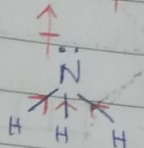


Crystal Field Theory: It is purely an electrostatic model which considers the metal-ligand bond to be ionic (via electrostatic interactions)

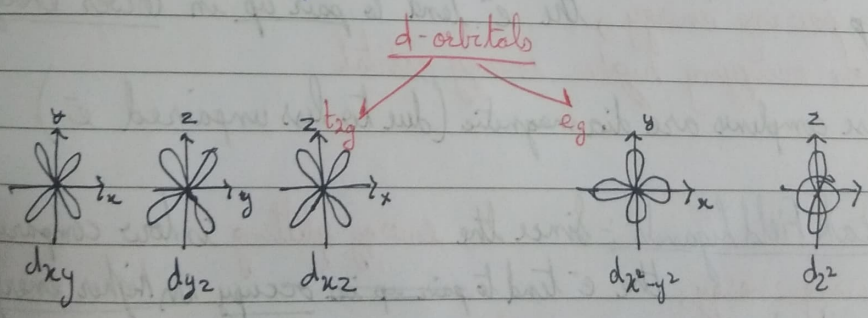
* On the basis of orientation of d-orbitals, they are classified as:-
(i) t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) \rightarrow lie betⁿ the axes
(ii) e_g orbitals ($d_{x^2-y^2}, d_{z^2}$) \rightarrow lie on the axes

Postulates of CFT:-

1. Anionic ligands are treated as -ve point charges & neutral ligands as point dipoles.
Eg for neutral ligand:  Overall e^- density is going up.
2. Interaction betⁿ metal & ligand is purely electrostatic
3. There is no intermixing of orbitals / no hybridization
4. When all 5 d-orbitals have same energy :- degeneracy
* When ligands approach the C.M.A, this degeneracy is lost
In isolated state (degeneracy), there is no external influence
 \rightarrow (When C.M.A is in isolated state)
5. The pattern of splitting depends upon the nature of Crystal Field.

Crystal Field Splitting in Octahedral Complexes:-

In a free/isolated gaseous metal atom/ion, all 5 d-orbitals [$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$] are equal in energy i.e. they degenerate



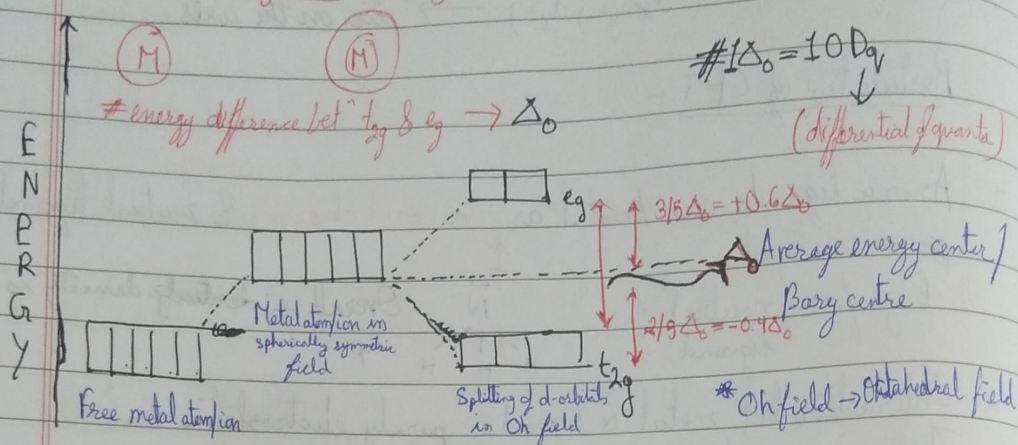
When ligands approach metal atom/ion, the e^- of C.M.A experience repulsion ~~from~~ from lone pairs of ligands
 \therefore d-orbital energy increases all the while maintaining same energy level

In octahedral, ligands approach along $+x, -x, +y, -y, +z, -z$ (x, y, z)

* This is because:

For octahedral, e_g orbitals \uparrow & t_{2g} orbitals \downarrow (energy)

CFSE diagram [Crystal Field Splitting Energy Diagram]



Magnitude of Δ_o (in Oh field) depends on:-

- (1) Nature of metal: whether metal belongs to 1st, 2nd, 3rd Transition series (Sc-Zn) (Y-Cd) (La-Hg)
- (2) Charges present on C.M.A: transition metals have variable valency [Bg: Fe^{2+}, Fe^{3+}]
- (3) Nature of ligand:
 - Strong ligands \rightarrow more splitting (Δ_o)
 - Weak ligands \rightarrow less splitting (Δ_o)

