① Explain crystal field splitting of octahedral and square planner complexes.

→ **Octahedral Complexes :-**

* In octahedral complexes, central metal ion is surrounded by six lone pairs of electrons. there are two types of electrostatic interactions in the complex.

① Attraction between positive metal ion and negitivity charged ligand

② Electrostatic repulsion b/w lone plains in ligands and electric in `d` orbital of metal.

* Since dx^2-y^2 and dz^2 orbitals are along axes, they experience much more repulsion then dxy, dyz, dzz, which are in b/w the axes

* As a result of these interactions, the equality in energy of five orbitals multifield, to give two different energy levell.

$$CFSE = [(-0.4 \times t_{2gn}) + (0.6 \times n\,e_g)]\,\Delta_0$$
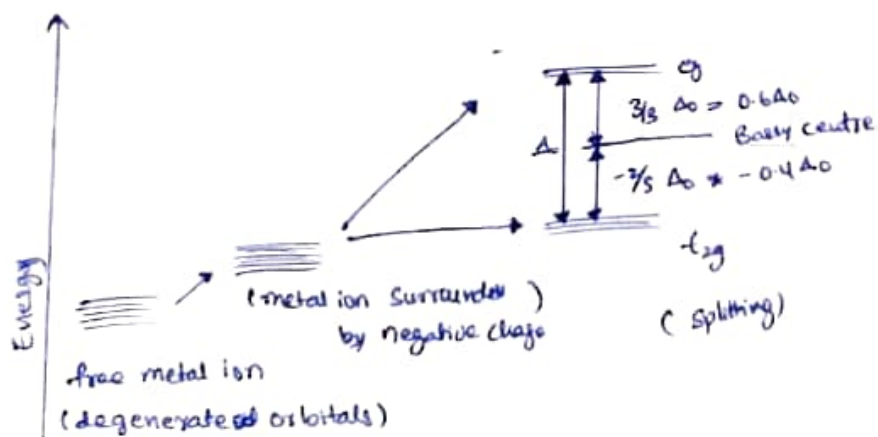
→ distribution of electron in complexes:

* the distribution of electrons depends on the type of ligand whether

is strong field or weak field.

for example for a d^4 electron system distribution is as follows:

d^4 (weak field):

e_g 1 —

t_{2g} 1 1 1

d^4 (strong field)

e_g — —

t_{2g} 1↟ 1 1

* for weak field ligands — high spin (Δ_o - less)

* for strong field ligands — low spin (Δ_o - more)

* Δ_o value depends on metal as well as ligand.

⟶ thus for metal, larger the size, large is Δ_o value

larger the oxidation state of metal, larger, is Δ_o value.

SQUARE PLANNER COMPLEXES:-

* the central metal ion is surrounded by 4 ligands

* the greater influence on a $d_{x^2-y^2}$ orbital so the energy of this orbital will be raised most

* the d_{xy} orbital lying in same plane but between the ligands will also have greatest energy. relatively lesser than $d_{x^2-y^2}$ orbital.

* d_{x^2} and d_{y_z} pair will always be effected equally and. therefore remain degenerate.

energy

$d_{x^2-y^2}$ ↑ Δ_1

d_{xy}

d_{y^2} Δ_2 Δ_{sp}

$d_{yz,dxz}$ Δ_3

(metal ion surrounded by negitive charge)

(freemetal ion)

