordinates for $c(r, \theta, t)$, three-dimensional cartesian coordinates for $c(x, y, z, t)$, cylindrical coordinates for $c(r, \theta, z, t)$, or spherical polar coordinates for $c(r, \theta, \phi, t)$, by simply using the appropriate form of the operator $\nabla^2$ (as provided in Complement C5).

\(^{12}\) As we assume diffusion in $x$ and $y$ is uncorrelated, the correlation coefficient $\rho_{xy} = 0$ and the covariance $\sigma_{xy} = 0$. 

![Figure 12.6: A concentration profile in the $xy$-plane represented by a two-dimensional gaussian distribution at times $t = 1, 2, 4, 8$ and $\infty$.](image)
12.3 The classical wave equation

Many systems involve interfaces separating one domain from another. Common examples include the surface of a liquid exposed to a gas, the interface between two immiscible liquids, and the surface of a membrane exposed to water. In each case, fluctuations of the interface involve the formation and propagation of wave forms that can be modeled using the classical wave equation. This section explores the classical wave equation and its solution in one and two dimensions.

12.3.1 The classical wave equation in one-dimension

The classical wave equation for the displacement \( h(x,t) \) of a string as a function of position \( x \) and time \( t \) is\(^\text{13}\)

\[
\frac{\partial^2 h(x,t)}{\partial t^2} = v^2 \frac{\partial^2 h(x,t)}{\partial x^2}
\]  

(12.14)

where \( v \) is a constant with units of speed, or length over time.\(^\text{14}\) We assume that the ends of the string are fixed so that the displacement is zero at \( x = 0 \) and \( x = L \). As such

\[
h(0,t) = h(L,t) = 0
\]

providing the boundary conditions (see Figure 12.7)

![Figure 12.7: The displacement \( h(x,t) \) of a classical wave over a length \( L \).](image)

To solve the wave equation, we follow the procedure used to solve the classical heat equation, Equation 12.1, by proposing a solution for the displacement \( h(x,t) \) that is separable in its dependence on position and time

\[
h(x,t) = X(x)T(t)
\]

Inserting this function into Equation 12.14 we find

\[
X(x) \frac{d^2 T(t)}{dt^2} = v^2 T(t) \frac{d^2 X(x)}{dx^2}
\]

Rearranging this equation so that the time dependence is on the left and the position dependence is on the right

\[
\frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2} = \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2}
\]

Since we expect \( x \) and \( t \) to be independent, the only way for this equality to hold is if each side of the equation is proportional to a constant\(^\text{15}\)

\[
\frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2} = -k^2 = \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2}
\]

(12.15)

\(^\text{13}\) The wave equation was discovered by French mathematician, physicist, philosopher, and music theorist Jean le Rond d’Alembert (1717-1783).

\(^\text{14}\) The classical heat equation may also be written \( u_t = \kappa u_{xx} \) using our compact notation for partial derivatives.

\(^\text{15}\) The use of a negative constant \( -k^2 \) will conveniently simplify our solution.
where $k$ is a constant that can be determined by initial or boundary conditions.

By assuming a separable solution, we have converted a single second order partial differential equation into two second order ordinary differential equations. We can now use the techniques we developed to solve second order ordinary differential equations of a single variable to determine solutions for $T(t)$ and $X(x)$. Those solutions can then be combined to determine the overall solution for $h(x, t) = X(x)T(t)$.

Let’s determine the solution for $X(x)$ by returning to Equation 12.15 and solving the second order ordinary differential equation

$$\frac{d^2X(x)}{dx^2} = -k^2X(x)$$

As the constant $k^2 > 0$, we draw on our experience in solving second order ordinary differential equations in Chapter 11 to propose a general solution of the form

$$X(x) = a_1 \cos(kx) + b_1 \sin(kx)$$

The constants $a_1$ and $b_1$ can be determined through the boundary conditions. We find

$$X(0) = a_1 = 0$$

Furthermore, since

$$X(L) = b_1 \sin(kL) = 0$$

it follows that

$$kL = n\pi \quad n = 1, 2, \ldots$$

providing an infinite number of possible values of our constant

$$k^2 = \frac{n^2\pi^2}{L^2} \quad n = 1, 2, \ldots$$

(12.16)

and an infinite number of potential solutions

$$X_n(x) = b_n \sin\left(\frac{n\pi}{L}x\right) \quad n = 1, 2, \ldots$$

Here $b_n$ are constant coefficients that must be determined by additional initial or boundary conditions.

Now let’s return to Equation 12.15 and determine the solution for $T(t)$ by solving the second order ordinary differential equation

$$\frac{d^2T(t)}{dt^2} = -v^2k^2T(t)$$

Having determined acceptable values of $k^2$ in Equation 12.16 we can rewrite this second order ordinary differential equation for $T(t)$ as

$$\frac{d^2T(t)}{dt^2} = -v^2 \frac{n^2\pi^2}{L^2}T(t) \quad n = 1, 2, \ldots$$

Drawing on our experience solving second order ordinary differential equations in Chapter 11, we propose an infinite number of potential solutions

$$T_n(t) = c_n \cos\left(\frac{n\pi}{L}vt\right) + d_n \sin\left(\frac{n\pi}{L}vt\right)$$

where $c_n$ and $d_n$ are constant coefficients that must be determined by additional initial or boundary conditions.

For a given value of $n$ we find that the product $X_n(x)T_n(t)$ is a solution of Equation 12.14. It follows that a sum of all possible solutions $X_n(x)T_n(t)$

\[\text{As } x \text{ is the sole variable, we have replaced the partial derivative with respect to } x \text{ in Equation 12.15 with a total derivative.}\]
represents a general solution for the time and position dependence of \( h(x,t) \), which can be written

\[
h(x,t) = \sum_{n=1}^{\infty} X_n(x) T_n(t) = \sum_{n=1}^{\infty} b_n \sin \left( \frac{n \pi x}{L} \right) \times \left[ c_n \cos \left( \frac{n \pi}{L} vt \right) + d_n \sin \left( \frac{n \pi}{L} vt \right) \right]
\]

where \( \omega_n = \frac{n \pi v}{L} \) and the constant coefficients \( s_n = b_n c_n \) and \( t_n = b_n d_n \).

To determine the values of the constant coefficients \( s_n \) and \( t_n \) we typically appeal to the initial conditions at \( t = 0 \) for our general solution

\[
h(x,0) = \sum_{n=1}^{\infty} s_n \sin \left( \frac{n \pi x}{L} \right)
\]

and its derivative in time

\[
\frac{\partial h}{\partial t}(x,0) = \sum_{n=1}^{\infty} t_n \omega_n \sin \left( \frac{n \pi x}{L} \right)
\]

Given a knowledge of \( h(x,0) \) and \( u_t(x,0) \) the parameters \( s_n \) and \( t_n \) are fit to provide an overall solution to \( h(x,t) \).

### 12.3.2 Application of the classical wave equation (plucked string)

Let’s consider the specific case of a plucked string. The ends of the string are fixed imposing the boundary conditions

\[
h(0,t) = 0 \quad h(L,t) = 0
\]

The initial condition for the displacement of the string is described by

\[
h(x,0) = \sin \left( \frac{2 \pi x}{L} \right) \cos \left( \frac{2 \pi x}{L} \right)
\]

with

\[
\frac{\partial h}{\partial t}(x,0) = 0
\]

Note that the first initial condition determines the initial displacement of the string \( h(x,0) \) while the second indicates that at \( t = 0 \) the string is drawn but not moving (heavy black line in Figure 12.8).

![Figure 12.8: The displacement of a string \( h(x,t) \) over a box of length \( L \), shown for the initial displacement (black) and at several times in the future (lighter and lighter shades of red).](image)

Once released the string moves through sinusoidal repeating oscillations.
We return to our general solution appropriate for these boundary conditions

\[ h(x, t) = \sum_{n=1}^{\infty} \sin \left( \frac{n\pi}{L} x \right) [s_n \cos (\omega_n t) + t_n \sin (\omega_n t)] \]

Taking the general solution at \( t = 0 \) and setting it equal to the initial distribution defined by Equation 12.17, we find

\[ h(x, 0) = \sum_{n=1}^{\infty} s_n \sin \left( \frac{n\pi}{L} x \right) = \sin \left( \frac{2\pi}{L} x \right) \cos \left( \frac{2\pi}{L} x \right) \]

Using our knowledge of trigonometric identities, we recognize that \( \sin(x) \cos(x) = \sin(2x)/2 \) so that

\[ h(x, 0) = \sin \left( \frac{2\pi}{L} x \right) \cos \left( \frac{2\pi}{L} x \right) = \frac{1}{2} \sin \left( \frac{4\pi}{L} x \right) \]

As such \( s_4 = 1/2 \) and all other coefficients \( s_n \neq 4 = 0 \). Applying the second initial condition, Equation 12.18, we find

\[ \frac{\partial u}{\partial t} (x, 0) = \sum_{n=1}^{\infty} t_n \omega_n \sin \left( \frac{n\pi}{L} x \right) = 0 \]

As such \( t_n = 0 \) for all \( n \). Having identified the coefficients of the series, we can write the general solution as a function of position and time

\[ h(x, t) = \frac{1}{2} \sin \left( \frac{4\pi}{L} x \right) \cos \left( \frac{4\pi}{L} vt \right) \]

This final result for the displacement of the string and its variation in time is shown in Figure 12.8. The solution is periodic in time with a period

\[ T = \frac{L}{2v} \]

proportional to \( L \) and inversely proportional to the speed of the wave \( v \).

12.3.3 The classical wave equation in two-dimensions

The classical wave equation in one-dimension describes the displacement \( h(x, t) \) of a string in position, \( x \), and time, \( t \), as

\[ \frac{\partial^2 h(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 h(x, t)}{\partial t^2} \]

Assuming that the ends of the string are fixed so that

\[ h(0, t) = 0 \quad h(L, t) = 0 \]

we identified the general solution

\[ h(x, t) = \sum_{n=1}^{\infty} \sin \left( \frac{n\pi}{L} x \right) [s_n \cos (\omega_n t) + t_n \sin (\omega_n t)] \]

where \( \omega_n = n\pi v / L \) and the constant coefficients \( s_n \) and \( t_n \) are defined by appealing to initial or boundary conditions.

Now consider the classical wave equation in two-dimensions expressed in cartesian coordinates

\[ \frac{\partial^2 h(x, y, t)}{\partial x^2} + \frac{\partial^2 h(x, y, t)}{\partial y^2} = \frac{1}{v^2} \frac{\partial^2 h(x, y, t)}{\partial t^2} \]  \[ (12.19) \]
Here \(h(x, y, t)\) describes the displacement of a two-dimensional sheet in position, \(x\) and \(y\), and time, \(t\). While our string was held fixed at two ends, leading to the boundary conditions \(h(0, t) = h(L, t) = 0\), we take our square sheet to be held fixed along each of four sides imposing the boundary conditions

\[
h(0, y, t) = h(L, y, t) = 0 \quad h(x, 0, t) = h(x, L, t) = 0
\]

An example of a wave form in our two-dimensional square sheet is shown in Figure 12.9.

Following our solution of the classical wave equation in one-dimension, we propose an ansatz for the displacement \(h(x, y, t)\) that is separable in position and time

\[
h(x, y, t) = X(x)Y(y)T(t)
\]

Inserting this function into Equation 12.19 we find

\[
Y(y)T(t) \frac{d^2X(x)}{dx^2} + X(x)Y(y) \frac{d^2Y(y)}{dy^2} = X(x)Y(y) \frac{1}{v^2} \frac{d^2T(t)}{dt^2}
\]

Dividing each term by \(h(x, y, t) = X(x)Y(y)T(t)\) leads to

\[
\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} = \frac{1}{v^2} \frac{d^2T(t)}{dt^2}
\]

Each of the terms depends solely on \(x\), \(y\), or \(t\) and can be solved independently. Our solutions for \(X(x)\) and \(Y(y)\) are

\[
X_n(x) = a_n \sin \left( \frac{n\pi x}{L} \right) \quad n = 1, 2, \ldots
\]

\[
Y_m(y) = b_m \sin \left( \frac{m\pi y}{L} \right) \quad m = 1, 2, \ldots
\]

where we have introduced indices \(n\) and \(m\) that independently track the number of half oscillations in the \(x\) and \(y\) directions. This leaves our equation in time to be

\[
\frac{d^2T(t)}{dt^2} = -v^2 \frac{\pi^2}{L^2} \left( n^2 + m^2 \right) T(t) = -\omega_{nm}^2 T(t)
\]

with the solution

\[
T_{nm}(t) = c_{nm} \cos \left( \omega_{nm} t \right) + d_{nm} \sin \left( \omega_{nm} t \right)
\]

where the frequencies

\[
\omega_{nm} = v \frac{\pi}{L} \left( n^2 + m^2 \right)^{1/2}
\]

are determined by the indices \(n\) and \(m\). As \(v\) has units of speed or length over time, the ratio \(L/v\) has units of time.

We can simplify our result as

\[
c_{nm} \cos \left( \omega_{nm} t \right) + d_{nm} \sin \left( \omega_{nm} t \right) = c_{nm} \sin \left( \omega_{nm} t + \varphi_{nm} \right)
\]

where

\[
c_{nm} = \sqrt{c_{nm}^2 + d_{nm}^2} \quad \varphi_{nm} = \tan^{-1} \left( c_{nm}/d_{nm} \right)
\]

Combining these results leads to the overall solution

\[
h(x, y, t) = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} X_n(x) Y_m(y) T_{nm}(t)
\]

\[
= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} u_{nm} \sin \left( \frac{n\pi x}{L} \right) \sin \left( \frac{m\pi y}{L} \right) \sin \left( \omega_{nm} t + \varphi_{nm} \right)
\]

Figure 12.10: The displacement \(h(x, y, t)\) for a classical wave in two-dimensions for \(n = 2\) and \(m = 4\). The wave is shown at five distinct times during one-half a period of oscillation.
where the coefficient $u_{nm} = a_n b_m c_{nm}$.

Let’s examine the properties of our solution to the two-dimensional wave equation by exploring the time evolution of the displacement $h(x,y,t)$. Consider the wave form $h(x,y,t)$ shown in Figure 12.10 for $n = 2$ and $m = 4$ and $\omega_{nm} = \omega_{24}$. The period of oscillation is defined

$$T = \frac{2\pi}{\omega_{24}}$$

The time evolution of the two-dimensional wave shown in Figure 12.10 represents one-half a period of oscillation. The maxima become minima and the minima become maxima.$^{18}$

At the initial time $t = 0$, the wave form is at maximum amplitude. As time evolves to $t = T/8$, the extrema in the wave are diminished while the nodal lines along which $h(x,y,t) = 0$ are maintained. At $t = T/4$ the wave form is flat. Further evolution to $t = 3T/8$ reverses the phase of the initial oscillations while maintaining the diminished amplitudes. As time evolves further to $t = T/2$, the full amplitude of the initial oscillation in the wave is restored. However, the wave is now inverted. Points that were originally maxima are minima, and vice versa. Further evolution of the wave over an additional time $T/2$ will restore the original wave form. This demonstrates the periodic nature of the general solution to the classical wave equation.

$^{18}$ Along the nodal lines defined by $x = 0$ and $y = 0$ the amplitude of the wave is zero at all times.

---

A Survey of partial differential equations in the physical sciences

Partial differential equations appear in all corners of the physical sciences including thermodynamics, kinetics, mechanics, and quantum theory. Examples include the classical heat equation, classical diffusion equation, classical wave equation, and quantum Schrödinger equation. In each case, a partial differential equation describes the variation in a function of two or more variables in terms of partial derivatives with respect to those variables. Here we explore the physical derivation of the classical heat equation, classical diffusion equation, and classical wave equation.

The classical heat equation in one-dimension

In the physical sciences, we are often interested in knowing how a distribution in space changes with time. For example, suppose we have a metal bar. The two ends of the bar are kept cold. The center of the bar is initially heated at time $t = 0$ creating a distribution of temperature that evolves in time as shown in Figure 12.11. The temperature in the center of the distribution decreases over time as heat flows toward the cold ends of the bar. Eventually, the entire bar is as cold as the ends.

How can we model this process as the temperature evolves in space and time? We expect that the rate of heat transfer is proportional to the temperature gradient

$$\text{temperature gradient} = \frac{\partial u(x,t)}{\partial x}$$

If the temperature gradient is zero, there will be no net heat flow and no change in temperature. If the temperature gradient is large, the temperature profile is expected to change as heat flows from the region of higher temperature to the region of lower temperature.

The heat energy in a length $\Delta x$ at position $x$ and time $t$ will be

$$\text{heat energy} = \Delta x \ u(x,t)$$

---

Figure 12.11: The temperature profile $u(x,t)$ is shown as a function of distance $x$ over a metal bar (thick gray line) of length $L$. At time $t = 0$, the bar is heated in the center while the ends are kept cold. Over time, the bar cools as depicted by profiles of temperature $u(x,t)$ that decrease with increasing time.
The classical diffusion equation in one-dimension

\[ \frac{\partial c(x, t)}{\partial t} = \kappa \frac{\partial^2 c(x, t)}{\partial x^2} \]

is the **classical heat equation**. This is known as **Fourier’s law of thermal conduction**.

The change in heat energy in a given segment of the bar of length \( \Delta x \) in time \( \Delta t \) will be proportional to the difference between the heat entering at one side, \( x \), and the other, \( x + \Delta x \), as

\[
\text{change in heat energy} = \text{difference in heat energy flux}
\]

or

\[
\Delta x \left[ \frac{\partial u(x, t)}{\partial t} + \frac{\partial u(x, t)}{\partial x} \right] = -\kappa \frac{\partial u(x, t)}{\partial x} \bigg|_{x} - \left( -\kappa \frac{\partial u(x, t)}{\partial x} \bigg|_{x+\Delta x} \right)
\]

which we can rearrange as

\[
\frac{1}{\Delta t} \left[ u(x, t + \Delta t) - u(x, t) \right] = \kappa \frac{1}{\Delta x} \left[ \frac{\partial u(x, t)}{\partial x} \bigg|_{x+\Delta x} - \frac{\partial u(x, t)}{\partial x} \bigg|_{x} \right]
\]

which takes the form of a finite difference approximation to the first derivative. When the width of the segment, \( \Delta x \), and the period of time, \( \Delta t \), are small enough this equation reduces to

\[
\frac{\partial u(x, t)}{\partial t} = \kappa \frac{\partial^2 u(x, t)}{\partial x^2}
\]

(12.20)

This is the **classical diffusion equation in one-dimension**.

The question of how much of the initial concentration is absorbed and how much diffuses away is equivalent to the problem known as the gambler’s ruin.

Figure 12.12: The concentration profile \( c(x, t) \) for particles diffusing on \( 0 < x < \infty \) with an absorbing boundary at \( x = 0 \). The distribution is shown as a function of \( x \) and \( t \). As time evolves, solutions are depicted in lighter and lighter shades of red.
where $D$ is the particle diffusion coefficient. Note that if the gradient is positive, the flux is in the negative direction and *vice versa*. This is known as *Fick's law of diffusion*.

The change in the distribution in a given length $\Delta x$ in time $\Delta t$ will be proportional to the difference between the number of particles entering at one side, $x$, and the other, $x + \Delta x$, as

change in number of particles = difference in particle flux

or

$$\Delta x c(x, t + \Delta t) - \Delta x c(x, t) = -D \Delta t \frac{\partial c(x, t)}{\partial x} \bigg|_x - \left( -D \Delta t \frac{\partial c(x, t)}{\partial x} \bigg|_{x+\Delta x} \right)$$

which we can rearrange as

$$\frac{1}{\Delta t} \left[ c(x, t + \Delta t) - c(x, t) \right] = D \frac{\Delta x}{\Delta t} \left[ \frac{\partial c(x, t)}{\partial x} \bigg|_{x+\Delta x} - \frac{\partial c(x, t)}{\partial x} \bigg|_x \right]$$

where we recognize *finite difference* approximations to the first derivatives with respect to $x$ and $t$. When the width of the segment, $\Delta x$, and the period of time, $\Delta t$, are small enough this equation reduces to

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}$$

(12.21)

This is the classical diffusion equation.

*The classical wave equation in one-dimension*

Now let’s consider the motion of a wave in a string. The wave is described by a displacement in the string, $h(x, t)$, as a function of position, $x$, and time, $t$, over a length, $L$ (see Figure 12.13). We consider the string to consist of a series of masses at positions $x - \Delta x$, $x$, $x + \Delta x$, and so on. Each mass is connected to the nearest neighboring masses by harmonic springs. How will the string move in space and time?

The motion of each mass is defined by Newton’s equation of motion. For a mass at point $x$ and time $t$ the acceleration in the displacement $h(x, t)$ is equal to the force divided by the mass

$$\frac{\partial^2 h(x, t)}{\partial t^2} = \frac{1}{m} F(x)$$

where $F(x)$ is the force and $m$ is the mass. The force resulting from the displacement of the mass at $x$ relative to the displacements of its nearest neighboring masses at $x + \Delta x$ and $x - \Delta x$ can be written

$$F(x) = k [h(x + \Delta x) - h(x)] - k [h(x) - h(x - \Delta x)]$$

where $k$ is the force constant. Combining these results leads to

$$\frac{\partial^2 h(x, t)}{\partial t^2} = \frac{k}{m} [h(x + \Delta x) - 2h(x) + h(x - \Delta x)]$$

The total length of the string is divided into $N = L/\Delta x$ segments so that the total mass of the string is $M = Nm$ while the total force constant is $K = km$. As such, we can write

$$\frac{1}{m} k = \frac{N}{M} KN = \frac{K}{M} N^2 = \frac{K}{M} \left( \frac{L}{\Delta x} \right)^2$$
This leads to the result
\[
\frac{\partial^2 h(x,t)}{\partial t^2} = \frac{KL^2}{M} \frac{[h(x + \Delta x) + 2h(x) + h(x - \Delta x)]}{\Delta x^2}
\]
which takes the form of a finite difference approximation to the second derivative.

When the width of the segment, \(\Delta x\), is small enough this equation reduces to
\[
\frac{\partial^2 h(x,t)}{\partial t^2} = v^2 \frac{\partial^2 h(x,t)}{\partial x^2}
\] (12.22)
where \(v^2 = KL^2 / M\). This is the classical wave equation.

B12 End-of-chapter problems

I have deeply regretted that I did not proceed far enough at least to understand something of the great leading principles of mathematics; for [those] thus endowed seem to have an extra sense.

Charles Darwin

Warm-ups

12.1 The one-dimensional classical heat equation
\[
\frac{\partial u(x,t)}{\partial t} = \kappa \frac{\partial^2 u(x,t)}{\partial x^2}
\]
describes the dependence of the temperature profile, \(u(x,t)\), as a function of position, \(x\), and time, \(t\). Note this equation can be written in the compact form \(u_t(x,t) = \kappa u_{xx}(x,t)\). The general solution for \(u(x,t)\) was found to be
\[
u(x,t) = u_0 + \sum_{n=1}^{\infty} u_n \cos \left( \frac{n\pi x}{L} \right) \exp \left( -\frac{n^2\pi^2}{L^2} \kappa t \right)
\]
for the temperature profile subject to the reflecting boundary conditions \(u(0,t) = u(L,t) = 0\).
(a) Consider the absorbing boundary conditions
\[
u(0,t) = 0 \quad u(L,t) = 0
\]
representing cold walls at \(x = 0\) and \(x = L\) where the temperature is always zero. Show that the general solution to the classical heat equation can be written
\[
u(x,t) = \sum_{n=1}^{\infty} u_n \sin \left( \frac{n\pi x}{L} \right) \exp \left( -\frac{n^2\pi^2}{L^2} \kappa t \right)
\]
(b) Consider the initial condition for the temperature profile
\[
u(x,0) = 4 \cos \left( \frac{2\pi x}{L} \right) \sin \left( \frac{2\pi x}{L} \right)
\]
Determine the values of the coefficients \(\{u_n\}\) for all \(n\) and express your final solution for \(u(x,t)\).

12.2 The one-dimensional classical wave equation
\[
\frac{\partial^2 h(x,t)}{\partial t^2} = v^2 \frac{\partial^2 h(x,t)}{\partial x^2}
\]
describes the dependence of the displacement, \(h(x,t)\), as a function of position, \(x\), and time, \(t\). Note this equation can be
written in the compact form $u_{tt}(x, t) = v^2 u_{xx}(x, t)$. The general solution for $h(x, t)$ was found to be

$$h(x, t) = \sum_{n=1}^{\infty} \sin \left( \frac{n\pi x}{L} \right) \left[ a_n \cos(\omega_n t) + b_n \sin(\omega_n t) \right]$$

where $\omega_n = \frac{n\pi v}{L}$ and the displacement $h(x, t)$ satisfies the boundary conditions $h(0, t) = h(L, t) = 0$.

Solve the one-dimensional classical wave equation for the displacement, $h(x, t)$, subject to the boundary condition $h(0, t) = h(L, t) = 0$ and initial conditions

$$h(x, 0) = 5 \sin \left( \frac{3\pi x}{L} \right)$$

and

$$\frac{\partial h(x, 0)}{\partial t} = 0$$

12.3 Consider the one-dimensional classical diffusion equation

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}$$

describing the dependence of the distribution, $c(x, t)$, as a function of position, $x$, and time, $t$. Note this equation can be written in the compact form $c_t(x, t) = Dc_{xx}(x, t)$.

(a) Show that the distribution

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left[ -\frac{(x-x_0)^2}{4Dt} \right]$$

is a solution to the diffusion equation.

(b) Show that the distribution is normalized by proving

$$\int_{-\infty}^{\infty} c(x, t) dx = 1$$

for all values of time.

(c) What is the functional form of the distribution at $t = 0$?

(d) Plot the distribution $c(x, t)$ for $t = 1/4D, 2/(4D)$, and $4/(4D)$ with $x_0 = 1$.

Homework exercises

12.4 In Chapter 3 we found that $\varphi(x, y, z) = (x^2 + y^2 + z^2)^{-1/2}$ satisfies

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = 0$$
which is known as Laplace’s equation. In doing so, we solved a second order partial differential equation. A simple extension of Laplace’s equation is

\[
\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} + \frac{8\pi^2 mE}{h^2} \varphi = 0
\]

which is the time-independent Schrödinger equation of quantum theory and \(\varphi(x, y, z)\) is the wave function for a free particle of mass \(m\). Show that

\[
\varphi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin \left(\frac{n_x \pi}{L} x \right) \sin \left(\frac{n_y \pi}{L} y \right) \sin \left(\frac{n_z \pi}{L} z \right)
\]

is a solution to this differential equation with the boundary conditions

\[
\varphi_{n_x, n_y, n_z}(x, y, z) = 0
\]

for \(x = 0, L, y = 0, L,\) or \(z = 0, L\) where \(n_x = 1, 2, 3, \ldots, n_y = 1, 2, 3, \ldots\) and \(n_z = 1, 2, 3, \ldots\). In doing so, find a relation for \(E\) in terms of the constants \(m, h, n_x, n_y,\) and \(n_z\).

12.5 Consider the one-dimensional classical diffusion equation

\[
\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}
\]

describing the dependence of the distribution, \(c(x, t)\), as a function of position, \(x\), and time, \(t\).

(a) Suppose that diffusion takes place on a semi-infinite plane \(0 \leq x < \infty\) where there is an absorbing boundary condition at \(x = 0\) defined by

\[
c(0, t) = 0
\]

Further assume the initial condition for \(x_0 > 0\)

\[
c(x, 0) = \delta(x - x_0)
\]

Consider the concentration profile

\[
c(x, t) = \frac{1}{\sqrt{4\pi D t}} \exp \left[ -\frac{(x - x_0)^2}{4D t} \right] - \frac{1}{\sqrt{4\pi D t}} \exp \left[ -\frac{(x + x_0)^2}{4D t} \right]
\]

shown in the figure below. The total distribution (black line) is composed of the difference of two gaussians, one centered at \(x_0 > 0\) (red line) and an image function centered at \(-x_0\) (blue line).

Demonstrate that the sum of the two functions meets the absorbing boundary condition that \(c(0, t) = 0\) and initial condition stated above.
(b) We can define the surviving population of the diffusing particles in terms of the survival probability

\[ p(t) = \int_0^\infty c(x,t)\,dx \]

which decreases with time. Determine a formula for \( p(t) \) in terms of the error function.

(c) Plot the survival probability \( p(t) \) as a function of \( t \) taking \( D = 1 \) for \( x_0 = 0.2, 1.0 \) and \( 2.0 \).

12.6 Consider the second order partial differential equation

\[ i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + E\psi(x,t) \]

which is the time-dependent Schrödinger equation of quantum theory and \( \psi(x,t) \) is the wave function for a free particle of mass \( m \). Note that \( \hbar = h/2\pi \).

(a) Show that

\[ \psi(x,t) = A \exp \left[ 2\pi i \left( \frac{x}{\lambda} - vt \right) \right] \]

is a solution to this differential equation if

\[ h\nu = \frac{h^2}{2m\lambda^2} \]

(b) For this free particle, the total energy \( E \) is the kinetic energy

\[ E = \frac{p^2}{2m} \]

where \( p \) is the particle’s momentum. Prove that the solution provided in (a) implies

\[ \lambda = \frac{h}{p} \]

which is the de Broglie relation between the particle’s momentum and wavelength.

12.7* Consider the time-dependent Schrödinger equation

\[ i\hbar \frac{\partial \psi(x,\tau)}{\partial \tau} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,\tau)}{\partial x^2} + V(x)\psi(x,\tau) = E\psi(x,\tau) \]

for a particle or mass \( m \) experiencing a potential energy \( V(x) \).

(a) Consider the imaginary time, \( \tau \), defined as

\[ \tau \equiv \frac{it}{\hbar} \]

Substitute \( t = -i\hbar \tau \) into the time-dependent Schrödinger equation above to prove that

\[ \frac{\partial \psi(x,\tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,\tau)}{\partial x^2} - V(x)\psi(x,\tau) = -E\psi(x,\tau) \]

(b) For a particle in a harmonic potential

\[ V(x) = \frac{1}{2}m\omega^2x^2 \]

the imaginary-time Schrödinger equation can be written

\[ \frac{\partial \psi(x,\tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,\tau)}{\partial x^2} - \frac{1}{2}m\omega^2x^2\psi(x,\tau) = -E\psi(x,\tau) \]

Prove that the function

\[ \psi(x,\tau) = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) \exp(-E\tau) \]

is a solution to this imaginary-time Schrödinger equation. In doing so, find a relation for \( E \) in terms of the frequency \( \omega \).
(c) Show that imaginary-time Schrödinger equation for a free particle, for which $V(x) = 0$, is isomorphic (of the same form) with the classical diffusion equation
\[
\frac{\partial \psi(x, t)}{\partial t} = D \frac{\partial^2 \psi(x, t)}{\partial x^2}
\]
where the diffusion constant is
\[
D = \frac{\hbar^2}{2m}
\]

(d) Consider the solution to the time-dependent Schrödinger equation for a free particle
\[
\psi(x, t) = A \exp \left[ 2\pi i \left( \frac{x}{\lambda} - vt \right) \right]
\]
Substitute $t = -i\hbar\tau$ and show that the resulting function is a solution to the imaginary-time Schrödinger equation for a free particle, derived in (c), where the energy is
\[
E = \hbar \nu = \frac{\hbar^2}{2m\lambda^2}
\]
13 Fourier series, Fourier transforms, and harmonic analysis

13.1 Fourier series 275
13.2 Fourier transforms 291
  A13 Orthogonal vectors and orthogonal functions 300
  B13 End-of-chapter problems 305

13.1 Fourier series

An infinite series of sine and cosine functions emerged as a general solution to a partial differential equation, such as the classical heat equation and classical wave equation, applied over a finite range. In this section, we expand upon this idea and explore ways to represent any periodic function as an infinite weighted sum of sines and cosines known as a Fourier series. The general study of Fourier series is known as harmonic analysis.

13.1.1 Periodic functions and Fourier series

In Chapter 12 we explored the general solution to the classical heat equation, describing the temperature, \( u(x) \), of some substance as a function of position, \( x \), as a weighted sum of sine and cosine terms. For example, the temperature profile of some substance bounded by insulated ends at \( x = 0 \) and \( x = L \) is shown in Figure 13.1 and written:

\[
    u(x) = \frac{1}{2} - \frac{1}{2} \cos \left( \frac{2\pi x}{L} \right)
\]

The temperature is never negative so that \( u(x) \geq 0 \). In addition, the fact that the temperature is reflected from the insulated ends means the slope of the temperature profile is zero at \( x = 0 \) and \( x = L \).

\[\text{Figure 13.1: The temperature profile } u(x) \text{ over a length } L \text{ with insulated ends.}\]

We also explored the classical wave equation describing the displacement of a string, \( h(x) \), as a function of position, \( x \), as a weighted sum of sine and cosine terms. For example, consider the displacement of a string with ends fixed at \( x = 0 \) and \( x = L \) shown in Figure 13.2 and written:

\[
    h(x) = \frac{1}{2} \sin \left( \frac{4\pi x}{L} \right)
\]

The displacement of the string varies, oscillating between positive and negative values, while being fixed at the end points \( x = 0 \) and \( x = L \).

The solutions above are defined over a finite interval \( 0 \leq x \leq L \). However, taking our solution over the interval \( 0 < x < L \) and repeating it over the
The Fourier series is named for French mathematician and physicist Joseph Fourier (1768-1830) who developed this harmonic analysis to study the flow of heat in a metal bar of finite length.

It turns out that periodic functions of interest in the physical sciences can be represented as an infinite sum of sines and cosines as

\[ f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi nx}{L} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{2\pi nx}{L} \right) \quad (13.1) \]

where the function \( f(x) \) is periodic over \((-\infty, \infty)\) with period \( L \). Each term represents the contribution of an oscillation of wavelength \( \lambda_n = \frac{L}{n} \) with amplitude defined by the coefficients \( a_n \) or \( b_n \). This decomposition of the function \( f(x) \) into waves of varying wavelengths is known as harmonic analysis. In this section, we develop a general approach to determine the infinity of coefficients \( \{a_n\} \) and \( \{b_n\} \) for any periodic function \( f(x) \).
13.1.2 Deriving the Fourier series for an arbitrary periodic function

Consider almost any function \( f(x) \) defined over the range \(-\pi \leq x \leq \pi\) and periodic over all \( x \).\(^4\) To determine the Fourier series we must evaluate the coefficients \( a_n \) and \( b_n \) that weight the contributions of the cosine and sine terms. We do that by determining the overlap of the function \( f(x) \) with each of the component functions that form the basis of the Fourier series. The relative overlap determines the magnitude of the coefficient \( a_n \) or \( b_n \) that weights each term in the series.\(^5\)

Evaluating the cosine coefficients \( a_n \) for \( n \geq 1 \)

Suppose we multiply the function \( f(x) \) by \( \cos(mx) \) and integrate over one period of oscillation as\(^6\)

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(mx) dx = \frac{1}{\pi} \int_{-\pi}^{\pi} \left[ \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx) \right] \cos(mx) dx
\]

\[
= \frac{1}{\pi} a_0 \int_{-\pi}^{\pi} \cos(mx) dx + \frac{1}{\pi} \sum_{n=1}^{\infty} a_n \int_{-\pi}^{\pi} \cos(nx) \cos(mx) dx + \frac{1}{\pi} \sum_{n=1}^{\infty} b_n \int_{-\pi}^{\pi} \sin(nx) \cos(mx) dx
\]

(13.2)

We can evaluate the three terms using our knowledge of integration and the Table of Indefinite Integrals in Supplement S.

There are three integrals to evaluate. The first integral is zero as integration performed over \( m \) periods of oscillation of the cosine is zero.\(^7\) The second integral can be evaluated for \( n = m \) using S\(_6\) #16 and for \( n \neq m \) using S\(_6\) #102 leading to\(^8\)

\[
\int_{-\pi}^{\pi} \cos(nx) \cos(mx) dx = \pi \delta_{nm}
\]

where \( \delta_{nm} \) is the Kronecker delta function that selects the single coefficient in the infinite series for which \( n = m \).\(^9\)

The third integral can be evaluated for \( n = m \) using S\(_6\) #17 and for \( n \neq m \) using S\(_6\) #103 leading to

\[
\int_{-\pi}^{\pi} \sin(nx) \cos(mx) dx = 0
\]

Inserting our results for the three integrals in Equation 13.2 results in

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(mx) dx = \frac{1}{\pi} \sum_{n=1}^{\infty} a_n \times \pi \delta_{nm} = a_m = a_n
\]

(13.3)

which defines the coefficients \( a_n \) weighting the cosine terms.

Evaluating the sine coefficients \( b_n \) for \( n \geq 1 \)

Suppose we multiply the function \( f(x) \) by \( \sin(mx) \) and integrate over one period of oscillation as

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(mx) dx = \frac{1}{\pi} \int_{-\pi}^{\pi} \left[ \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx) \right] \sin(mx) dx
\]

\[
= \frac{1}{\pi} a_0 \int_{-\pi}^{\pi} \sin(mx) dx + \frac{1}{\pi} \sum_{n=1}^{\infty} a_n \int_{-\pi}^{\pi} \cos(nx) \sin(mx) dx + \frac{1}{\pi} \sum_{n=1}^{\infty} b_n \int_{-\pi}^{\pi} \sin(nx) \sin(mx) dx
\]

(13.4)

\(^4\) Here we refer to those functions \( f(x) \) with a finite number of discontinuities for which

\[
\int_{-\pi}^{\pi} |f(x)| dx
\]

is finite.

\(^5\) We follow the procedure used to express a vector \( \mathbf{a} = a_x \hat{x} + a_y \hat{y} + a_z \hat{z} \) in terms of scalar coefficients \( a_x, a_y, \text{ and } a_z \) defined by the overlap of a when projected on each unit vector (see the Complements).

\(^6\) We have used the fact that

\[
\int_{-\pi}^{\pi} \cos(mx) dx = 0
\]

as it is taken over \( m \) full periods of the cosine, each with an area of zero.

\(^7\) This property of cosine functions is equivalent to orthogonality in vectors.

\(^8\) The properties of orthogonal functions are discussed in the Complements.

\(^9\) The Kronecker delta function is defined

\[
\delta_{nm} = \begin{cases} 
1 & n = m \\
0 & n \neq m 
\end{cases}
\]

Its properties are explored in Chapter 8.
The first integral is zero as integration performed over \(m\) periods of oscillation of the sine is zero.\(^{10}\) The second integral can be evaluated for \(n = m\) using \(S_6\) \#17 and for \(n \neq m\) using \(S_6\) \#103 leading to

\[
\int_{-\pi}^{\pi} \cos(nx) \sin(mx) \, dx = 0
\]

The third integral can be evaluated using for \(n = m\) using \(S_6\) \#14 and for \(n \neq m\) using \(S_6\) \#93 leading to\(^{11}\)

\[
\int_{-\pi}^{\pi} \sin(nx) \sin(mx) \, dx = \pi \delta_{nm}
\]

Inserting our results for the three integrals in Equation 13.4 results in

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(mx) \, dx = \frac{1}{\pi} \sum_{n=1}^{\infty} b_n \times \pi \delta_{nm} = b_m = b_n
\]

which defines the coefficients \(b_n\) weighting the sine terms.

**Evaluating the constant coefficient \(a_0\)**

Finally, note that

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \, dx = \frac{1}{\pi} \int_{-\pi}^{\pi} \left[ \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx) \right] \, dx
\]

\[
= \frac{1}{\pi} \frac{a_0}{2} \int_{-\pi}^{\pi} \, dx + \frac{1}{\pi} \sum_{n=1}^{\infty} a_n \int_{-\pi}^{\pi} \cos(nx) \, dx + \frac{1}{\pi} \sum_{n=1}^{\infty} b_n \int_{-\pi}^{\pi} \sin(nx) \, dx
\]

The first integral

\[
\int_{-\pi}^{\pi} \, dx = 2\pi
\]

while the second and third integrals, involving integration of cosine or sine over one period of oscillation, are zero. This leads to

\[
\frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \, dx = \frac{1}{\pi} \frac{a_0}{2} \times 2\pi = a_0
\]

which acts as a constant offset of the overall series also known as the zero frequency component.

We have arrived at a most remarkable result. We can express any function \(f(x)\) in terms of a Fourier series\(^{12}\)

\[
f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx)
\]

where the coefficients are determined using the integral relations provided by Equations 13.3, 13.5 and 13.6 and collected here\(^{13}\)

\[
a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) \, dx \quad b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) \, dx
\]

\[
\text{Our variable } x \text{ extends over the range } -\pi \leq x < \pi \text{ with a period of } 2\pi. \text{ As such, } x \text{ is dimensionless.}
\]

**Fourier series for functions of variables with units**

In the Fourier series defined by Equations 13.7 and 13.8, the variable \(x\) was dimensionless. Suppose we want to define a Fourier series representation of a function \(f(x)\) where the variable \(x\) has units of length over a range \(-\frac{1}{2} \leq x < \frac{1}{2}\).
We are substituting the range

\[-\pi \leq x < \pi \rightarrow \frac{L}{2} \leq x < \frac{L}{2}\]

As such, we must translate the argument of the sine and cosine functions as

\[nx \rightarrow \frac{2\pi nx}{L}\]

Note that the argument must be dimensionless as the sine and cosine functions require dimensionless arguments.

In that case, the Fourier series can be written

\[f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi nx}{L} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{2\pi nx}{L} \right) \quad (13.9)\]

where the coefficients are defined

\[a_n = \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \cos \left( \frac{2\pi nx}{L} \right) \, dx \quad b_n = \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \sin \left( \frac{2\pi nx}{L} \right) \, dx \quad (13.10)\]

Note that the coefficients are dimensionless. While the increment \(dx\) has units of length, the prefactor \(\frac{2}{L}\) has units of inverse length making the coefficients dimensionless.

Let's apply these results to determine the Fourier series of a periodic function \(f(x)\) known as the square wave.

### 13.1.3 Deconstructing the Fourier series of the square wave

Consider the periodic function of \(x\) known as the square wave function shown over two periods of oscillation in Figure 13.5 where the wavelength is \(L\). The function is written

\[f(x) = 2\theta \left( \frac{x}{L} \right) - 1 \quad \frac{L}{2} \leq x < \frac{L}{2}\]

where \(\theta (\frac{x}{L})\) is the Heaviside step function which is unity for \(x \geq 0\) and zero otherwise. It is one of the miracles of the Fourier series that a function composed of straight lines and right angles can be expressed as a sum of an infinite number of smooth sinusoidal functions.

![Figure 13.5: The square wave \(f(x)\) (red line) is an odd periodic function of \(x\) with wavelength \(L\).](image-url)

To represent the square wave using the Fourier series defined in Equation 13.9

\[f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi nx}{L} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{2\pi nx}{L} \right)\]

we must determine the coefficients by evaluating the integrals appearing in
Recall that for an odd function \( f \circ (-x) = -f \circ (x) \) so that
\[
\int_{-L}^{0} f \circ (x) \, dx = -\int_{0}^{-L} f \circ (x) \, dx
\]
and
\[
\int_{L}^{-L} f \circ (x) \, dx = 0
\]
In general, step functions with jump discontinuities have Fourier coefficients that vary as \( \frac{1}{n} \). The slow convergence of the series with increasing \( n \) reflects the difficulty in describing a discontinuous function using an infinite series of smoothly varying and continuous sine and cosine functions.

For the coefficients \( a_n \), the integrand is a product of the square wave, which is an odd function of \( x \), and a cosine wave, which is an even function of \( x \), making the integrand an odd function of \( x \). As such, the coefficients are
\[
a_n = 0
\]
for all \( n \) by symmetry.\(^{14} \) Noting that \( f(x) = -1 \) for \( x \in [-\frac{L}{2}, 0) \) and \( f(x) = 1 \) for \( x \in (0, \frac{L}{2}) \) the coefficients are
\[
b_n = -\frac{2}{L} \int_{-\frac{L}{2}}^{0} \sin \left( \frac{2\pi nx}{L} \right) \, dx + \frac{2}{L} \int_{0}^{\frac{L}{2}} \sin \left( \frac{2\pi nx}{L} \right) \, dx
\]
As the sine function is an odd function of \( x \) we have
\[
b_n = \frac{4}{L} \int_{0}^{\frac{L}{2}} \sin \left( \frac{2\pi nx}{L} \right) \, dx = -\frac{4}{L} \left( \frac{L}{2\pi n} \right) \cos \left( \frac{2\pi nx}{L} \right) \bigg|_{0}^{\frac{1}{2}}
\]
where \( \cos (\pi n) = (-1)^n \).

When \( n \) is even in Equation 13.11, the cosine term is unity and the coefficients are
\[
b_n = 0 \quad n = 2, 4, 6, \ldots
\]
When \( n \) is odd, the cosine term is \(-1\) and the coefficients are\(^{15} \)
\[
b_n = \frac{4}{n\pi} \quad n = 1, 3, 5, \ldots
\]
where \( n = 1, 3, 5, \ldots \) Inserting these results in Equation 13.9 leads to our final result
\[
f(x) = \sum_{n=1,3,5,\ldots}^{\infty} \frac{4}{n\pi} \sin \left( \frac{2n\pi x}{L} \right)
\]
for the Fourier series representation of the square wave function.

\[^{14}\text{Recall that for an odd function } f_0(-x) = -f_0(x) \text{ so that } \int_{0}^{L} f_0(x) \, dx = -\int_{0}^{L} f_0(x) \, dx \]
and
\[^{15}\text{In general, step functions with jump discontinuities have Fourier coefficients that vary as } \frac{1}{n^2}. \text{ The slow convergence of the series with increasing } n \text{ reflects the difficulty in describing a discontinuous function using an infinite series of smoothly varying and continuous sine and cosine functions.} \]
Harmonic analysis of the square wave

The square wave is represented as an infinite sum of harmonics where each harmonic has a characteristic wavelength \( \lambda_n = \frac{1}{n} L \) and amplitude \( b_n \propto \frac{1}{n} \). Figure 13.6 shows the square wave function compared with the partial sum defined

\[
f_N(x) = \sum_{n=1,3,5,...}^{N} \frac{4}{n\pi} \sin\left(\frac{2n\pi x}{L}\right)
\]

(13.14)

For \( N = 1 \), the partial sum is a single sine function

\[
f_1(x) = \frac{4}{\pi} \sin\left(\frac{2\pi x}{L}\right)
\]

representing a wavelength \( \lambda_1 = L \). The wavelength \( L \) of the square wave is captured exactly by this one term. However, the amplitude is too great as the coefficient \( b_1 = \frac{4}{\pi} > 1 \) causes \( f_1(x) \) to overshoot the bounds of the square wave that oscillates between \(-1\) and \(1\). In addition, the smooth sinusoidal form lacks the rectilinear square wave form.

