

# CHEM 344 FALL '09 PROBLEM SET #9

Due : Friday Nov 14 2009 @ 2pm before class!

## HW TO BE HANDED IN

Engel Chapter 16 : 7,15,18

Engel Chapter 17 : 3,4,17

Atkins Chapter 10 : 17,18,32,34,35

(copies attached)

## THINKING QUESTIONS DO NOT HAND IN

(practice for exams)

Engel Chapter 16 : 9,14,17

Engel Chapter 17 : 6,10,18

## STRETCH YOUR ABILITY DO NOT HAND IN

(NOT ON TEST EITHER)

Engel Chapter 16 : 22

Engel Chapter 17 : 11,14,16

- 10.17 Before doing the calculation below, sketch how the overlap between an  $1s$  orbital and a  $2p$  orbital can be expected to depend on their separation. The overlap integral between an  $1s$  orbital and a  $2p$  orbital on nuclei separated by a distance  $R$  is  $S = (R/a_0)\{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$ . Plot this function, and find the separation for which the overlap is a maximum.
- 10.18 Suppose that a molecular orbital has the form  $N(0.145A + 0.844B)$ . Find a linear combination of the orbitals  $A$  and  $B$  that is orthogonal to this combination.
- 10.32 Construct the molecular orbital energy level diagrams of (a) ethene (ethylene) and (b) ethyne (acetylene) on the basis that the molecules are formed from the appropriately hybridized  $CH_2$  or  $CH$  fragments.

**10.34** It is important to understand the origins of stabilization of linear conjugated molecules because they play important biological roles in plants and animals (see *Case study 9.1*). According to Hückel theory, the energies of the bonding  $\pi$  molecular orbitals of butadiene,  $\text{CH}_2=\text{CH}_2-\text{CH}_2=\text{CH}_2$ , are  $E = \alpha + 1.62\beta$  and  $\alpha + 0.62\beta$ . The energies of the antibonding  $\pi^*$  molecular orbitals are  $E = \alpha - 1.62\beta$  and  $\alpha - 0.62\beta$ . The total  $\pi$ -electron binding energy,  $E_\pi$ , is the sum of the energies of each  $\pi$  electron. Recalling that there are four electrons to accommodate in the  $\pi$  molecular orbitals, calculate the  $\pi$ -electron binding energy of ethene (see *Example 10.4*) and butadiene. Is the energy of the butadiene molecule lower or higher than the sum of two individual  $\pi$  bonds?

**10.35** Cyclic conjugated systems occur widely in biological macromolecules. Examples include the phenyl group of phenylalanine and a host of heterocyclic molecules, such as the purine and pyrimidine bases found in nucleic acids. In Exercise 10.34 you discovered that conjugation of double bonds lends extra stabilization to a molecule. We define the *delocalization energy* of a conjugated system as

$$E_{\text{deloc}} = E_\pi - N_{\text{db}}(2\alpha + 2\beta)$$

where  $N_{\text{db}}$  is the number of double bonds, each contributing an energy  $2\alpha + 2\beta$  in the absence

of conjugation. The most notable example of delocalization conferring extra stability is benzene and the aromatic molecules based on its structure. **(a)** Use valence bond and molecular orbital theory to describe the bonding in benzene. Does the formation of the cyclic structure strain the molecule? **(b)** The energies of the bonding  $\pi$  molecular orbitals of benzene are  $E = \alpha + 2\beta$ ,  $\alpha + \beta$ , and  $\alpha + \beta$  (note the degeneracy of the last two orbitals) and the energies of the  $\pi^*$  molecular orbitals are  $E = \alpha - 2\beta$ ,  $\alpha - \beta$ , and  $\alpha - \beta$  (note the presence of degenerate bonding and antibonding orbitals). **(c)** Recalling that there are six electrons to accommodate in the  $\pi$  molecular orbitals, calculate the delocalization energy of benzene. **(d)** Discuss the origins of aromatic stability in benzene by interpreting your results from parts (a)–(c). **(e)** Predict the electronic configurations of **(i)** the benzene anion, **(ii)** the benzene cation. Estimate the delocalization energy in each case.

---