

# Molecular Orbital Theory (MOT)

## Salient Features:-

In molecules,  $e^-$ s are present in new orbitals called molecular orbitals. Molecular orbitals like atomic orbitals are characterized by a set of quantum numbers.

- 1. Molecular Orbitals are formed by combination of atomic orbitals of nearly same energies and proper symmetry.
- 2. Nuclei of different atoms in the molecule behave as a Polycentric nucleus. Thus, an atomic orbital is monocentric while a molecular orbital is Polycentric.
- 3. The no. of molecular orbitals formed is equal to the no. of atomic orbitals undergoing combination. Half of the new molecular orbitals have energy lower than the combining atomic orbitals and are called Bonding orbitals. The other half of new molecular orbitals have energy greater than the combining atomic orbitals and are called anti-bonding orbitals.
- 4. The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals
- 5. ~~B.M.O~~ B.M.O named as  $\sigma$ ,  $\pi$ ,  $\delta$ ,  $w$  etc. while A.M.O. named as  $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$ ,  $w^*$  etc.

2. The electrons are re-distributed in M.O. acc. to Aufbau rule, Pauli's Exclusion Principle and Hund's rule = maximum multiplicity.

### Linear Combination of Atomic Orbital (LCAO)

Method: Equations for atomic and molecular orbitals

Molecular orbitals are formed by the combination of atomic orbitals of bonded atoms.

In wave mechanics atomic orbitals are expressed by wave functions ( $\Psi$ 's (Psi)).

Acc. to M.O.T atomic orbitals combine to form B MO & A MO which then participate in bond formation for eg: homonuclear diatomic molecule such  $H_2$  molecule.

Consider the two atoms of Hydrogen atom ~~part~~ in the molecule as A & B. These atomic orbitals may be represented by wave functions  $\Psi_A$  &  $\Psi_B$  respectively.

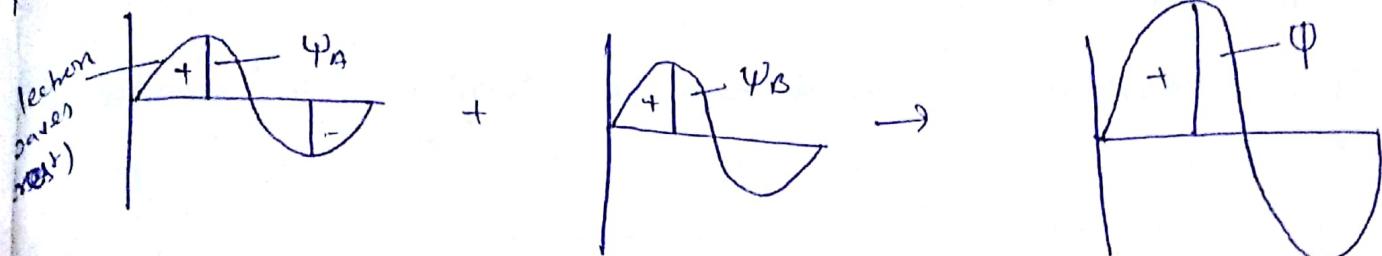
Then Acc. to LCAO. The M.O. ~~of~~  $H_2$  in the  $H_2$  molecule are given by linear combination (addition & subtraction) of wave functions of the individual atoms i.e. of  $\Psi_A$  &  $\Psi_B$  as shown below:

$$\Psi_{mo} = \Psi_A \pm \Psi_B$$

$$\Psi_b = \Psi_A + \Psi_B \quad (\text{constructive interference of waves}) \text{ BMO}$$

$$\Psi_a = \Psi_A - \Psi_B \quad (\text{destructive interference of waves}) \text{ A MO}$$

b)  $\text{BMO}$  → The molecular orbital  $\Psi_b$  formed by the addition overlap (constructive interference of waves) of atomic orbitals.



constructive interference

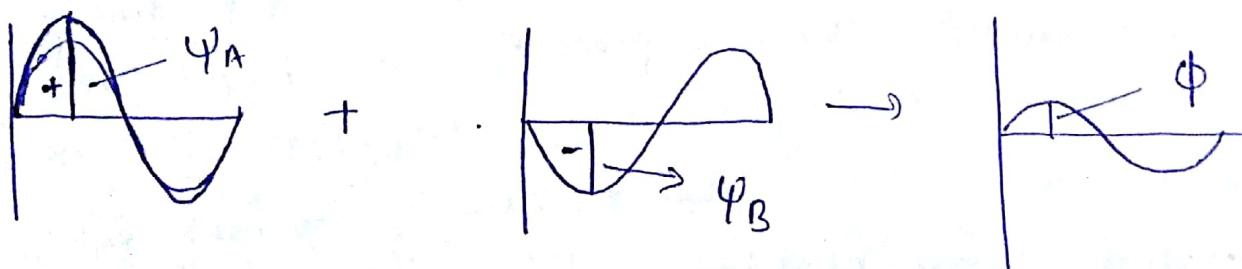
$$\Phi = \Psi_A + \Psi_B$$

→ If the crest of one wave overlaps with the crest of the other the two waves interact in a constructive interference and therefore the new resulting wave is reinforced. (Addition overlap)

### A $\text{BMO}$ (Anti-bonding molecular Orbital)

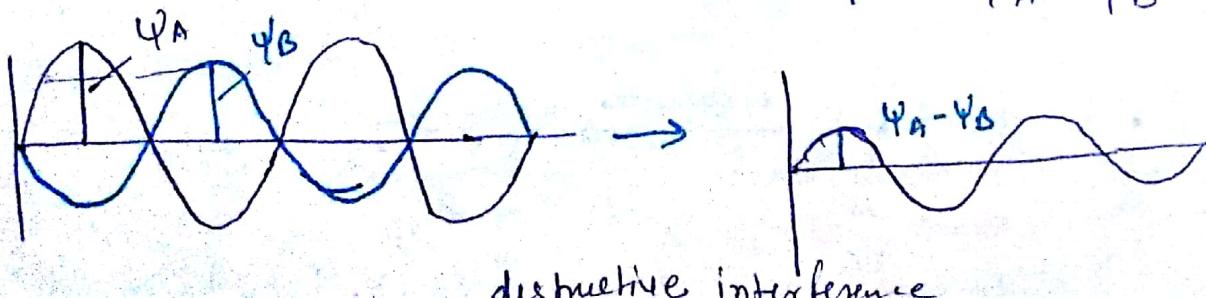
If the crest of one wave overlaps with the trough of the other, then two waves interact in a destructive manner. In other words, this is out of phase overlap or subtraction overlap and the resulting wave is weakened such type of subtraction overlap of atomic orbitals with opposite signs leads to the formation of

$\text{ABMO}$ .



$$\Phi = \Psi_A - \Psi_B$$

or



? Eg The combination of 1s orbitals of Hydrogen atoms to form molecular orbitals :-

The probability density of bonding molecular orbital ( $BMO$ ) is given by

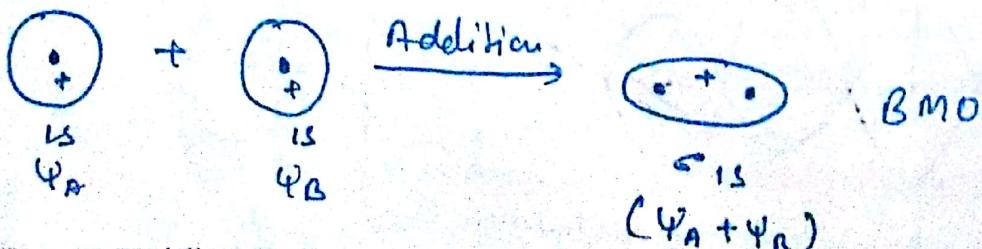
$$\Psi_b^2 \text{ or } (\Psi_A + \Psi_B)^2 \text{ or } (\Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B)$$

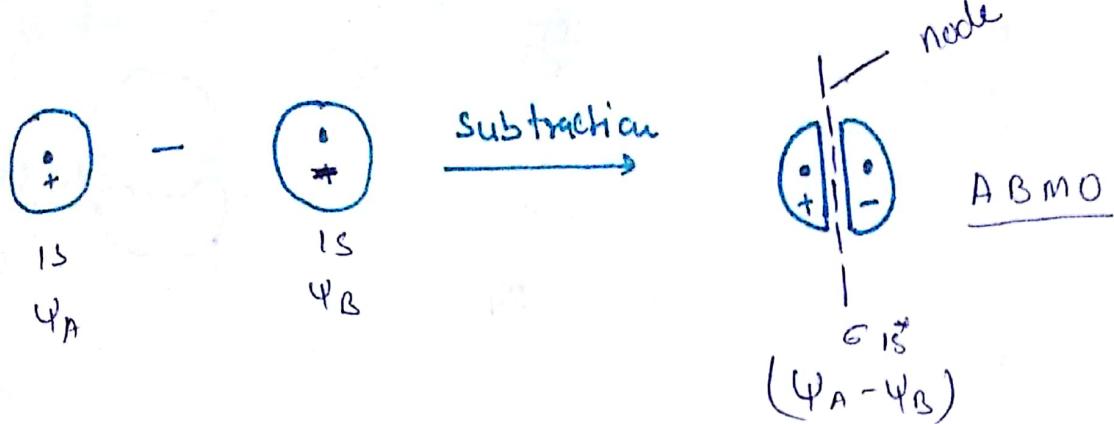
which means that shared e<sup>-</sup> density  $(\Psi_A + \Psi_B)^2$  is higher than the sum of the e<sup>-</sup> densities of two separate orbitals  $(\Psi_A^2 + \Psi_B^2)$ . Thus addition combination leads to ↑ in density b/w two nuclei A & B. In other words e<sup>-</sup> present in B MO experience greater force of attraction thereby lowering the energy of B MO as compared to individual atomic orbit

Why the probability density of AB MO is given by:

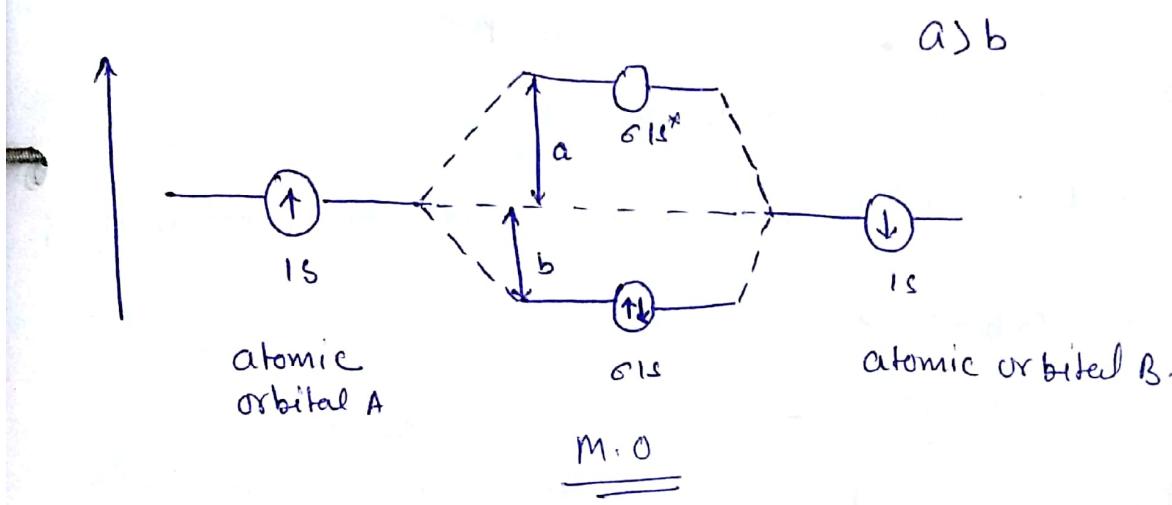
$$\Psi_a^2 \text{ or } (\Psi_A - \Psi_B)^2 \text{ or } (\Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B)$$

which means that shared e<sup>-</sup> density  $(\Psi_A - \Psi_B)^2$  is lower than sum of e<sup>-</sup> densities of separate orbitals  $(\Psi_A^2 + \Psi_B^2)$ . Thus subtraction combination leads to lowering of e<sup>-</sup> density in between the nuclei. The e<sup>-</sup>s present in the AB MO experience repulsive interaction thereby raising the energy of AB MO as compared to atomic orbitals. The e<sup>-</sup> density in fact is concentrated away from the nuclei creating a NODE in b/w the nuclei.





relative ~~Energy~~ Energies of atomic orbitals and M.O.  
in  $H_2$  molecule.



### Conditions for the Combination of atomic Orbitals

1. The combining atomic orbitals should have almost same energies.

eg: In 'homonuclear' nuclear diatomic molecule:-

$$1s + 1s = \text{Possible}$$

$$\text{but } 1s + 2s = \text{not possible}$$

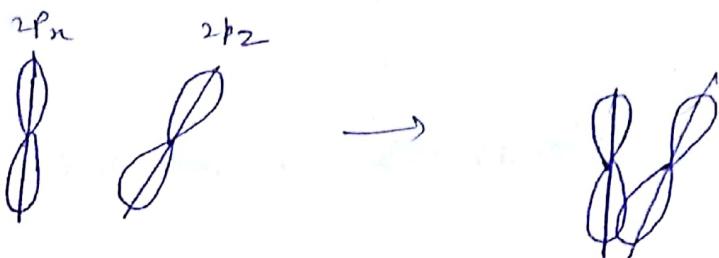
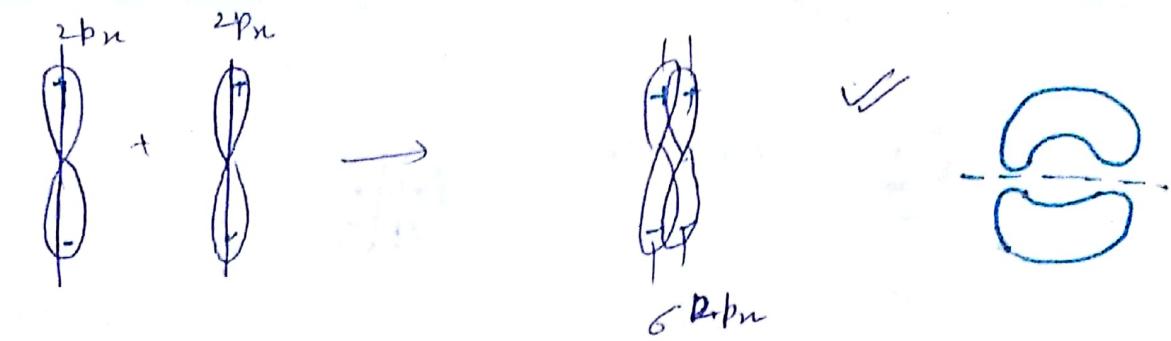
2. The extent of overlap b/w the AOs of the two atoms should be large.

