Chem 532: Problem Set #5

Due in class: Monday, Oct. 24

(1) Consider the diatomic molecule anharmonic oscillator with potential energy:

$V(x) = \frac{1}{2}k_2x^2 + \frac{1}{3!}k_3x^3$

Use your results from problem #3 from HW3 to

(a) Obtain an expression for the energy of vibrational state v correct to 2nd order in perturbation theory

(b) Use this expression to calculate the vibrational energies for v=0 and 1 (in terms of $\hbar\omega$).

(c) Compare the value of the v=0-1 fundamental frequency between the harmonic and cubic anharmonic approximations.

(2) Consider the simple harmonic oscillator. Use a trial function defined by $\phi = cos(\alpha x)$, where α is a variational parameter and *x* ranges from $-\frac{\pi}{2\alpha}$ to $+\frac{\pi}{2\alpha}$. Use the variation method to determine an approximation to the ground state energy. Compare your result to the known exact value.

(3) Apply the linear variation function

$$\phi = c_1x^2\left(L-x\right)+c_2x\left(L-x\right)^2 \qquad 0 \le x \le L$$

to the particle in a one-dimensional box.

(a) Calculate the percent errors for the *n*=1 and *n*=2 energies.

(b) Determine the coefficients c_1 and c_2 for the *n*=1 case.