

(Hückel Molecular Orbital Theory)

First application of quantitative quantum theory to chemical species is more complex than n -atom. It was given by Hückel working on unsaturated organic compounds in 1930-37. His approach focuses on p -electrons of double bonds, aromatic rings, heteroatoms, non-planar systems (applied occasionally).

- This theory is basically for planar systems with sp^2 -hybridized atoms & evaluates consequences of interaction of p -electrons.
- Hybridization concept is a major part of this theory.

~~ab initio~~

- ab initio, semi-empirical & Density functional theory methods are also based on molecular orbital approach.

Another approach to apply Schrödinger equation to chemistry is Valence Bond Theory (VBT) but fails to effectively explain phenomena like triplet state of oxygen, aromaticity of benzene & over cyclooctadiene.

Three major approximations are made to separate Schrödinger equation into a set of smaller equations before carrying out Hückel calculations. ②

This is done because Schrödinger equation is usually not separable into equations involving only one variable.

3 Approximations:

① Born-Oppenheimer Approximation:

This is used for almost all molecular orbital calculation & atomic energy calculations. Nuclei & electronic part are treated separately as nuclear motion is considered to be negligible in comparison to electronic motion.

$$\Psi_{\text{total}} = \Psi_{\text{nuclear}} \Psi_{\text{electronic}}$$

$$E_{\text{total}} = E_{\text{nuclear}} + E_{\text{electronic}}$$

- In evaluation of energy of the system, kinetic energy operator of nucleus is dropped & only internuclear repulsion term is retained.

- All terms involving electrons are retained in the operator i.e. kinetic energy operators for all electrons & potential energy terms for attractive forces between nuclei & electrons & also repulsive forces between electrons.

$$\hat{H}\Psi = E\Psi \quad (\text{only electronic part} + (\text{nuclear-nuclear repulsion term}))$$

② Independent Particle Approximation: ③

By analogy to atomic orbitals, we assume molecules to have molecular orbitals with electron probability distribution in space.

N n' -electrons.

$$\hat{H} = \hat{H}(1, 2, 3, \dots, n)$$

The main reason that Schrödinger equation for molecules cannot be separated is because of the potential energy term $\left(\frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}\right)$ for inter-electronic repulsions.

$i \rightarrow$ position of i th electron.

$j \rightarrow$ position of j th electron.

If we know the exact value of $\frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$, the problem would be solved but it would violate the Heisenberg Uncertainty Principle which states that exact position of electron cannot be determined. So this term is approximated to $V'(i)$

$$\hat{H}(i) = -\frac{1}{2} \nabla^2(i) + V'(i)$$

$V'(i)$ = Average potential due to core that consists of nuclei & all electrons other than i th electron.

ie. potential field experienced by i th electron due to other electrons & nuclei.

$$\hat{H}(i) \psi(i) = E(i) \psi(i) \quad (1)$$

(9)

This can be separated into 'n' equations but evaluation of $V(i)$ still poses a problem. One way to obtain approximate solution of equation (1) is to select any set of basis functions called basis set:

$$\psi = \sum_i a_i \phi_i$$

& then approximate it to true wavefunction by iterative procedure.

(3) π -electron Separation Approximation:

The 1st two approximations are for any molecular orbital theory. (including HMO)
This third approximation is unique only for HMO.

σ & π -electrons are separated.

π -electron containing system are more reactive.

$\text{H} \rightarrow \sigma$ -electrons are ignored (just used to calculate potential energy)
 $\rightarrow$ considered only for π -electrons.

$$\hat{H} = \sum_i^n \left[-\frac{1}{2} \nabla^2(i) + V_{\pi}(i) \right] + \frac{1}{2} \sum_{i,j} \frac{1}{r_{ij}} \quad (5)$$

kinetic energy
term for
all π -electrons

↓
intra electronic
repulsion term
for π -electrons.