3. The combining atomic orbitals should have the same symmetry about the molecular axis

$$\text{eg: } 2p_x + 2p_x = \text{Possible due to same symmetry}$$

$$2p_y + 2p_y = \text{Combination possible "}$$

$$\text{but } 2p_x + 2p_z = \text{not possible}$$

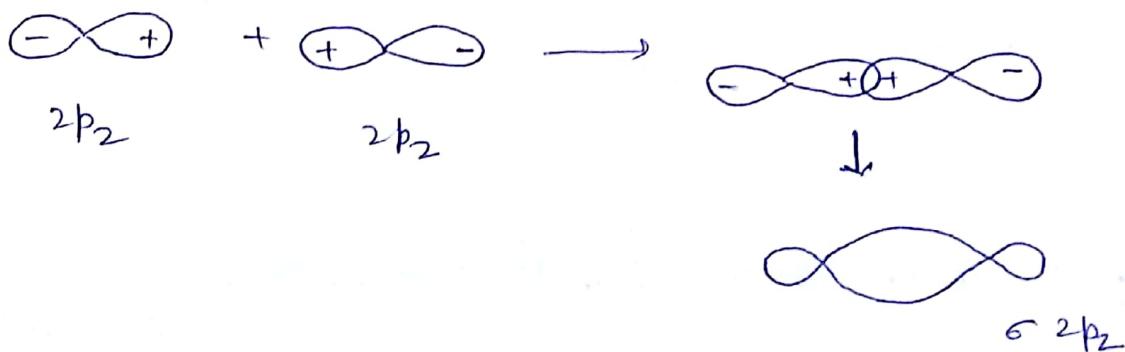


not possible.

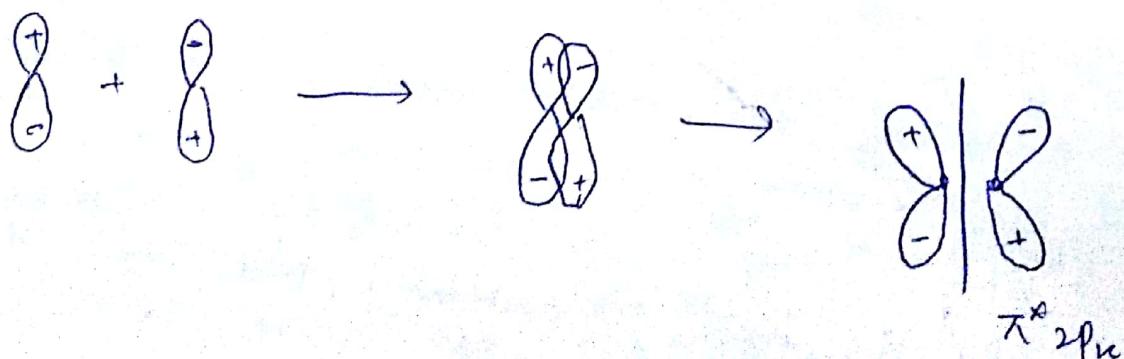
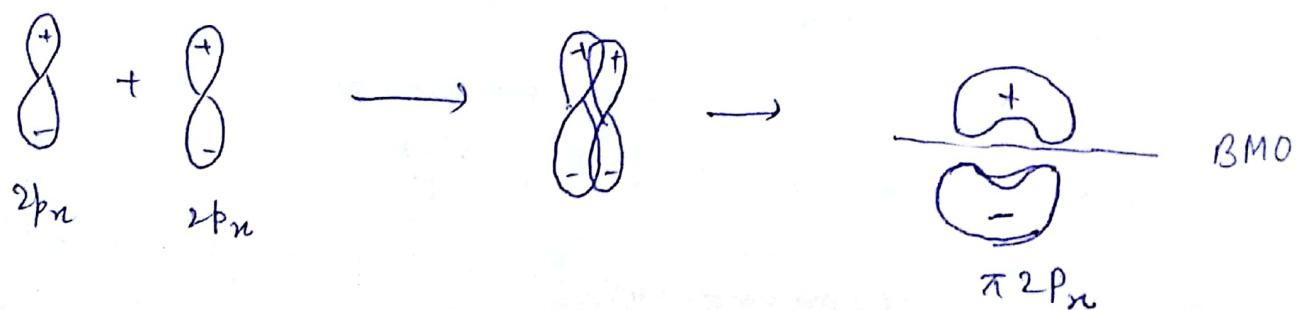
### Formation of some molecular Orbital

The molecular orbitals which is formed by overlapping of atomic orbitals along internuclear axis.

#### 6 molecular orbital



#### π molecular orbital



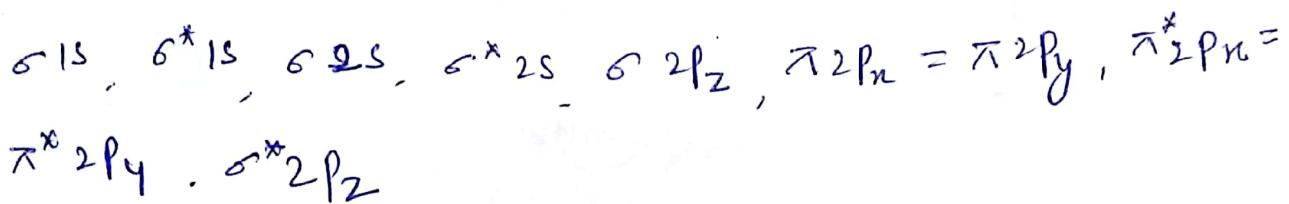
## Rules for filling e<sup>-</sup>s in M.O.

### a) Pauli Exclusion Principle:-

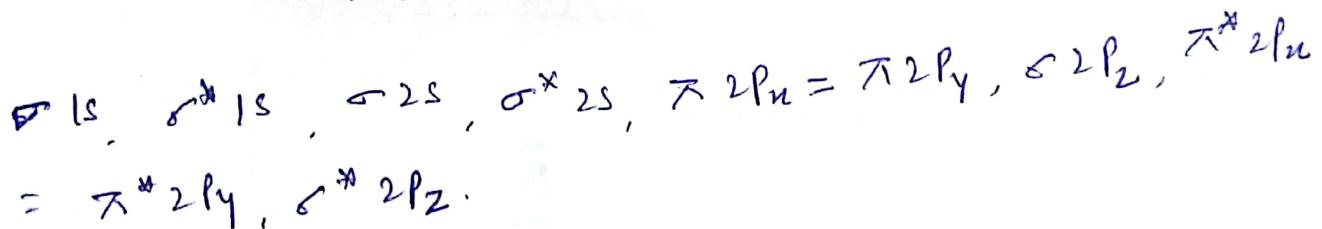
Acc. to this a 'MO' have maximum two e<sup>-</sup>s and that two are of opposite spin.

### b) Aufbau's Rule Acc. to this e<sup>-</sup>s are filled in various molecular orbitals in rising order of their energies

#### Order for O<sub>2</sub>, F<sub>2</sub>, Ne<sub>2</sub>



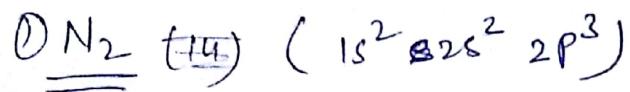
#### Other than O<sub>2</sub>, F<sub>2</sub>, Ne<sub>2</sub>



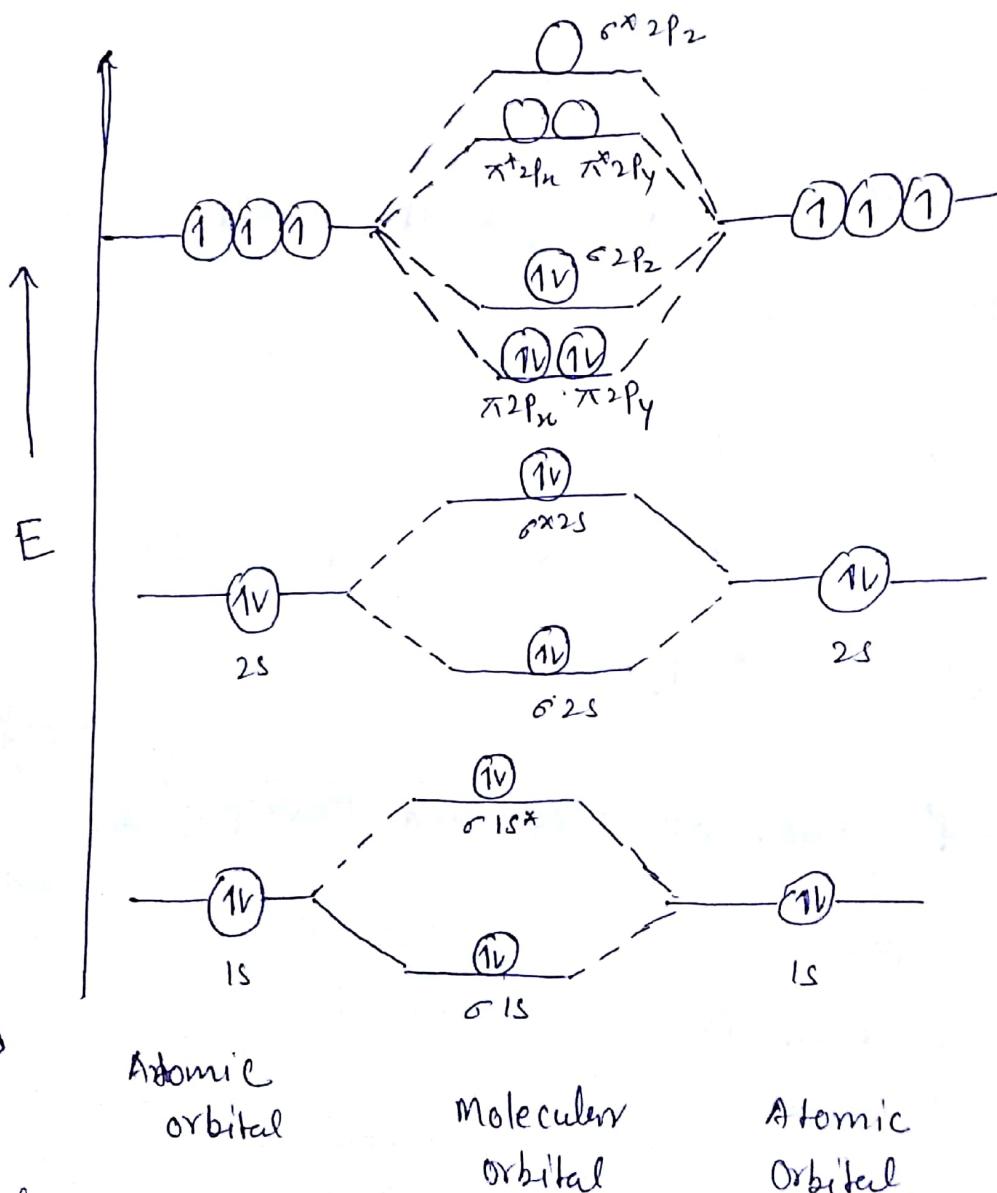
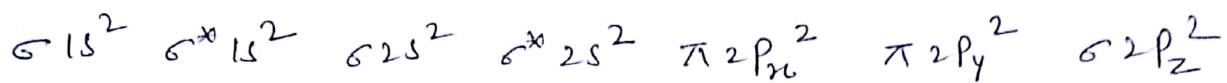
### c) Hund's Rule of Maximum Multiplicity:-

The pairing of e<sup>-</sup>s in degenerate orbitals does not take place until these are singly filled.

molecular orbital energy level diagram for diatomic homonuclear molecules such as :



Electronic configuration of N<sub>2</sub> (14)



No. of Bonding electrons = 10

No. of Antibonding electrons = 04

→ Bond energy is very high, about 945 KJ/mole

$$B.O. = \frac{1}{2} [N_b - N_a]$$

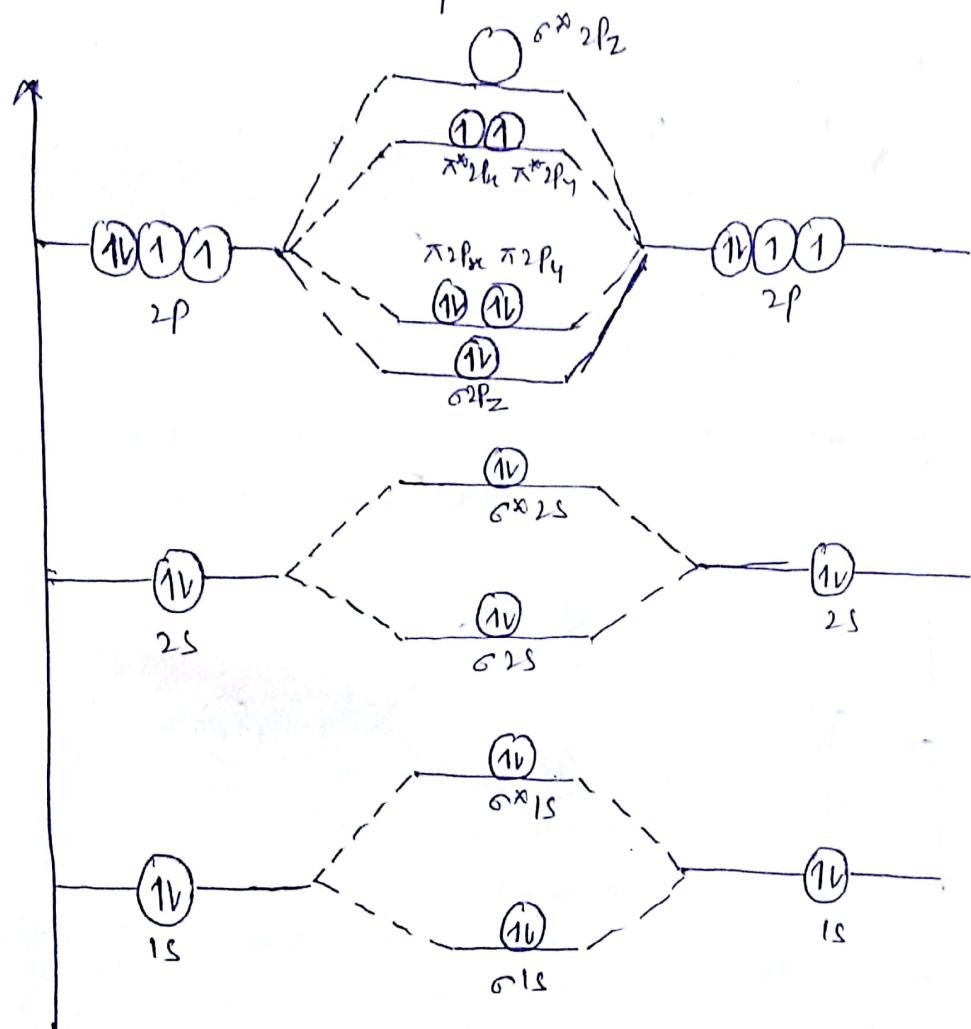
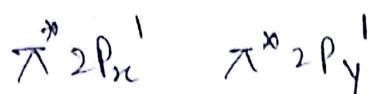
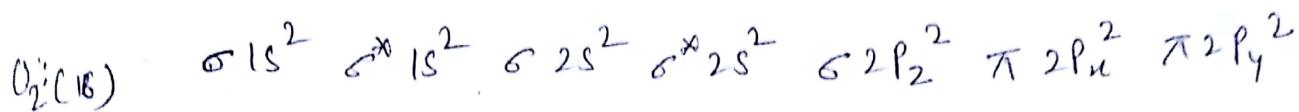
$$= \frac{1}{2} [10 - 4] = \frac{6}{2}$$

$$B.O. = 3 \boxed{N \equiv N}$$

→ All  $e^-$ 's are paired  $\rightarrow$  it is a diamagnetic molecule.

