CH651 Assignment 2, Due in Class, Monday November 9, 2015

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Q2.1 (i) Construct the harmonic oscillator potential energy matrix with elements $V_{i,j} = \langle i|V(\hat{x})|j\rangle$, where $V(x) = \frac{1}{2}m\omega^2 x^2$. Use the lowest four harmonic oscillator states: $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$ to build your matrix. (ii) Now construct the kinetic energy matrix $T_{i,j} = \langle i|\hat{p}^2/2m|j\rangle$ in this same eigenstate representation and sum your results to compute the total hamiltonian matrix.

Q2.2 To a good approximation the small amplitude intramolecular vibrations of molecules can be described by independent normal modes. This idea assumes that the vibrational hamiltonian can be written as a sum on independent harmonic oscillator terms, one for each normal mode of vibration. For a nonlinear triatomic, like water, there are three modes of vibration called the symmetric stretch, the antisymmetric stretch, and the bend and the normal mode hamiltonian has the form:

$$\hat{H}_{vib} = \frac{1}{2}(\hat{P}_S^2 + \omega_S^2\hat{Q}_S^2) + \frac{1}{2}(\hat{P}_A^2 + \omega_A^2\hat{Q}_A^2) + \frac{1}{2}(\hat{P}_B^2 + \omega_B^2\hat{Q}_B^2)$$

In this normal mode description the masses can be absorbed into the definition of the normal mode coordinate and momentum operators *e.g.* $\hat{Q}_S, \hat{P}_S$.

(i) Using the definitions of the coordinate and momentum operators for each mode in terms of their raising, $\hat{a}_k^+$, and lowering, $\hat{a}_k^-$, operators:

$$\hat{Q}_k = \sqrt{\frac{\hbar}{2\omega_k}}(\hat{a}_k^+ + \hat{a}_k^-) \quad \hat{P}_k = i\sqrt{\frac{\hbar\omega_k}{2}}(\hat{a}_k^+ - \hat{a}_k^-)$$

obtain an expression for the molecular vibrational hamiltonian of a water molecule written in terms of the number operators for each mode defined as $\hat{n}_k = \hat{a}_k^+\hat{a}_k^-$.

(ii) Compute the effect of the number operator for mode k, defined above, on energy eigenstate number n_k for this mode with wave function $\psi_{n_k}^{(k)}(Q_k)$.

(iii) Using the separation of variables idea, write down the general eigenfunction for this three mode problem. Give an expression for the general eigenstate energy of your eigenfunction.

(iv) From spectroscopy experiments, the normal mode vibrational frequencies of water are found to be $\bar{\nu}_S = 3652$ cm^{-1}, $\bar{\nu}_A = 3756$ cm^{-1}, and $\bar{\nu}_B = 1595$ cm^{-1}. (Here $\bar{\nu} = 1/\lambda$ is a convenient unit of frequency called the "wave number", it is the number of wavelengths of the exciting radiation that fit into a centimeter.) In a table give the energies and vibrational state assignments, *i.e.* the set of quantum number values (n_S, n_A, n_B) for the five lowest energy states: the ground state, the first excited state, *etc.* up to the fourth excited state.

Useful information: The raising and lowering operators for the different normal modes satisfy the following commutation relations:

$$[\hat{a}_j^-, \hat{a}_k^+] = \delta_{jk}$$

The effect of the raising and lowering operators for mode k on the energy eigen function number n_k for mode k are summarized below:

$$\hat{a}_k^+ \psi_{n_k}^{(k)}(Q_k) = \sqrt{n_k + 1}\, \psi_{n_k+1}^{(k)}(Q_k)$$
$$\hat{a}_k^- \psi_{n_k}^{(k)}(Q_k) = \sqrt{n_k}\, \psi_{n_k-1}^{(k)}(Q_k)$$

Q2.3 In class we employed a small τ approximation to the operator $\exp[-\tau(\hat{A} + \hat{B})]$ where the operators $\hat{A}$ and $\hat{B}$ did not commute *i.e.* $[\hat{A}, \hat{B}] \neq 0$. In particular we used the approximation $\exp[-\tau(\hat{A}+\hat{B})] = \exp[-\tau\hat{A}]\exp[-\tau\hat{B}] + \mathcal{O}(\tau^2)$, *i.e.* we used an approximation that was exact to first order in τ, so that the error was of order τ^2, *i.e.* $\mathcal{O}(\tau^2)$.

