Chemistry 562 **Spring 2012**

Problem Set 6

Due beginning of class on Wednesday, March 7

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. A fictional molecule HA (where H is hydrogen and A is a heavy atom) has a fundamental vibrational transition of 2000 cm^{-1}. Estimate the fundamental vibrational transition of DA (where D is deuterium (^2H)). Give your answer in units of cm^{-1} and nm.

2. For the Morse Potential,

$$V(x) = D_e(1 - e^{-ax})^2$$

where x is the displacement of the bond from its equilibrium position and D_e is the value of $V(x)$ at large separations. (Note that D_e in the above equation is in units of J.)

(a) Expand $V(x)$ in a Taylor Series about $x = 0$, through the x^2 term. (Taylor Series are discussed on page 462 in your book)

(b) Notice that the quadratic term looks like a harmonic oscillator. Write the force constant k as a function of D_e and a.

(c) Given that $D_e = 7.31 \times 10^{-19}$ J/molecule and $a = 1.82 \times 10^{10}$ m^{-1} for HCl, calculate the force constant of HCl.

(d) Using a graphing program, plot the Morse Potential (before the expansion) and plot the corresponding harmonic oscillator potential on the same graph. How do these two curves compare near the well minimum?

3. Using your notes from class, show that the classical expression for the energy of a hydrogenic atom can be written separably into one term that has the center-of-mass (X) kinetic energy and another term that has internal coordinates and the reduced mass (μ). Start from the equation

$$E = \frac{p_1^2}{m_1} + \frac{p_2^2}{m_2} + V(r)$$

4. *Atkins Problem 9.3*. Also predict the frequency (in Hz) and wavelength (in nm) of a photon that would excite the two longest-wavelength transitions of the Balmer series.

5. (a.) Use the Living Graphs feature of the textbook website to examine the 3s, 3p, and 3d radial wavefunctions $R_{n,l}(r)$ for a hydrogenic atom.

(i.) For hydrogen, how many radial nodes does each wavefunction have? Give the location *r* of each radial node to 3 significant figures. Give your answer in Å.

(ii.) How many angular nodes does each orbital have?

(iii.) What is the orbital angular momentum of an electron in each orbital?

(b.) Use the Living Graphs feature of the textbook website to examine the radial distribution functions $P_{n,l}(r)$ for these three wavefunctions.

(i.) In which orbital does an electron have the greatest probability of being near the nucleus?

(ii.) How do the radial distribution functions vary as a function of atomic number *Z*? (You are going from H to He^{+} to Li^{2+}, etc.) Does this make sense physically? Explain.