Adding additional terms to the sum with wavelengths \( L/n \) enhances the accuracy of the approximation. For example, including two terms

\[
f_3(x) = \frac{4}{\pi} \sin\left(\frac{2\pi x}{L}\right) + \frac{4}{3\pi} \sin\left(\frac{6\pi x}{L}\right)
\]

reduces the maximum amplitude of oscillation from \( \frac{4}{\pi} = 1.273 \ldots \) to \( \frac{8\sqrt{2}}{3\pi} = 1.2004 \ldots \), through destructive interference, while enhancing the square symmetry at the corners, through constructive interference. In the limit \( N \to \infty \) an accurate representation of the square wave function is achieved.

The first five terms in the partial sum are displayed individually in Figure 13.6 (blue lines). The partial sum \( f_9(x) \) over the five contributions (red line) is compared with the exact square wave function (gray line). The combination of destructive and constructive interference between the sinusoidal waves of varying wavelength and amplitude leads to an increasingly accurate representation of the square wave function with increasing \( N \).

Figure 13.7: The partial sum

\[
f_N(x) = \sum_{n=1,3,5,...}^{N} \frac{4}{n\pi} \sin\left(\frac{2n\pi x}{L}\right)
\]

formed from the infinite Fourier series for the square wave function (gray line). Increasing \( N \) from 1 (pale red) to 9 (red) to 60 (dark red line).

\[16\] This term is the fundamental or the first harmonic appearing in the Fourier series. It is the longest wavelength contribution with \( \lambda_1 = L \). The wavelength of other contributions are a fraction \( \lambda_n = \frac{1}{n} L \) of the fundamental.

\[17\] Even in the limit \( N \to \infty \) the Fourier series overshoots the square wave form at points of discontinuity where it is not possible to achieve uniform convergence. This is known as the Gibbs phenomenon.
13.1.4 Deconstructing the Fourier series of the triangle wave

Consider the periodic function known as the triangle wave shown over two periods of oscillation in Figure 13.8 where the period is T. It can be written over one period of oscillation as

\[
f(t) = \begin{cases} 
1 - \frac{4t}{T} & 0 \leq t < \frac{T}{2} \\
-1 + \frac{4}{T} \left( t - \frac{T}{2} \right) & \frac{T}{2} \leq t < T 
\end{cases}
\]

Remarkably, this function composed of straight lines and sharp angles can be represented as a sum of an infinite number of smooth sinusoidal functions.

![Triangle Wave Graph](image)

We can represent the triangle wave using a reformulation of Equation 13.9

\[
f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi nt}{T} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{2\pi nt}{T} \right)
\]

where the variable \( x \) is replaced by \( t \) and the wavelength \( L \) is replaced by the period \( T \). The coefficients are determined by a reformulation of Equation 13.10

\[
a_n = \frac{2}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t) \cos \left( \frac{2\pi nt}{T} \right) dt \quad b_n = \frac{2}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(t) \sin \left( \frac{2\pi nt}{T} \right) dt
\]

Let’s determine the Fourier coefficients for the periodic triangle wave.

Fourier coefficients for the triangle wave

Each coefficient \( b_n \) is an integral over a product of the triangle wave, which is an even function of \( t \), and a sine wave, which is an odd function of \( t \), making the integrand an odd function of \( t \). As such, the coefficients are

\[
b_n = 0
\]

for all \( n \) by symmetry.

Considering the coefficients \( a_n \), we note the integrand \( f(t) \cos \left( \frac{2\pi nt}{T} \right) \) is an even function of \( t \) about the point \( t = \frac{T}{2} \) so that the integral over \( [0, \frac{T}{2}] \) equals the integral over \( [-\frac{T}{2}, \frac{T}{2}] \). As such\(^{18}\)

\[
a_n = \frac{2}{T} \int_{0}^{\frac{T}{2}} \left( 1 - \frac{4t}{T} \right) \cos \left( \frac{2\pi nt}{T} \right) dt - \frac{2}{T} \int_{\frac{T}{2}}^{T} \left( -1 + \frac{4}{T} \left( t - \frac{T}{2} \right) \right) \cos \left( \frac{2\pi nt}{T} \right) dt
\]

\[
= \frac{4}{T} \int_{0}^{\frac{T}{2}} \left( 1 - \frac{4t}{T} \right) \cos \left( \frac{2\pi nt}{T} \right) dt \quad (13.15)
\]

\(^{18}\) This can be shown by substituting \( x = T - t \) and \( dx = -dt \) into the integral over \( \frac{T}{2} \leq t < T \) such that

\[
\int_{\frac{T}{2}}^{T} \left( 1 - \frac{4x}{T} \right) \cos \left( \frac{2\pi nx}{T} \right) dx
\]

For integer values of \( n \) we know that \( \cos(2\pi n - x) = \cos(-x) = \cos(x) \) so that

\[
\int_{0}^{\frac{T}{2}} \left( 1 - \frac{4x}{T} \right) \cos \left( \frac{2\pi nx}{T} \right) dx
\]

as we proposed based on symmetry.
The coefficients $a_n$ can now be evaluated by performing the two integrals

$$a_n = \frac{4}{T} \int_0^{\frac{T}{2}} \cos \left(\frac{2\pi nt}{T}\right) dt - \frac{4}{T} \int_0^{\frac{T}{2}} \cos \left(\frac{2\pi nt}{T}\right) dt$$

(13.16)

The first integral of a cosine function taken over an integer multiple of half periods is zero

$$\int_0^{\frac{T}{2}} \cos \left(\frac{2\pi nt}{T}\right) dt = 0$$

The second integral can be evaluated using the Table of Indefinite Integrals in Supplement S6 #96

$$\int x \cos(ax + b) dx = \frac{1}{a^2} \cos(ax + b) + \frac{x}{a} \sin(ax + b) + C$$

where $a = \frac{2\pi}{T}$ and $b = 0$ so that

$$\int_0^{\frac{T}{2}} \frac{4t}{T} \cos \left(\frac{2\pi nt}{T}\right) dt = \frac{T}{\pi^2 n^2} (\cos(n\pi) - 1)$$

Inserting our results in Equation 13.16 leads to

$$a_n = -\frac{4}{T} \times \frac{T}{\pi^2 n^2} (\cos(n\pi) - 1) = \frac{4}{\pi^2 n^2} (1 - (-1)^n)$$

where we have used the fact that $\cos(n\pi) = (-1)^n$. When $n$ is even the coefficients $a_n = 0$ and when $n$ is odd the coefficients are\(^{19}\)

$$a_n = \frac{8}{\pi^2 n^2} \quad n = 1, 3, 5, \ldots$$

(13.17)

Inserting the coefficients in Equation 13.9 leads to our final result

$$f(t) = \sum_{n=1,3,5,\ldots}^{\infty} \frac{8}{\pi^2 n^2} \cos \left(\frac{2\pi nt}{T}\right)$$

(13.18)

for the Fourier series representation of the triangle wave function.

**Harmonic analysis of the triangle wave**

The Fourier series expresses the function $f(t)$ as an infinite series of harmonics of wavelength $\lambda = \frac{T}{2}$ and amplitude $a_n \propto \frac{1}{n^2}$. Figure 13.9 shows the residual difference between the exact function $f(t)$ and the partial sum of the Fourier series representation $f_N(x)$ for $N = 1$ and 19. Note that the greatest difference between the exact function and the approximate Fourier series representation occurs at the sharp points where the derivative of the function is discontinuous. Even so as $N \to \infty$ the residual tends to zero.

We can also express the Fourier series in terms of the frequency of oscillation defined

$$\omega_0 = \frac{2\pi}{T}$$

so that

$$f(t) = \sum_{n=1,3,5,\ldots}^{\infty} \frac{8}{\pi^2 n^2} \cos (n\omega_0 t)$$

(13.19)

The first five terms in the partial sum are displayed in Figure 13.10 (blue lines). The partial sum $f_9(t)$ over the five contributions (red line) is compared with the exact triangle wave function (gray line). The coefficients $a_n$ for $n = 1$ through 9 are shown as blue bars. The amplitude of each term in the sum decreases as $n$.

\(^{19}\) In general, continuous *ramp functions* with discontinuities in the first derivative have Fourier coefficients that vary as $\frac{1}{n^2}$. The convergence of the Fourier series as $\frac{1}{n^2}$ with increasing $n$ is more rapid than the convergence as $\frac{1}{n}$ characteristic of discontinuous *step functions*.
and the frequency of oscillation, increases.

![Figure 13.10: The partial sum $f_N(t)$ of the Fourier series approximating the triangle wave (black line) for $N = 9$ (red line). The sum of the five blue curves of varying frequency forms the composite red curve. The height of the thick blue bars indicates the magnitude of the coefficients determining the oscillation amplitude.]

Note that for the triangle wave the magnitude of the non-zero Fourier coefficients for the continuous triangle wave diminishes as

$$\frac{a_n}{a_1} = \frac{1}{n^2} \quad n = 1, 3, 5, \ldots$$

while for the discontinuous square wave the magnitude of the Fourier coefficients diminishes as

$$\frac{b_n}{b_1} = \frac{1}{n} \quad n = 1, 3, 5, \ldots$$

As such, the Fourier series for the triangle wave converges faster to an accurate representation of the actual function.

**13.1.5 The sawtooth wave as an alternating sine series**

Consider the periodic function of $x$ known as the sawtooth wave. It is shown over three periods of oscillation in Figure 13.11 where the period is $L$.

![Figure 13.11: The sawtooth wave $f(x)$ (red line) is an odd periodic function of $x$ with period $2L$.]

The function can be written over one period as

$$f(x) = \frac{x}{L} \quad -L \leq x < L \quad (13.20)$$

The Fourier series is

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{n\pi x}{L} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{n\pi x}{L} \right)$$
where the coefficients are

\[ a_n = \frac{1}{L} \int_{-L}^{L} x \cos \left( \frac{n\pi x}{L} \right) \, dx \quad b_n = \frac{1}{L} \int_{-L}^{L} x \sin \left( \frac{n\pi x}{L} \right) \, dx \]

Let’s determine the Fourier coefficients for the periodic sawtooth wave.

**Fourier coefficients for the sawtooth wave**

Since \( f(x) \) is an odd function of \( x \), the Fourier series is an odd function of \( x \) and the coefficients multiplying the even cosine functions \( a_n = 0 \) for all \( n \). As such, the coefficients for the odd sine function can be evaluated using the Table of Indefinite Integrals in Supplement S89

\[
\int x \sin(ax + b) \, dx = \frac{1}{a^2} \sin(ax + b) - \frac{x}{a} \cos(ax + b) + C
\]

where \( a = \frac{\pi n}{L} \) and \( b = 0 \) so that

\[
b_n = \frac{1}{L^2} \int_{-L}^{L} x \sin \left( \frac{n\pi x}{L} \right) \, dx = -\frac{1}{L^2} \left[ \frac{L^2}{n\pi} \cos(n\pi) - \left( -\frac{L^2}{n\pi} \cos(-n\pi) \right) \right]
\]

\[ = -\frac{2}{\pi n} \cos(n\pi) = -\frac{2}{\pi n} (-1)^n = \frac{2}{\pi n} (-1)^{n+1} \]

This leads to our final result for the Fourier series of the odd sawtooth wave

\[
f(x) = \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin \left( \frac{n\pi x}{L} \right) \quad (13.21)
\]

The result is shown in Figure 13.12 where the exact function (gray line) is compared with the partial sum \( f_N(x) \) having \( N = 1 \) terms (light red), \( N = 5 \) terms (red), and \( N = 20 \) terms (dark red).

**Harmonic analysis of the sawtooth wave**

The harmonic analysis is summarized in Figure 13.12 showing the variation of the coefficients \( b_n \) with increasing frequency.

---

The magnitude of the Fourier coefficients diminishes as \( \frac{1}{n} \), as we found for the square wave in Equation 13.13. However, unlike the coefficients for the square wave which were positive, the coefficients for the sawtooth wave have

\[ f_N(x) = \frac{2}{\pi} \sum_{n=1}^{N} \frac{(-1)^{n+1}}{n} \sin \left( \frac{n\pi x}{L} \right) \]

approximating the sawtooth wave (gray line) for \( N = 1 \) (light red), \( N = 5 \) (red), and \( N = 20 \) (dark red). Also shown are the coefficients contributing to the series which alternate in sign.

**Figure 13.12:** The partial sum

\[ f_N(x) = \frac{2}{\pi} \sum_{n=1}^{N} \frac{(-1)^{n+1}}{n} \sin \left( \frac{n\pi x}{L} \right) \]
Alternating signs

\[ b_n = \frac{(-1)^{n+1}}{n} \quad n = 1, 2, 3, \ldots \]

As was observed for the square wave, the Fourier series overshoots the exact sawtooth wave form on either side of the discontinuity. In the case of the sawtooth wave, rather than stepping down from 1 to \(-1\) there is a step down from roughly 1.089 to \(-1.089\) making the overshoot approximately 9% of the magnitude of the discontinuity.

### 13.1.6 The shark fin wave as a series of sines and cosines

Now consider the periodic function of \(x\) known as the *shark fin wave* shown over three periods of oscillation in Figure 13.13 where the period is \(2L\).

\[ f(x) \]

![Figure 13.13: The shark fin wave (red line) is a periodic function of \(x\) with period \(2L\).](image)

The function can be written over one period as

\[
 f(x) = \begin{cases} 
 0 & -L \leq x < 0 \\ 
 \frac{x}{L} & 0 \leq x < L 
\end{cases} \quad (13.22)
\]

Since \(f(x)\) is neither an even function of \(x\) nor an odd function of \(x\), we expect the Fourier series

\[
 f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{n\pi x}{L} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{n\pi x}{L} \right) \quad (13.23)
\]

where the coefficients are defined by Equation 13.10

\[
 a_0 = \frac{1}{L} \int_{-L}^{L} x \, dx, \quad a_n = \frac{1}{L} \int_{-L}^{L} \cos \left( \frac{n\pi x}{L} \right) \, dx, \quad b_n = \frac{1}{L} \int_{-L}^{L} \sin \left( \frac{n\pi x}{L} \right) \, dx
\]

\[21\] The range of integration is \(0 \leq x \leq L\) since \(f(x) = 0\) for \(-L \leq x \leq 0\).

Let’s determine the Fourier coefficients for the periodic square wave.

**Fourier coefficients for the shark fin wave**

The coefficient for the constant term is

\[
 a_0 = \frac{1}{L^2} \int_{0}^{L} x \, dx = \frac{1}{L^2} \left[ \frac{x^2}{2} \right]_{0}^{L} = \frac{1}{2}
\]

We can evaluate the cosine coefficients using the Table of Indefinite Integrals in Supplement S6 #96

\[
 \int x \cos(ax + b) \, dx = \frac{1}{a^2} \cos(ax + b) + \frac{x}{a} \sin(ax + b) + C
\]
where \( a = \frac{2\pi}{L} \) and \( b = 0 \) so that

\[
a_n = \frac{1}{L^2} \int_0^L x \cos \left( \frac{n \pi x}{L} \right) \, dx = \frac{1}{\pi^2 n^2} (\cos(n\pi) - 1) = -\frac{1}{\pi^2 n^2} (1 - (-1)^n)
\]

As such, \( a_n = 0 \) for \( n \) even and for \( n \) odd

\[
a_n = -\frac{2}{\pi^2 n^2} \quad n = 1, 3, 5, \ldots \quad (13.25)
\]

We can evaluate the sine coefficients \( b_n \) using the Table of Indefinite Integrals in Supplement S6 #89

\[
\int x \sin(ax + b) \, dx = \frac{1}{a^2} \sin(ax + b) - \frac{x}{a} \cos(ax + b) + C
\]

where \( a = \frac{2\pi}{L} \) and \( b = 0 \) so that

\[
b_n = \frac{1}{L^2} \int_0^L x \sin \left( \frac{n \pi x}{L} \right) \, dx = -\frac{1}{\pi n} \cos(n\pi) = -\frac{1}{\pi n} (-1)^n = \frac{1}{\pi n} (-1)^{n+1}
\]

As such

\[
b_n = \frac{1}{\pi n} (-1)^{n+1} \quad n = 1, 2, 3, \ldots \quad (13.26)
\]

Inserting the coefficients defined by Equations 13.24, 13.25 and 13.26 in Equation 13.23 leads to the Fourier series for the shark fin wave

\[
f(x) = \frac{1}{4} - \sum_{n=1,3,5,\ldots}^{\infty} \frac{2}{\pi^2 n^2} \cos \left( \frac{n \pi x}{L} \right) + \sum_{n=1}^{\infty} \frac{1}{\pi n} (-1)^{n+1} \sin \left( \frac{n \pi x}{L} \right) \quad (13.27)
\]

Three realizations of the partial sum representing the Fourier series for the shark fin wave are shown in Figure 13.14. The Gibbs phenomenon is apparent at the discontinuities.

Harmonic analysis of the shark fin wave

The behavior of the Fourier coefficients of the shark fin wave can be summarized as

\[
a_0 = \frac{1}{2} \quad \text{for} \quad n = 0, \quad \frac{a_n}{a_1} = \frac{1}{n^2} \quad \text{for} \quad n = 1, 3, 5, \ldots, \quad \frac{b_n}{b_1} = \frac{(-1)^{n+1}}{n}, \quad n = 1, 2, 3, \ldots
\]

The coefficients vary as depicted in Figure 13.15.

After \( a_0 = \frac{1}{4} \) the coefficients for the cosine terms are uniformly negative, decaying in magnitude as \( \frac{1}{n^2} \) due to discontinuities in the derivative of the function. Coefficients for the sine terms have alternating signs, decaying in magnitude more gradually as \( \frac{1}{n} \) due to discontinuities in the function itself. In
addition, since the coefficients for the cosine series vary as \( a_n \propto \frac{1}{n} \) while the coefficients of the sine series vary at \( b_n \propto \frac{1}{n} \), the sine series makes the greater overall contribution.

In contrast to the Fourier series for the square wave and sawtooth wave, which are odd functions represented by sine series, and the triangle wave, which is an even function represented by a cosine series, the Fourier series for the shark fin wave includes both even cosine terms and odd sine terms. In fact, the shark fin wave, \( f(x) \), can be expressed as a linear sum of a constant, the triangle wave, \( f_T(x) \), and the sawtooth wave, \( f_S(x) \), as

\[
f(x) = \frac{1}{4} - \frac{1}{4} f_T(x) + \frac{1}{2} f_S(x)
\]

Similarly, the Fourier series of the shark fin wave, Equation 13.27, can be expressed as a linear sum of a constant term, the Fourier series of the triangle wave, Equation 13.18, and the Fourier series of the sawtooth wave, Equation 13.21.

### 13.1.7 The complex Fourier series

So far we have discussed Fourier series of real functions in terms of sine and cosine series. We will not consider a convenient compact definition of the Fourier series of real functions known as the complex Fourier series. We begin with

\[
f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx)
\]

Substituting \( \cos(nx) = \frac{1}{2} (e^{inx} + e^{-inx}) \) and \( \sin(nx) = \frac{1}{2i} (e^{inx} - e^{-inx}) \) we find

\[
f(x) = \frac{1}{2} a_0 + \frac{1}{2} \sum_{n=1}^{\infty} a_n (e^{inx} + e^{-inx}) + \frac{1}{2i} \sum_{n=1}^{\infty} b_n (e^{inx} - e^{-inx})
\]

Rearranging terms we have

\[
f(x) = \frac{1}{2} a_0 + \frac{1}{2} \sum_{n=1}^{\infty} (a_n - ib_n) e^{inx} + \frac{1}{2} \sum_{n=1}^{\infty} (a_n + ib_n) e^{-inx}
\]  \hspace{1cm} (13.28)

Let’s take the second series in Equation 13.28 above and substitute \( n \rightarrow -n \) as

\[
\sum_{n=1}^{\infty} (a_n + ib_n) e^{-inx} = \sum_{n=-1}^{-\infty} (a_{-n} + ib_{-n}) e^{inx}
\]

As the cosine function is even, the coefficients \( a_{-n} = a_n \) are even, and as the sine function is odd, the coefficients \( b_{-n} = -b_n \) are odd. As such, we find

\[
\sum_{n=-1}^{-\infty} (a_{-n} + ib_{-n}) e^{inx} = \sum_{n=-1}^{-\infty} (a_n - ib_n) e^{inx}
\]

Substituting this result in Equation 13.28 we find

\[
f(x) = \frac{1}{2} a_0 + \frac{1}{2} \sum_{n=1}^{\infty} (a_n - ib_n) e^{inx} + \frac{1}{2} \sum_{n=-1}^{-\infty} (a_n - ib_n) e^{inx}
\]

Defining the coefficient \( b_0 = 0 \), inserting in the series, and reordering terms we have

\[
f(x) = \frac{1}{2} \sum_{n=-1}^{\infty} (a_n - ib_n) e^{inx} + \frac{1}{2} (a_0 - ib_0) + \frac{1}{2} \sum_{n=1}^{\infty} (a_n - ib_n) e^{inx}
\]

Combining the three sums we arrive at a single series with an index running
from $-\infty$ to $\infty$ as

$$f(x) = \frac{1}{\pi} \sum_{n=-\infty}^{\infty} (a_n - ib_n) e^{inx} = \sum_{n=-\infty}^{\infty} c_n e^{inx} \quad (13.29)$$

We have previously shown in Equation 13.8 that

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) \, dx \quad b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) \, dx \quad (13.30)$$

Substituting these relations for $a_n$ and $b_n$ we find

$$c_n = \frac{1}{2} (a_n - ib_n) = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) \, dx - i \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) \, dx$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) (\cos(nx) - i \sin(nx)) \, dx$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) e^{-inx} \, dx$$

Note that we can also define the complex Fourier series over the range $-\frac{L}{2} \leq x < \frac{L}{2}$ as

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \exp \left( \frac{i2\pi nx}{L} \right) \quad (13.31)$$

where the coefficients are defined as

$$c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) e^{-\frac{i2\pi nx}{L}} \, dx \quad (13.32)$$

The complex Fourier series provides a compact representation of the Fourier series of a periodic function. It also provides a foundation for the harmonic analysis of aperiodic functions explored in the next section.

### 13.1.8 Complex Fourier series of the sawtooth wave

Consider again the sawtooth wave which is a periodic function of $x$. It can be written over one period as

$$f(x) = \frac{x}{L} \quad -L \leq x < L \quad (13.33)$$

The function is shown over three periods of oscillation in Figure 13.11 where the period is $2L$.

The complex Fourier series defined by Equations 13.31 and 13.32 can be extended to treat functions with a period $2L$ over a range $-L \leq x < L$ as

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \exp \left( \frac{i\pi nx}{L} \right) \quad (13.34)$$

where the corresponding Fourier coefficients are

$$c_n = \frac{1}{2L} \int_{-L}^{L} x \frac{1}{L} \exp \left( -\frac{i\pi nx}{L} \right) \, dx \quad (13.35)$$

Let’s determine the coefficients for complex Fourier series of the periodic sawtooth wave.

#### Coefficients for the complex Fourier series of the sawtooth wave

For $c_0$ we find

$$c_0 = \frac{1}{2L} \int_{-L}^{L} x \frac{1}{L} \, dx = 0 \quad (13.36)$$
as the integrand is an odd function of \( x \). We can evaluate the remaining coefficients \( c_n \) for \( n > 0 \) using the Table of Indefinite Integrals in Supplement S,

\[
\int x e^{bx} \, dx = \frac{x}{b} e^{bx} - \frac{1}{b^2} e^{bx} + C
\]

where \( b = -\frac{i\pi}{L} \) so that

\[
c_n = \frac{1}{2L^2} \left[ -\frac{xL}{i\pi} \exp\left(-\frac{i\pi nx}{L}\right) + \frac{L^2}{n^2\pi^2} \exp\left(-\frac{i\pi nx}{L}\right) \right]_L^{L} = \frac{1}{2L^2} \left[ -\frac{L^2}{i\pi} \left(e^{-in\pi} + e^{in\pi}\right) + \frac{L^2}{n^2\pi^2} \left(e^{-in\pi} - e^{in\pi}\right) \right]
\]

which can be reformed as

\[
c_n = -\frac{1}{i\pi} \frac{\sin(n\pi)}{n^2\pi^2} - i\frac{1}{n^2\pi^2} \sin(n\pi)
\]

for \( n \neq 0 \) and \( c_0 = 0 \). Since \( \sin(n\pi) = 0 \) for any integer \( n \) and \( \cos(n\pi) = (-1)^n \) we find\(^{24}\)

\[
c_n = -\frac{1}{i\pi} (-1)^n = \frac{1}{i\pi} (-1)^{n+1}
\]

With this result we can write the complex Fourier series of the sawtooth wave as

\[
f(x) = \frac{1}{i\pi} \sum_{n=-\infty}^{n} (-1)^{n+1} \frac{1}{n} \exp\left(\frac{i\pi nx}{L}\right) \quad (13.37)
\]

where the primed sum is restricted to \( n \neq 0 \).

**Harmonic analysis of the complex Fourier series of the sawtooth wave**

The Fourier series expresses the function \( f(x) \) as an infinite series of harmonics of wavelength \( \lambda = \frac{2}{L} \) and amplitude \( a_n \propto \frac{1}{n} \). Figure 13.16 shows the residual difference between the exact function \( f(x) \) and the partial sum of the Fourier series representation \( f_N(x) \) for \( N = 1 \) and 20. Note that the greatest difference between the exact function and the approximate Fourier series representation occurs at the sharp points where the function is discontinuous.

Note that for every term \( n \) in the sum there is a term \( -n \). Grouping the \( n \) and \( -n \) terms together we can rewrite the sum as

\[
f(x) = \frac{1}{i\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \left[ \exp\left(\frac{i\pi nx}{L}\right) - \exp\left(-\frac{i\pi nx}{L}\right) \right]
\]

Given that

\[
\frac{1}{2\pi} \left[ \exp\left(\frac{i\pi nx}{L}\right) - \exp\left(-\frac{i\pi nx}{L}\right) \right] = \sin\left(\frac{n\pi x}{L}\right)
\]

the complex Fourier series becomes

\[
f(x) = \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin\left(\frac{n\pi x}{L}\right) \quad (13.38)
\]

Our result is identical to that previously derived for the Fourier series representation of the sawtooth wave given by Equation 13.21. In the next section, we will use the complex Fourier series to extend the harmonic analysis of periodic functions using Fourier series to aperiodic functions using Fourier transforms.
13.2 Fourier transforms

The Fourier series can be used to represent an infinitely repeating periodic function in terms of an infinite sum of periodic waves. The coefficients weight the contributions of the component harmonics to sum to the total function. The Fourier transform extends the harmonic analysis to aperiodic functions by including a continuum of component frequencies. It has widespread application in the solution of differential equations, the formulation of quantum theory, and signal processing and analysis, including vibrational spectroscopy.

13.2.1 Fourier integral transforms

In this section, we extend our harmonic analysis of infinitely periodic functions, using Fourier series, to aperiodic functions, using Fourier transforms. We start from the complex Fourier series over the range \(-\frac{L}{2} \leq x < \frac{L}{2}\) in Equation 13.31 as

\[
f(x) = \sum_{n=-\infty}^{\infty} c_n \exp \left( \frac{i2\pi nx}{L} \right)
\]

with the coefficients defined in Equation 13.32 as

\[
c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \exp \left( -i \frac{2\pi nx}{L} \right) dx
\]

where \(n\) is an integer.

Let’s define a new variable called the wave number\(^{25}\)

\[
k_n = \frac{2\pi n}{L}
\]

(13.39)

As \(k_n\) is a real number that depends on the integer index \(n\), we write the coefficient \(c_n\) as a function of \(k_n\), \(c(k_n)\). The result is

\[
c(k_n) = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) e^{-ik_n x} dx
\]

so that our complex Fourier series is

\[
f(x) = \sum_{n=-\infty}^{\infty} c(k_n) e^{ik_n x}
\]

Now let’s convert the sum over \(n\) to an integral over \(k_n\). Noting that the increment in the sum \(\Delta n = (n_i + 1) - n_i = 1\) we write

\[
f(x) = \sum_{n=-\infty}^{\infty} c(k_n) e^{ik_n x} = \sum_{n=-\infty}^{\infty} c(k_n) e^{ik_n x} \Delta n
\]

Inserting the formula for \(c(k_n)\) we have\(^{26}\)

\[
f(x) = \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x') e^{-i\frac{2\pi x}{L} x'} dx' e^{ik_n x} \Delta n
\]

where the bracketed term is a function of \(k_n\) and independent of \(x\). Finally, let’s substitute\(^{27}\)

\[
1 = \Delta n = \frac{1}{2\pi} \Delta k_n
\]

to find\(^{28}\)

\[
f(x) = \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x') e^{-i\frac{2\pi x}{L} x'} dx' e^{ik_n x} \Delta k_n
\]

25 The wave number, \(k\), is the spatial frequency of the wave. It is defined in terms of the wavelength, \(\lambda\), as

\[
k = \frac{2\pi}{\lambda}
\]

The wave number is the analog of the angular frequency, \(\omega\), that is related to the period of oscillation, \(T\), in time as

\[
\omega = \frac{2\pi}{T}
\]

The wave number is a measure of the number of waves per unit distance.

26 Note the difference between \(x'\) and \(x\). We integrate over the variable \(x'\) to determine the coefficient \(c(k_n)\) used in the expression for \(f(x)\).

27 This is equivalent to the derivative

\[
\frac{dk_n}{n} = \frac{2\pi}{L}
\]

using Equation 13.39.

28 Note that

\[
\int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) e^{-i\frac{2\pi x}{L} x'} dx' = \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x') e^{-i\frac{2\pi x}{L} x'} dx
\]
Suppose we take the limit that \( L \to \infty \). Our steps in \( k_n \) become infinitesimally small as \( L \to \infty \) and

\[
\Delta k_n = \frac{2\pi n}{L} \to dk
\]

As such, we can convert the sum to an integral as

\[
\lim_{n \to \infty} \sum_{n=-\infty}^{\infty} c(k_n)e^{ik_n x} \Delta k_n \to \int_{-\infty}^{\infty} c(k)e^{ikx}dk
\]

where

\[
c(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x)e^{-ikx}dx
\]

Combining our results we find the overall formula

\[
f(x) = \int_{-\infty}^{\infty} \left[ \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x')e^{-ik'x'}dx' \right] e^{ikx}dk = \int_{-\infty}^{\infty} F(k)e^{ikx}dk
\]

The inner integral transforms \( f(x) \) from a function of \( x \) to a function of \( k \) that we write \( F(k) \). The outer integral reverses the transformation and returns our original function \( f(x) \). The result is the Fourier transform pair defined\(^{29}\)

\[
F(k) = \int_{-\infty}^{\infty} f(x)e^{-ikx}dx \quad (13.40)
\]

and

\[
f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(k)e^{ikx}dk \quad (13.41)
\]

where \( F(k) \) is the Fourier transform of \( f(x) \) and \( f(x) \) is the inverse Fourier transform of \( F(k) \).

### 13.2.2 Correspondence between the Fourier transform and Fourier series

What is the correspondence between the Fourier series of a periodic function and the Fourier transform over one period of that function? Noting that

\[
F(k) = \int_{-\infty}^{\infty} f(x)e^{-ikx}dx \quad (13.42)
\]

and from Equation 13.32 that

\[
c_n = \frac{1}{2}(a_n - ib_n) = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x)e^{-inx}dx
\]

we arrive a relationship between the Fourier series coefficients \( a_n \) and \( b_n \) and the Fourier transform \( F(k) \) evaluated at discrete values of the wave number\(^{30}\)

\[
k = n
\]

where

\[
c_n = \frac{1}{2}(a_n - ib_n) = \frac{1}{2\pi} F(n) \quad (13.43)
\]

There are two alternative conventions for expressing Fourier transform pairs. One is based on dividing the reciprocal of \( 2\pi \) evenly between the integrals as

\[
F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{-ikx}dx \quad (13.44)
\]

and

\[
f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)e^{ikx}dk \quad (13.45)
\]

The wave number is\(^{31}\)

\[
k = \frac{2\pi}{\lambda} = \frac{2\pi n}{L}
\]

corresponds to allowed wavelengths \( \lambda = L/n \).

---

\(^{29}\) Integral transforms first explored by the great Leonhard Euler (1707–1783) were used by Joseph Fourier (1768–1830) to study heat flow in an unbounded semi-infinite domain as an extension of his Fourier series.

\(^{30}\) The wave number

\[
k = n = \frac{2\pi}{\lambda}
\]

corresponds to wavelengths \( \lambda = 2\pi/n \).

\(^{31}\) The wave number

\[
k = \frac{2\pi}{\lambda} = \frac{2\pi n}{L}
\]

corresponds to allowed wavelengths \( \lambda = L/n \).
We see the Fourier transform

\[ F = \frac{2\pi n}{L} \]

where

\[ c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \exp \left( -i \frac{2\pi nx}{L} \right) \, dx \]  

(13.46)

so that\(^{32}\)

\[ c_n = \frac{1}{2} (a_n - ib_n) = \sqrt{\frac{2\pi}{L}} F \left( \frac{2\pi n}{L} \right) \]  

(13.47)

Another is based on explicitly including a factor of 2\(\pi\) in the argument of the exponential. In that form the Fourier transform pairs are written

\[ F(k) = \int_{-\infty}^{\infty} f(x) e^{-i2\pi kx} \, dx \]  

(13.48)

and

\[ f(x) = \int_{-\infty}^{\infty} F(k) e^{i2\pi kx} \, dk \]  

(13.49)

which is the most symmetric form of the reciprocal pair.

The wave number is\(^{33}\)

\[ k = \frac{n}{L} \]

where\(^{34}\)

\[ c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \exp \left( -i \frac{2\pi nx}{L} \right) \, dx \]  

(13.50)

so that

\[ c_n = \frac{1}{2} (a_n - ib_n) = \frac{1}{L} F \left( \frac{n}{L} \right) \]  

(13.51)

We see the Fourier transform \(F(k)\) provides a harmonic analysis of the function \(f(x)\) where \(F(k)\) is proportional to the amplitude of the contribution of a given wave number to the function.

Harmonic analysis is commonly used in the study of molecular vibrations and the application of various spectroscopies. Let’s apply the Fourier transform to the harmonic analysis of a variety of functions commonly used in the physical sciences. The results of these and other examples are tabulated in the Table of Fourier Transforms in Supplement S0.

13.2.3 Deconstructing the Fourier transform of the square wave

In the previous section, we derived the Fourier series of the infinite periodic square wave function (see Figure 13.5). Let’s define the aperiodic function of \(x\) consisting of one oscillation of the square wave defined over the range \(-\frac{L}{2} < x < \frac{L}{2}\) and shown in Figure 13.17. It is written in terms of a difference

\[ f(x) = 2\theta \left( \frac{x}{L} \right) - 1 \quad -\frac{L}{2} \leq x < \frac{L}{2} \]  

(13.52)

where \(\theta(x)\) is the Heaviside step function that is unity for \(x \geq 0\) and zero otherwise.

Computing the Fourier transform of the aperiodic square wave

The Fourier transform of the square wave function is defined by the integral

\[ F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left[ 2\theta \left( \frac{x}{L} \right) - 1 \right] e^{-ikx} \, dx \]

The integrand is zero other than over the interval \(-\frac{L}{2} < x < \frac{L}{2}\). The function is

\[ c_n = \frac{1}{2L} F \left( \frac{n}{2L} \right) \]
The rapid oscillation or ringing is a signature of the abrupt steps in the square wave function.

Relating the Fourier transform to the Fourier series

To extend our harmonic analysis of periodic functions, using Fourier series, to aperiodic functions, using Fourier series, we must extend the finite interval of the Fourier series to \((-\infty, \infty)\). In essence, we have replaced one order of infinity, the integer coefficients used in Fourier series, with another, the real wave numbers used in Fourier transforms.\(^3\)

We found the Fourier series of the periodic square wave function defined in Equation 13.13 to be

\[
f(x) = \sum_{n=1,3,5,...}^{\infty} \frac{4}{n\pi} \sin\left(\frac{2n\pi x}{L}\right)
\]

where the coefficients were defined in Equation 13.11 as

\[
b_n = \frac{2}{n\pi} \left[1 - \cos\left(\pi n\right]\right] = \frac{4}{L} \left(1 - \cos\left(\frac{kL}{2}\right)\right)
\]

Here we use the definition of the wave number

\[
k = \frac{2\pi n}{L}
\]

The Fourier coefficients \(b_n\) and the Fourier transform \(F(k)\) are related

\[
\text{Figure 13.17: Comparison of the square wave function } f(x) = 2\theta\left(\frac{x}{L}\right) - 1 \text{ and the imaginary Fourier transform complement } iF(k) = \sqrt{\frac{2}{\pi}} \left(1 - \cos\left(\frac{kL}{2}\right)\right).
\]
through Equation 13.47 as

\[-\frac{i}{2} b_n \frac{\sqrt{2\pi}}{L} F\left(\frac{2\pi n}{L}\right)\]  \hspace{1cm} (13.54)

where we have accounted for the fact that the Fourier coefficients are scaled by \(\frac{1}{L}\) while the Fourier transform is scaled by \(\frac{1}{\sqrt{2\pi}}\).

The coefficients \(b_n\) and Fourier transform \(F(k)\) appropriately scaled using Equation 13.54 are compared in Figure 13.18. The Fourier coefficients represent points located near the top of the peaks of the continuously oscillating Fourier transform.

**13.2.4 Fourier transform of the impulse function is the sampling function**

Consider the aperiodic function of \(t\) known as the impulse function which is unity in the range \(-a < t < a\) and zero otherwise (see Figure 13.19). It can be written in terms of a difference

\[f(t) = \theta(t + a) - \theta(t - a)\]  \hspace{1cm} (13.55)

where \(\theta(t)\) is the Heaviside step function which is unity for \(t \geq 0\) and zero otherwise.

The Fourier transform of the impulse function is defined by the integral

\[F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} [\theta(t + a) - \theta(t - a)] e^{-i\omega t} dt\]

The integrand is zero other than over the interval \(-a < x < a\) where it is unity.
As such, the integral can be written

\[ F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{2\pi} \left( -\frac{1}{i\omega} \right) e^{-i\omega t} \bigg|_{-\infty}^{\infty} = \frac{1}{2\pi} \left( e^{i\omega \alpha} - e^{-i\omega \alpha} \right) \]

where we substitute \( \sin(x) = (e^{ix} - e^{-ix})/2i \) to form our final result\(^{36}\)

\[ F(\omega) = \frac{\sqrt{2}}{\pi} \sin(\alpha \omega) \frac{1}{\omega} \]

(13.57)

which is shown in Figure 13.19 and recorded in Supplement S\( _9 \)#5. The period of oscillation is inversely proportional to the width \( \alpha \). The ringing on the flanks of the central peak is a signature of the discontinuous steps in the impulse function.

### 13.2.5 Fourier transform of the gaussian is a gaussian

Consider the aperiodic function of \( t \) known as the gaussian function (see Figure 13.20) written

\[ f(t) = e^{-\alpha t^2} \quad (13.58) \]

The Fourier transform of the gaussian function is defined by the integral

\[ F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\alpha t^2} e^{-i\omega t} dt \]

![Figure 13.20: Comparison of the gaussian function \( f(t) = e^{-\alpha t^2} \) and its Fourier transform complement \( F(\omega) = \frac{1}{\sqrt{2\pi}} e^{-\omega^2/4\alpha} \) for three values of \( \alpha \). Darker shades of red indicate larger values of \( \alpha \).](image)

We can evaluate this integral using the Table of Definite Integrals in Supplement S\( _9 \)#11 where

\[ \int_{-\infty}^{\infty} e^{-ax^2+bx} dx = \sqrt{\frac{\pi}{a}} e^{b^2/4a} \]

Setting \( a = \alpha \) and \( b = -i\omega \) we find the final result

\[ F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\alpha t^2} e^{-i\omega t} dt = \frac{1}{\sqrt{2\alpha}} e^{-\omega^2/4\alpha} \quad (13.59) \]

which is shown in Figure 13.20 and recorded in Supplement S\( _9 \)#2.\(^{37}\) The smooth variation of the gaussian function translates to an equally smooth variation in its Fourier transform.

### 13.2.6 Fourier transform of an exponential is a lorentzian

Consider the aperiodic function of \( t \) known as the symmetric exponential function (see Figure 13.21) written

\[ f(t) = e^{-\alpha t} \quad (13.60) \]

\[ \text{The function } \sin(x) = \begin{cases} 1 & x = 0 \\ \sin \frac{x}{x} & \text{otherwise} \end{cases} \]

(13.56)

is called the sinc function and is also known as the sampling function.

\[ F(\omega) = \frac{1}{\sqrt{2\pi}} e^{-\omega^2/4\alpha} \]

(13.59)
where the absolute value $|t|$ guarantees that the exponential function decreases to zero as $t \to \pm\infty$.

The Fourier transform of the exponential function is defined by the integral

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi} \sqrt{a^2 + \omega^2}}$$

To eliminate the absolute value we can divide the integral in two as

$$\int_{-\infty}^{\infty} e^{-a|t|} e^{-i\omega t} dt = \int_{0}^{\infty} e^{-at} e^{-i\omega t} dt + \int_{-\infty}^{0} e^{at} e^{-i\omega t} dt = \frac{1}{a - i\omega} + \frac{1}{a + i\omega}$$

Combining these terms leads to the final result

$$F(\omega) = \sqrt{\frac{2}{\pi}} \left( \frac{a}{a^2 + \omega^2} \right)$$

which is shown in Figure 13.21 and recorded in Supplement S9 #3. The smooth variation of the exponential function translates to the smooth variation in its Fourier transform.

The motion of a harmonic oscillator experiencing frictional damping was explored in Complement C11. The time-dependence of the position and momentum of the oscillator were described in terms of an exponentially damped sinusoidal function. In that model, the frictional damping coefficient and force constant of the oscillator define the rate of exponential decay, $\alpha$, and the frequency of oscillation, $\omega$.

### 13.2.7 Fourier transform of a sinusoid and Dirac delta functions

Now let’s consider a periodic function of $t$ such as

$$f(t) = \cos(\omega_0 t)$$

shown in Figure 13.22. The Fourier transform is defined by the integral

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \cos(\omega_0 t) e^{-i\omega t} dt$$
We have considered the Fourier transform of the exponential function, Equation 13.61, and the Fourier transform of the cosine function, Equation 13.63.

Now consider the exponentially damped sinusoidal function

$$f(t) = e^{-|t|} \cos(\omega_0 t)$$

where the Fourier transform is defined

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt$$

As in evaluating the Fourier transform of the cosine function, we employ the identity $\cos(x) = (e^{ix} + e^{-ix})/2$ to find

$$\int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{2} \left[ \int_{-\infty}^{\infty} e^{-|t|} e^{-i(\omega - \omega_0) t} dt + \frac{1}{2} \int_{-\infty}^{\infty} e^{-|t|} e^{-i(\omega + \omega_0) t} dt \right]$$

This identity allows us to reform our result as

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \left[ \frac{1}{2} \int_{-\infty}^{\infty} e^{-i(\omega - \omega_0) t} dt + \frac{1}{2} \int_{-\infty}^{\infty} e^{-i(\omega + \omega_0) t} dt \right]$$

which is shown in Figure 13.22 and recorded in Supplement S9 #10. The cosine function has a single characteristic frequency $\omega_0$ leading to a single representative harmonic frequency in the Fourier transform. Note the symmetric pair of peaks at $\omega_0$ and $-\omega_0$. The Fourier transform cannot differentiate between positive and negative frequencies.

### 13.2.8 Fourier transform of a damped oscillator

We have considered the Fourier transform of the exponential function, Equation 13.61, and the Fourier transform of the cosine function, Equation 13.63.

Now consider the exponentially damped sinusoidal function

$$f(t) = e^{-|t|} \cos(\omega_0 t)$$

where the Fourier transform is defined

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt$$

As in evaluating the Fourier transform of the cosine function, we employ the identity $\cos(x) = (e^{ix} + e^{-ix})/2$ to find

$$\int_{-\infty}^{\infty} e^{-|t|} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{2} \left[ \int_{-\infty}^{\infty} e^{-|t|} e^{-i(\omega - \omega_0) t} dt + \frac{1}{2} \int_{-\infty}^{\infty} e^{-|t|} e^{-i(\omega + \omega_0) t} dt \right]$$

**Figure 13.22:** Comparison of sinusoidal function $f(t) = \cos(\omega_0 t)$ and its Fourier transform complement $F(\omega) = \sqrt{2/\pi} [\delta(\omega - \omega_0) + \delta(\omega + \omega_0)]$ for three values of $\omega_0$. 

\[\delta(\omega - \omega_0)\delta(\omega + \omega_0)\]
As in evaluating the Fourier transform of the exponential function, we eliminate the absolute value by dividing each integral in two so that

\[
\int_{-\infty}^{\infty} e^{-a|t|} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{2} \int_{-\infty}^{0} e^{at} e^{-i(\omega-\omega_0)t} dt + \frac{1}{2} \int_{0}^{\infty} e^{-at} e^{-i(\omega-\omega_0)t} dt \\
+ \frac{1}{2} \int_{-\infty}^{0} e^{at} e^{-i(\omega+\omega_0)t} dt + \frac{1}{2} \int_{0}^{\infty} e^{-at} e^{-i(\omega+\omega_0)t} dt
\]

Combining these terms leads to the final result

\[
\int_{-\infty}^{\infty} e^{-a|t|} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{a-i(\omega-\omega_0)} + \frac{1}{a+i(\omega-\omega_0)} \\
+ \frac{1}{a-i(\omega+\omega_0)} + \frac{1}{a+i(\omega+\omega_0)}
\]

Evaluating the integrals leads to

\[
\int_{-\infty}^{\infty} e^{-a|t|} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{a-i(\omega-\omega_0)} + \frac{1}{a+i(\omega-\omega_0)} \\
+ \frac{1}{a-i(\omega+\omega_0)} + \frac{1}{a+i(\omega+\omega_0)}
\]

We can simply this result by multiplying by the complex conjugate to form a real common denominator and combining terms where

\[
\frac{1}{a-i(\omega\pm\omega_0)} + \frac{1}{a+i(\omega\pm\omega_0)} = \frac{2a}{a^2+(\omega\pm\omega_0)^2}
\]

Combining these terms leads to the final result

\[
F(\omega) = \sqrt{\frac{2}{\pi}} \left[ \left( \frac{a/2}{a^2+(\omega-\omega_0)^2} \right) + \left( \frac{a/2}{a^2+(\omega-\omega_0)^2} \right) \right]
\]

which is shown in Figure 13.23 and recorded in Supplement S9 #12. The cosine function has a single characteristic frequency \(\omega_0\) leading to peaks in its transform at \(\pm\omega_0\). The exponential decays leads to a broadened line. The more rapid the decay, the broader the line. The result is a Fourier transform with peaks at \(\pm\omega_0\) with widths proportional to the rate of decay \(a\).

13.2.9 Fourier transformation turns differentiation into multiplication

Consider the Fourier transform of a differentiable function \(f(x)\)

\[
F(k) = \int_{-\infty}^{\infty} f(x) e^{-ikx} dx
\]
What is the Fourier transform of the derivative of \( f(x) \) with respect to \( x \)?