$d_{x^2-y^2} > d_{xy} > d_{y^2} > d_{xz} = d_{yz}$

$\boxed{\Delta_{sp} = 1.3\,\Delta_o}$
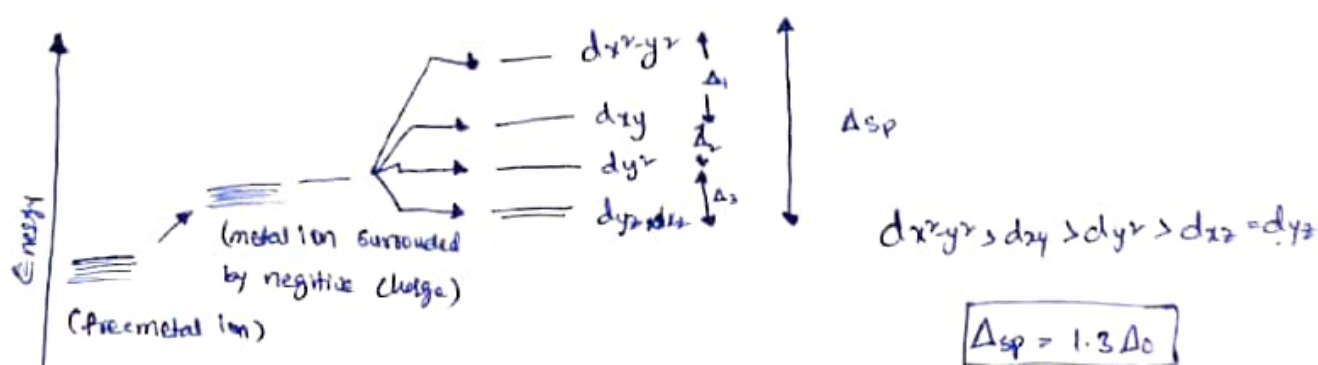
→ **molecular orbital theory**:-

* molecular orbitals are formed by the combination of atomic orbitals

* molecular orbitals can accomdate two electrons with opposite spin

* Each and every electron in the Mo belongs to all the nuclei of molecule.

* Mo is the region where electron resides Each M.O is described by a wave function ψ

* Mo are associated with the entire molecule.

* Conditions for overlapping of atomic orbitals:

  → Same energy

  → Same Symmetry

  → Extent of over lapping between atomic orbitals.

* the number of molecules orbitals formed is equal to the number of over lapping atomic formed is orbitals.

* the shape of Mo depends on shape, size and orientation of atomic orbitals.

* Mo are arranged is increasing order of their energy

  types of mo:-

According to LCAO, Mo. are formed by addition or substraction of wave functions of atomic orbitals.

① Bonding Mo

② non-Bonding Mo

③ Anti Bonding Mo

   $BM_0 < NBM_0 < ABM_0$.

Bonding MO:

$\sigma, \pi, \sigma \ldots \ldots$

* formed by addition of wave function of AO Constructive interface

$$\psi MO = \psi_A + \psi_B$$

* Posses high electron density in region b/w nucleus and their imparts ability to the molecule.

Anti Bonding MO:

$\sigma^*, \pi^*, \delta^* \ldots \ldots$

* formed by Substration of wave forms of AO, destructive influence

$$\psi^*_{MO} = \psi_A - \psi_B$$
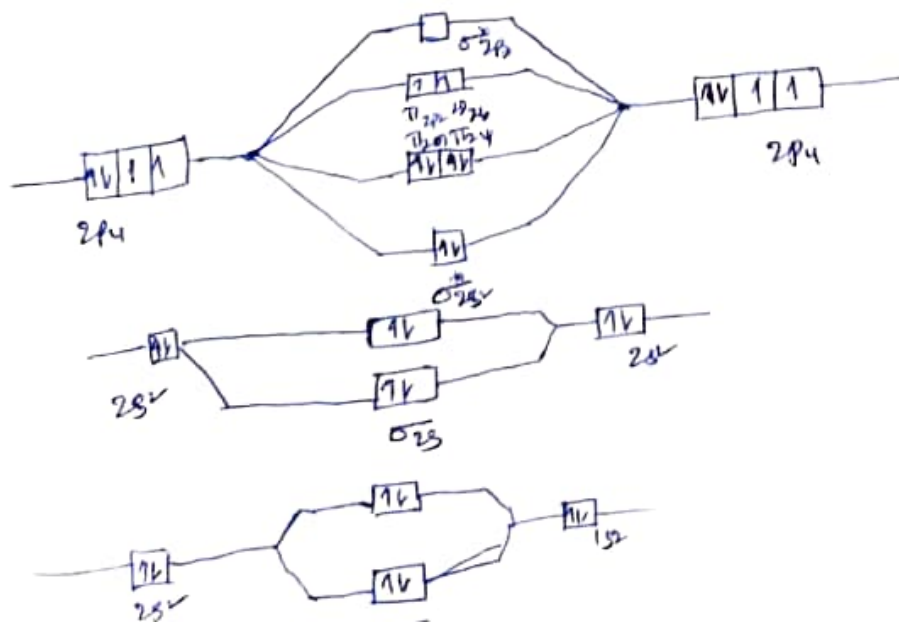
* Posses less electron density in the region b/w nucleus

