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Subject	PHYSICAL CHEMISTRY
Paper No and Title	2, PHYSICAL CHEMISTRY-I
TOPIC	QUANTUM CHEMISTRY
Sub-Topic (if any)	Hückel Molecular orbital Theory – Application PART III
Module No.	33

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	MODULE: 33 ,Hückel Molecular orbital Theory – Application PART III

1. Learning Outcomes

After studying this module, you shall be able to

- Find the π-electron energy and wavefunction for cyclopropenyl radical
- Understand the basis of molecular orbital diagram for π-electron systems

2. Hückel Molecular orbital theory

HMO theory is an approximate method which simplifies variation method to treat planar conjugated hydrocarbons. The Hückel theory treats only π- electrons in a planar conjugated molecule. HMO calculations are carried out using variation method and LCAO(π)-MO approximation. The basis set for MO approximation consists of one $p\pi$-orbital on each atom. The σ skeleton of the conjugated molecule is assumed frozen.

According to LCAO-MO approximation, the MO is written as,

$$\varphi_a = \sum_{i=1}^{n} c_i \psi_{2p_z i} \qquad \text{-(1)}$$

And the approximate energy is given by,

$$E_a = \frac{\int \varphi_a^* \widehat{H} \varphi_a \, d\tau}{\int \varphi_a^* \varphi_a \, d\tau} \qquad \text{-(2)}$$

The Hamiltonian $\widehat{H}$ incorporates the effect of the interaction of π electron with the rest of the molecule (nuclei, inner electrons, σ bonds) in an average way. In HMO method, π electrons are assumed to be moving in a potential generated by the nuclei and σ electrons

of the molecule. In addition, electron-electron repulsions are neglected in π-Hamiltonian of conjugated molecule.

For a planar conjugated hydrocarbon, the only atomic orbitals of π symmetry are the $2p\pi$ orbtials on carbon. In this module, we have consistently assumed the plane of the molecule as x-y plane with π orbital in the z axis, perpendicular to the molecular plane.

A trial function that depends linearly on the variational parameters leads to a secular determinant which gives secular equation as an approximation to the energy.

$$
\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \dots\dots & H_{1n} - ES_{1n} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & \dots\dots & \dots\dots \\
\dots\dots & \dots\dots & \dots\dots & \dots\dots \\
H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots\dots & H_{nn} - ES_{nn}
\end{vmatrix} = 0 \qquad \text{-(3)}
$$

To solve the Secular determinant for an n-π electron system, Hückel treated the H_{ii}, H_{ij}, S_{ij} and S_{ij} integrals as parameters that can be evaluated empirically by fitting the theory to experimental results.

1. $H_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau$

$$
H_{ij} = \begin{cases} \alpha & (i = j) \quad \text{Coulomb integral} \\ \beta & (i \neq j) \quad \text{Resonance integral} \end{cases}
$$

2. $S_{ij} = \int \psi_i^* \psi_j d\tau$

$$
S_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases} \quad \text{Overlap integral}
$$

The expansion of an *n* x *n* Hückel determinant yields a polynomial equation which has *n* real roots giving *n* energy levels and *n* molecular orbitalsfor the *n*-π electron system. The energy of any a[th] molecular orbital (MO) is given by

$E_a = \alpha + x_a \beta$, where x_a is the ath root of the polynomial.   -(4)

3. Application of HMO theory

In this section, we shall apply HMO theory to a cyclic conjugated molecule viz., cyclopropenyl radical.
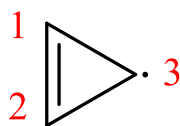
3.1 Cyclopropenyl radical

We consider here the case of cyclopropenyl radical.

Cyclopropenyl radical is a 3 π-electron cyclic system where the carbon atoms are adjacent with each carbon $2p_z$ orbital contributing 1 electron to the HMO π-electron system.

The three atomic orbitals (AOs) combine to form molecular orbitals (MOs).

