Bharathidasan University
Tiruchirappalli -620 024

Programme : M.Sc. Chemistry

Course Title : Applications of Physical Chemistry Concepts
Course Code : CHE632CC

Unit-I Applications of Quantum Chemistry

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Hückel molecular orbital theory:

One of the principle assumptions of Hückel molecular-orbital theory is that the π electrons move in a fixed, electrostatic, effective potential due to the σ framework of the molecule. The σ electrons are described in terms of localized hybrid bond orbitals and the π electrons are described by molecular wave functions that extend over each of the atoms that contributes a π electron. Thus, the π electrons are delocalized.

Main assumptions:

* HMOT applied to conjugated system and only carbon P orbitals used in basic set.

* $S_{ij} = \delta_{ij}$ (no overlap of adjacent P orbitals)

S = overlap integral

$$\boxed{\begin{array}{l} \delta_{ij} = 0 : \text{if } i \neq j \\ \delta_{ij} = 1 : \text{if } i = j \end{array}}$$

* $H_{ij} = 0$ for all p-orbitals not adjacent to each other

$H_{ii} = \alpha$ (constant for all i)

$H_{ij} = \beta$ (constant for all i, j) : $i \neq j$

α = Coulomb integral

β = resonance integral (energy stabilisation of parallel p-orbitals)

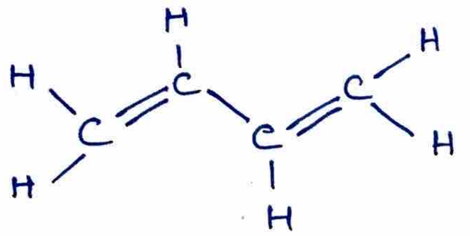
~~$H_{ij} = \int \psi$~~

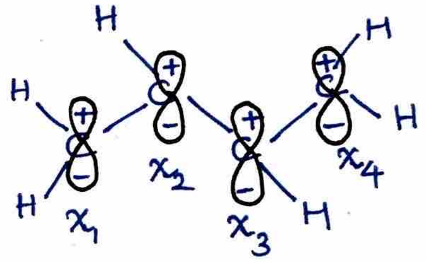
$$H_{ij} = \int \phi_i \hat{H} \phi_j \, d\tau$$

$$S_{ij} = \int \phi_i \phi_j \, d\tau$$

Example:

1, 3 - butadiene





Each carbon atom contributes a $2p_z$ orbital to the delocalized π orbital as similar to the molecular orbital treatment of H_2.

$$\phi_1 = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

where, χ_1, χ_2, ... are the carbon $2p_z$ orbitals.

$$\varepsilon(c_1, c_2, c_3, c_4)$$

we can minimize the energy with respect to each one of them will give four equations. These four equations can be rewritten in the form of matrix.

$$\begin{bmatrix} H_{11}-\varepsilon S_{11} & H_{12}-\varepsilon S_{12} & H_{13}-\varepsilon S_{13} & H_{14}-\varepsilon S_{14} \\ H_{12}-\varepsilon S_{12} & H_{22}-\varepsilon S_{22} & H_{23}-\varepsilon S_{23} & H_{24}-\varepsilon S_{24} \\ H_{13}-\varepsilon S_{13} & H_{23}-\varepsilon S_{23} & H_{33}-\varepsilon S_{33} & H_{34}-\varepsilon S_{34} \\ H_{14}-\varepsilon S_{14} & H_{24}-\varepsilon S_{24} & H_{34}-\varepsilon S_{34} & H_{44}-\varepsilon S_{44} \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

This matrix does not have an inverse. So,

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{vmatrix} = 0$$

by applying HMOT assumptions and approximations,

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

If we factor β from each column, let $x = \frac{(\alpha-E)}{\beta}$

then

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

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In the similar manner

For ethene,

$H_2C=CH_2$

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

For allyl,

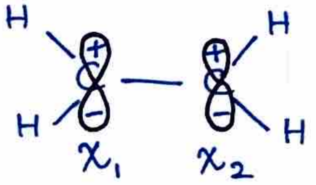
$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

For benzene,

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

Ethene:-

$H_2C = CH_2$



Each carbon atom contributes a $2p_z$ orbital to the delocalized π orbital.

$$\phi = c_1\chi_1 + c_2\chi_2$$

then the secular determinant becomes

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

$$x^2 - 1 = 0$$

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

If $x = -1$,

$$\frac{\alpha - \varepsilon}{\beta} = -1$$

$$\boxed{\varepsilon = \alpha + \beta}$$

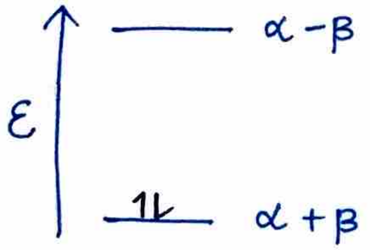
If $x = +1$,

$$\frac{\alpha - \varepsilon}{\beta} = 1$$

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

Both α and β are negative, the lowest energy is $\alpha+\beta$.

