to molecular orbitals ψ_i

→ ε_i → ideally negative of energy needed to remove electron from orbital (i). i.e. negative of ionisation energy for that orbital. It is ideally energy of an electron attracted to nuclei & repelled by other electrons, relative to energy of that electron & corresponding ionized molecule, infinitely separated from one another.

$$[H - S\varepsilon]C = 0$$

$$HC - S\varepsilon C = 0$$

$$HC = S\varepsilon C$$

& or $H_{ij} c_{ij} = S_{ij} \varepsilon_i c_{ij}$

$S_{ij} = \delta_{ij}$ $\quad \delta = 1$ if $i = j$

$\delta = 0$ if $i \neq j$

$\therefore S = S_{ij} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ = unit matrix

$$HC = \varepsilon C$$

→ Here ψ has to be orthonormal.

$\int \phi_i \phi_j dv = 0$ i.e. orthogonal atomic or molecular orbitals or function ϕ have zero net overlap.

$\int \phi_i \phi_i dv = 1$ → normalized orbital or function ϕ.

We can take normalized but not orthogonal ψ as it would mean zero overlap.

Orthonormality is a drastic approximation but works here for basis functions on adjacent atoms.

Basis functions on same atom (same orbital) → normalisation (appreciable overlap)

Basis functions on different atoms → orthogonal i.e. zero overlap. (& different orbitals)

$H_{ii} = \alpha$ = Coulomb Integral

$H_{ij} = \beta$ = Resonance Integral

So matrix (V) becomes

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

α → negative energy as it is the decrease in energy when e⁻ falls from infinity (with 0 Energy) into an orbital. It is negative of ionization energy of the orbital:

β → negative energy as it is the energy of electron in overlap region of adjacent p-orbitals relative to zero of energy.

Here 'zero' of energy is of electron & 2-center molecular orbital at infinite separation.

It is negative of average of ionization energy of two orbitals involved.

If we want to replace α & β by numbers, we can write '0' for α & '-1' for β. β value is '-1' relative to '0' value of α.

Only i-type interactions i.e. H_{ii} (like H_{11}, H_{22}) $= \alpha = 0$

ij type interactions i.e. H_{ij} (like H_{12}, H_{21}) $= \beta = -1$

Calculation of energies of molecular orbitals of Ethene

from equation (A.)

$$\left[\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} - \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} E\right] \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

$$E = \mathcal{E} = \begin{pmatrix} \mathcal{E}_1 & 0 \\ 0 & \mathcal{E}_2 \end{pmatrix}$$

$$\left[\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} - \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} \mathcal{E}_1 & 0 \\ 0 & \mathcal{E}_2 \end{pmatrix}\right] \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

$H_{11} - \mathcal{E}_1$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

$(\because S_{12} = S_{21} = 0)$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} \\ H_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

$$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \quad (\because S_{11} = S_{22} = 1,\ H_{11} = H_{22} = \alpha,\ H_{12} = H_{21} = \beta)$$

divide by β

$$\begin{pmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E}{\beta} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \quad (5)$$

Let $\frac{\alpha - E}{\beta} = x$, equation (5.) becomes.

$$\begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (6.)$$

$x^2 - 1 = 0$

$x = \pm 1$

$\frac{\alpha - E}{\beta} = 1$ & $\frac{\alpha - E}{\beta} = -1$

$E = \alpha - \beta$ $\quad E = \alpha + \beta$

Calculation of co-efficients:

For $x = 1$, eq. (6.) becomes

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

$c_1 + c_2 = 0$

$c_1 = -c_2$

$c_1^2 + c_2^2 = 1$

$2c_1^2 = 1$

$c_1 = \frac{1}{\sqrt{2}} = 0.707$

$c_2 = -0.707$

$\psi_2 = 0.707\phi_1 - 0.707\phi_2$ (from $\psi = c_1\phi_1 + c_2\phi_2$)

for $E = \alpha - \beta$

(higher energy)

Anti-bonding molecular orbital

For $x = -1$, equation (6.) becomes

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

$-c_1 + c_2 = 0$

$c_1 = c_2$

$c_1^2 + c_2^2 = 1$

$2c_2^2 = 1$

$c_2 = \frac{1}{\sqrt{2}} = 0.707$

$c_1 = 0.707$

$\psi_1 = 0.707\phi_1 + 0.707\phi_2$

for $E = \alpha + \beta$

(lower energy)

Bonding molecular orbital

Atomic orbital 1 (+) Atomic orbital 2 (+) $\xrightarrow{C_{12}\phi_1 + C_{22}\phi_2}$ (+) ! (−) Node — Anti-bonding molecular orbital