Starting from

\[
\int_{-\infty}^{\infty} \frac{d}{dx} f(x) e^{-ikx} \, dx
\]

we can integrate by parts to find

\[
\int_{-\infty}^{\infty} \frac{d}{dx} f(x) e^{-ikx} \, dx = f(x) e^{-ikx} \bigg|_{-\infty}^{\infty} + ik \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx
\]

The first term is zero if \( \lim_{x \to \pm \infty} f(x) = 0 \) and the second term is the Fourier transform of \( f(x) \) times a factor \( ik \). The final result is

\[
\int_{-\infty}^{\infty} \frac{d}{dx} f(x) e^{-ikx} \, dx = ik\mathcal{F}(f)(k) \tag{13.67}
\]

which is recorded in Supplement S9 #13. We see that the Fourier transform turns differentiation into multiplication.

---

**A13 Orthogonal vectors and orthogonal functions**

Any vector in three-dimensional space can be expressed as a weighted sum over orthonormal unit vectors multiplied by scalar coefficients. We call the unit vectors *basis vectors* as they provide a basis for the representation of any vector in three-dimensional space. Functions of continuous variables can be expressed as a weighted sum over continuous orthonormal *basis functions*. The properties of basis vectors and commonly used basis functions are explored below.

**Orthonormal sets of vectors**

In Chapter 4 we considered the unit vectors \( \hat{x}, \hat{y} \) and \( \hat{z} \) with the property that they were *normalized* so that

\[
\hat{x} \cdot \hat{x} = 1 \quad \hat{y} \cdot \hat{y} = 1 \quad \hat{z} \cdot \hat{z} = 1
\]

and *orthogonal* such that

\[
\hat{x} \cdot \hat{y} = \hat{y} \cdot \hat{z} = \hat{z} \cdot \hat{x} = 0
\]

We refer to \( \hat{x}, \hat{y} \) and \( \hat{z} \) as orthonormal vectors.

In three-dimensional space any vector can be written in terms of the three unit vectors \( \hat{x}, \hat{y} \) and \( \hat{z} \) as

\[
a = a_x \hat{x} + a_y \hat{y} + a_z \hat{z}
\]

where the scalar coefficients \( a_x, a_y \) and \( a_z \) are defined in terms of the projection of the vector \( \mathbf{a} \) on each of the unit vectors as

\[
a_x = \mathbf{a} \cdot \hat{x} \quad a_y = \mathbf{a} \cdot \hat{y} \quad a_z = \mathbf{a} \cdot \hat{z}
\]

as shown in Figure 13.24.

Suppose we define the unit vectors \( \mathbf{e}_n \) where \( \mathbf{e}_1 = \hat{x}, \mathbf{e}_2 = \hat{y} \) and \( \mathbf{e}_3 = \hat{z} \). Then we can state the orthonormality condition as

\[
\mathbf{e}_n \cdot \mathbf{e}_m = \delta_{nm}
\]

Any vector \( \mathbf{a} \) can be represented in terms of the unit vectors as

\[
\mathbf{a} = \sum_{n=1}^{3} a_n \mathbf{e}_n
\]
where the scalar coefficients are defined
\[ a_n = \mathbf{a} \cdot \mathbf{e}_n \]

In the sections that follow we will explore extensions of this idea to orthonormal functions of continuous variables.

**Orthonormal sets of sinusoidal functions**

In this chapter we found that many functions can be accurately expressed in terms of a weighted sum over sine and cosine functions. The sine and cosine function are orthogonal and normalized. The orthonormality conditions are written
\[ \frac{1}{\pi} \int_{-\pi}^{\pi} \cos(nx) \cos(mx) \, dx = \delta_{nm} \]
\[ \frac{1}{\pi} \int_{-\pi}^{\pi} \sin(nx) \sin(mx) \, dx = \delta_{nm} \]
where \( \delta_{nm} \) is the Kronecker delta function. In addition
\[ \frac{1}{\pi} \int_{-\pi}^{\pi} \cos(nx) \sin(mx) \, dx = 0 \]
for any \( n \) and \( m \). The properties of orthonormality are presented graphically in Figure 13.25.

\[ \delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases} \]

Its properties are explored in Chapter 8.

**Figure 13.25:** Visualizing the property of orthogonality for continuous functions. Variation in the normalized sine and cosine functions over the range \( x \in [-\pi, \pi] \) (left). The integral over the product formed by two orthogonal functions equals zero (right), shown as the sum of positive (red) and negative (gray) areas.

We can express any function \( f(x) \) in terms of a Fourier series
\[ f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx) \]
where the coefficients are determined using the integral relations provided by
Equations 13.3, 13.5 and 13.6 and collected here

\[ a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) \, dx \quad b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) \, dx \]

In Figure 13.25 is shown the normalized sine and cosine basis functions (left) and three products of two orthogonal functions. When vectors in three-dimensional space are orthogonal they are perpendicular. When two continuous functions are orthogonal the integral over their product is zero.

In the following section we will explore polynomial functions, derived in Chapter 11 to solve second order differential equations, in forming sets of orthonormal basis functions.

**Orthonormal sets of Hermite, Laguerre and Legendre polynomial functions**

We can build alternative sets of orthonormal basis functions based on the Hermite polynomials, Laguerre polynomials, and Legendre polynomials derived in Chapter 11 as the solutions of second order ordinary differential equations. With the proper weighting those polynomial functions are orthogonal and normalized. Any function can be expressed as an infinite sum over the set of polynomial functions.

The orthonormality condition for the Hermite polynomials is written

\[ \frac{1}{\sqrt{\pi} 2^n n!} \int_{-\infty}^{\infty} H_n(x) H_m(x) e^{-x^2} \, dx = \delta_{nm} \]

where the first five Hermite polynomials are

\[
\begin{align*}
H_0(x) &= 1 \\
H_1(x) &= 2x \\
H_2(x) &= 4x^2 - 2 \\
H_3(x) &= 8x^3 - 12x \\
H_4(x) &= 16x^4 - 48x^2 + 12
\end{align*}
\]

and the gaussian \( e^{-x^2} \) is the weighting function. The integral defining orthonormality includes a product of two Hermite polynomials and the gaussian weighting function. Figure 13.26 shows the first five Hermite polynomials each multiplied by the square root of the weighting function \( e^{-x^2/2} \). Note that \( n \) is the number of nodes or zeros.

![Figure 13.26: Variation in the first five weighted and normalized Hermite polynomials proportional to \( e^{-\frac{x^2}{2}} \) \( H_n(x) \) over the range \( x \in [-5, 5] \) (left). The equal areas of opposite sign observed in the product of the first two polynomials demonstrates the orthogonality of those functions (right).](image)
The Hermite polynomials are used to represent the wave function of the quantum harmonic oscillator.

The orthonormality condition for the Laguerre polynomials is written

$$\int_0^\infty L_n(x) L_m(x)e^{-x}dx = \delta_{nm}$$

where the first five Laguerre polynomials are

$$L_0(x) = 1$$
$$L_1(x) = -x + 1$$
$$L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$$
$$L_3(x) = \frac{1}{6}(-x^3 + 9x^2 - 18x + 6)$$
$$L_4(x) = \frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24)$$

and the exponential $e^{-x}$ is the weighting function. The integral defining orthonormality includes a product of two Laguerre polynomials and the exponential weighting function. Figure 13.27 shows the first five Laguerre polynomials each multiplied by the square root of the weighting function $e^{-x/2}$.

Figure 13.27: Variation in the first five weighted and normalized Laguerre polynomials proportional to $e^{-\frac{x^2}{2}}L_n(x)$ over the range $x \in [0, 22]$ (left). The equal areas of opposite sign observed in the product of the first two polynomials demonstrates the orthogonality of those functions (right).

The Laguerre polynomials are used to represent the radial component of the wave function of the quantum one electron atom.

The orthonormality condition for the Legendre polynomials is written

$$\frac{2n + 1}{2} \int_{-1}^1 P_n(x) P_m(x)dx = \delta_{nm}$$

where the first five Legendre polynomials are

$$P_0(x) = 1$$
$$P_1(x) = x$$
$$P_2(x) = \frac{1}{2}(3x^2 - 1)$$
$$P_3(x) = \frac{1}{2}(5x^3 - 3x)$$
$$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

and the weighting function is unity. The integral defining orthonormality includes a product of two Legendre polynomials and a weighting function of
unity. Figure 13.28 shows the first five Legendre polynomials each multiplied by the square root of the weighting function 1.

\[ Y_l^m(\theta, \phi) \]

\[ Y_l^0(\theta, \phi) \]

\[ Y_l^1(\theta, \phi) \]

\[ Y_l^2(\theta, \phi) \]

\[ Y_l^3(\theta, \phi) \]

\[ Y_l^4(\theta, \phi) \]

The Legendre polynomials are used in the multipole expansion of the electrostatic potential and in representing the quantum wave functions of electrons in atoms.

**Orthonormal sets of spherical harmonic functions**

Angular functions \( f(\theta, \phi) \) can be expressed in terms of an infinite set of spherical harmonic functions. Those functions are orthogonal and normalized and can be used to express any angular function in terms of an infinite sum over the set of spherical harmonic functions.

The orthonormality condition is written

\[ \int_0^{2\pi} \int_0^\pi Y_l^m(\theta, \phi) Y_{l',m}'(\theta, \phi) \sin(\theta) d\theta d\phi = \delta_{l,l'} \delta_{m,m'} \]

where the spherical harmonic for specific \( l \) and \( m \) can be written equivalently as \( Y_l^m(\theta, \phi) \) or \( Y_l^m(\theta, \phi) \). The first six spherical harmonic functions are shown in Figure 13.29 where the red and white surfaces indicate the sign of the function for the specific \( (\theta, \phi) \).

\[ \delta_{l,l'} \delta_{m,m'} \]

The functions depicted above and defined by the functions below. The integral defining orthonormality includes a product of one spherical harmonic function
and the complex conjugate of a second spherical harmonic function so that the resulting integral is real.

\[ Y_0^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{1}{\pi}} \]

\[ Y_1^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos(\theta) \quad Y_1^1(\theta, \phi) = \mp \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin(\theta)e^{\pm i\phi} \]

\[ Y_2^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2(\theta) - 1) \quad Y_2^1(\theta, \phi) = \pm \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin(\theta) \cos(\theta)e^{\pm i\phi} \quad Y_2^{-1}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2(\theta)e^{\pm 2i\phi} \]

To perceive the orthogonality of these functions, imagine overlapping \( Y_0^0(\theta, \phi) \), which is even over all space, with \( Y_1^1(\theta, \phi) \), which is an odd function of \( z \) (see variation in sign between the two lobes). An integral over all space of the product of the two functions will therefore be zero making the functions orthogonal.

Any function \( f(\theta, \phi) \) can be expanded as an infinite series using the set of orthogonal spherical harmonic functions

\[ f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_l^m Y_l^m(\theta, \phi) \]

where the coefficients \( f_l^m \) are defined

\[ f_l^m = \frac{2l+1}{4\pi} \int_0^{2\pi} \int_0^{\pi} f(\theta, \phi) Y_l^m(\theta, \phi) \sin(\theta) \sin(\phi) d\theta d\phi \]

Just as one carries out harmonic analysis using Fourier transforms one can carry out spherical harmonic analysis in decomposing an angular distribution in terms of the contribution of each spherical harmonic.

The spherical harmonic functions are the angular component of the solutions of Laplace's equation

\[ \nabla^2 f(r, \theta, \phi) = 0 \]

in spherical polar coordinates. In addition to forming a complete set of basis functions for the representation of angular functions \( f(\theta, \phi) \), the spherical harmonics are commonly used to represent the multipole expansion of the electrostatic potential, the fluctuations in the surface of a spherical droplet, and the distribution of electrons in atomic orbital electron configurations.

B13 End-of-chapter problems

The profound study of nature is the most fertile source of mathematical discoveries.

Joseph Fourier

Warm-ups

13.1 Find the Fourier series representing the periodic step function

\[ f(x) = \begin{cases} 
0 & -\pi \leq x < 0 \\
1 & 0 \leq x < \pi 
\end{cases} \]

defined over the range \(-\pi \leq x < \pi\) and repeating with a period of \(2\pi\) as shown below. Compare your resulting
coefficients with those of the square wave in Equation 13.12. Explain the observed differences.

13.2 Find the Fourier series representing the periodic positive triangle wave function

\[ f(x) = \begin{cases} \frac{x}{L} & 0 \leq x < L \\ \frac{2L-x}{L} & L \leq x < 2L \end{cases} \]

defined over the range \(0 \leq x < 2L\) and repeating with a period of \(2L\) as shown below.

13.3 Use the Table of Fourier transform pairs in Supplement S9 to determine the Fourier transform of the function

\[ f(t) = 0.5e^{-t/10} \cos(12t) + 1.8e^{-t/4} \cos(20t) + 0.7e^{-3t/4} \cos(26t) \]

Sketch the form of the function \(f(t)\) over the range \(0 \leq t \leq 10\) and its Fourier transform \(F(\omega)\) over the range \(0 \leq \omega < 30\).

13.4 Consider the general Fourier series of Equation 13.7

\[ f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx) \]

where the coefficients are defined by Equation 13.8

\[ a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos(nx) \, dx \quad b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin(nx) \, dx \]

Show that \(a_n = 0\) for \(n = 0, 1, 2, \ldots\) for any odd function of \(x\) (sine transform). Similarly, show that \(b_n = 0\) for \(n = 1, 2, 3, \ldots\) for any even function of \(x\) (cosine transform).
13.5 The Fourier transform of the damped cosine function \( e^{-at} \cos(\omega_0 t) \) is a Lorentzian function of the form

\[
I(\omega) = \frac{a}{a^2 + (\omega - \omega_0)^2}
\]

Determine the position of the maximum of \( I(\omega) \), the maximum value of \( I(\omega) \), and the width of \( I(\omega) \) at half of its maximum value known as the full width at half maximum (FWHM).

13.6 Consider the function \( f(t) \) with Fourier transform \( F(\omega) \). Show that the Fourier transform of \( f(t + t_0) \) is \( F(\omega) e^{i\omega t_0} \).

**Homework exercises**

13.7 Consider the Fourier series of the periodic sawtooth wave function, Equation 13.21, over the range \(-L \leq x < L\) where

\[
f(x) = 2 \pi \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \left( \frac{n\pi x}{L} \right)
\]

Set \( x = \frac{L}{2} \) and show that

\[
\frac{\pi}{4} = 1 - \frac{1}{3} + \frac{1}{5} - \frac{1}{7} + \frac{1}{9} - \frac{1}{11} + \ldots
\]

which is Leibniz’s formula for \( \pi \).

13.8 Find the Fourier series representing the periodic parabolic wave function

\[
f(x) = x^2 \quad -\pi \leq x < \pi
\]

defined over the range \(-\pi \leq x < \pi\) and repeating with a period of \(2\pi\) as shown below.

13.9 Consider the exponentially damped cosine function

\[
f(t) = e^{-at} \cos(\omega_0 t)
\]

defined over the range \(0 \leq t < \infty\) with \( a = \frac{1}{3} \) and \( b = \frac{1}{3} \). Determine its cosine transform defined

\[
F_c(\nu) = \int_{0}^{\infty} f(t) \cos(2\pi\nu t) dt
\]

Sketch the form of the function \( f(t) \) over the range \(0 \leq t \leq 20\) and the cosine transform \( F_c(\nu) \) over the range \(-1 \leq \nu \leq 1\).

13.10 Find the Fourier series representing the periodic positive sawtooth wave function

\[
f(x) = x \quad 0 \leq x < 2L
\]

defined over the range \(0 \leq x < 2L\) and repeating with a period of \(2L\) as shown below. Unlike the sawtooth wave shown in Figure 13.9 that is an odd function of \( x \), this sawtooth wave is not even or odd.
13.11 Find the Fourier series representing the periodic odd triangle wave function

\[ f(t) = \begin{cases} 
 t & -\frac{T}{2} \leq t < \frac{T}{2} \\
 \frac{T}{2} - t & \frac{T}{2} \leq t < \frac{3T}{2} 
\end{cases} \]

declared over the range \(-\frac{T}{2} \leq t < \frac{T}{2}\) and repeating with a period of \(T\) as shown below.

13.12 Consider the function \(f(t)\) with Fourier transform \(F(\omega)\). Show that the Fourier transform of \(f(st)\) is

\[ \frac{1}{s} F \left( \frac{\omega}{s} \right) \]

when \(s > 0\).

13.13* Consider the exponential function \(f(t) = e^{-|t|}\) with Fourier transform \(F(\omega)\). Starting from the definition of the Fourier transform of the derivative of \(f(t)\) written

\[ G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left( \frac{d}{dt} e^{-|t|} \right) e^{-i\omega t} dt \]

demonstrate that \(G(\omega) = i\omega F(\omega)\).

13.14 Consider the sine series solution to the classical wave equation

\[ u(x) = \sin \left( \frac{\pi x}{L} \right) \]

declared over the range \(0 \leq x < L\). We can make this a periodic function by repeating the behavior over \(0 \leq x < L\) with a period of \(L\) as shown below.
Derive the Fourier series representation of this solution to the wave equation.

13.15 Consider the cosine series solution to the classical heat equation

\[ u(x) = \frac{1}{2} - \frac{1}{2} \cos \left( \frac{2\pi x}{L} \right) \]

defined over the range \( 0 \leq x < L \). We can make this a periodic function by repeating the behavior over \( 0 \leq x < L \) with a period of \( L \) as shown below.

Derive the Fourier series representation of this solution to the heat equation.

13.16* Find the Fourier series representing the inverted parabolic wave function

\[ f(x) = L^2 - (x - 2n)^2, \quad n = \ldots, -2, -1, 0, 1, 2, \ldots \]

defined over the range \( (2n - 1)L \leq x < (2n + 1)L \) and repeating with a period of \( 2L \) as shown below.

Prove that your answer satisfies the boundary conditions \( f(0) = L^2 \) and \( f(-L) = f(L) = 0 \).

13.17 Complete the following steps to derive the energy theorem, also known as Parseval’s theorem, and explore its meaning.
(a) Evaluate the integral over the square of the function $f(t)$ written

$$E = \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} (f(t))^2 \, dt$$

when $f(t)$ is expressed as a Fourier series

$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi nt}{T} \right) + \sum_{n=1}^{\infty} b_n \sin \left( \frac{2\pi nt}{T} \right)$$

(b) Evaluate the integral defining the mean square residual difference written

$$\Delta E = \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} \left[ f(t) - f_N(t) \right]^2 \, dt$$

where $f(t)$ is expressed as a Fourier series and $f_N(t)$ is the partial sum.

(c) Evaluate $E$ for the square wave Fourier series. Do that by evaluating the integral as well as by summing the infinite series. Demonstrate that your results are equal.

13.18 Let’s consider another representation of the Fourier cosine series of a function $f(t)$ in terms of a function $g(\omega)$ defining a spectrum of frequencies $\omega$ contributing to the Fourier series. The function can be written as

$$f(t) = \sum_{n=-\infty}^{\infty} a_n \cos \left( \frac{2\pi nt}{T} \right) \cos(\omega t) \, d\omega$$

Derive $g(\omega)$. HINT: Consider the possibility of a weighted sum over Dirac delta functions.

13.19* Consider the sinusoidal function $\cos(\omega_0 t)$ sampled over $N + 1$ periods of oscillation and written

$$f(t) = \begin{cases} 0 & t < -\frac{N\pi}{\omega_0} \\ \cos(\omega_0 t) & -\frac{N\pi}{\omega_0} < t < \frac{N\pi}{\omega_0} \\ 0 & t > \frac{N\pi}{\omega_0} \end{cases}$$

The Fourier transform $F(\omega)$ of $f(t)$ can be written

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \left[ \sin \left( \frac{N\pi}{\omega_0} (\omega + \omega_0) \right) + \sin \left( \frac{N\pi}{\omega_0} (\omega - \omega_0) \right) \right]$$

(a) Plot the function $f(t)$ and its Fourier transform $F(k)$ for $N = 1$ over the range $-60 < \omega < 60$.

(b) Plot the function $f(t)$ and its Fourier transform $F(k)$ for $N = 11$ over the range $-15 < \omega < 15$.

(c) Determine the form of the Fourier transform in the limit

$$\lim_{N \to \infty} F(\omega)$$

where we have sampled an infinity of oscillations of the sinusoidal wave. HINT: Equation 8.17 will be useful.

(d) What feature of this function is responsible for the ringing oscillations observed in the Fourier transform?

13.20* Consider the two functions $f(t)$ and $g(t)$ with Fourier transforms $F(\omega)$ and $G(\omega)$, respectively. The integral convolution of the two functions $f(t)$ and $g(t)$ is

$$(f * g)(t) = \int_{-\infty}^{\infty} f(s)g(t-s) \, ds$$
where we use the notation \( f \ast g \) to denote convolution and write \((f \ast g)(t)\) to emphasize that the result is a function of \( t \). Prove that the Fourier transform of the convolution \((f \ast g)(t)\) is the product \( \sqrt{2\pi} F(\omega)G(\omega) \).

13.21∗ The complex Fourier series is defined
\[
f(x) = \sum_{m=-\infty}^{\infty} c_m e^{imx}
\]
where \( e^{imx} = \cos(mx) + i \sin(mx) \) and the coefficients \( c_m \) are complex numbers. Prove that
\[
c_m = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) e^{-inx} \, dx
\]
HINT: Do this by inserting the equation above for \( f(x) \) into the proposed definition of \( c_m \) and evaluating the integrals.

13.22∗ The aperiodic sawtooth function shown below can be written for one period of oscillation over \(-L \leq x < L\) as
\[
f(x) = \begin{cases} 
0 & x < -L \\
\frac{x}{L} & -L \leq x < L \\
0 & x > L
\end{cases}
\]
(a) Derive the Fourier transform of the aperiodic sawtooth function \( f(x) \) defined
\[
F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx
\]
as a function of \( k \).

(b) We derived the Fourier series of the periodic sawtooth wave function shown in Figure 13.9. The resulting Fourier series defined in Equation 13.21 is
\[
f(x) = \sum_{n=1}^{\infty} b_n \sin \left( \frac{\pi nx}{L} \right) = \frac{2}{\pi} \sum_{n=1}^{\infty} \left( -1 \right)^{n+1} \frac{n}{n} \sin \left( \frac{\pi nx}{L} \right)
\]
Show that the Fourier series coefficients \( b_n \) are related to the value of the Fourier transform evaluated at \( k = \frac{\pi n}{L} \) through the relation
\[
c_n = \frac{\sqrt{2\pi}}{2L} F \left( \frac{\pi n}{L} \right)
\]
13.23∗ The orthonormality condition for the Hermite polynomials is
\[
\frac{1}{\sqrt{\pi 2^n n!}} \int_{-\infty}^{\infty} H_n(x) H_m(x) e^{-x^2} \, dx = \delta_{nm}
\]
where \( \delta_{nm} \) is the Kronecker delta function which is unity when \( n = m \) and zero otherwise. Show that the Hermite polynomials \( H_1(x) = 2x \) and \( H_2(x) = 4x^2 - 2 \) are normalized and orthogonal over \(-\infty < x < \infty\).
13.24* The orthonormality condition for the Laguerre polynomials is

$$
\int_0^\infty L_n(x) L_m(x)e^{-x}dx = \delta_{nm}
$$

Show that the Laguerre polynomials $L_1(x) = 1 - x$ and $L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$ are normalized and orthogonal over $0 \leq x < \infty$.

13.25* The orthonormality condition for the Legendre polynomials is

$$
\frac{2n + 1}{2} \int_{-1}^{1} P_n(x) P_m(x)dx = \delta_{nm}
$$

Show that the Legendre polynomials $P_1(x) = x$ and $P_2(x) = \frac{1}{2}(3x^2 - 1)$ are normalized and orthogonal over $-1 \leq x \leq 1$.

13.26* The orthonormality condition for the spherical harmonic functions is

$$
\int_0^{2\pi} \int_0^{\pi} Y_{l,m}(\theta, \varphi) Y_{l',m'}(\theta, \varphi) \sin(\theta) d\theta d\varphi = \delta_{l,l'}\delta_{m,m'}
$$

where $Y_{l,m}^*(\theta, \varphi)$ is the complex conjugate of $Y_{l,m}(\theta, \varphi)$. Show that the spherical harmonic functions $Y_{1,0}(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta$ and $Y_{1,1}(\theta, \varphi) = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{i\varphi}$ are normalized and orthogonal over $0 \leq \theta < \pi$ and $0 \leq \varphi < 2\pi$. 
14 Matrices and matrix algebra

14.1 Vectors, matrices, and determinants

Linear algebra involves the study of linear equations. We have seen that linear equations naturally arise in the physical sciences in the form of linear polynomial equations, linear operators, and linear differential equations. Of particular interest is the solution of systems of coupled linear equations in many variables. This section explores methods for solving systems of linear equations in a way that naturally leads to the definition of the matrix and the determinant.

14.1.1 The vector and the matrix

In exploring the properties of vectors and the principles of vector algebra in Chapter 4, we expressed a vector shown in Figure 14.1 as

\[ \mathbf{a} = a_x \hat{x} + a_y \hat{y} + a_z \hat{z} \]

An alternative notation for the vector \( \mathbf{a} \) is

\[ \mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \]

Using this notation the unit vectors are written

\[ \hat{x} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \hat{y} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \hat{z} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \]

Thinking of \( \mathbf{a} \) as the sum \( \mathbf{a} = a_x \hat{x} + a_y \hat{y} + a_z \hat{z} \) we can write

\[ \mathbf{a} = a_x \hat{x} + a_y \hat{y} + a_z \hat{z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} \]

This demonstrates how these two distinct representations of the vector \( \mathbf{a} \) are equivalent.

We can generalize the concept of the vector to form a matrix. A matrix is a two dimensional array of terms forming \( m \) rows and \( n \) columns. We say that the matrix order is \( m \times n \) for a matrix with \( m \) rows and \( n \) columns. Consider the example

\[ \mathbf{A} = \begin{pmatrix} a_{11} \\ a_{21} \\ a_{31} \\ a_{41} \end{pmatrix} \]

\( \mathbf{A} \) is a column matrix or equivalently a column vector and its order is \( 4 \times 1 \). The position of each element \( a_{ij} \) is identified by a row index \( i \) and a column index \( j \).\(^1\)

\(^1\) We write the element in the \( i \)th row and \( j \)th column of the matrix as \( [\mathbf{A}]_{ij} \).
Now consider a related example of

\[ B = \begin{pmatrix} b_{11} & b_{12} & b_{13} \end{pmatrix} \]

\( B \) is formed from a row rather than a column and is referred to as a row matrix or equivalently a row vector. Its order is 1 \times 3. Finally, consider

\[ C = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \]

\( C \) is a square matrix and its order is 3 \times 3. \( C \) can be thought of as being formed from three row vectors of order 1 \times 3. It can also be thought of as being formed from three column vectors of order 3 \times 1.

Note that we can also form more general rectangular matrices such as

\[ D = \begin{pmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \\ d_{41} & d_{42} & d_{43} \end{pmatrix} \]

which is a matrix of order 4 \times 3 and

\[ E = \begin{pmatrix} e_{11} & e_{12} & e_{13} & e_{14} \\ e_{21} & e_{22} & e_{23} & e_{24} \end{pmatrix} \]

which is a matrix of order 2 \times 4.

**14.1.2 The matrix determinant**

For any square matrix we can calculate a property called the determinant.\(^2\)

Consider the determinant \( |A| \) of the 2 \times 2 square matrix \( A \) defined as

\[ |A| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21} \quad (14.1) \]

We encountered the determinant in Chapter 4 while exploring the vector cross product. We learned to express the vector cross product as the determinant of a 3 \times 3 matrix (see Equation 4.9). In addition, we learned how the determinant of a 3 \times 3 matrix can be written in terms of the determinants of three 2 \times 2 matrices as in this expression for the cross product

\[ a \times b = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} \]

\[ = \hat{x} \begin{vmatrix} a_y & a_z \\ b_y & b_z \end{vmatrix} - \hat{y} \begin{vmatrix} a_x & a_z \\ b_x & b_z \end{vmatrix} + \hat{z} \begin{vmatrix} a_x & a_y \\ b_x & b_y \end{vmatrix} \]

\[ = (a_y b_z - a_z b_y) \hat{x} + (a_z b_x - a_x b_z) \hat{y} + (a_x b_y - a_y b_x) \hat{z} \]

Let’s consider another use of the matrix determinant. Suppose we have a set of linear equations

\[ a_{11}x + a_{12}y = d_1 \\ a_{21}x + a_{22}y = d_2 \quad (14.2) \]

where the goal is to solve the equations for the variables \( x \) and \( y \) in terms of the various coefficients (see Figure 14.2). We can multiply the first equation by \( a_{22} \)
and the second by \(a_{12}\) (noted in red) as
\[
\begin{align*}
\quad a_{11}a_{22}x + a_{12}a_{22}y &= d_1a_{22} \\
\quad a_{21}a_{12}x + a_{22}a_{12}y &= d_2a_{12}
\end{align*}
\]

Subtracting the two equations we find
\[
(a_{11}a_{22} - a_{21}a_{12}) x = d_1a_{22} - d_2a_{12}
\]
Solving this equation for \(x\) leads to
\[
x = \frac{d_1a_{22} - d_2a_{12}}{a_{11}a_{22} - a_{21}a_{12}} \quad \text{(14.3)}
\]

Suppose we start again, this time multiplying the first equation by \(a_{21}\) and the second equation by \(a_{11}\) as
\[
\begin{align*}
\quad a_{11}a_{21}x + a_{12}a_{21}y &= d_1a_{21} \\
\quad a_{21}a_{11}x + a_{22}a_{11}y &= d_2a_{11}
\end{align*}
\]

Subtracting the two equations we find
\[
(a_{12}a_{21} - a_{22}a_{11}) y = d_1a_{21} - d_2a_{11}
\]
or
\[
y = \frac{d_1a_{21} - d_2a_{11}}{a_{12}a_{21} - a_{22}a_{11}} = \frac{d_2a_{11} - d_1a_{21}}{a_{11}a_{22} - a_{12}a_{21}} \quad \text{(14.4)}
\]
which completes our solution to Equation 14.2 for \(x\) and \(y\).

---

The common denominator in Equations 14.3 and 14.4 is the determinant of the \(2 \times 2\) square matrix
\[
|A| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}
\]

Geometrically, the determinant \(|A|\) can be interpreted as the area of a parallelogram with edges defined by the column vectors forming the matrix \(A\)

\[
a = \begin{pmatrix} a_{11} \\ a_{21} \end{pmatrix} \quad \text{and} \quad b = \begin{pmatrix} a_{12} \\ a_{22} \end{pmatrix}
\]

as shown in Figure 14.3. 

---

3 Our approach is readily generalized to the solution of \(n\) linear algebraic equations in \(n\) unknowns through a similar treatment of \(n \times n\) square matrix determinants. The resulting method will be discussed later in this Chapter.
For the determinant of a $3 \times 3$ matrix we write

$$
\begin{vmatrix}
 a_{11} & a_{12} & a_{13} \\
 a_{21} & a_{22} & a_{23} \\
 a_{31} & a_{32} & a_{33}
\end{vmatrix}
= a_{11} \begin{vmatrix}
 a_{22} & a_{23} \\
 a_{32} & a_{33}
\end{vmatrix} - a_{12} \begin{vmatrix}
 a_{21} & a_{23} \\
 a_{31} & a_{33}
\end{vmatrix} + a_{13} \begin{vmatrix}
 a_{21} & a_{22} \\
 a_{31} & a_{32}
\end{vmatrix} 
= a_{11} (a_{22}a_{33} - a_{23}a_{32}) - a_{12} (a_{21}a_{33} - a_{23}a_{31}) + a_{13} (a_{21}a_{32} - a_{22}a_{31})
$$

(14.5)

as we encountered previously in our definition of the vector cross product (see Equation 4.9). Geometrically, the determinant $|A|$ of a $3 \times 3$ matrix $A$ can be interpreted as the volume of a parallelepiped with edges defined by the three column vectors forming the matrix (see Figure 14.4).

This geometric interpretation is a useful qualitative guide in the quantitative evaluation of matrix determinants.

### 14.1.3 Matrix determinants of arbitrary dimension

We can extend this approach to computing determinants of $n \times n$ square matrices to arbitrarily large $n$. To do so, we introduce the cofactor $A_{ij}$ of the matrix $A$, where $A_{ij}$ is the determinant of an $(n-1) \times (n-1)$ square matrix, formed by deleting the $i$th row and $j$th column of $A$, multiplied by $(-1)^{i+j}$. The determinant of a $n \times n$ square matrix $A$ can then be written

$$|A| = a_{11}A_{11} + a_{12}A_{12} + \ldots + a_{1n}A_{1n}$$

To determine the $n$ cofactors, we need to evaluate $n$ determinants of $(n-1) \times (n-1)$ matrices. For each of these determinants we need to compute $n-1$ determinants of $(n-2) \times (n-2)$ matrices. And so on.

For example, returning to the case above we can express the determinant of the $3 \times 3$ matrix $A$ in terms of 3 cofactors as

$$
\begin{vmatrix}
 a_{11} & a_{12} & a_{13} \\
 a_{21} & a_{22} & a_{23} \\
 a_{31} & a_{32} & a_{33}
\end{vmatrix}
= a_{11} \begin{vmatrix}
 a_{22} & a_{23} \\
 a_{32} & a_{33}
\end{vmatrix} - a_{12} \begin{vmatrix}
 a_{21} & a_{23} \\
 a_{31} & a_{33}
\end{vmatrix} + a_{13} \begin{vmatrix}
 a_{21} & a_{22} \\
 a_{31} & a_{32}
\end{vmatrix} 
= a_{11} (a_{22}a_{33} - a_{23}a_{32}) - a_{12} (a_{21}a_{33} - a_{23}a_{31}) + a_{13} (a_{21}a_{32} - a_{22}a_{31})
$$

where the cofactors are

$$
A_{11} = (-1)^2 \begin{vmatrix}
 a_{22} & a_{23} \\
 a_{32} & a_{33}
\end{vmatrix},
A_{12} = (-1)^3 \begin{vmatrix}
 a_{21} & a_{23} \\
 a_{31} & a_{33}
\end{vmatrix},
A_{13} = (-1)^4 \begin{vmatrix}
 a_{21} & a_{22} \\
 a_{31} & a_{32}
\end{vmatrix}
$$

4 This method was developed by the French mathematician, physicist and astronomer Pierre-Simon Laplace (1749-1827).
Evaluating the $2 \times 2$ determinants and watching our signs leads to the final result

$$|A| = a_{11}A_{11} + a_{12}A_{12} + a_{13}A_{13}$$

$$= a_{11} [a_{22}a_{33} - a_{23}a_{32}] + a_{12} [-a_{21}a_{33} + a_{23}a_{31}] + a_{13} [a_{21}a_{32} - a_{22}a_{31}]$$

which is identical to our earlier result in Equation 14.5, validating our method.

Consider the determinant of the $3 \times 3$ matrix

$$|A| = \begin{vmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{vmatrix}$$

that can be evaluated as

$$|A| = 2(-1)^2 \begin{vmatrix} 2 & -1 \\ -1 & 2 \end{vmatrix} + (-1)(-1)^3 \begin{vmatrix} -1 & -1 \\ -1 & 2 \end{vmatrix} + (-1)(-1)^4 \begin{vmatrix} -1 & 2 \\ -1 & -1 \end{vmatrix}$$

$$= 6 - 3 - 3 = 0$$

This demonstrates how the determinant of the $3 \times 3$ matrix is evaluated in terms of three $2 \times 2$ determinants. In the end, our goal is to reduce the determinant of any size matrix to $2 \times 2$ determinants.

Now let’s consider the determinant of a $4 \times 4$ matrix

$$|A| = \begin{vmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{vmatrix} = a_{11}A_{11} + a_{12}A_{12} + a_{13}A_{13} + a_{14}A_{14}$$

where the cofactors are

$$A_{11} = (-1)^2 \begin{vmatrix} 2 & -1 \\ -1 & 2 \end{vmatrix} = 4 \quad A_{12} = (-1)^3 \begin{vmatrix} -1 & -1 \\ -1 & 2 \end{vmatrix} = 4$$

$$A_{13} = (-1)^4 \begin{vmatrix} -1 & 2 \\ -1 & 0 \end{vmatrix} = 4 \quad A_{14} = (-1)^5 \begin{vmatrix} -1 & 2 \\ -1 & 0 \end{vmatrix} = 4$$

This leads to the final result

$$|A| = 2(4) + (-1)(4) + 0(4) + (-1)(4) = 0$$

The determinant of this $4 \times 4$ matrix required the calculation of four $3 \times 3$ determinants that required the calculation of three $2 \times 2$ determinants. Ultimately, we reduced the determinant of the $4 \times 4$ matrix to twelve $2 \times 2$ determinants.

Another approach to computing $|A|$ is to simply expand the larger determinant as

$$|A| = +2 \begin{vmatrix} -1 & -1 & 0 \\ 0 & 2 & -1 \\ -1 & -1 & 2 \end{vmatrix} - (-1) \begin{vmatrix} 1 & 0 & -1 \\ 0 & -1 & 1 \\ 1 & 0 & 1 \end{vmatrix}$$

This is equivalent to the approach using cofactor matrices but treats the alternating signs in the initial expansion. This makes a sign error less likely. These examples demonstrate how our method for computing matrix determinants works for $2 \times 2$, $3 \times 3$, $4 \times 4$, and matrices of arbitrary dimension.

The calculation of matrix determinants is involved in many applications of linear algebra in the physical sciences. As such, it is critical to become efficient
in the calculation of matrix determinants and familiar with their properties. The next section surveys the basic properties of matrix determinants.

### 14.1.4 Special properties of matrix determinants

We identify five fundamental properties of the matrix determinant. Terms in a determinant that have been transformed are highlighted in red.

1. If we change the rows of a matrix $A$ to the columns of a matrix in the same order, we create the transpose matrix $A^T$. The determinant of $A$ and $A^T$ are identical. Compare the determinant

\[
|A| = \begin{vmatrix}
a & b & c \\
d & e & f \\
g & h & i \\
\end{vmatrix}
= a(ei - fh) - b(di - fg) + c(dh - eg)
\]

to the determinant of the transpose matrix

\[
|A^T| = \begin{vmatrix}
a & d & g \\
b & e & h \\
c & f & i \\
\end{vmatrix}
= a(ei - fh) - d(bi - hc) + g(bf - ec)
\]

While the terms in blue have changed order, the determinants $|A|$ and $|A^T|$ are identical.

2. If any row or column of a square matrix is multiplied by a constant $k$, then the determinant is multiplied by $k$. Consider that

\[
|B| = \begin{vmatrix}
a & b & kc \\
d & e & kf \\
g & h & ki \\
\end{vmatrix}
= a(eki - kfh) - b(dki - kfg) + kc(dh - eg)
= k\left[a(ei - fh) - b(di - fg) + c(dh - eg)\right]
= k|A|
\]

Geometrically, the multiplication of one column vector by a constant $k$ corresponds to scaling one side of the parallelepiped by $k$. This increases the volume of the parallelepiped, equal to the magnitude of the determinant, by the same factor (see Figure 14.5).\(^6\)

3. If any two rows or columns of a square matrix are identical, the determinant

Figure 14.5: Interpreted geometrically, multiplying one column by a constant $k$ increases the length of one side of the parallelepiped, and its volume, by the same constant $k$. The difference in volume is shaded blue.

5 Consider a matrix $A$

\[
A = \begin{pmatrix}
a & b & c \\
d & e & f \\
g & h & i \\
\end{pmatrix}
\]

By changing the rows of the matrix to columns, we create the matrix transpose $A^T$ as

\[
A^T = \begin{pmatrix}
a & d & g \\
b & e & h \\
c & f & i \\
\end{pmatrix}
\]

In compact notation we write $[A^T]_{ij} = [A]_{ji}$.

6 Note that if each element of an $n \times n$ determinant is multiplied by a constant $k$, then the determinant is multiplied by $k^n$.

Figure 14.6: Interpreted geometrically, when two columns of the matrix are identical the three-dimensional parallelepiped is reduced to a two-dimensional parallelogram of zero volume.
is zero. Consider the determinant with two identical columns

$$|B| = \begin{vmatrix} a & b & a \\ d & e & d \\ g & h & g \end{vmatrix} = a(eh - dh) - b(dg - dg) + a(dh - eg) = 0$$

where the first term is equal in magnitude and opposite in sign to the third term, and the second term is zero. Geometrically, this corresponds to a parallelepiped of zero volume (see Figure 14.6).

4. If two rows or columns of a matrix $A$ are interchanged to form a matrix $B$, the sign of the determinant changes. Consider that

$$|B| = \begin{vmatrix} a & c & b \\ d & f & e \\ g & i & h \end{vmatrix} = a(fh - ei) - c(dh - eg) + b(di - fg) = -|A|$$

where relative to the standard determinant $|A|$ each of the three terms has the sign reversed.

5. If one row or column is added to or subtracted from another row or column the determinant is unchanged. Consider the matrix $B$ formed from matrix $A$ by adding the first column to the second column

$$|B| = \begin{vmatrix} a & b+a & c \\ d & e+d & f \\ g & h+g & i \end{vmatrix} = a((e+d)i - f(h+g)) - (b+a)(di - fg) + c(d(h+g) - (e+d)g) = |A|$$

where the six terms involving a red coefficient sum to zero. Geometrically, this corresponds to a transformed parallelepiped of equal volume (see Figure 14.7).

Let’s practice computing determinants while exploring a number of square matrices that commonly occur in the physical sciences.

14.1.5 Applications to determinants of common square matrices

Consider the set of $2 \times 2$ complex matrices known as the Pauli matrices$^7$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We can compute the determinant of each matrix as

$$|\sigma_x| = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} = |\sigma_y| = \begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix} = |\sigma_z| = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} = -1$$

Now consider another set of $2 \times 2$ square matrices known as quaternions$^8$

$$U = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad I = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \quad J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad K = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$$

Figure 14.7: Interpreted geometrically, when the elements of one column of the matrix are added to the corresponding elements of another column the volume of the parallelepiped, and the determinant of the matrix, is unchanged. The volume shaded red is equal to the volume shaded blue.

$^7$ Named for Austrian physicist Wolfgang Pauli (1900-1958) who discovered the law of nature known as the Pauli exclusion principle.

$^8$ Quaternions were discovered by Irish mathematician, astronomer and physicist William Rowan Hamilton (1805-1865).
that are related to the Pauli matrices as $I = i\sigma_z$, $J = i\sigma_y$, and $K = i\sigma_x$. The matrix determinants of the quaternions are

$$|U| = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = |I| = \begin{vmatrix} i & 0 \\ 0 & -i \end{vmatrix} = |J| = \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} = |K| = \begin{vmatrix} 0 & i \\ i & 0 \end{vmatrix} = 1$$

Quaternions have a variety of interesting properties and can be used to model rotations in three dimensional space.

Another group of matrices commonly employed in the physical sciences are the rotation matrices. In two dimensions the rotation matrix is defined

$$R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$$

for counter-clockwise rotation through an angle $\theta$ in the $xy$-plane. Note that the elements of the matrix are functions of the variable $\theta$ making the matrix itself a matrix function of $\theta$. For example, depending on the specific value of $\theta$ the rotation matrix can take on a variety of values including

$$R(0) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad R\left(\frac{\pi}{2}\right) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \quad R\left(\frac{3\pi}{2}\right) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

This matrix has interesting properties that we will explore in the context of the rotation of vectors in a plane. For now we compute the determinant of $R(\theta)$ as

$$|R(\theta)| = \begin{vmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{vmatrix} = \cos^2 \theta + \sin^2 \theta = 1$$

a result that is independent of the value of $\theta$ as shown in Figure 14.8.

In this section, we have defined the matrix as a higher dimensional generalization of the concept of the vector. The determinant provides us with insight into the nature of the underlying matrix. In the next section, we explore the rules for adding, subtracting, multiplying and dividing matrices.

### 14.2 Basic properties of matrix algebra

Systems of linear equations may be compactly expressed using matrices. Matrices have an algebra all their own, and may be added, subtracted, multiplied and divided. They may also be real or complex. Some properties of matrix algebra are shared by scalars, while other properties are distinctly different. This section explores the fundamental properties of matrix algebra.

#### 14.2.1 Addition and subtraction of matrices

Recall the rules for adding and subtracting vectors. Two vectors $a$ and $b$ can be added to form a new vector $c$ by adding each of the components as

$$c = a + b = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} + \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} = \begin{pmatrix} a_x + b_x \\ a_y + b_y \\ a_z + b_z \end{pmatrix} = \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix}$$

In a similar way we can add two $2 \times 2$ matrices $A$ and $B$ to form a new $2 \times 2$ matrix $C$ as

$$C = A + B = [A]_{ij} + [B]_{ij}.$$
In compact notation we write
\[
C_{ij} = A_{ij} - B_{ij}
\]
where specific elements involved in the operation are highlighted in red. This process can be generalized to higher order \(m \times n\) matrices. For example, we can subtract one \(3 \times 2\) matrix from another \(3 \times 2\) matrix as

\[
C = A - B = \begin{pmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22} \\
a_{31} & a_{32}
\end{pmatrix} - \begin{pmatrix}
b_{11} & b_{12} \\
b_{21} & b_{22} \\
b_{31} & b_{32}
\end{pmatrix} = \begin{pmatrix}
c_{11} & c_{12} \\
c_{21} & c_{22}
\end{pmatrix}
\]

For a specific example of addition and subtraction of matrices, consider the addition of two \(2 \times 3\) matrices

\[
A + B = \begin{pmatrix}
-3 & 6 & 4 \\
1 & 0 & 2
\end{pmatrix} + \begin{pmatrix}
2 & 1 & 1 \\
-6 & 4 & 3
\end{pmatrix} = \begin{pmatrix}
-1 & 7 & 5 \\
-5 & 4 & 5
\end{pmatrix}
\]

Note that in adding and subtracting matrices the two matrices must have the same order.

If we multiply or divide a matrix by a constant, we multiply or divide each of the elements of that matrix by the same constant. For example

\[
cA = \begin{pmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22} \\
a_{31} & a_{32}
\end{pmatrix} = \begin{pmatrix}
c_{a_{11}} & c_{a_{12}} \\
c_{a_{21}} & c_{a_{22}} \\
c_{a_{31}} & c_{a_{32}}
\end{pmatrix}
\]

This property along with the rules for addition and subtraction allow us to form linear equations involving matrices, such as \(A\) and \(B\), just as we have formed linear equations involving constants such as \(a\) and \(b\). Consider the equation

\[
C = 3A - 2B = 3 \begin{pmatrix}
-3 & 6 & 4 \\
1 & 0 & 2
\end{pmatrix} - 2 \begin{pmatrix}
-1 & 7 & 5 \\
-5 & 4 & 5
\end{pmatrix} = \begin{pmatrix}
-7 & 4 & 2 \\
13 & -8 & -4
\end{pmatrix}
\]

These examples demonstrate how the rules of addition and subtraction of scalars and vectors can be extended to the addition and subtraction of matrices and scaling of vectors.