Oxygen ( $O_2$ ) molecule ( $1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_u^2 \pi^* 2p_y^2$ )

Electronic configuration of  $O_2$ :



Atomic  
orbital

Molecular  
orbital

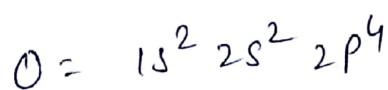
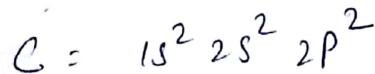
Atomic  
orbital

$$\text{no. of Bonding electrons} = 10$$

$$\text{no. of Antibonding } e^- \text{'s} = 6$$

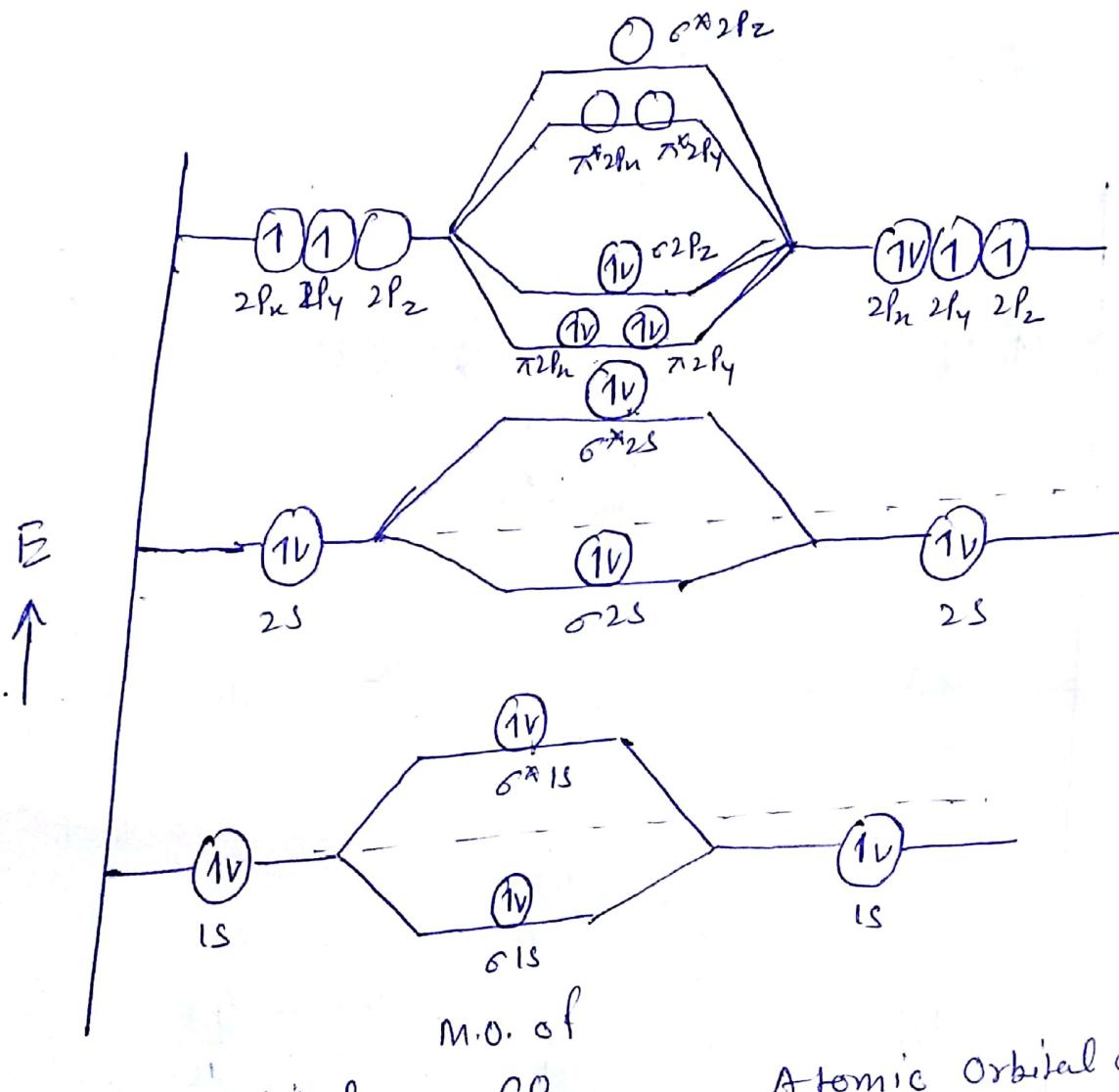
$$\text{B.O.} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 6] = \frac{4}{2} = 2$$

Molecular Orbital of CO [CO is isoelctric with N<sub>2</sub>]



$$CO(14) = \text{C } 1s^2 \text{ } 6^* 1s^2 \text{ } 6 \text{ } 2s^2 \text{ } 6^* 2s^2 \text{ } \pi^* 2p_x^2 = \pi^* 2p_y^2 \text{ } 6 \text{ } 2p_z$$

$$\pi^* 2p_x^0 = \pi^* 2p_y^0 \text{ } 6^* 2p_z$$



Atomic Orbital  
of C

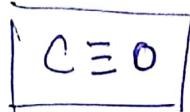
(less electronegative  
atom)

M.O. of  
CO

Atomic Orbital of  
'O'

(more Electronegative  
atom)

$$\begin{aligned}
 \text{Bond order} &= \frac{1}{2} [N_b - N_a] \\
 &= \frac{1}{2} [10 - 4] \\
 &= \frac{6}{2} = 3
 \end{aligned}$$



→ Diamagnetic

Note: Bond order :- It may be defined as the half of difference b/w the no. of e<sup>-</sup>s present in the bonding orbitals and the antibonding orbitals.

$$\frac{1}{2} [\text{no. of e}^- \text{ in BMO} - \text{no. of e}^- \text{ in A(BMO)}]$$

Those with positive bond order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

Magnetic Behaviour :- If all the molecular orbitals in species are spin paired, the substance is diamagnetic.

But if one or more molecular orbitals are singly occupied it is paramagnetic.

Paired e <sup>-</sup> s	=	diamagnetic nature
Unpaired e <sup>-</sup> s	=	Paramagnetic nature

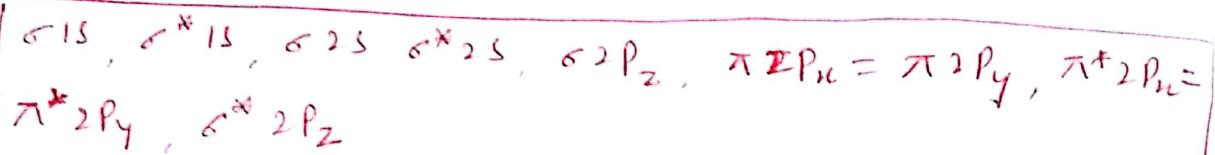
CO molecule is diamagnetic as all the e<sup>-</sup>s in CO are paired.

Before M.O. of diatomic molecule.

## Energy level diagram of diatomics

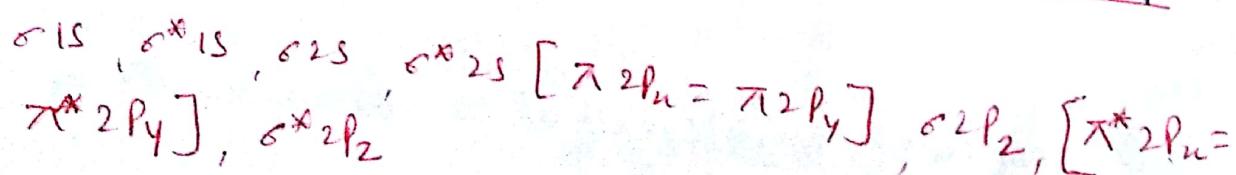
The factors upon which relative energies of molecular orbitals depend are:

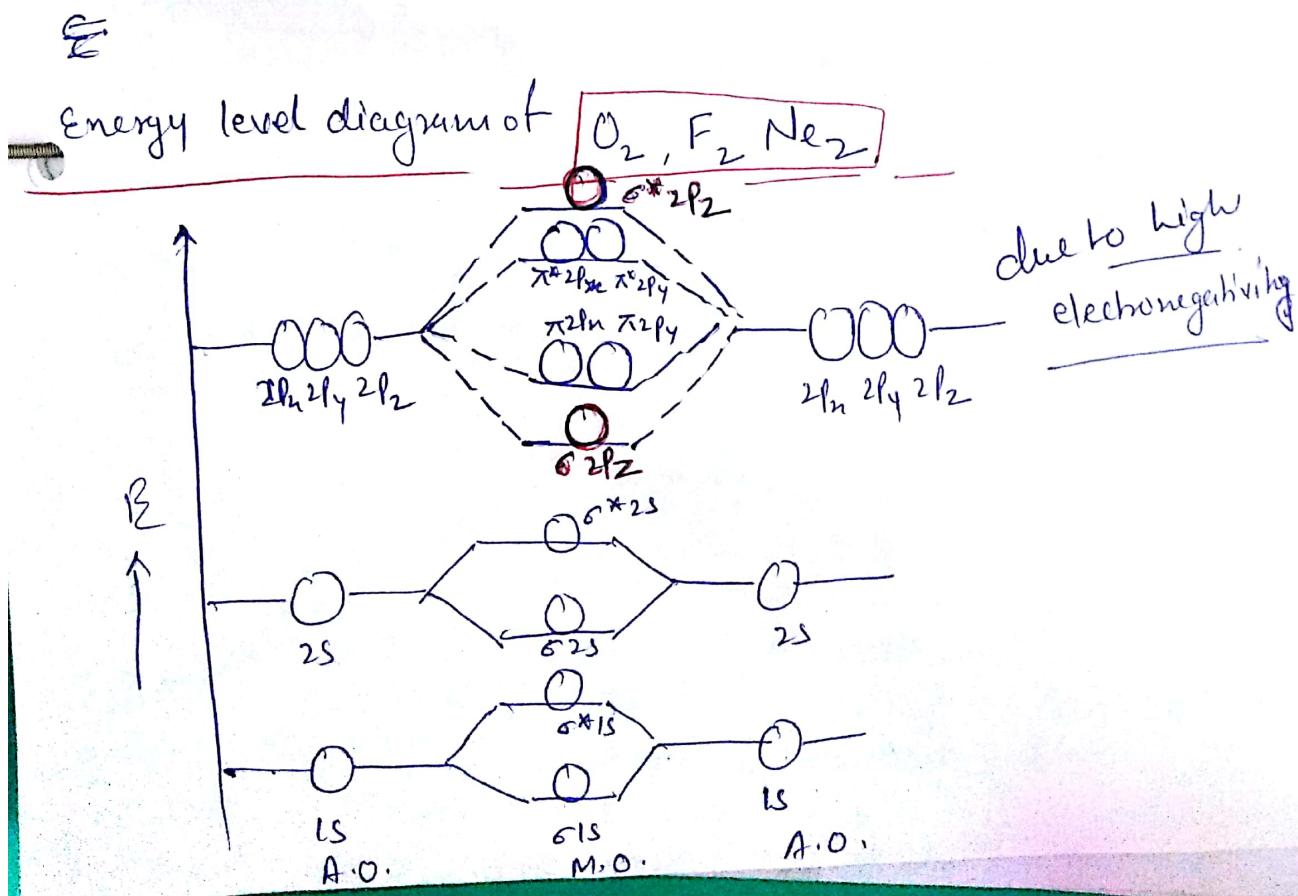
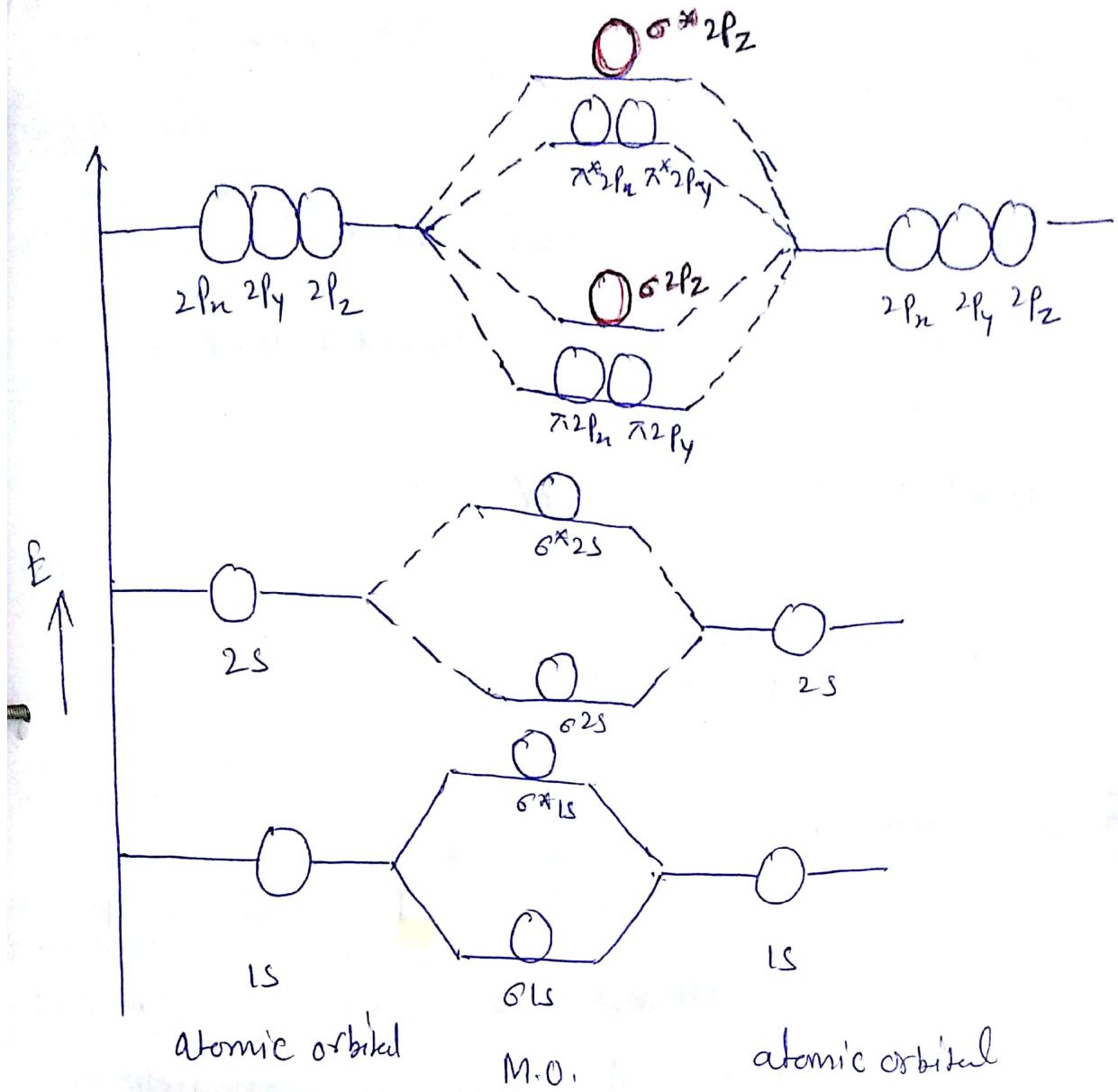
- I) Energies of the atomic orbitals combining to form molecular orbitals
- II) The extent of overlapping between the atomic orbitals.  
The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs
- III) The order of ~~Ring~~ energy of m.o. obtained by combination of 1s, 2s + 2p orbitals of two atoms :-



