Atoms, Molecules & Reactions, Spring 2006

Quantum Mechanics Homework –Week 7

Using Huckel molecular orbital theory, calculate the energy of the π electrons for 1,3 butadiene. Use the following stepwise process.

- Step 1: Recognize that 1,3 butadiene is a planar, conjugated, hydrocarbon. Hence σ-π separability can be applied. Each carbon atom has an unhybridized 2p orbital containing one electron available for π bonding. Draw 1,3 butadiene.

- Step 2: Write a trial wavefunction for the π electron system of 1,3 butadiene (look up what you did for ethylene).

- Step 3: Write the secular determinant you would obtain, if you used the variation method to obtain the energy of the π electrons of 1,3 butadiene, with the trial wavefunction you wrote above. (Do this by analogy, by comparing with ethylene. No need to do this from scratch).

- Step 4: Simplify the secular determinant, using the Huckel approximations (Huckel assumptions).

- Step 5: Divide each term in the above determinant by β

- Step 6: Use the following substitution and re-write the determinant. $x = \frac{\alpha - E}{\beta}$

- Step 7: Expand the determinant and obtain values for x (this will take some work. Be patient! The reward is worth it!). There will be four different values for x.

- Step 8: Use the above values of x to obtain the corresponding values for E (There will be four different values for E).

- Step 9: Recognizing that $\beta < 0$, draw a ladder type energy diagram to show the energy levels of 1,3 butadiene. Be sure to include the π electrons in this diagram.

- Step 10: Use the above diagram to determine the energy of the π electrons in 1,3 butadiene. Is this equal to twice the π electron energy for ethylene? Why is this significant?

- Step 11: Since you obtained four different energy levels for 1,3 butadiene, you should have four distinct wavefunctions to describe those energy levels. Starting from your trail wavefunction, obtain these four wavefunctions. (hint: the lowest energy level has zero nodes, the next one up has one node, etc.). This step should take less than 15 minutes.

- Step 12: Draw rough sketches of the wavefunctions you obtained above.