### 14.2.2 Multiplication of matrices

The rule for multiplying two matrices is similar to the rule for multiplying two vectors using the dot product. Consider the dot product between two vectors \(a\) and \(b\) that we express

\[
a \cdot b = \begin{pmatrix}
a_x \\
a_y \\
a_z
\end{pmatrix} \begin{pmatrix}
b_x \\
b_y \\
b_z
\end{pmatrix} = a_x b_x + a_y b_y + a_z b_z
\]
Note that while the vector \( \mathbf{b} \) is standing straight, the vector \( \mathbf{a} \) is laying on its side. Recall the relationship between a \( 2 \times 2 \) matrix \( \mathbf{A} \) and its transpose \( \mathbf{A}^T \) written\(^{12}\)

\[
\mathbf{A} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad \mathbf{A}^T = \begin{pmatrix} a & c \\ b & d \end{pmatrix}
\]

The \( 3 \times 1 \) matrix \( \mathbf{A} \) and its transpose \( \mathbf{A}^T \) can be written

\[
\mathbf{A} = \begin{pmatrix} a \\ d \\ g \end{pmatrix} \quad \mathbf{A}^T = \begin{pmatrix} a & d & g \end{pmatrix}
\]

So we see that we can multiply two \( 3 \times 1 \) matrices just as we multiply two vectors using the dot product

\[
\mathbf{C} = \mathbf{A}^T \mathbf{B} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ b_{11} & b_{12} & b_{13} \end{pmatrix} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}
\]

Now consider multiplying two \( 2 \times 2 \) matrices \( \mathbf{A} \) and \( \mathbf{B} \) to form a third \( 2 \times 2 \) matrix \( \mathbf{C} \) as\(^{14}\)

\[
\mathbf{C} = \mathbf{A} \mathbf{B} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}
\]

The multiplication of a particular row and column, and the resulting product matrix element, are highlighted in red, demonstrating that matrix multiplication is a series of vector multiplications.

This approach is readily generalized to the multiplication of a matrix of order \( m \times k \) by a matrix of order \( k \times n \) to form a matrix of order \( m \times n \). Consider the example of a \( 2 \times 3 \) matrix multiplying a \( 3 \times 4 \) matrix to yield a \( 2 \times 4 \) matrix

\[
\mathbf{C} = \mathbf{A} \mathbf{B} = \begin{pmatrix} -4 & 3 & 1 \\ 0 & -2 & 1 \end{pmatrix} \begin{pmatrix} 2 & 1 & -1 & 0 \\ 4 & -2 & 1 & -1 \\ -3 & 0 & 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 & -10 & 9 & -2 \\ -11 & 4 & 0 & 3 \end{pmatrix}
\]

Note that the product \( \mathbf{B} \mathbf{A} \) is not possible using the rules of matrix multiplication.

Let’s compare the basic properties of matrix multiplication with the familiar properties of scalar multiplication. The multiplication of scalars has the \textit{associative property} defined

\[ a(bc) = (ab)c \]

The same associative property is true for matrices where

\[ \mathbf{A} (\mathbf{B} \mathbf{C}) = (\mathbf{A} \mathbf{B}) \mathbf{C} \quad (14.6) \]

As in scalar multiplication, multiplying a matrix \( \mathbf{A} \) times itself is squaring the matrix so that

\[ \mathbf{A} \mathbf{A} = \mathbf{A}^2 \quad (14.7) \]

In general, we can raise a matrix to arbitrary powers as \( \mathbf{A}^n \).
The multiplication of scalars has the *distributive property* defined
\[ a(b + c) = ab + ac \]
The same distributive property is true for matrices where
\[ A(B + C) = AB + AC \]
as well as
\[ (A + B)C = AC + BC \]
This is where the similarity between scalar and matrix multiplication ends.

The multiplication of scalars has the *commutative property* defined
\[ ab = ba \]
which can also be expressed in terms of the *commutator* defined
\[ [a, b] = ab - ba = 0 \]

Matrix multiplication does not share this general commutative property. Earlier we multiplied the \( 2 \times 2 \) matrices \( A \) and \( B \) to find \( C = AB \). Reversing the order of multiplication we find
\[
D = BA = \begin{pmatrix}
    b_{11} & b_{12} \\
    b_{21} & b_{22}
\end{pmatrix}
\begin{pmatrix}
    a_{11} & a_{12} \\
    a_{21} & a_{22}
\end{pmatrix}
= \begin{pmatrix}
    b_{11}a_{11} + b_{12}a_{21} & b_{11}a_{12} + b_{12}a_{22} \\
    b_{21}a_{11} + b_{22}a_{21} & b_{21}a_{12} + b_{22}a_{22}
\end{pmatrix}
= \begin{pmatrix}
    d_{11} & d_{12} \\
    d_{21} & d_{22}
\end{pmatrix}
\]
Comparing the elements of the resulting matrices \( C \) and \( D \), it is clear that in general \( C \neq D \) and the commutator
\[ [A, B] = AB - BA \neq 0 \]
where \( O \) is the *zero matrix* for which all elements are zero. For example, consider the \( 2 \times 2 \) matrices
\[ A = \begin{pmatrix}
    0 & 2 \\
    1 & 0
\end{pmatrix} \quad B = \begin{pmatrix}
    3 & 0 \\
    0 & -1
\end{pmatrix} \]
where
\[ AB = \begin{pmatrix}
    0 & 2 \\
    1 & 0
\end{pmatrix}
\begin{pmatrix}
    3 & 0 \\
    0 & -1
\end{pmatrix}
= \begin{pmatrix}
    0 & -2 \\
    3 & 0
\end{pmatrix} \]
while
\[ BA = \begin{pmatrix}
    3 & 0 \\
    0 & -1
\end{pmatrix}
\begin{pmatrix}
    0 & 2 \\
    1 & 0
\end{pmatrix}
= \begin{pmatrix}
    0 & 6 \\
    -1 & 0
\end{pmatrix} \]
so that
\[ [A, B] = AB - BA = \begin{pmatrix}
    0 & -2 \\
    3 & 0
\end{pmatrix} - \begin{pmatrix}
    0 & 6 \\
    -1 & 0
\end{pmatrix}
= \begin{pmatrix}
    0 & -8 \\
    4 & 0
\end{pmatrix} \neq O \]
Since \( [A, B] \neq O \), the matrices \( A \) and \( B \) do not commute.

Another property of matrix multiplication that differs from the multiplication of scalars is uncovered by the following example. For scalars, the equation
\[ ab = 0 \]
is only satisfied when \( a \) or \( b \) are equal to zero. For matrix multiplication we can
satisfy the equivalent relation

\[ AB = O \]  \hspace{1cm} (14.10)

even when neither \( A \) or \( B \) are the zero matrix. For example, consider

\[
\begin{pmatrix}
1 & 1 & 1 \\
3 & 0 & -1 \\
-1 & -1 & 2
\end{pmatrix}
\begin{pmatrix}
-3 & 0 & -1 \\
1 & 4 & 0 \\
1 & 1 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix} = O
\]

14.2.3 Survey of matrix multiplication

Let’s look at an example of multiplying two 3×3 matrices

\[
A = \begin{pmatrix}
1 & 2 & 1 \\
3 & 0 & -1 \\
-1 & -1 & 2
\end{pmatrix} \quad B = \begin{pmatrix}
-3 & 0 & -1 \\
1 & 4 & 0 \\
1 & 1 & 1
\end{pmatrix}
\]

as

\[
AB = \begin{pmatrix}
1 & 2 & 1 \\
3 & 0 & -1 \\
-1 & -1 & 2
\end{pmatrix}
\begin{pmatrix}
-3 & 0 & -1 \\
1 & 4 & 0 \\
1 & 1 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
-3 + 2 + 1 & 0 + 8 + 1 & -1 + 0 + 1 \\
-9 + 0 - 1 & 0 + 0 - 1 & -3 + 0 - 1 \\
3 - 1 + 2 & 0 - 4 + 2 & 1 + 0 + 2
\end{pmatrix}
= \begin{pmatrix}
0 & 9 & 0 \\
-10 & -1 & -4 \\
4 & -2 & 3
\end{pmatrix}
\]

We have tracked the center 1×3 row vector in \( A \) and center 3×1 column vector in \( B \) to show how they are multiplied as a dot product to form the central element of the resulting matrix. Let’s explore the properties of matrix multiplication for three special classes of matrices.

Identity matrices

Now consider the identity matrix in which all diagonal elements are unity and all off-diagonal elements are zero

\[
I = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

The identity matrix derives its name from the fact that any matrix \( A \) multiplied by the identity matrix \( I \) equals the original matrix as

\[
AI = \begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\]

and

\[
IA = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\]

\[
= \begin{pmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{pmatrix}
\]

The identity matrix commutes with all matrices. The geometric interpretation of the determinant of the identity matrix is shown in Figure 14.9.

Block matrices

First consider a square block matrix that can be divided into blocks of largely
non-zero elements and blocks in which all elements are zero. For example

\[
A = \begin{pmatrix}
-2 & 1 & 0 & 0 \\
6 & 5 & 0 & 0 \\
0 & 0 & 9 & 2 \\
0 & 0 & 1 & 4 \\
\end{pmatrix}
\]

\[
B = \begin{pmatrix}
1 & 3 & 0 & 0 \\
6 & -2 & 0 & 0 \\
0 & 0 & 4 & 1 \\
0 & 0 & 9 & -2 \\
\end{pmatrix}
\]

In the product matrix \(AB\) the only non-zero elements will be those that are non-zero in the block matrices. The non-zero elements may be efficiently found by multiplying the two upper submatrices

\[
\begin{pmatrix}
-2 & 1 \\
6 & 5 \\
\end{pmatrix}
\begin{pmatrix}
1 & 3 \\
6 & -2 \\
\end{pmatrix} = \begin{pmatrix}
4 & -8 \\
36 & 8 \\
\end{pmatrix}
\]

and two lower submatrices

\[
\begin{pmatrix}
9 & 2 \\
1 & 4 \\
\end{pmatrix}
\begin{pmatrix}
4 & 1 \\
9 & -2 \\
\end{pmatrix} = \begin{pmatrix}
54 & 5 \\
40 & -7 \\
\end{pmatrix}
\]

The resulting products of submatrices can be combined to form the product matrix

\[
AB = \begin{pmatrix}
-2 & 1 & 0 & 0 \\
6 & 5 & 0 & 0 \\
0 & 0 & 9 & 2 \\
0 & 0 & 1 & 4 \\
\end{pmatrix}
\begin{pmatrix}
1 & 3 & 0 & 0 \\
6 & -2 & 0 & 0 \\
0 & 0 & 4 & 1 \\
0 & 0 & 9 & -2 \\
\end{pmatrix} = \begin{pmatrix}
4 & -8 & 0 & 0 \\
36 & 8 & 0 & 0 \\
0 & 0 & 54 & 5 \\
0 & 0 & 40 & -7 \\
\end{pmatrix}
\]

This efficiency can be extended to block matrices that are not square, as long as the submatrix products are defined by the normal rules for matrix multiplication.

**Orthogonal matrices**

Finally, let’s explore the properties of **orthogonal matrices** in which each column of the matrix, viewed as a vector, is orthogonal to every other column in the matrix. For example, consider the rotation matrix

\[
R(\theta) = \begin{pmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta \\
\end{pmatrix}
\]

which we can view as being composed of two vectors

\[
a = \begin{pmatrix}
\cos \theta \\
\sin \theta \\
\end{pmatrix}
\]

\[
b = \begin{pmatrix}
-\sin \theta \\
\cos \theta \\
\end{pmatrix}
\]

If we take the dot product of the two vectors we see that

\[
a \cdot b = \begin{pmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta \\
\end{pmatrix} = -\cos \theta \sin \theta + \sin \theta \cos \theta = 0
\]

so that the vectors \(a\) and \(b\) are orthogonal. In addition, we find

\[
a \cdot a = \begin{pmatrix}
\cos \theta & \sin \theta \\
\sin \theta & \cos \theta \\
\end{pmatrix} = \cos^2 \theta + \sin^2 \theta = 1
\]

and

\[
b \cdot b = \begin{pmatrix}
-\sin \theta & \cos \theta \\
-\sin \theta & \cos \theta \\
\end{pmatrix} = \sin^2 \theta + \cos^2 \theta = 1
\]
so that the vectors \( a \) and \( b \) are normalized.

As the vectors \( a \) and \( b \) are mutually orthogonal and individually normalized they are orthonormal vectors (see Chapter 4). It follows that the matrix \( R(\theta) \) multiplied by its transpose leads to the identity matrix as

\[
R(\theta)^T R(\theta) = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I
\]

and

\[
R(\theta) R(\theta)^T = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I
\]

In fact, an orthonormal matrix times its transpose is always the identity matrix.

Given that \( R(\theta)^T R(\theta) = R(\theta) R(\theta)^T = I \), it follows that the commutator

\[
\left[ R(\theta)^T, R(\theta) \right] = R(\theta)^T R(\theta) - R(\theta) R(\theta)^T = I - I = 0
\]

so that the orthogonal matrices \( R(\theta) \) and \( R(\theta)^T \) commute.

Consider one more example involving the matrix

\[
A = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

We can demonstrate that \( A \) is an orthogonal matrix since

\[
\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 1 & \frac{1}{2} + \frac{1}{2} = 1 \\ \frac{1}{2} - \frac{1}{2} = 0 \end{pmatrix}
\]

and

\[
\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} - \frac{1}{2} = 0 \\ \frac{1}{2} + \frac{1}{2} = 1 \end{pmatrix}
\]

As expected for an orthogonal matrix we find that

\[
A^T A = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

and

\[
A A^T = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

The geometric interpretation of the determinant of the orthogonal matrix \( A \) is shown in Figure 14.10. This is a special case of the general observation that the determinant \(|A|\) of the \( 2 \times 2 \) matrix \( A \) is the area of a parallelogram (see Figure 14.3). Orthogonal vectors form a right angle. In addition, the vectors are normalized. As such, the determinant is the area of a unit square. Orthogonal matrices commonly arise in problems in the physical sciences including quantum theory and the vibrational dynamics of molecules.
14.2.4 Matrix division and the inverse matrix

In considering the division of scalars we recognize that
\[
\frac{1}{a} = a a^{-1} = 1
\]
where we say that \(a^{-1}\) is the inverse of \(a\) and the product of a scalar and its inverse is unity. For matrices the equivalent expression is
\[
AA^{-1} = I
\]
where \(I\) is the identity matrix and \(A^{-1}\) is known as the matrix inverse of \(A\).

While it is a simple matter to determine the inverse of a scalar \(a\), as long as \(a \neq 0\), finding the inverse of a matrix takes more effort. Fortunately, as long as the matrix \(A\) is non-singular meaning that \(|A| \neq 0\) there is a systematic method for determining the matrix inverse, \(A^{-1}\).

Recall the definition of a matrix \(A\) and its transpose \(A^T\)
\[
A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \quad A^T = \begin{pmatrix} a_{11} & a_{21} \\ a_{12} & a_{22} \end{pmatrix}
\]

Further recall that the cofactor of a matrix \(A\), written \(A_{ij}\), is the determinant of an \((n-1) \times (n-1)\) square matrix, formed by deleting the \(i\)th row and \(j\)th column of \(A\), multiplied by \((-1)^{i+j}\). We can define the cofactor matrix as
\[
A_{\text{cof}} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}
\]
where each element is the corresponding matrix cofactor, \(A_{ij}\). It can be shown that the inverse of a non-singular matrix \(A\), for which the determinant \(|A| \neq 0\), can be written
\[
A^{-1} = \frac{1}{|A|} A_{\text{cof}}^T
\]
where \(A_{\text{cof}}^T\) is the transpose of the cofactor matrix. Geometrically, the magnitude of the determinant of the matrix \(A\) and that of its inverse matrix \(A^{-1}\) are related by \(|A^{-1}| = |A|^{-1}\) (see Figure 14.11).
Let’s use this definition to determine the inverse of the matrix

\[ A = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \]

for which the determinant is

\[ |A| = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = 4 - 6 = -2 \]

The matrix cofactors are \( A_{11} = 4, A_{21} = -2, A_{12} = -3, \) and \( A_{22} = 1. \) As such, the cofactor matrix is

\[ A_{\text{cof}} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = \begin{pmatrix} 4 & -3 \\ -2 & 1 \end{pmatrix} \]

Taking the transpose of the cofactor matrix and dividing by the determinant leads to the final result

\[ A^{-1} = \frac{1}{|A|} A_{\text{cof}} = \frac{1}{-2} \begin{pmatrix} 4 & -3 \\ -2 & 1 \end{pmatrix} = \begin{pmatrix} -2 & 3 \\ 2 & -1 \end{pmatrix} \]

We can validate our solution by determining the product of the matrix \( A \) and its inverse matrix \( A^{-1} \) as

\[ AA^{-1} = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} -2 & 3 \\ 2 & -1 \end{pmatrix} = \begin{pmatrix} -2 + 3 & 1 - 1 \\ -6 + 6 & 3 - 2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I \]

as well as

\[ A^{-1}A = \begin{pmatrix} -2 & 3 \\ 2 & -1 \end{pmatrix} \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} = \begin{pmatrix} -2 + 3 & -4 + 4 \\ 3 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I \]

Given that \( A^{-1}A = AA^{-1} = I, \) it follows that the commutator

\[ [A^{-1}, A] = A^{-1}A - AA^{-1} = I - I = O \]

so that a matrix \( A \) and its matrix inverse \( A^{-1} \) always commute.

This approach to finding the matrix inverse is generally applicable to any \( n \times n \) non-singular square matrix. We will find that determining the matrix inverse has great utility in solving algebraic equations involving matrices that commonly arise in the physical sciences.

### 14.2.5 Multiplication of matrices by vectors

By the rules of matrix algebra the multiplication of a matrix of order \( m \times k \) by a matrix of order \( k \times n \) results in a matrix of order \( m \times n \). For example, consider the multiplication of a \( 2 \times 3 \) matrix \( A \) and a \( 3 \times 2 \) matrix \( B \) as

\[ AB = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \\ b_{31} & b_{32} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31} & a_{11}b_{12} + a_{12}b_{22} + a_{13}b_{32} \\ a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31} & a_{21}b_{12} + a_{22}b_{22} + a_{23}b_{32} \end{pmatrix} \]

which results in a third matrix of order \( 2 \times 2 \).

A special case of multiplication of matrices of differing order involves the
multiplication of a square matrix by a row or column vector such as

\[
AB = \begin{pmatrix}
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
  b_{11} \\
  b_{21} \\
  b_{31}
\end{pmatrix}
= \begin{pmatrix}
  a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31} \\
  a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31} \\
  a_{31}b_{11} + a_{32}b_{21} + a_{33}b_{31}
\end{pmatrix}
= \begin{pmatrix}
  c_{11} \\
  c_{21} \\
  c_{31}
\end{pmatrix} = C
\]

where a \(3 \times 3\) matrix \(A\) is multiplied by a \(3 \times 1\) column vector \(B\) to yield a new \(3 \times 1\) column vector \(C\). Similarly, multiplying a \(1 \times 2\) row vector \(D\) by a \(2 \times 2\) square matrix \(E\) results in a \(1 \times 2\) row vector \(F\) as

\[
DE = \begin{pmatrix}
  d_{11} & d_{12}
\end{pmatrix}
\begin{pmatrix}
  e_{11} \\
  e_{21}
\end{pmatrix}
= \begin{pmatrix}
  d_{11}e_{11} + d_{12}e_{21} \\
  d_{11}e_{12} + d_{12}e_{22}
\end{pmatrix} = \begin{pmatrix}
  f_{11} \\
  f_{12}
\end{pmatrix} = F
\]

Let’s practice multiplying matrices by vectors while exploring the properties of rotation matrices in two and three dimensions. Recall the \(2 \times 2\) rotation matrix

\[
R(\theta) = \begin{pmatrix}
  \cos \theta & -\sin \theta \\
  \sin \theta & \cos \theta
\end{pmatrix}
\]

Now consider \(R(\theta)\) multiplied by a vector \(x_1\) in two-dimensional cartesian space as

\[
R(\theta)x_1 = x_2
\]

The rotation matrix acts as a matrix operator by transforming vector \(x_1\) into a new vector \(x_2\) by a counter-clockwise rotation in space through an angle \(\theta\). For example, suppose \(x_1\) is aligned along the \(x\)-axis and \(\theta = \frac{\pi}{2}\) then

\[
R\left(\frac{\pi}{2}\right)x_1 = \begin{pmatrix}
  0 & -1 \\
  1 & 0
\end{pmatrix}
\begin{pmatrix}
  1 \\
  0
\end{pmatrix}
= \begin{pmatrix}
  0 \\
  1
\end{pmatrix} = x_2
\]

The rotation matrix acts to rotate vector \(x_1\), aligned along the positive \(x\)-axis, counter-clockwise through an angle \(\theta = \frac{\pi}{2}\) to form \(x_2\), aligned along the positive \(y\)-axis (see Figure 14.12).

Now suppose \(R(\theta)\) acts on \(x_2\), aligned along the positive \(y\)-axis, with \(\theta = \pi\). The result is

\[
R(\pi)x_2 = \begin{pmatrix}
  -1 & 0 \\
  0 & -1
\end{pmatrix}
\begin{pmatrix}
  0 \\
  1
\end{pmatrix}
= \begin{pmatrix}
  0 \\
  -1
\end{pmatrix} = x_3
\]

where the rotation matrix acts to rotate \(x_2\), aligned with the positive \(y\)-axis, counter-clockwise through an angle \(\theta = \pi\) to form \(x_3\), aligned with the negative \(y\)-axis.

Now consider the extension of the rotation matrix in two dimensions to three dimensions. In two dimensions, we rotate about a single axis. In three dimensions, three matrices are required for rotation about the \(x\), \(y\), or \(z\) axes. Consider the matrix for counter-clockwise rotation about the positive \(x\)-axis

\[
R_x(\theta) = \begin{pmatrix}
  1 & 0 & 0 \\
  0 & \cos \theta & -\sin \theta \\
  0 & \sin \theta & \cos \theta
\end{pmatrix}
\]

Note that the terms in red mark the components of the two-dimensional rota-
A symmetric matrix satisfies the equality 
\[ A_{ij} = A_{ji}. \]

The unit element acts to maintain the current value of \( x \) while the red terms act to rotate the vector in the \( yz \)-plane.

Suppose \( x_1 \) is aligned along the positive \( z \)-axis and \( \theta = \pi \) then

\[
R_x(\theta)x_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} = x_2
\]

where the rotation matrix acts to rotate \( x_1 \), aligned with the positive \( z \)-axis, through an angle \( \theta = \pi \) to form \( x_2 \), aligned with the negative \( z \)-axis.

### 14.2.6 Applications involving complex matrices

Until now we have largely considered matrices for which the elements are real. However, as we found in the case of Pauli matrices and quaternions we can also form matrices where the elements are imaginary or complex. In fact, matrices with complex elements are common in the physical sciences and complex matrices have many useful properties.

For a complex number \( z = x + iy \) the absolute value is

\[
|z| = \sqrt{z \bar{z}} = \sqrt{(x - iy)(x + iy)} = \sqrt{x^2 + y^2}
\]

where \( z^* = x - iy \) is the complex conjugate of \( z \). This result led to

\[
|z|^2 = z^*z = x^2 + y^2 = r^2 = re^{-i\theta}re^{i\theta}
\]

where \( z = re^{i\theta} \) and \( z^* = re^{-i\theta} \). We think of \( |z| \) as the magnitude of the complex number \( z \).

Recall that for a vector \( a \) the absolute value \( |a| \) is defined in terms of the dot product

\[
|a|^2 = a \cdot a
\]

where \( |a| \) is the magnitude. If we have a complex column vector \( c \) we can define the absolute value of \( c \) by combining the concepts of the complex conjugate and the vector magnitude as

\[
|c|^2 = c^*c = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = a^*a + b^*b
\]

where the result is a real scalar.

Consider the example of the complex vector

\[
c = \begin{pmatrix} c_{11} \\ c_{21} \\ c_{31} \end{pmatrix} = \begin{pmatrix} 2i \\ 4 \\ 2 + i \end{pmatrix}
\]

for which the absolute value \( |c| \) is defined in terms of

\[
|c|^2 = c^*c = \begin{pmatrix} -2i & 4 & 2 - i \end{pmatrix} \begin{pmatrix} 2i \\ 4 \\ 2 + i \end{pmatrix}
\]

\[
= (-2i)(2i) + (4)(4) + (2 - i)(2 + i)
\]

\[
= 4 + 16 + (4 + 1) = 25
\]

As such the absolute value and magnitude \( |c| = \sqrt{|c|^2} = \sqrt{25} = 5 \).

For real matrices, a symmetric matrix is equal to its matrix transpose\(^\text{16}\)
For a complex matrix there is a corresponding property relating a matrix $C$ and its complex conjugate $C^∗$. When a matrix $C$ is equal to the transpose of its complex conjugate as

$$C = (C^∗)^T$$

we say that $C$ is a hermitian matrix. The matrix $(C^∗)^T$ is called the hermitian conjugate of $C$ just as $z^∗$ is referred to as the complex conjugate of $z$. Hermitian matrices are common in the physical sciences and a simplified notation has been developed to express them

$$C^\dagger = (C^∗)^T$$

so that we can write

$$C^\dagger C = (C^∗)^T C$$

When a matrix $D$ is both hermitian and orthogonal it is called a unitary matrix. In that case, the matrix has the property that

$$D^\dagger D = D D^\dagger = I$$

As we found for real orthogonal matrices, the unitary matrix is composed of columns having the properties of orthonormal vectors, namely that they are mutually orthogonal and individually normalized.

Consider the complex matrix

$$E = \frac{1}{5} \begin{pmatrix} -1 + 2i & -4 - 2i \\ -2 - 4i & -2 - i \end{pmatrix}$$

We can demonstrate that $E$ is a unitary matrix by proving that the set of column vectors composing the matrix has the properties of a set of orthonormal vectors, namely normalization

$$\frac{1}{5^2} \begin{pmatrix} -1 - 2i & 2 + 4i \\ -4 + 2i & -2 + i \end{pmatrix} \begin{pmatrix} -1 + 2i \\ 2 - 4i \end{pmatrix} = \frac{1}{25} [(1 + 4) + (4 + 16)] = 1$$

$$\frac{1}{5^2} \begin{pmatrix} -1 - 2i & 2 + 4i \\ -4 + 2i & -2 + i \end{pmatrix} \begin{pmatrix} -4 - 2i \\ -2 - i \end{pmatrix} = \frac{1}{25} [(16 + 4) + (4 + 1)] = 1$$

and mutual orthogonality

$$\frac{1}{5^2} \begin{pmatrix} -1 - 2i & 2 + 4i \\ -4 + 2i & -2 + i \end{pmatrix} \begin{pmatrix} -4 - 2i \\ -2 - i \end{pmatrix} = \frac{1}{25} [(4 - 4) + (-4 + 4)] = 0$$

$$\frac{1}{5^2} \begin{pmatrix} -1 - 2i & 2 + 4i \\ -4 + 2i & -2 + i \end{pmatrix} \begin{pmatrix} -1 + 2i \\ 2 - 4i \end{pmatrix} = \frac{1}{25} [(4 - 4) + (-4 + 4)] = 0$$

Furthermore, as expected for a unitary matrix we find that the product of the matrix, $E$, and its hermitian conjugate, $(E^\dagger)^T$, in any order results in the identity matrix as

$$(E^\dagger)^T E = \frac{1}{5^2} \begin{pmatrix} -1 + 2i & -4 - 2i \\ -2 - 4i & -2 - i \end{pmatrix} \begin{pmatrix} -1 - 2i \\ 2 - 4i \end{pmatrix} \begin{pmatrix} -4 + 2i \\ 2 + 4i \end{pmatrix} \begin{pmatrix} -1 - 2i & 2 + 4i \\ -4 + 2i & -2 + i \end{pmatrix}$$

$$= \frac{1}{25} \begin{pmatrix} (1 + 4) + (16 + 4) & (-2 - 8) + (8 + 2) \\ (-2 - 8) + (8 + 2) & (4 + 16) + (4 + 1) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$
and
\[
E(E^*)^T = \frac{1}{52} \begin{pmatrix}
-1 - 2i & 2 + 4i \\
-4 + 2i & -2 + i
\end{pmatrix}
\begin{pmatrix}
-1 + 2i & -4 - 2i \\
2 - 4i & -2 - i
\end{pmatrix}
= \frac{1}{25} \begin{pmatrix}
(1 + 4) + (4 + 16) & (4 - 4) + (-4 + 4) \\
(4 - 4) + (-4 + 4) & (16 + 4) + (4 + 1)
\end{pmatrix}
= \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\]

This example demonstrates how the properties of real orthogonal matrices can be generalized to the case of complex matrices.

14.3 Solving coupled linear equations using Cramer’s rule

Our study of linear algebra began with the solution of two coupled linear equations and led to the definition of the determinant. We return to the topic to apply our methods of matrix algebra to the general solution of systems of linear equations. We will develop a general method for solving for an arbitrary number of independent linear equations with the same number of unknown variables.

14.3.1 Solving coupled linear equations using determinants

We found that determinants naturally appear in the process of solving coupled linear equations. Let’s reconsider Equation 14.2 consisting of two equations with two unknown variables \(x\) and \(y\)

\[
\begin{align*}
a_{11}x + a_{12}y &= d_1 \\
a_{21}x + a_{22}y &= d_2
\end{align*}
\]

Now consider the determinant
\[
\mathcal{D} = \begin{vmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}
\]

We know that if we multiply a column of the matrix by a constant, \(x\), the determinant of the new matrix will be
\[
\begin{vmatrix}
a_{11}x & a_{12} \\
a_{21}x & a_{22}
\end{vmatrix} = a_{11}a_{22}x - a_{12}a_{21}x = \mathcal{D}x
\]

Furthermore, we know that if we add one column of the matrix to another the determinant is unchanged as
\[
\begin{vmatrix}
a_{11}x + a_{12}y & a_{12} \\
a_{21}x + a_{22}y & a_{22}
\end{vmatrix} = (a_{11}x + a_{12}y) a_{22} - a_{12} (a_{21}x + a_{22}y)
\]
\[
= a_{11}a_{22}x + a_{12}a_{22}y - a_{12}a_{21}x - a_{12}a_{22}y
\]
\[
= a_{11}a_{22}x - a_{12}a_{21}x = \mathcal{D}x
\]

Noting that \(a_{11}x + a_{12}y = d_1\) and \(a_{21}x + a_{22}y = d_2\) we can reform the determinant as
\[
\mathcal{D}x = \begin{vmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{vmatrix} = \begin{vmatrix}
d_1 & a_{12} \\
d_2 & a_{22}
\end{vmatrix}
\]

which can be solved for \(x\) as
\[
x = \frac{1}{\mathcal{D}} \begin{vmatrix}
d_1 & a_{12} \\
d_2 & a_{22}
\end{vmatrix} = \frac{d_1a_{22} - d_2a_{12}}{a_{11}a_{22} - a_{21}a_{12}}
Similar manipulations lead to a solution for $y$ as

$$y = \frac{1}{D} \begin{vmatrix} a_{11} & d_1 \\ a_{21} & d_2 \end{vmatrix} = \frac{d_2 a_{11} - d_1 a_{21}}{a_{11} a_{22} - a_{12} a_{21}}$$

These results agree with the previously derived expressions Equations 14.3 and 14.4. Our general solution expressed in terms of determinants is known as Cramer’s rule.\(^9\) In principle, Cramer’s rule allows us to solve an arbitrarily large system of linear equations defining the same number of unknown variables.

### 14.3.2 Generalization of Cramer’s rule to arbitrary dimension

Using our knowledge of matrix algebra and the properties of determinants, our derivation of Cramer’s rule can be generalized to $n$ coupled equations in $n$ variables. We start by generalizing the expression for our coupled equations in Equation 14.2 to an arbitrary number of variables as

$$Ax = d \quad (14.11)$$

where

$$x = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}$$

is a vector of $n$ unknown variables $x_1, x_2, \ldots, x_n$ and

$$A = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \quad (14.12)$$

is an $n \times n$ matrix of coefficients defining the $n$ linear equations represented by $Ax$. Finally, the vector

$$d = \begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_n \end{pmatrix}$$

represents the $n$ constants that complete the linear equations. The general solution for the $n$ unknown variables can be written

$$x_k = \frac{1}{|A|} |A_k| \quad (14.13)$$

where

$$A_k = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1(k-1)} & d_1 & a_{1(k+1)} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2(k-1)} & d_2 & a_{2(k+1)} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{n(k-1)} & d_n & a_{n(k+1)} & \cdots & a_{nn} \end{vmatrix} \quad (14.14)$$

is the matrix $A$ in which the $k$th column has been replaced by the vector $d$. Note that for a system of $n$ equations with $n$ unknowns, Cramer’s rule requires the evaluation of $n + 1$ determinants. As such, the application of Cramer’s rule can be costly for systems of equations where $n$ is large. In those cases, more efficient approaches can be considered. In the next section we explore a few of the many applications of Cramer’s rule.
Let's explore an application of Cramer's rule by solving the following set of coupled linear equations

\begin{align*}
3x - y &= 6 \\
x + 2y &= 5
\end{align*} \quad (14.15)

We can rewrite these equations in matrix form as

\[ Ax = \begin{pmatrix} 3 & -1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 6 \\ 5 \end{pmatrix} = d \]

Using Cramer's rule, the solution for $x$ and $y$ can be written

\[ x = \frac{1}{|A|} |A_1| = \frac{6 - 1}{3 - 1} = \frac{12 + 5}{6 + 1} = \frac{17}{7} \]

and

\[ y = \frac{1}{|A|} |A_2| = \frac{3 - 6}{3 - 1} = \frac{15 - 6}{6 + 1} = \frac{9}{7} \]

and verified by inserting in Equation 14.15 to show

\[ 3x - y = 3 \left( \frac{17}{7} \right) - \frac{9}{7} = 6 \quad x + 2y = \frac{17}{7} + 2 \left( \frac{9}{7} \right) = 5 \]

Now consider the set of equations

\begin{align*}
x + 2y + 3z &= -5 \\
3x + y - 3z &= 4 \\
-3x + 4y + 7z &= -7
\end{align*} \quad (14.16)

Each equation defines a plane in three-dimensional cartesian space. Geometrically, we seek the point in space $(x, y, z)$ representing the intersection of the three planes defined by the three independent equations of three variables (see Figure 14.13). The point of intersection is the solution to our set of coupled equations.

Figure 14.13: In three dimensions, points representing the solution to a linear equation form a plane. The point of intersection of the three planes (black dot) represents the common solution $(x, y, z)$ to the three linear equations.
variables \(x, y,\) and \(z\) defining the point of intersection of the three planes

\[
x = \frac{1}{|A|} |A_1| = \begin{vmatrix}
-5 & 2 & 3 \\
4 & 1 & -3 \\
-7 & 4 & 7 \\
\end{vmatrix} = -40 = -1
\]

\[
y = \frac{1}{|A|} |A_2| = \begin{vmatrix}
1 & -5 & 3 \\
3 & 4 & -3 \\
-3 & -7 & 7 \\
\end{vmatrix} = 40 = 1
\]

\[
z = \frac{1}{|A|} |A_3| = \begin{vmatrix}
1 & 2 & -5 \\
3 & 1 & 4 \\
-3 & 4 & -7 \\
\end{vmatrix} = -80 = -2
\]

This result can be verified by substituting into Equation 14.16 as

\[
(-1) + 2(1) + 3(-2) = -5 \\
3(-1) + (1) - 3(-2) = 4 \\
-3(-1) + 4(1) + 7(-2) = -7
\]

validating our result.

---

**A14 Applications of determinants in Hückel theory**

Matrix algebra is used in the study of Hückel theory used to estimate the electronic energy of conjugated organic molecules. In that context, we find matrix equations such as

\[
\begin{vmatrix}
\alpha - E & \beta - SE \\
\beta - SE & \alpha - E \\
\end{vmatrix} = 0
\]

where \(E\) is a variable and \(\alpha, \beta\) and \(S\) are constants. The determinant is

\[
\begin{vmatrix}
\alpha - E & \beta - SE \\
\beta - SE & \alpha - E \\
\end{vmatrix} = (\alpha - E)^2 - (\beta - SE)^2 = 0
\]

For the case \(S = 0\) this expression reduces to

\[(\alpha - E)^2 = \beta^2\]

The roots of this equation can be solved for \(E\) using the quadratic formula resulting in \(E_{\pm} = \alpha \pm \beta\).

In another example

\[
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & 0 \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E \\
\end{vmatrix} = 0
\]
Expanding the $4 \times 4$ determinant we find

$$
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 \\
\beta & \alpha - E & \beta & \beta \\
0 & \beta & \alpha - E & \beta \\
0 & 0 & \beta & \alpha - E \\
\end{vmatrix} = 0
$$

Expanding the $3 \times 3$ determinants we find

$$
\begin{vmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E \\
\end{vmatrix} - \beta^2
\begin{vmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E \\
\end{vmatrix} = 0
$$

which can be reduced to the polynomial equation in $E$

$$(\alpha - E)^4 - (\alpha - E)^2 \beta^2 - (\alpha - E)^2 \beta^2 - \beta^2 (\alpha - E)^2 + \beta^4 = 0$$

where

$$
(\alpha - E)^4 - 3 (\alpha - E)^2 \beta^2 + \beta^4 = 0
$$

Simplifying the equation by making the substitution

$$x = \left(\frac{\alpha - E}{\beta}\right)^2$$

results in

$$x^2 - 3x + 1 = 0$$

which yields the roots

$$x_\pm = \frac{3 \pm \sqrt{9 - 4}}{2} = \begin{cases} 2.62 \\ 0.38 \end{cases}$$

and the final result

$$E = \begin{cases} \alpha \pm 1.62\beta \\ \alpha \pm 0.62\beta \end{cases}$$

as $\sqrt{2.62} = 1.62$ and $\sqrt{0.38} = 0.62$. This matrix algebra can be used to study the energetics and spectroscopy of conjugated organic molecules.

---

**B.14 End-of-chapter problems**

You shouldn’t do science just to improve wealth - do science for the sake of human culture and knowledge. There must be some purpose in life that is higher than just surviving.

Gerhard Herzberg

---

**Warm-ups**

**14.1 Evaluate the following determinants**

<table>
<thead>
<tr>
<th>(a)</th>
<th>1 2 3</th>
<th>(b)</th>
<th>4 2 1</th>
<th>(c)</th>
<th>x 1 0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 0 1</td>
<td></td>
<td>-1 6 3</td>
<td></td>
<td>-1 x 1</td>
</tr>
<tr>
<td>-1 4 2</td>
<td></td>
<td>-1 5 -1</td>
<td></td>
<td>0 1 x</td>
<td></td>
</tr>
</tbody>
</table>
14.2 Solve the following determinants for $x$

(a) $\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$

(b) $\begin{vmatrix} x & -2 \\ 1 & x \end{vmatrix} = 6$

(c) $\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 2$

(d) $\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 0 & 0 \\ 1 & 0 & x & 0 \\ 1 & 0 & 0 & x \end{vmatrix} = 0$

14.3 Add the pair of matrices

$\begin{pmatrix} 0 & 1 & 2 \\ 2 & 4 & -3 \\ 6 & 3 & 5 \end{pmatrix} + \begin{pmatrix} 6 & 3 & -7 \\ -1 & 1 & -1 \\ -5 & 2 & 7 \end{pmatrix}$

14.4 Multiply the following pairs of matrices

(a) $\begin{pmatrix} 1 & 4 \\ 3 & 2 \end{pmatrix} \begin{pmatrix} 6 & -3 \\ -3 & 1 \end{pmatrix}$

(b) $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 4 & -1 \\ 2 & 3 \end{pmatrix}$

(c) $\begin{pmatrix} 4 & -1 & -1 \\ 1 & 2 & 5 \end{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ -2 & 1 & 6 \\ 3 & 4 & 5 \end{pmatrix}$

(d) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & x & 0 \\ 0 & 0 & x \end{pmatrix}$

14.5 Given the matrices

$A = \begin{pmatrix} 1 & 1 & 4 \\ 2 & -6 & 10 \\ 4 & -1 & -1 \end{pmatrix}$

$B = \begin{pmatrix} 6 & 1 & 0 \\ 4 & 2 & -1 \\ 8 & -4 & 3 \end{pmatrix}$

calculate the matrix defined by the commutator $[A, B] = AB - BA$.

14.6 Find the inverse of the following matrix

$\begin{pmatrix} 1 & 0 & -1 \\ 3 & 2 & 4 \\ -2 & 1 & 0 \end{pmatrix}$

14.7 Solve the following sets of equations using Cramer’s rule

(a) $x + y = 3$

$4x - 3y = 5$

(b) $x \sin \theta + y \cos \theta = x'$

$-x \cos \theta + y \sin \theta = y'$

Check your solutions by inserting them into the original equations.

Homework exercises

14.8 Consider the rotation matrix

$R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$

and the vector

$x_1 = \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$
Apply the rotation matrix to the following vectors $x_1$ to determine the vectors $x_2 = R(\theta)x_1$ for the stated value of $\theta$. (a) $x_1 = (1 \ 0)^T$ for $\theta = \pi$, (b) $x_1 = (0 \ 1)^T$ for $\theta = \pi/4$, (c) $x_1 = (1 \ -1)^T$ for $\theta = \pi/2$.

14.9 Prove that for

$$R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$$

the matrix product $R(\theta)R(\theta) = R^2$ equals

$$R^2 = \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ \sin 2\theta & \cos 2\theta \end{pmatrix} = R(2\theta)$$

14.10 Consider the matrix

$$A = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & 1 \\ 2 & 2 & 0 \end{pmatrix}$$

(a) Find the inverse matrix $A^{-1}$.
(b) Verify your answer by demonstrating that $A^{-1}A = AA^{-1} = I$ where $I$ is the identity matrix.

14.11 The rotation matrix in three dimensions for counter-clockwise rotation about the positive $z$-axes can be written

$$R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(a) Show that $|R| = 1$.
(b) Show that $R$ is composed of column vectors that are orthonormal.
(c) Show that $R^T = R^{-1}$ by showing that $R^TR = I$.

14.12 Consider the matrices

$$A = \begin{pmatrix} 2 & -1 \\ 1 & 2 \end{pmatrix} \quad B = \begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$$

and show that $|AB| = |BA| = |A||B|$.

14.13 An orthogonal matrix is composed of columns that form a set of orthonormal vectors that are individually normalized and mutually orthogonal. Orthogonal matrices have the property that the transpose of the matrix is also its inverse or $A^T = A^{-1}$.

Consider the matrix

$$A = \frac{1}{9} \begin{pmatrix} 1 & 8 & -4 \\ 4 & -4 & -7 \\ 8 & 1 & 4 \end{pmatrix}$$

(a) Prove orthogonality by taking each of the three column vector pairs and showing the dot product is zero.
(b) Prove normalization by showing that each column vector has a magnitude of unity.
(c) Demonstrate that the matrix transpose $A^T = A^{-1}$ by showing that $A^TA = AA^T = I$.

14.14 A real orthogonal matrix has the property that

$$A^T = A^{-1}$$

For matrices with complex elements the equivalent property is

$$(A^*)^T = A^{-1}$$
where $A^*$ is the complex conjugate of $A$, in which each element of $A^*$ is the complex conjugate of the corresponding element of $A$. A matrix satisfying this property is called a unitary matrix. Show that the complex matrix

$$A = \frac{1}{6}\begin{pmatrix} 2 - 4i & 4i \\ -4i & -2 - 4i \end{pmatrix}$$

is a unitary matrix by demonstrating that $(A^*)^T A = I$.

14.15 Show that the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are unitary matrices for which $(A^*)^T A = I$.

14.16 Solve the following sets of equations using Cramer’s rule

(a) \[ \begin{align*} x + 2y + 3z &= -5 \\ -x - 3y + z &= -14 \\ 2x + y + z &= 1 \end{align*} \]

(b) \[ \begin{align*} x + 2y - z + t &= 2 \\ x - 2y + z - 3t &= 6 \\ 2x + y + 2z + t &= -4 \\ 3x + 3y + z - 2t &= 10 \end{align*} \]

Check your solutions by inserting them into the original equations.

14.17 Consider two points $(x_1, y_1)$ and $(x_2, y_2)$ in two-dimensional cartesian coordinates. Suppose we are asked to determine the parameters $m$ and $b$ defining the equation of a line $y(x) = mx + b$ containing the two points. We can do this using Cramer’s rule.

As each point is on the line defined by $y = ax + b$ we know that

$$y_1 = mx_1 + b$$
$$y_2 = mx_2 + b$$

or that

$$-mx_1 + y_1 = b$$
$$-mx_2 + y_2 = b$$

which can be written in the matrix form $Ax = b$ as

$$Ax = \begin{pmatrix} -mx_1 & y_1 \\ -mx_2 & y_2 \end{pmatrix} = \begin{pmatrix} x_1 & y_1 \\ x_2 & y_2 \end{pmatrix} \begin{pmatrix} -m \\ 1 \end{pmatrix} = \begin{pmatrix} b \\ b \end{pmatrix} = b$$

(a) Use Cramer’s rule to solve for the parameters $m$ and $b$ in terms of $x_1, x_2, y_1$ and $y_2$.

(b) Determine the equation for a line $y(x) = mx + b$ passing through the two points $(5, 2)$ and $(3, -4)$ by determining the values of $m$ and $b$ using Cramer’s rule.

14.18 Consider the three points $(x_1, y_1, z_1)$, $(x_2, y_2, z_2)$ and $(x_3, y_3, z_3)$ in three-dimensional cartesian coordinates. Suppose we are asked to determine the parameters $a, b$ and $c$ defining the equation of a plane $z(x, y) = ax + by + c$ containing the three points. We can do this using Cramer’s rule.

As each point is on the plane defined by $z = ax + by + c$, we know that

$$z_1 = ax_1 + by_1 + c$$
$$z_2 = ax_2 + by_2 + c$$
$$z_3 = ax_3 + by_3 + c$$
or that

\[-ax_1 - by_1 + z_1 = c\]
\[-ax_2 - by_2 + z_2 = c\]
\[-ax_3 - by_3 + z_3 = c\]

which can be written in the matrix form \( Ax = c \) as

\[
Ax = \begin{pmatrix}
-ax_1 - by_1 + z_1 \\
-ax_2 - by_2 + z_2 \\
-ax_3 - by_3 + z_3
\end{pmatrix} = \begin{pmatrix} x_1 & y_1 & z_1 \\
x_2 & y_2 & z_2 \\
x_3 & y_3 & z_3 \end{pmatrix} \begin{pmatrix} -a \\
-b \\
1 \end{pmatrix} = \begin{pmatrix} c \\
c \\
c \end{pmatrix} = c
\]

(a) Use Cramer’s rule to solve for the parameters \(a, b\) and \(c\) in terms of \(x_1, x_2, x_3, y_1, y_2, y_3, z_1, z_2\) and \(z_3\).

