ORGANIC

MO theory (Delocalisation energy)

Sem - II

(S.P)

Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

($\hat{H}$ = Hamiltonian operator E = energy value Ψ = electronic wave function)

Multiple each side by Ψ and then integrate over all space

$$\int \Psi\hat{H}\Psi \, d\tau = \int \Psi E\Psi \, d\tau$$

$$E = \frac{\int \Psi\hat{H}\Psi \, d\tau}{\int \Psi\Psi \, d\tau}$$

If consider a diatomic molecule with LCAO, $\Psi_{MO} = c_1\varphi_1 + c_2\varphi_2$

$$E = \frac{\int (c_1\varphi_1 + c_2\varphi_2)\hat{H}(c_1\varphi_1 + c_2\varphi_2) \, d\tau}{\int (c_1\varphi_1 + c_2\varphi_2)^2 \, d\tau}$$

$$E = \frac{\int (c_1\varphi_1\hat{H}c_1\varphi_1 + c_1\varphi_1\hat{H}c_2\varphi_2 + c_2\varphi_2\hat{H}c_1\varphi_1 + c_2\varphi_2\hat{H}c_2\varphi_2) \, d\tau}{\int (c_1^2\varphi_1^2 + 2c_1\varphi_1c_2\varphi_2 + c_2^2\varphi_2^2) \, d\tau}$$

$$E = \frac{c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}}{c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}$$

Overlap Integral

$$\int \varphi_1 \varphi_2 d\tau = S_{12}$$

Coulomb Integral and Resonance Integral

$$\int \varphi_i \, H\varphi_j \, d\tau = H_{ij} \qquad H_{ij} = \alpha \; (i = j) \text{ Coulomb Integral}$$

$$\beta (i \neq j) \text{ Resonance Integral}$$

The Coulomb integral α gives the energy of an electron occupying the orbital ϕi in the isolated atom i . α is always negative and its absolute value increases with the electronegativity of i.

Resonance Integral , an intregal that determine energy of a electron in the field of two atom i and j involving the orbital φ_i and φ_j

Solving , secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Ethylene

$H_2C{=}{=}CH_2$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

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

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

$x^2 - 1 = 0$

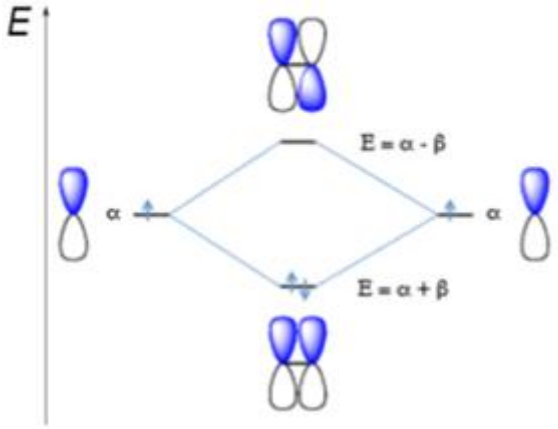
$x = \pm 1$

$x = \pm 1$

Putting the value into $x = \frac{\alpha - E}{\beta}$

$E_1 = \alpha + \beta$

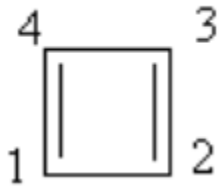
$E_2 = \alpha - \beta$



Total π energy $E_\pi = 2\alpha + 2\beta$

Energy level diagram for Ethylene

Cyclobutadiene



secular determinant

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

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

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

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

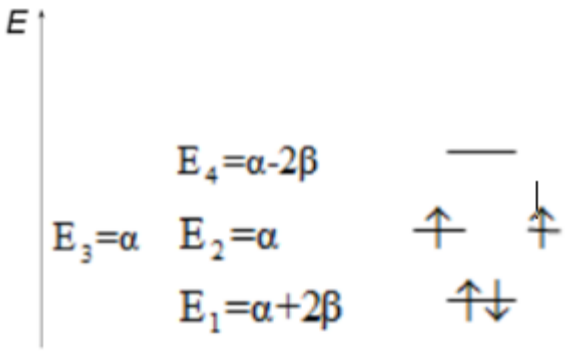
$X = -2\,,\qquad E_1 = \alpha + 2\beta$

$X = 0,\qquad E_2 = E_3 = \alpha$

$X = 2,\qquad E4 = \alpha - 2\beta$

The two energy levels E_2 and E_3 are degenerate (doubly degenerate non-bonding levels).

