

E-Learning materials by Dr. Ashok Kr. Acharya, Asst. Professor, University Department of Chemistry, DSPMU, Ranchi. **Electronic Structure of atoms**

M.Sc. Chapter - 6

The distribution of electron in various orbitals is known as electronic configuration of atoms and the process of filling of orbitals with electrons which takes place according to the following rules:

(i) The maximum number of electrons in any orbit is  $2n^2$  where  $n$  is the number of orbit or principal quantum number.

(ii) The maximum number of electrons in a sub-shell (s,p,d and f) is  $2(2l+1)$  where  $l$  is the azimuthal quantum number having the values,  $l=0,1,2,3$  for s,p,d and f sub-shell respectively.

(iii) The maximum number of orbitals in a given sub-shell is given by  $(2l+1)$  where  $l=0,1,2$  or  $3$  s,p,d, and f sub-shell respectively. Hence s,p,d, and f sub-shells have 1,3,5, and 7 orbitals respectively.

(iv) The orbitals are filled in order of their increasing energy as follows:  
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 4f < 5d < 6p < 7s < 5f < 6d < 7p < \dots$

(v) An orbital can have a maximum of two electrons of opposite spins (Pauli's exclusion principle)

(vi) The pairing of electrons will not occur in any orbitals until all the available orbitals have one electron each (Hund's rule)

(vii) The electronic configuration of an atom is written as  $n l^m$  where  $n$  is the principal quantum number (1,2,3,...),  $l$  is the sub-shell (s,p,d or f) and  $m$  is the total number of electrons present in sub-shell.

Deviation from filling normal sequence of filling of orbitals these deviations may be due to the following factors:

1. To explain the properties of lanthanum and actinium. This explains irregularity in the electronic configuration of La and Ac.
2. Extra stability of half filled and full filled d-orbitals. This explains irregularity in the configuration of Cr, Cu, Mo, Pd, Ag and Au.
3. To explain diamagnetic nature of the atom. This explains configuration of Pt.

Examples:-

Element	Expected Electronic configuration	Actual Electronic Configuration
Cr <sub>24</sub>	$3d^4 4s^2$	$3d^5 4s^1$
Cu <sub>29</sub>	$3d^9 4s^2$	$3d^{10} 4s^1$

Mo <sub>42</sub>	4d <sup>4</sup> 5s <sup>2</sup>	4d <sup>4</sup> 5s <sup>1</sup>
Pd <sub>46</sub>	4d <sup>8</sup> 5s <sup>2</sup>	4d <sup>10</sup> 5s <sup>0</sup>
Ag <sub>47</sub>	4d <sup>9</sup> 5s <sup>2</sup>	4d <sup>10</sup> 5s <sup>1</sup>
La <sub>57</sub>	4f <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup> 6s <sup>2</sup>
Pt <sub>78</sub>	5d <sup>8</sup> 6s <sup>2</sup>	5d <sup>9</sup> 6s <sup>1</sup>
Au <sub>79</sub>	5d <sup>9</sup> 6s <sup>2</sup>	5d <sup>10</sup> 6s <sup>1</sup>
Ac <sub>89</sub>	5f <sup>1</sup> 7s <sup>2</sup>	6d <sup>1</sup> 7s <sup>2</sup>

### Coupling Schemes

In an atom, the electron spin angular momentum may couple with the total angular momentum as follows:

The coupling of spin angular momenta of two electrons, called s-s coupling, give rise to a quantum number S (called total spin number), where  $S = 1/2 + 1/2$  or  $-1/2 - 1/2$ , i.e., 1, 0, or -1 ....(1)

Similarly, the coupling of orbital angular momenta of two electrons known as l-l coupling gives a quantum number L, called total orbital angular momentum quantum number where

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \dots, |l_1 - l_2| \quad \dots(2)$$

The term  $|l_1 - l_2|$  represents absolute value of  $l_1 - l_2$ .