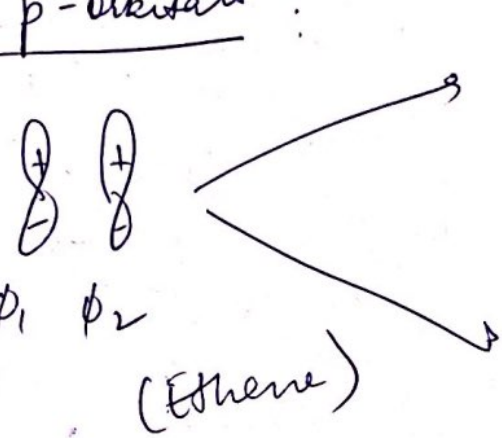
ϕ_1 ϕ_2 ψ_2

s s

(Two s-orbitals) $\xrightarrow{C_{11}\phi_1 + C_{21}\phi_2}$ (+)—(+) Bonding molecular orbital.

ψ_1

2 p-orbitals



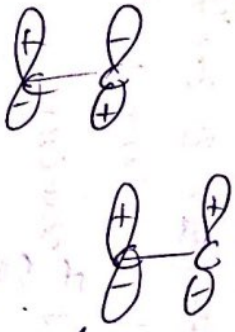
ϕ_1 ϕ_2 (Ethene)

ψ_2 Anti-Bonding

ψ_1 Bonding

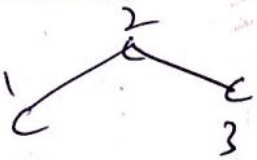
E. $\alpha-\beta$ — $\psi_2 = 0.707\phi_1 - 0.707\phi_2$ Anti-bonding molecular orbital

$\alpha+\beta$ — $\psi_1 = 0.707\phi_1 + 0.707\phi_2$ Bonding molecular orbital



Propenyl System (Acyclic 3-p orbitals)

$H_2C - CH = CH_2$



Each carbon atom will contribute 1 p-orbital each for π-electron delocalization

$$\left[\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} - \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} E\right]\begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0$$

for $x=0$

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

$c_2=0,\ c_1=-c_3$

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

$c_1=\frac{1}{\sqrt{2}}=0.707$

$c_3=-0.707$

$c_2=0$

$\psi_2=0.707\phi_1+0\phi_2-0.707\phi_3$

for $E=\alpha$

for $x=\sqrt{2}$

$$\begin{pmatrix} \sqrt{2} & 1 & 0 \\ 1 & \sqrt{2} & 1 \\ 0 & 1 & \sqrt{2} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}=0$$

$\sqrt{2}c_1+c_2=0$

$c_1+\sqrt{2}c_2+c_3=0$

$c_2=-\sqrt{2}c_1$

$c_1=c_3$

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

$c_1=\frac{1}{2},\ c_3=\frac{1}{2}$

$c_2=-0.707$

$\psi_3=0.500\phi_1-0.707\phi_2+0.500\phi_3$

for $E=\alpha-\sqrt{2}\beta$

for $x=-\sqrt{2}$

$E=\alpha+\sqrt{2}\beta$

$$\begin{pmatrix} -\sqrt{2} & 1 & 0 \\ 1 & -\sqrt{2} & 1 \\ 0 & 1 & -\sqrt{2} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}=0$$

