

## UNIT - I

### STRUCTURE AND BONDING MODELS

Plank's Quantum theory :- (1901) CO<sub>1</sub> - Explain short notes of different theories along with their applications.

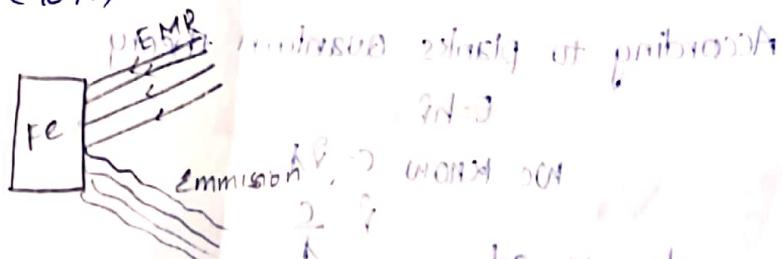
James Clark Maxwell explains wave character is continuous manner like pumping of water.

Max Planck explains wave nature is in discontinuous manner like throwing of small stones.

Postulates

#### \* Black body + radiation :-

The substance which acts as a perfect absorber and perfect emitter is known as Black body. There is no 100% perfect black body but we use carbon powder acts as a black body (90%).



#### \* Postulates :-

1. The EMR (Electro magnetic Radiation) is not emitted or absorbed continuously but it is possible due to release of small energy packets is known as Quantum (plural - Quanta)
2. The Energy of EMR is directly proportional to frequency of radiation.  $E \propto v$

$$E = hv$$

Where  $E$  = Energy of radiation

$v$  = Frequency of radiation

$h$  = Planck's constant.

$$h = 6.625 \times 10^{-34} \text{ erg.sec or } 6.625 \times 10^{-34} \text{ Joules.sec}$$

3. The energy of EMR is equal to integral multiple of frequency of radiation.

$$E = nhv$$

$$E = n \frac{hc}{\lambda}$$



Difficult to From classical physicist to cont. world but

$$(hc = 2.1 \times 10^{-34}) \text{ To explanation of shape of}$$

$$\theta = \frac{c}{\lambda}$$

\* From (E=mc²) Einstein's assumption [Then] light packet is known to have a photon. (singular is photon),

Dual nature of matter (or) De-broglie's equation :- (1923)

Whenever material is in movement manner which exhibits wave nature and particle nature.



particle nature

wave nature

Derivation :- On a particle basis it has mass & momentum side

According to Einstein mass energy relation having two  
 $E = mc^2$  — ①

According to planks quantum theory

$$E = h\nu$$

$$\text{We know } c = \lambda\nu$$

$$\nu = \frac{c}{\lambda}$$

Now we get

$$E = hc — ②$$

When we observe 1<sup>st</sup> & 2<sup>nd</sup> equations energy of radiation is same that's why we equate 1<sup>st</sup> & 2<sup>nd</sup> eqs.

$$① = ②$$

① It is used to calculate particle having low mass

$$mc^2 = \frac{hc}{\lambda} \quad \text{by using } \lambda = \frac{h}{mv}, \text{ where } m = \text{mass of electron}$$

v = velocity h = plank's constant

② It is used to calculate particles having high mass

$$\lambda = \frac{h}{mc^2} \quad \text{like, Iron ball having } 100\text{ gm mass and move with } 100\text{ cm/sec}$$

by using  $\lambda = \frac{h}{mv}$  formula

$$\lambda = \frac{h}{mc^2} \quad \text{to calculate angular momentum of an electron}$$

mc <sup>2</sup> <sub>2πr</sub> Bohr's atomic theory

where c is speed of light which explains only light

property so we replace 'c' term with 'v' (velocity of matter)

$$\lambda = \frac{h}{mv}$$

We know mass of the matter and velocity of matter is equals to momentum of matter (p)

$\lambda = \frac{h}{P}$  l = p/q total path length over period of time from given history

The above formula also explains wave nature &  $p$  explains

comparticle nature.

~~UVI~~ Schrödinger wave equation:-

whenever electron movement around the nucleus in continuous manner which possess wave nature, discontinuous manner which gives particle nature

Derivation

According to classical wave function

$$\text{Equation } \psi = A \sin \frac{2\pi x}{\lambda} \rightarrow ①$$

partial differentiate with respect to  $x$

$$\frac{\partial \psi}{\partial x} = A \cos \frac{2\pi x}{\lambda} \times \frac{2\pi}{\lambda}$$

Again partial differentiate with respect to  $x$

$$\frac{\partial^2 \psi}{\partial x^2} = -A \sin \frac{2\pi x}{\lambda} \times \frac{2\pi}{\lambda} \times \frac{2\pi}{\lambda} = -A \sin \frac{2\pi x}{\lambda} \times \frac{4\pi^2}{\lambda^2} \rightarrow ②$$

from eq. ①  $\psi = A \sin \frac{2\pi x}{\lambda}$ , so  $\frac{\partial^2 \psi}{\partial x^2} = -\psi \times \frac{4\pi^2}{\lambda^2}$

$$\frac{\partial^2 \psi}{\partial x^2} = -\psi \times \frac{4\pi^2}{\lambda^2}$$

not going nisologal

$$\frac{\partial^2 \psi}{\partial x^2} + \psi \times \frac{4\pi^2}{\lambda^2} = 0 \rightarrow ③$$

According to de Broglie's equation:

$\lambda = \frac{h}{mv}$  l = p/q total path length over time

$$l^2 = \frac{h^2}{m^2 v^2} \rightarrow ④$$

Substitute eq. ④ value in eq. ③.  $l^2 = \frac{h^2}{m^2 v^2}$

$$\frac{\partial^2 \psi}{\partial x^2} + \psi \times \frac{4\pi^2}{\lambda^2} = 0$$

unit of wave =  $\psi$

total path length =  $\lambda$

momentum =  $P$

$$\frac{\partial^2 \psi}{\partial x^2} + \psi \times \frac{4\pi^2 m^2 v^2}{h^2} = 0 \rightarrow ⑤$$

We know that total energy is nothing but sum of the potential energy and kinetic energy.

$$T.E = K.E + P.E$$

$$\therefore E = \frac{1}{2}mv^2 + V$$

$$E - V = \frac{1}{2}mv^2$$

$$2(E - V) = mv^2$$

Substitute eq. ④ value in eq. ③

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

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

Now if axes are 3 so we include we have 3 imaginary axes.