The coupling of S and L is known as Russel-Saunders coupling which gives a new quantum number, J where  $J = (L + S), (L + S - 1), \dots, |L - S| \quad \dots(3)$

The term L, S and J jointly form an important symbol known as atomic term symbol which is generally designated as  $^{2s+1}L_J$ . The superscript represents the multiplicity of the term and subscript is the value of J as given by equation (3). Just as  $l = 0, 1, 2$  and 3 corresponds to the atomic orbital s, p, d and f, respectively, similarly,  $L = 0, 1, 2, 3$ , correspond to atomic states S, P, D and F, respectively. (The state S should not be confused with the total spin quantum number S)

### R-s coupling ( Russel saunder's coupling)

it is known as l-s coupling according to this coupling :

(i) All the  $l$  vector ( $l$  = orbital angular momentum quantum number ) of the electrons couple together electrostatically to give the resultant L, called resultant orbital angular momentum quantum number. Different values of  $l$  define the state of the electrons only while those of L define the state of the free atom or ion as a whole. L is always an integer including Zero. Different values of L are represented by capital letter known as mulliken notations as shown below:

value of L = 0 1 2 3 4 5.....

Mulliken notation = S P D F G H....

L value of electrons in filled s, p, d, etc, orbital is zero e.g., for the six electrons in a completely filled p orbital for which  $l = 1$ , the value of L is zero as shown below:

$$= +\underbrace{1+1}_{p_x} + \underbrace{0+0}_{p_y} + \underbrace{1-1}_{p_z} = 0$$

where +1, +1,0,0,-1 and -1 represent the magnetic quantum number (M) value for the electrons number as (1,4) in  $P_x$  orbital, (1,5) in  $p_y$  orbital and (3,6) in  $P_z$  orbital as shown in table 1,

**Table 1:** different M and s value for six electrons in three P orbital's

$P_x$ -orbital - orbital	$P_y$ -orbital	$P_z$
$m = +1$	$m = 0$ $m = -1$	

$$s = +\frac{1}{2} (\uparrow \downarrow \text{ for } 1^{\text{st}} \text{ electron}) \quad s = +\frac{1}{2} (\uparrow \downarrow \text{ for } 1^{\text{st}} \text{ electron})$$

$$s = +\frac{1}{2} (\uparrow \downarrow \text{ for } 3^{\text{rd}} \text{ electron})$$

$$s = -\frac{1}{2} (\uparrow \downarrow \text{ for } 4^{\text{th}} \text{ electron}) \quad s = -\frac{1}{2} (\uparrow \downarrow \text{ for } 5^{\text{th}} \text{ electron})$$

$$s = -\frac{1}{2} (\uparrow \downarrow \text{ for } 6^{\text{th}} \text{ electron})$$

The calculation of L values for  $d^n$  configuration (for d 0-orbitals  $l = 2$ ,  $m = +2, +1, 0, -1$  and  $-2$ ) has been shown in table 2:

Table 2: calculation of L values for  $d^n$  configuration

$d^n$ configurati on	$D_z$ ( $m = +$ 2)	$D_{xy}$ ( $m = +1$ )	$D$ ( $m = 0$ )	$I$ ( $m =$ -1)	$I$ ( $m =$ -2)	Re sultant L and term symbol
$d^1$	( +2)					$2_D$
$d^2$	( +2)	+ (+1)				$3_F$
$d^3$	( +2)	+ (+1)	+ (0)			$3_F$





$d^4$	( +2)	(+1) +	(0) +	(-1) +		$2D$
$d^5$	( +2)	(+1) +	(0) +	(-1) +	(-2) +	$0_s$
$d^6$	( +2,+ 2)	(+1) +	(0) +	(-1) +	(-2) +	$2D$
$d^7$	( +2,+ 2)	(+1,+ 1)	(0) +	(-1) +	(-2) +	$3F$
$d^8$	( +2,+ 2)	(+1,+ 1)	(0,0) +	(-1) +	(-2) +	$3F$
$d^9$	( +2,+ 2)	(+1,+ 1)	(0,0) +	(- 1,- 1)	(-2) +	$2D$
$d^{10}$	( +2,+ 2)	(+1,+ 1)	(0,0) +	(- 1,- 1)	(- 2,- 2)	$0_s$

(ii) Similarly all S vectors (s=spin angular momentum quantum number) also combine to give the resultant spin angular momentum quantum number, s which is an integer or half integer depending upon the number of electron involved and the direction of the

spine vectors. s is equal to half the number of unpaired electron, n i.e  $S = \frac{n}{2}$ . the value of S for the electrons in any of the completely filled. s, p, d etc. orbital's is zero e.g., for a completely filled p- orbital for which l= S is equal to zero as shown below :

$$\text{value of } S = +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 0$$

Number of electron = 1<sup>st</sup> 4<sup>th</sup> 2<sup>nd</sup> 5<sup>th</sup> 3<sup>rd</sup> 6<sup>th</sup>

The calculation of s values for  $d^n$  configuration has been shown in table 3.

