# Huckel Molecular Orbital Theory (HMOT)

HMOT was proposed by Erich Huckel in 1930. It is a method for calculating molecular orbitals as linear combinations of atomic orbitals. The theory predicts the molecular orbitals for $\pi$-electrons in $\pi$-delocalised molecules like butadiene, benzene, ethene, pyrrole etc. It provides the theoretical proof for Huckel's rule of aromaticity.

The aim of HMOT are:-

1) To identify $\pi$ energy of a system.
2) To identify energy of a particular molecular orbital
3) - " - delocalisation energy
4) - " - energy for a particular transition.

order = no. of rows x columns

Ex:- 1)

| | $C_1$ ↓ | $C_2$ |
|---|---|---|
| $R_1$ → | a | b |
| $R_2$ → | c | d |

$R_1$ & $R_2$ = Row 1 & 2
$C_1$ & $C_2$ = column 1 & 2.

order = 2 x 2

2) $\begin{vmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{vmatrix}$ order = 2 x 3
[∵ 2 rows & 3 columns]

In organic molecules,
order = no. of C atoms.

In ethene, $CH_2 = CH_2$
order = 2 x 2

In benzene, $C_6H_6$, order = 6 x 6

* Secular determinant of ethene

$CH_2 = CH_2$

order = $2 \times 2$ [∵ 2 'C' atoms]

$$\begin{vmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{vmatrix}$$

$C = H - ES$ (E: Energy corresponding to mo)

$C_{11} = H_{11} - ES_{11}$ (H: Hamiltonian matrix element)

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$$

a) coulomb integral : $\alpha$

$\alpha = H_{ii}$ [row = column, when row & column values are same]

$$\begin{vmatrix} \alpha - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & \alpha - ES_{22} \end{vmatrix}$$

b) overlap integral : $[S_{ij}]$

$S_{ij}$ → = 1 [if $i = j$]

→ = 0 [if $i \neq j$]

$$\begin{vmatrix} \alpha - E.1 & H_{12} - E.0 \\ H_{21} - E.0 & \alpha - E.1 \end{vmatrix}$$

$$\begin{vmatrix} \alpha - E & H_{12} \\ H_{21} & \alpha - E \end{vmatrix}$$

c) Resonance integral : $(H_{ij})(\beta)$

$H_{ij} = \beta$ [If $c_i$ & $c_j$ are connected]

$H_{ij} = 0$ [If $c_i$ & $c_j$ are not connected]

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

$H_{12} = \beta$ (∵ $C_1$ & $C_2$ are attached)

$H_{21} = \beta$ (∵ $C_2$ & $C_1$ are connected by a bond)

∴ This is the secular determinant for ethene.

* Calculation of transition energy, total π energy, total π-bond energy & delocalisation energy for ethene.

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

÷ by $\beta$

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

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

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

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

$$x^2 = 1$$

$$x = \sqrt{1}$$

$$\underline{x = \pm 1}$$

$$\frac{\alpha - E}{\beta} = x = \pm 1$$

When $x = +1$, $\frac{\alpha - E}{\beta} = 1$

$$\alpha - E = \beta$$

$$\underline{\alpha - \beta = E}$$

When $x = -1$, $\frac{\alpha - E}{\beta} = -1$

$$\alpha - E = -\beta$$

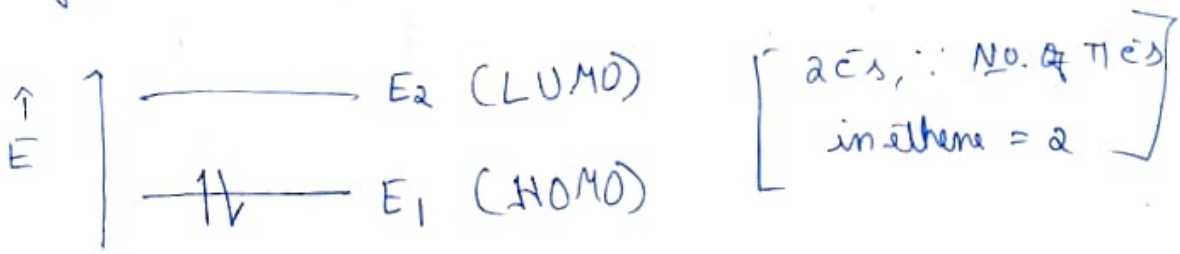
$$\underline{\alpha + \beta = E}$$

Ethene has two 'C' atoms, ∴ it has 2 energy levels $E_1$ & $E_2$.