* Probability of formation of Bonding molecule orbital (

$(\psi^2) >$ Probability of formation of ABMO.

MO Energy diagrams:-

i) O_2 E.c: $1s^2 2s^2 2p^4 - 2\#$ is the electronic configuration of O

E.C of O_2: $\sigma 1s^2 \, \sigma^*_{6}^2 \, \sigma 2s^2 \, \sigma^*_{2s}^2 \, \sigma_{2z}^2 \left(\pi_{2p_x}^2 \, \pi_{2p_y}^2 \right) \left(\pi_{2p_x}^{*1} - \pi_{2p_y}^{*1} \right)$

$N_b = 8$

$N_a = 4$

$\therefore$ Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-4)$

$= 2$, which justifies the

Presence of a double bond b/w oxygen
molecule (O_2)

(iii) $\underline{N_2}$:-

E_c of N : $1s^2 2s^2 2p3$

E_c of $N_2 = \sigma_{1s^2}\ \sigma^*_{2s^2}\ \sigma^*_{2s2}\ \sigma^y_{2s2}\ \left(\dfrac{\pi^2}{2\pi m} - \dfrac{\pi^2}{2p_y}\right)\ \sigma^2_{2p_z}$
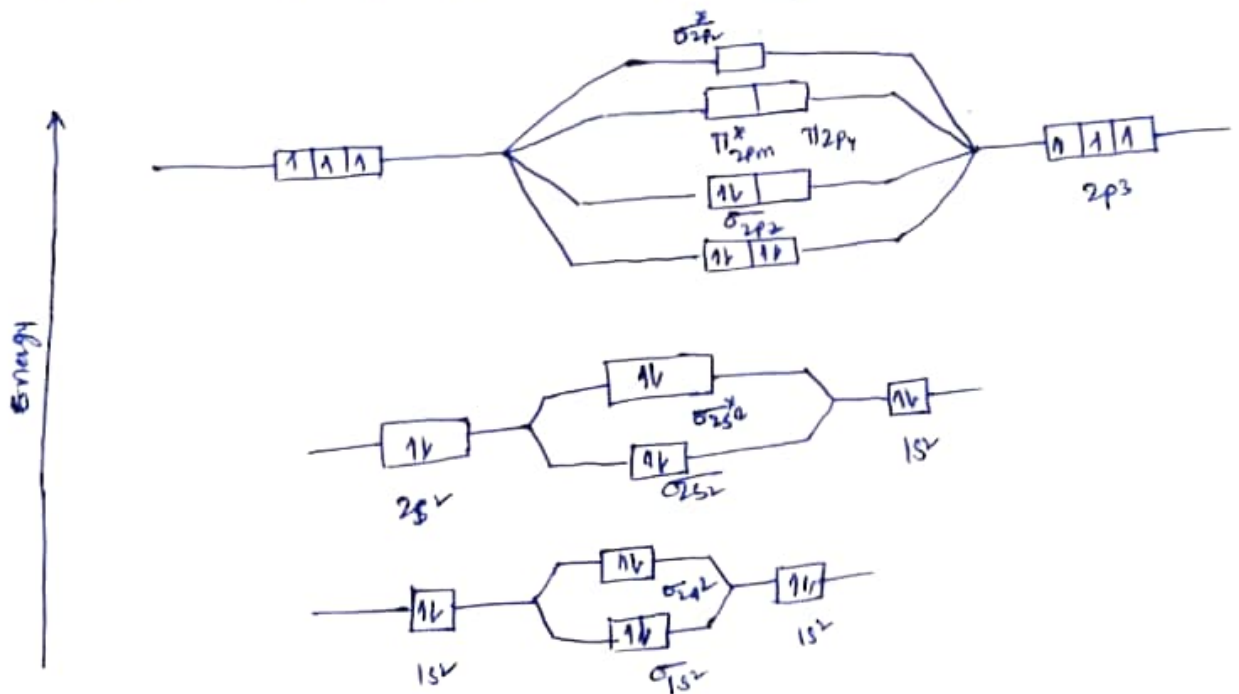
$N_b = 10$