Table 3. Determination of multiplicity, J values and ground state terms for  $d^n$  configuration

Con figuratio n	No of unpair ed electro ns	S=n/2	Mult iplicity =2s +1 =n+ 1	v alues of L from Table	Diff erent 'J' values	e te
$d^1$	1	$\frac{1}{2}$	2	$2D$	$\frac{5}{2}, \frac{3}{2}$	
$d^2$	2	$\frac{2}{2}=1$	3	$3F$	$\frac{4}{2}, \frac{3}{2}, \frac{2}{2}$	

$d^3$	3	$\frac{3}{2}$	4	$3_F$	$\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$	atom. The process of L and S coupling may be represented as below:
$d^4$	4	$\frac{4}{2}=2$	5	$3_D$	4,3,2,1,0	$(S_1+S_2+S_3+..) + (l_1+l_2+l_3+.....)= s+ L= J$
$d^5$	5	$\frac{5}{2}$	6	$0_s$	$\frac{5}{2}$	The values of J are $(2S+1)$ when $L \geq S$ and $(2L+1)$ when $L \leq S$ . when $L = 0$ , J can have only one value viz. $j = S$ . The value of J is always positive, never negative since it represents the total angular momentum of atom and its values vary in integral step between $(L+s)$ and $(L-s)$ i.e., J can have the following values:
$d^6$	4	$\frac{4}{2}=2$	5	$3_D$	4,3,2,1,0	$J=(L+s), (L+S-1) \dots 0 \dots (L-S+2), (L-S+2), (L-s)$
$d^7$	3	$\frac{3}{2}$	4	$3_F$	$\frac{9}{2}, \frac{7}{2}$	The values of $d^n$ configuration have been calculated on the basis of the above rules and are given in Table 3.
$d^8$	2	$\frac{2}{2}=1$	3	$3_F$	4,3,2	
$d^9$	1	$\frac{1}{2}$	2	$3_D$	$\frac{5}{2}, \frac{3}{2}$	
$d^{10}$	0	0	1	$0_s$	0	

The quantity  $(2s+1)$  is known as multiplicity of L state. This quantity gives the permitted values of given values L. J is called resultant inner quantum number obtained by coupling L and S vectors.

when L and S vectors couple together, they give a result vector J which is known as resultant quantum number or total momentum quantum number of the

Ground state term of atom or ions : The ground state terms of an atom or ion is written as ground state term = multiplicity  $L_J = (2S+1) L_J = (n+1)L_J$

following rules are observed to write to write the ground state term:

(i) The ground state terms will be that which has the maximum number of unpaired electrons or which has the highest values of spin multiplicity .

(ii) For a half filled or less than half filled orbital, the ground state terms is that which has the lowest values of J and for a more than half filled orbital, the ground state is that which has the highest value of J.

On the basis of the above rules, the ground , state terms for  $d^n$  configuration have been determined are given in Table3.

### Spin Multiplicity

Spine multiplicity of the electronic state is the values of  $(2S+1)$  where  $S$  is the absolute value of the algebraic sum of the spins of the individual electrons. For example, for  $d^1$  configuration,  $S = \frac{1}{2}$  and spin multiplicity is  $(2 \times \frac{1}{2} + 1) = 2$ .

For a  $d^2$  system where spins are parallel,  $S = \frac{1}{2} + \frac{1}{2} = 1$  and spin multiplicity is  $(2 \times 1 + 1) = 3$ .

The relation between unpaired electrons ( $n$ ), resultant spin quantum number ( $s$ ) and multiplicity is given in Table 4.

