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SEM-II

Physical Chemistry

Unit - IV

**Huckel Molecular
Orbital Theory**

**Huckel Theory Of
Conjugated System**

Huckel Theory of p-system

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This theory is popular method for planar organic compounds containing conjugated carbon chain which may be linear as well as cyclic. (conjugation through $p-\pi e^-$) It is based upon the following assumption:-

(1) The Huckel molecular orbital theory applied only to $p-\pi$ electron.

(2) The total π -electron wave function is product of one electron function as

$$\Psi_{\pi} = \Psi_1(1) \cdot \Psi_2(2) \cdot \Psi_3(3) \dots$$

(3) The total energy is the sum of one electron energy.

$$E = n_1 E_1 + n_2 E_2 + \dots + n_n E_n$$

(4) Where, E_i = energy of single electron in Ψ_i wave function for the factor n_i may be 0, 1, 2, 3... depending upon Huckel molecular orbital is unoccupied, singly occupied, doubly occupied etc.

(5) Each HMO is taken as a linear combination of carbon $2p_z$ atomic orbital.

$$\Psi_i = a_1 p_1 + a_2 p_2 + a_3 p_3 + \dots$$

where a_1, a_2, a_3, \dots are the coefficient of atomic orbital.

(5) Energy of HMO is calculated by the formulae

$$E = \frac{\int \psi_i H \psi_i d\tau}{\int \psi_i \psi_i d\tau}$$

(6) The variation treatment leads to n -secular equation.

$$a_1 (H_{11} - ES_{11}) + a_2 (H_{12} - ES_{12}) + \dots + a_n (H_{1n} - ES_{1n}) = 0$$

$$a_1 (H_{21} - ES_{21}) + a_2 (H_{22} - ES_{22}) + \dots + a_n (H_{2n} - ES_{2n}) = 0$$

$$a_1 (H_{n1} - ES_{n1}) + a_2 (H_{n2} - ES_{n2}) + \dots + a_n (H_{nn} - ES_{nn}) = 0$$

The secular determinant may be written as

$(H_{11} - ES_{11})$	$(H_{12} - ES_{12})$	\dots	$(H_{1n} - ES_{1n})$	$= 0$
$(H_{21} - ES_{21})$	$(H_{22} - ES_{22})$	\dots	$(H_{2n} - ES_{2n})$	
$---$	$---$	$---$	$---$	
$(H_{n1} - ES_{n1})$	$(H_{n2} - ES_{n2})$	\dots	$(H_{nn} - ES_{nn})$	

Huckel introduced some more drastic approx-
imation :-

(a) All integrals of the type H_{rr} are
assume to be equal.

i.e $H_{11} = H_{22} = H_{33} = \alpha$ (suppose)

(b) All integral of the type H_{rs} are
the same if r and s are neighbour.

$H_{12} = H_{23} = H_{34} = \dots = \beta$ (suppose)

If r and s are not neighbour, then
 $H_{rs} = 0$

(c) integral of the type S_{rr} are equal to
unity.

(d) Integral of the type S_{rs} equal to zero.

$\alpha - E$	β	0	0	= 0
β	$\alpha - E$	β	0	
0	β	$\alpha - E$	β	
0	0	β	$\alpha - E$	

dividing by β , we get

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

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

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

Expanding the determinant, we will get solution of x .

⇒ for the -ve value of x

$$\boxed{E < \alpha}$$

and it correspond to the bonding level.

⇒ for the +ve value of x

$$E > \alpha$$

It correspond to the antibonding level.

⇒ for the zero value of x , $E = \alpha$

It correspond to the non-bonding level.

Calculating the value of coefficient, we will get, the wave function of Hückel molecular orbital

x