$N_a = 4$

$\therefore$ Bond order $= \frac{1}{2}(10-4) = 3$ which Justifies the pertence of a.

triple Bond. b/w nitroge molecule (N_2)
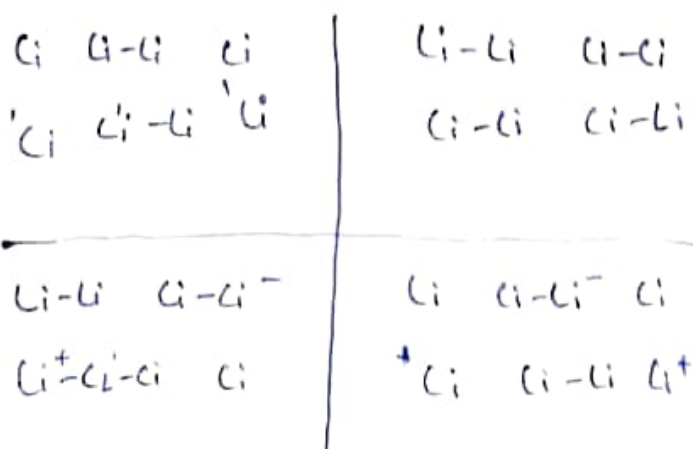
theories of metalic bonds

① free electron theory:

* Positive metal ions are suspended in sea of electron
* Attractions held electrons near cations but not so tightly so as impede flow
* thus valence electrons are delocalized and dont confine to single metal.
* this is because of decrease delocalized and dont confine resulat in metalic bond.
* matallic bond occus where these is atraction between kernels and occuse whese repluon of electron in that gas
* electral conductivity thermal conductivity dultility mallability is explaned through electron sea model.

Limitations:

① Cu is 50 times better conductor than Bi
② metals like Na and k are soft if can easy cut with a knofe, osmium is hard it can even scoetch glass

② VBT:
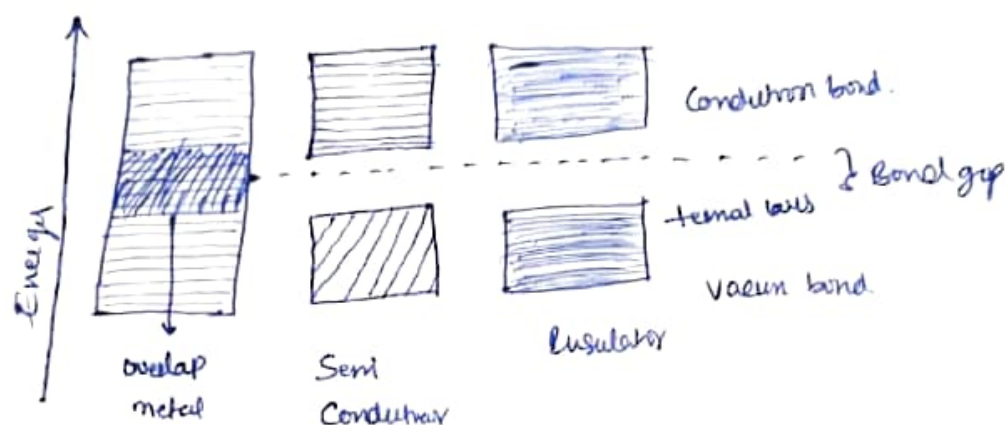
* in Li metal coystal. each atom is surrounded by 8 Li atoms
* So resonance of electron pair bond takes places

