

ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS, SPRING 2006, HW-WEEK 7

HW sheet

9

$$\psi_{sp^2}^{(1)} = \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z$$

$$\int \psi_{sp^2}^{(1)*} \psi_{sp^2}^{(1)} d\tau = \int \left( \frac{1}{\sqrt{3}} 2s^* + \sqrt{\frac{2}{3}} 2p_z^* \right) \left( \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z \right) d\tau$$

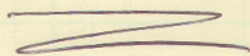
$$= \frac{1}{3} \int (2s^*)(2s) d\tau + \frac{\sqrt{2}}{3} \int 2s^* 2p_z d\tau + \frac{\sqrt{2}}{3} \int 2p_z^* 2s d\tau$$

$$+ \frac{2}{3} \int 2p_z^* 2p_z d\tau$$

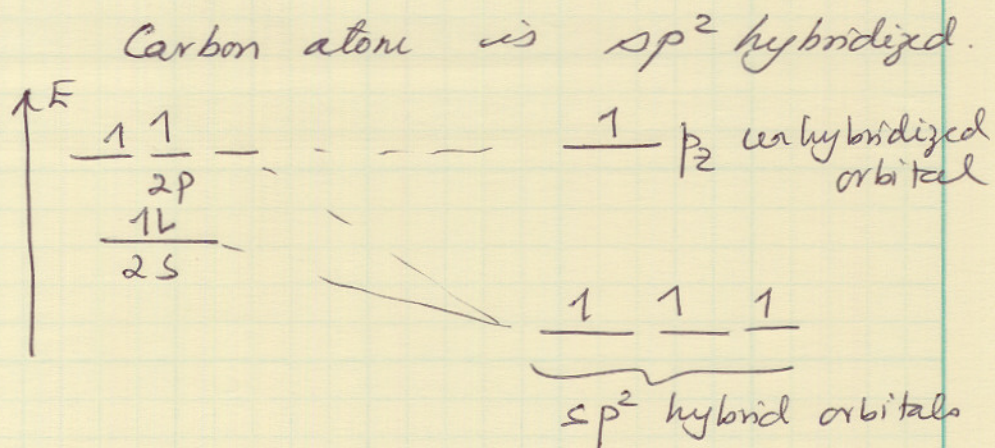
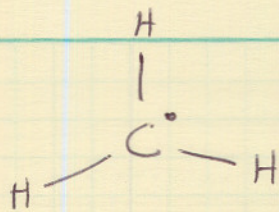
$$= \frac{1}{3} (1) + \frac{\sqrt{2}}{3} (0) + \frac{\sqrt{2}}{3} (0) + \frac{2}{3} (1)$$

Since  $2s$  and  $2p_z$  orbitals form an orthonormal set

$$= \frac{1}{3} + \frac{2}{3} = 1 \quad \therefore \psi_{sp^2}^{(1)} \text{ is normalized.}$$



(12)



are

There are 3 electrons in the  $sp^2$  hybrid orbitals of C. Each hybrid orbital overlaps with the  $1s$  orbital of the H atom forming 3  $\sigma$  bonds in  $CH_3$ . The unhybridized  $2p_z$  orbital, which is perpendicular to the plane of the  $CH_3$  radical carries the unpaired electron of the radical.

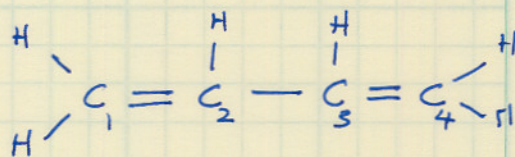
a

Downloaded sheet

Using Hückel M.O. theory, calculate the energy of the  $\pi$  electrons for 1,3 butadiene.

Step 1 -

Recognize that 1,3 butadiene is a planar, conjugated, hydrocarbon.

Step 2

write a trial wavefunction for the  $\pi$  electron system (similar to ethylene)

$$\psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4$$

Step 3

Write the secular determinant that you would obtain, if you were to use the variation method to obtain the energy of the  $\pi$  electrons using the trial wavefunction you wrote above. (do this by analogy, by comparing with ethylene. No need to do this from scratch)

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & H_{34} - ES_{34} \\ H_{41} - ES_{41} & H_{42} - ES_{42} & H_{43} - ES_{43} & H_{44} - ES_{44} \end{vmatrix} = 0$$

b

Hückel

Step 4 - Use the assumptions to simplify the secular determinant.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Step 5

Divide each term of this determinant by  $\beta$

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

Step 6 let  $\frac{\alpha - E}{\beta} = x$  and re-write the determinant.