There are two π electrons in ethylene and both occupies the lowest energy level.



The π-electronic energy of ethylene is

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

$$= 2\alpha + 2\beta$$

The value of β approximately $-75\ \text{kJ mol}^{-1}$

If we substitute the value of x in the matrix equation

$\underline{x=1}$

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

$$c_1 = -c_2$$

$\underline{x=-1}$

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

$$c_1 = c_2$$

then $\phi = c_1(\chi_1 + \chi_2)$

~~Molecular orbila~~

ϕ be normalised

$$\int \phi^2 d\tau = 1$$

$$\int [c_1(\chi_1+\chi_2)]^2 d\tau = 1$$

$$c_1^2 \int (x_1^2 + x_2^2 + 2x_1x_2)\, d\tau = 1$$

$$c_1^2 (1 + 1 + 0) = 1$$

$$2c_1^2 = 1$$

$$c_1^2 = \frac{1}{2}$$

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

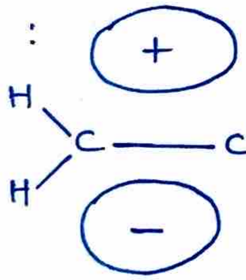
then

$x = -1$: $\varepsilon_1 = \alpha + \beta$: $\phi_1 = \frac{1}{\sqrt{2}}(x_1 + x_2)$

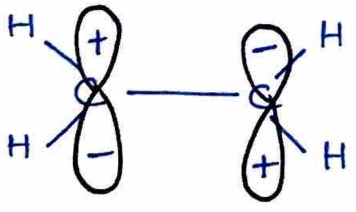
$x = +1$: $\varepsilon_2 = \alpha - \beta$: $\phi_2 = \frac{1}{\sqrt{2}}(x_1 - x_2)$

then the shape of the orbital becomes

ϕ_1 :



ϕ_2 :



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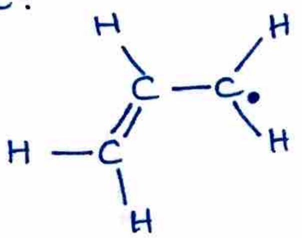
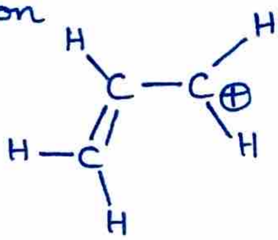
Allyl :

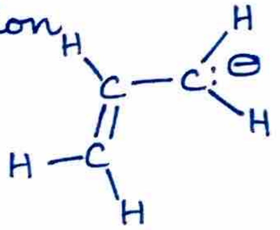
Allyl radical :

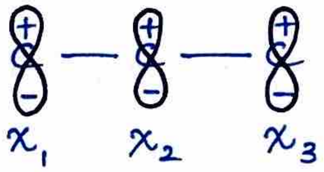


Allyl cation



Allyl anion





$$\phi = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3$$

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

It doesn't have an inverse. then,

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

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

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

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

$$x = 0$$

$$x = +\sqrt{2}$$

			allyl cation	allyl radical	allyl anion
$x = +\sqrt{2}$:	$\varepsilon_3 = \alpha - \sqrt{2}\beta$	:	___	___	___
$x = 0$:	$\varepsilon_2 = \alpha$	:	___	↑	↑↓
$x = -\sqrt{2}$:	$\varepsilon_1 = \alpha + \sqrt{2}\beta$	:	↑↓	↑↓	↑↓

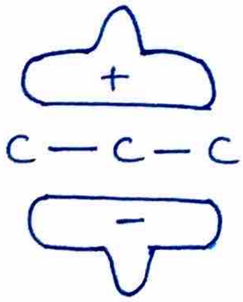
ϕ be normalised

$\varepsilon_3 = \alpha - \sqrt{2}\beta$: $\phi_3 = \frac{1}{2}(x_1 - \sqrt{2}x_2 + x_3)$