(Energy rises from left to right)

But experimental evidence for some diatomic molecules have shown that the above sequence of energy levels of MOs is not correct for all the molecules, for e.g. homonuclear diatomic molecules of 2nd row elements like  $[Li_2, Be_2, B_2, C_2, N_2]$ , the  $\sigma 2p_z$  MOs is higher in energy than  $\pi 2p_n$  &  $\pi 2p_y$  MOs.  
Order is





Analysis done by Bond Order (significance of M)

① Positive B.O. = Stable molecule

negative or zero B.O. = Unstable molecule

2) Bond dissociation energy of  $\text{BeO}_2$

③  $\text{B.O.} \propto \frac{1}{\text{Bond length}}$

4) magnetic character :

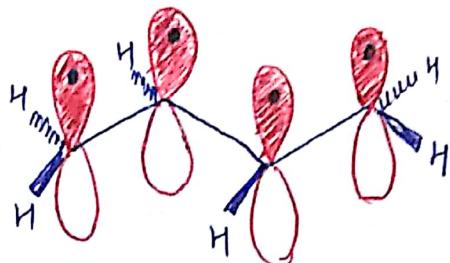
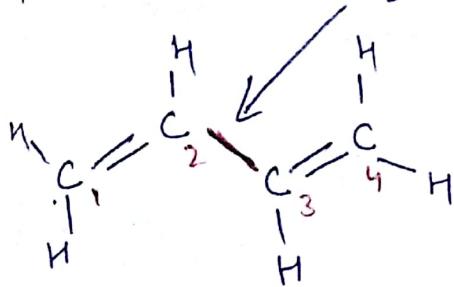
~~all  $e^-$ 's paired  $\rightarrow$  Diamagnetic (repelled by magnetic field)~~

unpaired  $e^-$ 's  $\Rightarrow$  Paramagnetic (molecule will be attracted by magnetic field)

will be attracted by magnetic field)

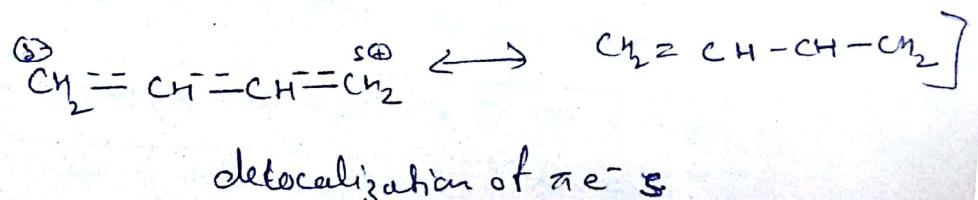
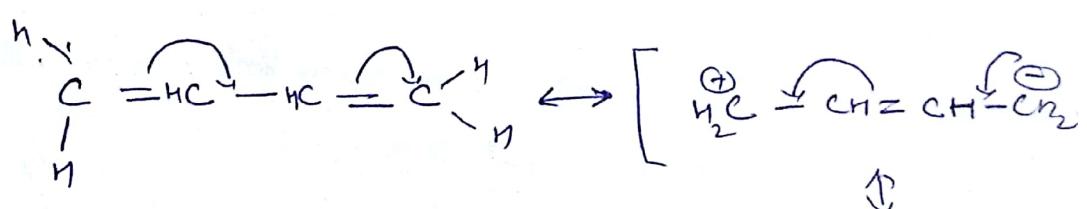
$\pi(\pi)$  molecular Orbitals of butadiene

1, 3 butadiene barrier of rotation



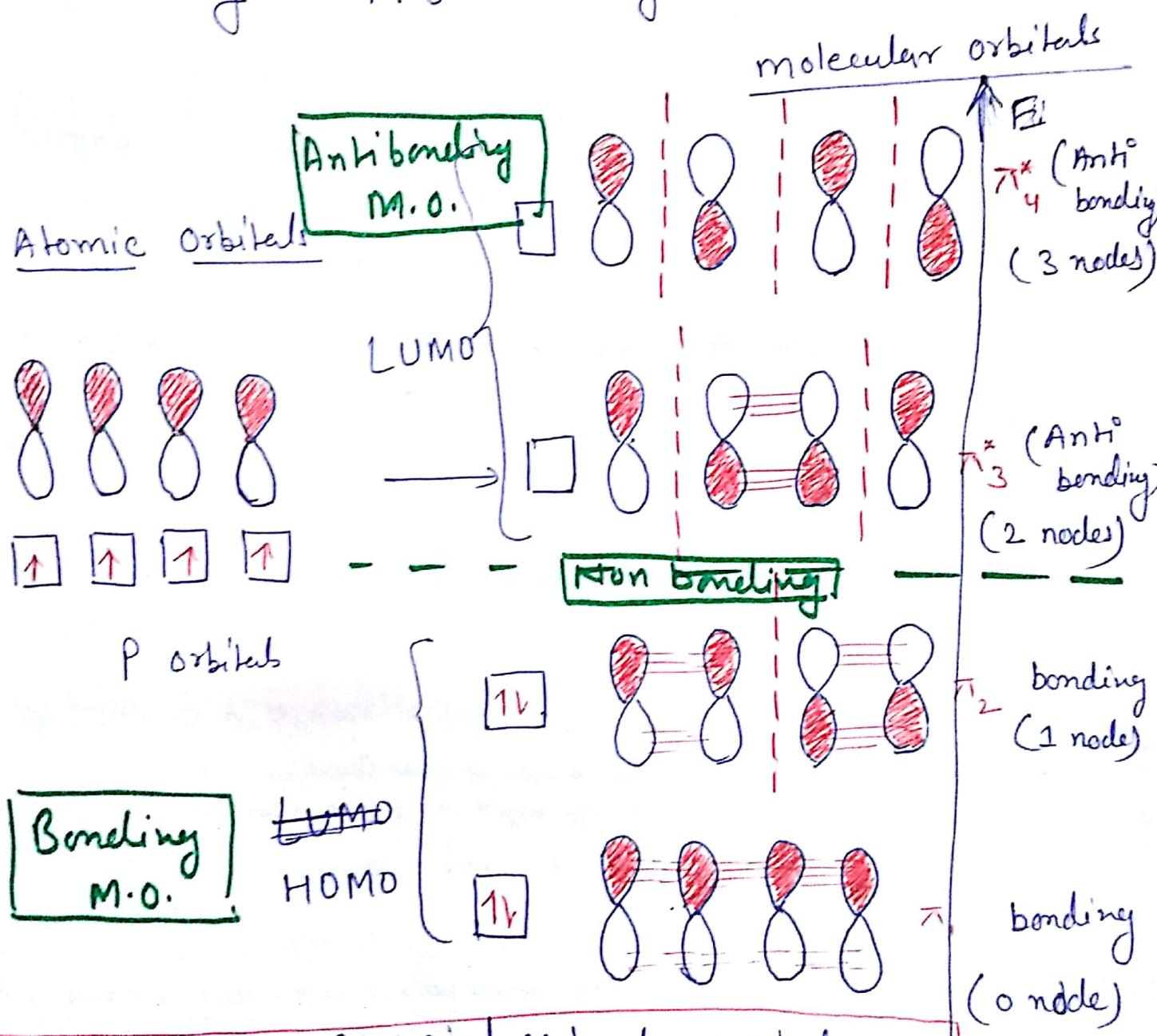
1, 3 butadiene

In 1, 3 butadiene molecule, From valence orbital theory alone we might expect that the  $C_2 - C_3$  bond in this molecule, because it is a sigma bond, would be able to rotate freely. Experimentally, however, it is observed that there is a significant barrier to rotation about the  $C_2 - C_3$  bond due to delocalization of  $\pi e^-$ s. and that the entire molecule is planar. In addition, the  $C_2 - C_3$  bond is 148 pm long (shorter than a typical C-C single bond 154 pm) and longer than a typical double bond 134 pm). due to delocalization of  $\pi e^-$ s.



Acc. to MOT

The four  $2p$  atomic orbitals combine mathematically to form  $4\pi$  molecular orbitals of increasing energy. Two of these are bonding M.O. having lower energy than the  $p$  atomic orbitals from which they are formed, while two of the antibonding  $\pi^*$  M.O. are higher in energy.



HOMO - Highest Occupied Molecular Orbital

LUMO - Lowest Unoccupied Molecular Orbital

The lowest energy M.O.,  $\pi_1$ , has only constructive interaction and "0" node.

$\pi_2$  Orbital has '1' node but two constructive interactions thus it is still a bonding orbital overall.

The Two antibonding orbitals,  $\pi_3^*$  has "2" nodes and one constructive interaction, while  $\pi_4^*$  has "3" nodes and zero constructive interaction.

By the Aufbau principle, the 4  $\pi$ e<sup>-</sup>s from the isolated  $2p_{\pi}$  atomic orbitals are placed in the bonding  $\pi_1$  &  $\pi_2$  MOs. b/w  $\pi_1$  includes constructive interaction b/w  $C_2$  &  $C_3$ . There is a degree, in the 1,3 butadiene molecule, of  $\pi$  bonding interaction b/w these two carbons. which accounts for its shorter length and barrier to rotation. However, MOT predicts that the 4  $\pi$ e<sup>-</sup>s are to some extent delocalized or "spread out", over the whole  $\pi$  system.

### Note:

- The no. of M.O. for a  $\pi$  system is equal to the no. of contributing P orbitals.  
For butadiene, we had 4 contributing P orbitals and thus 4  $\pi$  m.o. are formed
- The no. of nodes b/w P orbitals increases by 1 for each successive energy level such that the highest energy orbital has (n-1) nodes.

## (π) molecular Orbitals of benzene and aromaticity

A molecular Orbital description of benzene provides a more satisfying and more general treatment of "aromaticity".

