

### CH342 Handin Homework 6

1. Hooke's Law is only an approximation of the true vibrational potential energy of a molecule. There are many other possible forms for the potential energy function of a chemical bond. Use perturbation theory to calculate the small change in energy for the harmonic oscillator ground state that is perturbed by the addition of a term  $= b x^4$  to the potential energy function:

$$V(x) = \frac{1}{2} k x^2 + b x^4$$

[Hint: Remember that the wavefunction is  $\Psi(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha^2 x^2}$  where  $\alpha^2 = \left(\frac{m\omega_0}{\hbar}\right)$ . Just leave  $\alpha^2$

as a parameter until the last step and then substitute in at the last for  $\alpha^2$  to find that the change in energy is  $\frac{3b}{4} \left(\frac{\hbar}{m\omega_0}\right)^2$  ]

2. The following problem explores the Pauli Exclusion Principle and wavefunction symmetry. Let  $\psi_1$  and  $\psi_2$  be the functions for a particle in a one-dimensional particle in a box with  $n=1$  and  $n=2$ , respectively. If one electron is in each of these orbitals, the space part of the triplet and singlet wavefunctions is:

$$\psi_A = \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)] \quad \text{and} \quad \psi_S = \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)]$$

respectively. Suppose that particle 1 is in a small element of length  $dx$  at  $x=0.250 a$  and particle 2 is in a small element of length  $dx$  at  $x=0.255 a$ . The quantity  $a$  is the length of the box. Show that  $\psi_A$  has a very small value under these conditions while  $\psi_S$  can be large. What happens to  $\psi_A$  if both electrons are at  $x=0.250 a$ ? This problem shows how an anti-symmetric spacial wavefunction keeps the electrons apart.

A note on nomenclature: example-  $\psi_1(2)$  means wavefunction 1 (in this case with  $n=1$ ) is used for electron 2. Since this wavefunction is for electron 2 it should be evaluated at  $x=0.255 a$ .

3. Write a spreadsheet to plot the 3-21G Gaussian orbital for a  $2p_x$  orbital on carbon.

4. Show that the spin-orbit coupling operator,  $\vec{\hat{l}} \cdot \vec{\hat{s}}$ , can be given as:  $\vec{\hat{l}} \cdot \vec{\hat{s}} = \frac{1}{2} (\hat{j}^2 - \hat{l}^2 - \hat{s}^2)$  with eigenvalue:

$$|\ell s| = \frac{1}{2} \hbar^2 (j(j+1) - \ell(\ell+1) - s(s+1))$$

where the total angular momentum operator is the vector sum:  $\vec{j} = \vec{\hat{l}} + \vec{\hat{s}}$ .