Labeling the three carbons as 1, 2 and 3,

The Hückel molecular orbital wavefunction for this system becomes

$$\varphi_a = c_1 \psi_{2p_{z1}} + c_2 \psi_{2p_{z2}} + c_3 \psi_{2p_{z3}}$$

The Secular equations obtained for cyclopropenyl radical are of the form:

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 + (H_{13} - ES_{13})c_3 = 0$$
$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 + (H_{23} - ES_{23})c_3 = 0$$
$$(H_{31} - ES_{31})c_1 + (H_{32} - ES_{32})c_2 + (H_{33} - ES_{33})c_3 = 0$$

which can be written in the form of secular determinant of order three as shown below,

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = 0 \qquad -(5)$$

Now, in the case of cyclopropenyl radical, carbon atom 1 is connected to carbon atom 3, i.e., the *C1* and *C3* are neighbors.

Taking into account the assumptions of HMO theory, the secular determinant transforms into Hückel determinant as,

$$H_{11} = H_{22} = H_{33} = \alpha \quad H_{12} = H_{21} = H_{13} = H_{31} = H_{23} = H_{32} = \beta$$
$$S_{11} = S_{22} = S_{33} = 1 \quad S_{12} = S_{21} = S_{13} = S_{31} = S_{23} = S_{32} = 0$$

$$\begin{bmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = 0$$

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \neq 0 \Rightarrow \begin{bmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{bmatrix} = 0$$

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0 \qquad \text{-(6)}$$

Let, $\lambda = \dfrac{\alpha - E}{\beta}$ \qquad -(7)

This reduces the Hückel determinant as,

$$\begin{vmatrix} \lambda & 1 & 1 \\ 1 & \lambda & 1 \\ 1 & 1 & \lambda \end{vmatrix} = 0 \qquad \text{-(8)}$$

Note: For all cyclic π molecules, the element 1 will appear in Hückel determinant at positions 1 X n as well as n X 1, because the position 1 and position n are neighbors.

The Hückel determinant leads to a polynomial equation,

$$\lambda^3 + 3\lambda + 2 = 0 \qquad \text{-(9)}$$

which gives,

$$(\lambda + 2)(\lambda^2 - 2\lambda + 1) = 0$$

$$(\lambda + 2)(\lambda^2 - \lambda - \lambda + 1) = 0$$

$$(\lambda + 2)(\lambda - 1)(\lambda - 1) = 0$$

Thus, we have three roots of the polynomial equation as:

$$\lambda_1 = -2; \; \lambda_2 = 1; \; \lambda_3 = 1 \qquad \text{-(10)}$$

We assumed earlier while simplifying the Hückel determinant that

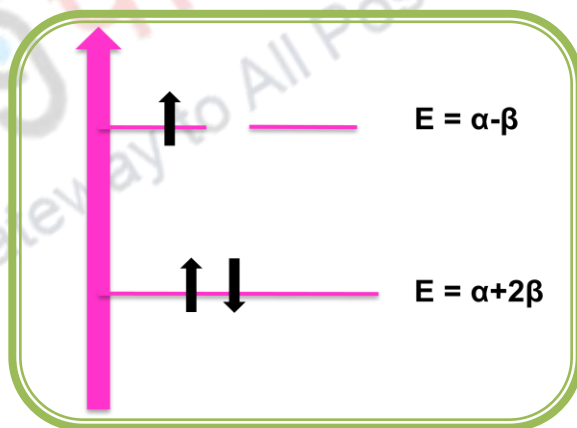$$\lambda = \frac{\alpha - E}{\beta}$$

So, the energies of the molecular orbitals of cyclopropenyl radical are of the form,

$$\lambda_1 = -2 \qquad E_1 = \alpha + 2\beta \qquad \text{-(11)}$$

$$\lambda_2 = \lambda_3 = 1 \qquad E_2 = E_3 = \alpha - \beta \qquad \text{-(12)}$$

The two energy levels viz., E_2 and E_3 are degenerate.

The Hückel energy level diagram for cyclopropenyl radical is shown below:

HMO energy level diagram for cyclopropenyl radical

The *total π electron energy E_π* is taken as the sum of the energies corresponding to occupancy of each π electron.

