Nov. 26 2007

Chem. 1410

Problem Set 10, due Dec. 3, 2007

Do the following problems; these are *not* to be handed in for grading; solutions will be distributed via .pdf.

Engel: P12.5, P12.6, P13.2, P13.5, P13.8

The following two problems are to be handing in for grading:

1) **Huckel Theory of π bonding in cyclobutadiene.** Engel, Problem P14.15

2) **Variational approximation to the ground state energy of the H_2^+ molecule ion**. In class we studied the electronic ground state properties of the H_2^+ molecule ion with the two nuclei (denotes as A and B) separated by an internuclear distance R using an un-normalized variational electronic trial function:

$$\psi_T(\vec{r}) = c_A 1s_A(\vec{r}) + c_B 1s_B(\vec{r})$$

Here $1s_{A,B}(\vec{r})$ is a (normalized) 1s hydrogen orbital (corresponding to atomic number Z=1) centered at nucleus A,B, and $c_{A,B}$ are variational parameters. Using the Variational Principle with linear variation of parameters, we determined that for the electronic ground state of the molecule, $c_A = c_B$ (again modulo normalization) at any internuclear separation R, and the ground state energy of the molecule is given (in a.u., i.e. Hartrees) by:

$$E(R) = -\frac{1}{2} + \frac{J'(R) + K'(R)}{1 + S(R)}$$

where $S(R), J'(R), K'(R)$ are precisely defined 3-dimensional integrals which are parametric in R. In fact, these integrals can be performed analytically, yielding:

$$S(R) = e^{-R}(1 + R + R^2/3)$$

$$J'(R) = e^{-2R}(1 + \frac{1}{R})$$

$$K'(R) = \frac{S(R)}{R} - e^{-R}(1 + R)$$

where R is measured in a.u. = Bohr radii. [N.B: You do not have to derive these integrals here!]

a) Given the formulae for $S(R), J'(R), K'(R)$, plot the ground state electronic energy *E(R)* vs. *R*. Show (via your graph) that this curve has a minimum. Determine the position of (i.e., the internuclear separation at) the minimum in Å , and the dissociation energy of the molecule in eV which are predicted from this simple model. [Note: For the purposes of this problem, define dissociation energy as the energy difference between the asymptotic value at *E* at $R = \infty$ (when the two H atoms are completely separated) and the energy at the equilibrium position of the molecule (i.e., where *E* is a minimum).]

b) Now, consider a slightly more sophisticated ansatz for the (un-normalized) ground state electronic state wavefunction of H_2^+, namely:

$$\psi_T(\vec{r}) = 1s_A(\vec{r};\xi) + 1s_B(\vec{r};\xi) \qquad [1]$$

Here $1s_A(\vec{r};\xi)$ is a (normalized) 1s hydrogenic orbital centered on nucleus A and corresponding to effective nuclear charge ξ, and analogously for $1s_B(\vec{r};\xi)$. With some effort (which you do not have to repeat here!), it can be shown that the expectation value of the electronic Hamiltonian in the state $\psi_T(\vec{r})$ (appropriately normalized) is given by:

$$E(R;\xi) = -\frac{\xi^2}{2} + \frac{J'(R;\xi) + K'(R;\xi)}{1 + S(R;\xi)}$$

with:

$$S(R;\xi) = e^{-\xi R}[1 + \xi R + (\xi R)^2 / 3]$$

$$J'(R;\xi) = (\xi - 1)\xi + (1 + \frac{1}{\xi R})e^{-2\xi R}$$

$$K'(R;\xi) = \frac{S(R;\xi)}{R} + (\xi - 2)\xi(1 + \xi R)e^{-\xi R}$$

The Variational Principle (using non-linear variation of parameters) then says that for a given value of *R*, the best estimate of the ground state electronic energy with a trial function of the type given in Eq. 1 is obtained by *minimizing* $E(R;\xi)$ vs. ξ. So …

i) For concreteness, set *R=2*. Plot $E(2;\xi)$ vs. ξ. Show that it does have a minimum, at $\xi \cong 1.24$, and that $E(2;1.24) \cong -0.588$ a.u.

ii) Repeat this calculation for the values R=1,1.25,1.5 … 3 (a total of 9 values including the one at *R=2*). Plot the 9 data points *(R,E)* on the same graph as the function $E(R)$ [based on the choice $\xi = 1$] which you plotted in part a). [Hint: You should find that the improved energy curve obtained using the procedure in part b) is lower at every internuclear separation R than the one computed in part a).]

iii) Estimate the position of (i.e., the internuclear separation at) the minimum in Å, and the dissociation energy of the molecule in eV which are predicted from the improved ("optimized ξ") model.

iii) Do you expect the experimentally measured dissociation energy of the H_2^+ molecule to be larger or smaller then the value estimated in iii)?