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

Laplacian operator

$$\Delta^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

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

It is known as time independent Schrodinger

wave equation

$$\textcircled{1} \quad \Delta^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where

$\Delta^2$  = Laplacian operator

$\psi$  = wave function

$m$  = mass of electron

$h$  = planks constant

$E$  = Total Energy

$V$  = Potential Energy

## Significance of $\psi$ :-

1.  $\psi$  is wave function (or) amplitude of wave
2.  $\psi$  Must be possess single values.
3.  $\psi$  has no physical significance
4.  $\psi$  values +ve, -ve and Imaginary.
5. In wave formation we have different displacements in their position.
6. So we get different wave function values, is known as eigen values.

## Significance of $\psi^2$ :-

1.  $\psi^2$  is probability function which explains finding of electrons present in wave.
2.  $\psi^2$  value is 0 which indicates finding of electron is negligible.
3.  $\psi^2$  value is high which indicates the probability of finding of electron is maximum.
4.  $\sin \psi^2$  value is low which indicates the probability of finding of electron is minimum.
5. By using Probability function we find out electron position entire wave in infinite manner.

$$\int_{-\infty}^{+\infty} \psi^2 dx dy dz = 1 //$$

## Molecular orbital theory (MOT)

### Introduction :-

#### Draw backs of valency Band theory :-

- \* It could not explain magnetic nature of oxygen molecule.
- \* It could not explain the formation of ionic crystals.
- \* It could not explain the formation of antibonding molecular orbitals.
- \* It could not explain the formation of bonding molecular orbitals.

Assumption of MOT :- To overcome the drawbacks of valency band theory Hund & Mulliken proposed the Molecular orbital theory, later Jons & Coulson modified.

#### Postulates or Salient features :-

1. Atoms combine together to form molecules.
2. Atoms produce atomic orbitals designated as  $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5s, 5p, 5d, 6s, 6p, 6d, 7s, 7p$  molecules.
3. The total no. of atomic orbitals is always equals to total no. of molecular orbitals.
4.  $\psi_1, \psi_2$  are 2 atomic orbitals which are combined in constructive Interphase we get bonding molecular orbitals these are low energy and stable orbitals.

Atomic orbitals are combined in destructive interface. We get bonding molecular orbitals these have high energy & unstable orbitals.

5. Bond order (Bo) =  $\frac{N_B - N_A}{2}$

where  $N_B$  = No. of electrons present in bonding molecular orbitals  
 $N_A$  = No. of electrons present in antibonding molecular orbitals

6. Linear combination of atomic orbitals (LCAO) stated three conditions those are same energy, similar energy, same shape.

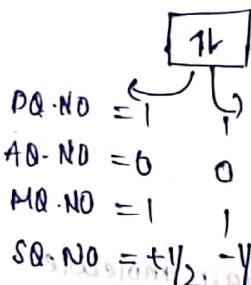
7. In molecular orbital theory to fulfill the electrons in molecular orbitals we should follow Hartree-Fock's principle, Hund's principle and Pauli's exclusion principle.

\* Hartree-Fock's principle: the electrons enter into lower energetic orbitals before entering into higher energetic orbitals based upon  $(n+l)$  value.

\* Hund's principle: whenever degenerate orbitals available for electrons the pairing of electrons takes place after all orbitals are filled with one electron each two orbitals.

\* Pauli's exclusion principle: It knows 2 electrons can have same set of all four quantum numbers.

Ex: He — 2 1s<sup>2</sup>



\* Energy level order of diatomic molecules upto Nitrogen elements:  
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \pi_{2p_z}^*$

\* Energy level order of diatomic molecules after Nitrogen element:  
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_1} < \pi_{2p_1} = \pi_{2p_2} < \pi_{2p_3} < \pi_{2p_1}^* = \pi_{2p_2}^* < \pi_{2p_3}^*$

Diatomic molecules:

The combination of 2 atoms those are same or different to form diatomic molecules.

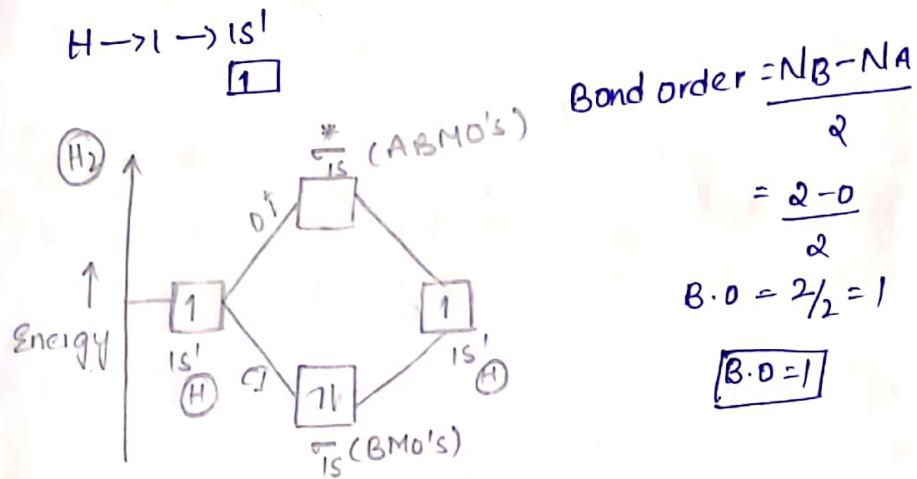
Ex:- H<sub>2</sub>, HCl etc

Homonuclear diatomic molecules:

The combination of 2 same elements having same energy to form homonuclear diatomic molecules.

