CHEMISTRY 163A
PROBLEM SET

36. McQ #9-21

37. McQ #9-24. Would NO^+ or NO have a higher vibrational frequency?

*38. Assume that a molecular orbital for the famous diatomic molecule A–B is a linear combination of an atomic orbital χ_A on atom A on atomic orbital χ_B on atom B; i.e.,

$$\phi = N(c_A\chi_A + c_B\chi_B).$$

1) What is the normalization coefficient, N, if χ_A and χ_B are each individually normalized and the overlap integral is represented by the symbol

$$S_{AB} = \int \chi_A\chi_B d\tau.$$

2) The energy of a single electron in this orbital is $\tilde{E} = \int \phi\hat{h}_f\phi d\tau$ where $\hat{h}_f$ is an "effective hamiltonian" which includes the kinetic energy and the attraction of the two nuclei for our electron and takes into account the average repulsive force of the other electrons on the one in orbital ϕ. Show that

$$\tilde{E} = \frac{1}{\left(c_A^2 + c_B^2\right)}\left[c_A^2 h_{AA} + 2c_A c_B h_{AB} + c_B^2 h_{BB}\right]$$

where $h_{AA} = \int \chi_A\hat{h}_f\chi_A d\tau$, $h_{BB} = \int \chi_B\hat{h}_f\chi_B d\tau$

$h_{AB} = \int \chi_A\hat{h}_f\chi_B d\tau = h_{BA}$ and where we have used the approximation $S_{AB} = 0$.

3) Apply the variation principle to $\tilde{E}$ above, i.e., set $\frac{\partial\tilde{E}}{\partial c_A} = 0$ and $\frac{\partial\tilde{E}}{\partial c_B} = 0$ to derive the equations.

$$c_A(h_{AA} - \tilde{E}) + c_B h_{AB} = 0$$

$$c_A h_{AB} + c_B(h_{BB} - \tilde{E}) = 0$$

(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 $c_A, c_B \neq 0$

a) $$-c_A = c_B \frac{h_{AB}}{\left(h_{AA} - \tilde{E}\right)} = c_B \frac{\left(h_{BB} - \tilde{E}\right)}{h_{AB}}$$

thus

b) $$\left(h_{AA} - \tilde{E}\right)\left(h_{BB} - \tilde{E}\right) - h_{AB}^2 = 0$$

This equation also follows from Kramer's rule that

c) $$\begin{vmatrix} h_{AA} - \tilde{E} & h_{AB} \\ h_{AB} & h_{BB} - \tilde{E} \end{vmatrix} = 0 \text{ for } c_A \text{ and } c_B \neq 0$$

Solve the above quadratic equation (b) to show that the *only* allowed values for the energy of ϕ are

d) $$E_{\pm} = \frac{1}{2}\left\{h_{AA} + h_{BB} \pm \left[(h_{AA} - h_{BB})^2 + 4h_{AB}^2\right]^{1/2}\right\}$$

5) For the homonuclear diatomic where χ_A and χ_B are the same orbital (although centered on nuclei at different positions), what relationship must hold between h_{AA} and h_{BB} (use physical insight)? What are $E_{\pm}$ for this homonuclear case? Use this result and the relationship (4, a) to get the ratios $\frac{c_A}{c_B}$ corresponding to $E_{\pm}$. In terms of the respective energies and coefficients, discuss which of the two solutions corresponds to a bonding and which to antibonding m.o.

6) Since $h_{AA} = \int \chi_A \hat{h}_f \chi_A d\tau$ involves the energy of interaction for atomic orbital on center A with an effective hamiltonian, most of the important contributions to h_{AA} come from the nuclear charge of atom A and electrons centered around atom A. A good approximation to h_{AA} is the energy of an electron in orbital χ_A of the free atom A; that is, the ionization potential of an electron from atomic orbital χ_A.

Similar statements apply to h_{BB}, and thus the relative magnitudes of h_{AA} and h_{BB} are determined by the electronegativities of atoms A and B. h_{AB} involves an orbital on A and one on B and thus depends not only on the electronegativities of atoms A and B but also on the overlap of the orbitals χ_A and χ_B. Consider the heteronuclear diatomic molecule B–F where $\chi_A = 2s_{\text{flouroine}}$ and $\chi_B = 2s_{\text{boron}}$.

a) What will be the value of h_{AB} for *very large* values of the internuclear B–F distance?

b) What will $E_{\pm}$ and $\left(\frac{c_A}{c_B}\right)_{\pm}$ be for these large internuclear distances (use 4a, d)? Interpret these results.

c) Qualitatively, how do h_{AA} and h_{BB} (and thus $E_{\pm}$) compare in magnitude?

d) At normal bonding distances where $h_{AB} \neq 0$ the trends evident in part 6(b) 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 antibonding combination?

❁ *FINIS* ❁