Benzene has cyclic

- Planar hexagonal structure in which all the carbon atom  $sp^2$  hybridized.
- All carbon-carbon bonds are equal in length due to delocalization of  $\pi$  e<sup>-</sup>s.
- Stable compound

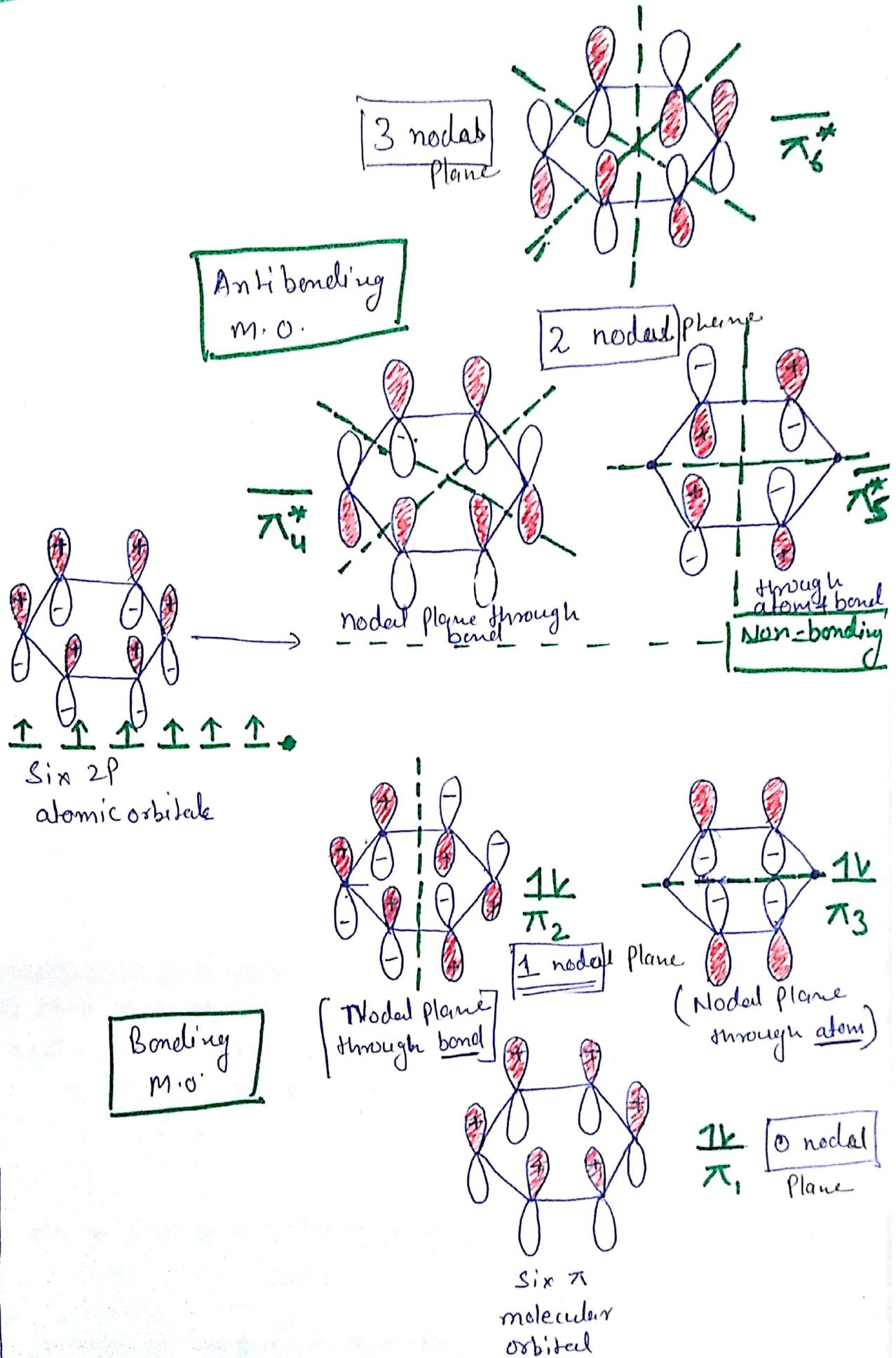
"Aromaticity" - To be aromatic a compound must conform to all ~~the~~ of the following criteria:

- Cyclic arrangement of p orbitals
- There is a p orbital on every atom of an aromatic ring.
- Planar structure.
- Conjugation
- must follow Hückel  $(4n+2)\pi e^-$  Rule.

$(4n+2)\pi e^-$  where n is any integer (0, 1, 2, 3, 4)

In other words aromatic compounds have 2, 6, 10, 18 —  $\pi$  e<sup>-</sup>s.

It is clear that Benzene is ~~an~~ aromatic compound and shows Aromaticity. ~~because~~ it shows all the above



is impossible to draw a cyclic pi-system with one node, but we can draw a system with one nodal plane. For instance, we draw a nodal plane that cuts through two single bonds ( $\pi_2 \rightarrow$  through bond). We can also draw a nodal plane through atoms as in ( $\pi_3 \rightarrow$  through atoms).

These two molecular orbital ( $\pi_2$  &  $\pi_3$ ) have same no. of nodal plane, therefore same energy. So these orbitals are degenerate.

→ This is the key difference in molecular orbital picture of cyclic system vs acyclic ~~the~~ systems. The next level up has two nodal planes. Again there are two ways to cut it, cut through the bonds ( $\pi_4^* \rightarrow$  through bonds) or through the atoms ( $\pi_5^* \rightarrow$  through atoms)

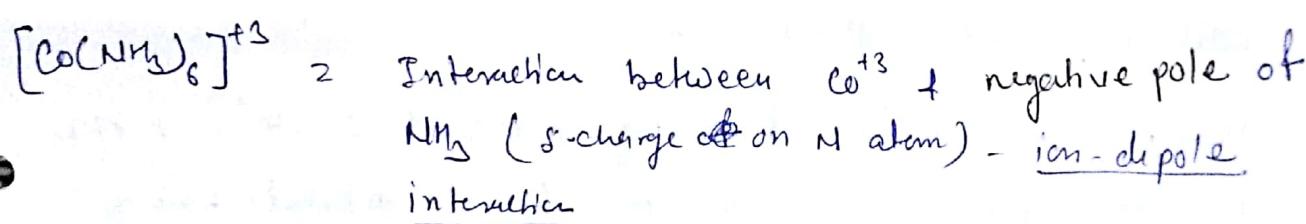
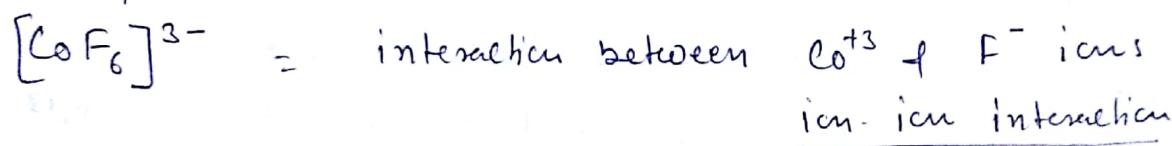
# CRYSTAL FIELD THEORY (CFT)

Dr. Poornam

The valence bond theory considers the bonding b/w the metal ion and the ligands are purely covalent. On the other hand, CFT is based on the assumption that the metal ion and the ligands act as point charges and the interactions between them are purely electrostatic.

- In case of negative ligands (anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CN}^-$ ) the interactions with  $M^{+n}$  are ion-ion interaction.
- If the ligands are neutral molecules (such as  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ), the interactions with the metal ions are ion-dipole interaction.

for e.g.:-



## 1. Degenerate Orbitals :-

In the case of free metal ion, all the five d-orbitals have the same energy, are called degenerate orbitals. This means that an  $e^-$  can occupy any one of these orbitals ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$ ,  $d_{z^2}$ ).

However, on the approach of the ligands, the orbital  $e^-$ s will be repelled by the lone pair of the ligands.

The repulsion will raise the energy of the d-orbitals. If all the ligands approaching the central metal ion are at equal distance from each of the d orbitals, the

of each orbital will increase by the same amount due to symmetrical field of ligand. Therefore, these orbitals will still remain degenerate, but they will have higher energy than that of the free ion.

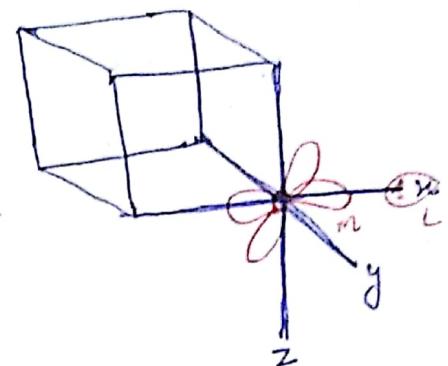
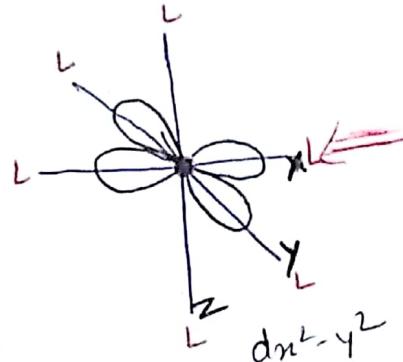
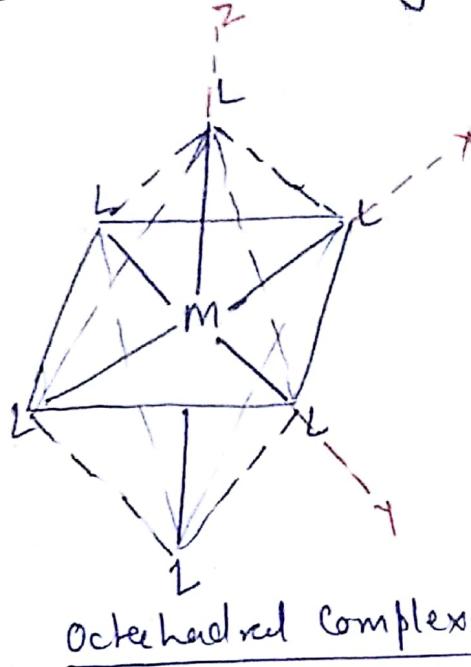
### Crystal field splitting

We know that d-orbitals have different orientations and therefore, these orbitals will experience different interactions from the ligand. The orbital lying in the direction of the ligand, will experience greater repulsion and their energies will be raised relative to their positions in a symmetrical field. On the other hand, the orbitals lying away from the approach of the ligands ~~would be lower~~ ~~they would~~ will have lesser interactions with the -ve charge of donor atoms and therefore their energies will be lower than they would be in spherical field.

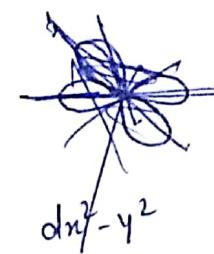
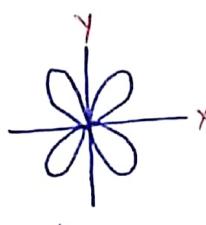
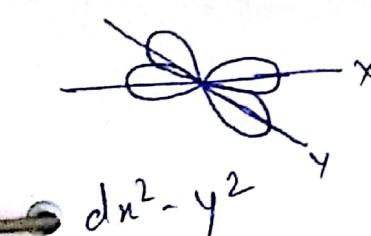
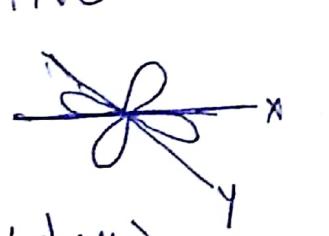
This conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electrical field of ligands is called crystal field splitting. This concept forms the basis of CFT.

The Crystal field splitting will be different in different structures with different co-ordination numbers.

## Crystal field splitting in Octahedral Complex.



five d orbitals (shapes)



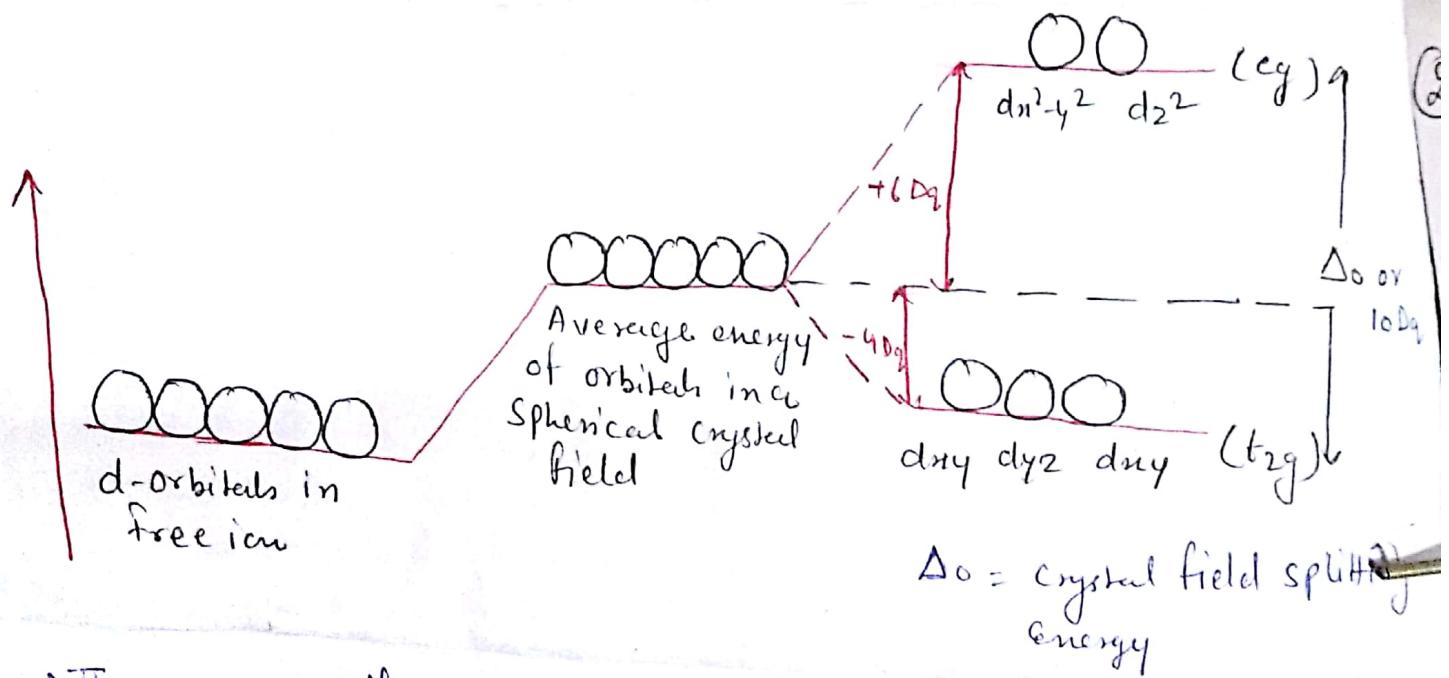
In case of Octahedral complexes, the five d-orbitals split up into two sets:

eg set of orbitals consisting of two orbitals ( $d_{x^2-y^2} + d_{z^2}$ ) of higher energy, called eg set. & These orbitals have their lobes arranged along the axis. These orbitals are also called named as axial orbitals. Term eg refers to doubly degenerate according to group theory (e = doubly degenerate set)

(cont'd)

$t_{2g}$  set of orbital:- This set consisting of three orbitals ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) of lower energy. These orbitals have lobes lie b/w the axes. ~~and~~ These orbitals are also ~~b/w~~ or non-axial orbitals. Group theory calls three orbitals as  $t_{2g}$  where "t" refers to triply degenerate.

### ① The splitting of d-orbitals in octahedral molecule



→ The energy difference b/w the two sets of energy levels is called crystal field splitting energy and is represented as  $\Delta_0$  ("o" stands for octahedral). It measures the crystal field strength of the ligands.