Ex:- H<sub>2</sub>O, O<sub>2</sub> etc

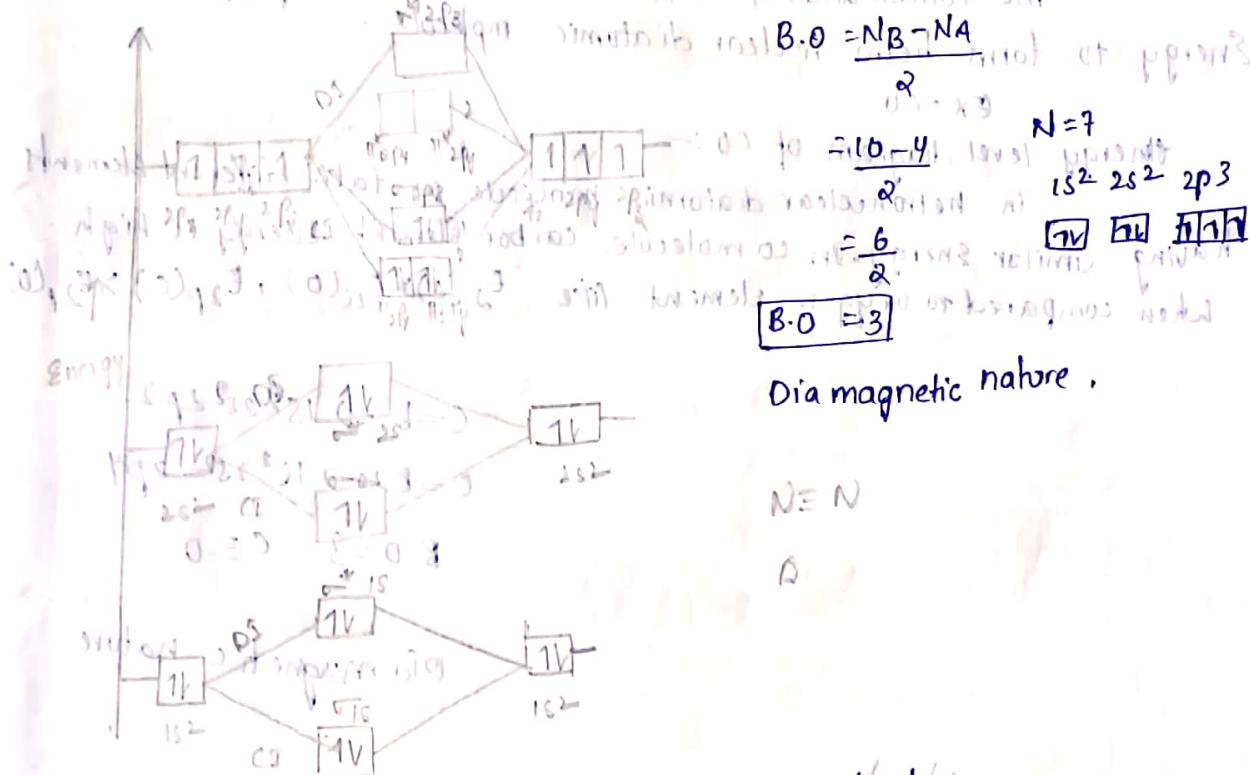
## Energy level diagram of hydrogen molecule.



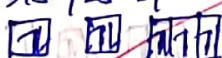
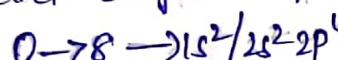
### Magnetic nature :-

1. In case of lone pair of electrons present in BMOS or ABMOS which exhibits paramagnetic nature.
2. In case of no lone pair of electrons present in BMOS and ABMOS which exhibits diamagnetic nature.

## Energy level diagram of Nitrogen molecule



## Energy level diagram of oxygen molecule



~~$$B.O = \frac{NB - NA}{2} = \frac{10 - 6}{2} = \frac{4}{2} = 2$$~~

~~$$\therefore B.O = 2.$$~~

Paramagnetic nature.

Energy level diagram for oxygen atom



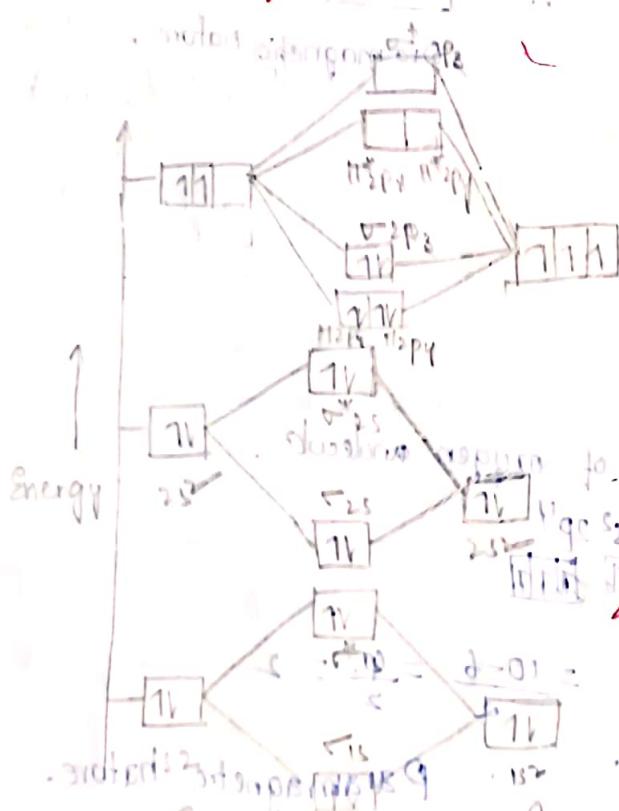
LOMIAE 80 2011  
In the same way for nitrogen atom to form nitro radical, i.e.,  
Nitrogen atom + hydrogen atom  $\rightarrow$  Nitrogen-hydrogen bond  
Nitrogen atom + oxygen atom  $\rightarrow$  Nitrogen-oxygen bond  
Nitrogen atom + chlorine atom  $\rightarrow$  Nitrogen-chlorine bond

Heteronuclear diatomic molecule,  
the combination of different elements having similar  
Energy to form heteronuclear diatomic molecule.

Ex :- CO

Energy level diagram of CO :-

In heteronuclear diatomic molecule we take different elements having similar energy. In CO molecule carbon element energy is high when compared to oxygen element like  $E_{2s}(C) > E_{2s}(O)$ ,  $E_{2p}(C) > E_{2p}(O)$ .



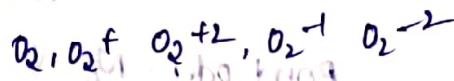
$$C = b \rightarrow 1s^2 2s^2 2p^2$$

$$O = e \rightarrow 1s^2 2s^2 2p^4$$

$$B - D = 3 \quad C \equiv O$$

Diamagnetic nature

calculate the bond order of molecular species.



$$\text{O}_2 \rightarrow \text{B.O} = \frac{10 - 6}{2} = \frac{4}{2} = 2$$

$$\text{O}_2^+ \rightarrow \text{B.O} = \frac{10 - 5}{2} = \frac{5}{2} = 2.5$$

$$\text{O}_2^{+2} \rightarrow \text{B.O} = \frac{10 - 4}{2} = \frac{6}{2} = 3$$

$$\text{O}_2^- \rightarrow \text{B.O} = \frac{10 - 7}{2} = \frac{3}{2} = 1.5$$

$$\text{O}_2^{-2} \rightarrow \text{B.O} = \frac{10 - 8}{2} = \frac{2}{2} = 1$$

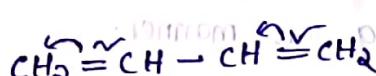
Two molecular orbitals of 1,3 Butadiene: - is aliphatic compound straight chain manner