For cyclopropenyl radical, the total π electron energy E_π is given by

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

$E_\pi = 3\alpha + 3\beta$ -(13)

Resonance energy (or delocalization energy D.E.) is defined as the difference in the energy of π electrons in a given molecule and the sum of energies of isolated double bond

The energy of two π electrons in ethylene is

$E_{ethylene} = 2\alpha + 2\beta$

$E_{D.E.} = E_\pi - E_{ethylene} = 3\alpha + 3\beta - 2\alpha - 2\beta = \alpha = \beta$ -(14)

Hence, we can say that the cyclopropenyl radical is stable by a factor β in comparison to an isolated double bond.

Another related term *is π bond formation energy* which is the energy released when a π bond is formed. Since the contribution of α is same in the molecules as in the atoms, so we can consider the energy of three electrons, each one in isolated and non-interacting atomic orbitals as 3α, then the *π bond formation energy* becomes,

$E_{\pi(bond\ formation)} = E_\pi - E_{isolated}$

$E_{\pi(bond\ formation)} = 3\alpha + 3\beta - 3\alpha = 3\beta$

Now, we solve for HMO coefficients,

In terms of λ given by

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

the secular equations for cyclopropenyl radical are as follows,

$$\begin{bmatrix} \lambda & 1 & 1 \\ 1 & \lambda & 1 \\ 1 & 1 & \lambda \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = 0 \qquad \text{-(15)}$$

$$\lambda c_1 + c_2 + c_3 = 0$$

$$c_1 + \lambda c_2 + c_3 = 0 \qquad \text{-(16)}$$

$$c_1 + c_2 + \lambda c_3 = 0$$

$For, \lambda = -2$, the secular equations become,

$$-2c_1 + c_2 + c_3 = 0 \qquad \text{-(17)}$$

$$c_1 - 2c_2 + c_3 = 0 \qquad \text{(18)}$$

$$c_1 + c_2 - 2c_3 = 0 \qquad \text{-(19)}$$

Subtracting equation (18) from equation (17) respectively gives,

$$-3c_1 - 3c_2 = 0$$

$$c_1 = c_2 \qquad \text{-(20)}$$

Subtracting equation (19) from equation (18) respectively gives,

$$-3c_2 - 3c_3 = 0$$

$$c_2 = c_3 \qquad \text{-(21)}$$

Now, we know that the sum of squares of coefficients is always unity, i.e., from normalization condition,

$$c_1{}^2 + c_2{}^2 + c_3{}^2 = 1 \qquad \text{-(22)}$$

Now, using equations (20) and (21), we get normalization condition for $\lambda = -2$ as,

$$3c_1{}^2 = 1 \quad or \quad c_1 = c_2 = c_3 = {}^1\!/_{\sqrt{3}} \qquad \text{-(23)}$$

So, we get the wavefunction corresponding to $\lambda = -2$ as,

$$\varphi_1 = \frac{1}{\sqrt{3}}(\psi_{2p_{z1}} + \psi_{2p_{z2}} + \psi_{2p_{z3}}) \qquad \text{-(24)}$$

$For, \lambda = 1$, the secular equations become,

$$c_1 + c_2 + c_3 = 0$$

$$c_1 + c_2 + c_3 = 0 \qquad \text{-(25)}$$

$$c_1 + c_2 + c_3 = 0$$

The value of the coefficients corresponding to $\lambda = 1$ cannot be determined using the set of equations as given in expression (25) alone. We know that the energy levels corresponding to $\lambda = 1$ ($E_2 \ and \ E_3$) are degenerate. And in case of degenerate orbitals, HMO method cannot determine the coefficients uniquely. One can choose any value for c_1, c_2 and c_3 provided that they satisfy the conditions of normalization and orthogonality as well as the values of c_1, c_2 and c_3 must satisfy the expression (25).