The Hückel energy level diagram for cyclobutadiene is shown below



$$Total\ \pi\ energy\ (E_\pi) = 2(\alpha + 2\beta) + 2\alpha = 4\alpha + 4\beta$$

$$D.E = E_\pi - Eethylene = 4\alpha + 4\beta - 4\alpha - 4\beta = 0$$

1, 3- butadiene

CH_2= CH-CH= CH_2

secular determinant of 1, 3- butadiene

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

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

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

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

$x = 1.618, -0.618, 0.618, +1.618$

$Putting\ the\ value\ into\ x = \dfrac{\alpha - E}{\beta}$

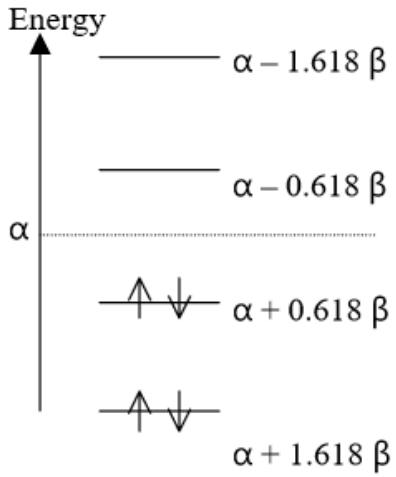
$E1 = \alpha + 1.618\beta$

$E_2 = \alpha + 0.618\beta$

$E_3 = \alpha - 0.618\beta$

$E_4 = \alpha - 1.618\beta$

Energy level diagram for 1, 3- butadiene



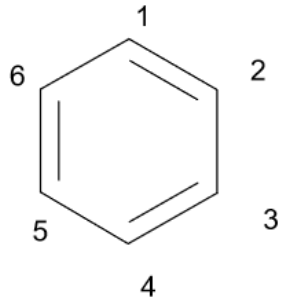
$Total$ π electron energy

$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

$E_\pi = 4\alpha + 4.48\beta$

$D.E = (4\alpha + 4.48\beta) - (4\alpha + 4\beta) = 0.48\beta$

Benzene



secular equation for benzene

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

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

S.P

$$x = \pm 1, \pm 1, \pm 2$$

Putting the value into $x = \dfrac{\alpha - E}{\beta}$

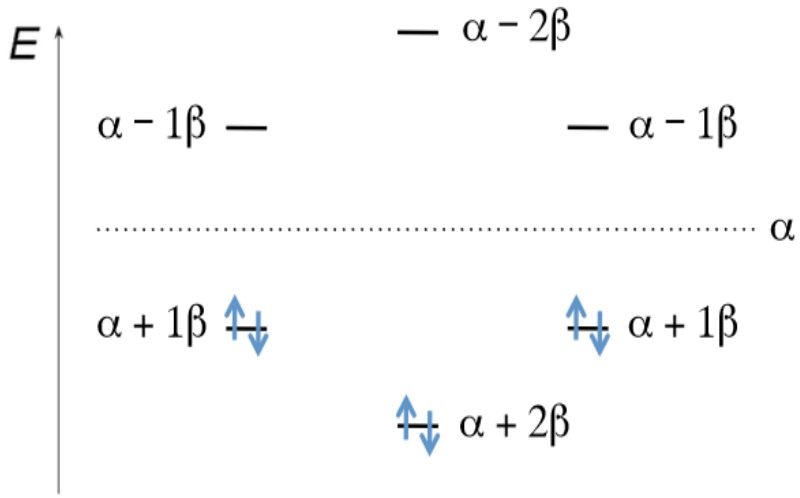
$E_1 = \alpha + 2\beta$

$E_2 = E_3 = \alpha + \beta$

$E_4 = E_5 = \alpha - \beta$

$E_6 = \alpha + 2\beta$

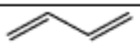
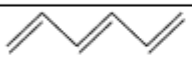
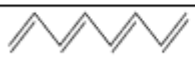
Energy level diagram for Benzene



Total π *energy* $E_\pi = 6\,\alpha + 8\,\beta$

D.E =2β

Energy of cyclic and acyclic planar systems

Planar systems	n_π	ε_j	ε_k
C═C (01)	2	$\varepsilon_1 = \alpha+\beta$ $\varepsilon_2 = \alpha-\beta$	
 (02)	4	$\varepsilon_1 = \alpha+1.6180\beta$ $\varepsilon_2 = \alpha+0.6180\beta$ $\varepsilon_3 = \alpha-0.6180\beta$ $\varepsilon_4 = \alpha-1.6180\beta$	
 (03)	4		$\varepsilon_0 = \alpha+2\beta$ $\varepsilon_1 = \varepsilon_{-1} = \alpha$ $\varepsilon_2 = \alpha-2\beta$
 (04)	6	$\varepsilon_1 = \alpha+1.7974\beta$ $\varepsilon_2 = \alpha+1.2494\beta$ $\varepsilon_3 = \alpha+0.4214\beta$ $\varepsilon_4 = \alpha-0.4214\beta$ $\varepsilon_5 = \alpha-1.2494\beta$ $\varepsilon_6 = \alpha-1.7974\beta$	
 (05)	6		$\varepsilon_0 = \alpha+2\beta$ $\varepsilon_1 = \varepsilon_{-1} = \alpha+\beta$ $\varepsilon_2 = \varepsilon_{-2} = \alpha-\beta$ $\varepsilon_3 = \alpha-2\beta$
 (06)	8	$\varepsilon_1 = \alpha+1.8792\beta$ $\varepsilon_2 = \alpha+1.5320\beta$ $\varepsilon_3 = \alpha+\beta$ $\varepsilon_4 = \alpha+0.3472\beta$ $\varepsilon_5 = \alpha-0.3472\beta$ $\varepsilon_6 = \alpha-\beta$ $\varepsilon_7 = \alpha-1.5320\beta$ $\varepsilon_8 = \alpha-1.8792\beta$	