1) bonding molecular orbital (in phase) - no nodes

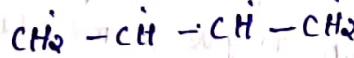
2) antibonding molecular orbital (out of phase) - one node

primary carbon (C) - anti bonding molecular orbital (nodes)

1,3 Butadiene has two double bonds in a conjugated system.



ratio of electron pair to bonding molecular orbitals is 2:1



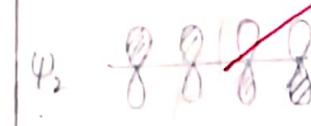
② bonding molecular orbital

ABNI = 3

BNI = 1

ABNI = 2

energy barrier



1

ABNI = 2

BNI = 1

ABNI = 1

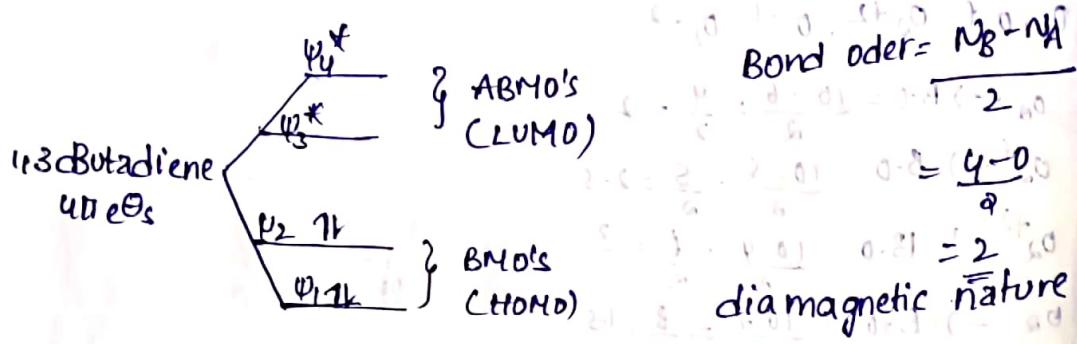


6

BNI = 3

ABNI = 0

## Energy level diagram of 1,3 Butadiene

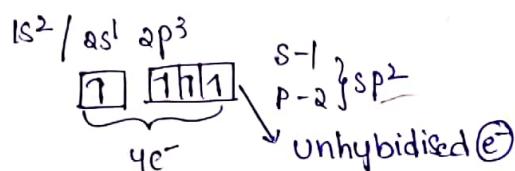
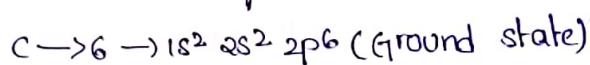


1. In 1,3 di Butadiene 4 carbons are arranged in 2 alternative double bonds.
2. In these 2 double bonds undergoes homolytic cleavage. to form  $\varphi\pi$  electrons.
3. In these  $4\pi$  electrons to form  $\psi_1, \psi_2$  as highest occupied molecular orbitals (HOMO) and  $\psi_3^*, \psi_4^*$  as lowest unoccupied molecular orbitals.
4. In 1,3 di butadiene we have  $4\pi$  electrons. These  $4\pi$  electrons entering into homo  $\ominus$

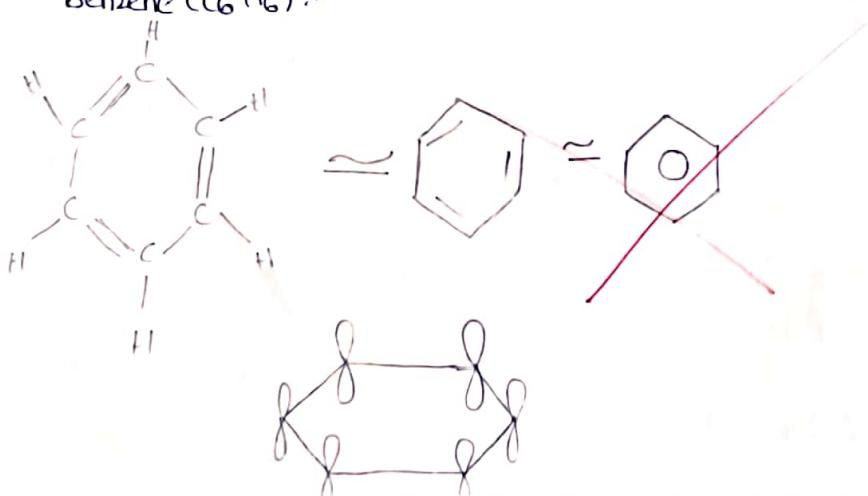
## $\pi$ molecular orbitals of Benzene:-

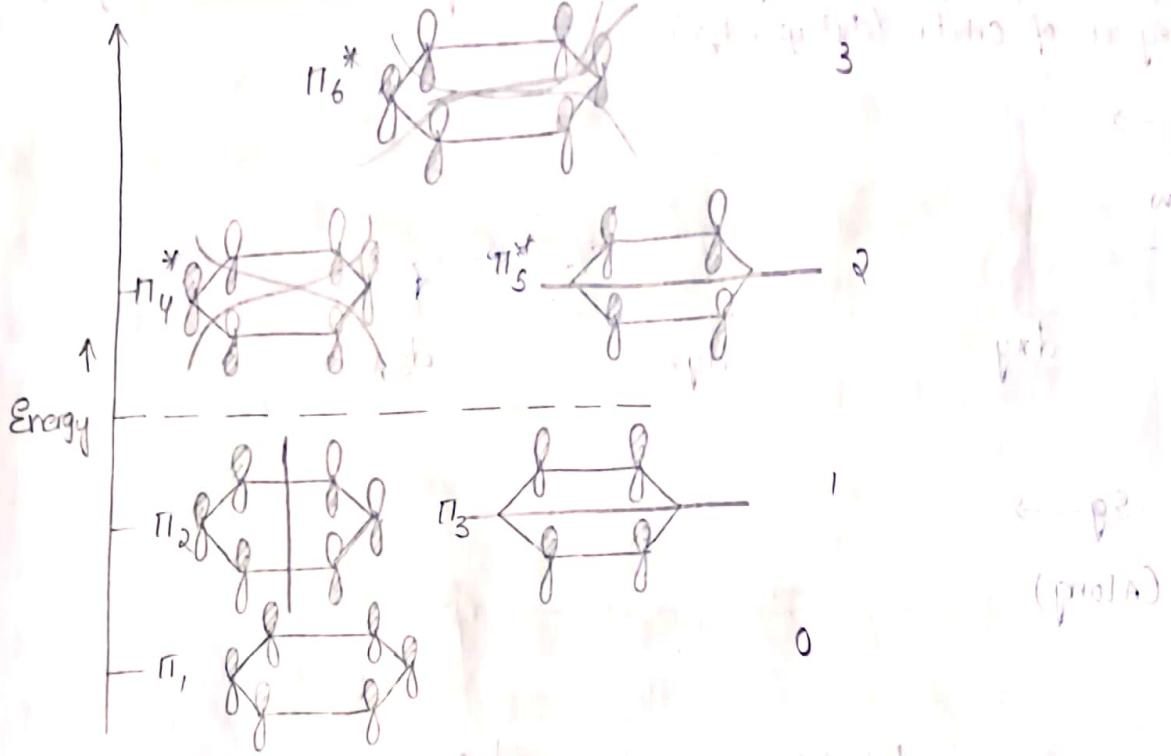
In Benzene 6 carbon elements are (attached) attached with 3 alternative double bonds . in ring wise manner.