(b) Determine the equation for a plane \(z(x, y) = ax + by + c\) that contains the three points \((5, 2, 1), (3, -4, 2)\) and \((-2, 1, -3)\) by determining the values of \(a, b\) and \(c\) using Cramer’s rule.

14.19* Determinants commonly appear in the Hückel theory of molecular orbitals of \(\pi\)-systems. Determine which values of \(x\) satisfy each of the following equations expressed in the form of determinants.

(a) The determinant equation for triethylenemethane

\[
\begin{vmatrix}
x & 1 & 0 & 1 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
1 & 0 & 1 & x
\end{vmatrix} = 0
\]

(b) The determinant equation for cyclobutadiene

\[
\begin{vmatrix}
x & 1 & 1 & 1 \\
1 & x & 0 & 0 \\
1 & 0 & x & 0 \\
1 & 0 & 0 & x
\end{vmatrix} = 0
\]

(c) The determinant equation for benzene

\[
\begin{vmatrix}
x & 1 & 0 & 0 & 1 \\
1 & x & 1 & 0 & 0 \\
0 & 1 & x & 1 & 0 \\
0 & 0 & 1 & x & 1 \\
1 & 0 & 0 & 0 & 1
\end{vmatrix} = 0
\]

14.20* Consider the following set of linear equations arising in Hückel theory

\[
\begin{align*}
(\alpha - E)c_1 + \beta c_2 &= 0 \\
\beta c_1 + (\alpha - E)c_2 + \beta c_3 &= 0 \\
\beta c_2 + (\alpha - E)c_3 &= 0
\end{align*}
\]

for the variable \(E\) in terms of the constant parameters \(\alpha\) and \(\beta\).

(a) Set the determinant of the matrix of coefficients equal to zero and solve for \(E\) in terms of \(\alpha\) and \(\beta\). You should find three values \(E_1, E_2,\) and \(E_3\).

(b) The column vectors formed by the coefficients are normalized as

\[
\sum_{k=1}^{3} c_k^2 = 1
\]

Determine the set of coefficients \(c_1, c_2,\) and \(c_3\) that satisfy the linear equations for each value of \(E\).
14.21* In analyzing the determinant $|A|$ of the $2 \times 2$ matrix

$$A = \begin{pmatrix} a & c \\ b & d \end{pmatrix}$$

we found that the magnitude of the determinant was equal to the area of a parallelogram formed by the vectors $\mathbf{a} = a \hat{x} + b \hat{y}$ and $\mathbf{b} = c \hat{x} + d \hat{y}$. Prove that the area of the parallelogram is equal to the magnitude of the determinant $|ad - bc|.$

HINT: Consider making a geometric argument using the partitioning of space suggested in the figure above.
15 Eigenvalues and eigenvectors

15.1 Matrix eigenvalues and eigenvectors

Many problems in the physical sciences can be expressed as a set of linear equations. A special class of homogeneous linear equations are known as eigenvalue problems. In an eigenvalue problem, an operator acts on a function resulting in the same function (the eigenfunction) times a constant (the eigenvalue). Matrix eigenvalue problems can be solved using the special properties of determinants and matrix algebra. In this section, we develop general methods for solving matrix eigenvalue problems.

15.1.1 The characteristic equation and eigenvalues

In the physical sciences we commonly encounter problems that can be written in the form of the homogeneous equation

$$Ax = \lambda x \quad (15.1)$$

The matrix $A$ multiplies the vector $x$ resulting in the same vector $x$ times a constant $\lambda$. As such, the magnitude of the vector is multiplied by a scalar constant $\lambda^2$

$$|Ax| = |\lambda x| = \lambda |x|$$

while the orientation defined by the unit vector $\hat{x}$

$$\hat{x} = \frac{1}{|x|}x$$

is unchanged since

$$\frac{1}{|Ax|}Ax = \frac{1}{\lambda |x|} \lambda x = \frac{1}{|x|}x = \hat{x}$$

These qualitative properties of Equation 15.1 and its solution are shown in Figure 15.1.

It is convenient to rewrite Equation 15.1 as

$$Ax = \lambda Ix$$

where $I$ is the identity matrix and we have used the fact that $x = Ix$. Subtracting $\lambda Ix$ from each side results in

$$Ax - \lambda Ix = (A - \lambda I)x = 0 \quad (15.2)$$

where 0 is the zero vector in which all elements of the vector are zero. This expression, which is equivalent to our original Equation 15.1, can be used to determine eigenvectors from known eigenvalues.
Let’s consider the specific example

\[ \mathbf{A} \mathbf{x} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \mathbf{x} \]

where

\[ \mathbf{x} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \]

The goal is to solve for \( \mathbf{x} \) by identifying \( c_1 \) and \( c_2 \). Returning to our example we find

\[ (\mathbf{A} - \lambda \mathbf{I}) \mathbf{x} = \begin{pmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = \mathbf{0} \]

A general solution for the elements of \( \mathbf{x} \) is provided by Cramer’s rule (see Chapter 14) as

\[ c_k = \frac{1}{|\mathbf{A} - \lambda \mathbf{I}|} |(\mathbf{A} - \lambda \mathbf{I})_k| \quad (15.3) \]

where \( (\mathbf{A} - \lambda \mathbf{I})_k \) is the matrix \( (\mathbf{A} - \lambda \mathbf{I}) \) in which the \( k \)th column has been replaced by the vector \( \mathbf{0} \). For our specific example we find

\[ c_1 = \frac{1}{|\mathbf{A} - \lambda \mathbf{I}|} \begin{vmatrix} 0 & a_{12} \\ 0 & a_{22} - \lambda \end{vmatrix} \quad c_2 = \frac{1}{|\mathbf{A} - \lambda \mathbf{I}|} \begin{vmatrix} a_{11} - \lambda & 0 \\ a_{21} & 0 \end{vmatrix} \]

However, since the determinants \( |\mathbf{A} - \lambda \mathbf{I}|_1 = |\mathbf{A} - \lambda \mathbf{I}|_2 = 0 \) it appears that we have only the trivial solution \( c_1 = c_2 = 0 \).

Not so fast! It turns out that our equations for \( c_1 \) and \( c_2 \) can have a non-trivial solution when the denominator \( |\mathbf{A} - \lambda \mathbf{I}| = 0 \). Viewed through Cramer’s rule, the non-trivial solution for \( c_k \) results from dividing \( |(\mathbf{A} - \lambda \mathbf{I})_k| = 0 \) by \( |\mathbf{A} - \lambda \mathbf{I}| = 0 \) to arrive at a non-zero result for \( c_k \).

Based on these specific observations we can form a general rule. The condition for identifying a non-trivial solution to our original Equation 15.1

\[ \mathbf{A} \mathbf{x} = \lambda \mathbf{x} \]

is expressed

\[ |\mathbf{A} - \lambda \mathbf{I}| = 0 \quad (15.4) \]

and known as the characteristic equation.\(^3\) As the matrix \( \mathbf{A} \) defines the particular problem we wish to solve, the characteristic equation is used to identify those values of \( \lambda \), known as eigenvalues, for which a non-trivial solution for \( \mathbf{x} \) exists. As such, we refer to Equation 15.1 as an eigenvalue problem and Equation 15.4 forms the starting point for its solution.

### 15.1.2 Eigenvalues and eigenvectors

Let’s see how this works for the specific case

\[ \mathbf{A} \mathbf{x} = \lambda \mathbf{x} \]

where the matrix

\[ \mathbf{A} = \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \quad (15.5) \]

We expect a non-trivial solution for \( \mathbf{x} \) only for values of \( \lambda \) satisfying the charac-
teristic equation defined by Equation 15.4. We first form the matrix
\[
A - \lambda I = \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} a - \lambda & 1 \\ 1 & a - \lambda \end{pmatrix}
\]
Taking the determinant
\[
|A - \lambda I| = \begin{vmatrix} a - \lambda & 1 \\ 1 & a - \lambda \end{vmatrix} = (a - \lambda)^2 - 1 = 0
\]
results in a quadratic equation in the parameter \(\lambda\)
\[
\lambda^2 - 2a\lambda + (a^2 - 1) = 0
\]
with roots defined by the quadratic formula
\[
\lambda = \frac{a \pm \sqrt{a^2 - (a^2 - 1)}}{2} = a \pm 1
\]
The two values of \(\lambda\) for which the characteristic equation is satisfied are \(\lambda_1 = a + 1\) and \(\lambda_2 = a - 1\). As such, there are two equations
\[
Ax_1 = \lambda_1 x_1 \quad Ax_2 = \lambda_2 x_2
\]
leading to two solutions \(x_1\) and \(x_2\). The scalars \(\lambda_1\) and \(\lambda_2\) are the *eigenvalues* of the matrix \(A\) while \(x_1\) and \(x_2\) are the corresponding *eigenvectors*. Let’s determine the explicit form of the eigenvectors \(x_1\) and \(x_2\) and explore their general properties.

### 15.1.3 Eigenvectors and their properties

To determine the eigenvectors \(x_1\) and \(x_2\) we turn to Equation 15.2. For \(\lambda_1 = a + 1\) and \(x_1\) we have
\[
(A - \lambda_1 I) x_1 = \begin{pmatrix} a - \lambda_1 & 1 \\ 1 & a - \lambda_1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} -c_1 + c_2 \\ c_1 - c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution \(c_1 = c_2\). To normalize our eigenvectors we also impose the condition
\[
x_1^T x_1 = \begin{pmatrix} c_1 & c_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1^2 + c_2^2 = 1
\]
Solving for \(c_1 = c_2 = 1/\sqrt{2}\) leads to the final result for the eigenvector
\[
x_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]
For \(\lambda_2 = a - 1\) and \(x_2\) we have
\[
(A - \lambda_2 I) x_2 = \begin{pmatrix} a - \lambda_2 & 1 \\ 1 & a - \lambda_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} c_1 + c_2 \\ c_1 + c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution \(c_1 = -c_2\). We want our eigenvectors to have an absolute value of unity so we also demand
\[
x_2^T x_2 = (c_1 \ c_2) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1^2 + c_2^2 = 1
\]

Solving for \( c_1 = -c_2 = 1/\sqrt{2} \) leads to the final result for the eigenvector
\[
x_2 = \begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]

In addition to being individually normalized our eigenvectors are mutually orthogonal as
\[
x_1^T x_2 = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix} = x_2^T x_1 = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} = 1 - 1 = 0
\]

Finally, we insert our eigenvectors \( x_1 \) and \( x_2 \) in the original Equation 15.5 as
\[
A x_1 = \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} (a + 1)
\]
\[= \frac{1}{\sqrt{2}} (a + 1) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \lambda_1 x_1
\]

and
\[
A x_2 = \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \begin{pmatrix} -1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} (a - 1)
\]
\[= \frac{1}{\sqrt{2}} (a - 1) \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \lambda_2 x_2
\]
validating our solution. Our final result takes the form of a pair of eigenvalues, \( \lambda_1 \) and \( \lambda_2 \), and the corresponding eigenvectors, \( x_1 \) and \( x_2 \).

Under the transformation \( A x = \lambda x \) the orientation of each vector satisfying the transformation is preserved. This is a special property of specific eigenvectors \( x \) that is valid only for particular eigenvalues \( \lambda \). For all other vectors \( x \) and for all other constants \( \lambda \) we find that \( A x \neq \lambda x \) (see Figure 15.2). Just as polynomial equations have characteristic roots, the eigenvalues are the roots of the characteristic equation.
15.1.4 Eigenvectors and the eigenvector matrix

We can build a matrix $C$ out of columns formed by our eigenvectors $x_1$ and $x_2$

$$C = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

which is an orthogonal matrix as the columns form a set of vectors that are individually normalized and mutually orthogonal. $C$ is known as the eigenvector matrix.

As $C$ is an orthogonal matrix its transpose matrix is also its inverse

$$C^T = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = C^{-1}$$

which we can demonstrate as

$$CC^{-1} = \begin{pmatrix} \frac{1}{2} & 1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & 1 & 1 \\ 1 & 1 & -1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I$$

Similarly $C^{-1}C = I$. This suggests an alternative approach to the solution of our original problem $Ax = \lambda x$ where $A$ is defined by Equation 15.5.

Suppose we multiply the coefficient matrix $A$ from the right by our eigenvector matrix $C$. The result is

$$AC = \frac{1}{\sqrt{2}} \begin{pmatrix} a & 1 \\ 1 & a \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} (a+1) & (a-1) \\ (1+a) & (1-a) \end{pmatrix}$$

Now suppose we multiply the resulting matrix $AC$ from the left by the inverse of our eigenvector matrix $C^{-1}$. We find the remarkable result

$$C^{-1}AC = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} (a+1) & (a-1) \\ (1+a) & (1-a) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 2(a+1) & 0 \\ 0 & 2(a-1) \end{pmatrix} = \begin{pmatrix} a+1 & 0 \\ 0 & a-1 \end{pmatrix}$$

The matrix transformation $C^{-1}AC$ leads to a diagonal matrix where the elements are the eigenvalues $\lambda_1 = a+1$ and $\lambda_2 = a-1$ of the matrix $A$. We refer to the result

$$C^{-1}AC = \Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

as the eigenvalue matrix.

Given this result, if we know the orthonormal eigenvectors $x_1$ and $x_2$ we can form the eigenvector matrix $C$ and determine the eigenvalues $\lambda_1$ and $\lambda_2$ by evaluating $C^{-1}AC = \Lambda$. This general approach is useful in the evaluation of quadratic polynomials of many variables known as quadratic forms.\textsuperscript{6} We will explore the use of quadratic polynomials in eigenvalue problems modeling the vibrational motion of masses on springs and molecules.

\textsuperscript{6} We can express multidimensional quadratic functions in the form of the equation $x^T Ax$ where $x$ is a coordinate vector, $x^T$ is its vector transpose, and $A$ is a matrix of constant coefficients. By identifying the eigenvectors of the matrix $A$, building the eigenvector matrix $C$, and employing the identity $CC^{-1} = C^{-1}C = I$ we can write $x^T Ax = x^T I A I x = x^T C^{-1} A C^{-1} x$ which can also be written $y^T Ay$ where $C^{-1}AC = \Lambda$ is a diagonal matrix, $y = C^{-1} x$ is the normal coordinate vector, and $y^T = \left( C^{-1} x \right)^T = x^T C$. In this way, we can transform a set of coupled quadratic equations in $x$ into a set of uncoupled quadratic equations in the normal coordinates $y$. 
15.1.5 Solving eigenvalue problems of arbitrary dimension

The method we have developed for solving eigenvalue problems of the form

\[ Ax = \lambda x \]  

(15.7)

is generally applicable to the case of \( n \) coupled equations in \( n \) unknown variables where

\[
A = \begin{pmatrix}
  a_{11} & a_{12} & \cdots & a_{1n} \\
  a_{21} & a_{22} & \cdots & a_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{n1} & a_{n2} & \cdots & a_{nn}
\end{pmatrix}
\]  

(15.8)

is an \( n \times n \) matrix of coefficients, \( \lambda \) is an eigenvalue, and

\[
x = \begin{pmatrix}
  c_1 \\
  c_2 \\
  \vdots \\
  c_n
\end{pmatrix}
\]

is the corresponding eigenvector.

In general we expect to find \( n \) eigenvalues and \( n \) corresponding eigenvectors. The eigenvalues are solutions to the characteristic equation defined in Equation 15.4 as

\[
|A - \lambda I| = \begin{vmatrix}
  a_{11} - \lambda & a_{12} & \cdots & a_{1n} \\
  a_{21} & a_{22} - \lambda & \cdots & a_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{n1} & a_{n2} & \cdots & a_{nn} - \lambda
\end{vmatrix} = 0
\]  

(15.9)

which is an \( n \)th order polynomial equation in \( \lambda \) having \( n \) roots corresponding to a set of \( n \) eigenvalues \( \{\lambda_k\} \). The eigenvalues have the special properties that the sum of all eigenvalues equals the trace of \( A \)

\[
\sum_{k=1}^{n} \lambda_k = \text{Tr} A
\]

while the product of all eigenvalues equals the determinant of \( A \)

\[
\prod_{k=1}^{n} \lambda_k = |A|
\]

These rules can be used to check the validity of a proposed set of eigenvalues \( \{\lambda_k\} \).

Each of the \( n \) eigenvalues, \( \lambda_k \), is used to define a corresponding eigenvector, \( x_k \), through Equation 15.2 as

\[
(A - \lambda_k I) x_k = 0
\]  

(15.10)

The set of orthonormal eigenvectors \( \{x_k\} \) can be used to form the columns of the orthogonal eigenvector matrix \( C \). Finally, the eigenvector matrix and its inverse \( C^{-1} = C^T \) are used to diagonalize the matrix \( A \) as

\[
C^{-1} A C = \Lambda
\]  

(15.11)

The set of \( n \) eigenvalues and corresponding eigenvectors forms a complete solution to our eigenvalue problem.
15.2 Matrix methods for coupled differential equations

Sets of homogeneous coupled linear algebraic equations can be solved using matrix methods when formed as an eigenvalue problem. The same methods can be used to solve sets of coupled linear ordinary differential equations. In this section, use matrix methods to solve eigenvalue problems involving coupled linear ordinary differential equations describing physical kinetics and dynamics.

15.2.1 Chemical kinetics revisited (as an eigenvalue problem)

In our explorations of first order differential equations in Chapter 10 we analyzed the chemical kinetic scheme

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

by solving the set of three coupled linear first order ordinary differential equations for the time-dependent concentrations of each species

\[
\begin{align*}
\frac{d}{dt} A(t) &= -k_1 A(t) \\
\frac{d}{dt} B(t) &= k_1 A(t) - k_2 B(t) \\
\frac{d}{dt} C(t) &= k_2 B(t)
\end{align*}
\]

originally presented in Equation 10.9. The initial conditions define the concentration of each species at time \( t = 0 \) as \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \). With our knowledge of matrix algebra we can rewrite this set of coupled linear differential equations as

\[
\frac{d}{dt} \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix}
\]

which can be reformed as

\[
\frac{d}{dt} x(t) = Kx(t) \quad (15.12)
\]

where we have defined the composition vector

\[
x(t) = \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix}
\]

and the rate constant matrix

\[
K = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix}
\]

We anticipate exponential time dependence for the concentrations. As such, we substitute into Equation 15.12 an ansatz for \( x(t) \) in the form

\[
e^{at}
\]

and find

\[
\frac{d}{dt} x(t) = ax(t) = Kx(t) \quad (15.13)
\]

This equation has the form of an eigenvalue problem (see Equation 15.7) and

\[
7 \text{ This follows from the fact that the time derivative of } x(t) \text{ is proportional to } x(t) \text{ itself, a property of the exponential function.}
\]

\[
8 \text{ Taking } x(t) = x_0 e^{at} \text{ we find }
\]

\[
\frac{d}{dt} x(t) = x_0 \frac{d}{dt} e^{at} = ax_0 e^{at} = ax(t)
\]

by design.
can be solved using the general methods we have developed for the solution of ordinary differential equations and matrix eigenvalue problems.

Equation 15.13 can be rewritten in the form of Equation 15.10 as

\[(K - aI)x(t) = 0\]

This expression will have non-trivial solutions only for cases where the determinant

\[|K - aI| = 0\]

which is the characteristic equation defined in Equation 15.9.

Inserting the rate constant matrix \(K\) in the characteristic equation and evaluating the determinant leads to a cubic polynomial equation in \(a\)

\[
|K - aI| = \begin{vmatrix}
-k_1 - a & 0 & 0 \\
-k_2 - a & 0 & 0 \\
0 & k_2 & 0 - a
\end{vmatrix} = -(k_1 + a)(k_2 + a) = 0
\]

The roots of this equation are the three eigenvalues \(a_1 = 0, a_2 = -k_1\) and \(a_3 = -k_2\). We can now identify the eigenvectors \(x_k\) corresponding to each of the eigenvalues \(a_k\) using Equation 15.10 where

\[(K - a_kI)x_k = 0\]

For \(a_1 = 0\) we have

\[
(K - a_1)x_1 = \begin{pmatrix}
-k_1 & 0 & 0 \\
k_1 & -k_2 & 0 \\
0 & k_2 & 0
\end{pmatrix} \begin{pmatrix}
c_1 \\
c_2 \\
c_3
\end{pmatrix} = \begin{pmatrix}0 \\
0 \\
0
\end{pmatrix} = 0
\]

leading to a set of equations defining the coefficients

\[-k_1c_1 = 0 \\
k_1c_1 - k_2c_2 = 0 \\
k_2c_2 = 0
\]

The first equation leads to \(c_1 = 0\) while the third equation leads to \(c_2 = 0\). No constraint is placed on \(c_3\). As such, we arbitrarily and for convenience we set \(c_3 = 1\). This results in the eigenvector

\[x_1 = \begin{pmatrix}0 \\
0 \\
1
\end{pmatrix}\]

For \(a_2 = -k_1\) we have

\[
(K - a_2)x_2 = \begin{pmatrix}
0 & 0 & 0 \\
k_1 & -k_2 + k_1 & 0 \\
0 & k_2 & k_1
\end{pmatrix} \begin{pmatrix}
c_1 \\
c_2 \\
c_3
\end{pmatrix} = \begin{pmatrix}0 \\
0 \\
0
\end{pmatrix} = 0
\]

leading to a set of equations defining the coefficients

\[0 = 0 \\
k_1c_1 - (k_2 - k_1)c_2 = 0 \\
k_2c_2 + k_1c_3 = 0
\]

We arbitrarily set \(c_1 = 1\) to find \(c_2 = k_1/(k_2 - k_1)\) and \(c_3 = -k_2/(k_2 - k_1)\)
leading to the eigenvector

\[ \mathbf{x}_2 = \begin{pmatrix} 1 \\ k_1 \\ \frac{k_2 - k_1}{k_2 - k_1} \\ \frac{-k_1 - k_2}{k_2 - k_1} \end{pmatrix} \]

Finally, for \( \alpha_3 = -k_2 \) we have

\[ (\mathbf{K} - \alpha_3) \mathbf{x}_3 = \begin{pmatrix} -k_1 + k_2 & 0 & 0 \\ k_1 & 0 & 0 \\ 0 & k_2 & k_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{0} \]

leading to a set of equations defining the coefficients

\[-(k_2 - k_1)c_1 = 0 \\
- k_1 c_1 = 0 \\
k_2 c_2 + k_2 c_3 = 0 \]

The first and second equations lead to \( c_1 = 0 \). We arbitrarily set \( c_2 = -k_1 / (k_2 - k_1) \) to find \( c_3 = k_1 / (k_2 - k_1) \) leading to the eigenvector

\[ \mathbf{x}_3 = \begin{pmatrix} 0 \\ -k_1 \\ k_2 - k_1 \\ k_1 \\ \frac{k_1}{k_2 - k_1} \end{pmatrix} \]

Having defined the three eigenvalues and corresponding eigenvectors we can write the solution for the time-dependence of the composition vector

\[ \mathbf{x}(t) = \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} = d_1 \mathbf{x}_1 e^{\alpha_1 t} + d_2 \mathbf{x}_2 e^{\alpha_2 t} + d_3 \mathbf{x}_3 e^{\alpha_3 t} \]

\[ = d_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + d_2 \begin{pmatrix} 1 \\ \frac{k_1}{k_2 - k_1} \\ \frac{-k_1 - k_2}{k_2 - k_1} \end{pmatrix} e^{-k_1 t} + d_3 \begin{pmatrix} 0 \\ -k_1 \\ k_2 - k_1 \end{pmatrix} e^{-k_1 t} \]

where the coefficients \( d_1, d_2 \) and \( d_3 \) must be determined by the initial conditions. Returning to the initial conditions \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \) at \( t = 0 \) we find

\[ \mathbf{x}(0) = d_1 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + d_2 \begin{pmatrix} 1 \\ \frac{k_1}{k_2 - k_1} \\ \frac{-k_1 - k_2}{k_2 - k_1} \end{pmatrix} + d_3 \begin{pmatrix} 0 \\ -k_1 \\ k_2 - k_1 \end{pmatrix} = \begin{pmatrix} A_0 \\ 0 \\ 0 \end{pmatrix} \]

leading to a set of equations defining the coefficients

\[ d_2 = A_0 \]

\[ d_2 \frac{k_1}{k_2 - k_1} - d_3 \frac{k_1}{k_2 - k_1} = 0 \]

\[ d_1 - d_2 \frac{k_2}{k_2 - k_1} + d_3 \frac{k_1}{k_2 - k_1} = 0 \]

The first equation sets \( d_2 = A_0 \), the second equation sets \( d_3 = d_2 = A_0 \) and the
third equation defines
\[ d_1 = A_0 \frac{k_2}{k_2 - k_1} - A_0 \frac{k_1}{k_2 - k_1} = A_0 \]

This leads to our result for the time dependence of the reaction composition
\[
 x(t) = \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} = A_0 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + A_0 \begin{pmatrix} \frac{1}{k_1} \\ \frac{1}{k_2 - k_1} \\ \frac{1}{k_2 - k_1} \end{pmatrix} e^{-k_1 t} + A_0 \begin{pmatrix} 0 \\ \frac{-k_1}{k_2 - k_1} \\ \frac{k_2}{k_2 - k_1} \end{pmatrix} e^{-k_2 t}
\]

or
\[
 A(t) = A_0 e^{-k_1 t}
 B(t) = A_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})
 C(t) = A_0 + A_0 \frac{k_1}{k_2 - k_1} \left( e^{-k_1 t} - \frac{k_2}{k_1} e^{-k_2 t} \right)
\]

The result is shown in Figure 15.3.

In the limit that \( t = 0 \) the solution respects the initial conditions \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \). Over time, the solution also respects the condition that \( A(t) + B(t) + C(t) = A_0 \). In the long time limit, we find \( A(\infty) = B(\infty) = 0 \) and \( C(\infty) = A_0 \). This result derived using matrix algebra as an eigenvalue problem is identical to Equations 10.10, 10.11 and 10.12 derived in Chapter 10 by successively solving the series of first-order ordinary differential equations.

### 15.2.2 Oscillating masses on springs revisited (as an eigenvalue problem)

In our explorations of **second order differential equations** in Chapter 11 we analyzed the dynamics of a mass on a spring governed by Newton’s equation of motion
\[
m \frac{d^2 x(t)}{dt^2} = -\kappa (x(t) - x_0)
\]
where \( x(t) \) is the displacement of the oscillator from its mechanically stable position at \( x_0 \) and \( \kappa \) is the force constant (see Figure 15.4). We solved this linear second order ordinary differential equation by inserting the ansatz for the time dependence of the solution
\[
e^{\alpha t}
\]

to derive the auxiliary equation with roots \( \alpha = \pm i \sqrt{\frac{\kappa}{m}} \), leading to a final solution
\[
x(t) = x_0 + \left( x(0) - x_0 \right) \cos \left( \sqrt{\frac{\kappa}{m}} t \right)
\]

for an oscillator initially in position \( x(0) \) with velocity \( \frac{d}{dt} x(0) = 0 \).

Now consider the case of two masses connected to solid supports and each other by springs (see Figure 15.5). The potential energy is
\[
V(x_1, x_2) = \frac{1}{2} \kappa x_1^2 + \frac{1}{2} \kappa (x_2 - x_1)^2 + \frac{1}{2} \kappa x_2^2
\]

where \( x_1 \) and \( x_2 \) are the displacements of the oscillators from the points of mechanical equilibrium at which the potential energy \( V(0, 0) = 0 \) is a minimum.
The equations of motion for the displacements of the two masses are

\[
\begin{align*}
 m \frac{d^2}{dt^2} x_1(t) &= - \frac{dV}{dx_1} = -\kappa x_1 + \kappa (x_2 - x_1) = -2\kappa x_1 + \kappa x_2 \\
 m \frac{d^2}{dt^2} x_2(t) &= - \frac{dV}{dx_2} = -\kappa (x_2 - x_1) - \kappa x_2 = \kappa x_1 - 2\kappa x_2
\end{align*}
\]

We can rewrite these equations in compact form as

\[
\frac{d^2}{dt^2} \mathbf{x}(t) = -\mathbf{K} \mathbf{x}(t) \tag{15.14}
\]

where we have defined the displacement vector

\[
\mathbf{x}(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix}
\]

and the force constant matrix

\[
\mathbf{K} = \begin{pmatrix} \frac{2\kappa}{m} & -\frac{\kappa}{m} \\ -\frac{\kappa}{m} & \frac{2\kappa}{m} \end{pmatrix}
\]

Equation 15.14 has the form of an eigenvalue problem defined by Equation 15.7 and can be treated using the general methods we have developed for solving ordinary differential equations and matrix eigenvalue problems.

As we anticipate sinusoidal time dependence for the mass displacements, we substitute into Equation 15.14 an ansatz for the time dependence of \( \mathbf{x}(t) \) of the form\(^9\)

\[
e^{i\omega t}
\]

and find\(^10\)

\[
\frac{d^2}{dt^2} \mathbf{x}(t) = -\omega^2 \mathbf{x}(t) = -\mathbf{K} \mathbf{x}(t) \tag{15.15}
\]

which can be rewritten as

\[
\left( \mathbf{K} - \omega^2 \mathbf{I} \right) \mathbf{x}(t) = 0
\]

This expression will have non-trivial solutions only for cases where the determinant

\[
\begin{vmatrix} \mathbf{K} - \omega^2 \mathbf{I} \end{vmatrix} = 0
\]

which is the characteristic equation defined in Equation 15.9.

Inserting the force constant matrix \( \mathbf{K} \) in the characteristic equation and evaluating the determinant leads to a quartic polynomial equation in \( \omega \)

\[
\begin{vmatrix} \mathbf{K} - \omega^2 \mathbf{I} \end{vmatrix} = \begin{vmatrix} \frac{2\kappa}{m} & -\frac{\kappa}{m} \\ -\frac{\kappa}{m} & \frac{2\kappa}{m} \end{vmatrix} - \begin{vmatrix} \omega^2 & 0 \\ 0 & \omega^2 \end{vmatrix} = \frac{4\kappa^2}{m^2} - \frac{\kappa^2}{m^2} = 0
\]

The roots of this quartic equation in \( \omega \) are two pairs of eigenvalues \( \pm \omega_1 = \pm \sqrt{\frac{\kappa}{m}} \) and \( \pm \omega_2 = \pm \sqrt{\frac{3\kappa}{m}} \). We can now identify the eigenvectors corresponding to each of the eigenvalue pairs \( \omega_k^2 \) by solving the eigenvector equation defined by Equation 15.10 where

\[
\left( \mathbf{K} - \omega_k^2 \mathbf{I} \right) \mathbf{x}_k = 0
\]

and the solutions are the eigenvectors \( \mathbf{x}_k \).

---

\(^9\) The second derivative with respect to time of \( \mathbf{x}(t) \) is proportional to \( -\mathbf{x}(t) \), a property of sinusoidal functions.

\(^10\) Taking \( \mathbf{x}(t) = \mathbf{x}_0 e^{i\omega t} \) we find

\[
\frac{d^2}{dt^2} \mathbf{x}(t) = \mathbf{x}_0 \frac{d^2}{dt^2} e^{i\omega t} = -\omega^2 \mathbf{x}_0 e^{i\omega t} = -\omega^2 \mathbf{x}(t)
\]

by design.
For $\omega_1^2 = \frac{k}{m}$ we have

\[
(K - \omega_1^2) x_1 = \begin{pmatrix} \frac{k}{m} & -\frac{k}{m} \\ -\frac{k}{m} & \frac{k}{m} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

leading to a set of equations defining the coefficients

\[
\frac{k}{m} c_1 - \frac{k}{m} c_2 = 0 \\
-\frac{k}{m} c_1 + \frac{k}{m} c_2 = 0
\]

Both equations lead to $c_1 = c_2$ and the eigenvector

\[
x_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]

For $\omega_2^2 = \frac{3k}{m}$ we have

\[
(K - \omega_2^2) x_2 = \begin{pmatrix} \frac{k}{m} & -\frac{k}{m} \\ -\frac{k}{m} & \frac{k}{m} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

leading to a set of equations defining the coefficients

\[
-\frac{k}{m} c_1 - \frac{k}{m} c_2 = 0 \\
-\frac{k}{m} c_1 + \frac{k}{m} c_2 = 0
\]

Both equations lead to $c_1 = -c_2$ and the eigenvector

\[
x_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]

Having defined the two eigenvalues and corresponding eigenvectors we can write the solution for the time-dependence of the displacement vector as

\[
x(t) = x_1 \left[ d_1 \cos(\omega_1 t) + d_2 \sin(\omega_1 t) \right] + x_2 \left[ d_3 \cos(\omega_2 t) + d_4 \sin(\omega_2 t) \right]
\]

where the coefficients $d_1, d_2, d_3$ and $d_4$ must be determined by the initial conditions.

The initial conditions for the displacements and velocities of the masses are

\[
x_1(0) \quad \frac{dx_1(t)}{dt} x_1(0) = 0 \quad x_2(0) \quad \frac{dx_2(t)}{dt} x_2(0) = 0
\]

where the masses are initially at rest. Applying the initial conditions for the displacements we find

\[
x(0) = d_1 \begin{pmatrix} 1 \\ 1 \end{pmatrix} + d_3 \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \begin{pmatrix} x_1(0) \\ x_2(0) \end{pmatrix}
\]

leading to a set of equations defining the coefficients $d_1$ and $d_3$ in terms of the initial displacements

\[
x_1(0) = d_1 + d_3 \\
x_2(0) = d_1 - d_3
\]

Figure 15.6: The trajectory of a symmetric displacement of the two masses leading to in-phase sinusoidal oscillation with angular frequency $\omega_1 = \sqrt{k/m}$ and period $T_1 = 2\pi \sqrt{m/k}$. 
so that the coefficients are
\[ d_1 = \frac{1}{2} (x_1(0) + x_2(0)) \quad d_3 = \frac{1}{2} (x_1(0) - x_2(0)) \]

Applying the initial conditions for the velocities of the displacements we find
\[ \frac{d}{dt}x(0) = d_2 \omega_1 \begin{pmatrix} 1 \\ 1 \end{pmatrix} + d_4 \omega_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \]

so that \( d_2 = d_4 = 0 \). Our final result for the general solution to Equation 15.14 is
\[ x(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix} = d_1 \begin{pmatrix} 1 \\ 1 \end{pmatrix} \cos(\omega_1 t) + d_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} \cos(\omega_2 t) \]

or
\[ x(t) = \frac{1}{2} (x_1(0) + x_2(0)) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \cos \left( \sqrt{\frac{k}{m}} t \right) + \frac{1}{2} (x_1(0) - x_2(0)) \begin{pmatrix} 1 \\ -1 \end{pmatrix} \cos \left( \sqrt{\frac{3k}{m}} t \right) \]

Note that our general solution has two frequencies of motion defined by \( \omega_1 \) and \( \omega_2 = \sqrt{3} \omega_1 \). In general, the motion of the two masses will be defined by oscillatory motion on both time scales.

To gain insight into our solution, let’s analyze the time dependence for two initial displacements. Suppose we choose the initial condition \( x_1(0) = x_2(0) = \Delta x(0) \). Our general solution reduces to
\[ x(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix} = \Delta x(0) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \cos \left( \sqrt{\frac{k}{m}} t \right) \]

where the displacement of each mass undergoes sinusoidal oscillation with a period
\[ T_1 = 2\pi \sqrt{\frac{m}{k}} \]
during which both masses oscillate in phase as shown in Figure 15.6.

Now suppose we choose the initial condition \( x_1(0) = -x_2(0) = \Delta x(0) \). Our general solution reduces to
\[ x(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix} = \Delta x(0) \begin{pmatrix} 1 \\ -1 \end{pmatrix} \cos \left( \sqrt{\frac{3k}{m}} t \right) \]

where the displacement of each mass undergoes sinusoidal oscillation with a period
\[ T_2 = 2\pi \sqrt{\frac{m}{3k}} = \frac{1}{\sqrt{3}} T_1 \]
during which both masses oscillate out-of-phase as shown in Figure 15.7.

These oscillations represent normal modes of vibration. Each mode has a unique frequency, \( \omega_1 \) or \( \omega_2 \), and corresponding eigenvector, \( x_1 \) or \( x_2 \). The eigenvectors are mutually orthogonal and can be normalized as
\[ x_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad x_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \]

These modes have the characteristics of vibrations in solids. The lower frequency in-phase oscillation has the characteristic of a lower frequency acoustic mode where atoms move together (see Figure 15.6). The higher frequency out-of-phase motion has the characteristic of a higher frequency acoustic mode where atoms move out-of-phase (see Figure 15.7).
phase oscillation has the characteristic of a higher frequency optical mode where atoms move against each other (see Figure 15.7).

Note that the same time evolution of the displacements can be viewed on the two-dimensional plane where the abscissa is the displacement $x_1$ and the ordinate the displacement $x_2$ as shown in Figure 15.8. The diagonal red line represents the dynamics of the in-phase oscillation depicted in Figure 15.6 and the diagonal blue line represents the dynamics of the out-of-phase oscillation depicted in Figure 15.7.

Now consider the initial displacement $x_1(0) = x(0)$ and $x_2(0) = 0$ shown in Figure 15.9. The oscillators are coupled and the initial displacement of $x_1$ away from the point of mechanical equilibrium, $(x_1, x_2) = (0, 0)$, leads to the displacement of $x_2$. As the trajectory defined by the point $(x_1(\tau), x_2(\tau))$ evolves in time it explores an area defined by the set of displacements consistent with the constraint that the total energy of the system is constant in time. The bounding lines known as caustics form a square region in $xy$-plane.

Let’s return to Equation 15.14 defining the motion of our two masses

$$\frac{d^2}{dt^2} x(t) = -Kx(t) \quad (15.16)$$

Suppose we form an orthogonal matrix from our two orthonormal eigenvectors $x_1$ and $x_2$ as

$$C = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

The inverse of our orthogonal matrix is its transpose $C^{-1} = C^T$. Now recall that $C$ and $C^{-1}$ can be used to diagonalize the force constant matrix $K$ using Equation 15.6

$$C^{-1}KC = \Lambda \quad (15.17)$$

where

$$C^{-1}KC = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \frac{2\kappa}{m} - \frac{\kappa}{m} & \frac{2\kappa}{m} \\ \frac{2\kappa}{m} & \frac{2\kappa}{m} \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \frac{\kappa}{m} & \frac{3\kappa}{m} \\ \frac{\kappa}{m} & \frac{3\kappa}{m} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 2\kappa \frac{m}{m} & 0 \\ 0 & 6\kappa \frac{m}{m} \end{pmatrix} = \Lambda$$

which defines the diagonal matrix

$$\Lambda = \begin{pmatrix} \frac{\kappa}{m} & 0 \\ 0 & \frac{3\kappa}{m} \end{pmatrix} = \begin{pmatrix} \omega_1^2 & 0 \\ 0 & \omega_2^2 \end{pmatrix}$$

with diagonal elements equal to the eigenvalues found through the solution of the secular equation. We see that one way of finding the eigenvalues is to diagonalize the force constant matrix $K$.

Now let’s use the eigenvector matrix $C$ to transform the equation of motion Equation 15.14 by multiplying from the left by $C^{-1}$ as

$$\frac{d^2}{dt^2} C^{-1} x(t) = -C^{-1}Kx(t)$$
and inserting the identity matrix \( I = CC^{-1} \) between \( K \) and \( x(t) \) as

\[
\frac{d}{dt} C^{-1} x(t) = -C^{-1} K x(t) = -C^{-1} K C C^{-1} x(t)
\]

We have shown that \( C^{-1} K C = \Lambda \) so that

\[
\frac{d}{dt} C^{-1} x(t) = -\Lambda C^{-1} x(t)
\]

Finally, let’s define a new displacement vector

\[
y(t) = \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = C^{-1} x(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} x_1 + x_2 \\ x_1 - x_2 \end{pmatrix}
\]

Following this transformation the equations of motion for our two masses take on the simple form

\[
\frac{d^2}{dt^2} y(t) = \frac{d^2}{dt^2} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = -\Lambda y(t) \tag{15.18}
\]

where

\[
\frac{d^2}{dt^2} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = -\begin{pmatrix} \frac{\kappa}{m} & 0 \\ 0 & \frac{3\kappa}{m} \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}
\]

where the components are known as the normal modes of oscillation.

We began with two coupled second order ordinary differential equations describing the local modes displacements \( x_1(t) \) and \( x_2(t) \). Following the transformation defined by the orthogonal eigenvector matrix \( C \) we arrive at two uncoupled second order ordinary differential equations for the motion of the normal modes

\[
y_1(t) = \frac{1}{\sqrt{2}} (x_1(t) + x_2(t)) \quad y_2(t) = \frac{1}{\sqrt{2}} (x_1(t) - x_2(t))
\]

The trajectory shown in Figure 15.9 as a function of local modes \( x_1 \) and \( x_2 \) is represented as a function of normal modes \( y_1 \) and \( y_2 \) in Figure 15.10. Transformation of the local mode displacement vector \( x(t) \) to the normal mode displacement vector \( y(t) \) leads to a rotation such that the bounding caustics form a square with sides parallel to the normal mode axes.

Finally, let’s return to the symmetric and asymmetric motions displayed in Figures 15.6, 15.7 and 15.8. The same time evolution of the displacements can be viewed on the two-dimensional plane where the abscissa is the displacement \( y_1 \) and the ordinate the displacement \( y_2 \) as shown in Figure 15.11. The horizontal red line represents the dynamics of the in-phase oscillation depicted in Figure 15.6 and the vertical blue line represents the dynamics of the out-of-phase oscillation depicted in Figure 15.7. When compared with Figure 15.8 we see that the transformation to normal mode coordinates converts coupled motion of two local mode coordinates to uncoupled motion of two one-dimensional normal mode coordinates.

We can extend this approach to the general case of \( N \) masses coupled to one another in three dimensions. In that case, the positions of the \( N \) masses are described by a vector \( x \) with \( 3N \) elements. When the coupling is quadratic, we express the equations of motion in terms of a \( 3N \times 3N \) force constant matrix \( K \). Solution of the secular equation \( |K - \omega^2 I| = 0 \) results in \( 3N \) eigenvalues and corresponding eigenvectors forming the frequencies and coordinates of \( 3N \) independent normal modes of motion.
Scalar operators and eigenfunctions

Eigenvalue problems are not restricted to the solution of matrix equations defined by real coefficients. More generally, eigenvalue problems may involve scalar operators rather than matrices and scalar functions rather than vectors. Moreover, eigenvalue problems are broadly defined for both real and complex matrices and functions. In this section, we explore the diverse applicability of the eigenvalue problem.

15.3.1 Eigenvalues and eigenfunctions of scalar operators

In Chapter 5 we explored the use of linear operators, including scalar operators, such as \( \hat{d}_x = \frac{d}{dx} \), and vector operators, such as the gradient \( \nabla \). The notion of a linear operator can be extended to the matrix eigenvalue problem

\[
A \mathbf{x} = \lambda \mathbf{x}
\]

(15.19)

where the matrix \( A \) can be thought of as a matrix operator.\(^{11}\)

Conversely, we can imagine forming an eigenvalue problem when no matrices are involved. For example, consider \( \hat{d}_x \phi(x) = a \phi(x) \) where \( \hat{d}_x \) acts on the scalar function \( \phi(x) \) resulting in the same function multiplied by a constant \( a \). We consider \( \phi(x) \) to be an eigenfunction and \( a \) to be the corresponding eigenvalue.\(^{12}\)

Let’s look at a few examples. Consider the operator \( \hat{p}_x = -i\hbar \hat{d}_x \) where \( \hbar \) is a constant. We can write the eigenvalue problem

\[
\hat{p}_x \phi(x) = -i\hbar \frac{d}{dx} \phi(x) = \hbar k \phi(x)
\]

(15.20)

where \( k \) is another constant and the goal is to identify the eigenfunction \( \phi(x) \). Using our knowledge of the solution of first order ordinary differential equations we propose

\[
\phi(x) = \exp(ikx)
\]

(15.22)

which has \( \hbar k \) as its corresponding eigenvalue.

Now consider the eigenvalue problem

\[
\hat{M} \Phi(\varphi) = \frac{d^2}{dx^2} \Phi(\varphi) = -m^2 \Phi(\varphi)
\]

(15.23)

where we seek the eigenfunction of the operator \( \hat{M} \). Using our knowledge of the solution of second order ordinary differential equations we propose

\[
\Phi(\varphi) = \exp(im\varphi)
\]

(15.24)

which has \( -m^2 \) as its corresponding eigenvalue.

As a final example, consider the eigenvalue problem arising in the quantum theory of a particle in a box where

\[
\hat{H} \psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)
\]

(15.25)

\( \hat{H} \) is the energy operator that acts on the wave function \( \psi(x) \) resulting in the function times the constant \( E \) corresponding to the energy of the particle. We
propose the sinusoidal function

\[ \psi(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{\pi}{L} x \right) \]  

(15.26)

which we can demonstrate to be an eigenfunction of the operator \( \hat{H} \) as

\[
\hat{H} \psi(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sqrt{\frac{2}{L}} \sin \left( \frac{\pi}{L} x \right) = -\frac{\hbar^2}{2m} \left[ -\left( \frac{\pi}{L} \right)^2 \sqrt{\frac{2}{L}} \sin \left( \frac{\pi}{L} x \right) \right]
\]
\[
= \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 \psi(x) = E \psi(x)
\]

This allows us to identify the corresponding eigenvalue

\[ E = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 = \frac{\hbar^2}{8mL^2} \]

where we have used the identity \( \hbar = \hbar/2\pi \).

### 15.3.2 Special properties and forms of hermitian operators

In Chapter 14 we explored the properties of complex matrices. We found that when a matrix \( C \) is equal to the transpose of its complex conjugate\(^{13}\)

\[ C = (C^*)^T \]

it is known as a **hermitian matrix**.\(^{14}\) The matrix \((C^*)^T = C^\dagger\) is called the **hermitian conjugate** of \( C \).

Consider the eigenvalue problem

\[ \hat{\sigma}_x \psi_+ = \lambda \psi_+ \]

where the matrix operator

\[ \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]

is hermitian since

\[ (\sigma_x^*)^T = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}_x \]

and the eigenvector is defined

\[ \psi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \]

Evaluating the expression

\[ \hat{\sigma}_x \psi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \psi_+ \]

allows us to identify the eigenvalue as the real number 1. In fact, for any eigenvalue problem in which the operator is hermitian the eigenvalues are real.

