

## Unit -I

### Molecular structure theories of Bonding

→ Democritus a Greek philosopher proposed that matter can be divided to smallest particle called "atom" which can't be further divided. Democritus idea was ignored.

In Greek "atom" means not able to divide or "indivisible"

→ Later "John Dalton" (1776-1844) <sup>given</sup> explanations about atom. This theory is called as John Dalton theory.

→ structure of the atom :-

Atom consist of a nucleus containing protons, neutrons which is surrounded by e<sup>-</sup>s.

proton carries +ve, neutron zero, e<sup>-</sup> -ve

These are called Fundamental particles.

Concept of orbital :- / Atomic orbitals :-

orbit :- 1) orbit defined as a circular path around the nucleus.

2) orbits are represented by <sub>n=1 n=2 n=3 n=4</sub> K, L, M, N notations.

maximum no. of e<sup>-</sup>s that can be accommodated in given orbit =  $2n^2$

## Solar system

The paths on the planets revolve are called orbits.

## Orbitals :-

- orbital is a 3-dimensional space around the nucleus. It gives maximum probability of finding of  $e^-$ s.
- "In quantum mechanics atomic orbital is a mathematical function that describes the wave like behaviour of either one  $e^-$  or a pair of  $e^-$ s in an atom"
- Atomic orbital may also refer to the physical region or space where the  $e^-$ s are ~~per~~ can be found to be present.
- Each orbital in an atom is characterised by quantum numbers. ( $n, l, m_s$ ).
- principle quantum number  $\rightarrow$  Given ~~shapes~~ sizes ( $n$ ) of orbitals
- Azumutal quantum number ( $l$ )  $\rightarrow$  Given shapes of orbitals
- Magnetic quantum number ( $M$ )/( $m_s$ )  $\rightarrow$  orientation of orbitals determined.
- spin quantum number ( $s$ )  $\rightarrow$  It determines spin of an electron.

## Differences between orbit & orbital :-

### orbit

- 1) It is a circular path
- 2) orbits designated by Capital letters (K, L, M, N etc)
- 3) An orbit indicates the exact position of  $e^-$ s of atom  
does not
- 4) Orbit follows uncertainty principle
- 5) circular path around the nucleus in which an electron moves

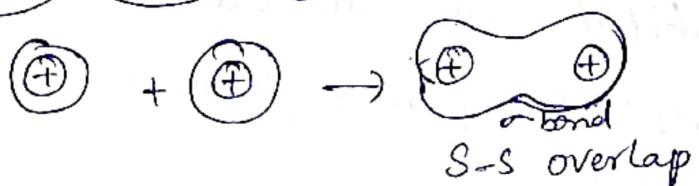
### orbital

- 1) It have different types of shapes.
- 2) orbitals designated by S, P, d, f etc.
- 3) An orbital does not specify the exact position of an  $e^-$  of an atom
- 4) Orbital follows the uncertainty principle
- 5) Specific region of Space around nucleus in an atom, where there is maximum prop probability of finding an electron is called orbital.

~~Orbital overlap theory~~

molecular orbitals of  $Br_2$  atomic molecule

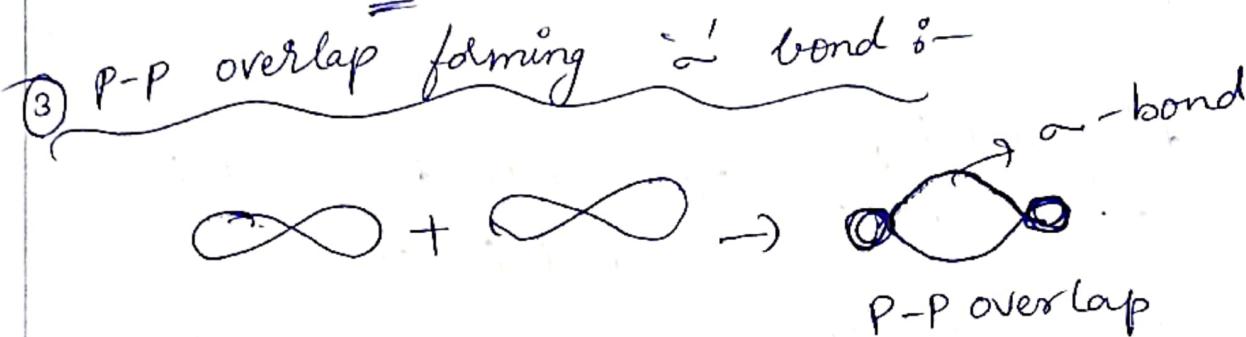
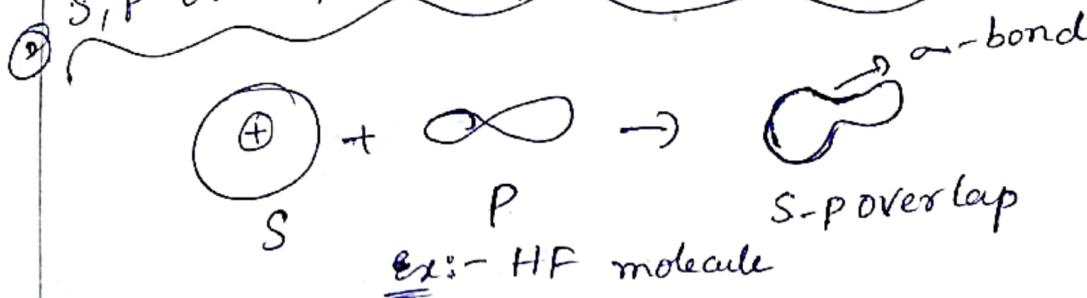
①  $\rightarrow$  S, S over lap in the formation of  $\sigma$  bond



ex:-  $H_2$  molecule

S orbitals are spherically symmetrical & shows head on overlapping

S,P overlap along axis forming  $\sigma$  bond



Ex:-  $F_2, N_2, O_2$  etc.

Molecular orbitals :-

① Molecular orbitals can be obtained from the combination of atomic orbitals which predict the location of an electron in an atom.

→ Atomic orbitals are found in atoms & molecular orbitals in molecules.

→ Atomic orbitals join together to form molecular orbitals.

→ Atomic orbitals containing valence electrons combine to produce molecular orbitals.

(5)

→ \* the number of atomic orbitals combining is equal to the number of molecular orbitals formed.

Ex:- 2 atomic orbitals containing e<sup>-</sup> combine to produce 2 molecular orbitals.

molecular orbitals classified as bonding & anti bonding.

molecular orbitals can change their shapes depending on the hybridisation they undergo.

molecular orbitals are can be explained by

MOT theory ~~(Molecular orbital theory.)~~ <sup>Robert</sup>

this theory proposed by Hunds, Mulliken & Jones

this theory also known as Hunds Mulliken theory.

postulates:-

→ Atomic orbitals of atoms overlap to form molecular orbitals.

→ Filling of e<sup>-</sup>s in various MOs obey Aufbau & Hund's rule & pauli's principle.

→ The number of molecular orbitals formed is equal to the number of overlapping atomic orbitals.

## MOT Postulates :-

(6)

Ex:- 2 atomic orbitals overlapping yield 2 molecular orbitals - I) Bonding molecular orbital with lowest energy & II) Anti Bonding molecular orbital with higher energy.

→ Each molecular orbital can accommodate 2 electrons with opposite spin just like atomic orbitals.

→ Depending on the type of overlapping molecular orbitals are designated as  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$

$\delta, \delta^*$

$\rightarrow \overline{\overline{\delta}}$



atomic orbitals



Bonding molecular orbital

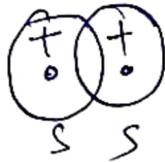
node



Anti Bonding Molecular

orbital

→



atomic  
orbitals.

→ MOT deals with LCAO.

## Linear Combination of Atomic orbital (LCAO)

Linear combination of atomic orbitals (LCAO) is a simple method of quantum chemistry.

- It gives qualitative picture of the molecular orbitals in a molecule.
- Atomic orbitals combine to form molecular orbitals.
- the no. of mos formed is equal to the no. of overlapping atomic orbitals.
- MOT theory deals with a linear combination of atomic orbitals (LCAO).
- According to quantum mechanics atom has ~~the~~ wave nature, denoted by  $\Psi$
- $\Psi_a, \Psi_b$  are the wave functions of 2 overlapping atomic orbitals & the process of their overlapping is called Linear Combination of Atomic Orbitals (LCAO) method.
- According to LCAO method, linear combination of atomic orbitals can take place either by addition (Constructive) or subtraction (destruction) of wave functions of atomic orbitals involved.
- Bonding molecular orbital  $\Psi$
- Anti Bonding molecular orbital  $\Psi^*$
- Bonding molecular orbitals represented by  $\sigma, \pi, \delta$
- Anti Bonding molecular orbitals represented by  $\sigma^*, \pi^*, \delta^*$

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(Bonding molecular orbital)

→ BMO formed by addition of wave function of atoms.

$$\boxed{\Psi_{BMO} = \Psi_A + \Psi_B}$$

Orbital

is called bonding molecular  
(constructive interaction)

- 1) It possess lower energy than that of combining atomic orbitals.
- 2) It possess high  $\epsilon$  density
- 3) It has stability to the molecule
- 4) BMO contributes to attraction b/w the 2 atoms.
- 5) BMO formed only when the lobes of atomic orbitals possess the same sign.