Li Li-Li Li | Li-Li Li-Li
Li Li-Li Li | Li-Li Li-Li
_____|
Li-Li Li-Li⁻ | Li Li-Li⁻ Li
Li⁺-Li-Li Li | Li Li-Li Li⁺

MOTs.

* MOT of metals Crystals is like MOT of Covalent molecules

* the electrons in metal are considered to long to the Crystals a whole not to Individual Cons any Pair of atoms.

* matallic bond result from delocaltion of free electron orbitals over all the atoms of a metal Structure.

Conduction bond.

Bond gap

-termal tails

vacun bond

Insulator

overlap metal

Semi Conductour

Energy

* In Li Crystal $Li-1s^2 2s^1 2p^0$

* 1s band: formd by Combination of $1s^2$ orbitals As it is Completely filled. It is non-Conduction bond.

* 2s bond: 2s orbital of each Li atom has 1 electron

2s and 2p orbi bonds are near In energ. Iso 2p bonds overlap with 2s bond Called overlapping zone.

* the level below which all energy levels are filled it termed as femi level.

(1) LCAO :-

* molecular orbitals can be obtained by several methods most Convinient way to describe them is LCAO

* According to LCAO, atomic orbitals can be represented by wave fuction ψ

* In LCAO method, the atoms are brought from a distance to equalibrium internuclear distance where the probability of formation of bond, which deals to form a molecule.

* Consider a molecule AB formed from atoms A and B with wave fuctions ψ_A and ψ_B respectively

$$\psi_{AB} = N[(c_A \psi_A + c_B \psi_B)]$$

where c_A and c_B and constants used to give minimum energy for ψ_{AB}

→ N - normalizing constant

* the probability of finding an electron in a volume of space (du) is $\int u^2 du$

$$\int_0^\infty u^2 du = 1$$

* form (1) we have two assumptions

if $(c_A = c_B)$

$$\psi_b = N_b[A(\psi_A + \psi_B)] \cdots ①$$

if $(c_A = -c_B)$

$$\psi_a = N_a c_A (\psi_A - \psi_B) \cdots ②$$

* for homonuclear diatomic molecules $c_A^2 = c_B^2$

$$\Rightarrow c_A = 1, c_B = \pm 1$$

if $c_A = 1$ & $c_B = 1$:

$$\psi_a = N_b (\psi_A + \psi_B)$$

If $C_A = 1$ & $C_B = -1$:-

$$\psi_a = N_a (\psi_A - \psi_B)$$

* ψ^2 is probability of finding an electron

$$\psi_b^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2 \quad -- ④$$

$$\psi_a^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2 \quad -- ⑤$$

* ψ^2 is probability of finding or finding an electron

$$\psi_b^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2 \quad ---4$$

* form (4) and ⑤ it is clear that finding an electron in bonding orbitals is greater than that an antibonding orbitals by an amount of $2\psi_A\psi_B$

Rules of LCAO :-

* the AO's must roughly of energy when considering overlap b/o too different atoms

* for effective overlap orbitals must overlap one another as must overlap one another as much as possible.

* in order to produce BO and ABMO either symetry of two AO remain uncharged (on both AOs must challenge symmetry in an identical manner

⑤ Bonding in metals:

Bonding in metals should explain the high mobility of electrons and non-directional manner of electrons

→