Chemistry 60649 Fall 2008
Professor J. Daniel Gezelter Due Mon. 10/13/2008

Problem Set 4

These problems will concentrate entirely on the Harmonic oscillator.

1. Consider a one-dimensional harmonic oscillator of frequency ω and mass m.

   a) Prove that the expectation value of any odd power of the position, $\hat{x}$, or the momentum, $\hat{p}$ is zero. Discuss the reason for your answer.

   b) Obtain the expectation values of $\hat{x}^2$ and $\hat{x}^4$ in any state. Is there any relation between the two of them?

2. Use operator methods in order to obtain the probability amplitudes $\langle p|0\rangle$ where $|p\rangle$ is an eigenstate of momentum. Use superposition to show how $\langle p|0\rangle$ (also known as $\psi_0(p)$) is related to $\langle x|n\rangle$ (also known as $\psi_n(x)$).

3. The harmonic oscillator is a rough approximation to the vibrations of a diatomic molecule if we choose the mass m to be the reduced mass for the diatomic:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1}$$

   where m_1 and m_2 are the masses of the two atoms in the diatomic. Compare the total probability of H_2 in the region where it is classically forbidden when it is in its ground vibrational state with that of T_2 in its ground state. Discuss your answer.

4. This clever problem has been stolen from Sakurai: Consider a particle of mass m subject to a one-dimensional potential of the following form:

$$V(x) = \begin{cases} \frac{1}{2}kx^2 & \text{for } x > 0 \\ \infty & \text{for } x < 0 \end{cases} \tag{2}$$

   Use what you have learned about both the ordinary harmonic oscillator and the particle-in-a-box boundary conditions to answer the following questions:

   a) What is the ground state energy?

   b) What is the expectation value of $\langle x^2\rangle$ for the ground state?

   c) Relate your answers to those of an equivalent harmonic oscillator that is symmetric around $x = 0$.

5. A simple potential function which models many of the properties of diatomic molecules is the *Morse potential*,
$$V(x) = D_e\left(1 - e^{-\beta x}\right)^2 \tag{3}$$
where x is the displacement of the bond from its equilibrium position and D_e is the value of $V(x)$ at large separations. Expand $V(x)$ in a Taylor series about $x = 0$ to obtain
$$V(x) = D_e\beta^2 x^2 - D_e\beta^3 x^3 + \cdots \tag{4}$$
Given that $D_e = 7.31 \times 10^{-19}$ J $\cdot$ molecule^{-1} and $\beta = 1.82 \times 10^{10}$ m^{-1} for HCl, calculate the force constant of HCl. Plot the Morse potential for HCl and plot the corresponding harmonic oscillator potential on the same graph.

6. Consider a harmonic oscillator that is operating under classical mechanics. The probability $(P(x)dx)$ of being found between x and $x + dx$ is proportional to $1/v(x)$ where $v(x)$ is the velocity at point x. Suppose our classical harmonic oscillator is given the same total energy as the ground state of the quantum harmonic oscillator, $E = \hbar\omega/2$.
   a) Where are the classical turning points at this energy?
   b) Derive the expression for $v(x)$ between the classical turning points.
   c) Plot on the same graph, the potential energy, the classical probability distribution, and the quantum probability distribution, $|\psi_0(x)|^2$. Compare your graph to Liboff's figure 7.11. Discuss your findings.

7. Use what you've done in problems 1 and 2 as well as the creation and annihilation operator methods to derive the uncertainty product $\sigma_x\sigma_p$ for the harmonic oscillator.