(Anti Bonding molecular orbital)

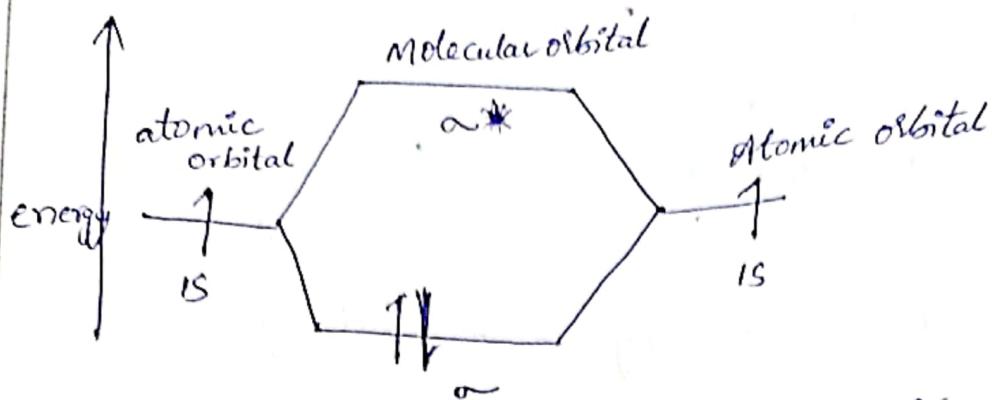
→ ABMO formed by subtraction of wave functions of atoms. designated ( $\Psi^*_{ABMO}$ )

$$\boxed{\Psi^*_{ABMO} = \Psi_A - \Psi_B}$$

(destructive interaction)

- 1) It possess higher Energy than that of combining atomic orbitals.
- 2) It possess low  $\epsilon$  density
- 3) It has instability
- 4) ABMO contributes to repulsion of 2 combining atoms.
- 5) ABMO formed only when the lobes of atomic orbitals possess opposite sign.

Ex:-



$\rightarrow$  Probability of finding an  $e^-$  is  $(\Psi)^2$

where  $(\Psi_A)^2$  is the probability of finding an electron  
an atom A

$(\Psi_B)^2$  is the probability of finding an electron  
an atom B

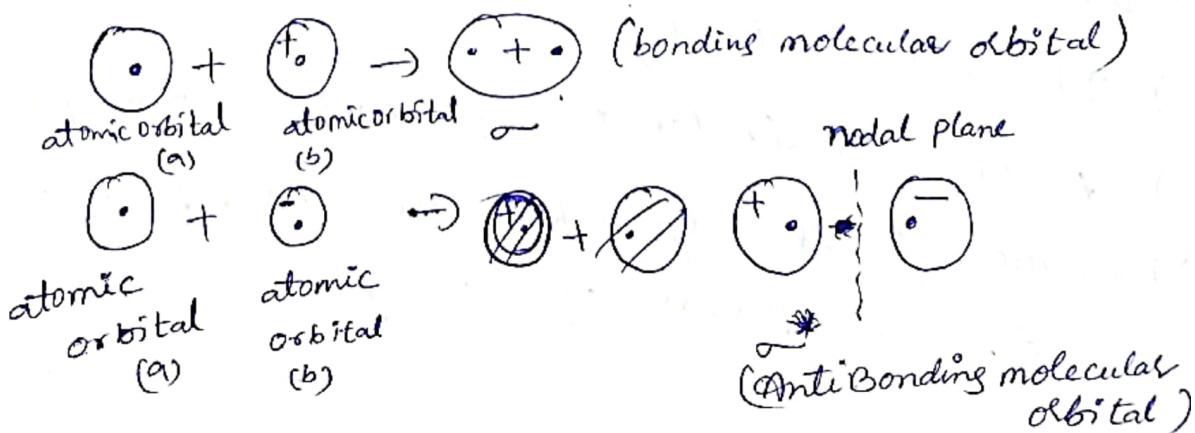
finding an  $e^-$  on atom

$2\Psi_A\Psi_B$  is the overlap integral.

$$(\Psi)^2 = (\Psi_A + \Psi_B)^2 = (\Psi_A)^2 + (\Psi_B)^2 + 2\Psi_A\Psi_B$$

Larger the overlap integral stronger is the bond  
that formed.

$$(\Psi^*)^2 = (\Psi_A - \Psi_B)^2 = (\Psi_A)^2 + (\Psi_B)^2 - 2\Psi_A\Psi_B$$



(Q)

## Energy level Diagrams of molecular orbitals

Energy level diagrams of molecular orbitals

Homo di atomic molecules  $N_2, O_2, F_2$  etc.

Energy level diagrams of molecular orbitals

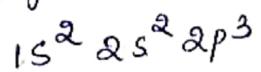
Hetero di atomic molecules  $CO, NO$  etc

### Molecular orbital Energy level diagrams of $N_2^{+}$

The atomic no. of Nitrogen = 7

$N_2 \rightarrow$  Homo nuclear di atomic molecule

→ Electron configuration of N is

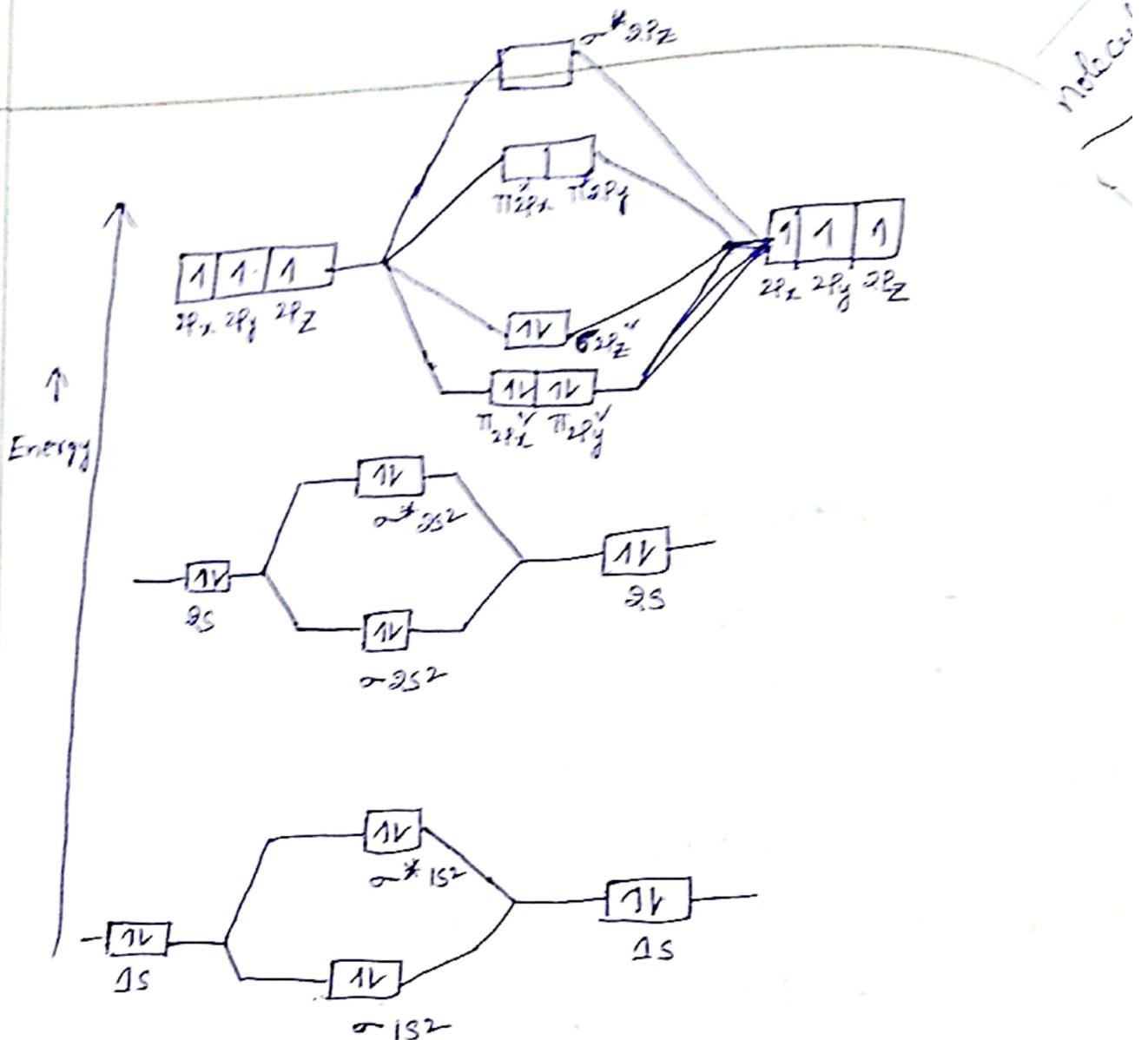


→ The electron configuration  $N_2$  according to molecular orbital approach is

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 (\pi 2p_x)^2 = (\pi^* 2p_y)^2, (\sigma^* 2p_z)^2$$

The total number of  $\bar{e}s$  are

$$N+N=7+7=14 \bar{e}s$$



Number of  $\sigma$ s in bonding molecular orbital

$$N_b = 10$$

no. of  $\sigma$ s in anti bonding molecular orbital

$$N_a = 4$$

$$\text{Bond order} = \frac{N_b - N_a}{2} \Rightarrow \frac{10 - 4}{2} \Rightarrow \frac{6}{2} \Rightarrow 3$$

Bond order = 3  $\Rightarrow$  Triple bond

$\Rightarrow$  presence of  $N_2$  all paired  $\sigma$ s shows that " $N_2$  is diamagnetic"

$\Rightarrow$  bond length is inversely proportional to the bond order.

# Molecular orbital energy level diagram of oxygen ( $O_2$ ) :-

$O_2$  is homonuclear diatomic molecule.