(i) Compute the error term that is $\mathcal{O}(\tau^2)$ with this approximation.

(ii) Suppose we were to use the following approximation:

$\exp[-\tau(\hat{A} + \hat{B})] \sim \exp[-\frac{\tau}{2}\hat{A}]\exp[-\tau\hat{B}]\exp[-\frac{\tau}{2}\hat{A}]$.

Compute error term that is $\mathcal{O}(\tau^2)$ with this approximation. Comment on the accuracy of this approximate form.

Q2.4 Consider a time dependent hamiltonian in which the potential energy depends on time so $\hat{H}(t) = \hat{p}^2/2m + V(\hat{x}, t)$.

(i) For this hamiltonian, compute the commutator $[\hat{H}(t_1), \hat{H}(t_2)]$ for $t_1 \neq t_2$.

(ii) In class we realized that when the hamiltonian is time dependent the propagator for the time dependent Schrödinger equation should take the form $\exp[-(i/\hbar)\int_0^\infty \hat{H}(t)dt]$. Consider two times t_1 and t_2 that are infinitesimally displaced so $t_2 = t_1 + \tau$, where τ is the small positive displacement in time. Write down an approximation, accurate to first order in τ, to the propagator $K(x_2, t_2, x_1, t_1)$ that evolves the system from x_1 at t_1 to x_2 at t_2.

(iii) Show how you would use your approximate propagator from (ii) to evolve the wave function from its initial shape at t_1 to its final shape at t_2.

Q2.5 In class we made use of the complete orthogonal set of eigenfunctions of the momentum operator to transform between position and momentum representations. In the position representation, the momentum eigenstates have the following form: $\langle x|k\rangle = \frac{1}{\sqrt{2\pi}}\exp[ikx]$.

(i) Show that these functions are eigenfunctions of the momentum operator and give their eigenvalues. Show that these functions are also eigenfunctions of the free particle hamiltonian operator. Further, show that they CAN NOT be normalized in the usual sense. What does this tell you about a free particle of mass M with a definite energy $E = \hbar^2 k^2/2M$.

(ii) Despite these problems of normalization, the momentum eigenfunctions are particularly useful for their mathematical properties. Linear combinations of these un-normalizable functions can actually be used to represent normalized wave packets. For example, let $C(k)$ be the coefficient function that gives the amplitude of each free particle energy or momentum eigenstate in an expansion of a wave packet of the following form:

$\psi(x, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} C(k)\exp[i(kx - \frac{\hbar k^2}{2M}t)]dk$

Suppose the coefficients of the different momentum eigenfunctions are given by

$C(k) = N \exp[-a(k - k_0)^2]$.

Using the following result: $I = \int_{-\infty}^{\infty} \exp[-\alpha x^2 + \beta x] dx = \sqrt{\pi/\alpha} \exp[\beta^2/4\alpha]$, obtain an expression for the resulting wave packet, $\psi(x, t)$.

(iii) Set $t = 0$ and show that the wave packet constructed in this way can be normalized

(iv) You should be able to rearrange your expression for the time dependent wave packet to show that it has the form of a real valued function multiplied by a phase factor. The real valued function will have the form of a traveling gaussian with time dependent mean position, $x_0(t)$, and variable width, $\sigma(t)$, *i.e.* the real valued part will have the form $\exp[-(x - x_0(t))^2/2\sigma^2(t)]$. Obtain simple expressions for $x_0(t)$ and $\sigma(t)$ and interpret your results.

Q2.6 Consider a particle of mass M moving in quartic well so the potential has the form $V(x) = cx^4$ where c is a positive constant. Obtain an estimate for the ground state energy of this oscillator by using a normalized Gaussian variational function.