In Benzene carbon element undergoes  $\varphi_2$  hybridization after that which forms one unhybridised electron to give  $\pi$  molecular orbital.



## Benzene ( $C_6 H_6$ ):-





for the given defined  $\pi_6^*$  LUMO (muon)  $\rightarrow$  382  
 : ~~lumino~~  $\pi_6^*$  (muon)  $\rightarrow$  ~~lumino~~ (muon's) formed in diaction

Benzene  
 diaction  $\rightarrow$   $\pi_6^*$   $\pi_5^*$   $\pi_4^*$   $\pi_3^*$   $\pi_2$   $\pi_1^*$  HOMO (BMO's)  
~~but only~~  $\pi_6^*$  diaction  $\rightarrow$  ~~lumino~~ (muon's) formed in diaction

Cristal field theory (CFT) :-  
 Bethe & vanvleck proposed crystal field theory to explain coordination covalent compounds (crystals) in 1930.

### Postulates of crystal field theory :-

1. Transition metals can be taken as lewis acids and ligands taken as

a lewis bases.

2. Transition metals <sup>always</sup> exhibit positive charge and ligands sometimes possess negative charge and sometimes (positive cha) neutral charge

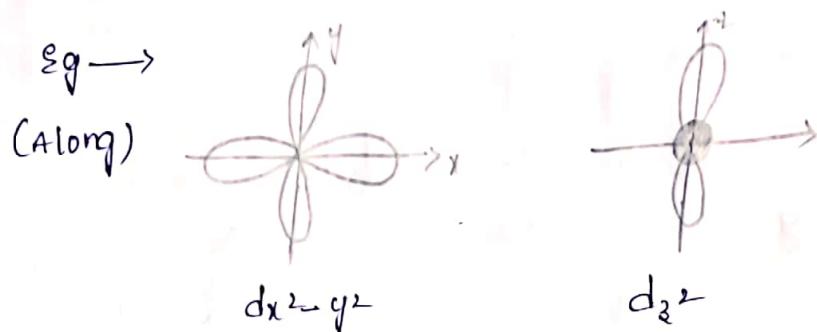
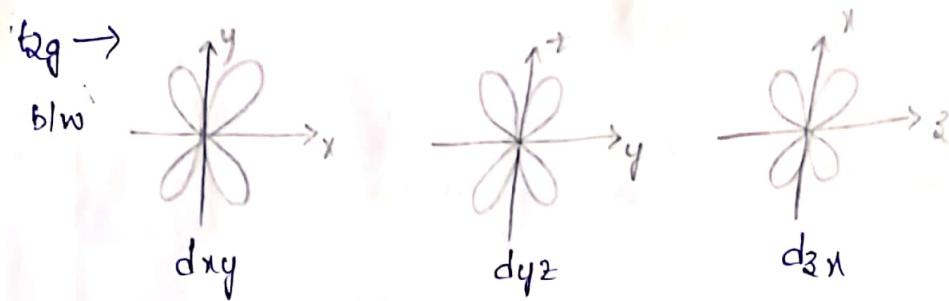
3. a) attraction :- the transition metals possess positive charge and ligands

b) repulsions :- the transition metal possess positive charge and ligands

4. The transition metals have 5 degeneracy orbitals like  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$

$d_{z^2}$ ,  $y^2$ ,  $d_{3x}$

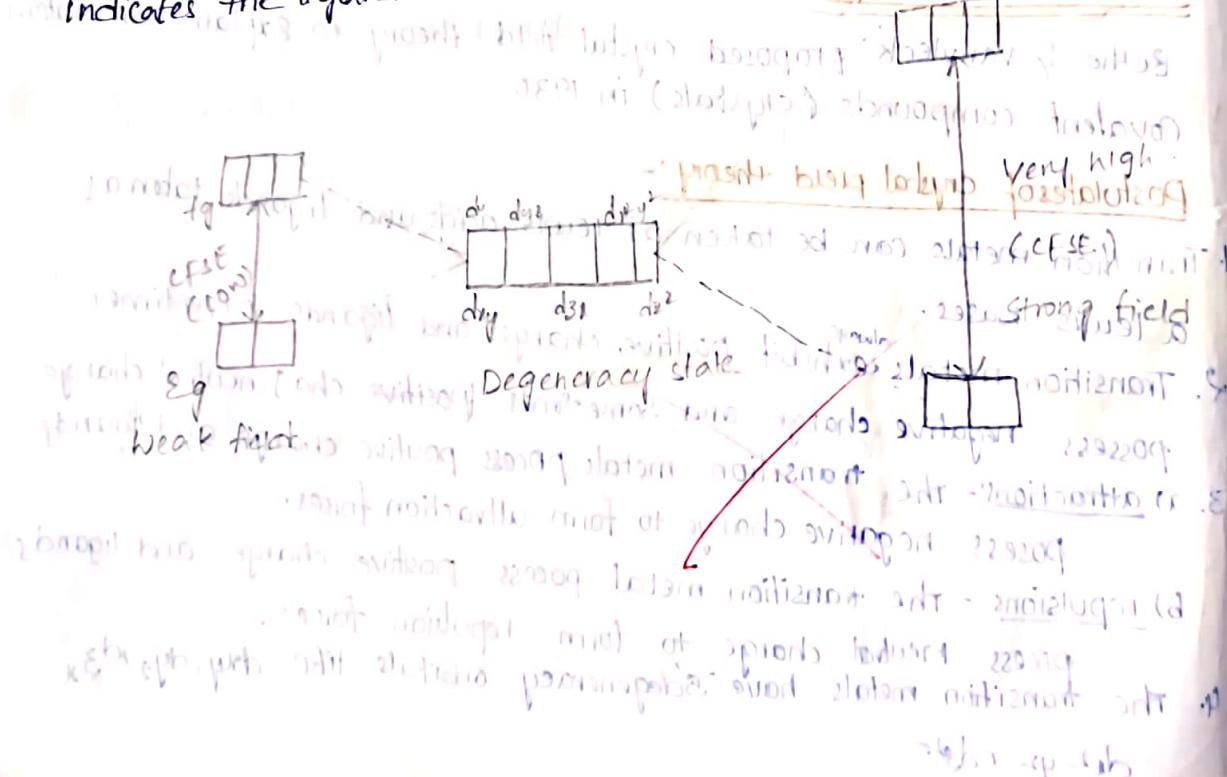
5 Whenever ligand approaches to the central metal atom the degeneracy of d orbitals get destroyed, to form t<sub>2g</sub> set of orbitals ( $d_{xy}, d_{yz}, d_{zx}$ ) eg set of orbitals ( $d_{x^2-y^2}, d_{z^2}$ )