→ Splitting occurs in such a way that the average energy of ~~the~~ d-orbitals does not change. This means that the three orbitals lie at an energy that is  $\frac{2}{5} \Delta_0$  below the

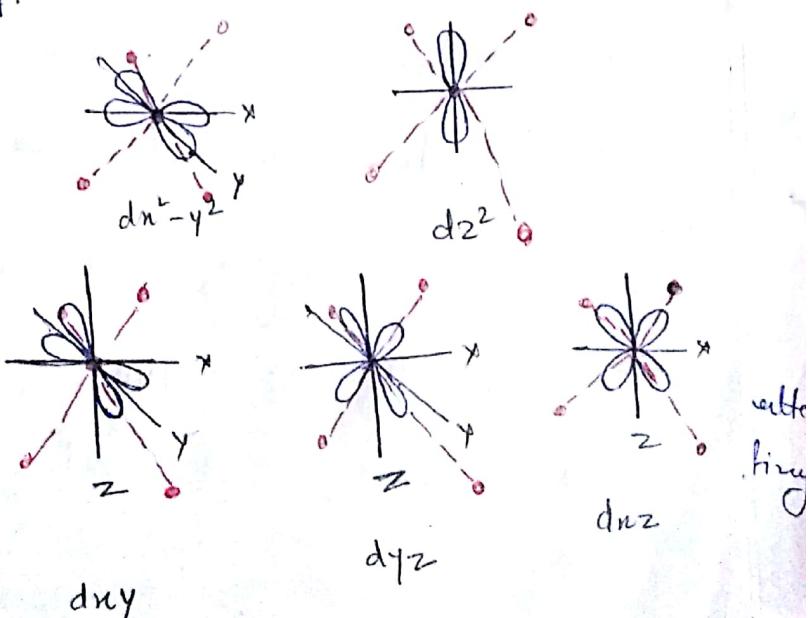
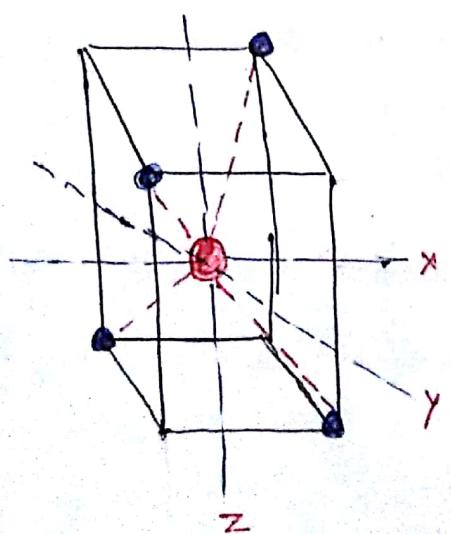
The average d-orbital energy and the two d-orbitals lie at an energy  $\frac{3}{5}\Delta_0$  above the average energy.

In an octahedral, the e<sup>-</sup>'s are attracted to the axes.

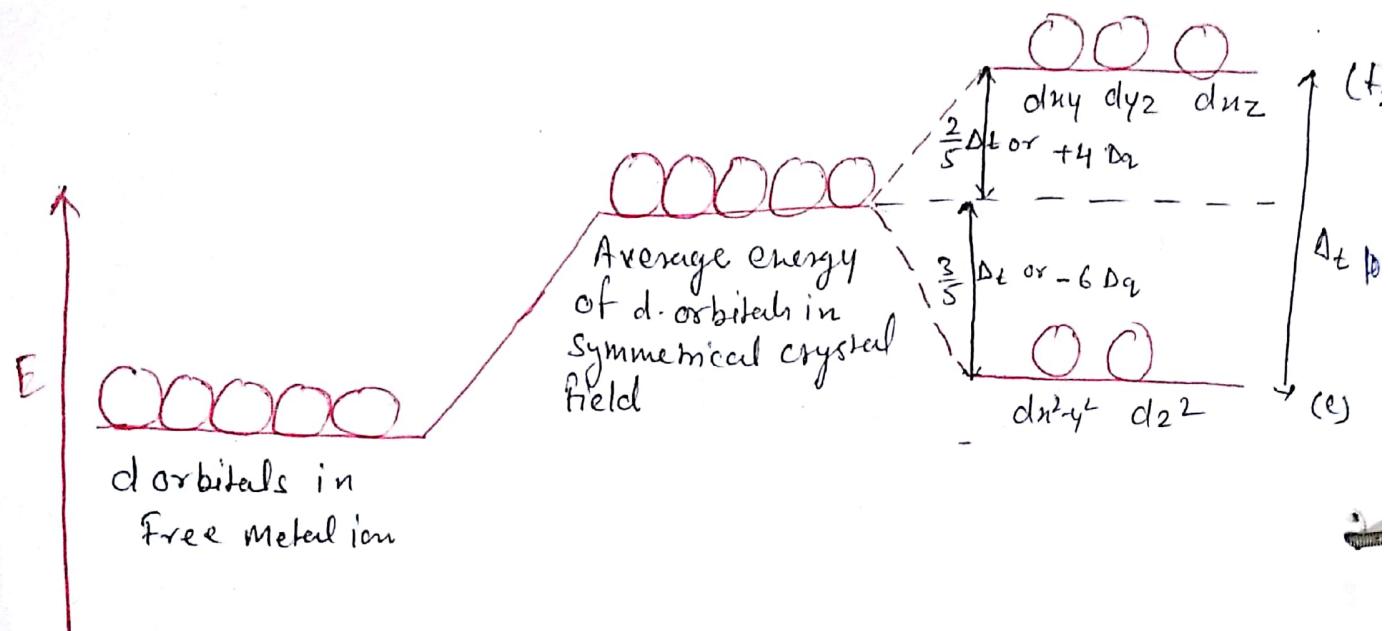
Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of eg are higher ( $0.6\Delta_0$ ) while t<sub>2g</sub> is lower ( $0.4\Delta_0$ )

## ② Splitting of d Orbitals in the Tetrahedral Molecule

In a tetrahedral complex, there are 4 ligands attached to the central metal. The d orbitals also split into two different sets of energy levels. The top three consist of the d<sub>xy</sub>, d<sub>nz</sub>, d<sub>y<sup>2</sup></sub>(t<sub>2</sub>) orbitals. The bottom two consist of the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and d<sub>z<sup>2</sup></sub> orbitals(e). The reason for this is due to poor orbital overlap b/w the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligand are not.



→ Splitting of the degenerate d-orbitals in tetrahedral field



In tetrahedral field,  $t_{2g}$  set has higher energy.

The magnitude of  $\Delta_t$  is considerably less than in octahedral field, which is mainly due to reason:-

- 1) In tetrahedral complex, there are only 4 ligands instead of six.
- 2) In tetrahedral complex, the direction of orbitals does not coincide with the direction of ligand. Both factors reduces CFSE by  $\frac{2}{3}$  rd so  $\Delta_t$  is roughly  $\frac{4}{9}$  times to  $\Delta_O$  OR

The difference in the splitting energy is tetrahedral splitting constant ( $\Delta_t$ ), which less than  $\Delta_O$  for the same ligand.

$$\boxed{\Delta_t = 0.44 \Delta_O}$$

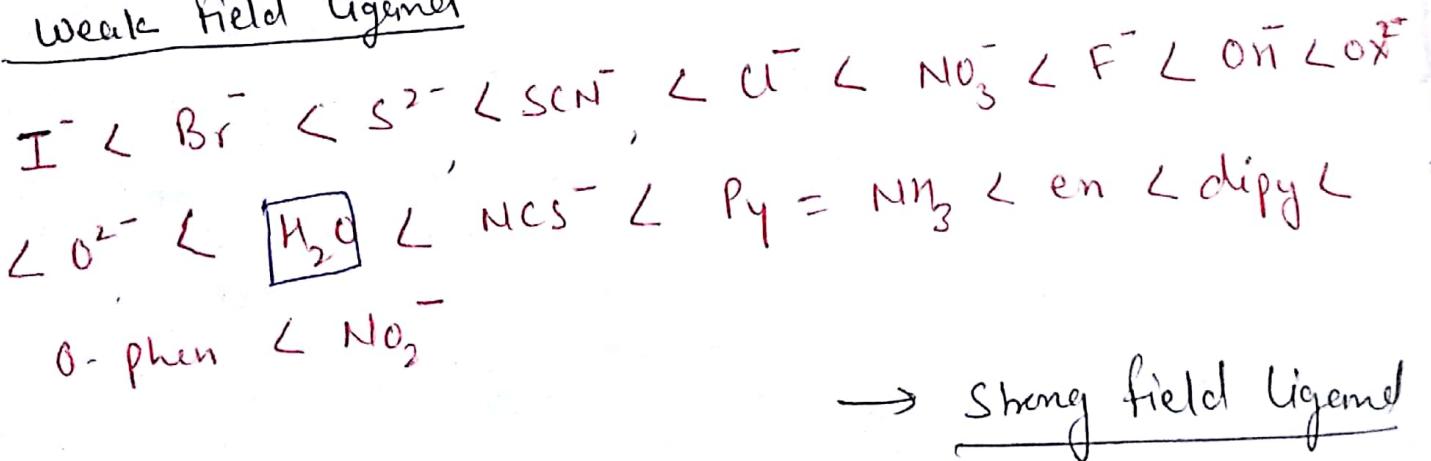
Consequently,  $\Delta_t$  is typically smaller than the spin pairing energy, so tetrahedral complexes are usually high spin.

## Spectrochemical series

The CFT depends upon the nature of the ligands. The greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it. The ligands which cause only a small degree of crystal field splitting are called weak field ligands while those which cause a large splitting are called strong field ligands.

Thus, ligands can be arranged acc. to the magnitude of the  $\Delta_o$  and this arrangement is called spectrochemical series.

### Weak field ligand



Note:- Ligands lying above  $H_2O$  are called strong field ligand and they cause greater crystal field splitting (or high  $\Delta_o$ ). On the other hand the ligands below  $H_2O$  and below it are called weak field ligands & they cause lesser crystal field splitting (or low  $\Delta_o$ )

## Important Postulate of CFT :-

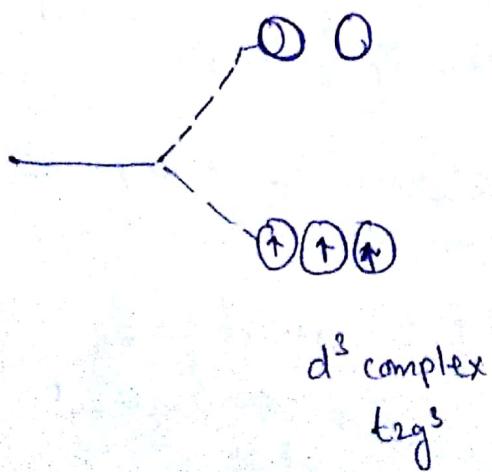
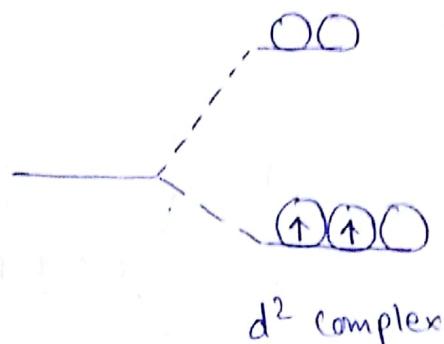
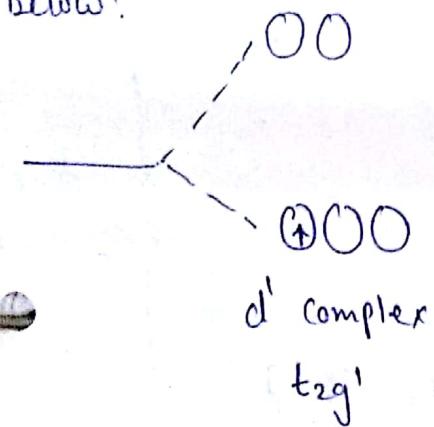
- ① The five d-orbitals in an isolated gaseous metal have same energy and are degenerate. The degeneracy is maintained till metal ion is surrounded by symmetrical field.
- ② When a complex is formed, the metal ion is surrounded by ligands. If this field produced by ligands is symmetrical then d-orbitals remain degenerate but ~~but~~ in most of the complexes, the field produced by ligand is not symmetrical, so degeneracy is lost b/c as the d-orbitals are not affected equally by ligand field.
- ③ The removal of degeneracy of d-orbitals leads the splitting of d-orbitals and their energies. It is known as crystal field splitting (CFS). The pattern of splitting depends upon nature of crystal field.

## Electronic structures and Properties of complexes according to CFT (Consequences of d-orbital splitting $\rightarrow$ Magnetic behaviour and magnetic behaviour of)

The electronic configuration of complexes depend upon the crystal field splitting.

In Octahedral complexes, the 3 orbitals are of lower energy and two orbitals are of higher energy.

Acc. to Hund's Rule,  $e^-$ 's occupy a set of orbitals of same energy one at a time with their spins parallel. The  $e^-$ 's only pair up after each orbital gets one electron. So, for Complexes having upto three d-electrons ( $d^1, d^2, d^3$ ) each  $e^-$  can occupy a separate orbital in the lower set as shown below:



For a  $d^4$  complex, there are two Possibilities:

i) All the 4  $e^-$ 's may occupy lower set of orbitals with one  $e^-$  gets paired i.e  $t_{2g}^4$ . It experiences a strong repulsion from the  $e^-$  already there.

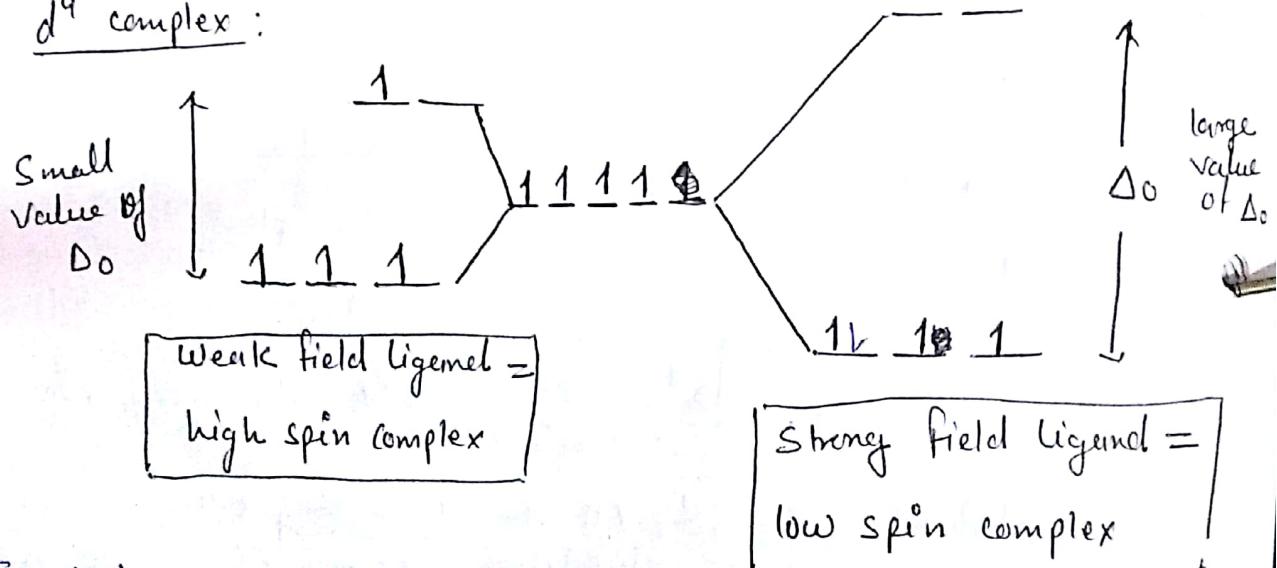
ii) The 3  $e^-$ 's occupy lower set of orbitals and the 4th  $e^-$  goes to one of the higher set of orbitals i.e.  $t_{2g}^3$  e.g.