Atomic number of oxygen ( $O$ ) = 8

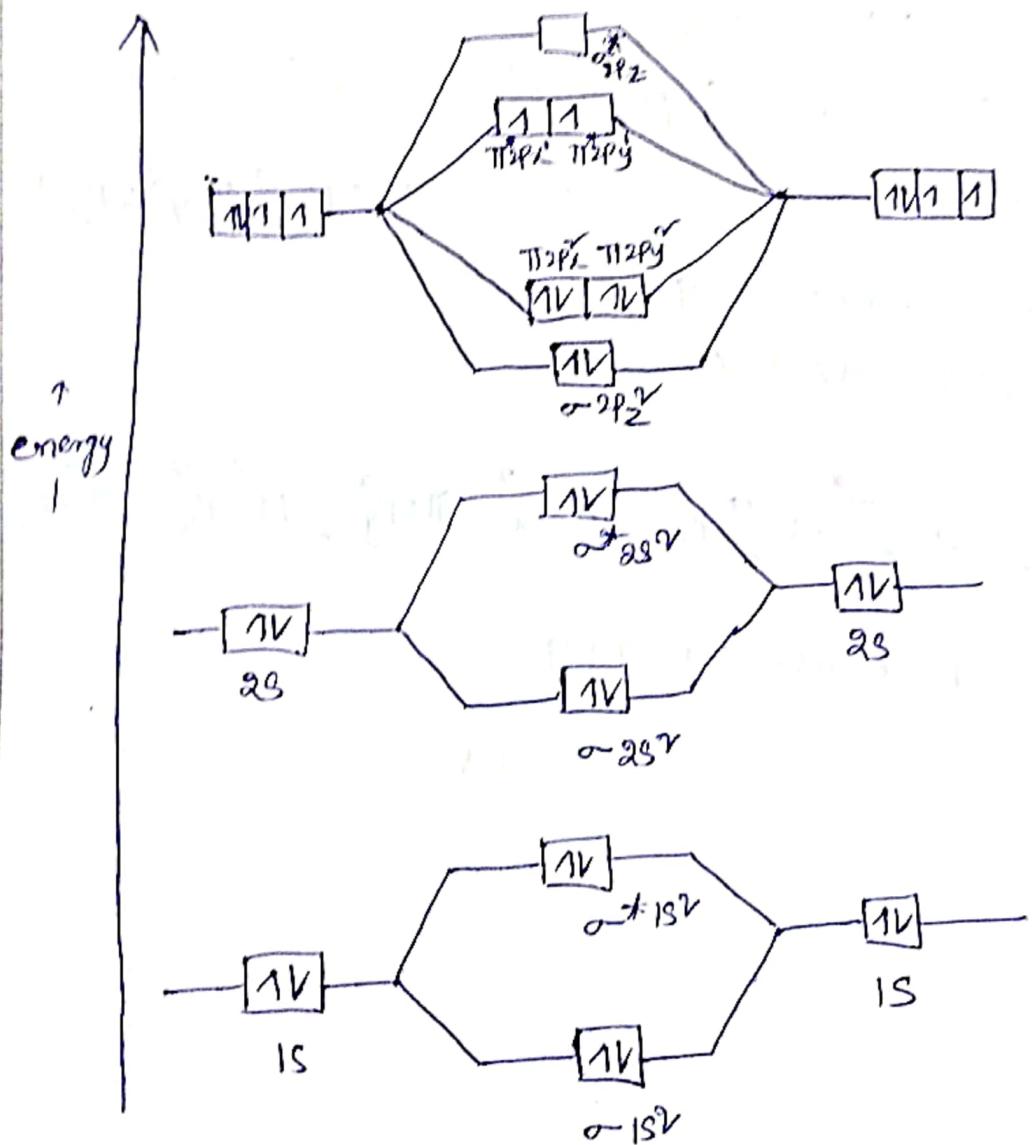
$$O \Rightarrow e^- \text{ configuration} = 1s^2 2s^2 2p^4$$

$$\Rightarrow 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$

The  $e^-$  configuration of  $O_2$  according to molecular orbital

$$O_2 = 16 e^- S.$$

$$1s^2 \rightarrow 1s^2, 2s^2 \rightarrow 2s^2, 2p_x^2 \rightarrow 2p_x^2, (2p_y)^2 = (1p_{2p_y})^2, (2p_z)^1 = (1p_{2p_z})^1$$



number of bonding electrons  $N_b = 10$

number of anti bonding Electrons  $N_a = 6$

$$\text{Bond order} \Rightarrow \frac{1}{2} (N_b - N_a)$$

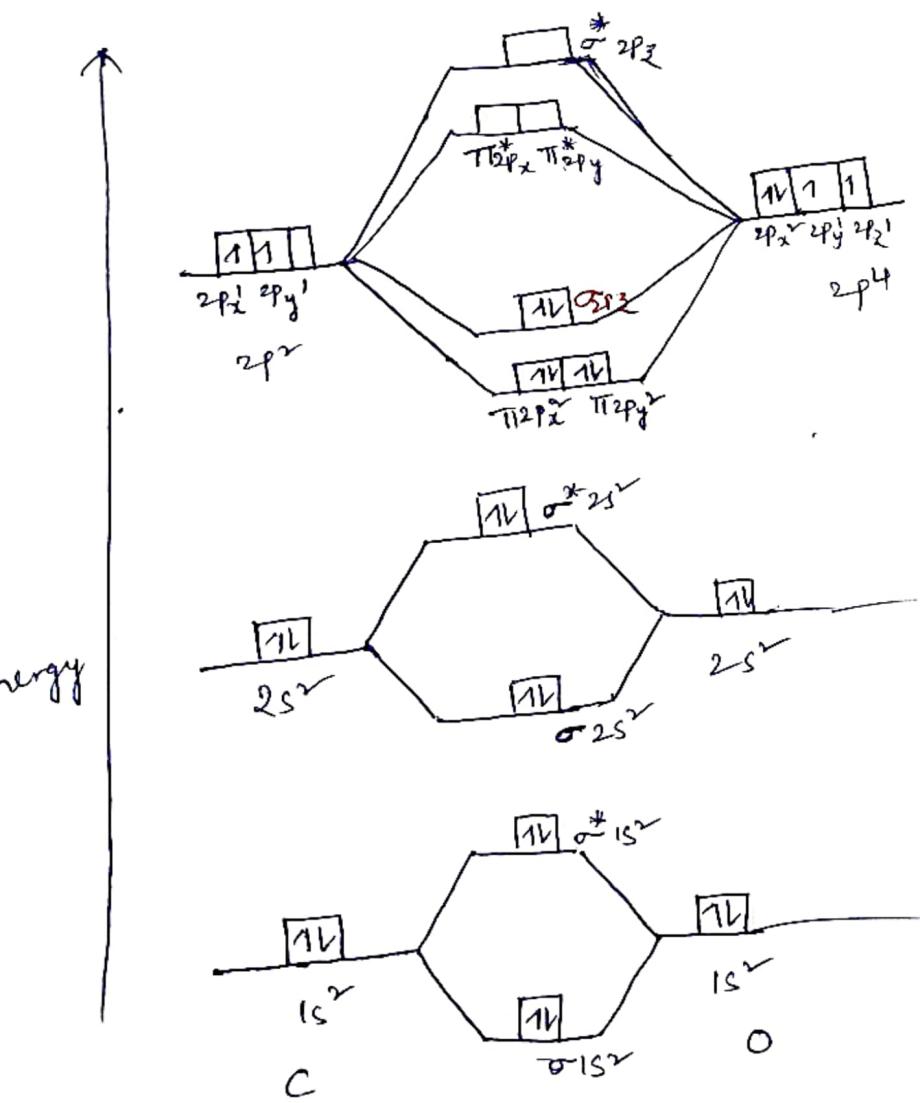
$$\Rightarrow \frac{10 - 6}{2} \Rightarrow \frac{4}{2} \Rightarrow 2$$

the bond order 2  $\Rightarrow$  double bond.

$O_2$  molecule is para magnetic because it contains 2 un paired  $e^-$ s. ( $\pi^*_{2p_x}, \pi^*_{2p_y}$  MO)

## Molecular Energy level Diagram of CO :-

- It is an example of Hetero di atomic molecule. 'C' atomic number = 6, 'O' atomic number = 8
- the electronic configuration of 'C' is  $= 1s^2 2s^2 2p^2$   
no. of e<sup>-</sup>s in 'C' is = 6
  - the electronic configuration of 'O' is  $= 1s^2 2s^2 2p^4$   
no. of e<sup>-</sup>s in 'O' is = 8
  - the total no. of e<sup>-</sup> is in CO =  $6 + 8 = 14$ e<sup>-</sup>s  
So it is iso electronic Configuration with N<sub>2</sub>



$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{10 - 4}{2}$$

$$= \frac{6}{2}$$

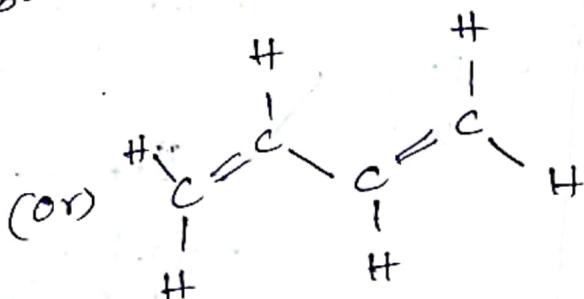
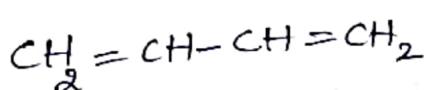
$$= 3$$

→ presence of paired  $\bar{e}$  ns shows that  
 $'CO'$  molecule is diamagnetic  
in nature.