$E_1 = \alpha + \beta$

$E_2 = \alpha - \beta$

Energy level diagram for ethene,




Transition Energy = $E_2 - E_1$

$= \alpha - \beta - (\alpha - \beta)$

$= \underline{-2\beta}$

Total π energy = No. of electrons in $E_1$ + No. of e's in $E_2$

$= 2E_1 + 0 \cdot E_2$

$= 2[\alpha + \beta] + 0$

$= \underline{2\alpha + 2\beta}$

Total π-bond energy = No. of π bonds $[2\alpha + 2\beta]$

$= 1[2\alpha + 2\beta]$

$= \underline{2\alpha + 2\beta}$

[$2\alpha + 2\beta$ energy is required to form 1 π bond]

Delocalisation energy = Total π-bond energy − Total π energy

$= 2\alpha + 2\beta - (2\alpha + 2\beta)$

$= \underline{0}$

# H-MOT

## Delocalisation Energy

URBAN EDGE

* For linear molecule:

$$E_K = \alpha + 2\beta \cos\left(\frac{K\pi}{n+1}\right)$$

$K = 1, 2, 3 \ldots$

$n =$ no. of C atoms

1. for ethene $CH_2 = CH_2$

$K = 1$ & $2$, $n = 2$

$K=1$, $E_1 = \alpha + 2\beta \cos\left(\frac{1\cdot\pi}{2+1}\right) = \alpha + 2\beta \cos\left(\frac{\pi}{3}\right)$

$E_1 = \alpha + 2\beta \cos 60^\circ$

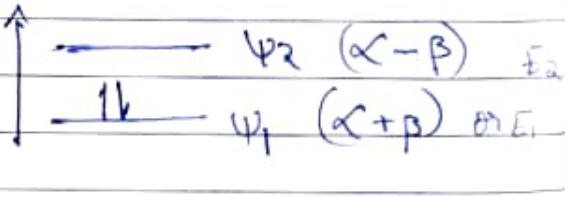
$= \alpha + 2\beta \cdot \frac{1}{2} \Rightarrow \boxed{E_1 = \alpha + \beta}$ | $\cos 60 = \frac{1}{2}$

$K=2$, $E_2 = \alpha + 2\beta \cos\left(\frac{2\pi}{2+1}\right) = \alpha + 2\beta \cos\left(\frac{180\times 2}{3}\right)$

$E_2 = \alpha + 2\beta \cos 120^\circ = \alpha + 2\beta \cdot -\frac{1}{2}$ | $\cos 120 = -\frac{1}{2}$

$\boxed{E_2 = \alpha - \beta}$

The 2 energy levels are,




$\beta$ is $-$ ve

$\therefore \psi_1$ will be having lower energy.

a) Transition energy $= E_2 - E_1 = \alpha - \beta - (\alpha - \beta)$

$= -2\beta$

b) Total $\pi$ energy = No. of e's in $E_1$ + No. of e's in $E_2$

$= 2 \cdot E_1 + 0 \cdot E_2 = 2(\alpha + \beta)$

$= 2\alpha + 2\beta$

c) Total $\pi$ bond energy = No. of $\pi$ bonds $(2\alpha + 2\beta)$

$= 1(2\alpha + 2\beta) = 2\alpha + 2\beta$

d) Delocalisation energy = Total $\pi$ bond energy − Total $\pi$ energy

$= 2\alpha + 2\beta - (2\alpha + 2\beta)$

$= 0$

$\cos 45 = \frac{1}{\sqrt{2}}$ | $\cos 135 = -\frac{1}{\sqrt{2}}$ | $\cos 180 = -1$

$\cos 90 = 0$ | $\cos 0 = 1$ | $\cos 60 = \frac{1}{2}$

$\cos 120 = -\frac{1}{2}$

URBAN EDGE

2. For allylic radical.

$n = 3$, $K = 1, 2, 3$

$K=1$, $E_K = \alpha + 2\beta \cos\left(\frac{K\pi}{n+1}\right)$

$E_1 = \alpha + 2\beta \cos\left(\frac{1 \cdot \pi}{3+1}\right) = \alpha + 2\beta \cos\left(\frac{180}{4}\right)$

$E_1 = \alpha + 2\beta \cos 45 = \alpha + 2\beta \cdot \frac{1}{\sqrt{2}}$

$E_1 = \underline{\alpha + \sqrt{2}\beta}$

$K=2$, $E_2 = \alpha + 2\beta \cos\left(\frac{2\pi}{3+1}\right) = \alpha + 2\beta \cos\left(\frac{2 \cdot 180}{4}\right)$

