



CHEMISTRY 273

PROBLEM SET #1

- According to the pi-electron coefficients listed in the handout, which of the three carbon atoms would have the greatest positive charge in the allyl cation $C_3H_5^+$ ? Is this consistent with the charge distribution predicted from resonance structures?
- What are the charges on the various carbon atoms in the pentadienyl cation, $C_5H_7^+$ ?
 - In the ground state which of the two non-equivalent bonds contains the most double-bond characters?
 - Are the bond orders and charge distributions in (a) and (b) consistent with the resonance structures of $C_5H_7^+$?
- Assume the molecular orbitals for the famous diatomic molecule A-B can be written as a linear combination of an atomic orbital χ_1 on atom A and atomic orbital χ_2 on atom B:

$$\phi = N(c_1\chi_1 + c_2\chi_2)$$

- What is the normalization coefficient, N , if χ_1 and χ_2 are each individually normalized and the overlap integral is represented by S_{12} :

$$S_{12} = \int \chi_1\chi_2 d\tau \equiv \langle \chi_1 | \chi_2 \rangle$$

- The energy of a single electron in this orbital is:

$$\tilde{E} = \int \phi \hat{h}_f \phi d\tau \equiv \langle \phi | \hat{h}_f | \phi \rangle$$

where h_f is an "effective hamiltonian" which includes kinetic energy, the attraction of the two nuclei for the electron, and the *average (effective)* repulsive force of the other electrons for the one in orbital ϕ . Show that:

$$\tilde{E} = \frac{1}{c_1^2 + c_2^2} [c_1^2 h_{11} + 2c_1 c_2 h_{12} + c_2^2 h_{22}]$$

where

$$h_{11} \equiv \int \chi_1 \hat{h}_f \chi_1 d\tau \quad h_{22} \equiv \int \chi_2 \hat{h}_f \chi_2 d\tau$$

$$h_{12} \equiv \int \chi_1 \hat{h}_f \chi_2 d\tau \quad h_{21} \equiv \int \chi_2 \hat{h}_f \chi_1 d\tau \equiv h_{12}$$

and the approximation $S_{12} = 0$ has been used.

- (3) Apply the variation principle to:

$$\tilde{E} \text{ above; i.e., set } \frac{\partial \tilde{E}}{\partial c_1} = 0, \quad \frac{\partial \tilde{E}}{\partial c_2} = 0.$$

to derive the equations:

$$c_1(h_{11} - \tilde{E}) + c_2 h_{12} = 0$$

$$c_1 h_{21} + c_2(h_{22} - \tilde{E}) = 0$$

(*HINT*: Use the result of part 2 to substitute \tilde{E} for a messy quantity which arises in the straightforward evaluation of the derivatives.)

- (4) For the non-trivial case $c_1, c_2 \neq 0$

$$(a) \quad -c_1 = c_2 \frac{h_{12}}{(h_{11} - \tilde{E})} = c_2 \frac{(h_{22} - \tilde{E})}{h_{12}}$$

thus

$$(b) \quad (h_{11} - \tilde{E})(h_{22} - \tilde{E}) - h_{12}^2 = 0.$$

This equation also follows from Kramer's rule that:

$$(c) \quad \begin{vmatrix} h_{11} - \tilde{E} & h_{12} \\ h_{21} & h_{22} - \tilde{E} \end{vmatrix} = 0 \text{ for } c_1, c_2 \neq 0.$$

Solve the quadratic (b) to show that the allowed values for the energy of \tilde{E} are:

$$(d) \quad \tilde{E}_{\pm} = \frac{(h_{11} + h_{22})}{2} \pm \left\{ 1/2[(h_{11} - h_{22})^2 + 4h_{12}^2]^{1/2} \right\}$$

- (5) For the homonuclear diatomic where χ_1 and χ_2 are the same orbital (although centered on nuclei at different positions), what must be the relation between h_{11} and h_{22} ? What are \tilde{E}_{\pm} for the homonuclear case? Which energy corresponds to \tilde{E}_b , the energy of the bonding m.o., and which \tilde{E}_a , the antibonding m.o.? Use this result and the relationships 4(a) to get the ratios c_1/c_2 corresponding to \tilde{E}_b and \tilde{E}_a .
- (6) Since $h_{11} = \langle \chi_1 | \hat{h}_f | \chi_1 \rangle$ involves the energy of interaction of an electron in an orbital on atom A with an effective hamiltonian, the most important contributions to h_{11} come from the nuclear charge of atom A and the repulsions of electrons on this atom. A good approximation to h_{11} is the energy of an electron in the orbital χ_1 of the free atom A, *i.e.*, the ionization of an electron from atomic orbital χ_1 . Similar statements apply to h_{22} , and thus the relative electronegativities of atoms A and B (h_{11} and h_{22} are almost always negative due to the nuclear attraction terms).

h_{12} involves the interaction of an orbital on atom A and one on B and depends not only on the electronegativities of A and B but also the overlap of χ_1 and χ_2 . Consider the heteronuclear diatomic molecule B-F where $\chi_1 = 2s_{\text{fluorine}}$ and $\chi_2 = 2s_{\text{boron}}$.

- (a) Qualitatively, how do h_{11} and h_{22} compare in magnitude?
- (b) What is the value for h_{12} for very large values of the internuclear B-F distance?
- (c) What are \tilde{E}_b and \tilde{E}_a and the corresponding c_1/c_2 for these large internuclear distances (use 4a, d)? Interpret these results.
- (d) At normal bond distances where $h_{12} \neq 0$, the trends in 6(c) still apply. Would you expect the 2σ bonding orbital of B-F to be made up mostly of the fluorine 2s or the boron 2s? What about the 2σ antibonding?