↓
Potential energy of single 'i' π -electron in average field of framework of nuclei & all other electrons including σ & π -electrons.

p-orbitals are considered to be independent of σ -bond framework except for potential energy of charge-charge interaction term i.e. $V_{\pi}(i)$.

Simple Hückel Method
or

Simple Hückel Theory
or

Hückel π -electron Theory

This theory shows how with simple arguments one can use Schrödinger equation to develop a method that gives useful results & which can be extended to more powerful methods with retention of many useful concepts ~~of~~ from simple approach.

Schrödinger equation :

$$\nabla^2 \psi + \frac{8\pi^2m}{h^2} (E - V) \psi = 0$$

$$\text{or } \left(\frac{-h^2}{8\pi^2m} \nabla^2 + V \right) \psi = E \psi$$

$$\text{or } \hat{H} \psi = E \psi$$

If ψ is exact, Energy would be exact & if ψ is approximate, Energy would be upper bound of true energy i.e. equal to greater than true energy (variational theorem).

$$E = \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau} \quad (\text{one of the postulates of Quantum Mechanics})$$

- The concept of molecular orbital as a tool ⑦ in interpreting electronic spectra was given by Mulliken, who coined the term 'orbital'.
- Molecular orbital can be synthesized by combining simpler functions called basis functions. Basis functions are located on atoms of molecules, which may or may not be atomic orbitals. These basis functions comprise a basis set (just like ^{or analogous to} LCAO-MO theory i.e. linear combination of atomic orbitals - molecular orbital theory).
- This concept of basis set was suggested by Pauling & Leonard-Jones.
- Early application of LCAO in SHM was when p-type atomic orbitals were combined to give π -atomic orbitals.
- Molecular orbitals: weighted sum of atomic orbitals with optimized co-efficient.
- Ψ can in principle be approximated by using enough suitable basis functions.
- Basis functions on different atoms are combined to give molecular orbitals spread over the molecule, analogous to combining

atomic orbitals on same atom to give hybrid atomic orbitals.

'n' basic functions gives 'n' Molecular orbitals.

Using LCAO approximation:

$$\Psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n$$

$\phi_1, \phi_2, \dots, \phi_n \rightarrow$ basis functions on atoms 1, 2, ..., n, respectively.

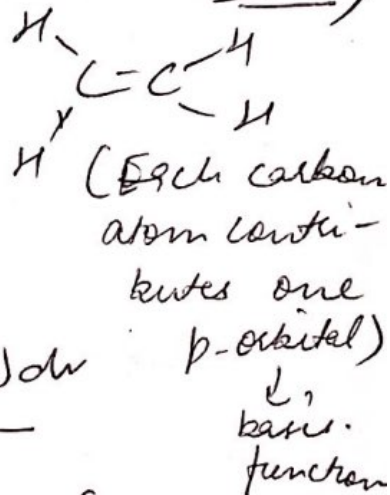
$c_1, c_2, \dots, c_n \rightarrow$ weighting co-efficient to be adjusted to get best Ψ .

Let us take an example of a molecule with 2 atoms & each atom contributes 1 basis function to molecular orbital. (Ethene)

$$\Psi = c_1 \phi_1 + c_2 \phi_2$$

$$E = \frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi^2 d\tau}$$

$$= \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) d\tau}{\int (c_1 \phi_1 + c_2 \phi_2)^2 d\tau}$$



(Here $\sigma - \pi$ basis function)

Basis function is expressed by ϕ .