6. CFSE: The distance between t<sub>2g</sub> set of orbitals and e<sub>g</sub> set of orbitals is known as crystal field splitting energy or crystal field stabilisation energy.

case 1:- If the gap b/w t<sub>2g</sub> and e<sub>g</sub> set of orbitals is low which indicates ligand character is weak field.

case 2:- If the gap b/w t<sub>2g</sub> + e<sub>g</sub> set of orbitals is high which indicates the ligand character is strong field.

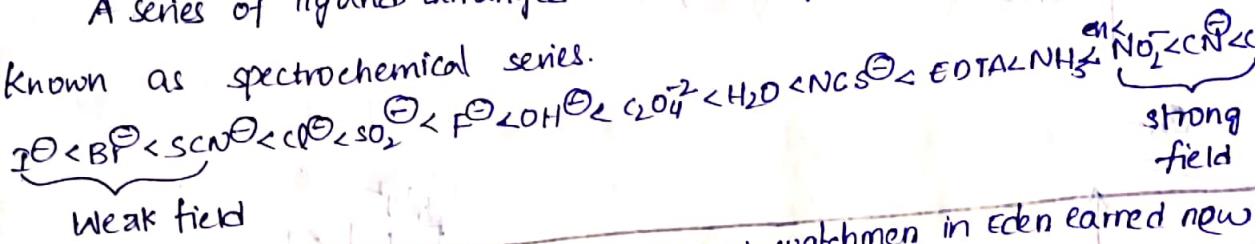


S.No	electronic configuration	t <sub>2g</sub>	e <sub>g</sub>	t <sub>2g</sub>	e <sub>g</sub>
1.	3d <sup>1</sup>	1	□	1	□
2.	3d <sup>2</sup>	11	□	11	□
3.	3d <sup>3</sup>	111	□	111	□
4.	3d <sup>4</sup>	1111	□	111	1
5.	3d <sup>5</sup>	1111	□	111	11
6.	3d <sup>6</sup>	1111	□	111	11
7.	3d <sup>7</sup>	11111	1	1111	11
8.	3d <sup>8</sup>	11111	11	11111	11
9.	3d <sup>9</sup>	11111	111	11111	111
10.	3d <sup>10</sup>	11111	1111	11111	111

### Spectrochemical series:-

A series of ligands arranged in increasing order of energy is

known as spectrochemical series.



weak field

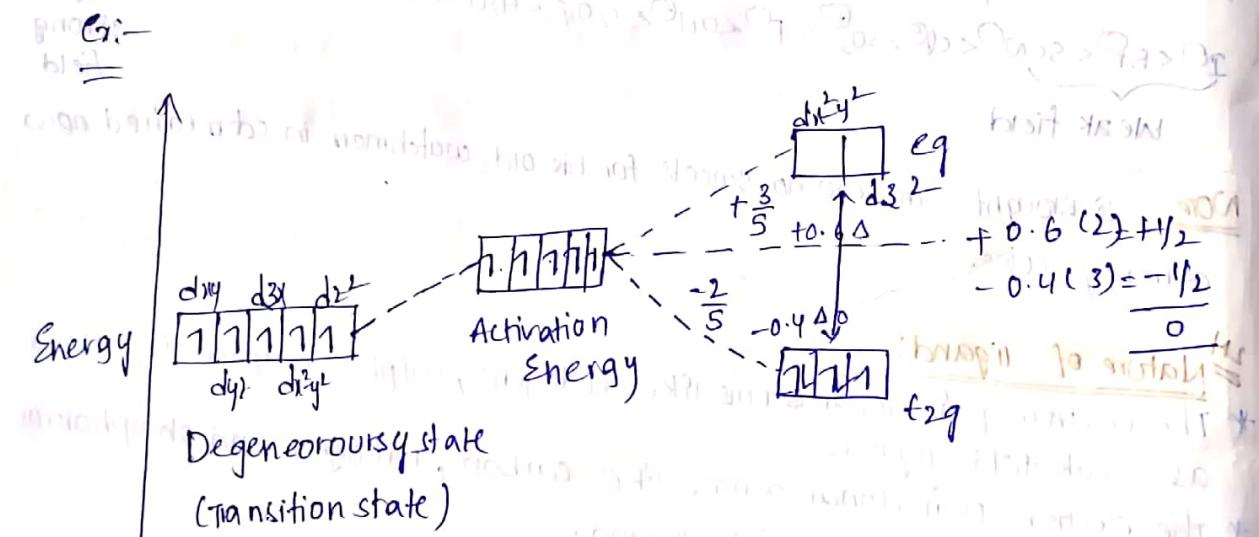
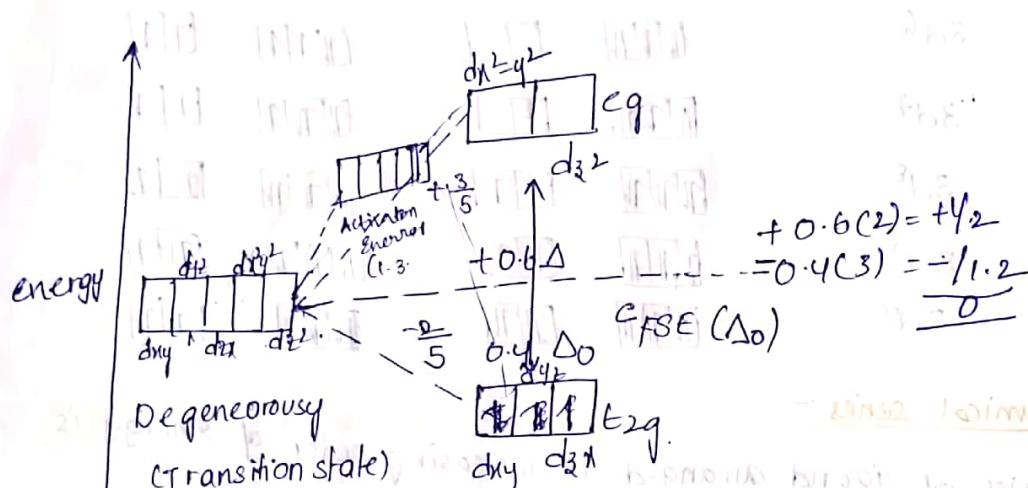
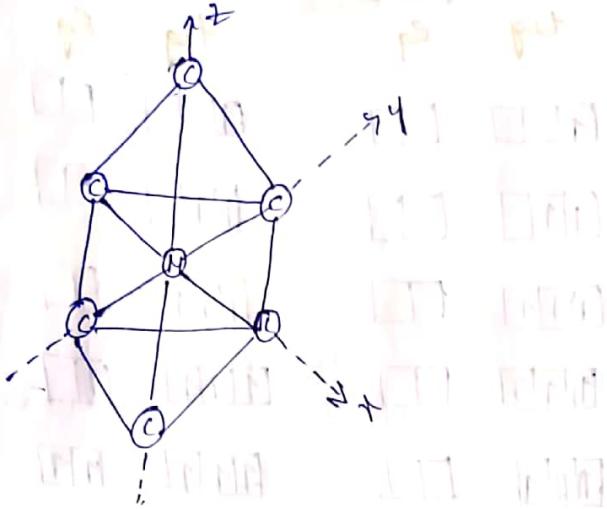
Note:- I brought some chocho sweets for his old watchmen in Eden earned now currency coins.