This is an important property of operators in the physical sciences where we encounter eigenvalue problems such as

\[ \hat{A} x = \lambda x \]  

(15.27)

in which \( \hat{A} \) is an **observable operator** meaning that the associated eigenvalue \( \lambda \) is a physical property that can be experimentally measured. As such, the eigenvalue...
A_15

End-of-chapter problems

“Mathematizing” may well be a creative activity of man, like language or music, of primary originality, whose historical decisions defy complete objective rationalization.

Herman Weyl

Warm-ups

15.1 Show that the eigenvector matrix

\[
\mathbf{C} = \begin{pmatrix}
\sqrt{6} & \sqrt{6} \\
\sqrt{15} & \sqrt{10} \\
3 & -2 \\
\sqrt{15} & \sqrt{10}
\end{pmatrix}
\]

has the inverse matrix

\[
\mathbf{C}^{-1} = \begin{pmatrix}
\sqrt{6} & 3 \\
\sqrt{15} & \sqrt{15} \\
\sqrt{6} & -2 \\
\sqrt{10} & \sqrt{10}
\end{pmatrix}
\]

by proving that \(\mathbf{C}^{-1}\mathbf{C} = \mathbf{I}\).

15.2 Show that the eigenvector matrix

\[
\mathbf{C} = \begin{pmatrix}
\sqrt{6} & \sqrt{6} \\
\sqrt{15} & \sqrt{10} \\
3 & -2 \\
\sqrt{15} & \sqrt{10}
\end{pmatrix}
\]
will diagonalize the matrix

\[ A = \begin{pmatrix} 1 & \sqrt{6} \\ \sqrt{6} & 2 \end{pmatrix} \]

by demonstrating that \( C^{-1}AC = \Lambda \), where \( \Lambda \) is the diagonal eigenvalue matrix.

15.3 Show that \( c \) and \( \lambda c \), where \( \lambda \) is a scalar, are parallel vectors in space. HINT: Make use of the definition of the scalar dot product.

15.4 Consider the matrix

\[ A = \begin{pmatrix} -1 & 2 \\ 2 & 2 \end{pmatrix} \]

(a) Determine the eigenvalues of \( A \) by finding the roots, \( \lambda_1 \) and \( \lambda_2 \), of the characteristic equation

\[ |A - \lambda I| = 0 \]

(b) For each eigenvalue, \( \lambda_1 \) and \( \lambda_2 \), find the corresponding normalized eigenvector, \( x_1 \) and \( x_2 \).

15.5 Consider the matrix

\[ A = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \]

(a) Determine the eigenvalues of \( A \) by finding the roots, \( \lambda_1 \) and \( \lambda_2 \), of the characteristic equation

\[ |A - \lambda I| = 0 \]

(b) For each eigenvalue, \( \lambda_1 \) and \( \lambda_2 \), find the corresponding normalized eigenvector, \( x_1 \) and \( x_2 \).

15.6 Consider the matrix

\[ A = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \]

(a) Determine the eigenvalues of \( A \) by finding the roots, \( \lambda_1 \), \( \lambda_2 \) and \( \lambda_3 \), of the characteristic equation

\[ |A - \lambda I| = 0 \]

(b) For each eigenvalue, \( \lambda_1 \), \( \lambda_2 \) and \( \lambda_3 \), find the corresponding normalized eigenvector, \( x_1 \), \( x_2 \) and \( x_3 \).

15.7 Show that \( y = \sin ax \) is not an eigenfunction of the operator \( d/dx \), but is an eigenfunction of the operator \( d^2/dx^2 \).

15.8 Show that the function \( \Phi(\varphi) = Ae^{im\varphi} \), where \( i, m, h, \) and \( A \) are constants, is an eigenfunction of the operator

\[ \hat{M}_z = \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \]

Determine the eigenvalue.

**Homework exercises**

15.9 Consider the matrix

\[ A = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \]

(a) Determine the eigenvalues of \( A \) by finding the roots, \( \lambda_1 \), \( \lambda_2 \) and \( \lambda_3 \), of the characteristic equation

\[ |A - \lambda I| = 0 \]
(b) For each eigenvalue, \(\lambda_1, \lambda_2\) and \(\lambda_3\), find the corresponding normalized eigenvector, \(x_1, x_2\) and \(x_3\).

15.10 Show that the matrix \(C\) and the corresponding inverse matrix \(C^{-1}\) defined

\[
C = \begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{2}}{2} & 1 \\
\frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} & 0 \\
1 & -\frac{\sqrt{2}}{2} & \frac{1}{2}
\end{pmatrix}, \quad C^{-1} = \begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{2}}{2} & 1 \\
\frac{\sqrt{2}}{2} & 0 & -\frac{\sqrt{2}}{2} \\
1 & -\frac{\sqrt{2}}{2} & \frac{1}{2}
\end{pmatrix}
\]

will put the matrix

\[
A = \begin{pmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E
\end{pmatrix}
\]

into diagonal form and that the diagonal elements are the roots of the characteristic equation \(|A - \lambda I| = 0\).

15.11 Solve the simultaneous equations

\[
\frac{d}{dt} x = Ax = \frac{1}{2} \begin{pmatrix} 1 & \sqrt{5} \\ \sqrt{5} & 1 \end{pmatrix} x
\]

for the initial condition \(x(0) = (1 \quad 0)^T\).

15.12 Solve the simultaneous equations

\[
\frac{d}{dt} x = Ax = \begin{pmatrix} -1 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -1 \end{pmatrix} x
\]

for the initial condition \(x(0) = (1 \quad 0 \quad 0)^T\).

15.13 Consider the case of two masses moving on a line and connected by springs to solid supports and each other (see Figure 15.5). The potential energy of interaction is given by

\[
V(x_1, x_2) = \frac{k_1}{2} x_1^2 + \frac{k}{2} (x_2 - x_1)^2 + \frac{k_2}{2} x_2^2
\]

where \(x_1\) and \(x_2\) are the displacements of each mass from the minimum of energy \(V(0, 0) = 0\). Rewrite the potential energy in terms of the variables \(y_1 = x_1 + x_2\) and \(y_2 = x_1 - x_2\). Interpret your result.

15.14 Consider the equation of motion for two masses moving on a line and coupled by springs to solid supports and each other (see Figure 15.5)

\[
\frac{d^2}{dt^2} x = \frac{d^2}{dt^2} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = -\frac{k}{m} \begin{pmatrix} 2 & -1 \\ -1 & 2 \end{pmatrix} x = -Kx
\]

(a) Show that the corresponding orthogonal eigenvector matrix

\[
C = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}
\]

can be used to diagonalize \(K\) as

\[
C^{-1} KC = \Lambda
\]

where \(\Lambda\) is the eigenvalue matrix the elements of which are the eigenvalues.

(b) Prove that the equation of motion can be rewritten in diagonalized form

\[
\frac{d^2}{dt^2} y = \Lambda y
\]
where

\[ y(t) = Cx = \begin{pmatrix} y_1(t) \\ y_2(t) \end{pmatrix} \]

(c) Interpret the character of \( y_1 \) and \( y_2 \) by relating the nature of the motion (in-phase or out-of-phase) to the time scales of motion implied by the corresponding eigenvalues.

15.15 Consider two masses moving on a line and coupled by springs to solid supports and each other (see Figure 15.5). The potential energy is given by

\[ V(x_1, x_2) = 5k x_1^2 + 6k (x_2 - x_1)^2 + \frac{3k}{2} x_2^2 \]

where \( x_1 \) and \( x_2 \) are the displacements of each mass from the minimum of energy \( V(0,0) \). Take the masses to be \( m_1 = m_2 = m = 1 \). The corresponding equations are motion for the two masses are

\[ \frac{d^2}{dt^2} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = -\frac{k}{m} \begin{pmatrix} 22 & -12 \\ -12 & 15 \end{pmatrix} x = -Kx \]

Note that a matrix

\[ \begin{pmatrix} a + b & -b \\ -b & b + c \end{pmatrix} \]

for which \( a - c, 2b, \) and \( \sqrt{(a-c)^2 + 4b^2} \) form a Pythagorean triple will result in integer eigenvalues. In this case, \( a = 10, b = 12, \) and \( c = 3 \) forming the Pythagorean triple \((7, 24, 25)\) since \( 7^2 + 24^2 = 25^2 \). As such, we expect to find integer eigenvalues.

(a) Solve the characteristic equation

\[ |K - \omega^2 I| = 0 \]

to find the eigenvalues represented as the allowed squared frequencies \( \omega_1^2 \) and \( \omega_2^2 \).

(b) Use the eigenvector equation

\[ (K - \omega_k^2 I) x_k = 0 \]

to identify the eigenvector corresponding to each eigenvalue.

15.16 Consider the generalization of the system shown in Figure 15.5 to a system consisting of three masses moving on a line and connected by springs to solid supports and each other. The potential energy of interaction is given by

\[ V(x_1, x_2, x_3) = k x_1^2 + \frac{k}{2} (x_2 - x_1)^2 + \frac{k}{2} x_2^2 + \frac{k}{2} (x_3 - x_2)^2 + k x_3^2 \]

where \( x_1, x_2, \) and \( x_3 \) are the displacements of each mass from the minimum of energy \( V(0,0,0) = 0 \).

\[ x_1 = 0 \quad x_2 = 0 \quad x_3 = 0 \quad x \]

(a) Derive the equations of motion

\[ m_1 \frac{d^2 x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \quad m_2 \frac{d^2 x_2}{dt^2} = -\frac{\partial V}{\partial x_2} \quad m_3 \frac{d^2 x_3}{dt^2} = -\frac{\partial V}{\partial x_3} \]
where \( m_1 = m_2 = m_3 = m = 1 \) are the three masses.

(b) Rewrite the equations of motion in the matrix format

\[
\frac{d^2}{dt^2} \mathbf{x} = -\mathbf{Kx}
\]

where \( \mathbf{x} \) is the displacement vector

\[
\mathbf{x}(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \end{pmatrix}
\]

and \( \mathbf{K} \) is the force constant matrix.

(c) Propose a solution of the form

\[
\mathbf{x}(t) = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} e^{i\omega t}
\]

and insert it into the equation you derived in (b). Rearrange the terms to find the equation

\[
\omega^2 \mathbf{x} = \mathbf{Kx}
\]

(d) Solve the characteristic equation

\[
|\mathbf{K} - \omega^2 I| = 0
\]

to find the eigenvalues represented as the allowed squared frequencies \( \omega_1^2, \omega_2^2 \) and \( \omega_3^2 \).

(e) Use the eigenvector equation

\[
\left( \mathbf{K} - \omega_k^2 \mathbf{I} \right) \mathbf{x}_k = 0
\]

to identify the eigenvector corresponding to each eigenvalue.

(f) Interpret the motions associated with each eigenvector \( \mathbf{x}_1, \mathbf{x}_2, \) and \( \mathbf{x}_3 \) and its corresponding vibrational frequency \( \omega_1, \omega_2, \) and \( \omega_3 \).

15.17 Consider the generalization of the system shown in Figure 15.5 to a system consisting of three masses moving on a line and connected by springs to each other. The potential energy of interaction is given by

\[
V(x_1, x_2, x_3) = \frac{k}{2} (x_2 - x_1)^2 + \frac{k}{2} (x_3 - x_2)^2
\]

where \( x_1, x_2, \) and \( x_3 \) are the displacements of each mass from the minimum of energy \( V(0,0,0) = 0 \).

\[
\begin{array}{ccc}
& & \\
m & m & m \\
& \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet
\end{array}
\]

\[
x_1 = 0 \\ x_2 = 0 \\ x_3 = 0 \\ x
\]

(a) Derive the equations of motion

\[
m_1 \frac{d^2 x_1}{dt^2} = -\frac{\partial V}{\partial x_1} \\
m_2 \frac{d^2 x_2}{dt^2} = -\frac{\partial V}{\partial x_2} \\
m_3 \frac{d^2 x_3}{dt^2} = -\frac{\partial V}{\partial x_3}
\]

where \( m_1 = m_2 = m_3 = m = 1 \) are the three masses.
(b) Rewrite the equations of motion in the matrix format
\[ \frac{d^2}{dt^2} \mathbf{x} = -\mathbf{Kx} \]
where \( \mathbf{x} \) is the displacement vector
\[ \mathbf{x}(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \end{pmatrix} \]
and \( \mathbf{K} \) is the force constant matrix.

(c) Solve the characteristic equation
\[ |\mathbf{K} - \omega^2 \mathbf{I}| = 0 \]
to find the eigenvalues represented as the allowed squared frequencies \( \omega_1^2, \omega_2^2 \) and \( \omega_3^2 \).

(d) Use the eigenvector equation
\[ (\mathbf{K} - \omega_k^2 \mathbf{I}) \mathbf{x}_k = \mathbf{0} \]
to identify the eigenvector corresponding to each eigenvalue.

(e) Interpret the motions associated with each eigenvector \( \mathbf{x}_1, \mathbf{x}_2, \) and \( \mathbf{x}_3 \) and its corresponding vibrational frequency \( \omega_1, \omega_2, \) and \( \omega_3 \).

15.18 Consider a diatomic molecule such as dioxygen physisorbed to a metallic surface. We model the system as two masses constrained to move on a line. The two masses are bonded together by a spring, and one of the masses is bonded to the solid surface by a second spring (see below).

The potential energy of interaction is given by
\[ V(x_1, x_2) = \frac{39}{2} kx_1^2 + \frac{380}{2} k(x_2 - x_1)^2 \]
where \( x_1 \) and \( x_2 \) are the displacements of each mass relative to the minimum energy position \((0, 0)\) where \( V(0, 0) = 0 \).

The masses of the two atoms are \( m_1 = m_2 = m \). The equation of motion in matrix form is
\[ \frac{d^2}{dt^2} \mathbf{x} = \frac{d^2}{dt^2} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = -\frac{k}{m} \begin{pmatrix} 419 & -380 \\ -380 & 380 \end{pmatrix} \mathbf{x} = -\mathbf{Kx} \]

(a) Propose a solution of the form
\[ \mathbf{x}(t) = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} e^{i\omega t} \]
and insert it into the equation of motion above. Rearrange the terms to find the equation
\[ \omega^2 \mathbf{x} = \mathbf{Kx} \]
(b) Solve the characteristic equation
\[ |K - \omega^2 I| = 0 \]
to find the eigenvalues represented as the allowed squared frequencies \( \omega_1^2 \) and \( \omega_2^2 \).
(c) Use the eigenvector equation
\[ (K - \omega_k^2 I)x_k = 0 \]
to identify the eigenvector corresponding to each eigenvalue.
(d) Interpret the motions associated with each eigenvector \( x_1 \) and \( x_2 \) and its corresponding vibrational frequency \( \omega_1 \) and \( \omega_2 \).

15.19 Radioactive decay of a certain nucleus satisfies the following kinetic equations
\[
\begin{align*}
\frac{dA}{dt} &= -2A \\
\frac{dB}{dt} &= 2A - B \\
\frac{dC}{dt} &= B
\end{align*}
\]

(a) By defining the concentration vector
\[
x(t) = \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix}
\]
the rate equations can be written in the matrix form
\[
\frac{d}{dt} x = Kx
\]
where \( K \) is the rate coefficient matrix. What is \( K \)?
(b) By proposing a solution of the form
\[
x(t) = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} e^{at}
\]
where \( a, b, c \) and \( \alpha \) are constants, the rate equation can be written
\[
\frac{d}{dt} x = a x = Kx
\]
which puts it in the form of an eigenvalue problem
\[ Kx = \alpha x \]
Solve the characteristic equation
\[ |K - \alpha I| = 0 \]
to find the three eigenvalues \( \alpha_1, \alpha_2 \) and \( \alpha_3 \).
(c) Find the eigenvectors \( x_1, x_2 \) and \( x_3 \) corresponding to the eigenvalues \( \alpha_1, \alpha_2 \) and \( \alpha_3 \).
(d) The general solution capturing the time-dependent populations of the nuclear species can be written
\[
x(t) = \begin{pmatrix} A(t) \\ B(t) \\ C(t) \end{pmatrix} = d_1 x_1 e^{\alpha_1 t} + d_2 x_2 e^{\alpha_2 t} + d_3 x_3 e^{\alpha_3 t}
\]
where \( d_1, d_2 \) and \( d_3 \) are constant coefficients. Determine the values of the three coefficients given the initial conditions \( A(0) = A_0 \) and \( B(0) = C(0) = 0 \).

15.20∗ Two pendula of length \( l \) and mass \( m \) are coupled by a spring with force constant \( k \). The equations of motion for the displacements \( s_1 \) and \( s_2 \) along the arc of motion of each pendulum are
\[
\begin{align*}
m \frac{d^2}{dt^2} s_1 &= -\frac{mg}{l} s_1 + k(s_2 - s_1) \\
m \frac{d^2}{dt^2} s_2 &= -\frac{mg}{l} s_2 - k(s_2 - s_1)
\end{align*}
\]
(a) First divide each equation by the mass, \( m \). Reformulate the equations in matrix notation as
\[
\frac{d^2}{dt^2} \mathbf{x} = -\mathbf{K} \mathbf{x}
\]
where the displacement vector
\[
\mathbf{x}(t) = \begin{pmatrix} s_1(t) \\ s_2(t) \end{pmatrix}
\]
(b) By proposing a solution of the form
\[
\mathbf{x}(t) = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} e^{i\omega t}
\]
the equation of motion can be written
\[
\frac{d^2}{dt^2} \mathbf{x} = -\omega^2 \mathbf{x} = -\mathbf{K} \mathbf{x}
\]
leading to the characteristic equation
\[
|\mathbf{K} - \omega^2 \mathbf{I}| = 0
\]
Solve the characteristic equation to find the two eigenvalues \( \omega_1 \) and \( \omega_2 \).
(c) Find the eigenvectors \( \mathbf{x}_1 \) and \( \mathbf{x}_2 \) corresponding to the eigenvalues \( \omega_1 \) and \( \omega_2 \).
The general solution capturing the time-dependent displacements of the pendula can be written
\[
\mathbf{x}(t) = \begin{pmatrix} s_1(t) \\ s_2(t) \end{pmatrix} = d_1 \mathbf{x}_1 e^{i\omega_1 t} + d_2 \mathbf{x}_2 e^{i\omega_2 t}
\]
(d) What are the coefficients \( d_1 \) and \( d_2 \) for \( s_1(0) = s_2(0) = s_0 \). Describe the corresponding motion.
(e) What are the coefficients \( d_1 \) and \( d_2 \) for \( s_1(0) = -s_2(0) = s_0 \). Describe the corresponding motion.

15.21 Show that the functions
\[
\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}
\]
where \( L \) is a constant and \( n = 1, 2, 3, \ldots \) are eigenfunctions of the operator
\[
\hat{H} = -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2}
\]
when \( \hbar \) and \( m \) are constants. What are the eigenvalues?

15.22 Show that the function \( \varphi(x) = x e^{ax} \) is an eigenfunction of the operator
\[
\hat{O} = \frac{d^2}{dx^2} - \frac{2a}{x}
\]
where \( a \) is a constant. What is the eigenvalue?

15.23 Consider the Pauli matrices
\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]
(a) Prove the matrices are hermitian by showing that \((A^\dagger)^T = A\) for each matrix.
(b) Consider the eigenvalue problems
\[
\sigma_x \psi_{x^+} = \lambda \psi_{x^+} \quad \sigma_y \psi_{y^+} = \lambda \psi_{y^+} \quad \sigma_z \psi_{z^+} = \lambda \psi_{z^+}
\]
for the eigenvectors
\[
\psi_{x^+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \psi_{y^+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad \psi_{z^+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]
What is the corresponding eigenvalue for each eigenvector?
(c) For the eigenvalue problems
\[ \sigma_x \psi_x = -1 \psi_x \quad \sigma_y \psi_y = -1 \psi_y \quad \sigma_z \psi_z = -1 \psi_z \]
determine the normalized eigenvectors \( \psi_x \), \( \psi_y \) and \( \psi_z \).

15.24∗ Consider the eigenvalue problem
\[ \hat{\sigma} \psi = \lambda \psi \]
where \( \hat{\sigma} \) is a hermitian operator, \( \psi \) is the eigenvector, and \( \lambda \) is the corresponding eigenvalue. Prove that the eigenvalue \( \lambda \) is real.

15.25∗ Consider the eigenvalue problems
\[ \hat{\sigma} \psi_1 = \lambda_1 \psi_1 \quad \hat{\sigma} \psi_2 = \lambda_2 \psi_2 \]
where \( \hat{\sigma} \) is a hermitian operator, \( \psi_1 \) and \( \psi_2 \) are eigenvectors, \( \lambda_1 \) and \( \lambda_2 \) are the corresponding eigenvalues, and \( \lambda_1 \neq \lambda_2 \). Prove that the eigenvectors \( \psi_1 \) and \( \psi_2 \) are orthogonal.
16 Geometric transforms and molecular symmetry

16.1 Eigenvectors, geometric transforms, and symmetry

Matrices can be used to transform one orientation of a vector into another. In this section, we survey matrices describing fundamental geometric transformations in two-dimensions, including scaling, inversion, rotation, and reflection.

16.1.1 Using eigenvalues and eigenvectors to explore symmetry

In two-dimensions, geometric objects can be related to one another using transformations that scale the size of an object or invert, reflect or rotate its shape. Those transformations can be defined in terms of a geometric mapping

\[ T \mathbf{x} = \mathbf{x}' \quad (16.1) \]

where one point on the xy-plane, defined by the vector \( \mathbf{x} \), is mapped into another, \( \mathbf{x}' \), by a transformation defined by the matrix \( T \). Let’s explore how fundamental geometric transformations on the xy-plane can be performed using \( 2 \times 2 \) matrices and how those transformations can be characterized in terms of matrix eigenvalues and eigenvectors.

Scaling

Consider the scaling transformation defined by the matrix

\[ \mathbf{S}_v = \begin{pmatrix} k_1 & 0 \\ 0 & k_2 \end{pmatrix} \]

where \( k_1 \) and \( k_2 \) are constants.\(^1\) This matrix transforms one point \( \mathbf{x} \) into another \( \mathbf{x}' \) as

\[ \mathbf{S}_v \mathbf{x} = \begin{pmatrix} k_1 & 0 \\ 0 & k_2 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} k_1 x \\ k_2 y \end{pmatrix} = \mathbf{x}' \]

leading to scaling by a factor of \( k_1 \) in the x-direction and \( k_2 \) in the y-direction (see Figure 16.1).

Let’s characterize the transformation matrix \( \mathbf{S}_v \) in terms of its eigenvalues and eigenvectors. The eigenvalues are defined by the characteristic equation, Equation 15.9, and determined by solving the characteristic polynomial that is a quadratic equation in \( \lambda \)

\[ |\mathbf{S}_v - \lambda I| = \begin{vmatrix} k_1 - \lambda & 0 \\ 0 & k_2 - \lambda \end{vmatrix} = (k_1 - \lambda)(k_2 - \lambda) = 0 \]

The solutions of the characteristic polynomial are the eigenvalues \( \lambda_1 = k_1 \) and

\[ \mathbf{v} = \begin{pmatrix} k_1 \\ k_2 \end{pmatrix} \]

is a scaling vector with elements \( k_1 \) and \( k_2 \) that define the scaling factor in each dimension.

\( ^1 \) The transformation matrix \( \mathbf{S}_v \) can also be written

\[ \mathbf{S}_v = \mathbf{Iv} \]

where \( \mathbf{I} \) is the identity matrix and

\[ \mathbf{v} = \begin{pmatrix} k_1 \\ k_2 \end{pmatrix} \]
\[ \lambda_2 = k_2. \] The corresponding eigenvectors are defined by Equation 15.10 as

\[
(S_v - \lambda_1 I) \mathbf{x}_1 = \begin{pmatrix} 0 & 0 \\ 0 & k_2 - k_1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

and

\[
(S_v - \lambda_2 I) \mathbf{x}_2 = \begin{pmatrix} k_1 - k_2 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

leading to

\[
\mathbf{x}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \mathbf{x}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

We see that the orthonormal eigenvectors define the principal scaling directions and the eigenvalues the degree of scaling in each direction.

**Shear scaling**

Consider the shear transformation defined by the matrix

\[
S = \begin{pmatrix} 1 & k \\ 0 & 1 \end{pmatrix}
\]

where the characteristic equation is

\[
|S - \lambda I| = \begin{vmatrix} 1 - \lambda & k \\ 0 & 1 - \lambda \end{vmatrix} = (1 - \lambda)^2 = 0
\]

and the solutions of the characteristic polynomial are a single root \( \lambda_1 = \lambda_2 = 1. \)

![Figure 16.2: Shear scaling of an area (red) resulting in the sheared area (gray). The single eigenvector of the 2 x 2 shear matrix S is shown for k = 1/2 (red arrow).](image)

This degeneracy results in a single eigenvector defined by

\[
(S - \lambda I) \mathbf{x} = \begin{pmatrix} 0 & k \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

leading to

\[
\mathbf{x} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]

Transformation by \( S \) leads to shear scaling where for a given vector the \( y \)-component is unchanged while the \( x \)-component is scaled by a constant factor of \( 1 + k \) (see Figure 16.2).
Uniform scaling

Now consider the uniform scaling transformation matrix

\[ S_v = \begin{pmatrix} k & 0 \\ 0 & k \end{pmatrix} = kI \]

where I is the identity matrix. This is a special case of the general scaling transformation in which the diagonal elements are identical. The characteristic equation is defined

\[ |S_v - \lambda I| = \begin{vmatrix} k - \lambda & 0 \\ 0 & k - \lambda \end{vmatrix} = (k - \lambda)^2 = 0 \]

and the solutions of the characteristic polynomial are the eigenvalues \( \lambda_1 = \lambda_2 = k \). The corresponding eigenvectors are defined by

\[ (S_v - \lambda_1 I)x_1 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \]

and an identical equation for \( x_2 \). Any values of \( c_1 \) and \( c_2 \) satisfy the equation. As such, any vectors in the \( xy \)-plane are eigenvectors of the uniform scaling transformation that acts to scale all elements of any vector by a factor of \( k \) (see Figure 16.3).

Note that for \( k = 1 \) the uniform scaling transformation becomes the identity transformation

\[ S_v = E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

Normally we represent the identity matrix as I. In the context of geometric transforms, E is most commonly used rather than I to represent the identity transformation.\(^2\)

Rotation

Let’s evaluate the rotation transformation defined by

\[ R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \]

which we recognize to be the orthogonal \( 2 \times 2 \) rotation matrix defining counterclockwise rotation through an angle \( \theta \) in the \( xy \)-plane.\(^3\) The characteristic equation is

\[ |R(\theta) - \lambda I| = \begin{vmatrix} \cos \theta - \lambda & -\sin \theta \\ \sin \theta & \cos \theta - \lambda \end{vmatrix} = (\cos \theta - \lambda)^2 + \sin^2 \theta = 0 \]

Expanding the square leads to

\[ \lambda^2 - 2\lambda \cos \theta + \cos^2 \theta + \sin^2 \theta = \lambda^2 - 2\lambda \cos \theta + 1 = 0 \]

and the roots

\[ \lambda = \cos \theta \pm \sqrt{\cos^2 \theta - 1} = \cos \theta \pm \sqrt{-\sin^2 \theta} \\
= \cos \theta \pm i \sin \theta = e^{\pm i\theta} \]

defining the complex eigenvalues \( \lambda_1 = e^{-i\theta} \) and \( \lambda_2 = e^{i\theta} \). For \( \lambda_1 = e^{-i\theta} \) the

\(^2\) The E is taken from the German einheit meaning unity.

\(^3\) Eigenvectors were originally discovered by Italian mathematician and astronomer Joseph-Louis Lagrange (1736-1813) in the context of studying rigid body rotational motion.
eigenvector is defined by
\[
(R(\theta) - \lambda_1 I) \mathbf{x}_1 = \begin{pmatrix} i \sin \theta & - \sin \theta \\ \sin \theta & i \sin \theta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution \( c_1 = 1 \) and \( c_2 = i \). For \( \lambda_2 = e^{i \theta} \) the eigenvector is defined by
\[
(R(\theta) - \lambda_2 I) \mathbf{x}_2 = \begin{pmatrix} -i \sin \theta & - \sin \theta \\ \sin \theta & -i \sin \theta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution \( c_1 = i \) and \( c_2 = 1 \). The normalized complex eigenvectors can be written
\[
\mathbf{x}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad \mathbf{x}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} i \\ 1 \end{pmatrix}
\]
independent of the value of \( \theta \).

Transformation by \( R(\theta) \) leads to counter-clockwise rotation through an angle \( \theta \) in the \( xy \)-plane that preserves the length of the vector (see Figure 16.4). Note that the eigenvectors of the rotation matrix \( \mathbf{x}_1 \) and \( \mathbf{x}_2 \) are normalized and orthogonal.\(^4\)

Reflection

Let’s evaluate the reflection transformation defined by
\[
\sigma(\theta) = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}
\]
where \( \sigma(\theta) \) is the reflection matrix that performs a reflection across a line passing through the origin and making an angle \( \theta \) with the \( x \)-axis (see Figure 16.5). The characteristic equation is
\[
|\sigma(\theta) - \lambda I| = \begin{vmatrix} \cos 2\theta - \lambda & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta - \lambda \end{vmatrix}
= - (\cos 2\theta - \lambda)(\cos 2\theta + \lambda) - \sin^2 2\theta = 0
\]
Expanding the square leads to
\[
\lambda^2 - \cos^2 2\theta - \sin^2 2\theta = \lambda^2 - 1 = (\lambda + 1)(\lambda - 1) = 0
\]
with roots defining the eigenvalues \( \lambda_1 = 1 \) and \( \lambda_2 = -1 \).
Consider the specific case of $\theta = 3\pi/4$. The eigenvector corresponding to $\lambda_1 = 1$ is defined by
\[
\left(\sigma\left(\frac{3\pi}{4}\right) - \lambda_1 I\right) x_1 = \begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution $c_1 = -c_2 = 1$. For $\lambda_2$ the eigenvector is defined by
\[
\left(\sigma\left(\frac{3\pi}{4}\right) - \lambda_2 I\right) x_2 = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
with the solution $c_1 = c_2 = 1$. The normalized eigenvectors are
\[
x_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad x_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]
This transformation leads to a reflection across the diagonal defined by $x = -y$ that preserves the length of the vector (see Figure 16.5).

How can we interpret the eigenvalues and eigenvectors of $\sigma(\theta)$? Note that $x_1$ defines the line of reflection, while $x_2$ is perpendicular to the line of reflection. Any vector parallel to the line of reflection is unchanged as $\sigma(\theta)x_1 = x_1$, while any vector perpendicular to the line of reflection is reversed in orientation as $\sigma(\theta)x_2 = -x_2$.

**Inversion**

Let’s evaluate the inversion transformation defined by
\[
i = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\]
where $i$ is the inversion matrix resulting in inversion through the origin. The characteristic equation is
\[
|i - \lambda I| = \begin{vmatrix} -1 - \lambda & 0 \\ 0 & -1 - \lambda \end{vmatrix} = (1 + \lambda)^2 = 0
\]
with roots defining the eigenvalues $\lambda_1 = \lambda_2 = -1$.

The corresponding eigenvectors are defined
\[
(i - \lambda_1 I) x_1 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]
and an identical equation for $x_2$. Both equations are satisfied by any values of $c_1$ and $c_2$. As such, any vectors in the $xy$-plane are eigenvectors of the matrix $i$.

The inversion transformation is described graphically in Figure 16.6. The transformation leads to an inversion of any vector in the $xy$-plane preserving the vector magnitude. An object is said to possess inversion symmetry when the transformation
\[
x \rightarrow -x
\]
leaves the object unchanged.

**16.1.2 Geometric transformations in three-dimensions**

The geometric transformations that characterize scaling, rotation, reflection and inversion have been defined in two-dimensions. In this section, we extend our
definitions of symmetry operations from two-dimensions to three-dimensions.

Consider the identity transformation in three-dimensions defined by the identity matrix

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The identity transformation is a special case of the uniform scaling transformation that leaves the coordinate vector unchanged as $Ex = x$.

Now consider the rotation transformation in three-dimensions. The matrix

$$R_z(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

leads to counter-clockwise rotation of a vector through an angle $\theta$ about the z-axis. The x and y coordinates are transformed by counterclockwise rotation in the xy-plane, while the z-coordinate is left unchanged. Similar matrices lead to rotation of a vector about the x-axis or y-axis

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix} \quad R_y(\theta) = \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{pmatrix}$$

through an angle $\theta$ in the counter-clockwise direction.

The reflection transformation in three-dimensions is defined by the reflection matrix

$$\sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

that leads to the reflection of a vector across the xy-plane. Similar reflection matrices lead to reflection of a vector across the yz-plane or xz-plane

$$\sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In addition, compound improper rotations can be defined by successive rotation and reflection transformations.

Finally, consider the inversion transformation in three-dimensions is defined by the inversion matrix

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

resulting in inversion through the origin. The inversion transformation reverses the x, y, and z coordinates as $ix = -x$.

In considering molecular conformations, the principal symmetries of interest are characterized by the identity, rotation, reflection, and inversion transformations. By defining a molecular conformation in terms of vectors representing the position of each atom in three dimensional cartesian coordinates, we can use the transformation matrices defined above to rotate, reflect or invert the atomic positions and identify the underlying molecular symmetries.
16.2 Matrix transformations and molecular symmetry

Symmetry plays a critical role in defining the properties of molecular systems. Just as matrices can be used to transform one orientation of a vector into another, matrices can be used to transform one orientation of a molecule into another. In this section, we explore how vectors can be used to describe molecular orientations in three-dimensions and how matrix transforms can be used to define and assess molecular symmetry.

16.2.1 Using matrices to define symmetry in molecules

The basic structure of a molecule can be defined in terms of geometries such as trigonal planar, tetrahedral, trigonal bipyramidal and octahedral. Those geometries can be further analyzed in terms of symmetry transformations such as inversion, rotation, and reflection. The arrangement of atoms in a crystal, such as the carbon atoms forming a diamond lattice (see Figure 16.7), can also be described in terms of basic symmetries. In addition, symmetry plays a critical role in the interpretation of molecular spectra. We will use our knowledge of transformation matrices to explore and define molecular symmetry.

16.2.2 The symmetries of H₂O (water)

The point group of a molecule is defined by the set of symmetry transformations that result in a final orientation of the molecule that is indistinguishable from its initial orientation. The term point group is derived from the fact that all planes of reflection symmetry, axes of rotational symmetry, and planes and axes of improper rotational symmetry intersect at a single point.

For example, consider the water molecule (see Figure 16.8). We describe its conformation using vectors by placing the oxygen atom at the origin

\[ \mathbf{x}_O = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \]

and assigning vectors to describe the position of each hydrogen atom relative to the central oxygen atom\(^5\)

\[ \mathbf{x}_{H1} = \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix}, \quad \mathbf{x}_{H2} = \begin{pmatrix} -c_1 \\ 0 \\ c_2 \end{pmatrix} \]

where we have placed the hydrogen atoms in the \(xz\)-plane so that \(y = 0\).

\(^5\)The O–H bond lengths are \(r_{OH} = |\mathbf{x}_{H1}| = |\mathbf{x}_{H2}| = \sqrt{c_1^2 + c_2^2} = 96\text{pm}\) and the H–O–H angle is \(\theta_{HOH} = \cos^{-1}(\mathbf{x}_{H1} \cdot \mathbf{x}_{H2} / |\mathbf{x}_{H1}| |\mathbf{x}_{H2}|) = 104.5^\circ\).
The first symmetry of the water molecule that we note is the *identity symmetry* defined by

\[ E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  

(16.2)

The identity transformation applied to the position of each atom leads to

\[ E x_O = x_O \quad E x_{H_1} = x_{H_1} \quad E x_{H_2} = x_{H_2} \]

The final orientation of the water molecule is identical to and indistinguishable from the initial orientation. As such, we say that the water molecule possesses *E* identity symmetry.

In fact, every molecule we consider will possess identity symmetry.

We can also identify *rotational symmetry* of the water molecule. Suppose we apply a two-fold counter-clockwise rotation about the positive \( z \)-axis (the black rod in Figure 16.9) through an angle \( \theta = \pi \) defined by the \( 3 \times 3 \) rotation matrix

\[ C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  

(16.3)

to vectors describing the position of each atom in the water molecule as

\[ C_2 x_O = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} = x_O \]

and similarly

\[ C_2 x_{H_1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} -c_1 \\ 0 \end{pmatrix} = x_{H_1} \]

and

\[ C_2 x_{H_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = x_{H_2} \]

We find rotation through an angle \( \theta = \pi \) leaves the position of the oxygen atom unchanged while exchanging the positions of the two hydrogen atoms. Since we consider the hydrogen atoms to be indistinguishable, the transformed orientation of the water molecule is indistinguishable from the initial orientation. As a result, we say that the water molecule possesses \( C_2 \) rotational symmetry.

We can also consider *reflection symmetry*. Reflection transformations are defined by the matrices \( \sigma_{xz} \), for reflection across the \( xz \)-plane, and \( \sigma_{yz} \), for reflection across the \( yz \)-plane

\[ \sigma_{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  

(16.4)

Let’s see how this works. As the atoms of the water molecule are in the \( xz \)-plane (the red surface in Figure 16.10) we expect that reflection across the \( xz \)-plane will leave the orientation of the water molecule unchanged. Applying \( \sigma_{xz} \) to the...
position vector of the oxygen atom as
\[ \sigma_{xz} \mathbf{x}_O = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{x}_O \]
results in no change in the position of the oxygen atom. Similarly, applying \( \sigma_{xz} \) to the position vectors of the hydrogen atoms as
\[ \sigma_{xz} \mathbf{x}_{H_1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix} = \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix} = \mathbf{x}_{H_1} \]
and
\[ \sigma_{xz} \mathbf{x}_{H_2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -c_1 \\ 0 \\ c_2 \end{pmatrix} = \begin{pmatrix} -c_1 \\ 0 \\ c_2 \end{pmatrix} = \mathbf{x}_{H_2} \]
leads to no change in the positions of the hydrogen atoms. As the reflection transformation \( \sigma_{xz} \) leads to no change in the orientation of the water molecule, we say that the water molecule possesses \( \sigma_{xz} \) reflection symmetry.

Now let’s explore reflection across the \( yz \)-plane (the gray surface in Figure 16.10) defined by \( \sigma_{yz} \). Applying \( \sigma_{yz} \) to vectors defining the positions of atoms of the water molecule leads to
\[ \sigma_{yz} \mathbf{x}_O = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{x}_O \]
and similarly
\[ \sigma_{yz} \mathbf{x}_{H_1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix} = \begin{pmatrix} -c_1 \\ 0 \\ c_2 \end{pmatrix} = \mathbf{x}_{H_1} \]
and
\[ \sigma_{yz} \mathbf{x}_{H_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -c_1 \\ 0 \\ c_2 \end{pmatrix} = \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix} = \mathbf{x}_{H_2} \]
The transformation by \( \sigma_{yz} \) leads to exchange of the positions of the two hydrogens atoms. However, as the hydrogen atoms are indistinguishable there is no distinguishable change in the orientation of the water molecule. We say that the water molecule possesses \( \sigma_{yz} \) reflection symmetry.

Finally, let’s see what happens when evaluating a symmetry that the water molecule does not possess. Consider inversion symmetry defined by the inversion transformation matrix
\[ \mathbf{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \] (16.5)
which we apply to the water molecule as
\[ \mathbf{i} \mathbf{x}_O = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{x}_O \]
and similarly
\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
c_1 \\
0 \\
c_2
\end{pmatrix}
= \begin{pmatrix}
-c_1 \\
0 \\
-c_2
\end{pmatrix}
\]

and
\[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
-c_1 \\
0 \\
c_2
\end{pmatrix}
= \begin{pmatrix}
c_1 \\
0 \\
-c_2
\end{pmatrix}
\]

As the resulting orientation of the water molecule is distinguishably different from the initial orientation (see Figure 16.11), we say that the water molecule does not possess inversion symmetry.

16.2.3 The symmetries of BH$_3$ (borane)

Let’s consider the case of the BH$_3$ molecule known as borane (see Figure 16.12). We describe the orientation of the borane molecule by defining the positions of each atom in terms of a vector. We place the boron atom at the origin

\[
x_B = \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix}
\]

and assign a vector to describe the position of each hydrogen atom relative to the boron atom.
the central boron atom

\[
x_{H_1} = \begin{pmatrix} c_1 \\ 0 \\ 0 \end{pmatrix} \quad x_{H_2} = \begin{pmatrix} \frac{1}{2}c_1 \\ \sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} \quad x_{H_3} = \begin{pmatrix} \frac{1}{2}c_1 \\ -\sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix}
\]

where we have placed the hydrogen atoms in the \(xy\)-plane so that \(z = 0\).

Based on our experience in evaluating the symmetries of the water molecule, we expect to find three-fold rotational symmetry of the \(BH_3\) molecule defined by counter-clockwise rotation about the positive \(z\)-axis (the black rod in Figure 16.13) through an angle \(\theta = 2\pi/3\) defined by the matrix

\[
C_3 = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}
\]

(16.6)

We can demonstrate this symmetry by applying \(C_3\) to vectors describing the position of each atom in the molecule as

\[
C_3 x_B = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} c_1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = x_O
\]

and similarly

\[
C_3 x_{H_1} = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} \frac{1}{2}c_1 \\ \sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}c_1 \\ \sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} = x_{H_2}
\]

followed by

\[
C_3 x_{H_2} = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} \frac{1}{2}c_1 \\ -\sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}c_1 \\ -\sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} = x_{H_3}
\]

and finally

\[
C_3 x_{H_3} = \frac{1}{2} \begin{pmatrix} -1 & -\sqrt{3} & 0 \\ \sqrt{3} & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} \frac{1}{2}c_1 \\ -\sqrt{\frac{3}{2}}c_1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = x_{H_1}
\]

These results demonstrate that transformation of the borane molecule by rotation through an angle \(\theta = 2\pi/3\) leaves the position of the boron atom unchanged while the positions of the hydrogen atoms are exchanged. Since we consider the hydrogen atoms to be indistinguishable, the transformed orientation of the borane molecule is indistinguishable from the initial orientation. As a result, we say that the \(BH_3\) molecule possesses \(C_3\) rotational symmetry (see Figure 16.14).

The \(BH_3\) molecule possesses additional symmetries including identity symmetry and reflection symmetry for reflection across the \(xy\)-plane (see red

\[The B–H bond lengths are \(r_{BH} = \frac{|x_{H_1}|}{|x_{H_3}|} = c_1 = 119\) pm and the H-B-H angles are \(\theta_{HBH} = \cos^{-1} (\frac{|x_{H_1} \cdot x_{H_2}|}{|x_{H_1}| |x_{H_2}|}) = \cos (-\pi/2) = 2\pi/3.\]

\[For the general case of \(n\)-fold rotation
\[C_n = \begin{pmatrix} \cos \left(\frac{2\pi}{n}\right) & -\sin \left(\frac{2\pi}{n}\right) & 0 \\ \sin \left(\frac{2\pi}{n}\right) & \cos \left(\frac{2\pi}{n}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix}\]
defines counter-clockwise rotation about the positive \(z\)-axis through an angle \(\theta = 2\pi/n\). You may also encounter rotation matrices defined in terms of clockwise rotation. Those matrices have the same form where \(-\sin \theta\) is substituted for \(\sin \theta\).]
surface in Figure 16.14) defined by

\[
\sigma_{xy} = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]  

(16.7)

and known as \(\sigma_h\) symmetry. The borane molecule is also symmetric to two-fold rotation about any of the three axes defined by the three B–H bonds (see red rods in Figure 16.15), known as \(C_2\) symmetry, and reflection across any of the three planes defined by the \(z\)-axis and one of the three B–H bond axes (see gray surfaces in Figure 16.15), known as \(\sigma_v\) symmetry.

Finally, there is one additional symmetry of the BH\(_3\) molecule known as an improper rotation. This particular improper rotation is a compound transformation that consists of counter-clockwise rotation by \(C_3\), through an angle \(2\pi/3\) about the positive \(z\)-axis, followed by reflection by \(\sigma_{xy}\) across the \(xy\)-plane (see red surface in Figure 16.15). We can represent this compound transformation by the matrix product

\[
S_3 = \sigma_{xy} \ C_3 = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix} \begin{pmatrix}
-1 & -\sqrt{3} & 0 \\
\sqrt{3} & -1 & 0 \\
0 & 0 & 2
\end{pmatrix}
\]

The orientation of the borane molecule is not distinguishably changed by the improper rotation defined by \(S_3\). As such, we say that borane has \(S_3\) improper rotational symmetry.

In general, the \(S_n\) improper rotation involves rotating the molecule by \(C_n\) through \(\theta = \frac{2\pi}{n}\) radians followed by reflection through the plane perpendicular to the \(C_n\) rotational axis. In this case, rotation by \(C_3\) through \(\frac{2\pi}{3}\) radians about the \(z\)-axis was followed by reflection through the \(xy\)-plane perpendicular to the \(z\)-axis.

Overall, we find that the structure of the BH\(_3\) molecule possesses identity symmetry \(E\), rotational symmetries \(C_2\) and \(C_3\), reflection symmetries \(\sigma_h\) and \(\sigma_v\), and improper rotational symmetry \(S_3\). These symmetries characterize the point group \(D_{3h}\). In the next section, we develop a systematic approach to the identification of the point group of any molecule.
16.3 Point groups and the symmetry decision tree

Point groups represent a set of symmetries that are shared by all members of a given group, which may include identity, inversion, reflection, rotation, and improper rotation symmetries. The point group of a given molecule in a specific conformation can be determined through a series of yes or no decisions determining whether the molecule does or does not possess a specific symmetry. Those decisions can be organized in a decision tree that can be used to uniquely identify the symmetry of the molecule. In this section, the symmetry decision tree is introduced and explored through a variety of examples.

16.3.1 The symmetry decision tree

The point group of a molecule can be determined by answering a series of questions regarding the presence or absence of the fundamental symmetries, including identity, inversion, reflection, rotation, and improper rotation symmetries. Those questions are conveniently organized in a decision tree (see Figure 16.16).

![Symmetry Decision Tree Diagram]

Starting at the top of the tree and descending, each branch point represents a decision related to whether the molecule possesses a particular symmetry (in
which case we move to the right) or does not (in which case we move to the left).
At each successive branch point another question is answered until we reach a terminal point at a branch tip identifying the symmetry point group for that molecule.

The decision tree begins with the separation of linear (branch right) from non-linear (branch left) molecules. In the subset of linear molecules possessing $C_{\infty}$ rotational symmetry, there are those lacking or possessing inversion symmetry $i$ leading to point groups $C_{\infty v}$ or $D_{\infty h}$.

Consider the linear molecules shown in Figure 16.17. The nitrous oxide molecule, $N_2O$, has identity symmetry $E$, $C_{\infty}$ rotational symmetry, and $\sigma_v$ reflection symmetry. From the perspective of the symmetry decision tree (see Figure 16.18), $N_2O$ is linear (branch to the right) but lacks inversion symmetry (branch to the left), leading to point group $C_{\infty v}$.