Separation approximation is used, where $\sigma - e^-$ are ignored & only $\pi - e^-$ of p-orbital are considered.

$$E = \frac{C_1^2 H_{11} + 2C_1 C_2 H_{12} + C_2^2 H_{22}}{C_1^2 S_{11} + 2C_1 C_2 S_{12} + C_2^2 S_{22}} \quad \text{--- (1)}$$

or $E(C_1^2 S_{11} + C_1 C_2 S_{12} + C_1 C_2 S_{21} + C_2^2 S_{22}) = C_1^2 H_{11} + C_1 C_2 H_{12} + C_1 C_2 H_{21} + C_2^2 H_{22}$ --- (2)

where,

$$\begin{cases} H_{11} = \int \phi_1 \hat{H} \phi_1 d\tau, & H_{12} = \int \phi_1 \hat{H} \phi_2 d\tau, \\ H_{21} = \int \phi_2 \hat{H} \phi_1 d\tau, & H_{22} = \int \phi_2 \hat{H} \phi_2 d\tau \quad (H_{12} = H_{21}) \\ S_{11} = \int \phi_1^2 d\tau, & S_{22} = \int \phi_2^2 d\tau \\ S_{12} = S_{21} = \int \phi_1 \phi_2 d\tau \end{cases}$$

They are not operators but integrals involving $\hat{H}$ & basis function ϕ .

For any particular molecular geometry, Energy of ground electronic state is minimum Energy possible for that particular nuclear arrangement & collection of electrons that goes with it. (using Born-Oppenheimer Approximation).

We need to minimize Energy with respect to basis set co-efficients (C_1, C_2)

$$\frac{\partial E}{\partial C_1} = 0, \quad \frac{\partial E}{\partial C_2} = 0 \quad \text{(To get lowest energy).}$$

Differentiate eq. (2) with respect to C_1 & put it equal to zero

$$\frac{\partial E}{\partial c_1} (c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}) + E (2c_1 S_{11} + c_2 S_{12} + c_2 S_{21}) = 2c_1 H_{11} + c_2 H_{12} + c_2 H_{21} \quad (10)$$

$$2c_1 H_{11} - 2E c_1 S_{11} + c_2 H_{12} - E c_2 S_{12} + c_2 H_{21} - E c_2 S_{21} = 0$$

$$2c_1 (H_{11} - E S_{11}) + c_2 (H_{12} - E S_{12}) = 0$$

$$\text{or } (H_{11} - E S_{11}) c_1 + (H_{12} - E S_{12}) c_2 = 0 \quad (2)$$

Now differentiate equation (1) with respect to c_2 & put it equal to zero.

$$\text{i.e. } \frac{\partial E}{\partial c_2} = 0$$

$$\frac{\partial E}{\partial c_2} (c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}) + E (c_1 S_{12} + c_1 S_{21} + 2c_2 S_{22}) = c_1 H_{12} + c_1 H_{21} + 2c_2 H_{22}$$

Rearranging, we get:

$$(H_{21} - E S_{21}) c_1 + (H_{22} - E S_{22}) c_2 = 0 \quad (3) \quad \begin{matrix} \text{using} \\ H_{12} = H_{21} \\ \& S_{12} = S_{21} \end{matrix}$$

from (2) & (3)

$$\begin{pmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{21} - E S_{21} & H_{22} - E S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\text{or } \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} - \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (A)$$

$$\text{or } \boxed{(H - SE) = 0}$$

where, $H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$ = Fock matrix = Energy elements matrix & each element represents interactions between two orbitals. (4)

$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$ = Overlap matrix & each element is overlap integral.

$C = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$ = Column matrix.

→ System of 2 basis functions i.e. 2 molecular orbitals each with its energy & 2 co-efficients.
 $\epsilon = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix}$ $\epsilon_1, \epsilon_2 \rightarrow$ Energies.
 → electron spin is not taken into consideration.
 → $C_{11} \rightarrow$ co-efficient of ϕ_1 (basis function) in ψ , (molecular orbital)
 similarly C_{12}, C_{21}, C_{22} .

$S \rightarrow$ measure of how well pairs of basis function overlap.

$S_{ii} = 1$ (like S_{11} & S_{22})

perfect overlap between identical function on the same atom.

$S_{ij} = 0$ (like S_{12}, S_{21})

overlap between different function on the same atom or well-separated function on different atoms.

→ $\epsilon \rightarrow$ Energy level matrix $\rightarrow$ diagonal elements are molecular orbital energy levels (ϵ_i) corresponding