Chemistry 30321 Fall 2012
Professor J. Daniel Gezelter Due Fri. 10/12/2012

Problem Set 6
(More in-depth problems on the Harmonic Oscillator, Rotational Levels)

Pick ***one*** of the first three problems, but do problems 4, 5, 6, 7 and 8.

1. For this problem you should strongly consider using expressions for $\hat{x}$ and $\hat{p}$ in terms of the creation and annihilation operators $\hat{a}^\dagger$ and $\hat{a}$.
   (a) Calculate the average kinetic energy, $\langle \hat{p}^2/2m \rangle$ and the average potential energy, $\langle k\hat{x}^2/2 \rangle$ for the ground state of the harmonic oscillator.
   (b) Repeat the analysis for the n = 4 state of the harmonic oscillator.

2. The harmonic oscillator is a good approximation to the vibrational motion of a diatomic molecule if we choose the mass μ to be the reduced mass:

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

where m_1 and m_2 are the masses of the two atoms in the diatomic. The ground state *wavefunction* is given by:

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \tag{2}$$

where $\alpha = \sqrt{k\mu}/\hbar$.

For the H_2 molecule, find the *total probability* for the ground vibrational state to be found in the region where it is classically forbidden.

What I'm asking for is the *total probability* that the ground state will be found *outside* the classical turning points:

$$P_{forbidden} = \int_{-\infty}^{-x_t} p(x)dx + \int_{x_t}^{\infty} p(x)dx \tag{3}$$

where x_t is the classical turning point for the ground state energy, and $p(x)$ is the *probability distribution* for the ground state.) You'll need a calculator and some knowledge of the *error function* to do this problem.

3. Consider a particle of mass m subject to a one-dimensional potential of the following form:

$$V(x) = \begin{cases} \frac{1}{2}kx^2 & \text{for } x > 0 \\ \infty & \text{for } x < 0 \end{cases} \tag{4}$$

This is a combination of the particle in a box and the harmonic oscillator that works better as a model for real diatomics than the standard harmonic oscillator. On the right side of $x = 0$, the Hamiltonian is exactly the same as a harmonic oscillator Hamiltonian. The hard wall at $x = 0$, however, introduces a *boundary condition*.

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 does this boundary condition require the wave functions to do at $x = 0$?

b) Which of the normal harmonic oscillator wavefunctions have the property required in part a) and would then be valid functions in the new Hamiltonian?

c) If the lowest of these “allowed” states is the ground state, what is the ground state energy of this system?

d) What would the energy of the first excited state be?

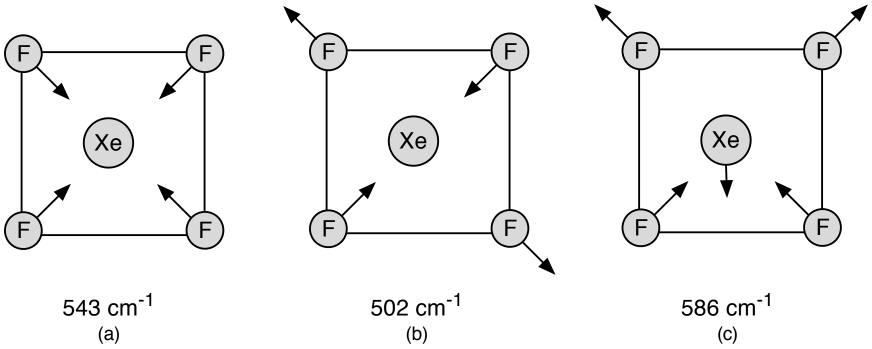
e) What is the spacing in energy between any two adjacent levels?

f) What would we need to do the “allowed” wavefunctions to make them usable for calculations of $\langle x \rangle$ or $\langle x^2 \rangle$?

(Hint: You don’t need to solve *any* integrals to do this problem. You do, however, need to think a little more deeply about this one than you would for a standard plug-and-chug problem.)

4. Are the stretching modes of the diatomic molecules O_2 and N_2 infrared active? Why or why not? Are the stretching modes of O_2 and N_2 Raman active? Why or why not?

5. Determine the IR and Raman activity of three of the vibrational modes of the square planar molecule XeF_4 shown below: (a) the symmetric stretching mode; (b) one of the antisymmetric stretching modes; (c) another antisymmetric stretching mode. Explain your reasoning.



6. Do problem 5-34 in McQuarrie and Simon

7. Do problem 5-35 in McQuarrie and Simon

8. Do problem 5-37 in McQuarrie and Simon

9. Extra Credit: Do the other two problems that you *didn’t* pick from the first three.