**Table 4. Relation between unpaired electron, resultant spin quantum number and multiplicity**

Unpaired electrons (n)	Resultant Spin quantum No. (s)	Multiplicity
0	0	1
1	$\frac{1}{2}$	2
2	1	3
2	1	4
4	$1\frac{1}{2}$	5
	2	

### Self Consistent field (SCF) Methods

Schrodinger's equation can not be solved exactly for atoms containing more than one electron. Even in case of He atom, which has two electrons, the Schrodinger's equation can be solved only by approximation methods but can not be solved exactly. The reason is due to the presence of the potential energy function present in the expression . for example, the potential energy of He atom is given by



$$V(r_1, r_2, r_{12}) = \frac{Ze^2}{4\pi\epsilon_0 r_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

.....(1)

The above equation containing three terms. The first terms is the attractive potential of electron 1 for the nucleus of charge + Ze(Z=2), the second term is attractive potential of electron 2 for the two electrons form the nucleus while  $r_{12}$  is the inter-electron distance. Using the potential given by the equation (1), the Schrodinger's equation for He may be written as follows:

$$\left[ (\nabla_1^2 + \nabla_2^2) + \frac{2m}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \right] \Psi = 0$$

..... (2)

Since the potential energy contains inter -electron repulsion term the motion of each electron is affected by the position of the other. thus equation (2) cannot be separated into two equation. If the inter - electron repulsion terms were neglected the above equation could be separated into two one- electron equation like like that of the H- atom could be solved easily.

Atoms beyond He atom (Li, Be, B etc.) would have many inter- electron terms in the potential energy and

would be more difficult to separator into individual equations. to solve the schrodinger equation for may electron atom. Hartree (1928) suggested self consistent filed (SCF) method. according to this method each electon is supposed to move in a spherically symmetricla potential due to the nucleus and the average potential of all the electron except the one under consideration. We start with an approximate wave function by the guessing it. Thos wave function is used to calculate the average potential of electron due to all the other electron. The schrodinger's equation for this nucleus. In this way, the wave function (orbitals ) for all the electrons are calculated. from these one electron obital. a nbew wave function which is a product of N one electron obritatls. is constructed. This wave function is now used to calculate the effective potential and the process is repeated several time until the new set of wave function is obtained. These new wave function are called self consistent filed orbitals and the calculation is stopped.

From the Hartree SCF method, we obtain a seri3es of atomic orbitals, each contains four quantum numbers as in hydrogen atom and hydrogen like ions. However, the energie of H actom depends only upon the principle quantum number n and the azimuthal

quantum number,  $l$  for a given value of  $l$ , there are  $(2l+1)$  values of the magnetic quantum number,  $m$  and  $(2l+1)$  orbitals. Thus, three p orbital ( $l=1$ ) are degenerate, similarly five d-orbital ( $l=2$ ) are degenerate.

The Hartree method was improved by Fock (1930) who united the spin of the electron into the wave function as suggested by Slater. The Hartree-Fock self-consistent field methods are successfully used to solve the Schrödinger's equation for many electron atoms. The energy of the many electron atom is given by

$$E_n = -$$

## Molecular Orbital Theory

The carbon compounds containing alternate double and single bonds are called conjugate molecules.

The

carbon atoms of these molecules are  $sp^2$  hybridised to form three hybrid orbitals which are directed towards perpendicular to the molecular plane. These orbitals overlap together to form  $\pi$  bonds. The orbital formed from the unhybridised  $2p_z$  orbitals are called  $\pi$  orbitals and electrons in these orbitals lie above and below the molecular plane. Since  $\sigma$  and  $\pi$  electrons are in the planes perpendicular to each other. The interaction between them may be neglected in the planar conjugate molecule. Therefore, the MOs for  $\pi$  electrons in a conjugated system may be considered independently of  $\sigma$  - electrons. These orbitals are set up according to linear combination of  $2p_z$  AOs of each C-atom in a conjugated molecule. This concept was first introduced by Hückel (1931) and later developed by Coulson and Higgins (1947).

Let us consider a conjugated system of double and single bonds containing carbon atoms. Each C-atom contributes one  $2p_z$  AO with one  $\pi$  electron. According to LCAO, the MO may be written as:

atom contributes one  $2p_z$  AO with one  $\pi$  electron. According to LCAO, the MO may be written as:

$$\Psi_i = \sum_{j=1}^n c_{ij} \Phi_j$$

Where  $i = 1, 2, 3, \dots, N$  and  $j = 2p_z$  orbital on C-atom  $j$ .