$-\sqrt{2}c_1+c_2=0$

$c_2=\sqrt{2}c_1$

$c_2=\sqrt{2}c_3$

$c_1=c_3$

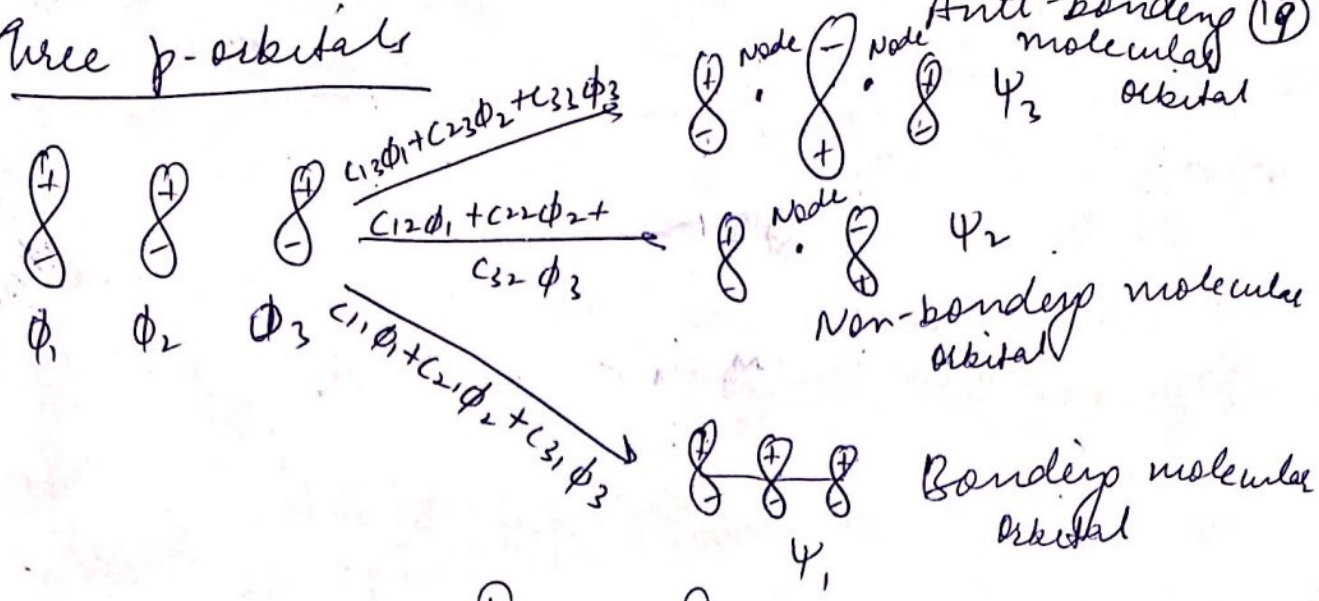
$c_1^2+c_2^2+c_3^2=1$

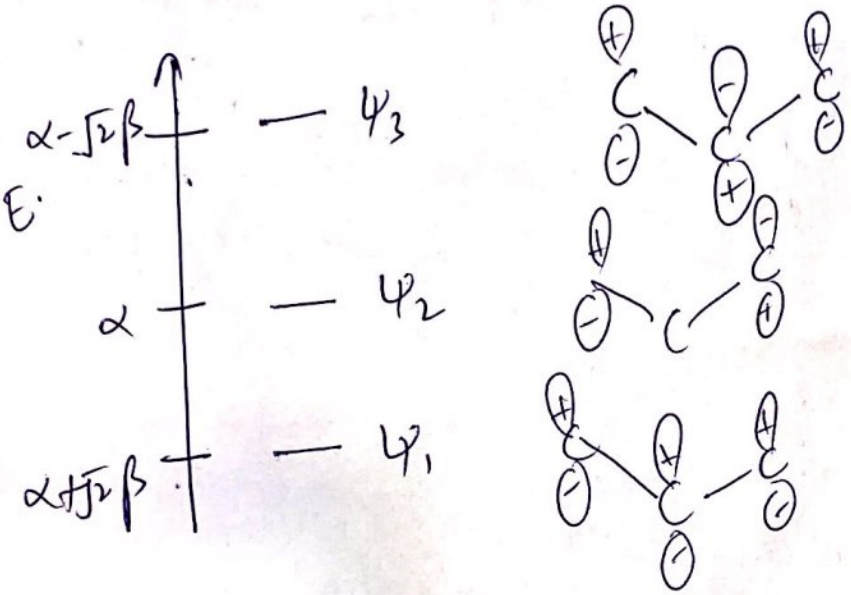
$c_1=\frac{1}{2},\ c_2=\frac{\sqrt{2}}{2}=0.707$

$c_3=0.500$

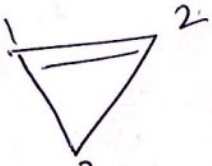
$\psi_1=0.500\phi_1+0.707\phi_2+0.500\phi_3$

Three p-orbitals





Cyclopropenyl system



$$\begin{pmatrix} \frac{\alpha - E}{\beta} & 1 & 1 \\ 1 & \frac{\alpha - E}{\beta} & 1 \\ 1 & 1 & \frac{\alpha - E}{\beta} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0$$

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

~~$x^3 - 3x + 2 = 0$~~

~~$x = 0, \pm\sqrt{3}$~~

$x = 1, \quad x^2 + x - 2 = 0$

$x = 1, -2.$

$E_1 = \alpha + 2\beta, \quad \psi_1 = \frac{\phi_1}{\sqrt{3}} + \frac{\phi_2}{\sqrt{3}} + \frac{\phi_3}{\sqrt{3}}$

$E_2 = E_3 = \alpha - \beta, \quad \psi_2 = 0.707\phi_1 - 0.707\phi_2$

$\psi_3 = \frac{1}{\sqrt{6}}\phi_1 + \frac{\phi_2}{\sqrt{6}} - \frac{2}{\sqrt{6}}\phi_3$

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

$E = \alpha - \beta$

$$c_1 + c_2 + c_3 = 0$$

We can choose, $c_3 = 0$

$$c_1 = -c_2$$

(or any co-efficient as zero)