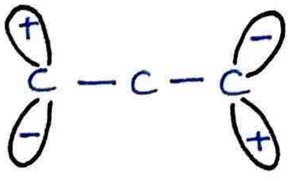
$\varepsilon_2 = \alpha$: $\phi_2 = \frac{1}{\sqrt{2}}(x_1 - x_3)$

$\varepsilon_1 = \alpha + \sqrt{2}\beta$: $\phi_1 = \frac{1}{2}(x_1 + \sqrt{2}x_2 + x_3)$

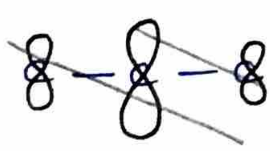
ϕ_1 :

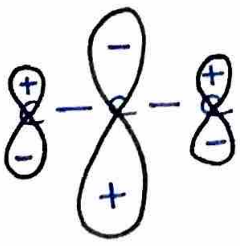


ϕ_2 :

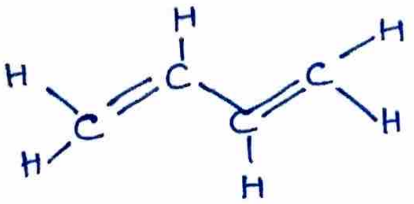


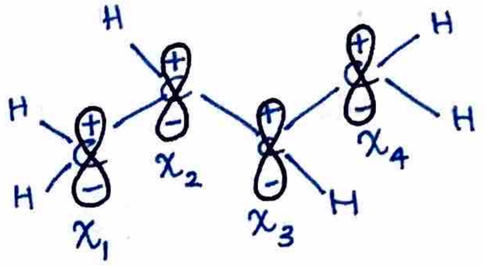
ϕ_3 :





1, 3-butadiene





~~X_1~~ $\phi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$

The secular determinant for the butadiene molecule is

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

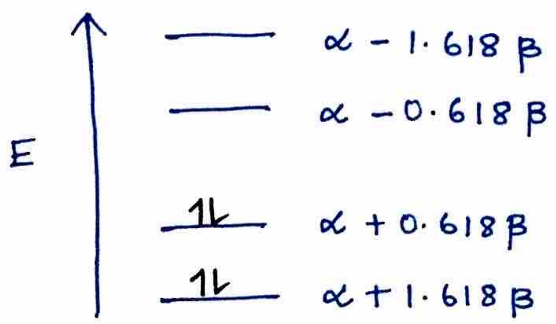
where, $x = \dfrac{\alpha - \varepsilon}{\beta}$

If the determinant is expanded,

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

Therefore, we get four roots for x

$$x = \pm 1.61804$$
$$= \pm 0.61804$$



There are four π electrons in butadiene. In the ground state, these four π electrons occupy the two orbitals of lowest energ

The total π electronic energy of butadiene is

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
$$= 4\alpha + 4.472\beta$$

In the simple Hückel theory, this localized structure is equivalent to two isolated ethene molecules.

$$2E_{\pi}(\text{ethene}) = 2(2\alpha + 2\beta)$$
$$= 4\alpha + 4\beta$$

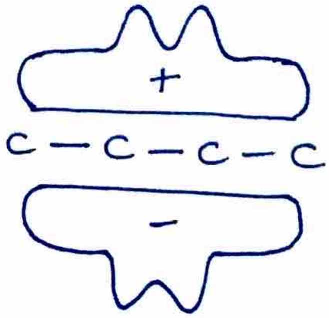
Therefore, the delocalization energy of 1,3-butadiene

$$= E_{\pi}(\text{butadiene}) - 2E_{\pi}(\text{Ethene})$$
$$= 0.472\beta$$

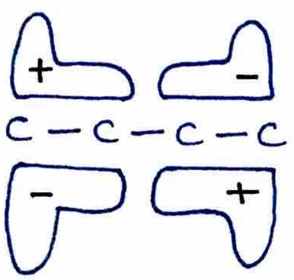
This is the energy by which butadiene is stabilised relative to two isolated double bonds or the stability that butadiene derives because its π electrons are delocalized over the entire length of the molecule instead of being localized to the two end bonds.

