CH651 Assignment 1, Thursday, September 25, 2014. Due Friday October 3, 2014

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Q1 In class we showed that the rate of change of the quantum mechanical average position, $\langle x \rangle(t) = \int \Psi^*(x,t)\hat{x}\Psi(x,t)dx$, when the system was in state $\Psi(x,t)$ was obtained as

$$\frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m}\int \Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t)dx = \frac{1}{m}\langle \hat{p} \rangle(t) \tag{1}$$

enabling us to identify the momentum operator as $\hat{p} = -i\hbar\partial/\partial x$.

Using the fact that $\hat{H}$ and $\hat{p}$ are hermitian operators, (i) find an expression for the average acceleration, $d^2\langle x \rangle(t)/dt^2$, in terms of the expectation of the commutator of $\hat{H}$ and $\hat{p}$, and (ii) simplify this commutator expression to obtain a classical-like equation of motion relating these quantum expectation values.

Q2 Suppose that $\psi_1(x)$ and $\psi_2(x)$ are normalized eigenfunctions of $\hat{H}$ with eigenvalues E_1 and E_2 respectively. (i) Compute the variance in the energy, $\sigma_H^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2$ when the system is prepared in (a) $\psi_1(x)$, and (b) $\psi_2(x)$.

(ii) Suppose the system is prepared in a linear combination state

$$\Psi(x,t) = a_1\psi_1(x)\exp[-\frac{i}{\hbar}E_1 t] + a_2\psi_2(x)\exp[-\frac{i}{\hbar}E_2 t] \tag{2}$$

Compute the expectation value of the energy, $\langle \hat{H} \rangle$, in this state and compute its variance, σ_H^2.

(iii) Write down an expression for the time dependent expectation value of the position $\langle x \rangle(t)$ when the system is prepared in the above superposition state $\Psi(x,t)$ and show that it can be written as a real valued function.

Q3 The action of the parity operator, $\hat{\Pi}$, is defined as follows:

$$\hat{\Pi}f(x) = f(-x)$$

(i) Show that the set of all even functions, $\{e_n(x)\}$, are degenerate eigenfunctions of the parity operator. What is their degenerate eigenvalue? The same is true for the set of all odd functions, $\{o_n(x)\}$, but their degenerate eigenvalue is different from that of the even functions, what is it?

(ii) Show that the parity operator is an hermitian operator.

(iii) In class we showed that eigenfunctions of an hermitian operator whose eigenvalues are different are orthogonal. What important integration result does this imply for the functions you considered in part (i) above?

Q4 Show which of the following operators are hermitian:

(i) $\hat{O}_1 = i\hat{x}$ (ii) $\hat{O}_2 = \hat{p}$ (iii) $\hat{O}_3 = \frac{d}{dx}$ (iv) $\hat{O}_4 = \frac{d^2}{dx^2}$

Q5 A particle of mass m in an infinite square well of length L starts out in the left half of the well, $(0 \leq x \leq L/2)$, and at $t = 0$ is equally likely to be found at any point in this left region.

(i) What is the initial wave function $\Psi(x, 0)$? (Assume it is real, and don't forget to normalize it!)

(ii) What is the probability that a measurement of the energy of this initial state would yield the value $\pi^2 \hbar^2 / 2mL^2$?

Q6 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.

Q7 (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.

Q8 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:

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

Q9 A particle in the harmonic oscillator potential with frequency ω starts out in the state

$$\Psi(x,0) \quad = \quad A[3\psi_0(x) + 4\psi_2(x)]$$

where $\psi_n(x)$ are the normalized eigen functions of the harmonic oscillator.

(i) Find the normalization constant A

(ii) Construct $\Psi(x,t)$ and $|\Psi(x,t)|^2$

(iii) Find $\langle \hat{x} \rangle(t)$ and $\langle \hat{p} \rangle(t)$ when the particle is in $\Psi(x,t)$.

(iv) If the energy of the particle is measured, what values do you expect, and what are their probabilities?

Q10 (i) In class we said that an operator, $\hat{O}$, was hermitian if it satisfied the following result for any arbitrary functions, $f(x)$ and $g(x)$

$$\int f^*(x)\hat{O}g(x)dx \quad = \quad \left(\int g^*(x)\hat{O}f(x)dx \right)^*$$

We can generalize this result to define hermitian conjugate operators. Thus, $\hat{A}$ and $\hat{B}$ are said to be hermitian conjugates of each other if they satisfy the following result

$$\int f^*(x)\hat{A}g(x)dx \quad = \quad \left(\int g^*(x)\hat{B}f(x)dx \right)^*$$

Show that the raising, $\hat{a}_+$, and lowering, $\hat{a}_-$, operators are hermitian conjugates of each other. Note the standard notation for the operator that is the hermitian conjugate of operator $\hat{A}$ is $\hat{A}^\dagger$, i.e. in the above we usually write $\hat{B} = \hat{A}^\dagger$.