→ If  $\Delta_0$  is large (as it is for strong field ligands),  
 The e<sup>-</sup>s will try to remain in the lower set of orbitals.  
 In this case, the complex has less no. of unpaired e<sup>-</sup>s  
 and is called low spin complex.

In this case the repulsion due to pairing of e<sup>-</sup>s will be less than  $\Delta_0$

→ If  $\Delta_0$  is small (as it is for weak field ligands)  
 then after filling the lower set of three orbitals with one e<sup>-</sup> each, the next e<sup>-</sup> goes to the higher set of orbitals. In this case, the repulsion due to pairing of e<sup>-</sup>s will be more than  $\Delta_0$ . The pairing of e<sup>-</sup>s will occur only after all the five orbitals are singly filled.

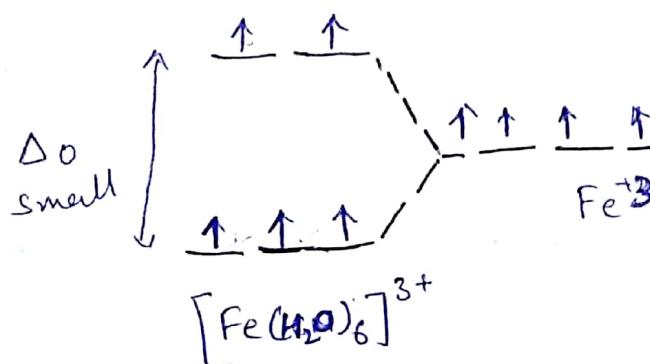
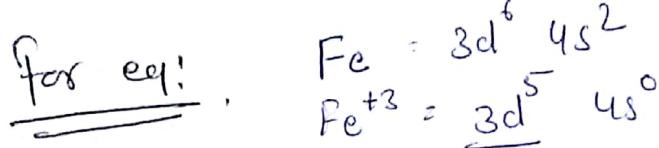
d<sup>4</sup> complex :



In this case, the complex will have maximum no. of unpaired e<sup>-</sup>s and is called high spin complex.

Hence: If  $\Delta_0$  is less  $\rightarrow$  4<sup>th</sup> e<sup>-</sup> will enter one of the eg orbitals giving configuration  $t_{2g}^3 eg'$  due to weak field ligand.  
 If  $\Delta_0$  is more  $\rightarrow$  The pairing will occur in the t<sub>2g</sub> orbital & configuration will

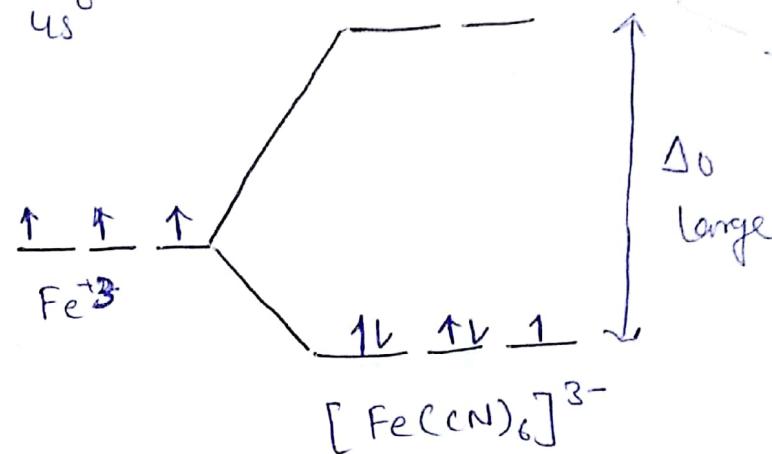
will be  $t_{2g}^4$  due to strong field ligand.



High spin complex

5 unpaired e<sup>-</sup>  
 Paramagnetism

$H_2O$  = weak field ligand

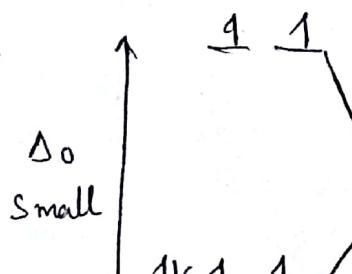
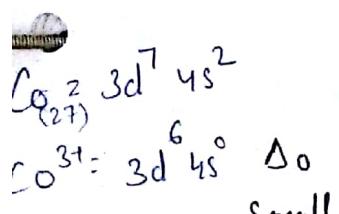


Low spin complex

1 unpaired e<sup>-</sup>

CN = Strong field ligand.

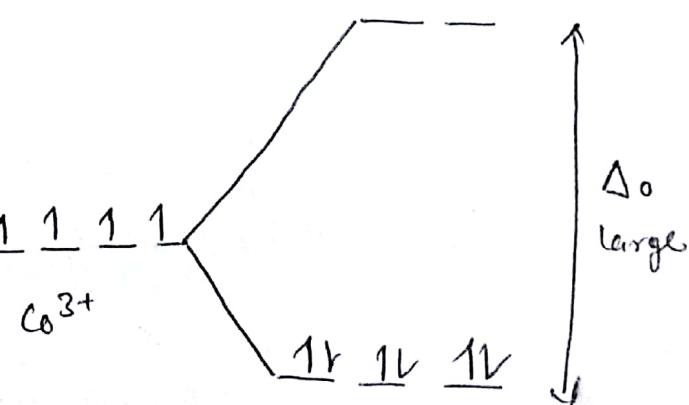
Let us consider the another eq:  $[\text{CoF}_6]^{3-}$  &  $[\text{Co(NH}_3)_6]^{3+}$  complexes:



High spin complex  
 4 unpaired e<sup>-</sup>s

Behaviour → Paramagnetism

F = weak field ligand



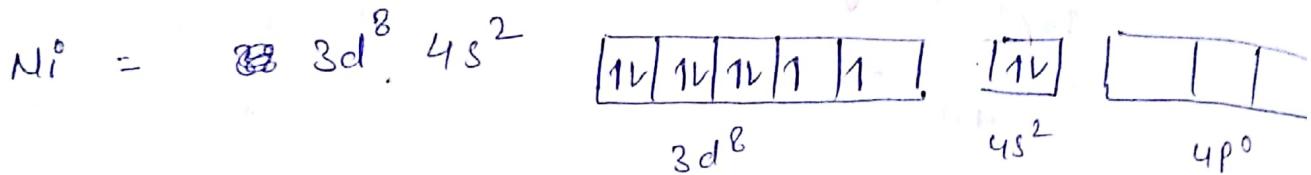
Low spin complex  
 No unpaired e<sup>-</sup>s

Behaviour → Diamagnetism

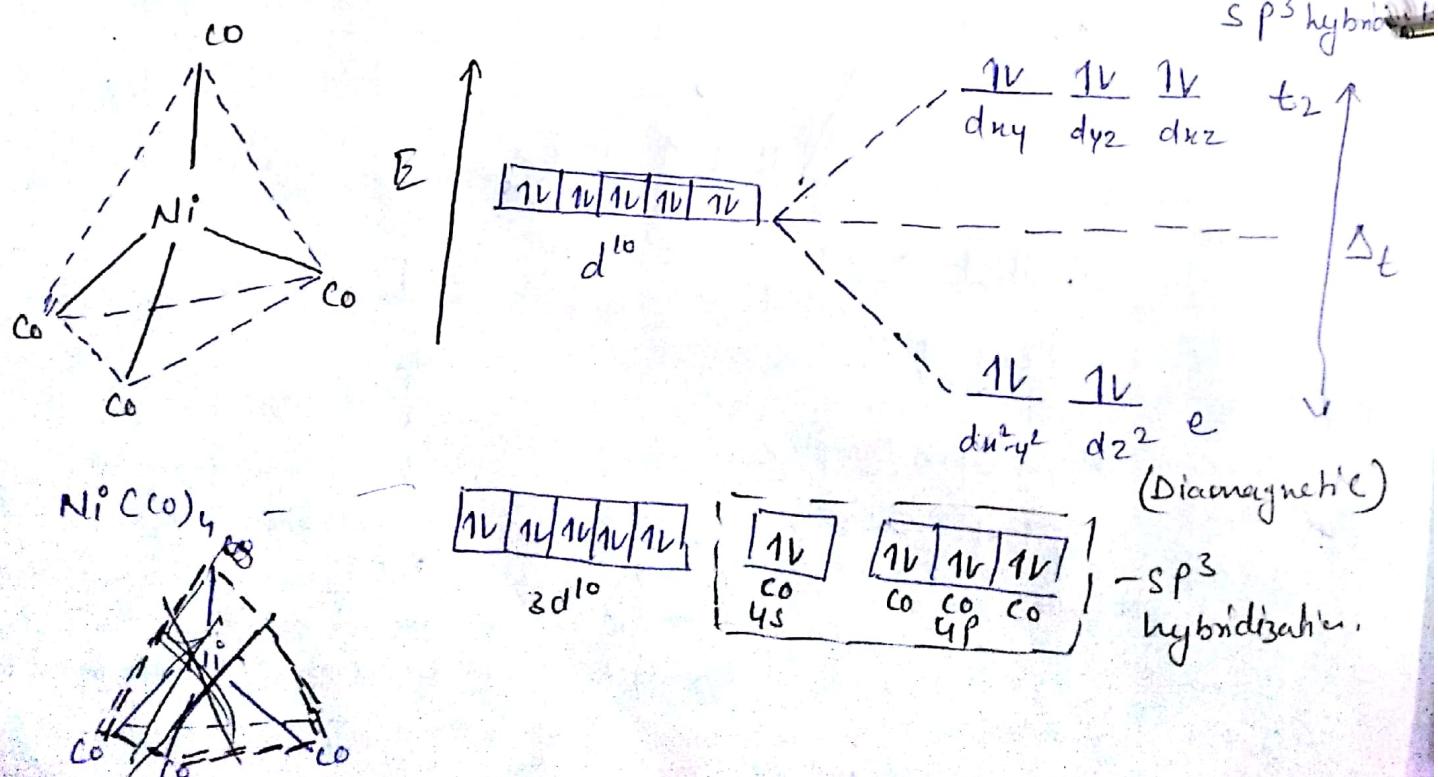
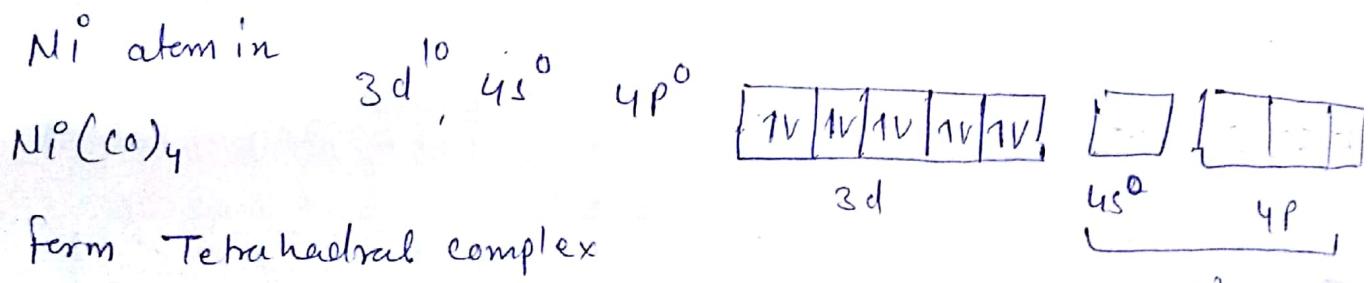
NH<sub>3</sub> → Strong field ligand

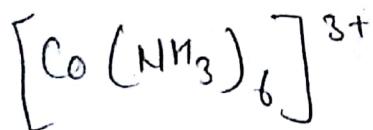
## Energy level diagram of $[\text{Ni}(\text{CO})_4]$

In  $\text{Ni}^0(\text{CO})_4$ , Ni has zero oxidation state and exists as  $\text{Ni}^0$ . Four ligands (CO) are attached to central metal atom Ni<sup>0</sup> and require four orbitals. The electronic configuration in  $\text{Ni}^0(\text{CO})_4$  can be written as:



In presence of 4 CO ligands, which is strong ligand, the e<sup>-</sup>'s pair up against Hund's Rule.



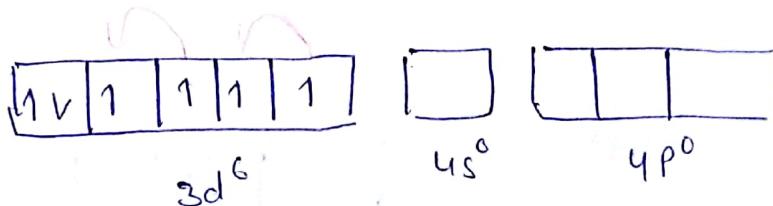


In  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , Co has +3 oxidation state and exist as  $\text{Co}^{3+}$ . Six  $\text{NH}_3$  ligands are attached to central metal ion and require 6 vacant orbitals.

The electronic configuration for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  may be written as

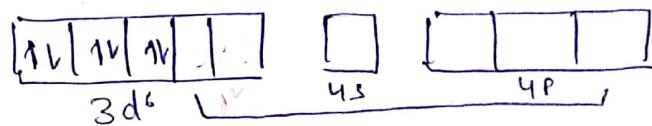
$$\text{Co} = 3d^7 4s^2$$

$$\text{Co}^{3+} = 3d^6 4s^0$$

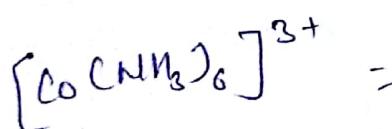


In the presence of  $\text{NH}_3$  ligands, the e<sup>-</sup> pair up  $\text{Co}^{3+}$  in such a way.