A simple method to satisfy the above mentioned three conditions is to set any one of the coefficients equal to zero. Let $c_3 = 0$, then we have from equation (25),

$$c_1 + c_2 = 0$$

$$c_2 = -c_1 \qquad \text{-(26)}$$

From normalization condition,

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

$$c_1{}^2 + c_2{}^2 + 0 = 1 \qquad (27)$$

Using equation (26) in equation (27) gives,

$$c_1{}^2 + c_1{}^2 + 0 = 1$$

$$2c_1{}^2 = 1 \ \ or \ \ c_1 = \frac{1}{\sqrt{2}} \ , c_2 = -\frac{1}{\sqrt{2}} \qquad \text{-(28)}$$

So, we get the wavefunction corresponding to $\lambda = 1$ assuming $c_3 = 0$ as,

$$\varphi_2 = \frac{1}{\sqrt{2}}(\psi_{2p_{z1}} - \psi_{2p_{z2}}) \qquad \text{-(29)}$$

We arbitrarily chose $c_3 = 0$ but we cannot repeat the same process for determining φ_3. This is because φ_3 must be orthogonal to φ_1 and φ_2.

$$\int \varphi_1 \varphi_3 d\tau = 0 \qquad \text{-(30)}$$

$$\int \varphi_2 \varphi_3 d\tau = 0 \qquad \text{-(31)}$$

For instance, taking equation (31), we get

$$\int \left[\frac{1}{\sqrt{2}}(\psi_{2p_{z1}} - \psi_{2p_{z2}}) \right] \left[c_1\psi_{2p_{z1}} + c_2\psi_{2p_{z2}} + c_3\psi_{2p_{z3}} \right] d\tau = 0 \qquad \text{-(32)}$$

On expanding the equation (32) we get,

$$\int \frac{1}{\sqrt{2}} c_1 \psi_{2p_{z1}}{}^2 d\tau + \int \frac{1}{\sqrt{2}} c_2 \psi_{2p_{z1}}\psi_{2p_{z2}} d\tau + \int \frac{1}{\sqrt{2}} c_3 \psi_{2p_{z1}}\psi_{2p_{z3}} d\tau$$
$$- \int \frac{1}{\sqrt{2}} c_1 \psi_{2p_{z2}}\psi_{2p_{z1}} d\tau - \int \frac{1}{\sqrt{2}} c_2 \psi_{2p_{z2}}{}^2 d\tau$$
$$- \int \frac{1}{\sqrt{2}} c_3 \psi_{2p_{z2}}\psi_{2p_{z3}} d\tau = 0$$

$$\int \frac{1}{\sqrt{2}} c_1 \psi_{2p_{z1}}{}^2 d\tau - \int \frac{1}{\sqrt{2}} c_2 \psi_{2p_{z2}}{}^2 d\tau = 0$$

$$\frac{1}{\sqrt{2}} c_1 - \frac{1}{\sqrt{2}} c_2 = 0$$

Or, we can write $c_1 = c_2$ -(33)

But, the value of coefficients must satisfy equation (25),

$$c_1 + c_2 + c_3 = 0$$

$$2c_1 + c_3 = 0$$

$$c_3 = -2c_1 \qquad \text{-(34)}$$

From normalization condition,

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

Substituting the values from equations (33) and (34) we get,

$$c_1{}^2 + c_1{}^2 + 4c_1{}^2 = 1$$

$$6c_1{}^2 = 1 \quad or \quad c_1 = c_2 = \frac{1}{\sqrt{6}}; \; c_3 = -\frac{2}{\sqrt{6}} \qquad \text{-(35)}$$

So, we get the wavefunction φ_3 as,

$$\varphi_3 = \frac{1}{\sqrt{6}} \psi_{2p_{z1}} + \frac{1}{\sqrt{6}} \psi_{2p_{z2}} - \frac{2}{\sqrt{6}} \psi_{2p_{z3}} \qquad \text{-(36)}$$

In general, any linear combinations of degenerate molecular orbitals (MO's), which satisfy the orthogonality and normalization conditions, will be equally valid MO's.

The pictorial representation of the three Hückel molecular orbitals for cyclopropenyl radical is shown below.

