Errata for First Edition of *Mathematical Methods for Molecular Science*

SUBSTANTIVE EDITS made to correct equations, clarify passages, or correct solutions to end-of-chapter problems are listed below.

CHAPTER 1

1. Page 17, in section 1.1.3, the last equation should read:

$$x = p_{\mathrm{Cl_2}} = p_{\mathrm{PCl_3}} = \frac{1}{2}K_p\left[-1+\sqrt{1+4/K_p}\right]$$

2. Page 26, notation in Figure 1.17 should read: $\pi + \tan^{-1}\left(\frac{y}{x}\right)$.
3. Page 27, the caption of Figure 1.18 should read: two lengths dr and $rd\theta$.
4. Page 31, in the first paragraph $x = r\cos\theta$ and $y = r\sin\theta$.
5. Page 32, end-of-chapter problem 1.5 should read: Identify the roots of the following equations in which $y = 0$.

CHAPTER 2

6. Page 43, in the caption of Table 2.1, replace "over six orders of magnitude" with "over seven orders of magnitude."
7. Page 48, replace "For very large N, we can approximate this sum in terms of an integral" with "We can approximate this sum as an integral that is readily evaluated" and so on.

CHAPTER 5

8. Page 104, the two references to Figure 5.6 should be to Figure 5.5.
9. Page 122, the equation for **f** should read:

$$\mathbf{f} = \frac{\partial V}{\partial r}\,\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial V}{\partial \theta}\,\hat{\boldsymbol{\theta}} + \frac{\partial V}{\partial z}\,\hat{\mathbf{z}} = f_r\,\hat{\mathbf{r}} + f_\theta\,\hat{\boldsymbol{\theta}} + f_z\,\hat{\mathbf{z}}$$

10. Page 124, in end-of-chapter problem 5.10, the passage "An interpretation of the *Heisenberg uncertainty principle* is that the operator..." should be replaced with "According to the *Heisenberg uncertainty principle*, the operator..." and so on.
11. Page 125, in end-of-chapter problem 5.16, the passage "and the vector $\mathbf{r} = x\,\hat{\mathbf{i}} + y\,\hat{\mathbf{j}} + z\,\hat{\mathbf{k}}$." is better written "and the vector $\mathbf{r} = x\,\hat{\mathbf{i}} + y\,\hat{\mathbf{j}} + z\,\hat{\mathbf{k}}$, where $\hat{\mathbf{i}} = \hat{\mathbf{x}}$, $\hat{\mathbf{j}} = \hat{\mathbf{y}}$, and $\hat{\mathbf{k}} = \hat{\mathbf{z}}$."

CHAPTER 6

12. Page 139, in end-of-chapter problem 6.4, the area formula should read: $A(x,y,z) = 2(xy + yz + zx)$.
13. Page 141, in end-of-chapter problem 6.10, the function should be: $V(x,y) = ((x-y)^2 - 1)^2 + 20x^2y^2$.

CHAPTER 7

14. Page 167, the first equation should read:

$$\int_{-\infty}^{\infty} \delta(x - x_0)\,dx = 1$$

Chapter 8

15. Page 177, replace "Every infinite series will converge, to a finite number, or diverge, to positive or negative infinity. How do we know if a given series, such as the harmonic series, will converge or diverge?" with "Every infinite series will converge, diverge to positive or negative infinity, or oscillate without approaching a limit. How do we know if a given series will converge?"
16. Page 188, four occurrences of $(x - x_0)$ should be replaced by $(x - \bar{x})$.

Chapter 9

17. Page 205, the passage "Now consider a crystal consisting of $N_0 = 6 \times 10^{23}$ indistinguishable atoms." should be replaced with "Now consider a crystal consisting of $N_0 = 6 \times 10^{23}$ distinguishable atoms."
18. Page 206, in the last paragraph, replace "three unique outcomes" with "three distinct classes of outcomes" and "N outcomes is $N!$" with "N distinguishable symbols is $N!$" and "any outcomes" with "before accounting for repeated outcomes."
19. Page 208, in the penultimate paragraph, replace "resulting in four heads and two tails" with "resulting in two heads and four tails."
20. Page 209, in the first full paragraph, replace "And what if the spins are indistinguishable, rather than distinguishable?" with "And what if we only care about the number of up and down spins?"
21. Page 209, in footnote 7, the second sentence should read: For a given choice of the down spin, permutations among the remaining 9 up spins do not generate distinct configurations.
22. Page 209, the two sentences beginning "For example, for $N = 3$ choices of $k = 4$ numbers ..." should read: For example, for $N = 3$ choices of $k = 4$ numbers from the set $\{1, 2, 3, 4\}$ the sequences $2, 3, 4$ and $1, 3, 4$ correspond to different outcomes, whereas the sequences $2, 3, 4$ and $3, 2, 4$ correspond to the same outcome. The probability of choosing a distinct outcome will be the probability of choosing that ordered sequence times the multiplicity of distinct orderings corresponding to that outcome.
23. Page 209, the two sentences beginning "For a sequence of N choices from a set $\{1, 2, 3, 4\}$ ..." should read: For a sequence of N choices from a set $\{1, 2, 3, 4\}$ having n_1 ones, n_2 twos, n_3 threes, and n_4 fours, there will be