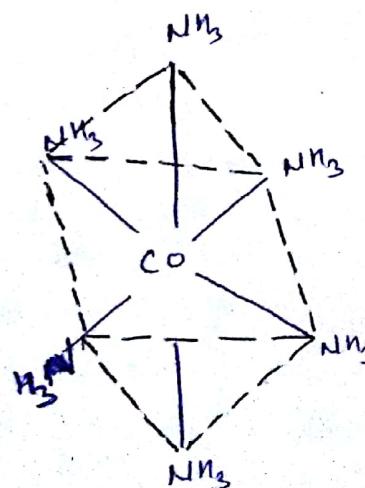
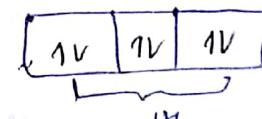
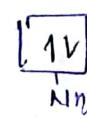
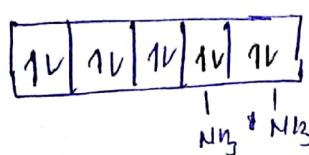
$$\text{Co}^{3+} \text{ in } [\text{Co}(\text{NH}_3)_6]^{3+} =$$



$d^2 sp^3$  hybridization

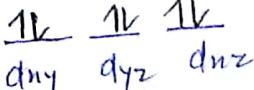
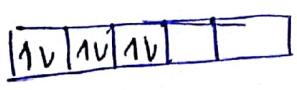
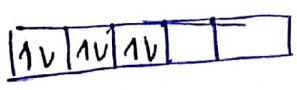
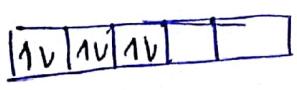


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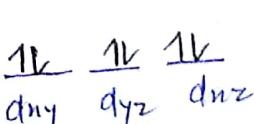
Octahedral complex

$E_g$



Low spin complex  
(Diamagnetic)

Large  $\Delta_o$  value



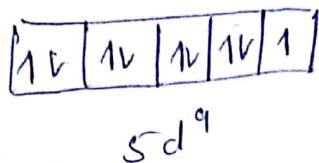
High spin complex  
(Paramagnetic)

## Energy level diagram of $[\text{PtCl}_2(\text{NH}_3)_2]$

Pt<sup>2+</sup> has d<sup>8</sup> as outer electronic configuration. This is the following scheme for formation of  $[\text{PtCl}_2(\text{NH}_3)_2]$

Free Pt<sup>2+</sup> ion (d<sup>9</sup>)

$[5\text{d}^9, 6\text{s}^1]$

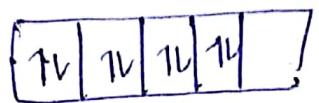


6P<sup>0</sup>

Excited

~~Free~~ Pt<sup>2+</sup> ion (d<sup>8</sup>)

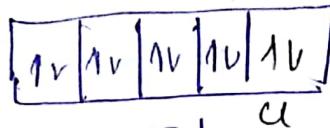
5d<sup>8</sup>, 6s<sup>0</sup>



dsp<sup>2</sup> hybridization

Pt Cl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>

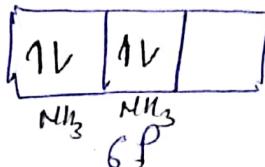
complex



5d



6s

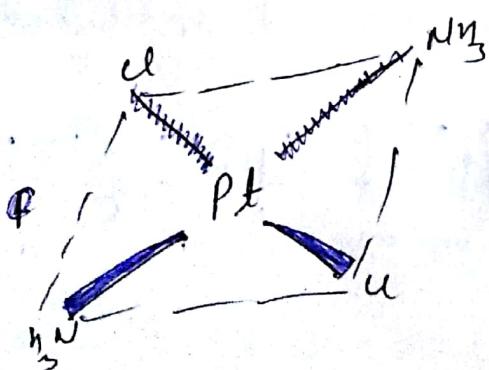


NH<sub>3</sub> NH<sub>3</sub>

6P

dsp<sup>2</sup> hybridization

Structure - Square planar



## Band Structure of Solids and Role of doping on band structure

The variation in the electrical conductivity of solids can be explained with the help of band theory.

\* In metals, the energy gap b/w the partially filled valence band and unoccupied conduction band is negligible.

\* The conductivity of a solid depends upon the energy gap between the different filled energy bands and the next vacant energy band. The outer filled energy band is called Valence band. and the next empty band in which e<sup>-</sup>s can move is called conduction band. The difference in energy b/w valence band and conduction band varies from one solid to another solid and determines the electrical conductivity.

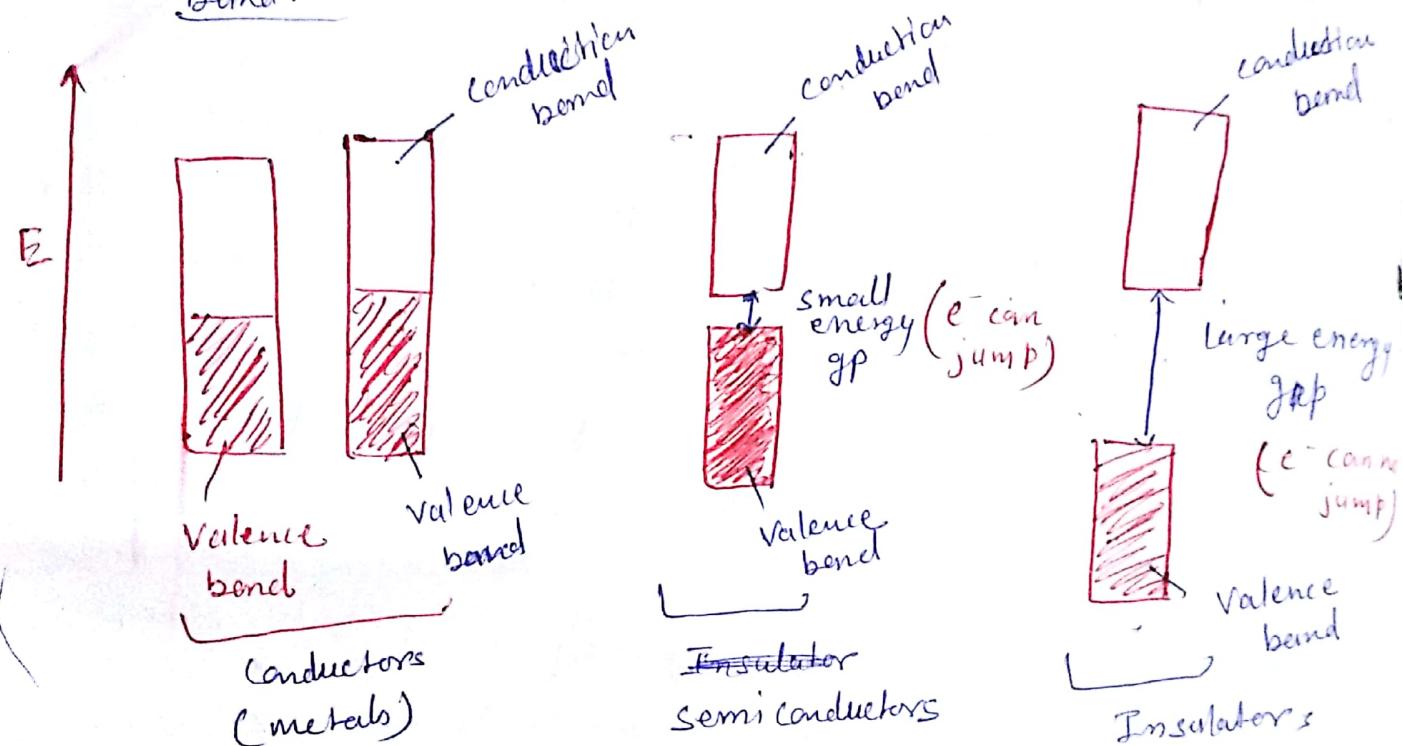
\* In metals:- The energy gap b/w the partially filled valence band and unoccupied conduction band is negligible. Rather they overlap and e<sup>-</sup> flow readily takes place.

In semi-conductor : There is small energy gap b/w valence band and conduction band. However some e<sup>-</sup>s may jump to the conduction band and these semi-conductors can exhibit a little electrical conductivity. e.g. In case of silicon and germanium, these are 111 kJ/mol and 63 kJ/mol respectively and the e<sup>-</sup> jump is feasible.

The conductivity of semi-conductor increases with rise in temp. b/c more e<sup>-</sup>s are now in a position to jump from the valence band to conduction band.

In Insulator : The energy gap are very large and no e<sup>-</sup> jump is feasible from the valence band to the conduction band.

Therefore insulators don't conduct electrically.  
 for e.g. - In case of diamond the energy gap  
 is the order of  $511 \text{ kJ/mol}$ . Therefore diamond  
 is an insulator. From the above discussion, we  
 conclude that conductivity in the solid is primarily  
linked with energy difference b/w valence and conduction  
bond.

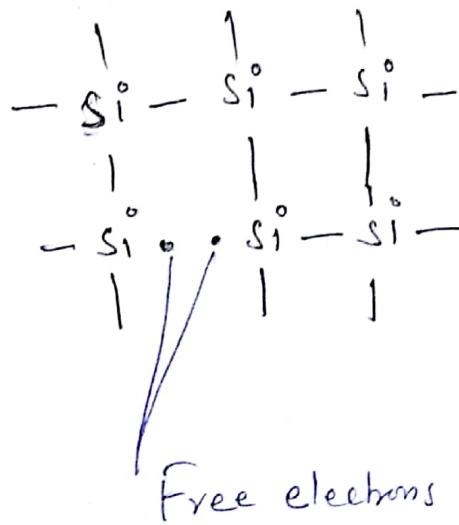


### Intrinsic and Extrinsic semiconductor

The insulators can be converted into semi-conductor in two ways. These are k/a/s Intrinsic & Extrinsic semi-conductors.

Intrinsic Semiconductor :- An insulator capable of conducting electric current at higher temp; is k/a/s intrinsic semi-conductor. This happens because certain covalent bonds are broken due to the energy supplied and the released electrons are in a position to conduct electric current. Silicon is one such example of

Intrinsic semi-conductors. The cleavage of only one Si-Si bond has been shown in fig:- )



### Extrinsic Semi-conductors :-

The extrinsic semi-conductors are formed when impurities of certain elements are added to the insulators. This process is known as doping which make electrons or holes available for conductivity.

Doping :- It is a process by which impurity is introduced in semiconductors to enhance their conductivity.

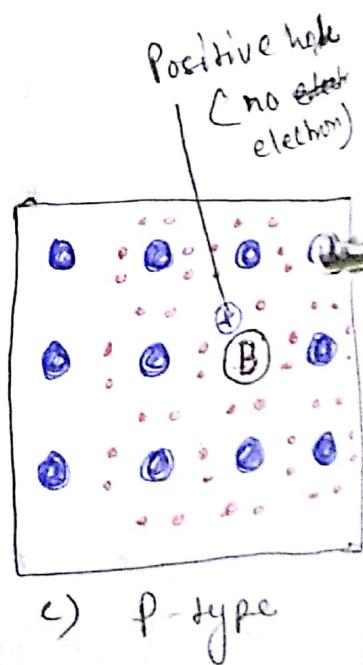
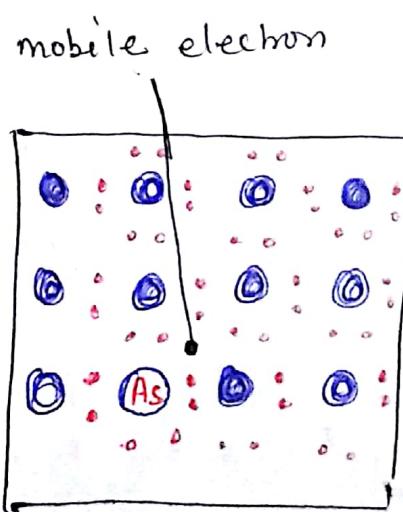
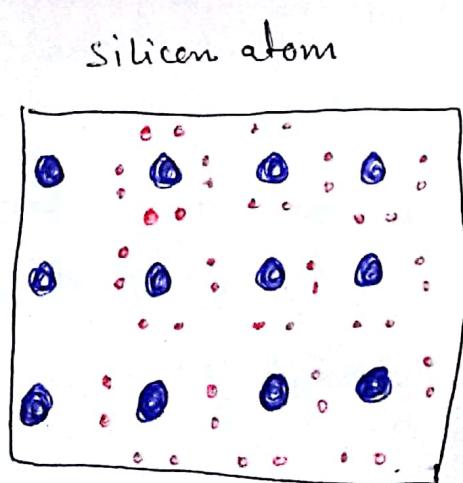
Doping leads to two types of semi-conductors.

- n-type semi-conductor
- p-type semi-conductor

n-type semi-conductor :- n-type semi-conductor are formed when impurity atoms containing more valence e<sup>-</sup>s than the atoms of the parent insulator are introduced in it.

These are called electron rich impurities.

for eg:- When Si or germanium crystal is doped with a Group 15 element like P or As, the dopant atom forms four co-valent bonds like Si or Ge atom but the 5<sup>th</sup> e<sup>-</sup> not used in bond becomes delocalised and contributes its share towards electrical conduction. Thus Si or Ge doped with P or As (having 5 valence e<sup>-</sup>s) is called n-type semiconductor. "n" indicates negative charge of electron. since it is the electron that conducts electricity.



### p-type semi-conductor

These are formed when impurity atoms containing lesser no. of valence electrons than the atoms of the parent insulator element are added to it. These are called e<sup>-</sup> deficient impurities.

for e.g.: When group 13 element such as B or Al are add to pure Si crystal (group 14 element), due to only three valence electrons of B or Al, dopant atom form three covalent bonds but at the place of 4<sup>th</sup> e<sup>-</sup> a hole is created. This hole moves through the crystal like a +ve charge giving rise to electrical conductivity. Thus Si or Ge doped with B or Al is called p-type semiconductor ("P" stands for positive charge); since positive hole is responsible for electrical conductivity.

### Uses of semi-conductor

1. Used in transistors, digital cameras, digital computers.
2. Also used in solar batteries, and television sets.
3. n-p junctions formed as a result of combination of n and p-type semi-conductors are employed in rectifiers.