Positive lobe
○ **Negative lobe**
- - - - **Base of nodal plane**
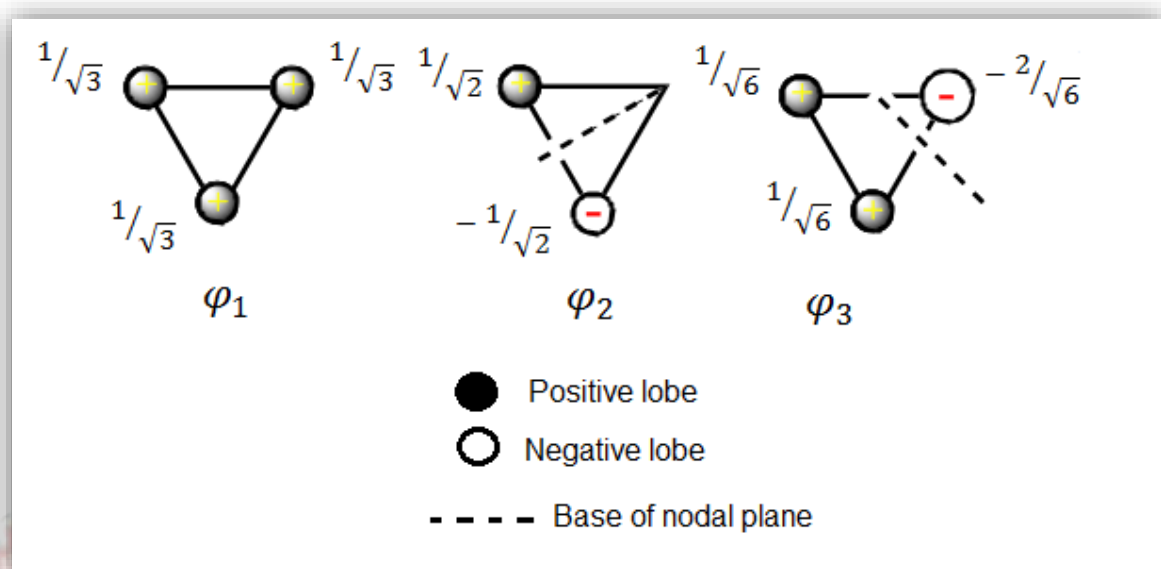
- Electron density:

$$\int \varphi^2 d\tau = \sum_n c_n^2 = {c_1}^2 + {c_2}^2 + {c_3}^2$$

This means that in LCAO-HMO approach, c_n^2 represents the electron density due to one electron at the atom n, but there may be several electrons in the system distributed in a number of HMO's. So, the total electron density is taken as the sum of electron densities contributed by different electron in each HMO.

$$q_n = \sum_i n_i c_{in}^2 \quad n_i \text{ is the number of electrons in ith HMO (0,1 or 2)}$$

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In case of cyclopropenyl radical, two π-electrons are in energy state E_1 while the third electron may be placed in either energy state E_2 or E_3 (degenerate). In such a case, electron density is calculated by assuming that half of the available electron is in each of the degenerate MO's.

$$q_1 = 2 \times \left(\frac{1}{\sqrt{3}}\right)^2 + \frac{1}{2} \times \left(\frac{1}{\sqrt{2}}\right)^2 + \frac{1}{2} \times \left(\frac{1}{\sqrt{6}}\right)^2 = 1$$

$$q_2 = 2 \times \left(\frac{1}{\sqrt{3}}\right)^2 + \frac{1}{2} \times \left(-\frac{1}{\sqrt{2}}\right)^2 + \frac{1}{2} \times \left(\frac{1}{\sqrt{6}}\right)^2 = 1$$

$$q_3 = 2 \times \left(\frac{1}{\sqrt{3}}\right)^2 + 0 + \frac{1}{2} \times \left(-\frac{2}{\sqrt{6}}\right)^2 = 1$$