The carbon dioxide molecule, $CO_2$, has identity symmetry $E$, inversion symmetry $i$, and $C_{\infty}$ rotational symmetry. It is also invariant to $S_{\infty}$ improper rotation defined by $C_{\infty}$ rotation about the bond axis and $\sigma_h$ reflection. From the perspective of the symmetry decision tree, $CO_2$ is linear (branch right) and possesses inversion symmetry (branch right), leading to point group $D_{\infty h}$.

From the set of non-linear molecules, a special subset of molecules possessing $n \geq 2$ equivalent axes of $n$-fold rotational symmetry ($C_n$) are selected. Those molecules form the point groups $T_d$, $O_h$, and $I_h$ characterizing the three underlying symmetries of the five platonic solids, the tetrahedron ($T_d$), cube ($O_h$), octahedron ($O_h$), dodecahedron ($I_h$), and icosahedron ($I_h$). These five solids are the only regular convex polyhedra formed by identical faces, of equal size, shape, and angles, and having an equal number of faces that meet to from each vertex. This regularity leads to exceptionally high symmetry with multiple rotational axes meeting at the center of the solid.

Consider the sulfur hexafluoride molecule, SF$_6$, shown in Figure 16.19.

The molecule is octahedral and highly symmetric, having inversion symme-
try $i$, multiple rotational symmetries $C_4$, $C_3$, and $C_2$, and multiple reflection symmetries $\sigma_h$ and $\sigma_v$. In fact, there are four $C_3$ rotational axes (one for every two opposing triangular faces of the octahedron), three $C_4$ rotational axes (one for every two opposing vertices of the octahedron), three planes of $\sigma_v$ reflection symmetry (one perpendicular to each of the $C_4$ axes), and six planes of $\sigma_h$ reflection symmetry (two parallel to each of the $C_4$ axes).

From the perspective of the symmetry decision tree, SF$_6$ is not linear (left), possesses multiple $C_3$ axes (right, see Figure 16.19), possesses inversion symmetry (right), and lacks $C_3$ symmetry (left), leading to point group $O_h$. This set of decisions is summarized in Figure 16.20.

The non-linear molecules lacking a symmetry of the platonic solids are separated into groups possessing or lacking a single principal axis of $n$-fold rotational symmetry, $C_n$. Molecules lacking $C_n$ symmetry are divided into point groups characterizing molecules having reflection symmetry, $C_n$, molecules lacking reflection symmetry but possessing inversion symmetry, $C_i$, and molecules possessing neither, $C_1$. The point group $C_1$ characterizes the least symmetric of all molecules, those possessing only identity symmetry, $E$.

Let’s evaluate the symmetry of the fluorochlorobromomethane molecule, CHFClBr, shown in Figure 16.21, using the decision tree. The molecule is not linear (left), it does not have multiple $C_3$ axes (left), it does not have a principal axis of rotational symmetry $C_n$ (left), it does not have horizontal reflection symmetry $\sigma_h$ (left), nor does it have inversion symmetry $i$ (left), making it a member of point group $C_1$ (see Figure 16.22).

The non-linear molecules possessing a single principal axis of $n$-fold rotational symmetry are divided into groups of molecules possessing or lacking $n$ axes of $C_2$ rotational symmetry perpendicular to the principal axis. Molecules possessing this special symmetry are further divided into a group possessing a plane of $\sigma_h$ reflection symmetry perpendicular to the principal axis, $D_{nh}$, a group lacking a horizontal plane of reflection symmetry but possessing $n$ vertical planes of $\sigma_v$ reflection symmetry, $D_{nv}$, and a group having no reflection symmetry, $D_n$.

Consider the allene molecule, $C_3H_4$, possessing a principal axis of $C_2$ rotational symmetry (see Figure 16.23). According to the symmetry decision tree the allene molecule is not linear (left), does not have multiple $C_3$ rotational axes (left), has a principal axis of $C_2$ symmetry (right), has two axes of $C_2$ rotational symmetry perpendicular to the principal axis (right), does not have a horizontal plane of $\sigma_h$ reflection symmetry (left), and does have two planes of $\sigma_v$ symmetry (right), making it a member of the $D_{2d}$ point group (see Figure 16.23).

The remaining non-linear molecules are divided into a group possessing a plane of $\sigma_h$ reflection symmetry perpendicular to the principal axis, $C_{nh}$, and a group lacking a horizontal plane of reflection symmetry but possessing $n$
vertical planes of reflection symmetry, $C_{nv}$. Finally, the subset of molecules possessing a single axis of $n$-fold rotational symmetry but lacking any reflection symmetry are divided into one group of molecules possessing improper rotational symmetry, $S_{2n}$, and another group lacking it, $C_n$.

Consider the boric acid molecule, $\text{B(OH)}_3$, possessing a principal axis of $C_3$ rotational symmetry (see Figure 16.24). According to the symmetry decision tree the boric acid molecule is not linear (left), does not have multiple $C_3$ rotational axes (left), has a principal axis of $C_3$ rotational symmetry (right), does not have axes of $C_2$ rotational symmetry perpendicular to the principal axis (left), and does have a horizontal plane of $\sigma_h$ reflection symmetry (right), characterized by the $C_{3h}$ point group.

By answering at most seven questions, related to fundamental inversion, reflection, rotation, or improper rotation symmetries of a given molecule, the point group of any molecule may be uniquely defined. Let’s practice the use of the decision tree by identifying the point groups of a number of common organic molecules.

16.3.2 The symmetries of $\text{CH}_4$ (methane) and substituted methanes

Let’s identify the point group of the tetrahedral methane molecule, $\text{CH}_4$, using the symmetry decision tree (see Figure 16.25). The molecule is nonlinear (left), has four axes of $C_3$ symmetry (right), and does not have inversion symmetry (left) leading to the tetrahedral point group, $T_d$.

Overall, the methane molecule has four axes of $C_3$ symmetry (right), three axes of $C_2$ symmetry, six planes of $\sigma_d$ reflection symmetry, and three axes of $S_4$ improper rotational symmetry. Now let’s consider how the symmetry is
impacted by the gradual substitution of H atoms with Cl atoms.

Substitution of a single Cl atom for a H atom results in chloromethane, CH$_3$Cl (see Figure 16.26). The chloromethane molecule is nonlinear (left), has a single principal axis of $C_3$ rotational symmetry (left then right), has no axes of $C_2$ rotational symmetry perpendicular to the principal axis (left), does not have $\sigma_h$ reflection symmetry (left), and does have three planes of $\sigma_v$ reflection symmetry (right), leading to the $C_{3v}$ point group. The substitution of a H atom for a Cl atom broke the tetrahedral symmetry of the methane molecule, leading to the $C_{3v}$ point group which has fewer symmetry operations than the $T_d$ point group.

Substituting a second Cl atom for a H atom results in dichloromethane, CH$_2$Cl$_2$ (see Figure 16.26). The CH$_2$Cl$_2$ molecule is nonlinear (left), has no axis of $C_3$ rotational symmetry (left), has a single principal axis of $C_2$ rotational symmetry (right), has no axes of $C_2$ rotational symmetry perpendicular to the principal axis (left), does not have $\sigma_h$ reflection symmetry (left), and does have two planes of $\sigma_v$ reflection symmetry (right), leading to the $C_{2v}$ point group. The substitution of a second H atom for a Cl atom lowered the symmetry from the $C_{3v}$ point group to the $C_{2v}$ point group.

Substituting a third Cl atom for a H atom results in trichloromethane, CHCl$_3$, also known as chloroform (see Figure 16.26). Note that chloroform shares the symmetries of chloromethane, making it a member of the $C_{3v}$ point group. We observe that the third substitution of a H atom for a Cl atom enhances the overall symmetry. That trend continues upon substitution of the sole remaining H atom for a Cl atom forming the tetrachloromethane molecule, CCl$_4$, also known as carbon tetrachloride (see Figure 16.26). Like methane, the tetrahedral carbon tetrachloride molecule is highly symmetric and characterized by the point group $T_d$.

### 16.3.3 The symmetries of $C_2H_6$ (ethane) and substituted ethanes

Consider the ethane molecule, C$_2$H$_6$, in the staggered conformation (see Figure 16.27). Let’s identify the symmetry point group using the symmetry decision tree.

This molecular conformation is nonlinear (left), does have a single principal axis of $C_3$ rotational symmetry (left then right), does have three axes of $C_2$ rotational symmetry perpendicular to the principal axis (right), does not have $\sigma_h$ reflection symmetry (left), and does have three planes of $\sigma_v$ reflection symmetry.
In addition, the molecule possesses inversion symmetry, \( i \). We conclude that ethane in the staggered conformation is characterized by the \( D_{3d} \) point group.

Now consider the impact of substituting four \( H \) atoms with two \( F \) and \( Br \) atoms to form \( \text{CH}_2\text{F}_2\text{Br}_2 \) as shown in Figure 16.28.

These substitutions break the \( C_3 \) and \( C_2 \) rotational symmetries of ethane in the staggered conformation. In addition, these substitutions eliminate all planes of \( \sigma_v \) reflection symmetry. Applying the symmetry decision tree, the molecule is nonlinear (left), has no axis of \( C_n \) rotational symmetry (left then left), does not have a plane of \( \sigma_h \) reflection symmetry (left), but does possess inversion symmetry \( i \) (right). As such, the \( \text{CH}_2\text{F}_2\text{Br}_2 \) molecule in the staggered conformation shown in Figure 16.28 is characterized by the \( C_i \) point group.

### 16.3.4 The symmetries of \( \text{C}_6\text{H}_{12} \) (cyclohexane)

It is possible to extend our analysis of molecular symmetry to more complex organic molecules. Let’s consider the example of the cyclohexane molecule, \( \text{C}_6\text{H}_{12} \), in the chair conformation (see Figure 16.29).

We describe the conformation of the molecule in terms of vectors defining the positions of the six carbon and twelve hydrogen atoms. In the cases of \( \text{H}_2\text{O} \) and \( \text{BH}_3 \) we placed one atom at the origin. In the case of cyclohexane, the \( z \)-axis...
passes through the center of the six-membered carbon ring. Six C–H bonds are oriented parallel to the z-axis, three in the positive z-direction and three in the negative z-direction. Finally, we place the first and fourth carbon atoms in the xz-plane.

We observe that the structure of the molecule possesses identity symmetry, \(E\), as well as inversion symmetry, \(i\). Looking down the z-axis we observe that the structure is symmetric to three-fold rotation defined by \(C_3\) about the z-axis (see Figure 16.29). In addition, we identify three axes of two-fold \(C_2\) rotational symmetry. Each axis bisects the center of two opposing \((i, j) – (i + 3, j + 3)\) C–C bonds.

Changing reference frames (see Figure 16.30), we identify other symmetries of the cyclohexane molecule in its chair conformation. For example, the structure lacks \(\sigma_h\) reflection symmetry as is altered by reflection across the horizontal plane. However, the structure is invariant to reflection across three vertical planes parallel to the z-axis and passing through opposing \((i, i + 3)\) carbon atoms. These planes are known as dihedral planes and the reflection symmetry operation is \(\sigma_d\).

The structure of cyclohexane in the chair conformation is also unchanged by the \(S_6\) improper rotational transformation (see Figure 16.31). This compound transformation is defined by rotation through an angle \(\pi/3\) about the z-axis, as found in a \(C_6\) rotational transformation, followed by reflection across the \(xy\)-plane defined by \(\sigma_h\).

Note that while the chair conformation of cyclohexane does not possess \(C_6\) rotational symmetry, it does possess \(S_6\) improper rotational symmetry combining \(C_6\) rotation with \(\sigma_h\) reflection. The structure of cyclohexane in the boat conformation does not possess improper rotational symmetry. These observations can be applied to the symmetry decision tree to determine the point group of cyclohexane in the chair conformation. The path through the decision tree is shown in Figure 16.32.

Starting at the top, the molecule is not linear (left), does not have 2 or more axes of \(C_3\) symmetry (left), does have a principal axis of \(C_3\) symmetry (right), does have three axes of \(C_2\) symmetry perpendicular to the principal axis (right), does not have horizontal \(\sigma_h\) reflection symmetry (left), and does have three planes of vertical \(\sigma_d\) reflection symmetry. These symmetries characterize the \(D_{3d}\) point group.

Overall, we find that the structure of the \(C_6H_{12}\) cyclohexane molecule in the chair conformation possesses identity symmetry \(E\), inversion symmetry \(i\), rotational symmetries \(C_2\) and \(C_3\), reflection symmetry \(\sigma_d\), and improper rotational symmetry \(S_6\).
16.3.5 The symmetries of the Posner molecule Ca$_9$(PO$_4$)$_6$

Consider the Posner molecule, Ca$_9$(PO$_4$)$_6$ (see Figure 16.33). The central calcium ion, Ca$^{2+}$ (orange), is surrounded by six phosphate groups, PO$_4^{3-}$, each composed of one phosphorus (yellow) and four oxygen (red) atoms. Each of the six phosphate groups coordinates a single calcium ion. Two additional calcium ions flank the central calcium making the molecule charge neutral. Let’s identify the symmetry point group of the Posner molecule using the symmetry decision tree.

The Posner molecule is not linear (left), does not have 2 or more axes of $C_3$ rotational symmetry (left), does have a principal axis of $C_3$ rotational symmetry (right), does not have three axes of $C_2$ rotational symmetry perpendicular to the principal axis (left), does not have horizontal $\sigma_h$ reflection symmetry (left), does not have three planes of vertical $\sigma_v$ reflection symmetry (left), and does have $S_6$ improper rotational symmetry. These symmetries characterize the point group $S_6$.

The examples above demonstrate a reliable method for determining the point group of any simple or complex molecule using the symmetry decision tree. Identification of the point group provides a foundation of knowledge for the study of many fundamental properties of molecules and solids.

A$_{16}$ End-of-chapter problems

The miracle of the appropriateness of the language of mathematics for the formulation of the laws of physics is a wonderful gift which we neither understand nor deserve.

Eugene Paul Wigner

Warm-ups

16.1 Consider the scaling transformation defined by

$$ S_v = \begin{pmatrix} 5 & 0 \\ 0 & 2 \end{pmatrix} $$

(a) For the vector $x = (1, 2)^T$ determine $x' = S_v x$.

(b) Solve the characteristic equation $|S_v - \lambda I| = 0$ to determine the eigenvalues $\lambda_1$ and $\lambda_2$.

(c) Determine the eigenvectors $x_1$ and $x_2$ satisfying the equations $(S_v - \lambda_1 I) x_1 = 0$ and $(S_v - \lambda_2 I) x_2 = 0$. 
16.2 Consider the shear transformation defined by
\[
S = \begin{pmatrix} 1 & 2 \\ 0 & 1 \end{pmatrix}
\]
(a) For the vector \( x = (1, 2)^T \) determine \( x' = S x \).
(b) Solve the characteristic equation \( |S - \lambda I| = 0 \) to determine the eigenvalues \( \lambda_1 \) and \( \lambda_2 \).
(c) Determine the eigenvectors \( x_1 \) and \( x_2 \) satisfying the equations \( (S - \lambda_1 I) x_1 = 0 \) and \( (S - \lambda_2 I) x_2 = 0 \).

16.3 Consider the rotation transformation defined by
\[
R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}
\]
(a) Take \( \theta = \frac{\pi}{4} \). For the vector \( x = \left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)^T \) determine \( x' = R \left( \frac{\pi}{4} \right) x \).
(b) Solve the characteristic equation \( |R \left( \frac{\pi}{4} \right) - \lambda I| = 0 \) to determine the eigenvalues \( \lambda_1 \) and \( \lambda_2 \).
(c) Determine the eigenvectors \( x_1 \) and \( x_2 \) satisfying the equations \( (R \left( \frac{\pi}{4} \right) - \lambda_1 I) x_1 = 0 \) and \( (R \left( \frac{\pi}{4} \right) - \lambda_2 I) x_2 = 0 \).

16.4 Consider the reflection transformation defined by
\[
\sigma(\theta) = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}
\]
(a) Take \( \theta = \frac{\pi}{2} \). For the vector \( x = \left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)^T \) determine \( x' = \sigma \left( \frac{\pi}{2} \right) x \).
(b) Solve the characteristic equation \( |\sigma \left( \frac{\pi}{2} \right) - \lambda I| = 0 \) to determine the eigenvalues \( \lambda_1 \) and \( \lambda_2 \).
(c) Determine the eigenvectors \( x_1 \) and \( x_2 \) satisfying the equations \( (\sigma \left( \frac{\pi}{2} \right) - \lambda_1 I) x_1 = 0 \) and \( (\sigma \left( \frac{\pi}{2} \right) - \lambda_2 I) x_2 = 0 \).

16.5 Consider the inversion transformation defined by
\[
i = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\]
(a) For the vector \( x = (1, 2)^T \) determine \( x' = i x \).
(b) Solve the characteristic equation \( |i - \lambda I| = 0 \) to determine the eigenvalues \( \lambda_1 \) and \( \lambda_2 \).
(c) Determine the eigenvectors \( x_1 \) and \( x_2 \) satisfying the equations \( (i - \lambda_1 I) x_1 = 0 \) and \( (i - \lambda_2 I) x_2 = 0 \).

16.6 Consider the ammonia molecule, \( \text{NH}_3 \), shown below. The nitrogen atom is placed at the origin and one hydrogen atom is placed in the \( xz \)-plane so that
\[
x_N = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \quad x_{H1} = \begin{pmatrix} c_1 \\ 0 \\ c_2 \end{pmatrix} \quad x_{H2} = \begin{pmatrix} -\frac{1}{2}c_1 \\ \frac{\sqrt{3}}{2}c_1 \\ c_2 \end{pmatrix} \quad x_{H3} = \begin{pmatrix} -\frac{1}{2}c_1 \\ -\frac{\sqrt{3}}{2}c_1 \\ c_2 \end{pmatrix}
\]
where we have taken the N-H bond length to be \( \sqrt{c_1^2 + c_2^2} \).
(a) Show that a three-fold rotation about the \( z \)-axis passing through the N atom transforms the molecule into an orientation indistinguishable from the initial orientation. Do this by applying
to each atom’s position to find $C_3 x_N = x'_N$, $C_3 x_{H1} = x'_{H1}$, $C_3 x_{H2} = x'_H$, and $C_3 x_{H3} = x'_H$ where $x'_N = x_N$, $x'_H = x_H$, $x'_H = x_{H3}$, and $x'_H = x_{H1}$.

(b) Consider reflection of the ammonia molecule across the $xy$-plane containing the central N atom. This results in the inversion of the ammonia molecule. Do this by applying

$$
\sigma_h = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
$$

to each atom’s position $\sigma_h x_N = x'_N$, $\sigma_h x_{H1} = x'_{H1}$, $\sigma_h x_{H2} = x'_{H2}$, and $\sigma_h x_{H3} = x'_{H3}$. Show that this transformation leaves the molecule in an orientation that is distinguishable from the initial orientation, thereby demonstrating that ammonia lacks $\sigma_h$ reflection symmetry.

(c) List all symmetry transformations that result in a final orientation of the NH$_3$ molecule that is indistinguishable from its initial orientation. Determine the point group for NH$_3$.

16.7 Consider the ethane molecule, C$_2$H$_6$, in the staggered conformation (see Figure 16.27) with symmetries characterized by the $D_{3d}$ point group. Then consider the related molecules

(a) 1-chloroethane, C$_2$H$_5$Cl
(b) gauche-1,2-dichloroethane, C$_2$H$_4$Cl$_2$
(c) trans-1,2-dichloroethane, C$_2$H$_4$Cl$_2$
(d) 1,1-dichloroethane, C$_2$H$_4$Cl$_2$

For each molecule, use the symmetry decision tree to determine the point group defining the symmetry of the molecule in its staggered conformation.

Homework exercises

16.8 Consider the xenon tetrafluoride molecule, XeF$_4$, shown below. The xenon atom is placed at the origin with the fluorine atoms at the corners of a square in the $xy$-plane.
One fluorine atom is placed on the positive $x$-axis so that

$$x_{Xe} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \quad x_{F1} = \begin{pmatrix} c_1 \\ 0 \\ 0 \end{pmatrix}$$

where we have taken the Xe-F bond length to be $c_1$.

(a) Construct the remaining vectors $x_{F2}$, $x_{F3}$, and $x_{F4}$ defining the positions of the fluorine atoms.

(b) Prove that the xenon tetrafluoride molecule exhibits $C_4$ rotational symmetry by showing that a four-fold $C_4$ rotation about the $z$-axis passing through the Xe atom transforms the molecule into an orientation that is indistinguishable from the initial orientation.

(c) List all symmetry transformations that result in a final orientation of the XeF$_4$ molecule that is indistinguishable from its initial orientation. Determine the point group for XeF$_4$.

16.9 Consider the ethane molecule, C$_2$H$_6$, in the eclipsed conformation shown below

with symmetries characterizing the $D_{3h}$ point group. Now consider the related molecules

(a) 1-chloroethane, C$_2$H$_5$Cl  
(b) cis-1, 2-dichloroethane, C$_2$H$_4$Cl$_2$

(c) gauche-1, 2-dichloroethane, C$_2$H$_4$Cl$_2$  
(d) 1,1-dichloroethane, C$_2$H$_4$Cl$_2$

For each molecular conformation, use the symmetry decision tree to determine the point group.

16.10 We considered the structure of the cyclohexane molecule, C$_6$H$_{12}$, in the chair conformation shown below. It was found it to possess identity symmetry $E$, inversion symmetry $i$, rotational symmetries $C_2$ and $C_3$, reflection symmetry $\sigma_d$, and improper rotational symmetry $S_6$. The symmetry decision tree was used to identify the point group $D_{3d}$.

Use the symmetry decision tree to identify the molecular symmetries and point group of the cyclohexane molecule in the boat conformation.
16.11 Consider the ethene molecule, $C_2H_4$, shown below with symmetries characterizing the $D_{2h}$ point group.

![Ethene molecule diagram]

Now consider the related molecules

(a) 1-chloroethene $C_2H_3Cl$
(b) cis-1,2-dichloroethene $C_2H_2Cl_2$
(c) trans-1,2-dichloroethene $C_2H_2Cl_2$
(d) 1,1-dichloroethene $C_2H_2Cl_2$

For each molecular conformation, use the symmetry decision tree to determine the point group.

16.12 The cyclopropane molecule, $C_3H_6$, has symmetry characterized by the $D_{3h}$ point group.

![Cyclopropane molecule diagram]

Now consider the related molecules

(a) 1-fluorocyclopropane, $C_3H_5F$
(b) 1,1-difluorocyclopropane, $C_3H_4F_2$
(c) cis-1,2-difluorocyclopropane, $C_3H_4F_2$
(d) trans-1,2-difluorocyclopropane, $C_3H_4F_2$

For each molecular conformation, use the symmetry decision tree to determine the point group.

16.13 Consider the cyclooctatetrene molecule, $C_8H_8$, shown below from two perspectives.

![Cyclooctatetrene molecule diagram]

Use the symmetry decision tree to determine the point group of $C_8H_8$. Consider the various symmetry operations, including inversion, reflection, rotation, and improper rotation. Identify all symmetry operations that leave the $C_8H_8$ structure unchanged.
16.14 Consider the sulfurhexafluoride molecule, \( \text{SF}_6 \), with symmetries characterizing the \( O_h \) point group.

(a) (b)

(c) (d)

In each of the figures above, rods or planes are shown to imply a particular rotational or reflection symmetry. In each case, identify the corresponding symmetry operation.

16.15 Consider the cyclooctasulfur molecule, \( \text{S}_8 \), shown below.

(a) An improper rotation is a combination of a rotation about an axis and a reflection in a plane perpendicular to that axis. For example, we found that borane has \( S_3 \) improper rotational symmetry defined by the transformation \( S_3 = \sigma_{xy} C_3 = C_3 \sigma_{xy} \). Define the improper rotational symmetry operation \( S_8 \) in terms of elementary operations of rotation and reflection.

(b) Determine the number of dihedral reflection planes \( \sigma_d \) that contain the principal \( C_4 \) rotation axis and bisect two horizontal \( C_2 \) rotation axes.

(c) List all symmetry transformations that result in a final orientation of the \( \text{S}_8 \) molecule that is indistinguishable from its initial orientation. Determine the point group for \( \text{S}_8 \).
Supplements

S1 Notes on notation  395
S2 Formulas from geometry  397
S3 Formulas from trigonometry  399
S4 Table of power series  401
S5 Table of definite integrals  402
S6 Table of indefinite integrals  403
S7 Error function table  410
S8 Complementary error function table  411
S9 Table of Fourier transform pairs  412

S1 Notes on notation

Common characters and mathematical symbols used throughout the text are collected here.

Greek characters (lower case and unique capitals)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Alpha</td>
</tr>
<tr>
<td>β</td>
<td>Beta</td>
</tr>
<tr>
<td>γ</td>
<td>Gamma</td>
</tr>
<tr>
<td>δ</td>
<td>Delta</td>
</tr>
<tr>
<td>ε</td>
<td>Epsilon</td>
</tr>
<tr>
<td>ζ</td>
<td>Zeta</td>
</tr>
<tr>
<td>η</td>
<td>Eta</td>
</tr>
<tr>
<td>θ</td>
<td>Theta</td>
</tr>
<tr>
<td>ι</td>
<td>Iota</td>
</tr>
<tr>
<td>κ</td>
<td>Kappa</td>
</tr>
<tr>
<td>λ</td>
<td>Lambda</td>
</tr>
<tr>
<td>μ</td>
<td>Mu</td>
</tr>
<tr>
<td>ν</td>
<td>Nu</td>
</tr>
<tr>
<td>ξ</td>
<td>Xi</td>
</tr>
<tr>
<td>ο</td>
<td>Omicron (=o, not used)</td>
</tr>
<tr>
<td>ζ</td>
<td>Xi</td>
</tr>
<tr>
<td>ζ</td>
<td>Xi</td>
</tr>
<tr>
<td>ξ</td>
<td>Xi</td>
</tr>
<tr>
<td>Κ</td>
<td>Kappa</td>
</tr>
<tr>
<td>Λ</td>
<td>Lambda</td>
</tr>
<tr>
<td>Μ</td>
<td>Mu</td>
</tr>
<tr>
<td>Ν</td>
<td>Nu</td>
</tr>
<tr>
<td>Ω</td>
<td>Omega</td>
</tr>
</tbody>
</table>

Mathematical symbols (basic)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>=</td>
<td>Equal</td>
</tr>
<tr>
<td>≠</td>
<td>Not equal</td>
</tr>
<tr>
<td>≈</td>
<td>Approximately equal</td>
</tr>
<tr>
<td>∝</td>
<td>Proportional</td>
</tr>
<tr>
<td>≡</td>
<td>Equivalent</td>
</tr>
<tr>
<td>∀</td>
<td>For all</td>
</tr>
<tr>
<td>&lt;</td>
<td>Less than</td>
</tr>
<tr>
<td>&gt;</td>
<td>Greater than</td>
</tr>
<tr>
<td>≥</td>
<td>Greater than or equal</td>
</tr>
<tr>
<td>≤</td>
<td>Less than or equal</td>
</tr>
<tr>
<td>≫</td>
<td>Much greater than</td>
</tr>
<tr>
<td>≪</td>
<td>Much less than</td>
</tr>
<tr>
<td>+</td>
<td>Plus</td>
</tr>
<tr>
<td>−</td>
<td>Minus</td>
</tr>
<tr>
<td>⊆</td>
<td>Subset</td>
</tr>
<tr>
<td>⊇</td>
<td>Superset</td>
</tr>
<tr>
<td>⊂</td>
<td>Proper subset</td>
</tr>
<tr>
<td>⊃</td>
<td>Proper superset</td>
</tr>
</tbody>
</table>

Mathematical symbols (linear algebra)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Scalar</td>
</tr>
<tr>
<td>a · b</td>
<td>Scalar product</td>
</tr>
<tr>
<td>a × b</td>
<td>Cross product</td>
</tr>
<tr>
<td>A</td>
<td>Matrix</td>
</tr>
<tr>
<td>A⁻¹</td>
<td>Matrix inverse</td>
</tr>
<tr>
<td>Aᵀ</td>
<td>Hermitian conjugate</td>
</tr>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>A</td>
</tr>
</tbody>
</table>

Mathematical symbols (number theory)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>z</td>
<td>Complex number</td>
</tr>
<tr>
<td>Z</td>
<td>Integers</td>
</tr>
<tr>
<td>Re(z)</td>
<td>Real part</td>
</tr>
<tr>
<td>Im(z)</td>
<td>Imaginary part</td>
</tr>
<tr>
<td>ℝ</td>
<td>Real numbers</td>
</tr>
<tr>
<td>ℂ</td>
<td>Complex numbers</td>
</tr>
</tbody>
</table>

Mathematical symbols (exponentials and logarithms)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>e^x</td>
<td>Exponential</td>
</tr>
<tr>
<td>ln(x)</td>
<td>Natural logarithm</td>
</tr>
<tr>
<td>x^n</td>
<td>nth power of x</td>
</tr>
<tr>
<td>log(x)</td>
<td>Base 10 logarithm</td>
</tr>
<tr>
<td>√x</td>
<td>nth root of x</td>
</tr>
</tbody>
</table>
Mathematical symbols (sums, products and combinatorial factors)

\[ \sum_{n=1}^{N} a_n \] Definite sum

\[ \prod_{n=1}^{N} a_n \] Definite product

\[ n! = n \times (n-1) \times \ldots \times 1 \] Factorial

\[ n!! = n \times (n-2) \times \ldots \times 2 \] Double factorial (n even)

\[ \Gamma(n) = (n-1)! \] Gamma function

\[ \binom{N}{n} = \frac{N!}{n!(N-n)!} \] Binomial coefficient

\[ \frac{N!}{n_1!n_2! \ldots n_m!} \] Multinomial coefficient

Mathematical symbols (calculus)

\[ \lim_{x \to a^+} f(x) \] Limit as \( x \to a \) from + or -

\[ \frac{df}{dx} \equiv f' \equiv \hat{D}_x f \] Derivative

\[ \frac{d^2f}{dx^2} \equiv f'' \equiv \hat{D}_x^2 f \] Second derivative

\[ \frac{dy}{dt} \equiv \dot{y} \] Time derivative

\[ \int f(x) \, dx \] Integral

\[ \int \int f(x,y) \, dxdy \] Double integral

\[ x \in (a,b) \quad \frac{a}{b} < x < b \quad x \in (a,b] \quad a < x \leq b \quad x \in [a,b) \quad a \leq x < b \quad x \in [a,b] \quad a \leq x \leq b \]

Mathematical symbols (vector calculus)

\[ \nabla V \] Gradient of \( V \)

\[ \nabla \times f \] Curl of \( f \)

\[ \nabla^2 V \] Laplacian of \( V \)

Mathematical constants

\[ e = 2.718281828 \ldots \] Euler’s number

\[ \gamma = 0.5772156649 \ldots \] Euler-Mascheroni constant

\[ \pi = 3.141592654 \ldots \] Pi

\[ \varphi = 1.6180339887 \ldots \] Golden ratio constant
S2 Formulas from geometry

Geometric relations are essential in modeling physical systems and problem solving in the physical sciences. A brief compilation of commonly used geometric identities is provided for convenience. The following notation is used to define these relations, where \( r \) is the radius, \( h \) is the height (or altitude), \( b \) (or \( a \)) is the base length, \( A \) is the area, \( C \) is the circumference, \( V \) is the volume, \( S \) is surface area (curved surface), and \( B \) is the base area. Volumes of polyhedra are defined in terms of polyhedron edge vectors \( a \), \( b \), and \( c \).

Two dimensions

<table>
<thead>
<tr>
<th>Shape</th>
<th>Formula for Area/Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triangle</td>
<td>( A = \frac{1}{2}bh )</td>
</tr>
<tr>
<td>Circle</td>
<td>( A = \pi r^2 ), ( C = 2\pi r )</td>
</tr>
<tr>
<td>Ellipse</td>
<td>( A = \pi ab ), ( C \approx \pi \sqrt{2(a^2 + b^2)} )</td>
</tr>
<tr>
<td>Parallelogram</td>
<td>( A = bh )</td>
</tr>
<tr>
<td>Trapezoid</td>
<td>( A = \frac{1}{2}(a + b)h )</td>
</tr>
</tbody>
</table>

Three dimensions (Platonic solids)

<table>
<thead>
<tr>
<th>Shape</th>
<th>Formula for Volume/Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron (regular)</td>
<td>( V = \frac{1}{12}\sqrt{2a^3} ), ( S = \sqrt{3}a^2 )</td>
</tr>
<tr>
<td>Cube</td>
<td>( V = a^3 ), ( S = 6a^2 )</td>
</tr>
<tr>
<td>Octahedron (regular)</td>
<td>( V = \frac{1}{3}\sqrt{2a^3} ), ( S = 2\sqrt{3}a^2 )</td>
</tr>
<tr>
<td>Dodecahedron (regular)</td>
<td>( V = \frac{1}{4}\left(15 + 7\sqrt{5}\right)a^3 ), ( S = 3\sqrt{25 + 10\sqrt{5}}a^2 )</td>
</tr>
<tr>
<td>Icosahedron (regular)</td>
<td>( V = \frac{5}{12}\left(3 + \sqrt{5}\right)a^3 ), ( S = 5\sqrt{3}a^2 )</td>
</tr>
</tbody>
</table>
Three dimensions (other solids)

<table>
<thead>
<tr>
<th>Shape</th>
<th>Volume Formula</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>( V = \frac{4}{3}\pi r^3 )</td>
<td>( S = 4\pi r^2 )</td>
</tr>
<tr>
<td>Right Circular Cylinder</td>
<td>( V = \pi r^2 h )</td>
<td>( S = 2\pi rh )</td>
</tr>
<tr>
<td>Right Circular Cone</td>
<td>( V = \frac{1}{3}\pi r^2 h )</td>
<td>( S = \pi r\sqrt{r^2 + h^2} )</td>
</tr>
<tr>
<td>Prism (rectangular)</td>
<td>( V = abh )</td>
<td>( S = 2ab + 2bh + 2ah )</td>
</tr>
<tr>
<td>Pyramid (square)</td>
<td>( V = \frac{1}{3}Bh )</td>
<td>( S = 2b\sqrt{(b/2)^2 + h^2 + b^2} )</td>
</tr>
<tr>
<td>Tetrahedron (general)</td>
<td>( V = \frac{1}{3!}</td>
<td>(a \times b) \cdot c</td>
</tr>
<tr>
<td>Parallelepiped</td>
<td>( V =</td>
<td>(a \times b) \cdot c</td>
</tr>
</tbody>
</table>
S3 Formulas from trigonometry

Trigonometric relations are commonly used in solving problems in the physical sciences. Familiarity with the unit circle and a knowledge of the most commonly encountered values of trigonometric functions is essential to efficient calculation. A brief summary of useful trigonometric identities is provided for convenience. The following notation uses standard abbreviations opp \equiv opposite, adj \equiv adjacent, and hyp \equiv hypotenuse, as well as \sin \equiv sine, \cos \equiv cosine, \tan \equiv tangent, \cot \equiv cotangent, \sec \equiv secant, and \csc \equiv cosecant.

\[ \theta (\text{rad}) \quad 0 \quad \frac{\pi}{6} \quad \frac{\pi}{4} \quad \frac{\pi}{3} \quad \frac{\pi}{2} \quad \frac{2\pi}{3} \quad \frac{3\pi}{4} \quad \frac{5\pi}{6} \quad \pi \quad \frac{3\pi}{2} \quad \frac{5\pi}{3} \quad \frac{7\pi}{4} \quad \frac{11\pi}{6} \quad 2\pi \]

\[ \theta (\text{deg}) \quad 0 \quad 30^\circ \quad 45^\circ \quad 60^\circ \quad 90^\circ \quad 120^\circ \quad 135^\circ \quad 150^\circ \quad 180^\circ \quad 210^\circ \quad 225^\circ \quad 270^\circ \quad 300^\circ \quad 315^\circ \quad 330^\circ \quad 360^\circ \]

<table>
<thead>
<tr>
<th>\theta (rad)</th>
<th>0</th>
<th>$\frac{\pi}{6}$</th>
<th>$\frac{\pi}{4}$</th>
<th>$\frac{\pi}{3}$</th>
<th>$\frac{\pi}{2}$</th>
<th>$\frac{2\pi}{3}$</th>
<th>$\frac{3\pi}{4}$</th>
<th>$\frac{5\pi}{6}$</th>
<th>$\pi$</th>
<th>$\frac{3\pi}{2}$</th>
<th>$\frac{5\pi}{3}$</th>
<th>$\frac{7\pi}{4}$</th>
<th>$\frac{11\pi}{6}$</th>
<th>$2\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\sin(\theta)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{\sqrt{3}}{2}$</td>
<td>$\frac{\sqrt{3}}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
</tr>
<tr>
<td>\cos(\theta)</td>
<td>1</td>
<td>$\frac{\sqrt{3}}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\sqrt{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
</tr>
<tr>
<td>\tan(\theta)</td>
<td>0</td>
<td>$\frac{1}{\sqrt{3}}$</td>
<td>1</td>
<td>$-\sqrt{3}$</td>
<td>$-1$</td>
<td>$\frac{1}{\sqrt{3}}$</td>
<td>0</td>
<td>$\frac{1}{\sqrt{3}}$</td>
<td>1</td>
<td>$-\sqrt{3}$</td>
<td>$-1$</td>
<td>$-\frac{1}{\sqrt{3}}$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Function Definitions

\[ \sin \theta = \frac{\text{opp}}{\text{hyp}} \quad \cos \theta = \frac{\text{adj}}{\text{hyp}} \quad \tan \theta = \frac{\text{opp}}{\text{adj}} \]

\[ \csc \theta = \frac{\text{hyp}}{\text{opp}} \quad \sec \theta = \frac{\text{hyp}}{\text{adj}} \quad \cot \theta = \frac{\text{adj}}{\text{opp}} \]

Function Relations

\[ \tan x = \frac{\sin x}{\cos x} \quad \cot x = \frac{\cos x}{\sin x} \]

\[ \csc x = \frac{1}{\sin x} \quad \sec x = \frac{1}{\cos x} \quad \cot x = \frac{1}{\tan x} \]

Negative Angle Formulas

\[ \sin(-x) = -\sin x \quad \cos(-x) = \cos x \quad \tan(-x) = -\tan x \]

\[ \csc(-x) = -\csc x \quad \sec(-x) = \sec x \quad \cot(-x) = -\cot x \]
Addition Formulas
\[
\sin(x \pm y) = \sin x \cos y \pm \cos x \sin y \\
\cos(x \pm y) = \cos x \cos y \mp \sin x \sin y \\
\tan(x \pm y) = \frac{\tan x \pm \tan y}{1 \mp \tan x \tan y}
\]

Double Angle Formulas
\[
\sin 2x = 2 \sin x \cos x \\
\cos 2x = \cos^2 x - \sin^2 x = 1 - 2 \sin^2 x = 2 \cos^2 x - 1 \\
\tan 2x = \frac{2 \tan x}{1 - \tan^2 x} = \frac{2 \sin x \cos x}{\cos^2 x - \sin^2 x}
\]

Half-Angle Formulas
\[
\sin^2 \frac{x}{2} = \frac{1 - \cos x}{2} \\
\cos^2 \frac{x}{2} = \frac{1 + \cos x}{2} \\
\tan \frac{x}{2} = \frac{1 - \cos x}{\sin x} = \frac{\sin x}{1 + \cos x}
\]

Product Formulas
\[
\sin x \cos y = \frac{1}{2} [\sin(x + y) + \sin(x - y)] \\
\cos x \sin y = \frac{1}{2} [\sin(x + y) - \sin(x - y)] \\
\cos x \cos y = \frac{1}{2} [\cos(x + y) + \cos(x - y)] \\
\sin x \sin y = \frac{1}{2} [\cos(x - y) - \cos(x + y)]
\]

Factoring Formulas
\[
\sin x \pm \sin y = 2 \cos \frac{x \mp y}{2} \sin \frac{x \pm y}{2} \\
\cos x \pm \cos y = 2 \cos \frac{x + y}{2} \cos \frac{x - y}{2} \\
\cos x - \cos y = 2 \sin \frac{x + y}{2} \sin \frac{x - y}{2}
\]
Table of power series

Power series representations of functions are useful in approximation as well as the exact solution of differential and integral equations. This table summarizes power series that most commonly appear in the physical sciences.

1. \[ \frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots = \sum_{n=0}^{\infty} x^n \]
2. \[ e^x = \exp(x) = 1 + x + \frac{1}{2!} x^2 + \frac{1}{3!} x^3 + \ldots = \sum_{n=0}^{\infty} \frac{1}{n!} x^n \]
3. \[ e^{-x} = \exp(-x) = 1 - x + \frac{1}{2!} x^2 - \frac{1}{3!} x^3 + \ldots = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} x^n \]
4. \[ e^{-x^2} = \exp(-x^2) = 1 - x^2 + \frac{1}{2!} x^4 - \frac{1}{3!} x^6 + \ldots = \sum_{n=0}^{\infty} (-1)^n \frac{1}{n!} x^{2n} \]
5. \[ \sin(x) = x - \frac{1}{3!} x^3 + \frac{1}{5!} x^5 - \frac{1}{7!} x^7 + \ldots = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1} \]
6. \[ \cos(x) = 1 - \frac{1}{2!} x^2 + \frac{1}{4!} x^4 - \frac{1}{6!} x^6 + \ldots = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n)!} x^{2n} \]
7. \[ \sinh(x) = x + \frac{1}{3!} x^3 + \frac{1}{5!} x^5 + \frac{1}{7!} x^7 + \ldots = \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} x^{2n+1} \]
8. \[ \cosh(x) = 1 + \frac{1}{2!} x^2 + \frac{1}{4!} x^4 + \frac{1}{6!} x^6 + \ldots = \sum_{n=0}^{\infty} \frac{1}{(2n)!} x^{2n} \]
9. \[ \ln(1+x) = x - \frac{1}{2} x^2 + \frac{1}{3} x^3 - \frac{1}{4} x^4 + \ldots = -\sum_{n=1}^{\infty} \frac{1}{n} x^n \]
10. \[ \tan^{-1}(x) = x - \frac{1}{3} x^3 + \frac{1}{5} x^5 - \frac{1}{7} x^7 + \ldots = \sum_{n=0}^{\infty} (-1)^n \frac{1}{2n+1} x^{2n+1} \]
S5 Table of definite integrals

Certain integrals are pervasive throughout the physical sciences. A brief table of the most frequently encountered definite integrals is provided for convenience. The integral identities listed below are derived in the text. Note the constant $a > 0$.

1. $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$
2. $\int_0^\infty e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$
3. $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \left( \frac{\pi}{a} \right)^{1/2}$
4. $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^n a^n} \left( \frac{\pi}{a} \right)^{1/2}$
5. $\int_0^\infty xe^{-ax^2} dx = \frac{1}{2a}$
6. $\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$
7. $\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left( \frac{1}{a^{n+1}} \right)$
8. $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^n a^n} \left( \frac{\pi}{a} \right)^{1/2}$
9. $\int_0^\infty x^{2n+1} e^{-ax^2} dx = 0$
10. $\int_0^\infty e^{-ax^2 + bx} dx = \left( \frac{\pi}{a} \right)^{1/2} e^{b^2/4a}$
11. $\int_0^\infty e^{-a(x-x_1)^2 - b(x-x_2)^2} dx = \left( \frac{\pi}{a+b} \right)^{1/2} \exp \left[ -\frac{ab}{a+b} (x_1 - x_2)^2 \right]$
12. $\int_0^\infty \frac{1}{x} \sin(ax) dx = \pi$
13. $\int_0^\infty \frac{a}{a^2 - x^2} dx = \pi$
14. $\int_0^\infty x^k e^{-ax^n} dx = \frac{1}{m} \lambda^{-\frac{k+1}{n}} \Gamma \left( \frac{k+1}{n} \right)$
Table of indefinite integrals

Integrals involving a variety of algebraic, trigonometric and exponential functions appear throughout the physical sciences. A brief table of the most frequently encountered indefinite integrals is provided for convenience.