Pi molecular orbitals of Butadiene & similar:

1,3 Butadiene :-

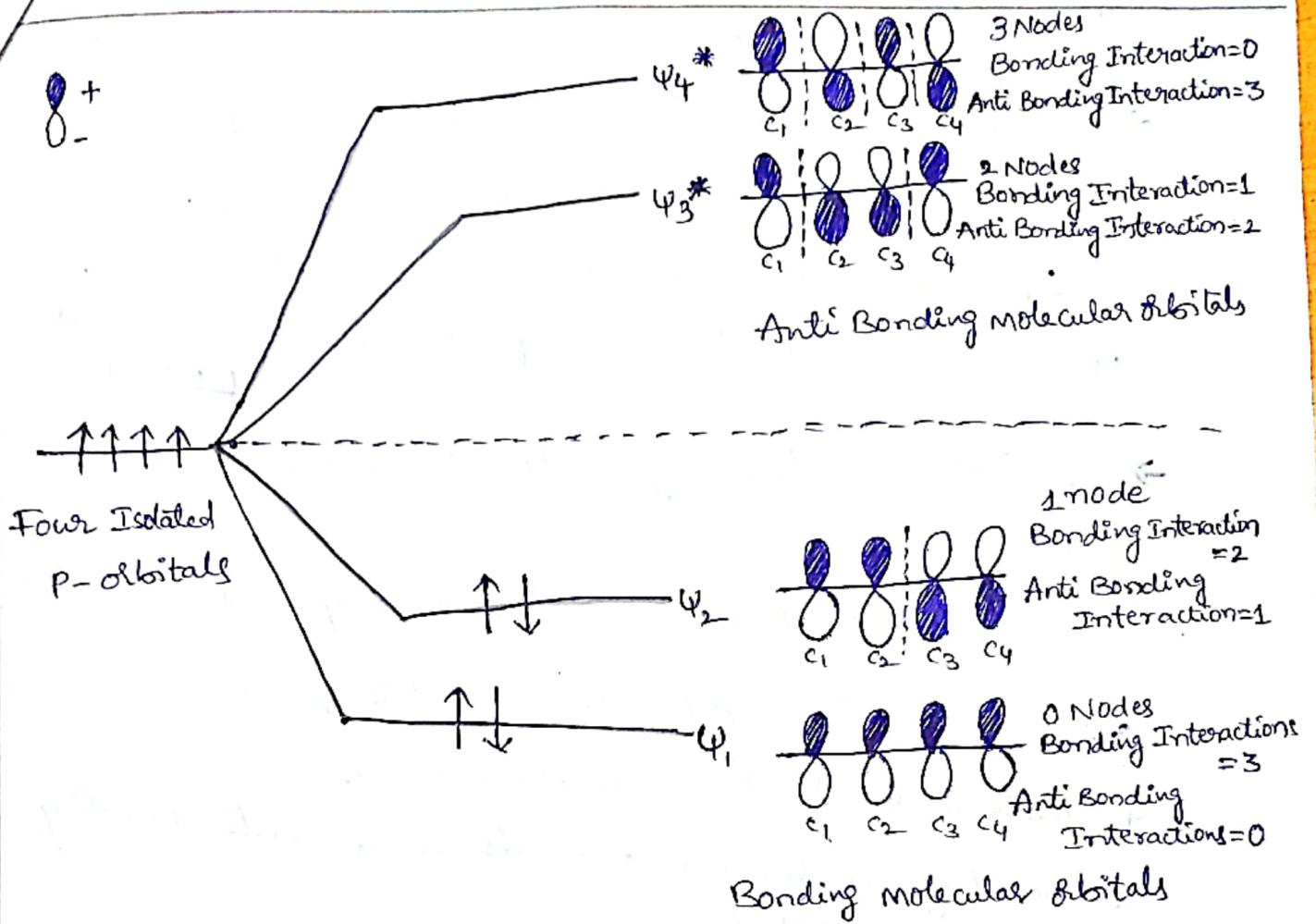
The structure of 1,3 Butadiene consists of 2 conjugated double bonds. The structure has 4  $sp^2$  hybridized carbon atoms. Each atom contributes a p atomic orbital consisting of one  $\pi$ .



1,3 Butadiene

one s & two p-orbitals undergo hybridisation and produce 3  $sp^2$  hybrid orbitals which form strong  $\sigma$  bonding with hydrogens & carbon with hybridised 4<sup>th</sup> p(II) atomic orbitals by overlapping forming molecular orbital above & below carbon bond.

The diagram represents the relative energies of  $\pi$  (II) molecular orbitals of 1,3 Butadiene which is derived compound of Ethene. The energy of the p-orbital of a C-atom is denoted by the horizontal centre line. The orbital lying below the horizontal line are bonding molecular orbitals whereas orbitals above the anti-bonding are called as anti-bonding molecular orbitals.



Each p-orbital contributes 1 e<sup>-</sup>, resulting in the arrangement of 4 e<sup>-</sup> from 4 p-orbitals which combine in 4 different ways & form 4 molecular orbitals designated by ψ<sub>1</sub>, ψ<sub>2</sub>, ψ<sub>3</sub>, ψ<sub>4</sub>

ψ<sub>1</sub> & ψ<sub>2</sub> = Bonding Molecular Orbitals

ψ<sub>3</sub> & ψ<sub>4</sub> = Anti-Bonding Molecular Orbitals.

→ ψ<sub>1</sub> has bonding interactions b/w C<sub>1</sub>-C<sub>2</sub>, C<sub>2</sub>-C<sub>3</sub> & C<sub>3</sub>-C<sub>4</sub> ∴ there exist 3 bonding interactions.

→ ψ<sub>2</sub> has bonding interactions b/w C<sub>1</sub>-C<sub>2</sub> & C<sub>3</sub>-C<sub>4</sub> & anti-bonding interactions b/w C<sub>2</sub>-C<sub>3</sub>.  
∴ they have single bond interaction.

It is the highest occupied molecular orbital (HOMO)  
→  $\psi_3$  has bonding interaction b/w  $C_2-C_3$  but Anti-bonding interactions b/w  $C_1-C_2$  &  $C_3-C_4$ .  
∴ they have single anti-bonding interaction.  
It is the lowest unoccupied molecular orbital (LUMO)

→  $\psi_4$  has antibonding interactions b/w  $C_1-C_2$ ,  $C_2-C_3$  &  $C_3-C_4$ .  
∴ they have 3-anti-bonding interactions.

out of the 4 orbitals available, the 4 molecular orbitals  $\psi_1, \psi_2, \psi_3, \psi_4$  2 bonding molecular orbitals & 2 anti-bonding molecular orbitals.

The energy in molecular orbital increases with the rise in the no. of nodes.

$$\text{Wave equation } \Psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4$$

- orbital.

## Crystal Field Theory :- (CFT) :-

This theory was proposed by Brethe and van Vleck in 1930s. It is applied mainly to ionic crystals, hence it is termed as the crystal field theory.

the main postulates of CFT :- (Salient features) :-

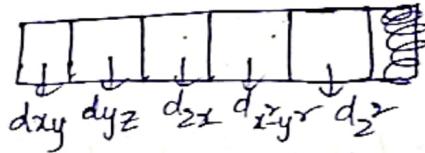
- ① A complex is considered as a combination of central metal ion surrounded by ligands.
- ② There is no overlap b/w the metal orbital & ligand orbitals & the interaction b/w metal ion & ligands is purely electrostatic in nature.
- ③ All the d-orbitals on the metal atom have equal energy (degenerate orbitals).
- ④ As the ligands approach the central metal atom

atom for complex formation, these orbitals lose their degeneracy & split into orbitals of different energies depending upon the direction from which the ligands approach the central metal atom. This phenomenon is called "CFT" theory.

⑤ This theory does not consider any orbital overlap unlike valence bond theory. This theory does not consider covalent ~~to~~ character of bond b/w metal & ligand. The metal ions & ligands do not mix their orbitals (or) share  $\pi$ ns.

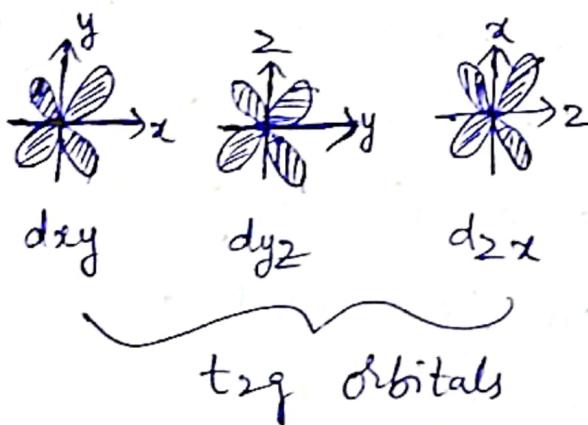
ex:-  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  etc.

⑥ neutral ligands  
metal consist of  
5 d-orbitals are

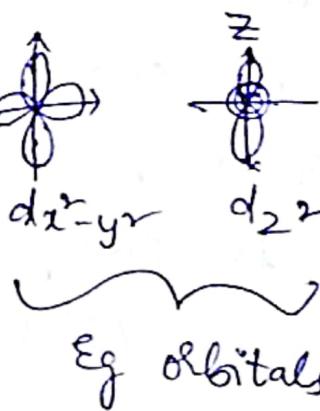


d-generated orbitals. (Same energy)

structures of d-orbitals :-



lobes are present  
between the axis



lobes are present  
along the axis  
(on)

→  $d_{z^2}$  &  $d_{x^2-y^2}$  orbitals have their lobes along the axis & are called axial orbitals  
eg orbital refers to doubly degenerate.