$$n_1! n_2! n_3! n_4!$$

equivalent orderings of the sequence that do not generate distinct outcomes, where $n_1 + n_2 + n_3 + n_4 = N$. It follows that the number of distinct sequences that can be chosen, having n_1 ones, n_2 twos, n_3 threes, and n_4 fours, is the total number of possible orderings $N!$ divided by the number of equivalent reorderings $n_1! n_2! n_3! n_4!$, or

$$\frac{N!}{n_1! n_2! n_3! n_4!}$$

24. Page 227, replace "wave functions for four possible states" to "wave functions for five possible states."
25. Page 231, replace "As N is increased, the normalized sum of the measured averages tends to a gaussian distribution" to "As N is increased, the distribution of the normalized sample mean approaches a gaussian distribution."

Chapter 11

26. Page 267, in Figure 11.5, replace the equation $y(x) = \cos(3x) + 2\sin(3x)$ with $y(x) = \cos(3x) + 2\sin(3x)$ and in the caption the equation should read: $y(x) = \cos(3x) + 2\sin(3x)$.
27. Page 289, the second Hermite polynomial should be $H_2(x) = 4x^2 - 2$.

Chapter 12

28. Page 315, below Equation (12.22) the paragraph should read: As such, we can readily express the wave equation in two-dimensional plane polar coordinates for $h(r, \theta, t)$, three-dimensional cartesian coordinates for $h(x, y, z, t)$, cylindrical coordinates for $h(r, \theta, z, t)$, or spherical polar coordinates for $h(r, \theta, \varphi, t)$, by simply using the appropriate form of the operator ∇^2 (as provided in Complement C5).

29. Page 318, the definitions of *heat energy* and *heat energy flux* have been updated as follows: The heat energy per unit length at a position x and time t for a material with heat capacity c and density ρ will be

$$\text{heat energy} = c\rho\, u(x,t)$$

The flux of heat energy passing any point x per unit time will be

$$\text{heat energy flux} = -k\, \frac{\partial u(x,t)}{\partial x}$$

where k is the *thermal conductivity* of the material.
The equality

$$\text{change in heat energy} = \text{difference in heat energy flux}$$

has been revised to read:

$$c\rho\, [u(x, t + \Delta t) - u(x,t)]\, \Delta x = -k \left[\frac{\partial u(x,t)}{\partial x}\bigg|_{x} - \left(-k \frac{\partial u(x,t)}{\partial x}\bigg|_{x+\Delta x} \right) \right] \Delta t$$

which we can rearrange as

$$\frac{1}{\Delta t}\, [u(x, t + \Delta t) - u(x,t)] = \kappa \frac{1}{\Delta x} \left[\frac{\partial u(x,t)}{\partial x}\bigg|_{x+\Delta x} - \frac{\partial u(x,t)}{\partial x}\bigg|_{x} \right]$$

where $\kappa = k/(c\rho)$ is the *thermal diffusion coefficient*.

30. Page 320, the definitions of *number of particles* and *particle flux* have been updated as follows: The number of particles per unit length at a position x and time t will be

$$\text{number of particles} = c(x,t)$$

The flux of particles passing any point x per unit time will be

$$\text{particle flux} = -D\, \frac{\partial c(x,t)}{\partial x}$$

where D is the *particle diffusion coefficient*.
The equality

$$\text{change in number of particles} = \text{difference in particle flux}$$

has been revised to read:

$$[c(x, t + \Delta t) - c(x,t)]\, \Delta x = -D \left[\frac{\partial c(x,t)}{\partial x}\bigg|_{x} - \left(-D \frac{\partial c(x,t)}{\partial x}\bigg|_{x+\Delta x} \right) \right] \Delta t$$