### Nature of ligand:-

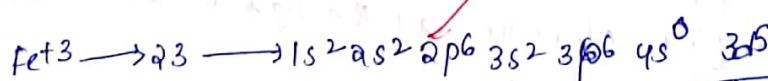
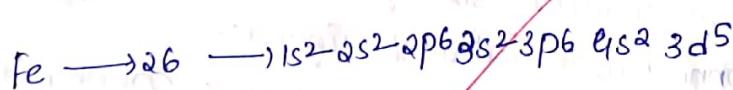
- \* The electron pair donor atoms like halogens, sulphur, oxygen is known as weak field ligands.
- \* the electron pair donor atoms like carbon, nitrogen, and phosphorous is known as strong field ligand.

### Splitting of d-orbitals in octahedral complex.

- In octahedral complex six ligands surrounded by transition metal and also connected to adjacent ligands.
- In this complex structure all the ligands connected to central metal atom. with 8 faces.
- In this complex ligands are arranged along the eq set of orbitals get excited



$$\text{Ex: } [\text{Fe}(\text{CN})_6]^{-3}$$

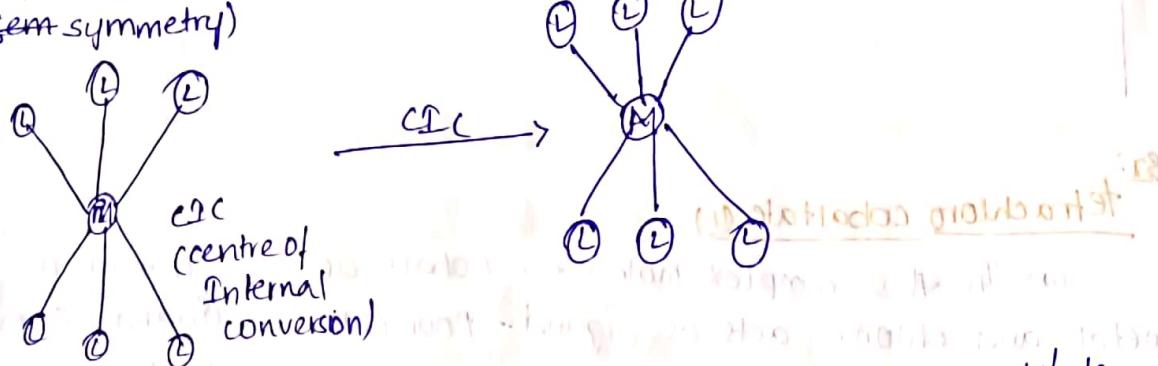


paramagnetic in nature

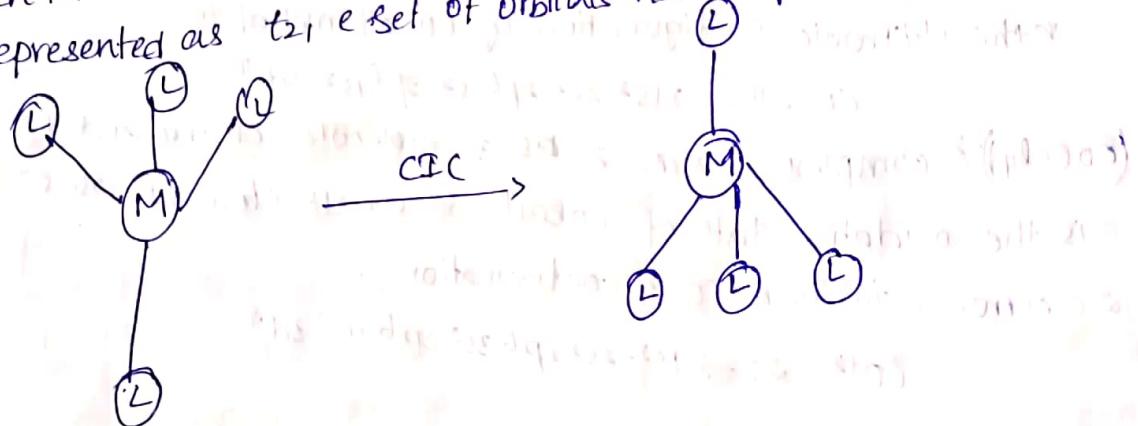
## splitting of d-orbitals in tetrahedral complex:-

- In tetrahedral complex molecule one transition metal surrounded by 4 ligands in four faces.
- the four ligands in tetrahedral complex molecule arranged b/w the axes so, in five degenerouse d-orbitals set of orbitals get excited when compared to set of orbitals.