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

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

$$\psi_2 = 0.707\phi_1 - 0.707\phi_2$$

Other degenerate ψ,

$E = \alpha - \beta$ Here $c_1 = c_2$

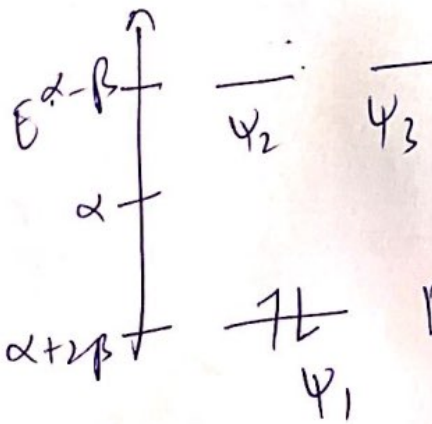
$$c_1 + c_2 + c_3 = 0$$

$$c_3 = -2c_1$$

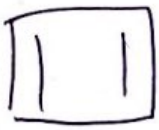
$$c_1^2 + c_2^2 + c_3^2 = 1$$

$$c_1 = \frac{1}{\sqrt{6}}, \quad c_2 = \frac{1}{\sqrt{6}}, \quad c_3 = -\frac{2}{\sqrt{6}}$$

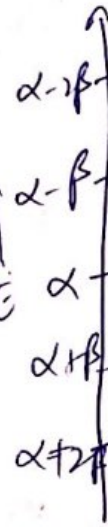
$$\psi_3 = \frac{\phi_1}{\sqrt{6}} + \frac{\phi_2}{\sqrt{6}} - \frac{2}{\sqrt{6}}\phi_3$$



Cyclobutadiene



$$\begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix}$$



Antibonding

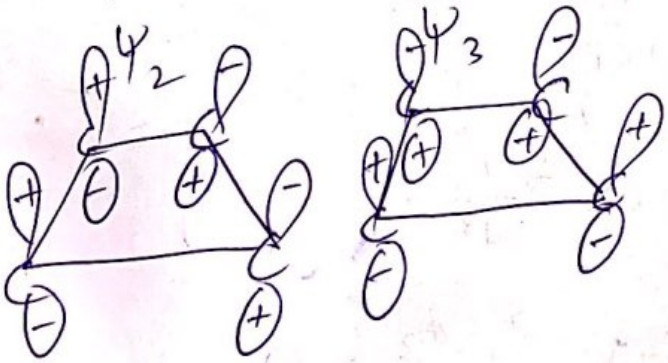
$\psi_4 = 0.500\phi_1 - 0.500\phi_2 + 0.500\phi_3 - 0.500\phi_4$

$\psi_3 = 0.500\phi_1 + 0.500\phi_2 - 0.500\phi_3 - 0.500\phi_4$

Non-bonding

$\psi_2 = 0.500\phi_1 - 0.500\phi_2 - 0.500\phi_3 + 0.500\phi_4$

$\psi_1 = 0.500\phi_1 + 0.500\phi_2 + 0.500\phi_3 + 0.500\phi_4$



Strengths of SHM :

- Extensively used to correlate, rationalize & predict many chemical phenomena.
- Used to detect dipole moment, bond lengths, ESR spectra, redox potential, UV, IR spectra, ionization potential, aromaticity, acidity or basicity & reactivity.
- It gives insight into any phenomena that involves predominantly π-electron system of conjugated molecules.

Not used nowadays as better semi-empirical & DFT methods & ab initio methods are available.

Weaknesses of SHM :

- It treats only π-electrons.
- It is an approximate method.
- Non-~~π~~ substituents like alkyl groups, halogens are treated as π centres. Their α & β values are altered (different from 0 & -1) but this is not a reliable method as values of α & β vary considerably.
- Completely ignores electron spin.
- Overlap matrix integrals & Fock matrix integrals are not exactly evaluated.

$H_{ij} = \alpha$, β or 0 → i & j on farther removed atoms
→ i & j on adjacent atoms
↓
i & j on same atom

$$\left[\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} E\right] \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0$$

$H_{13} = 0$ as 1 & 3 are not directly bonded

Similarly $H_{31} = 0$

$$\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0$$

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

Divide by β

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

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

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

$$x^3 - 2x = 0$$

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

$$x = 0, \pm\sqrt{2}$$

$x = 0, \frac{\alpha - E}{\beta} = 0, \quad E = \alpha$

$x = \sqrt{2}, \frac{\alpha - E}{\beta} = \sqrt{2}, \quad E = \alpha - \sqrt{2}\beta$

$x = -\sqrt{2}, \frac{\alpha - E}{\beta} = -\sqrt{2}, \quad E = \alpha + \sqrt{2}\beta$