The resulting wave functions for butadiene are

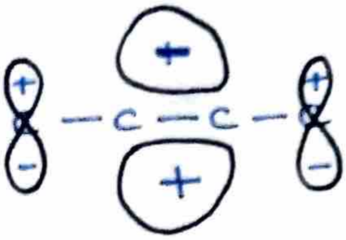
$$\phi_1 = 0.3717\,\chi_1 + 0.6015\,\chi_2 + 0.6015\,\chi_3 + 0.3717\,\chi_4$$



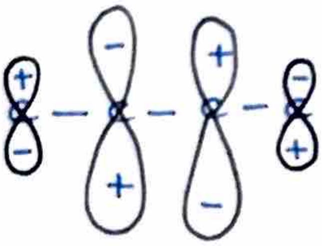
$$\phi_2 = 0.6015\,\chi_1 + 0.3717\,\chi_2 - 0.3717\,\chi_3 - 0.6015\,\chi_4$$



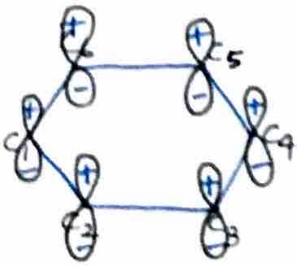
$$\phi_3 = 0.6015\,\chi_1 - 0.3717\,\chi_3 - 0.3717\,\chi_3 + 0.6015\,\chi_4$$



$$\phi_4 = 0.3717\,\chi_1 - 0.6015\,\chi_2 + 0.6015\,\chi_3 - 0.3717\,\chi_4$$



Benzene:-



$$\phi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4 + c_5\chi_5 + c_6\chi_6$$

The Hückel secular determinant for benzene.

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

where $x = \frac{\alpha - \varepsilon}{\beta}$

If we expand the determinant,

$$x^6 - 6x^4 + 9x^2 - 4 = 0$$

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

The six roots of the polynomial for E are

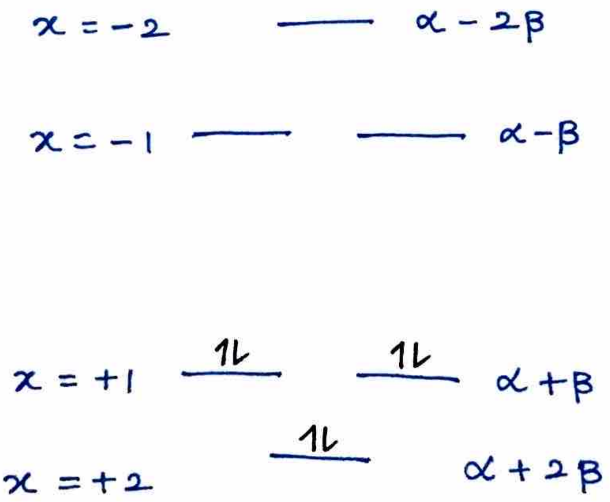
$$E_1 = \alpha + 2\beta$$

$$E_2 = E_3 = \alpha + \beta$$

$$E_4 = E_5 = \alpha - \beta$$

$$E_6 = \alpha - 2\beta$$

The Hückel energy level diagram of benzene is



The total π-electronic energy in benzene is

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

$$= 6\alpha + 8\beta$$

If the six π electrons were localized to three double bonds, then the π-electronic energy would be equal to the energy of three ethylene molecules.