Basic Forms and Most Common Functions (of \( x \))

1. \( \int x^p \, dx = \frac{1}{p+1} x^{p+1} + C, \quad \text{if } p \neq -1 \)
2. \( \int \frac{1}{x} \, dx = \ln |x| + C \)
3. \( \int (ax + b)^p \, dx = \frac{(ax + b)^{p+1}}{a(p+1)} + C, \quad \text{if } p \neq -1 \)
4. \( \int \frac{1}{ax + b} \, dx = \frac{1}{a} \ln |ax + b| + C \)
5. \( \int \frac{1}{x^2 + a^2} \, dx = \frac{1}{a} \arctan \frac{x}{a} + C \)
6. \( \int \frac{1}{x^2 - a^2} \, dx = \frac{1}{2a} \ln \left| \frac{x-a}{x+a} \right| + C = \frac{1}{a} \coth^{-1} \frac{x}{a} + C \)
7. \( \int \ln |ax + b| \, dx = \frac{ax + b}{a} \ln |ax + b| - x + C \)
8. \( \int e^{ax} \, dx = \frac{1}{a} e^{ax} + C \)
9. \( \int e^{ax} \sin bx \, dx = \frac{1}{a^2 + b^2} e^{ax} (a \sin bx - b \cos bx) + C \)
10. \( \int e^{ax} \cos bx \, dx = \frac{1}{a^2 + b^2} e^{ax} (a \cos bx + b \sin bx) + C \)
11. \( \int a^{bx} \, dx = \frac{a^{bx}}{b \ln a} + C, \quad \text{if } a > 0, a \neq 1 \)
12. \( \int x a^{bx} \, dx = \frac{x a^{bx}}{b \ln a} - \frac{a^{bx}}{b^2 (\ln a)^2} + C, \quad \text{if } a > 0, a \neq 1 \)
13. \( \int \sin(ax + b) \, dx = -\frac{1}{a} \cos(ax + b) + C \)
14. \( \int \sin^2(ax + b) \, dx = \frac{x}{2} - \frac{1}{2a} \cos(ax + b) \sin(ax + b) + C = \frac{x}{2} - \frac{1}{4a} \sin 2(ax + b) + C \)
15. \( \int \cos(ax + b) \, dx = \frac{1}{a} \sin(ax + b) + C \)
16. \( \int \cos^2(ax + b) \, dx = \frac{x}{2} + \frac{1}{2a} \cos(ax + b) \sin(ax + b) + C = \frac{x}{2} + \frac{1}{4a} \sin 2(ax + b) + C \)
17. \( \int \sin(ax + b) \cos(ax + b) \, dx = \frac{1}{2a} \sin^2(ax + b) + C \)

Algebraic Functions (of \( x \) and \( ax + b \))

18. \( \int \frac{x}{ax + b} \, dx = \frac{1}{a^2} [ax - b \ln |ax + b|] + C \)
19. \( \int \frac{x}{(ax + b)^2} \, dx = \frac{1}{a^2} \left( \ln |ax + b| + \frac{b}{ax + b} \right) + C \)
20. \( \int \frac{x}{(ax + b)^3} \, dx = \frac{1}{a^2} \left( \frac{b}{2(ax + b)^2} - \frac{1}{ax + b} \right) + C \)
21. \( \int (ax + b)^p \, dx = \frac{1}{a^{p+2}(p+2)} (ax + b)^{p+2} - \frac{b}{a^2(p+1)} (ax + b)^{p+1} + C, \quad \text{if } p \neq -1, p \neq -2 \)

22. \( \int \frac{x^2}{ax + b} \, dx = \frac{1}{a^2} \left( \frac{1}{2} (ax + b)^2 - 2b(ax + b) + b^2 \ln |ax + b| \right) + C \)

23. \( \int \frac{x^2}{(ax + b)^2} \, dx = \frac{1}{a^2} \left( ax + b - 2b \ln |ax + b| - \frac{b^2}{ax + b} \right) + C \)

24. \( \int \sqrt{ax + b} \, dx = \frac{2}{3a} \sqrt{(ax + b)^3} + C \)

25. \( \int \frac{1}{\sqrt{ax + b}} \, dx = \frac{2\sqrt{ax + b}}{a} + C \)

26. \( \int \sqrt{ax + b} \, dx = \frac{2(3ax - 2b)\sqrt{(ax + b)^3}}{15a^2} + C \)

27. \( \int \frac{1}{x} \sqrt{ax + b} \, dx = 2\sqrt{ax + b} + b \int \frac{dx}{\sqrt{ax + b}} \)

28. \( \int \frac{1}{x} \sqrt{ax + b} \, dx = \frac{2}{\sqrt{b}} \ln \left| \frac{\sqrt{ax + b} - \sqrt{b}}{\sqrt{ax + b} + \sqrt{b}} \right| + C = -\frac{1}{\sqrt{b}} \tanh^{-1} \left( \frac{\sqrt{ax + b}}{\sqrt{b}} \right) + C, \quad \text{if } b > 0 \)

29. \( \int \frac{1}{x}\sqrt{ax - b} \, dx = \frac{2}{\sqrt{b}} \arctan \sqrt{\frac{ax - b}{b}} + C, \quad \text{if } b > 0 \)

30. \( \int \frac{x^2}{\sqrt{ax + b}} \, dx = \frac{2}{105a^3} \sqrt{(ax + b)^3} \left( 15a^2x^2 - 12abx + b^2 \right) + C \)

31. \( \int \frac{x^2}{\sqrt{ax + b}} \, dx = \frac{2}{a(2n + 1)} \left[ x^n \sqrt{ax + b} - nb \int \frac{x^{n-1} \, dx}{\sqrt{ax + b}} \right] \)

**Algebraic Functions (of x and ax^2 + b)**

32. \( \int \frac{1}{ax^2 + b} \, dx = \frac{1}{\sqrt{ab}} \arctan \left( \frac{x}{\sqrt{ab}} \right) + C, \quad \text{if } ab > 0 \)

33. \( \int \frac{1}{ax^2 + b} \, dx = \frac{1}{2\sqrt{a}} \ln \left| \frac{b + x\sqrt{-ab}}{b - x\sqrt{-ab}} \right| + C = \frac{1}{\sqrt{-ab}} \tanh^{-1} \left( \frac{x\sqrt{-ab}}{b} \right) + C, \quad \text{if } ab < 0 \)

34. \( \int \frac{1}{ax^2 - b} \, dx = \frac{1}{2\sqrt{a}} \ln \left| \frac{x\sqrt{a} - \sqrt{b}}{x\sqrt{a} + \sqrt{b}} \right| + C, \quad \text{if } a > 0, b > 0 \)

35. \( \int \frac{1}{ax^2 + b} \, dx = \frac{1}{2a} \left( \frac{(ax + b)^{p+1}}{p+1} \right) + C, \quad \text{if } p \neq -1 \)

36. \( \int \frac{x}{ax^2 + b} \, dx = \frac{1}{2a} \ln |ax^2 + b| + C \)

37. \( \int \frac{x}{(ax^2 + b)^p} \, dx = \frac{1}{2pa(ax^2 + b)^p} + C, \quad \text{if } p > 0 \)

38. \( \int \frac{1}{\sqrt{ax^2 + b}} \, dx = \frac{1}{2b} \ln \left| \frac{x}{\sqrt{ax^2 + b}} \right| + C \)

39. \( \int \sqrt{ax^2 + b} \, dx = \frac{x}{2} \sqrt{ax^2 + b} + b \frac{1}{2\sqrt{a}} \ln |x\sqrt{a} + \sqrt{ax^2 + b}| + C, \quad \text{if } a > 0 \)

40. \( \int \sqrt{ax^2 + b} \, dx = \frac{x}{2} \sqrt{ax^2 + b} + b \frac{1}{2\sqrt{-a}} \arcsin \left( \frac{x\sqrt{-a}}{b} \right) + C, \quad \text{if } a < 0 \)

**Algebraic Functions (of x and ax^2 + bx + c)**

41. \( \int \frac{1}{ax^2 + bx + c} \, dx = \frac{2a + b}{\sqrt{Y}} \arctan \left( \frac{2ax + b}{\sqrt{Y}} \right) + C, \quad \text{if } Y > 0 \)

42. \( \int \frac{1}{ax^2 + bx + c} \, dx = \frac{2}{\sqrt{-Y}} \ln \left| \frac{2ax + b - \sqrt{-Y}}{2ax + b + \sqrt{-Y}} \right| + C = \frac{-2}{\sqrt{-Y}} \tan^{-1} \left( \frac{2ax + b}{\sqrt{-Y}} \right) + C, \quad \text{if } Y < 0 \)

\( X \equiv ax^2 + b + c, Y \equiv 4ac - b^2 \)
43. \[ \int \frac{1}{\sqrt{ax^2 + bx + c}} \, dx = \frac{1}{\sqrt{a}} \ln \left| X + x\sqrt{a} + \frac{b}{2\sqrt{a}} \right| + C, \text{ if } a > 0 \]
44. \[ \int \frac{1}{\sqrt{ax^2 + bx + c}} \, dx = \frac{1}{\sqrt{-a}} \arcsin \left( \frac{-2ax - b}{\sqrt{-Y}} \right) + C, \text{ if } a < 0 \]
45. \[ \int \frac{x}{ax^2 + bx + c} \, dx = \frac{1}{2a} \ln |X| - b \left( \frac{dx}{X} \right) \]

**Algebraic Functions (of x and \( x^2 \pm a^2 \))**

46. \[ \int \sqrt{x^2 \pm a^2} \, dx = \frac{1}{2} \left[ x\sqrt{x^2 \pm a^2} \pm a \ln |x + \sqrt{x^2 \pm a^2}| \right] + C \]
47. \[ \int \frac{1}{\sqrt{x^2 \pm a^2}} \, dx = \ln |x + \sqrt{x^2 \pm a^2}| + C \]
48. \[ \int x\sqrt{x^2 \pm a^2} \, dx = \frac{1}{3} \sqrt{(x^2 \pm a^2)^3} + C \]
49. \[ \frac{1}{x} \sqrt{x^2 + a^2} \, dx = \sqrt{x^2 + a^2} - a \ln \left( \frac{a + \sqrt{x^2 + a^2}}{x} \right) + C \]
50. \[ \frac{1}{x} \sqrt{x^2 - a^2} \, dx = \sqrt{x^2 - a^2} - a \arcsin \frac{x}{a} + C \]
51. \[ \int \frac{x}{\sqrt{x^2 \pm a^2}} \, dx = \sqrt{x^2 \pm a^2} + C \]
52. \[ \int \frac{1}{x\sqrt{x^2 \pm a^2}} \, dx = \frac{1}{a} \ln \left| \frac{\sqrt{x^2 \pm a^2} + a}{x} \right| + C = -\frac{1}{a} \sinh^{-1} \frac{a}{x} + C \]
53. \[ \int \frac{1}{x\sqrt{x^2 - a^2}} \, dx = \frac{1}{a} \arccos \frac{x}{a} + C = \frac{1}{a} \arccos \frac{a}{x} + C \]
54. \[ \int \sqrt{(x^2 \pm a^2)^3} \, dx = \frac{1}{8} \left[ 2x\sqrt{(x^2 \pm a^2)^3} \pm 3a^2 x\sqrt{x^2 \pm a^2} + 3a^4 \ln |x - \sqrt{x^2 \pm a^2}| \right] + C \]
55. \[ \frac{1}{\sqrt{(x^2 \pm a^2)^3}} \, dx = \frac{1}{a^2\sqrt{x^2 \pm a^2}} + C \]
56. \[ x\sqrt{(x^2 \pm a^2)^3} \, dx = \frac{1}{5} \sqrt{(x^2 \pm a^2)^5} + C \]
57. \[ \frac{x}{(x^2 \pm a^2)^3} \, dx = \frac{-1}{\sqrt{x^2 \pm a^2}} + C \]
58. \[ \frac{1}{a^2 - x^2} \, dx = \frac{1}{2a} \ln \left| \frac{a + x}{a - x} \right| + C = \frac{1}{a} \tanh^{-1} \frac{x}{a} + C \]
59. \[ \int \frac{1}{a^2 - x^2} \, dx = \arcsin \frac{x}{a} + C = -\arccos \frac{x}{a} + C \]

**Algebraic Functions (of x and \( a^2 - x^2 \))**

60. \[ \sqrt{a^2 - x^2} \, dx = \frac{1}{2} \left[ x\sqrt{a^2 - x^2} + a^2 \arcsin \frac{x}{a} \right] + C \]
61. \[ x\sqrt{a^2 - x^2} \, dx = -\frac{1}{3} \sqrt{(a^2 - x^2)^3} + C \]
62. \[ \frac{1}{x} \sqrt{a^2 - x^2} \, dx = \sqrt{a^2 - x^2} - a \ln \left( \frac{a + \sqrt{a^2 - x^2}}{x} \right) + C \]
63. \[ \frac{-x}{\sqrt{a^2 - x^2}} \, dx = -\sqrt{a^2 - x^2} + C \]
64. \[ \frac{1}{x\sqrt{a^2 - x^2}} \, dx = \frac{1}{a} \ln \left| \frac{a + \sqrt{a^2 - x^2}}{x} \right| + C = -\frac{1}{a} \cosh^{-1} \frac{a}{x} + C \]
65. \[ \sqrt{(a^2 - x^2)^3} \, dx = \frac{1}{8} \left[ 2x\sqrt{(a^2 - x^2)^3} + 3a^2 x\sqrt{a^2 - x^2} + 3a^4 \arcsin \frac{x}{a} \right] + C \]
46. \( \int \frac{1}{\sqrt{(a^2 - x^2)^3}} \, dx = \frac{x}{a^2 \sqrt{a^2 - x^2}} + C \)

67. \( \int x \sqrt{(a^2 - x^2)^5} \, dx = -\frac{1}{5} \sqrt{(a^2 - x^2)^3} + C \)

68. \( \int \frac{x}{\sqrt{(a^2 - x^2)^3}} \, dx = \frac{1}{\sqrt{a^2 - x^2}} + C \)

**Other Algebraic Functions**

69. \( \int 2ax - x^2 \, dx = \frac{1}{2} \left[ (x-a) \sqrt{2ax - x^2} + a^2 \arcsin \frac{x-a}{a} \right] + C \)

70. \( \int \frac{1}{\sqrt{2ax - x^2}} \, dx = \arccos \frac{a-x}{a} + C \)

71. \( \int \sqrt{\frac{1+x}{1-x}} \, dx = \arcsin x - \sqrt{1-x^2} + C \)

**Logarithmic Functions**

72. \( \int \log_a |x| \, dx = x \log_a |x| - \frac{x}{\ln a} + C, \quad \text{if } a \neq 1, a > 0 \)

73. \( \int (\ln |x|)^2 \, dx = x (\ln |x|)^2 - 2x \ln |x| + 2x + C \)

74. \( \int x \ln |x| \, dx = \frac{x^2}{2} \ln |x| - \frac{x^2}{4} + C \)

75. \( \int \frac{1}{x \ln |x|} \, dx = \ln |\ln |x|| + C \)

76. \( \int x^p \ln |x| \, dx = x^{p+1} \left[ \frac{\ln |x|}{p+1} - \frac{1}{(p+1)^2} \right] + C, \quad \text{if } p \neq -1 \)

77. \( \int \frac{(\ln |x|)^p}{x} \, dx = \frac{1}{p+1} (\ln |x|)^{p+1} + C, \quad \text{if } p \neq -1 \)

78. \( \int \sin(\ln |x|) \, dx = \frac{x}{2} (\sin(\ln |x|) - \cos(\ln |x|)) + C \)

79. \( \int \cos(\ln |x|) \, dx = \frac{x}{2} (\sin(\ln |x|) + \cos(\ln |x|)) + C \)

**Exponential Functions**

80. \( \int xe^{ax} \, dx = \frac{1}{a^2} x e^{ax} (ax - 1) + C \)

81. \( \int x^m e^{ax} \, dx = \frac{1}{a} x^m e^{ax} - \frac{m}{a} \int x^{m-1} e^{ax} \, dx, \quad m \geq 2 \)

82. \( \int \frac{1}{x} e^{ax} \, dx = \ln |x| + ax + \frac{1}{2(2!)a^2} (ax)^2 + \frac{1}{3(3!)a^3} (ax)^3 + \cdots + C \)

83. \( \int \frac{1}{1 + e^x} \, dx = x - \ln |1 + e^x| + C \)

84. \( \int \frac{1}{ae^{px} + b} \, dx = \frac{x}{b} - \frac{1}{bp} \ln |ae^{px} + b| + C, \quad \text{if } b \neq 0, p \neq 0 \)

85. \( \int \frac{1}{ae^{px} + be^{-px}} \, dx = \frac{1}{p \sqrt{ab}} \arctan \left( \frac{e^{px}}{\sqrt{ab}} \right) + C, \quad \text{if } ab > 0 \)

86. \( \int e^{ax} \ln |bx| \, dx = \frac{1}{a} e^{ax} \ln |bx| - \frac{1}{a} \int \frac{e^{ax}}{x} \, dx \)

**Trigonometric Functions**

87. \( \int \sin^3 (ax + b) \, dx = -\frac{1}{3a} \cos(ax + b) \left[ \sin^2 (ax + b) + 2 \right] + C \)

88. \( \int \sin^4 (ax + b) \, dx = \frac{3x}{8} - \frac{3}{16a} \sin 2(ax + b) - \frac{1}{4a} \sin^3 (ax + b) \cos(ax + b) + C \)
89. $\int x \sin(ax+b) \, dx = \frac{1}{a^2} \sin(ax+b) - \frac{x}{a} \cos(ax+b) + C$

90. $\int x \sin^2(ax+b) \, dx = \frac{x^2}{4} - \frac{1}{4a} x \sin 2(ax+b) - \frac{1}{8a^2} \cos 2(ax+b) + C$

91. $\int x^2 \sin^2(ax+b) \, dx = \frac{1}{6} x^3 - \left( \frac{1}{4a} x^2 - \frac{1}{8a^3} \right) \sin 2(ax+b) - \frac{1}{4a^2} x \cos 2(ax+b) + C$

92. $\int \frac{1}{x} \sin ax \, dx = ax - \frac{1}{3(3!)^a} (ax)^3 + \frac{1}{5(3!)^a} (ax)^5 + \cdots + C$

93. $\int \sin ax \sin bx \, dx = \frac{1}{2(a-b)} \sin(a-b)x - \frac{1}{2(a+b)} \sin(a+b)x + C$, if $a^2 \neq b^2$

94. $\int \cos^3(ax+b) \, dx = \frac{1}{a} \sin(ax+b) - \frac{1}{3a} \sin^3(ax+b) + C$

95. $\int \cos^4(ax+b) \, dx = \frac{3x}{8} + \frac{1}{16a} 3 \sin 2(ax+b) + \frac{1}{4a^2} \cos^3(ax+b) \sin(ax+b) + C$

96. $\int x \cos(ax+b) \, dx = \frac{1}{a^2} \cos(ax+b) + \frac{x}{a} \sin(ax+b) + C$

97. $\int x^2 \cos(ax+b) \, dx = \frac{x^2}{4} + \frac{1}{4a} x \sin 2(ax+b) + \frac{1}{8a^2} \cos 2(ax+b) + C$

98. $\int x^2 \sin^2(ax+b) \, dx = \frac{x^3}{6} + \left( \frac{x^2}{4a} - \frac{1}{8a^3} \right) \sin 2(ax+b) + \frac{1}{4a^2} x \cos 2(ax+b) + C$

99. $\int \frac{1}{x} \cos ax \, dx = \ln |ax| - \frac{1}{2(2!)} (ax)^2 + \frac{1}{4(4!)} (ax)^4 + \cdots + C$

100. $\int \frac{1}{1 + \cos(ax+b)} \, dx = \frac{1}{a} \tan \left( \frac{ax+b}{2} \right) + C$

101. $\int \frac{1}{1 - \cos(ax+b)} \, dx = -\frac{1}{a} \cot \left( \frac{ax+b}{2} \right) + C$

102. $\int \cos ax \cos bx \, dx = \frac{1}{2(a-b)} \sin(a-b)x + \frac{1}{2(a+b)} \sin(a+b)x + C$, if $a^2 \neq b^2$

103. $\int \sin ax \cos bx \, dx = -\frac{1}{2(a-b)} \cos(a-b)x - \frac{1}{2(a+b)} \cos(a+b)x + C$, if $a^2 \neq b^2$

104. $\int \sin^p(ax+b) \cos(ax+b) \, dx = \frac{1}{a(p+1)} \sin^{p+1}(ax+b) + C$, if $p \neq -1$

105. $\int \sin(ax+b) \cos^p(ax+b) \, dx = -\frac{1}{a(p+1)} \cos^{p+1}(ax+b) + C$, if $p \neq -1$

106. $\int \sin^2(ax+b) \cos^2(ax+b) \, dx = -\frac{1}{32a} \sin 4(ax+b) + \frac{x}{8} + C$

107. $\int \tan(ax+b) \, dx = -\frac{1}{a} \ln |\cos(ax+b)| + C$

108. $\int \tan^2(ax+b) \, dx = \frac{1}{a} \tan(ax+b) - x + C$

109. $\int \tan^3(ax+b) \, dx = \frac{1}{2a} \left[ \tan^2(ax+b) + 2 \ln |\cos(ax+b)| \right] + C$

110. $\int \cot(ax+b) \, dx = \frac{1}{a} \ln |\sin(ax+b)| + C$

111. $\int \cot^2(ax+b) \, dx = -\frac{1}{2a} \left[ \cot^2(ax+b) + 2 \ln |\sin(ax+b)| \right] + C$

112. $\int \sec(ax+b) \, dx = \frac{1}{a} \ln \left| \tan \left( \frac{ax+b}{2} + \frac{\pi}{4} \right) \right| + C$

113. $\int \sec^2(ax+b) \, dx = \frac{1}{a} \tan(ax+b) + C$

114. $\int \cot^2(ax+b) \, dx = -\frac{1}{a} \cot(ax+b) - x + C$
<table>
<thead>
<tr>
<th>Equation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\int \sec^3(ax + b) , dx = \frac{1}{2a} \left[ \sec(ax + b) \tan(ax + b) + \ln \left</td>
<td>\tan \left( \frac{ax + b}{2} + \frac{\pi}{4} \right) \right</td>
</tr>
<tr>
<td>$\int \sec x \tan x , dx = \sec x + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \csc(ax + b) , dx = \frac{1}{a} \ln \left</td>
<td>\tan \left( \frac{ax + b}{2} \right) \right</td>
</tr>
<tr>
<td>$\int \csc^2(ax + b) , dx = -\frac{1}{a} \cot(ax + b) + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \csc x \cot x , dx = -\csc x + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \csc^3(ax + b) , dx = \frac{1}{2a} \left[ -\csc(ax + b) \cot(ax + b) + \ln \left</td>
<td>\tan \left( \frac{ax + b}{2} \right) \right</td>
</tr>
<tr>
<td>$\int \arcsin \frac{x}{a} , dx = x \arcsin \frac{x}{a} + \sqrt{a^2 - x^2} + C$</td>
<td></td>
</tr>
<tr>
<td>$\int x \arcsin ax , dx = \frac{1}{4a^2} \left[ (2a^2x^2 - 1) \arcsin ax + ax \sqrt{1 - a^2x^2} \right] + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \frac{1}{x^2} \arcsin ax , dx = a \ln \left</td>
<td>\frac{1 - \sqrt{1 - a^2x^2}}{ax} \right</td>
</tr>
<tr>
<td>$\int \arccos \frac{x}{a} , dx = x \arccos \frac{x}{a} - \sqrt{a^2 - x^2} + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \arctan \frac{x}{a} , dx = x \arctan \frac{x}{a} - \frac{a}{2} \ln(a^2 + x^2) + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \arccot \frac{x}{a} , dx = x \arccot \frac{x}{a} + \frac{a}{2} \ln(a^2 + x^2) + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \arccsc \frac{x}{a} , dx = x \arccsc \frac{x}{a} - a \ln \left</td>
<td>x + \sqrt{x^2 - a^2} \right</td>
</tr>
<tr>
<td>$\int \arcsec \frac{x}{a} , dx = x \arcsec \frac{x}{a} + a \ln \left</td>
<td>x + \sqrt{x^2 - a^2} \right</td>
</tr>
</tbody>
</table>

**Hyperbolic Functions**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\int \sinh ax , dx = \frac{1}{a} \cosh ax + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \sinh^2 ax , dx = \frac{1}{4a} \sinh 2ax - \frac{1}{2} x + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \cosh ax , dx = \frac{1}{a} \sinh ax + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \cosh^2 ax , dx = \frac{1}{4a} \sinh 2ax + \frac{1}{2} x + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \tanh ax , dx = \frac{1}{a} \ln</td>
<td>\cosh ax</td>
</tr>
<tr>
<td>$\int \tanh^2 ax , dx = x - \frac{1}{a} \tanh ax + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \coth ax , dx = \frac{1}{a} \ln</td>
<td>\sinh ax</td>
</tr>
<tr>
<td>$\int \coth^2 ax , dx = x - \frac{1}{a} \coth ax + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \sech ax , dx = \frac{1}{a} \arctan(\sinh ax) + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \sech^2 ax , dx = \frac{1}{a} \tanh ax + C$</td>
<td></td>
</tr>
<tr>
<td>$\int \csch ax , dx = -\frac{1}{a} \ln</td>
<td>\coth ax + \csch ax</td>
</tr>
</tbody>
</table>
140. \[ \int \text{csch}^2 ax \, dx = -\frac{1}{a} \coth ax + C \]

141. \[ \int \text{sech} ax \tanh ax \, dx = -\frac{1}{a} \text{sech} ax + C \]

142. \[ \int \text{csch} ax \coth ax \, dx = -\frac{1}{a} \text{csch} ax + C \]
## Error function table

The error function is a common definite integral that frequently appears in the physical sciences

\[
erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt
\]

A tabulation of values of the error function is provided below.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(0)</th>
<th>(0.1)</th>
<th>(0.2)</th>
<th>(0.3)</th>
<th>(0.4)</th>
<th>(0.5)</th>
<th>(0.6)</th>
<th>(0.7)</th>
<th>(0.8)</th>
<th>(0.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.0)</td>
<td>0.00000</td>
<td>0.01228</td>
<td>0.02256</td>
<td>0.03384</td>
<td>0.04511</td>
<td>0.05637</td>
<td>0.06762</td>
<td>0.07886</td>
<td>0.09008</td>
<td>0.10128</td>
</tr>
<tr>
<td>(0.1)</td>
<td>0.11246</td>
<td>0.12362</td>
<td>0.13476</td>
<td>0.14587</td>
<td>0.15695</td>
<td>0.16800</td>
<td>0.17901</td>
<td>0.18999</td>
<td>0.20094</td>
<td>0.21184</td>
</tr>
<tr>
<td>(0.2)</td>
<td>0.22280</td>
<td>0.23402</td>
<td>0.24524</td>
<td>0.25647</td>
<td>0.26772</td>
<td>0.27896</td>
<td>0.29020</td>
<td>0.30145</td>
<td>0.31270</td>
<td>0.32395</td>
</tr>
<tr>
<td>(0.3)</td>
<td>0.33313</td>
<td>0.34439</td>
<td>0.35565</td>
<td>0.36691</td>
<td>0.37818</td>
<td>0.38944</td>
<td>0.40070</td>
<td>0.41197</td>
<td>0.42324</td>
<td>0.43451</td>
</tr>
<tr>
<td>(0.4)</td>
<td>0.44577</td>
<td>0.45702</td>
<td>0.46828</td>
<td>0.47954</td>
<td>0.49080</td>
<td>0.50205</td>
<td>0.51331</td>
<td>0.52457</td>
<td>0.53583</td>
<td>0.54709</td>
</tr>
<tr>
<td>(0.5)</td>
<td>0.55834</td>
<td>0.56959</td>
<td>0.58084</td>
<td>0.59209</td>
<td>0.60334</td>
<td>0.61459</td>
<td>0.62584</td>
<td>0.63709</td>
<td>0.64834</td>
<td>0.65959</td>
</tr>
<tr>
<td>(0.6)</td>
<td>0.67083</td>
<td>0.68208</td>
<td>0.69332</td>
<td>0.70457</td>
<td>0.71582</td>
<td>0.72707</td>
<td>0.73832</td>
<td>0.74956</td>
<td>0.76081</td>
<td>0.77205</td>
</tr>
<tr>
<td>(0.7)</td>
<td>0.78329</td>
<td>0.79453</td>
<td>0.80577</td>
<td>0.81701</td>
<td>0.82825</td>
<td>0.83949</td>
<td>0.85072</td>
<td>0.86195</td>
<td>0.87318</td>
<td>0.88441</td>
</tr>
<tr>
<td>(0.8)</td>
<td>0.89564</td>
<td>0.90686</td>
<td>0.91808</td>
<td>0.92930</td>
<td>0.94052</td>
<td>0.95174</td>
<td>0.96296</td>
<td>0.97418</td>
<td>0.98540</td>
<td>0.99662</td>
</tr>
<tr>
<td>(0.9)</td>
<td>0.99783</td>
<td>0.99905</td>
<td>0.99927</td>
<td>0.99949</td>
<td>0.99971</td>
<td>0.99993</td>
<td>1.00015</td>
<td>1.00037</td>
<td>1.00059</td>
<td>1.00081</td>
</tr>
</tbody>
</table>
supplements

411

S8 Complementary error function table
The complementary error function is a common definite integral that frequently appears in the physical
sciences
Z
2 ∞ − t2
e dt
erfc( x ) = √
π x
A tabulation of values of the error function is provided below.
Hundredths digit of x
4
5

x

0

1

2

3

0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2

1.00000
0.88754
0.77730
0.67137
0.57161
0.47950
0.39614
0.32220
0.25790
0.20309
0.15730
0.11979
0.08969
0.06599
0.04771
0.03389
0.02365
0.01621
0.01091
0.00721
0.00468
0.00298
0.00186
0.00114
0.00069
0.00041
0.00024
0.00013
0.00008
0.00004
0.00002
0.00001
0.00001

0.98872
0.87638
0.76648
0.66109
0.56203
0.47076
0.38832
0.31533
0.25200
0.19812
0.15319
0.11647
0.08704
0.06394
0.04615
0.03272
0.02279
0.01559
0.01048
0.00691
0.00448
0.00285
0.00178
0.00109
0.00065
0.00039
0.00022
0.00013
0.00007
0.00004
0.00002
0.00001
0.00001

0.97744
0.86524
0.75570
0.65087
0.55253
0.46210
0.38059
0.30857
0.24619
0.19323
0.14916
0.11321
0.08447
0.06193
0.04462
0.03159
0.02196
0.01500
0.01006
0.00662
0.00428
0.00272
0.00169
0.00103
0.00062
0.00037
0.00021
0.00012
0.00007
0.00004
0.00002
0.00001
0.00001

0.96616
0.85413
0.74498
0.64072
0.54311
0.45354
0.37295
0.30190
0.24048
0.18844
0.14522
0.11003
0.08195
0.05998
0.04314
0.03048
0.02116
0.01442
0.00965
0.00634
0.00409
0.00259
0.00161
0.00098
0.00059
0.00035
0.00020
0.00011
0.00006
0.00003
0.00002
0.00001
0.00000

0.95489
0.84305
0.73430
0.63064
0.53377
0.44506
0.36541
0.29532
0.23486
0.18373
0.14135
0.10692
0.07949
0.05809
0.04170
0.02941
0.02038
0.01387
0.00926
0.00608
0.00391
0.00247
0.00154
0.00094
0.00056
0.00033
0.00019
0.00011
0.00006
0.00003
0.00002
0.00001
0.00000

0.94363
0.83200
0.72367
0.62062
0.52452
0.43668
0.35797
0.28884
0.22933
0.17911
0.13756
0.10388
0.07710
0.05624
0.04030
0.02838
0.01962
0.01333
0.00889
0.00582
0.00374
0.00236
0.00146
0.00089
0.00053
0.00031
0.00018
0.00010
0.00006
0.00003
0.00002
0.00001
0.00000

6

7

8

9

0.93238
0.82099
0.71310
0.61067
0.51534
0.42838
0.35062
0.28246
0.22390
0.17458
0.13386
0.10090
0.07476
0.05444
0.03895
0.02737
0.01890
0.01281
0.00853
0.00557
0.00358
0.00225
0.00139
0.00085
0.00050
0.00029
0.00017
0.00009
0.00005
0.00003
0.00002
0.00001
0.00000

0.92114
0.81001
0.70258
0.60079
0.50625
0.42018
0.34337
0.27618
0.21856
0.17013
0.13023
0.09800
0.07249
0.05269
0.03763
0.02640
0.01819
0.01231
0.00818
0.00534
0.00342
0.00215
0.00133
0.00080
0.00048
0.00028
0.00016
0.00009
0.00005
0.00003
0.00001
0.00001
0.00000

0.90992
0.79906
0.69212
0.59099
0.49725
0.41208
0.33622
0.26999
0.21331
0.16577
0.12667
0.09516
0.07027
0.05098
0.03635
0.02545
0.01751
0.01183
0.00784
0.00511
0.00327
0.00205
0.00126
0.00076
0.00045
0.00026
0.00015
0.00008
0.00005
0.00003
0.00001
0.00001
0.00000

0.89872
0.78816
0.68172
0.58126
0.48833
0.40406
0.32916
0.26390
0.20816
0.16149
0.12320
0.09239
0.06810
0.04933
0.03510
0.02454
0.01685
0.01136
0.00752
0.00489
0.00312
0.00195
0.00120
0.00072
0.00043
0.00025
0.00014
0.00008
0.00004
0.00002
0.00001
0.00001
0.00000


## Table of Fourier transform pairs

Fourier transform pairs are useful in the harmonic analysis of functions and the solution of differential equations. This table summarizes Fourier transforms that most commonly appear in the physical sciences where the transform pairs are defined

\[
F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \quad f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} d\omega
\]

<table>
<thead>
<tr>
<th>(f(t))</th>
<th>(F(\omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (e^{-t^2/2})</td>
<td>(e^{-\omega^2/2})</td>
</tr>
<tr>
<td>2. (e^{-at^2}\ a &gt; 0)</td>
<td>(\frac{1}{\sqrt{2a}} e^{-\omega^2/4a})</td>
</tr>
<tr>
<td>3. (e^{-</td>
<td>t</td>
</tr>
<tr>
<td>4. (\left(\frac{a}{a^2 + t^2}\right)\ \text{Re}(a) &gt; 0)</td>
<td>(\sqrt{\frac{\pi}{2}} e^{-j</td>
</tr>
<tr>
<td>5. (\theta(t+a) - \theta(t-a) = \begin{cases} \frac{1}{2} &amp; -a &lt; t &lt; a \ 0 &amp; \text{otherwise} \end{cases})</td>
<td>(\sqrt{\frac{\pi}{2}} \sin(\omega a))</td>
</tr>
<tr>
<td>6. (\sin(at)/t\ a \in \mathbb{R})</td>
<td>(\sqrt{\frac{\pi}{2}} [\theta(\omega+a) - \theta(\omega-a)] = \begin{cases} \sqrt{\frac{\pi}{2}} &amp; -a &lt; \omega &lt; a \ 0 &amp; \text{otherwise} \end{cases})</td>
</tr>
<tr>
<td>7. (1)</td>
<td>(\sqrt{2\pi} \delta(\omega))</td>
</tr>
<tr>
<td>8. (\delta(t+a))</td>
<td>(\frac{1}{\sqrt{2\pi}} e^{i\omega t})</td>
</tr>
<tr>
<td>9. (e^{i\omega_0 t})</td>
<td>(\sqrt{2\pi} \delta(\omega - \omega_0))</td>
</tr>
<tr>
<td>10. (\cos \omega_0 t\ \omega_0 \in \mathbb{R})</td>
<td>(\sqrt{\frac{\pi}{2}} [\delta(\omega + \omega_0) + \delta(\omega - \omega_0)])</td>
</tr>
<tr>
<td>11. (\sin \omega_0 t\ \omega_0 \in \mathbb{R})</td>
<td>(\sqrt{\frac{\pi}{2}} i [\delta(\omega + \omega_0) - \delta(\omega - \omega_0)])</td>
</tr>
<tr>
<td>12. (e^{-</td>
<td>t</td>
</tr>
<tr>
<td>13. (\frac{d}{dt} f(t)\ \text{differentiable} f(t))</td>
<td>(i\omega F(\omega))</td>
</tr>
<tr>
<td>14. (f(t) e^{-i\omega_0 t})</td>
<td>(F(\omega + \omega_0))</td>
</tr>
<tr>
<td>15. (f(t + t_0))</td>
<td>(F(\omega) e^{i\omega t_0})</td>
</tr>
<tr>
<td>16. (f(st)\ s \in \mathbb{R})</td>
<td>(\frac{1}{</td>
</tr>
<tr>
<td>17. (\int_{-\infty}^{\infty} f(s) g(t-s) ds = (f \ast g)(t))</td>
<td>(\sqrt{2\pi} F(\omega) G(\omega))</td>
</tr>
<tr>
<td>18. (f(t)g(t))</td>
<td>(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) G(\omega - \omega) d\omega = \frac{1}{\sqrt{2\pi}} (F \ast G)(\omega))</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


Index

x-intercept, 13
68-95-99.7 rule (probability), 181

l'Hôpital's rule, 134

abscissa, 13, 21
absolute value, 30, 328
absorbance, 37
absorbing boundary condition (differential equations), 265, 267, 269
acoustic mode (oscillation), 353
al-Khwârîzmi, Muhammad ibn Mûsâ (780-850), 14
algebraic function, 18
algebraic substitution (integration), 150
alternating harmonic series, 122
angular frequency, 234
angular momentum, 73
ansatz (differential equations), 203
anticommutative property (vectors), 72
antiderivative, 203
auxiliary equation (differential equations), 220
Avogadro's number, 158
Barrow, Isaac (1630-1677), 144
base (logarithm), 34
basis functions, 298
basis vectors, 298
bell curve, 20
Bernoulli, Jacob (1655-1705), 16
Bessel's equation (differential equations), 250
binary logarithm, 34
Binet's formula, 250
binomial coefficient, 171
binomial distribution, 170, 171
birth-death process (kinetics), 204
blackbody radiation, 133, 139
block matrix, 322
Bohr model, 110
Bohr radius, 117, 188
Bohr, Niels (1885-1962), 111
Boltzmann entropy formula, 38
Boltzmann, Ludwig (1844-1906), 38
boundary condition (differential equations), 209, 220, 231
bounded (functions), 16
Box-Mueller method (random numbers), 193
bridge (card game), 197
Broglie, Louis (1892-1928), 111
butterfly potential, 116
Cantor, Georg (1845-1918), 292
capacity dimension, 136
carbon tetrachloride (CCl4), 383
Cardano, Gerolamo (1501-1576), 29
cartesian coordinates, 13, 23
Cauchy, Augustin-Louis (1789-1857), 122, 342
causic, 354
central limit theorem, 191
centripetal force, 112
centripetal force, 71, 112
chain rule (differentiation), 49, 50
characteristic, 35
characteristic equation, 342, 346, 348, 351, 367
characteristic polynomial, 367
chloroform (CHCl3), 383
 Clairaut's theorem, 53
classical diffusion equation, 254, 266
classical heat equation, 251, 265, 273, 307
classical wave equation, 267, 273, 306
Clairaut, Rudolf (1822-1888), 54
Clairaut-Clapeyron equation, 147
cofactor (matrices), 314, 325
column matrix, 311
column vector, 311
common logarithm, 34
commutative property (matrices), 321
commutative property (operators), 80
commutative property (vectors), 69
commutator (matrices), 321
commutator (operators), 80
comparison test, 121
complementary error function, 183, 257
completing the square, 15
complex conjugate, 30, 302, 328, 329
complex function, 33
complex number, 20, 33, 220
complex plane, 29
composite function, 49, 55
composition vector (kinetics), 347
coupled equation, 19, 50
coupland transformation, 378
compressibility factor, 165
Condorcet, Nicolas (1743-1794), 51
constructive interference, 279
continuous (functions), 16, 46
continuous variables, 119
correlation coefficient (statistics), 184
Coulomb's law, 90
Coulomb, Charles-Augustin (1736-1806), 90
coulombic potential, 90
countably infinite, 292
covariance (statistics), 184
Cramer's rule, 331, 342
Cramer, Gabriel (1704-1752), 331
critical point, 106
cross correlation (statistics), 184
cross product, 71, 312
cyclic rule (derivatives), 62
cylindrical coordinates, 25
d'Alembert, Jean le Rond (1717-1783), 120, 259
damped cosine, 19, 305
de Moivre's identity, 42
decision tree, 379
definite integral, 144
degree (polynomial), 15
derivative, 45
derivative notation, 46
Descartes, René (1596-1650), 13
destructive interference, 279
detailed balance (kinetics), 208
determinant, 72, 106, 312
differential, 54
differential operator, 80
diffusion coefficient, 254
Dirac delta function, 148, 162
Dirac, Paul (1902-1984), 149
direct dependence, 55
discovery (mathematics), 29
discrete variables, 119
discriminant, 14
displacement vector (dynamics), 351
distributive property (matrices), 321
distributive property (operators), 79
divergence operator (vectors), 86
domain (functions), 16
dot product, 69, 71, 319
double factorial, 166
double integral, 153
double roots (differential equations), 225
dummy variable (integration), 205
eigenfunction, 356
eigenvalue, 342, 343, 356
eigenvalue matrix, 345
eigenvalue problem, 342, 346
eigenvector, 343
eigenvector matrix, 345, 346
Einstein summation convention, 321
electromagnetic spectrum, 34
energy operator, 81, 358
eergy theorem (Fourier series), 307
equations of state, 59
equilibrium constant (kinetics), 208
equiprobable function, 138, 149, 183, 257, 408, 409
Euclid (circa 300 BCE), 23, 45, 119, 171
Euler's constant, 16
Euler's formula, 31
Euler's identity, 33
Euler's test, 56
Euler's theorem, 58
Euler, Leonard (1707-1783), 31, 137, 290
Noether’s theorem, 235
Noether, Emmy (1882-1935), 235
non-homogeneous equation (differential equations), 205
non-linear differential equation, 204
non-singular matrix, 325
non-trivial solution (differential equations), 252
non-trivial solution (linear equations), 342
normal (vector), 72
normal distribution, 20
normal distribution (probability), 191
normal modes (oscillation), 353, 355
normalization constant, 177
normalized (functions), 300
normalized (vectors), 65, 298
normalized distribution (probability), 177
observable operator, 357
odd function, 16
operator, 79
optical mode (oscillation), 354
ordered pair, 13
orders of magnitude, 34
ordinary (differential equations), 203
ordinate, 13, 21
Oresme, Nicole (circa 1320-1382), 121
orthogonal (functions), 300
orthogonal (vectors), 60, 298
orthogonal matrix, 323, 336, 345, 354
orthonormal vectors, 324
out-of-phase oscillation, 353
overdamped motion, 20, 238
parabola, 13
parabolic wave (function), 305, 307
parametric functions, 27
Parseval’s theorem (Fourier series), 281
partial derivative, 51
partial differential equation, 251
partial fractions (integration), 151
partial sum, 119
particle diffusion coefficient, 266
particle in a box, 47, 198, 356
Pascal’s triangle, 171
Pascal’s wager, 171
Pascal, Blaise (1623-1662), 171
Pauli exclusion principle, 317
Pauli matrices, 317, 328
Pauli, Wolfgang (1900-1958), 317
periodic step (function), 303
permittivity of a vacuum, 90
pH scale, 37
phase portrait, 236, 239
phase space, 236, 239
physical kinetics, 207
Planck’s constant, 165
plane polar coordinates, 21
plane waves, 82
platonic solids, 380, 381
point group, 373
polynomials, 15
potential energy, 89
potential energy landscape, 89
power series, 122, 227
probability, 169
probability distribution function, 177
product rule (differentiation), 48, 50
pseudorandom numbers, 192
Pythagoras (570-495 BCE), 22, 121
Pythagoras tree, 134
Pythagorean means, 194
Pythagorean theorem, 22
Pythagorean triple, 361
quadrant (cartesian coordinates), 21, 22
quadratic equation, 13, 343
quadratic forms, 345
quadratic formula, 14, 33, 220, 333, 343
quadratic mean, 194
quantization (angular momentum), 111
quantum number, 117
quantum fields, 237
quantum mechanics, 346
quantity, 45
quotient rule, 50
radioactive atomic nuclei, 179
radius of convergence, 222
rate constant (kinetics), 203
rate constant matrix (kinetics), 347
rate of change, 120
recurrence time (random numbers), 192
recursion relation (differential equations), 228
reduced equation (differential equations), 205
reflection matrix, 370, 372
reflection symmetry, 374
reflection transformation, 370, 372, 387
residual difference, 281, 288
Riemann sum, 145
Riemann surface, 40
Riemann, Bernhard (1826-1866), 40
right hand rule, 72
right hand rule (Fourier transform), 292, 294
root mean square, 194
roots (polynomials), 14
rotation matrices, 318
rotation transformation, 369, 372, 387
round functions, 21
row matrix, 312
row vector, 312
Rubik’s cube, 142
Rydberg constant, 113
Rydberg, Johannes (1854-1919), 113
saddle point (divergence), 87
saddle point (vector field), 83
sawtooth wave (function), 282, 305, 309
scalar operator, 79, 356
scalar product (vectors), 69
scalar triple product, 76
scalars, 65
scaling transformation, 367, 369, 386
secant line, 45
second derivative, 46
second order differential equation, 350
self-similarity, 134
semi-log plot, 18
semiclassical (quantum theory), 111
separable function, 155
shark fin wave, 284
shear transformation, 368, 387
Sierpinski carpet, 135, 141
Sierpinski gasket, 136, 141, 172
Sierpinski, Waclaw (1882-1969), 135
sifting property (delta function), 162
significant figures, 36
sine cardinal function, 294
sink (divergence), 87
sink (vector field), 83
smooth (functions), 46
source (divergence), 87
source (vector field), 83
special functions, 240
spherical harmonic analysis, 303
spherical harmonic functions, 310
square matrix, 312
square wave (function), 277, 291
square well potential, 165
standard deviation (statistics), 175
state function, 57
steady state (kinetics), 211
step function (Fourier series), 281, 285
Stevin, Simon (1548-1620), 14
Stirling’s approximation, 39, 197
Stirling, James (1692-1770), 39
superposition (differential equations), 204, 219, 241, 245
survival probability, 180, 270
symmetric matrix, 328
table of integrals, 156
tangent line, 45, 52, 59
tangent plane, 59
taylor polynomial, 130
taylor series, 128
taylor, Brook (1685-1731), 128, 152
thermal diffusion coefficient, 265
thermal diffusivity, 251
total derivative, 56
total differential, 54, 56
trace (matrices), 320, 346
transmittance, 37
transpose matrix, 316
triangle wave (function), 280, 304, 306
trigonomometric transformation (integration), 151
trivial solution (differential equations),
220, 252, 260
trivial solution (linear equations), 342
truncated series, 132

uncountably infinite, 292
underdamped motion, 19, 238
uniform distribution (probability), 177, 192
unit circle, 21, 26, 397
unit vectors, 65, 311
unitary matrix, 329, 337

variance (statistics), 174

variational principle, 111
vector field, 83
vector function, 82–84, 318
vector notation, 65
vector operator, 84, 356
vector product, 71
vector projection, 69
vector space, 299
vector-valued function, 82
vectors, 65, 311

virial expansion, 165

Von Neumann, John (1903-1957), 191

wave function, 187

wave number (Fourier transform), 289, 290
weighting function (orthogonal functions), 300, 301

Wiener, Norbert (1894-1964), 193
work, 70

y-intercept, 13

Zeno (circa 490-430 BCE), 119
Zeno’s paradox, 119
zero frequency component (Fourier series), 276
zero matrix, 321
COLOPHON

This book was typeset using the \LaTeX\ document preparation system\(^1\) authored by Leslie Lamport and released in 1985. The \LaTeX\ output is formatted using the \TeX\ computer typesetting system\(^2\) designed by Donald Knuth and released in 1978. In 1986, I was a graduate student at Columbia University preparing my doctoral dissertation in \LaTeX. At that time, I could call Leslie Lamport to ask why all of my tables were floating to the end of the document. Now we have Stack Exchange.

The text is set in the humanist Palatino font designed by Hermann Zapf and released in 1949. It includes roman, italic, text figures, and small caps. Bold fonts are avoided.\(^3\)

The text layout was inspired by The Feynman Lectures on Physics with its \(8\frac{1}{2} \times 11\) inch page size, ample margins and margin notes, and rich variety of figures. The typography and design were informed by the work of Edward R. Tufte\(^4\) and specifically grew from a modified version of the Tufte Book \LaTeX\ template.

Tufte has articulated design principles to be followed in the clear presentation of quantitative information including data and mathematical functions.

Graphical excellence is that which gives to the viewer the greatest number of ideas in the shortest time with the least ink in the smallest space.

Edward R. Tufte

In the design of figures for this text, I have aspired, however imperfectly, to follow this principle.

All figures were composed using the Asymptote vector graphics language\(^5\) within the \LaTeX\ programming environment. While most figures are original compositions, others are closely derived from examples provided by the Asymptote resource. I have benefited from wisdom and source code shared by active Asymptote users through Art of Problem Solving and Stack Exchange without which the graphics in this text would not have been possible.


\(^5\) John C. Bowman and Andy Hammer-lindl. Asymptote: A vector graphics language. TUGBOAT: The Communications of the \TeX\ Users Group, 29:288–294, 2008; and John C. Bowman and Orest Shardt. Asymptote: Lifting \TeX\ to three dimensions. TUGBOAT: The Communications of the \TeX\ Users Group, 30:58–63, 2009