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

Step 7 - expand the determinant and obtain values for  $x$  (this will take some doing. Be patient! The reward is worth it!). There are 4 different values for  $x$ .

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

$$x \left\{ x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} \right\} -$$

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

$$x \left\{ x(x^2 - 1) - (x) \right\} - \left\{ (x^2 - 1) - (0) \right\} = 0$$

$$x [x^3 - x - x] - [x^2 - 1] = 0$$

d

$$x^4 - 2x^2 - x^2 + 1 = 0$$

$$x^4 - 3x^2 + 1 = 0$$

$$\text{let } x^2 = A$$

$$A^2 - 3A + 1 = 0$$

$$A = \frac{3 \pm \sqrt{9-4}}{2} = 2.618 \text{ or } 0.3819$$

$$\Rightarrow x^2 = 2.618 \text{ or } x^2 = 0.3819$$

$$\Rightarrow x = \pm 1.618, \pm 0.618$$

Step 8

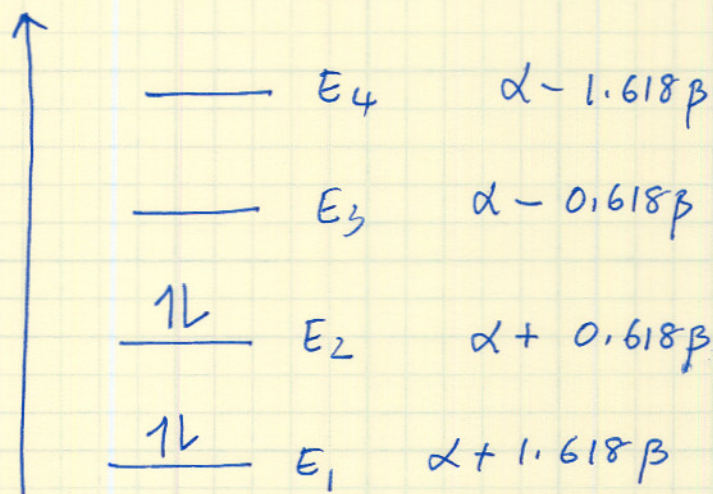
Use the values of  $\alpha$  to obtain the corresponding values for  $E$  (there are 4 different values for  $E$ )

$$\frac{\alpha - E}{\beta} = \alpha \quad E = \alpha - \beta\alpha$$

$$E_{\neq} = \begin{matrix} \alpha - 1.618\beta & , & \alpha + 1.618\beta \\ \alpha - 0.618\beta & & \alpha + 0.618\beta \end{matrix}$$

### Step 9

Recognizing that  $\beta < 0$ , draw a ladder type energy diagram to show the different energy levels for <sup>1,3</sup>butadiene. Be sure to include the  $\pi$  electrons in the diagram.



### Step 10

Use the above, to determine the energy of the  $\pi$  electrons. Is this equal to twice the  $\pi$  electron energy of ethylene?

$$\begin{aligned} \text{energy of } 1,3 \text{ butadiene} \} &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned}$$

$$\text{energy of ethylene} = 2(\alpha + \beta) = 2\alpha + 2\beta$$

$$\text{energy of two ethylene systems} \} = 2(2\alpha + 2\beta) = 4\alpha + 4\beta$$

f

∴ energy of 1,3 butadiene < energy of 2 ethylene molecules  
(since  $\beta < 0$ )

This additional stabilization of 1,3 butadiene is due to delocalization of the  $\pi$ -electrons!

Step 11

Since you obtained 4 different energy levels for 1,3 butadiene, you should have 4 distinct wavefunctions to describe them. Starting from your trial wavefunction, obtain these 4 wavefunctions (hint: the lowest energy level has zero nodes, the next one up has one node, the next one up has 2 nodes etc.). This exercise should not take more than 15 mins.

	# of nodes
$\psi_1 = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4$	0
$\psi_2 = c_1 \phi_1 + c_2 \phi_2 - c_3 \phi_3 - c_4 \phi_4$	1
$\psi_3 = c_1 \phi_1 - c_2 \phi_2 - c_3 \phi_3 + c_4 \phi_4$	2
$\psi_4 = c_1 \phi_1 - c_2 \phi_2 + c_3 \phi_3 - c_4 \phi_4$	3



Step 12

Draw rough sketches of the wavefunctions you obtained above.