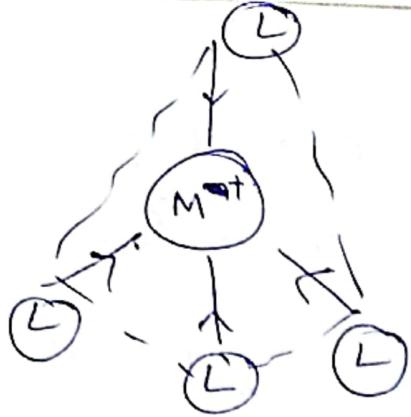
→  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  have their lobes b/w the axis hence referred to as non-axial orbitals  
 $t_{2g}$  orbital refers to triply degenerate

→ when ligand approach to metal atom 2 types of forces are takes place. They are "electrostatic forces & repulsion forces"  
Due to Repulsion forces splitting of  $d$ -orbitals ( $t_{2g}$ ,  $e_g$  orbitals).

### Splitting of $d$ -orbitals in Tetrahedral Complexes:-

In tetrahedral complex, the 4 ligands occupy alternate corners of a cube & the metal ion is placed in the center.

In tetrahedral complex 4 ligands attached to the central metal ion. The ligands approaches central metal ion b/w the axes of coordinate system. So the 3 orbitals namely  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  are oriented b/w the axis & near to 4 ligands & gets more interacting than the 2-d orbitals  $d_{x^2-y^2}$  &  $d_{z^2}$  which are along the axis.



a) Tetrahedral ligand field surrounded a central transitional metal ( $M^+$ )

The difference between  $e_g$  &  $t_{2g}$  orbitals (or) the difference in the splitting of  $e_g$  &  $t_{2g}$  orbitals in tetrahedral complexes splitting constant ( $\Delta_t$ ) / CFSE in loss their energy +

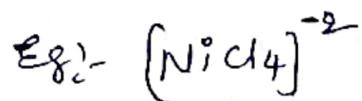
→ when ligands approach to metal ion  $\uparrow$  split into 2 set of d-orbitals  $e_g$  &  $t_{2g}$  orbitals.

→  $e_g$  orbitals have low energy,  $t_{2g}$  orbitals (bottom side) have high energy.  
(upper side)

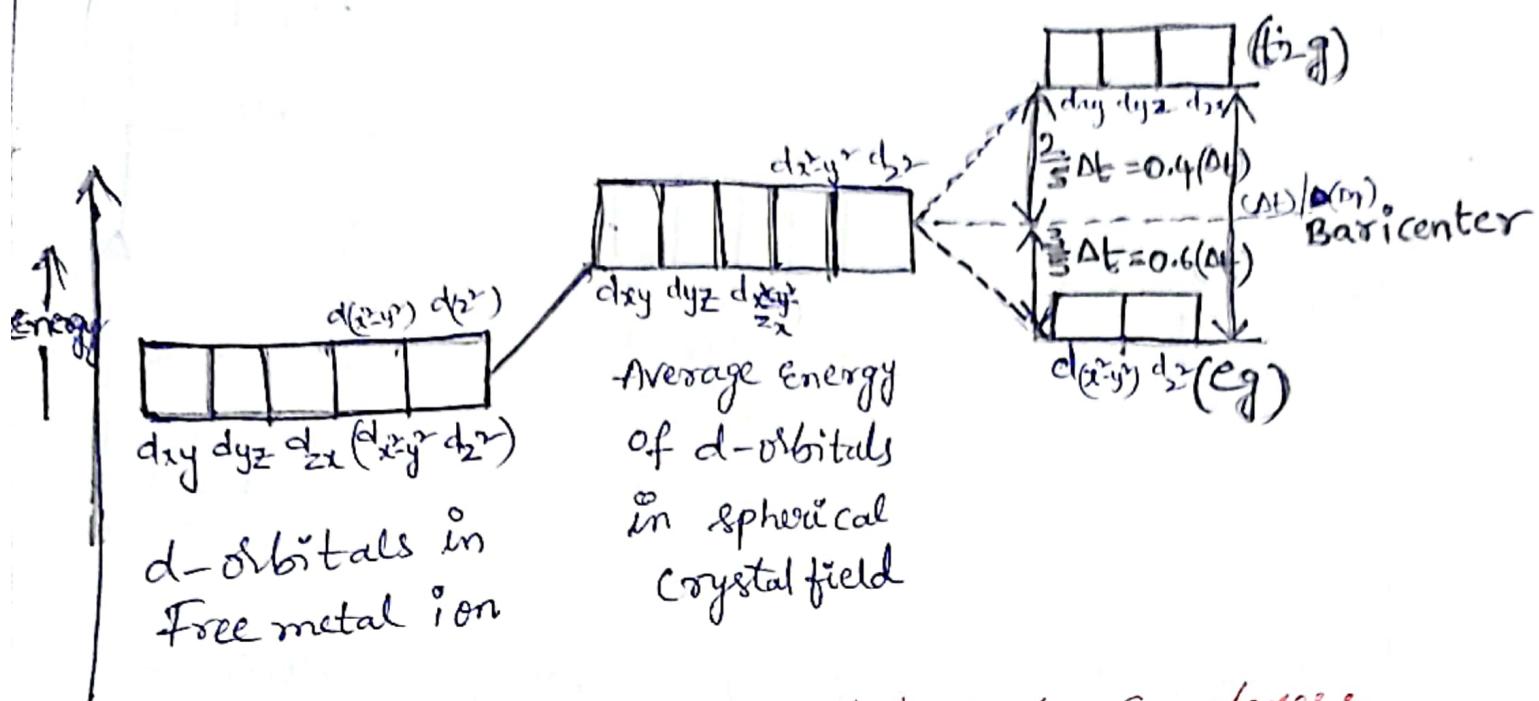
→ CFSE → crystal field stabilisation Energy (or) crystal field splitting energy. ( $\Delta$ )

In tetrahedral Complexes is represented by ( $\Delta_t$ ), t stands for tetrahedral

→ CFSE of tetra complexes  $\Delta_t$  which is less than ( $\Delta_0$ ) (CFSE of octahedral Complexes).

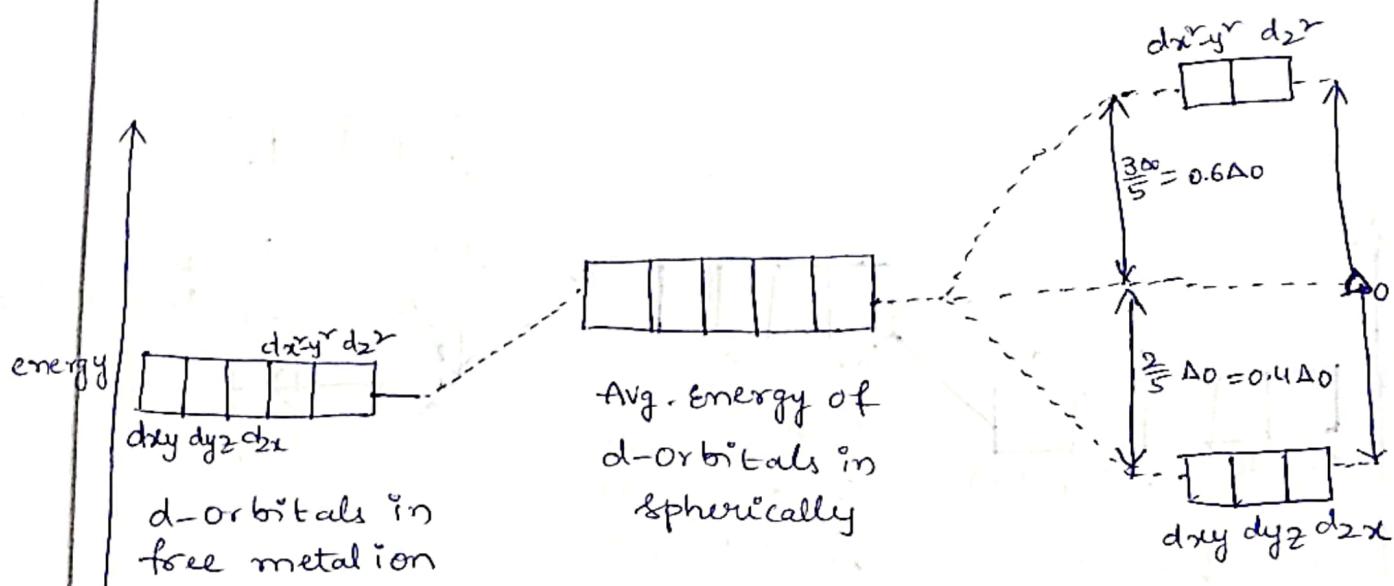


→ CFSE ( $\Delta$ ) depends on the fixed produced by the ligand & charge on the metal ion.



## Splitting of d-orbitals in octahedral Complexes:-

In octahedral complexes, the coordination number - 6. The 6 ligands approaching the central metal atom along the axis of co-ordinated system. So the 2 d-orbitals  $d_{x^2-y^2}$  &  $d_{z^2}$  oriented along the axis are directly pointed the ligands and remaining three d-orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  are oriented between the axis. Hence  $d_{x^2-y^2}$  and  $d_{z^2}$  are more repelled from ligands than  $d_{xy}$ ,  $d_{yz}$  &  $d_{zx}$ . Thus the energy of 2  $e_g$  orbitals is increased than the 3  $t_{2g}$  orbitals. Thus the 5 d-orbitals of the metal-ion splits into 2 sets of different energies.