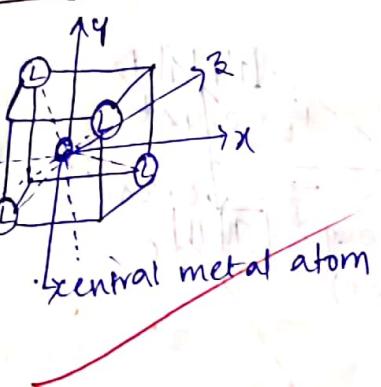
Note: ① In octahedral complex molecule our 5 degenerate orbitals represented as  $t_{2g}$  and  $e_g$  because of which obeys gerade condition (gem symmetry)

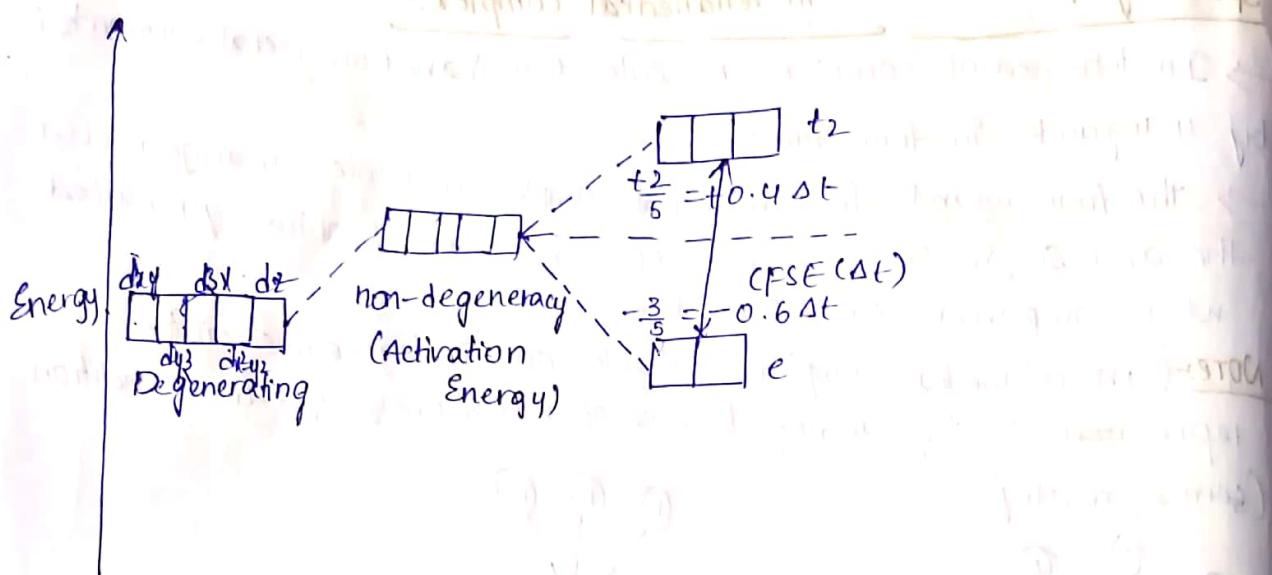


- ② In tetrahedral complex molecule our five degenerate d-orbitals represented as  $t_{2g}$ , the set of orbitals here symmetry is absent.



## Complex Structure:





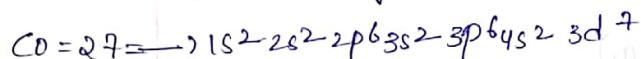
SQ:

### Tetrachloro cobaltate (II)

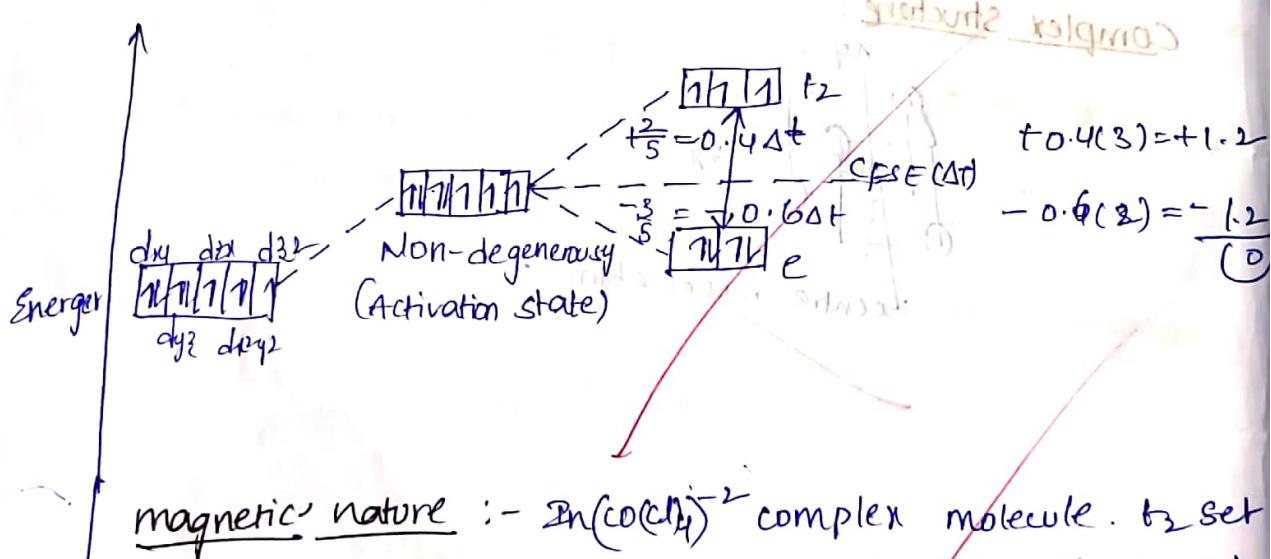
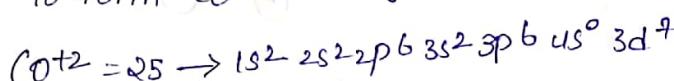
\* In this complex molecule, Cobalt acts as transition metal and chlorine acts as ligand. Four chlorine ligands surround by cobalt metal to form tetrahedral complex molecule.

\* The atomic number of cobalt is 27

\* The electronic configuration of Cobalt metal is



$(CoCl_4)^{+2}$  complex have -2 as a molecule charge and  $+2$  is the oxidation state of cobalt. So cobalt element loses 2 electrons. to form  $Co^{+2}$  configuration.



Magnetic nature :- In  $(CoCl_4)^{+2}$  complex molecule,  $t_2$  set of orbitals have 3 lone pair of electrons so this complex molecules undergoes paramagnetic nature.