Lect 10

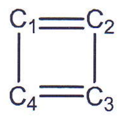
Homework

: The Hückel Model and other Semiempirical Methods

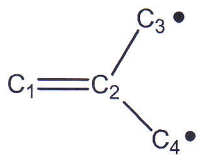
1. Write the Secular determinant for the following molecules in terms of (i) α, β and E, (ii) $x = (\alpha\text{-}E)/\beta$

   In molecules with heteroatoms, check PP slides for appropriate heteroatom parameters

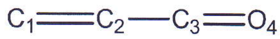
   (a) Square cyclobutadiene

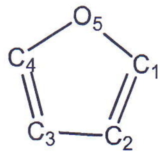
   (b) Trimethylenemethane
   This is a diradical species.
   I've drawn one of 3 resonance forms

   (c) Acrolein

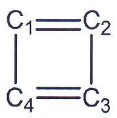
   

   (d) Furan

2. How many electrons does the oxygen atom in (a) Acrolein, (b) Furan, contribute to the pi electron system.

3. Let's consider Cyclobutadiene:

   In the solution to Prob. 1 (a), we showed that the secular determinant is:

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

   With a bit of algebra, it can be shown that the above determinant expands to give: $x^4\text{-}4x^2 = 0$

   (a) Solve this equation to obtain the 4 energy levels.
   Note: Two of the four energies are degenerate.

(b) It can be shown (with a bit more algebra) that the **non-normalized** molecular orbitals of cyclobutadiene are:

$$\phi_1 = c_1(\chi_1 + \chi_2 + \chi_3 + \chi_4)$$
$$\phi_2 = c_1(\chi_1 - \chi_3)$$
$$\phi_3 = c_2(\chi_2 - \chi_4)$$
$$\phi_4 = c_1(\chi_1 - \chi_2 + \chi_3 - \chi_4)$$

Determine the **normalized** molecular orbitals.

(c) Calculate the total π energy and the Delocalization energy.

(d) Calculate the π electron charge for each atom.

(e) Calculate the π bond order for each bond.

4. Consider 1,3-butadiene: $C_1{=}C_2{-}C_3{=}C_4$

Note: The solution to this problem is given in the Chap. 12 PowerPoint presentation.

(a) Write the Secular Determinant.

(b) Solve the Secular Determinant to obtain the 4 energy levels.

(c) Determine the normalized coefficients of the molecular orbitals corresponding to each energy.

(d) Calculate the total π energy and the Delocalization energy.

(e) Calculate the π electron charge for each atom.

(f) Calculate the π bond order for each bond.

5. Consider butadiene in the lowest excited state (figure to right).
Note: The energies and orbitals are the same as in the ground state.

(a) Calculate the π electron charge on each atom.

(b) Calculate the π bond order for each bond.