Among the 2 sets of different energies orbitals. One set consists of lower energy & more ~~er~~ stable are  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals ( $t_{2g}$  orbitals) & the other less stable higher energy  $d_{z^2}$ ,  $d_{x^2-y^2}$  ( $E_g$  orbitals). This splitting of degenerate orbitals under the influence of ligand is termed as crystal field splitting and the energy separation b/w them is denoted by  $\Delta_o$  ( $o$  means octahedral).

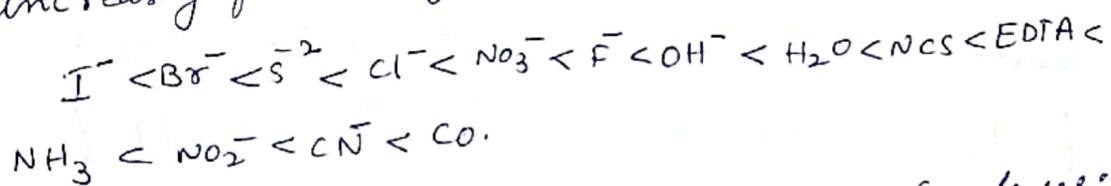
The energy of  $t_{2g}$  orbitals is decreased by  $\frac{2}{5} \Delta_o$  ( $\approx 0.4 \Delta_o$ ) & the energy of  $E_g$  orbitals rises by  $\frac{3}{5} \Delta_o$  ( $\approx 0.6 \Delta_o$ ) above the hypothetical degenerate orbitals.

It is important to note that the crystal field splitting energy  $\Delta_o$  depends on the field produced by the ligand & the charge on the metal ion.

Ligands that produce strong field & causes large splitting are called strong field ligands & those that produce weak field cause small degree of splitting & are termed as weak field ligands.

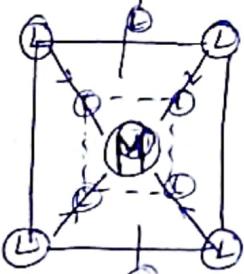
### Spectrochemical Series :-

Ligands are arranged in the order of increasing field strength is called Spectrochemical series.



### Splitting of d-orbitals in Square planar complexes :-

Square planar Complexes are derived from  $\text{O}^{\oplus}$  octahedral complexes by with drawing two trans ligands lying along the z-axis the with drawing of 2 trans ligands involves the following steps.

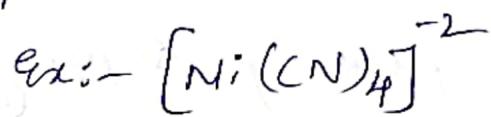


Step-I :- If the 2 trans ligands lying along the z-axis are moved away from central metal  $\text{O}^{\oplus}$  ion then the remaining ligands are in xy-plane & tends to approach the metal-ion very closely.

So the d-orbitals in xy-plane are more interacted with ligands than octahedral form structure. Thus the energies of  $d_{x^2-y^2}$  &  $d_{xy}$  is increased & remaining d-orbitals  $d_{yz}$ ,  $d_{zx}$  &  $d_{zz}$  energies decreased.

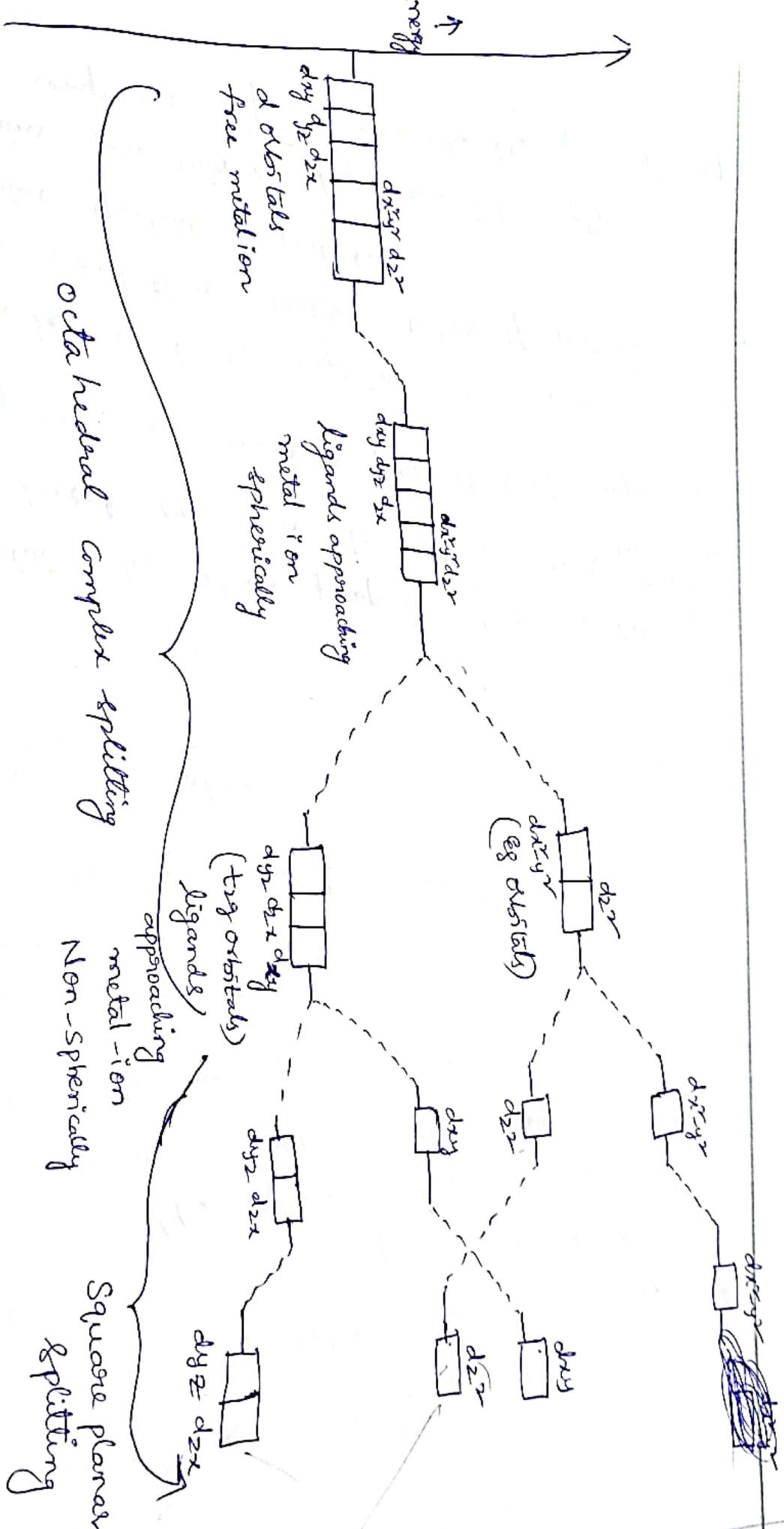
Step-II :- If the 2 trans ligands lying on z-axis are removed completely. As a result square planar field is formed. This leads the further rise & fall in the energies of  $d_{x^2-y^2}$  &  $d_{xy}$  & fall in the energy of  $d_{zx}$ ,  $d_{yz}$ ,  $d_{zz}$  i.e. more energy orbitals are =  $d_{x^2-y^2}$  &  $d_{xy}$  less energy orbitals are =  $d_{yz}$ ,  $d_{zx}$  &  $d_{zz}$

Square planar complex



Square planar complexes are formed by  $(d^8)$  ions with strong field ligands.

o Splitting of d-orbitals in Square Planar Compounds :-



# factors affecting the ~~max~~ CF splitting :-

## (i) Geometry of the Complex:-

In octahedral complex, the ligands approach along the axis influencing the axial d-orbitals directly, whereas in tetrahedral complexes those d-orbitals are not directly under the influence of ligands.

## (ii) Nature of ligands:-

## (iii) Charge on the central metal ion:-

## (iv) position of metal:-

## Applications of crystal field theory:-

- ① It explains the colour property of the metal complexes based on d-d transitions. Ex:-  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  blue colour.
- ② It explains the magnetic properties of complexes.
- ③ It can be used to explain the stability of various oxidation ~~state~~ states of metals.
- ④ It explains spectral properties.
- ⑤ It explains formation of high spin & low spin octahedral complexes.