The  $n\pi$  MOs are formed by the overlap of  $n$   $2p_z$  AOs.

Hückel MO theory is similar to the method of Homonuclear diatomic molecules. Hückel made the following postulates:

- (i) All overlap integrals are zero i.e.  $S_{ij} = 0$
- (ii) The Coulomb integral  $H_{ii}$  shows that the energy of an electron in  $2p_z$  orbital on the  $i$ th C-atom. All such integrals are equal and denoted by  $\alpha$ .
- (iii) The exchange integral indicates the energy of interaction of the  $i$ th and  $j$ th orbitals.
- (iv) All resonance integrals ( $\beta$ ) between non-neighboring atoms are set equal to zero.

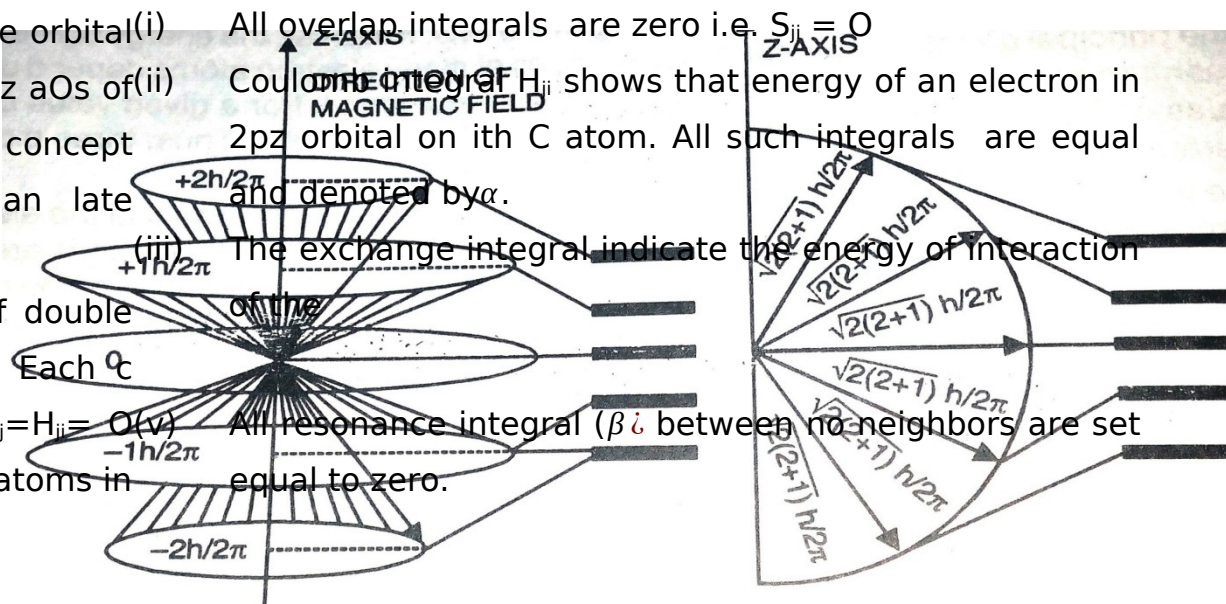


Fig. Five different space orientations corresponding to  $l = 2$ .

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & \dots 0\dots \\ \beta & \alpha-E & \beta & 0 & \dots 0\dots \\ 0 & \beta & \alpha-E & \beta & \dots 0\dots \\ 0 & 0 & \beta & \alpha-E & \beta\dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0 \quad \dots(1)$$

Defining a dimensionless parameter x as  $z = \frac{\alpha-\beta}{\beta}$ ,

the above equation (1) may be written as

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

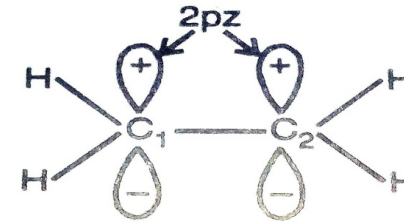
The conjugated system thus has n energy levels and n Mos. The energy of Kth Mos is given by

$$E_k = \alpha + x_k \beta$$

Where  $X_k$  is the kth root of the polynomial. Since coulomb integral  $\alpha$  and resonance integral  $\beta$  are negative. As positive value of  $X_k$  represents an energy level which is more negative and more stable. Such an energy level is called bonding molecular orbital (BMO). A negative value of  $X_k$  represents an energy level which has higher energy and hence less stability than an electron in a carbon 2pz orbital. Such level is called antibonding molecular orbital (ABMO). The energy level

corresponding to  $X_k$  being zero is called no bonding molecular orbital (NBMO).

