

## Homework H25 Solution

1. Problem 8.8.

**Solution:** Consider the 3 carbon atoms to have atomic orbitals  $\phi_n$ . We want to find the molecular orbitals  $\psi$ , by setting up the secular determinant to zero. Under the Hückel approximation, the diagonal terms in the Hamiltonian matrix are  $\alpha$ , and the neighboring terms are  $\beta$ , while the rest are zero. (Note: the book uses  $\alpha$  and  $\beta$ , whereas Gruebele uses a and b in class to avoid confusion with the common nomenclature for spin up and down wavefunctions)

Thus, the secular determinant is,

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \text{ or } \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0,$$

where we divided both sides by  $\beta$  and  $x = \frac{\alpha - E}{\beta}$ .

Expanding the determinant we have,

$$\begin{aligned} x^3 - 2x &= 0 \\ \text{or, } x(x^2 - 2) &= 0 \\ \text{or, } x &= 0, \pm\sqrt{2} \end{aligned}$$

Thus, the  $\pi$  electron energy levels are,

$$\begin{aligned} E_1 &= \alpha + \sqrt{2}\beta \text{ (when } x = -\sqrt{2}\text{)} \\ E_2 &= \alpha \text{ (when } x = 0 \text{)} \\ E_3 &= \alpha - \sqrt{2}\beta \text{ (when } x = \sqrt{2}\text{)} \end{aligned}$$

with two electrons in the lowest level, and one in the next.

To obtain the molecular orbitals, we need to solve the eigenvalue equation (same as the diagonalization procedure) for each value of  $x$ .

$$\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{aligned} \text{or, } c_1x + c_2 &= 0 \\ c_1 + c_2x + c_3 &= 0 \\ c_2 + c_3x &= 0 \end{aligned}$$

For  $x = -\sqrt{2}$ ,

$$c_1 = c_3; c_2 = \sqrt{2}c_1$$

$$c_1^2 + c_2^2 + c_3^2 = 1$$

$$\Rightarrow c_1 = c_3 = \frac{1}{2}; c_2 = \frac{1}{\sqrt{2}}$$

$$\text{Thus, } \psi_1 = \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$$

Similarly, for  $x = 0$ ,

$$c_2 = 0, c_1 = \frac{1}{\sqrt{2}} = -c_3$$

$$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$$

And for  $x = \sqrt{2}$ ,

$$c_1 = c_3 = \frac{1}{2}; c_2 = -\frac{1}{\sqrt{2}}$$

$$\text{Thus } \psi_3 = \frac{1}{2}\phi_1 - \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$$

For the delocalization energy, we need to compare with a system with 2  $\pi$  electrons of ethene (Energy  $\alpha + \beta$  each) and one non-bonded pi electron (Energy  $\alpha$ ).

$$\text{So, delocalization energy} = [2(\alpha + \beta) + \alpha] - [2(\alpha + \sqrt{2}\beta) + \alpha]$$

$$= 0.828 \beta \text{ (remember, } \beta = b \text{ is negative)}$$

## Turn in 2: IQMol benzene

### Questions:

1. What are the energies in eV of the HOMO and the LUMO? Note that both the HOMO and LUMO are doubly degenerate, just like the simple Hückel calculation showed. Look up the conversion from hartree to eV if you need to.

**Solution:** As seen from the MO surfaces tab, the energy of HOMO:

$$E_{HOMO} = -0.332 \text{ hartrees} = -9.03 \text{ eV}$$

and that of the LUMO:

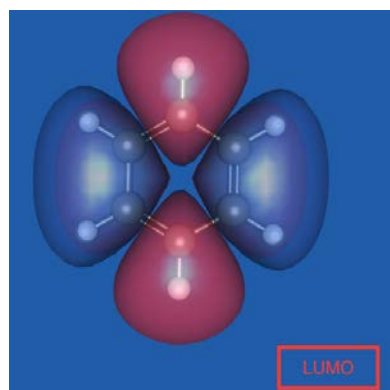
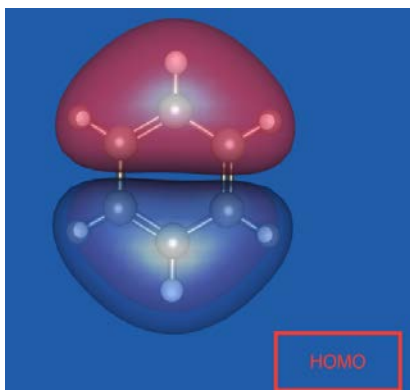
$$E_{LUMO} = 0.145 \text{ hartrees} = 3.94 \text{ eV}$$

2. What are the bond distances  $C_2-C_3$  and  $C_3-C_4$ ? Is there any difference  $> 0.01 \text{ \AA}$ ? The energy minimization took care of the fact that benzene is more stable than cyclo-hexatriene owing to delocalization /conjugation.

**Solution:** Clicking the appropriate tabs on the left, we see that both  $C_2-C_3$  and  $C_3-C_4$  bond distances are  $1.399 \text{ \AA}$ .

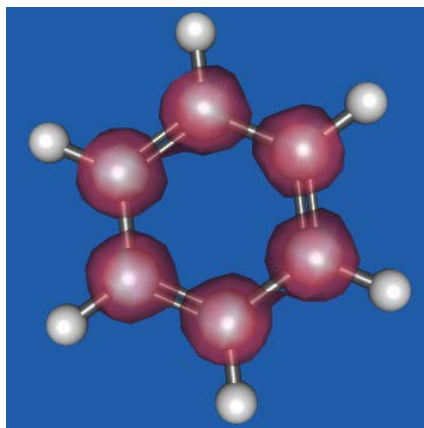
3. Check the boxes Alpha 21 and Alpha 22 separately. Draw the shapes of the HOMO and LUMO of benzene. You may capture the screenshots and paste them into your homework.

**Solution:** The HOMO and LUMO look like the following :



4. Click on the “MO surfaces” again and select orbital #1 this time. What atomic orbitals is benzene orbital #1 really made up from? Do you think it shows any significant bonding overlap?

**Solution:** The lowest lying orbital (#1) looks like



This molecular orbital is made up primarily from the lowest lying atomic orbitals, which are the carbon 1s orbitals, which is reflected from the MOs retaining roughly the shape of 1s orbitals. This does not show significant bonding because there is little overlap between the 1s wavefunctions. The energy of this orbital stays about the same, whether you bring the carbon atoms together to make benzene, or you leave them dissociated.

3. Problem 8.10.

**Solution:** The enthalpy change of hydrogenation is a measure of stability of the saturated hydrocarbon over the unsaturated one.

The enthalpy change of hydrogenation of cyclohexene corresponds to the reduction of one  $\pi$  bond, whereas that of benzene corresponds to three  $\pi$  bonds.

Hence, the stabilization of the delocalized benzene  $\pi$  system corresponds to the differences in enthalpy change of benzene and of three localized  $\pi$  bonds.

Therefore, stabilization energy of benzene,

$$\begin{aligned} E_{s,benzene} &= \Delta H_{benzene} - 3 \Delta H_{cyclohexene} \\ &= -209 - 3(-121) \text{ kJ/mol} \\ &= 154 \text{ kJ/mol} \end{aligned}$$