Chapter 14

31. Page 403, in section 14.2.7, starting with the first full sentence the text should read: When the hermitian conjugate of a matrix is equal to its inverse, it is called a *unitary matrix*. In that case, the matrix has the property that

$$\mathbf{D}^{\dagger}\mathbf{D} = \mathbf{D}\mathbf{D}^{\dagger} = \mathbf{I}$$

Chapter 15

32. Page 434, in the caption of Figure 15.4, the first equation should read: $V(x) = \frac{1}{2}\kappa(x - x_0)^2$.
33. Page 442, after Equation 15.27 insert the text "where $\psi(0) = \psi(L) = 0$."
34. Page 443, the phrase "The real *kinetic energy operator* in quantum theory is hermitian..." should be replaced by "For the particle in a box, the real *kinetic energy operator* is hermitian..." In addition, a footnote was added to read "In general, whether the kinetic energy operator is hermitian depends on the boundary conditions satisfied by the wave functions it operates on."
35. Page 447, in end-of-chapter problem 15.14, the conversion from local mode coordinates $\mathbf{x}$ to normal mode coordinates $\mathbf{y}$ should read:

$$\mathbf{y}(t) = \mathbf{C}^{-1}\mathbf{x} = \begin{pmatrix} y_1(t) \\ y_2(t) \end{pmatrix}$$

36. Page 451, in end-of-chapter problem 15.20, replace "The equations of motion for the displacements s_1 and s_2..." with "The equations of motion for the small displacements s_1 and s_2..." In addition, replace "Solve the characteristic equation to find the two eigenvalues ω_1 and ω_2." with "Solve the characteristic equation to find the two eigenvalues ω_1^2 and ω_2^2."

Supplements

37. Page 502, in Supplement S9 the following table entry should read:

12.	$f(t) = \mathrm{e}^{-a\|t\|}\cos(\omega_0 t)$	$a > 0,\ \omega_0 \in \Re$	$F(\omega) = \sqrt{\frac{2}{\pi}}\left[\left(\frac{a/2}{a^2 + (\omega + \omega_0)^2}\right) + \left(\frac{a/2}{a^2 + (\omega - \omega_0)^2}\right)\right]$

38. Page 508, in Supplement S_{10} the answer to end-of-chapter problem 3.17 should read: $\frac{\partial u}{\partial s} = 2st(e^{-s} + t)(1 - e^{-s^2 t}) - e^{-s}(e^{-s^2 t} + s^2 t)$ and $\frac{\partial u}{\partial t} = s^2(e^{-s} + t)(1 - e^{-s^2 t}) + e^{-s^2 t} + s^2 t$.
39. Page 511, in Supplement S_{10} the answer to end-of-chapter problem 6.2 should read: $x^* = \frac{1}{2}L$.
40. Page 511, in Supplement S_{10} the answer to end-of-chapter problem 6.10 should read: For $(x, y) = (1, 0), V = 0, V_x = 0, V_y = 0, V_{xx} = 8$ and $D = 320$ making the point a minimum. For $(x, y) = (0, 0), V = 0, V_x = 0, V_y = 0, V_{xx} = -4$ and $D = 0$ which is inconclusive. For $(x, y) = (1/3, -1/3), V = \frac{5}{9}, V_x = 0, V_y = 0, V_{xx} = \frac{52}{9}$ and $D = -\frac{640}{9}$ making the point a saddle.
41. Page 512, in Supplement S_{10} the answer to end-of-chapter problem 7.7 should be $\frac{4\pi}{15}a^5$.
42. Page 515, in Supplement S_{10} the answer to end-of-chapter problem 9.4 for the number of permutations of the letters in Laplace should be 1260.
43. Page 517, in Supplement S_{10} the answer to end-of-chapter problem 11.4(a) should be $x^2 \sum_{n=0}^{\infty} n a_n x^n$.
44. Page 525, in Supplement S_{10} the answer to end-of-chapter problem 15.16 should be

(a) $m_1 \frac{d^2 x_1}{dt^2} = -3kx_1 + kx_2$, $m_2 \frac{d^2 x_2}{dt^2} = kx_1 - 3kx_2 + kx_3$, $m_3 \frac{d^2 x_3}{dt^2} = kx_2 - 3kx_3$, (b) $\mathbf{K} = \begin{pmatrix} 3k & -k & 0 \\ -k & 3k & -k \\ 0 & -k & 3k \end{pmatrix}$,

(c) $\frac{d^2}{dt^2}\mathbf{x} = -\omega^2 \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} \mathrm{e}^{i\omega t} = -\omega^2 \mathbf{x}(t) = -\mathbf{K}\mathbf{x}$, (d) $\omega_1^2 = (3 - \sqrt{2})k$, $\omega_2^2 = 3k$, $\omega_3^2 = (3 + \sqrt{2})k$, (e) $\mathbf{x}_1 = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$,

$\mathbf{x}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}$, $\mathbf{x}_3 = \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$, (f) $\mathbf{x}_1$ is an asymmetric stretch, $\mathbf{x}_2$ is a symmetric stretch, $\mathbf{x}_3$ is an asymmetric stretch.