The application of the Huckel molecular orbital theory to ethylene: the ethylene molecule is shown in figure.



**Fig. Ethylene molecule**

In the case ethylene. Huckel approximation is :

$$\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} = 0 \quad \dots\dots(1)$$

The Huckel secular equation is given by

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad \dots\dots(2)$$

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

Equation (2) on expansion given

$$x^2 - 1 = 0$$

$$x = \pm 1$$

Or

For  $x=1, E_1 = \alpha + \beta$  (BMO)

$$\dots\dots(3)$$

And for  $x=+1, E_2 = \alpha + \beta$  (ABMO)

.....(4)

The two  $\pi$  electron of ethylene occupy the BMO as shown in figure.

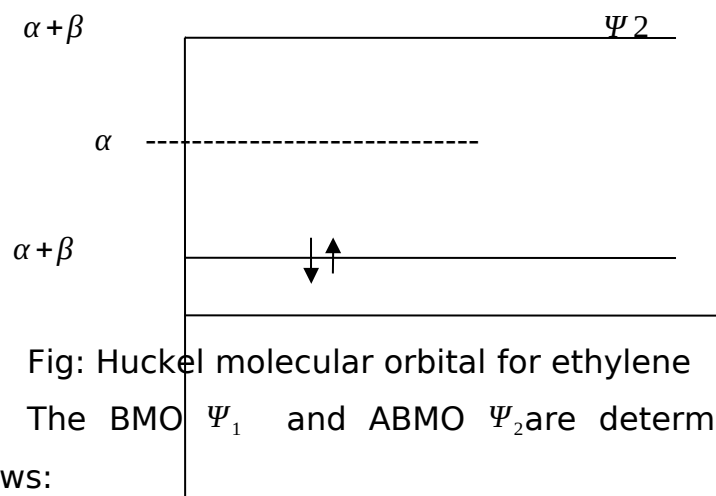


Fig: Huckel molecular orbital for ethylene

The BMO  $\Psi_1$  and ABMO  $\Psi_2$  are determined as follows:

The secular equation corresponds to the two linear equation viz.

$$c_1x + c_2 = 0 \text{ and } c_1 + c_2x = 0$$

For BMO  $\Psi_1, x=-1$ , Thus

$$-c_1 + c_2 = 0 \text{ and } c_1 - c_2 = 0$$

Or in both cases,  $c_1 = c_2$

since  $\Psi_1$  must be normalized i.e.  $\int \Psi_1 \Psi_2 d\tau = 1$ , we

get

$$\int (c_1\phi_1 + c_2\phi_2)(c_1\phi_1 + c_2\phi_2) d\tau = 1$$

$$\text{Or } c_1^2 \int \phi_1\phi_1 d\tau + c_2^2 \int \phi_2\phi_2 d\tau + 2c_1c_2 \int \phi_1\phi_2 d\tau = 1$$

.....(5)

Again  $\phi_1$ s from an orthogonal set i.e.

$$\int \phi_i \phi_j d\tau = \delta_{ij} = \begin{cases} 1, i=j \\ 0, i \neq j \end{cases}$$

.....(6)

Where  $\delta_{ij}$  is called Kronecker delta.

It means that  $\int \phi_i \phi_i d\tau = 1$  and  $\int \phi_i \phi_j d\tau = 0$

Substituting these values in equation (5), we get

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

$$\text{Or } c_2 = \frac{1}{\sqrt{2}} \text{ since } (c_1 = c_2)$$

$$\text{Hence } \Psi_1 = (\phi_1 + \phi_2) / \sqrt{2} \text{ .....(7)}$$

Similarly for  $x=1$ , we can show that

$$\Psi_2 = (\phi_1 - \phi_2) / \sqrt{2} \text{ .....}$$

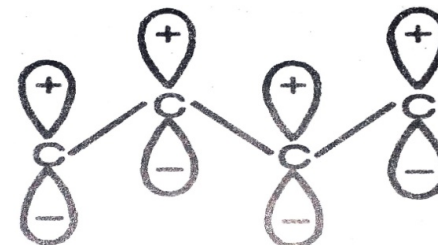
(8)

It is noted that the probability of finding  $\pi$  electrons is zero at the nodal planes. In ethylene each C atom is bonded to 2H atom hence total bond order with each C atom is four.

