

CH651 Assignment 1, Tuesday, October 1, 2013. Due Tuesday  
October 8, 2013

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- Q1** Consider a particle of mass  $m$  moving in a harmonic oscillator potential,  $V(x) = \frac{1}{2}m\omega^2x^2$ . Assume a normalized ground state variational wave function with the following form

$$\begin{aligned}\psi(x) &= 0 & x < -L/2 \\ \psi(x) &= \sqrt{\frac{2}{L}} \sin[\pi(x/L + 1/2)] & -L/2 \leq x \leq L/2 \\ \psi(x) &= 0 & x > L/2\end{aligned}$$

Where  $L$  is the variational parameter.

(i) Find the optimal value of  $L$ .

(ii) Compute the variational energy and verify that its value is appropriate compared to the true ground state energy.

**Useful information:**

$$\frac{2}{L} \int_{-L/2}^{L/2} x^2 \sin^2[\pi(x/L + 1/2)] dx = L^2 \left( \frac{1}{12} - \frac{1}{2\pi^2} \right)$$

**Hint:** The form of the variational wave function assumed here is the ground state of a particle in a square well potential, where  $L$  is the length of the well. Use the energy of this state,  $\hbar^2/(8mL^2)$ , to simplify your calculations.

- Q2** Show that  $\hat{l}^2$  and  $\hat{l}_x$  commute.

- Q3** Construct the harmonic oscillator potential energy matrix with elements  $V_{i,j} = \langle i|V(\hat{x})|j\rangle$ , where  $V(x)$  was given in Q1. Use the lowest four harmonic oscillator states:  $|0\rangle$ ,  $|1\rangle$ ,  $|2\rangle$ ,  $|3\rangle$  to build your matrix.

- Q4** 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

$$\Psi(x, t) = a_1\psi_1(x) \exp[-\frac{i}{\hbar}E_1t] + a_2\psi_2(x) \exp[-\frac{i}{\hbar}E_2t] \quad (1)$$

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

(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.

**Q5** 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?

**Q6** 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)  $\hat{O}_4 = \frac{d^2}{dx^2}$

**Q7** 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  $\pi^2\hbar^2/2mL^2$  ?

**Q8** To a good approximation the vibrations of small 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  $\bar{\nu}_S = 3652 \text{ cm}^{-1}$ ,  $\bar{\nu}_A = 3756 \text{ cm}^{-1}$ , and  $\bar{\nu}_B = 1595 \text{ cm}^{-1}$ . (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:

$$\begin{aligned}\hat{a}_k^+ \psi_{n_k}^{(k)}(Q_k) &= \sqrt{n_k + 1} \psi_{n_k+1}^{(k)}(Q_k) \\ \hat{a}_k^- \psi_{n_k}^{(k)}(Q_k) &= \sqrt{n_k} \psi_{n_k-1}^{(k)}(Q_k)\end{aligned}$$

**Q9** A particle in the harmonic oscillator potential with frequency  $\omega$  starts out in the state

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

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  $g(x)$

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

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

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

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  $\hat{B} = \hat{A}^\dagger$ .