$= \alpha + 2\beta \cos 90$

$\underline{E_2 = \alpha}$

$E_3 = \alpha + 2\beta \cos\left(\frac{3\pi}{3+1}\right) = \alpha + 2\beta \cos\left(\frac{3 \cdot 180}{4}\right)$

$E_3 = \alpha + 2\beta \cos(135)$ or $\cos\left(\pi - \frac{\pi}{4}\right)$

$E_3 = \alpha + 2\beta \cdot \frac{-1}{\sqrt{2}}$

$E_3 = \underline{\alpha - \sqrt{2}\beta}$

The 3 energy levels are.

——— $\psi_3$ $\alpha - \sqrt{2}\beta$

——— $\psi_2$ $\alpha$

——— $\psi_1$ $\alpha + \sqrt{2}\beta$

URBAN EDGE

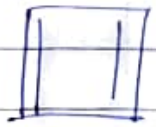
★ For cyclic systems :

$$E = \alpha + 2\beta \cos\left(\frac{2K\pi}{n}\right)$$

$K = 0, \pm 1, \pm 2 + \ldots$

$n =$ no. of C atoms :

1. cyclobutadiene = 4 Energy level:



If $K=0$, $E_0 = \alpha + 2\beta \cos\left(\frac{2 \cdot 0\pi}{n}\right)$

$E_0 = \alpha + 2\beta \cos 0$

$E_0 = \alpha + 2\beta$

First +1 must be taken (+ve first)

If $K=1$, $E_1 = \alpha + 2\beta \cos\left(\frac{2 \cdot 1\pi}{4}\right)$ :

$E_1 = \alpha + 2\beta \cos\left(\frac{\pi}{2}\right)$ $\left(\cos\frac{\pi}{2} = 0\right)$

$E_1 = \alpha$

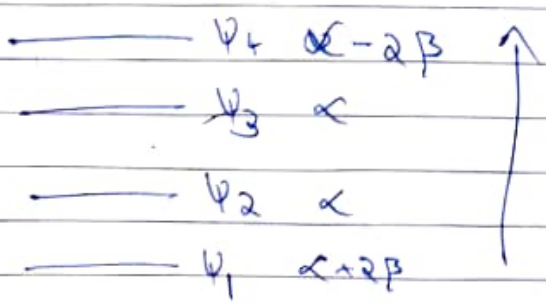
If $K=-1$ $E_{-1} = \alpha$

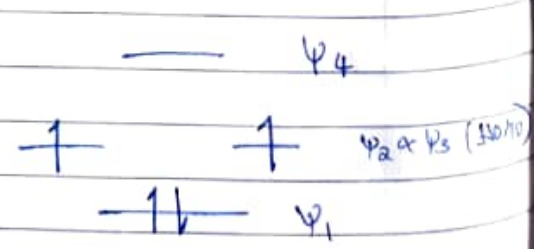
If $K=2$ $E_2 = \alpha + 2\beta \cos\left(\frac{2 \cdot 2\pi}{4}\right)$

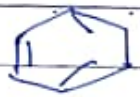
$E_2 = \alpha + 2\beta \cos\pi$

$E_2 = \alpha + 2\beta(-1)$

$E_2 = \alpha - 2\beta$



2.  6-energy level

$$E_K = \alpha + 2\beta \cos\left(\frac{2K\pi}{n}\right)$$

$n = 6$, $K = 0, \pm 1, \pm 2, 3$

$K = 0$, $E_0 = \alpha + 2\beta \cos\left(\frac{2.0.\pi}{6}\right)$

$E_0 = \alpha + 2\beta$

$K = 1$, $E_1 = \alpha + 2\beta \cos\left(\frac{2.1.\pi}{6}\right)$

$E_1 = \alpha + \beta$

$K = -1$ $E_{-1} = \alpha + 2\beta \cos\left(\frac{2.-1.\pi}{6}\right)$

$E_{-1} = \alpha + \beta$

$K = 2$ $E_2 = \alpha + 2\beta \cos\left(\frac{2.2.\pi}{6}\right)$

$E_2 = \alpha - \beta$

$K = -2$ $E_{-2} = \alpha - \beta$

$K = 3$ $E_3 = \alpha + 2\beta \cos\left(\frac{2.3.\pi}{6}\right)$

$E_3 = \alpha - 2\beta$