The application of the Huckel molecular orbital theory to 1,3 Butadiene: 1,3.

Butadiene contains four carbon 2pz orbitals and for  $\pi$  electrons as shown in figure.

Fig: 2pz orbitals of 1,3 Butadiene



Huckel secular determinant of 1,3 Butadiene is

$$(1) \begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \quad \dots\dots\dots$$

To simplify the solution of equation (1), we divide each row of the determination by  $\beta$  and then.

Substitute  $x = \frac{\alpha-E}{\beta}$ . The secular determinant then becomes.

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \quad \dots\dots\dots(2)$$

Expansion of this determinant gives the polynomial equation

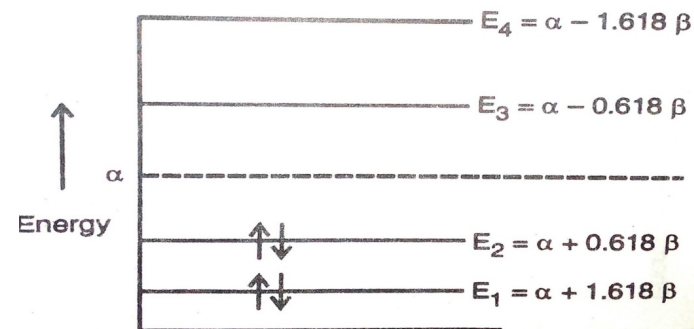
$$x^4 + 3x^2 + 1 = 0$$

This equation has the roots  $x = \pm 1.618$  and  $\pm 0.618$ . Thus, we get the following for energy levels.

- $E_1 = \alpha + 1.618\beta$  (BMO)
- $E_2 = \alpha + 0.618\beta$  (BMO)
- $E_3 = \alpha - 1.618\beta$  (ABMO)
- $E_4 = \alpha - 1.618\beta$  (ABMO)

The four  $\pi$  electrons of 1,3 - butadiene are filled in two BMOs  $\Psi_1$  and  $\Psi_2$  as shown in figure:

Fig: Four  $\pi$  electron of 1,3 - Butadiene  
Here, we add a quantity called delocalisation energy



(DE) which is defined as the difference between the total  $\pi$  electron energy of the molecule and the  $\pi$  electron energy of the same number of isolated double bonds. Thus, for butadiene .

The delocalisation energy is a measure of stability of the molecule. The higher the value of DE, more stable is the molecule. Thus butadiene is more stable than two ethylene molecule by an energy of  $0.472\beta$

Huckel molecular orbital theory applied to cyclo-butadiene : The Huckel secular equation is given by

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \quad \text{Where } x = \frac{\alpha-E}{\beta} \quad \dots\dots(i)$$

Expansion of this determinant gives the polynomial equation

$$X^4 - 4X^2 = 0$$

$$X = 0 \text{ (twice)}, \neq 2$$

Or

Thus, the energy levels are

$$X = -2, E_1 = \alpha + 2\beta \text{ (BMO)}$$

$$X = 0, E_2 + E_3 \text{ (degenerate Pair, NBMO)}$$

$$\begin{aligned} DE &= E_{\pi}(\text{butadiene}) - 2 E_{\pi}(\text{ethylene}) \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) - 2(2\alpha + 2\beta) \\ &= 4\alpha + 4.472\beta - 4\alpha - 4\beta = 0.472\beta \end{aligned}$$

$$X = +2, E_4 = \alpha + 2\beta \text{ (ABMO)}$$

: Cyclobutadiene

The molecular diagram for cyclobutadiene is shown in figure,

The  $\pi$  electrons are filled in BMO and NBMO as shown in figure. Two  $\pi$  electrons are filled in the lowest BMO of energy  $\alpha + 2\beta$  and two are filled in double degenerate NBMO of energy  $\alpha$ .