- Charge density

  In a conjugated molecule, a neutral carbon is associated with an electron density of 1.0 and the net charge density is defined as

  $$\varepsilon_n = 1 - q_n$$

  For cyclopropenyl radical,

  $\varepsilon_1 = 1 - 1 = 0 = \varepsilon_2 = \varepsilon_3$

- Π-bond order between adjacent carbon atoms is given by

  $$BO_{ab}^{\pi} = \sum_i n_i c_{ia} c_{ib}$$

  $where\ n_i\ is\ the\ number\ of\ \pi\ electrons\ in\ ith\ MO$
  $c_{ia} c_{ib}\ is\ the\ \pi - electorn\ charge\ in\ ith\ MO\ between\ adjacent$
  $carbon\ atoms\ a\ and\ b$

Π-bond order represents the extent of π-bonding between adjacent atoms.

For cyclopropenyl radical,

$$BO_{12}^{\pi} = \left(2 \times \frac{1}{\sqrt{3}} \times \frac{1}{\sqrt{3}}\right) + \left(\frac{1}{2} \times \frac{1}{\sqrt{2}} \times -\frac{1}{\sqrt{2}}\right) + \left(\frac{1}{2} \times \frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right)$$

$$BO_{12}^{\pi} = 0.5$$

$$BO_{23}^{\pi} = \left(2 \times \frac{1}{\sqrt{3}} \times \frac{1}{\sqrt{3}}\right) + \left(\frac{1}{2} \times -\frac{1}{\sqrt{2}} \times 0\right) + \left(\frac{1}{2} \times \frac{1}{\sqrt{6}} \times -\frac{2}{\sqrt{6}}\right)$$

$$BO_{23}^{\pi} = 0.5$$

$$BO_{31}^{\pi} = \left(2 \times \frac{1}{\sqrt{3}} \times \frac{1}{\sqrt{3}}\right) + \left(\frac{1}{2} \times 0 \times \frac{1}{\sqrt{2}}\right) + \left(\frac{1}{2} \times -\frac{2}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right)$$

$$BO_{31}^{\pi} = 0.5$$

There is a σ bond between two carbon atoms which is taken into account while reporting the total bond order. The total bond order is given by

$$BO_{ab}^{total} = 1 + BO_{ab}^{\pi}$$

A high bond order corresponds to large π-charge in the bond regions which means a shorter and stronger bond.

Exercise: Calculate the ground state energies, wavefunction, electron density, charge density and bond order for cyclopropenyl carbonium ion and carbanion respectively. Compare the results with cyclopropenyl radical and comment on the results.

4. Summary

- HMO theory is an approximate method which simplifies variation method to treat planar conjugated hydrocarbons.

- The Hückel theory treats only π- electrons in a planar conjugated molecule.

- HMO calculations are carried out using variation method and LCAO(π)-MO approximation.

- The basis set for MO approximation consists of one $p\pi$-orbital on each atom.

- **Application of HMO theory to cyclopropenyl radical**

✓ Cyclopropenyl radicalis a three electron system

✓ $E_1 = \alpha + 2\beta E_2 = E_3 = \alpha - \beta$

  The two energy levels viz., E_2 and E_3 are degenerate.

✓ $E_\pi = 3\alpha + 3\beta$

✓ $E_{D.E.} = \beta$

✓ In case of degenerate orbitals, HMO method cannot determine the coefficients uniquely. One can choose any value for c_1, c_2 and c_3 provided that they satisfy the conditions of normalization and orthogonality. In general, any linear combinations of degenerate molecular orbitals (MO's), which satisfy the orthogonality and normalization conditions, will be equally valid MO's.

✓ $\varphi_1 = \frac{1}{\sqrt{3}}(\psi_{2p_{z1}} + \psi_{2p_{z2}} + \psi_{2p_{z3}})$

  $\varphi_2 = \frac{1}{\sqrt{2}}(\psi_{2p_{z1}} - \psi_{2p_{z2}})$

  $\varphi_3 = \frac{1}{\sqrt{6}}\psi_{2p_{z1}} + \frac{1}{\sqrt{6}}\psi_{2p_{z2}} - \frac{2}{\sqrt{6}}\psi_{2p_{z3}}$