The π-electronic energy of three ethylene molecule is

$$E_{\pi} = 3(2\alpha + 2\beta)$$

$$= 6\alpha + 6\beta$$

Therefore, the delocalization (or resonance) energy in benzene is

$$DE = E_{\pi}\,(\text{benzene}) - 3E_{\pi}\,(\text{ethylene})$$

$$= 2\beta$$

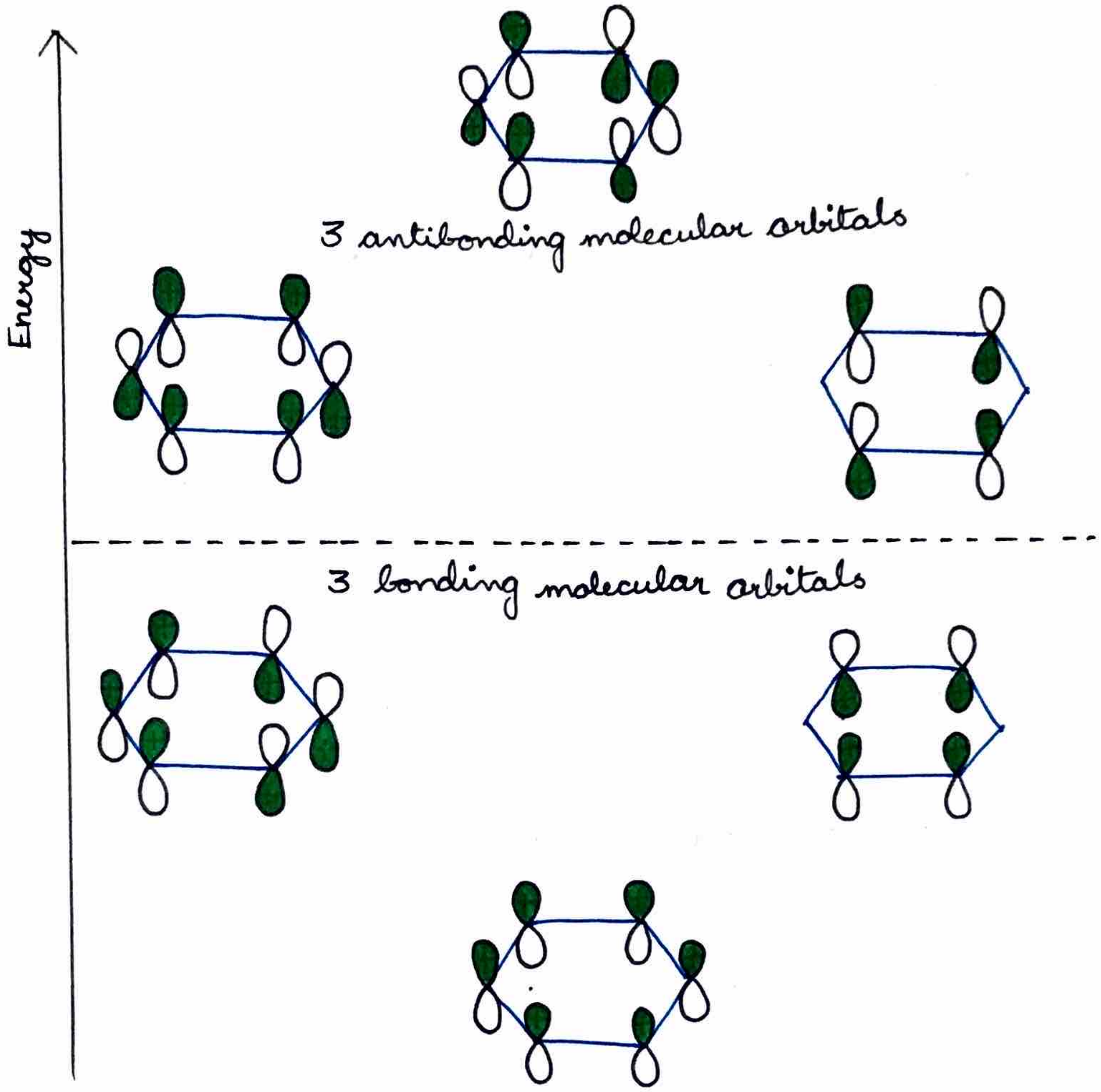
The Hückel molecular orbitals of benzene are

$$\psi_1 = \frac{1}{\sqrt{6}}\,(x_1 + x_2 + x_3 + x_4 + x_5 + x_6) \qquad E = \alpha + 2\beta$$

$$\left.\begin{aligned} \psi_2 &= \frac{1}{\sqrt{4}}\,(x_2 + x_3 - x_5 - x_6) \\ \psi_3 &= \frac{1}{\sqrt{3}}\left(x_1 + \frac{1}{2}x_2 - \frac{1}{2}x_3 - x_4 - \frac{1}{2}x_5 + \frac{1}{2}x_6\right) \end{aligned}\right\} E = \alpha + \beta$$

$$\left.\begin{aligned} \psi_4 &= \frac{1}{\sqrt{4}}\,(x_2 - x_3 + x_5 - x_6) \\ \psi_5 &= \frac{1}{\sqrt{3}}\left(x_1 - \frac{1}{2}x_2 - \frac{1}{2}x_3 + x_4 - \frac{1}{2}x_5 - \frac{1}{2}x_6\right) \end{aligned}\right\} E = \alpha - \beta$$

$$\psi_6 = \frac{1}{\sqrt{6}}\,(x_1 - x_2 + x_3 - x_4 + x_5 - x_6) \qquad E = \alpha - 2\beta$$


Energy
3 antibonding molecular orbitals
3 bonding molecular orbitals