Q2.7 (a) Solve Heisenberg's equations of motion

$$\frac{d\hat{A}_H}{dt} = \frac{i}{\hbar}[\hat{H}_H, A_H] \tag{1}$$

for the time evolution of the raising and lowering operators $\hat{A}_H = \hat{b}_H^+$ and $\hat{A}_H = \hat{b}_H$ for a harmonic oscillator where we can write the hamiltonian as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \frac{\hbar\omega}{2}(\hat{P}^2 + \hat{Q}^2) = \hbar\omega(\hat{b}^+\hat{b} + \frac{1}{2}) \tag{2}$$

so $A_H(t) = e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}$ and the Schrödinger operators for the transformed momentum and coordinates of the oscillator are $\hat{P} = \hat{p}/(\hbar\omega m)^{1/2}$ and $\hat{Q} = \hat{x}(m\omega/\hbar)^{1/2}$, so $\hat{b} = (\hat{Q} + i\hat{P})/\sqrt{2}$, $\hat{b}^+ = (\hat{Q} - i\hat{P})/\sqrt{2}$, and $[\hat{b}, \hat{b}^+] = 1$

(b) Show that $\hat{Q}_H(t) = \hat{Q}\cos\omega t + \hat{P}\sin\omega t$.

(c) Solve Heisenberg's equation of motion for the operators $\hat{A}_H = \hat{b}_H^+\hat{b}_H$ and $\hat{A}_H = \hat{b}_H\hat{b}_H^+$

Q2.8 (i) Using the same ideas as outlined in Q2.5 explain why it makes sense to write the normalized momentum eigen states as $\langle x_2|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp[\frac{i}{\hbar}px_2]$

(ii) Use the methods we employed in class to compute an exact, explicit form for the free particle propagator matrix elements $K(x_2, x_1, t) = \langle x_2|\exp[-i\hat{H}_{FP}t/\hbar]|x_1\rangle$ with $\hat{H}_{FP} = \hat{p}^2/2m$.

(iii) Use your free propagator to evolve the initial wave function $\psi(x_1, t = 0) = (2a/\pi)^{1/4}\exp[-ax_1^2]$ out to time t.

Q2.9 The Pauli spin matrices

$$\mathbf{S}_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \mathbf{S}_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \mathbf{S}_z = \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \text{ and } \mathbf{S}^2 = \frac{1}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{3}$$

are the matrix representations of the operators $\hat{\mathbf{S}}_x$, $\hat{\mathbf{S}}_y$, $\hat{\mathbf{S}}_z$, and $\hat{\mathbf{S}}^2$ in the basis set of spin functions $\{|\alpha\rangle, |\beta\rangle\}$.

(a) Diagonalize the $\mathbf{S}_x$, $\mathbf{S}_y$, $\mathbf{S}_z$ spin matrices to obtain the eigenvalues and eigenfunctions of the corresponding operators in terms of this basis set.

(b) Suppose a measurement of $\hat{\mathbf{S}}_z$ for an electron gives the value $+\frac{1}{2}\hbar$; if a measurement of $\hat{\mathbf{S}}_x$ is then carried out on the resulting state, give the probabilities for each possible outcome.

Q2.10 A model for conjugated polymers that are used in organic light emitting diodes (OLEDs) capable of qualitatively describing the optical absorption properties of these materials assumes that every time a carbon atom is added to the growing conjugated polymer chain, an additional electron joins the molecule's π-electron system, which can be treated as a system of independent electrons (non-interacting fermions) that is contained in a growing 1D infinite square well potential. Suppose each additional C atom adds one bond length, l, to the total growing length, L, of the 1D infinite square well, so for an N C-atom polymer, $L = Nl$. Compute the lowest excitation energy, ΔE, of the π-electron system of a conducting polymer containing N carbon atoms (assume that N is even to simplify the problem).

Hint: In the limit of large N you should find that your result predicts that the excitation energy goes like $\Delta E \sim 1/N$, NOT like $1/N^2$ as you might guess if the length were the only factor influencing the N dependence. The trick here is to use the Pauli exclusion principle.