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

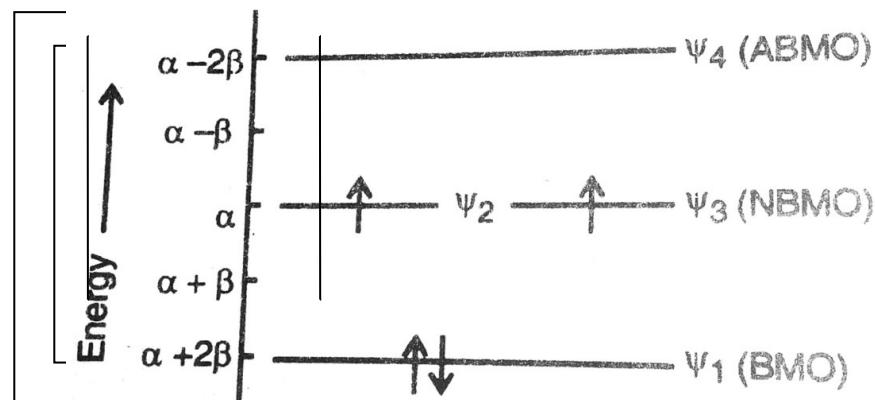
$$E_{\pi} = 4\alpha + 4\beta$$

Or

Thus delocalization energy (DE) is given by

$$DE = 4\alpha + 4\beta - 4(\alpha + \beta) = 0$$

Thus, according to HMO theory cyclobutadiene is unstable due to its  $DE = 0$ . Baeyer's strain theory also supports this view.



Fig

Huckel molecular orbital diagram for cyclobutadiene

Mention its applications. The extended huckel theory was proposed by Hoffmann (1962) This method used an effective AOs for valence electrons Hamiltonian and all the overlap integrals are retained. The EHT basis set consists of Slater AOs for valence electrons. Thus, for hydrogen only 1<sup>st</sup> orbital is considered. In the second period of the periodic table from lithium to fluorine, 2s and 2p orbital is considered. For the third period elements. We take 3s, 3p and 3d orbitals and some times 4s and orbital are also used. We can write each MO in the LCAO from as.

$$\Psi = \sum C_{iv} \phi_v$$

Where  $C_{iv}$  are the LCAO coefficients,  $\phi_v, \phi_v,$  are normalised slater AOs. On each centre (except H atom) there are more than one AO such as  $s, p_x, p_y, p_z,$  etc. open applying the variation theorem. We get as set of secular equations.

$$\sum_v (H_{\mu v} - \epsilon_i S_{\mu v}) C_{iv} = 0$$

Where  $\mu$  indicates MOs,  $v$  the AOs,  $S_{iv}$  is the AO overlap integral and  $\epsilon_i$  is the energy of  $i$ th MO. The matrix element  $H_{\mu v}$  is called defined by the following equation .

$$H_{\mu v} = \langle \phi_v | H | \phi_v \rangle$$

If we element  $C_{iv}$  from eq. (2), we get the following negative of the volence state ionization potential of the appropriate AO. The off diagonal elements  $H_{\mu v}$  are considered proportional to the overlap,  $S_{\mu v}$  following equation are known for off - diagonal elements.

$$H_{\mu v} = 0.5 [H_{\mu\mu} + H_{vv}] S_{\mu v} K \dots\dots\dots(5)$$

$$H_{\mu v} = K^1 S_{\mu v} (H_{vv} \cdot H_{vv})^{1/2} \dots\dots\dots(6)$$

$$H_{\mu v} = S_{\mu v} [2 - |S_{\mu v}|] \times 0.5 (H_{\mu\mu} + H_{vv}) \dots\dots\dots(6)$$

Equation (5) is used with a K value of 1.75. equation (6) is used for calculation of inorganic complexes. Equation (7) is generally used. The overlap integral can be calculated by using slater AOs and the secular

determinant is solved for the orbital energies and coefficients. We can then calculate total energy by adding the energies of the occupied orbitals. Thus, the total electronic energy is given by

$$E_{EHT} = 2 \sum_i^{occ} \epsilon_i$$

**Application :** this theory is successful in explaining conformation of molecules.