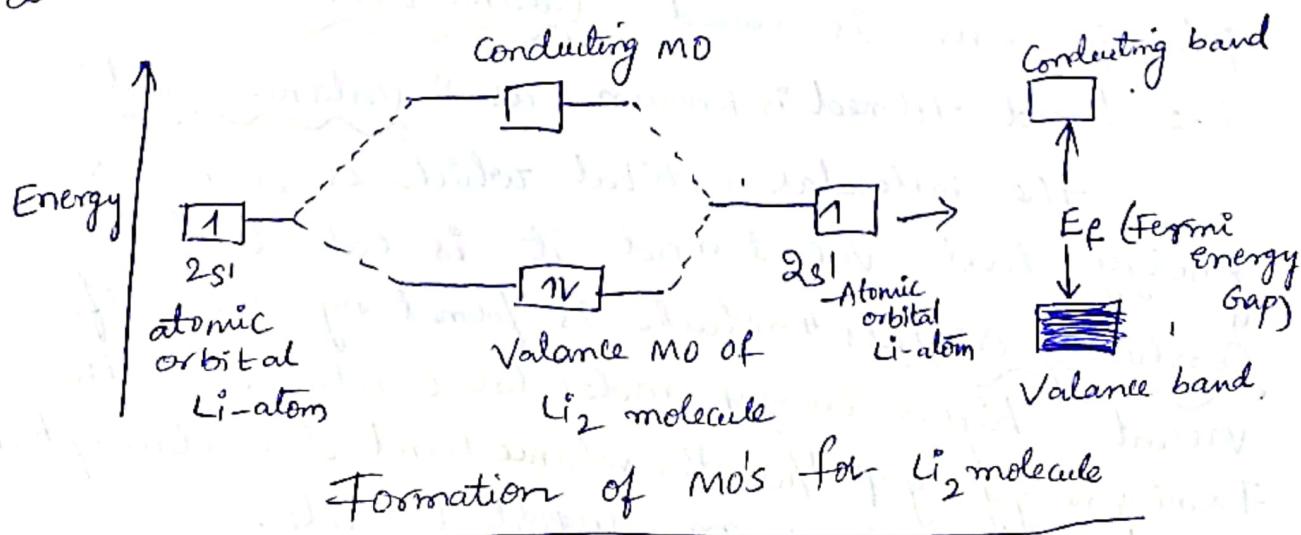
$$\boxed{\text{Spin formula } m_s = \sqrt{n(n+1)} \text{ B.M}}$$

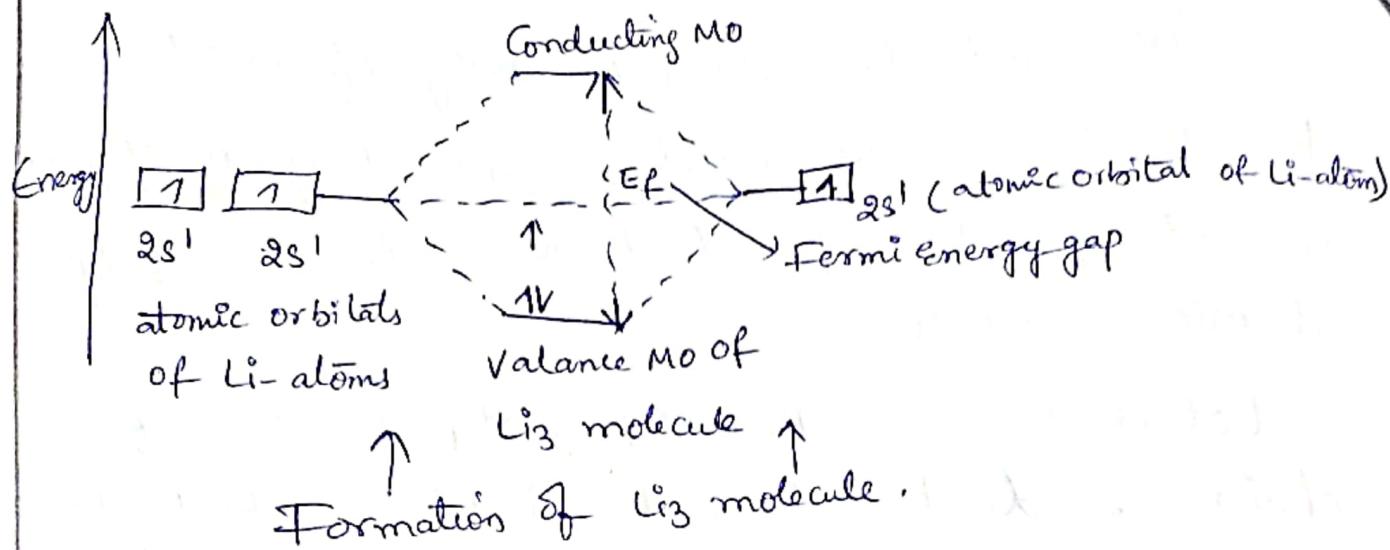
## Band structure of solids:-

the molecular orbital theory of metal is known as "band model". Since large no. of (MO's) molecular orbitals formed from a large no. of (AO's) atomic orbitals.

Let us consider the step by step formation of a chain of ~~Li~~ Li atoms  $\text{Li} - \text{Li} - \text{Li} - \dots - \text{Li} - \text{Li} - \text{Li}$ .

In this formation of this chain of Li-atoms, Li molecules is formed by the combination of 2 atomic orbitals producing 2 molecular orbitals among these 2 MO's. one MO with lower energy & the other with higher energy. the lower Energy MO will contain the  $e^-$  pair & the higher Energy MO is vacant. Attaching ~~another~~ another Li-atom the thin Li-atom to  $\text{Li}_2$  molecule gives the Linear  $\text{Li}_3$  molecule formed by the combination of 3  $\text{Li}(2s)$  atomic orbitals producing 3 Li-MO.



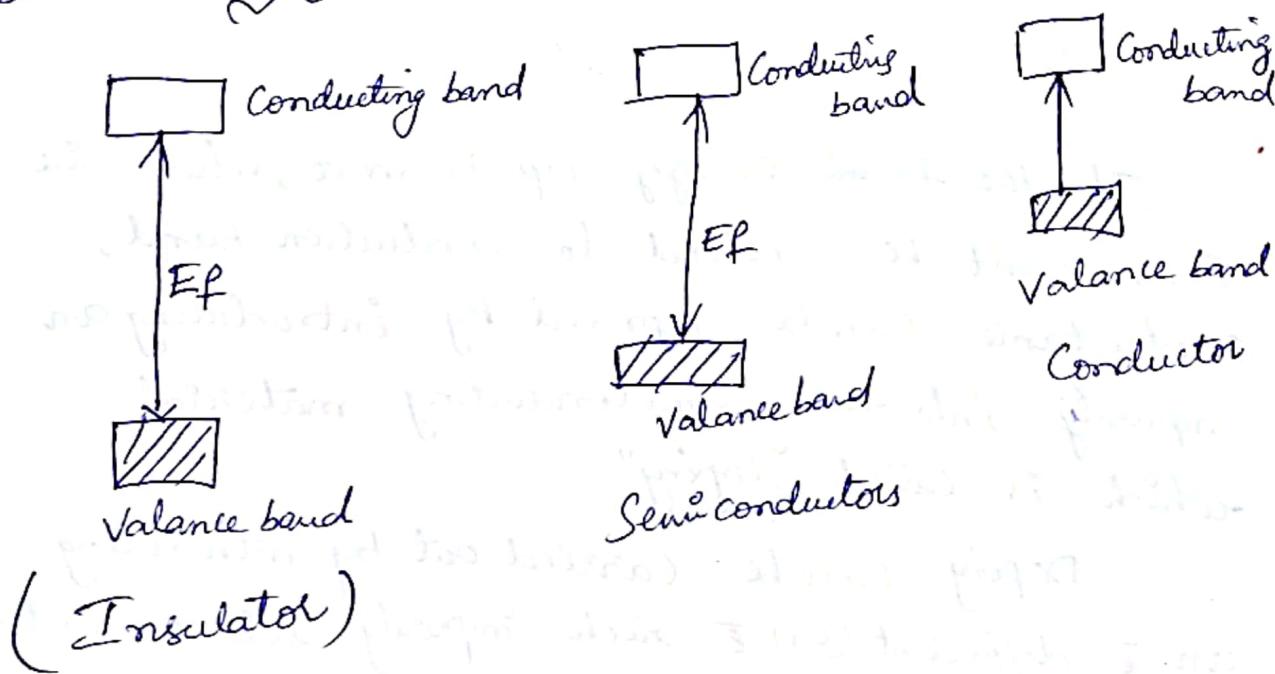


→ As the length of the chain increases by increasing the no. of Li-atoms we get a large no. of MOs closely spaced together. As the no. of Li-atoms increases the energy levels get closer & closer & ultimately becomes continuous. Such a group of continuous energy levels are known as "bands". The molecular orbital theory is known as "Band Model".

the molecular orbital which contains the pair of electrons is called "valence orbitals" & the band formed is known as "valence band".

the molecular orbital which is in higher energy level vacant and it is called "conducting orbitals" which is formed by the no. of vacant higher energy molecular orbitals. Now the Fermi energy gap b/w the valence band & conducting band ~~formed~~ plays an important role.

- If the Fermi energy gap ( $E_F$ ) is more the material becomes "insulator". If the Fermi energy gap ( $E_F$ ) is less the material becomes "conductor". If the Fermi energy  $\rightarrow (E_F)$  is in b/w a conductor and an insulator, then that material becomes "semiconductor"
- when the electrons in valence band are exposed to heat, light etc. they absorb the energy & excited to higher energy level, the conducting band causing the material to become a "conductor". when the Fermi energy gap ( $E_F$ ) is more , the e- can't be excited to the conducting band the material becomes "insulator"



## Types of Semiconductors :-

Semiconductors are 2 types

- 1) Intrinsic Semiconductors
- 2) Extrinsic Semiconductors.

### Intrinsic Semiconductors:-

If the Fermi energy gap is small b/w the Valence band & Conducting band, the  $e^-$  from Valence band is excited to Conduction band, it is called "Intrinsic Semiconductor". the hole left in the Valence band & excited  $e^-$ s to the Conduction band as a result ~~can~~ to get "conductivity"

As the temperature increases, the no. of  $e^-$ s promoted to the Conduction band increases in ~~conducting~~<sup>vib</sup> of Semiconductor.

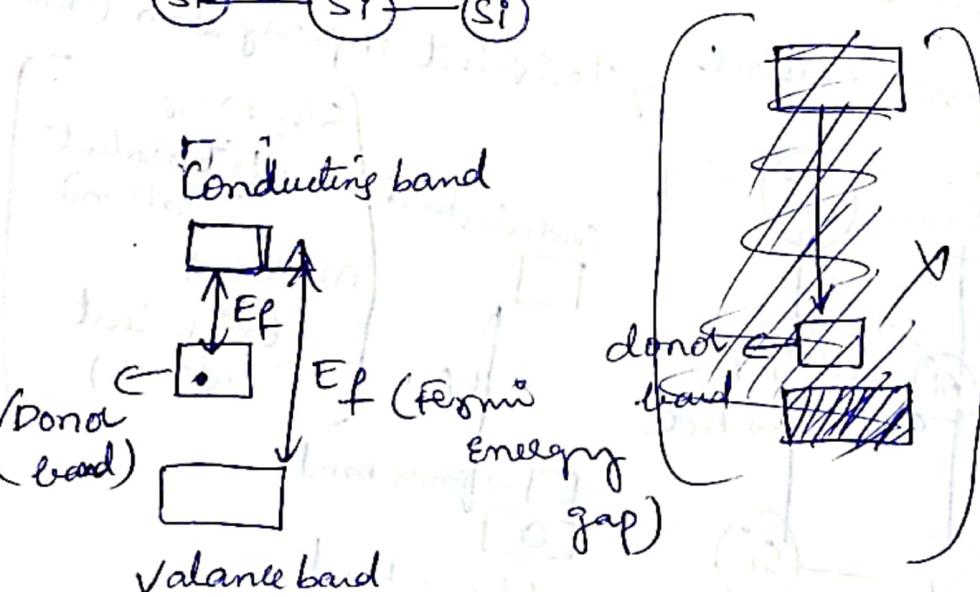
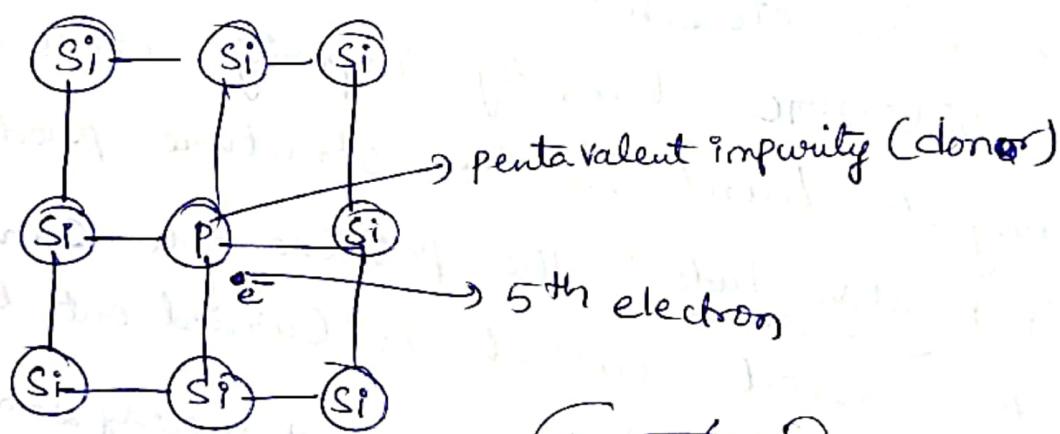
### Extrinsic Semiconductors (or) Effect of doping on Conductance:-

If the Fermi energy gap is more, where the  $e^-$ s can't be excited to Conduction band, conductance can be improved by introducing an impurity into the semiconducting material which is called "doping".

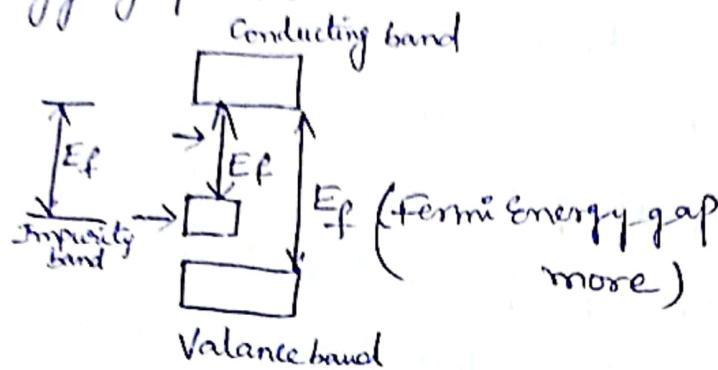
Doping can be carried out by introducing an  $e^-$  deficient (or)  $e^-$  rich impurity into the material which produces p-type & n-type semiconductors.

## n-type Semiconductors :-

In n-type Semiconductors were produced by (introducing) doping Si (or) Ge with Penta Valent impurity atoms like P (or) As etc. Si (or) Ge atoms are replaced by P (or) As 5 e<sup>-</sup>s in its outer shell. Only 4 e<sup>-</sup>s form covalent bonds with Si (or) Ge & the 5<sup>th</sup> e<sup>-</sup> is localised at absolute zero. At the Normal temp 5<sup>th</sup> e<sup>-</sup> ~~is~~ impurity promoted to conduction band, causing conduction. Since the conductivity of such Semiconductors are due to -ve electrons, they are called n-type Semiconductors.

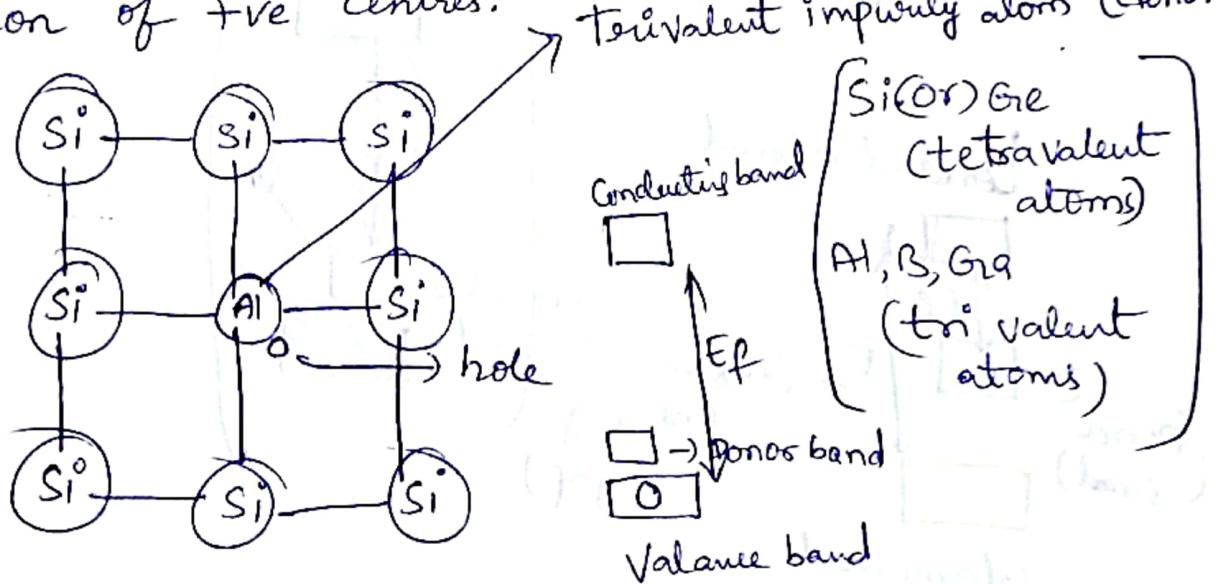


the impurity forms an impurity band called donor band b/w valence band & conducting band of the material, where by the fermi energy gap is reduced & conduction takes place.



### P-type Semiconductors:-

By introducing a trivalent impurity atom like Al, B, Ga etc. into Si (or) Ge, the replacement of these Si (or) Ge atoms by impurity produces an incomplete band in the structure producing a (+ve) "positive hole", the positive hole can migrate the crystal, current is carried out by migration of +ve centres.



# Differences between Bonding & Anti-Bonding molecular Orbitals

## Bonding molecular orbital

- ① Bonding molecular orbital is formed by the addition of overlapping atomic orbitals $\Psi_{mo} = \Psi_A + \Psi_B$
- ② It has greater density
- ③ It possesses lower energy
- ④ It is represented by  $\sigma, \pi$
- ⑤ Attraction b/w 2 atoms
- ⑥ It stabilizes the molecule

## Anti-Bonding molecular orbital

- ① Anti-Bonding molecular orbital is formed by subtraction of overlapping atomic orbitals. $\Psi_{mo}^* = \Psi_A - \Psi_B$
- ② It has lower density
- ③ It possesses higher energy
- ④ It is represented by  $\sigma^*, \pi^*$
- ⑤ Repulsion b/w 2 atoms
- ⑥ It de-stabilizes the molecule.

## Differences b/w Atomic orbitals & molecular orbitals:-

### ① Atomic orbitals

① An e in atomic orbital is under the influence of only one positive nucleus of the atom.

② ~~Molecular~~ Atomic orbitals inherent property of an atom

③ they have simple shapes (type of atomic orbital S, P, d, f) <sup>(fixed)</sup>

④ Mono centric. Found around a single nucleus

⑤ Atomic orbitals are found in atoms

⑥ probability of finding any e of an atom in any specific region around the nucleus of the atom.

⑦ Atomic orbitals are named S, P, d, f.

### Molecular Orbitals

① An e molecular orbital is under the influence of 2 (or) more nuclei depending upon the no. of atoms present in the molecule.

② Molecular orbital are formed by combination of atomic orbitals.

③ they have complex shapes. changed their shapes depending on the hybridisation

④ Poly centric. It is found around different nuclei

⑤ Molecular orbitals are found in molecules

⑥ Molecular orbitals formed from the combination of atomic orbitals.

⑦ molecular orbitals are classified bonding & anti bonding. ~~Note~~