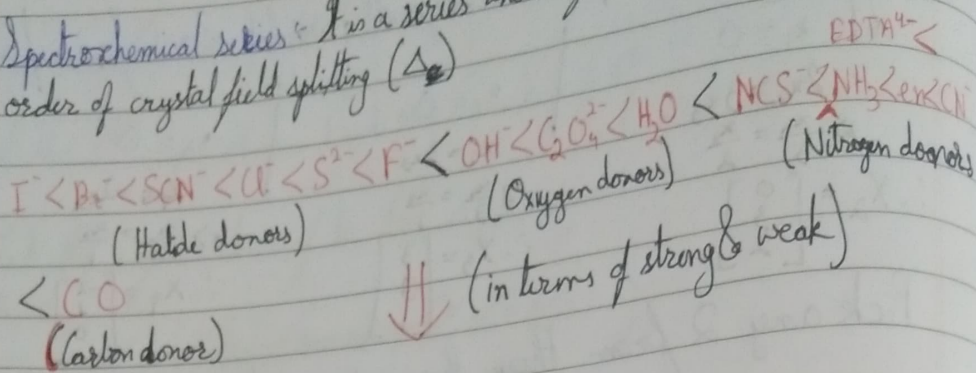
Strong Field Ligands: Since the energy splitting is high & compared to pairing energy, the e^- tend to pair up in lower energy orbitals before occupying higher energy orbitals.

These complexes are diamagnetic (due to less unpaired e^-)

Weak Field Ligands: Since the energy splitting is low compared to pairing energy, the e^- tend to pair up in occupy in higher energy orbitals in order to maximise no of unpaired e^- before pairing up in t_{2g} orbitals. These complexes are paramagnetic (due to more unpaired e^-)


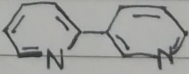
Diamagnetic: less magnetic behaviour & paramagnetic: more magnetic behavior

Spectrochemical series: It is a series where ligands are arranged in increasing order of crystal field splitting (Δ_o)



1. I^- (Iodide)
 2. Br^- (Bromide)
 3. S^{2-} (Sulfide)
 4. Cl^- (Chloride)
 5. F^- (Fluoride)
 6. OH^- (Hydroxide)
 7. $C_2O_4^{2-}$ (Oxalate)
 8. H_2O (Water)
- \Rightarrow Weak ligand considered during CFT

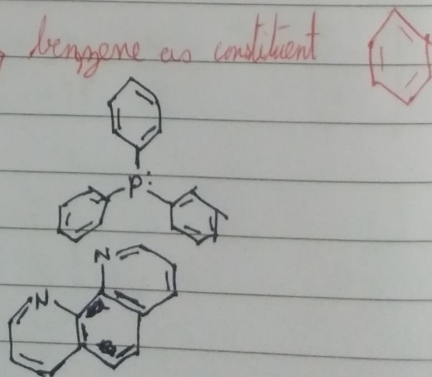
9. NCS^- (Thiocyanate)
 10. NH_3 (Ammonia)
 11. en (Ethylenediamine)
 12. $bipy$ (2, 2'-Bipyridine)
 13. $phen$ (1, 10-Phenanthroline)
 14. NO_2^- (Nitrite)
 15. PPh_3 (Triphenylphosphine)
 16. CN^- (Cyanide)
 17. CO (Carbon monoxide)
- \Rightarrow Strong ligand considered during CFT

Here, • pyridine $\rightarrow C_5H_5N$  • bipy:  $(C_5H_4N)_2$

• $en \rightarrow NH_3-CH_2-CH_2-NH_3$

• $PPh_3 \rightarrow 1 \text{ Phosphorus} + 3 \text{ phenyl group}$

• $phen \rightarrow C_{12}H_8N_2$ (heterocyclic)
 (phenyl group in left)
 two pyridine groups



Magnitude of Δ_o depends on:-

① Charge on metal :-

M^{2+} complex



M^{3+} complex

Δ : 50% rise in splitting

② Whether metal belongs to which 3d, 4d, 5d series

3d $\xrightarrow{\text{30\% rise in splitting } (\Delta)}$ 4d $\xrightarrow{\text{30\% rise in splitting } (\Delta)}$ 5d

③ Nature of ligand :-

- Strong Field Ligand / Low spin complexes :- more splitting, lesser magnetic field
- Weak Field Ligand / High spin complexes :- less splitting, higher magnetic field

Calculation of CFSE :- (in O_h field)

$$\text{CFSE in } O_h \text{ field} = [-0.4 (n_{t_{2g}}) + 0.6 (n_{e_g})] \Delta_o$$

here, $n_{t_{2g}} \rightarrow$ no. of e^- in t_{2g} & $n_{e_g} \rightarrow$ no. of e^- in e_g

Calculation of Magnetic Moment :- (μ_s)

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.} \text{ where } n \rightarrow \text{no. of unpaired } e^-$$

here, B.M. \rightarrow Bohr's Magnetron (unit of μ_s)

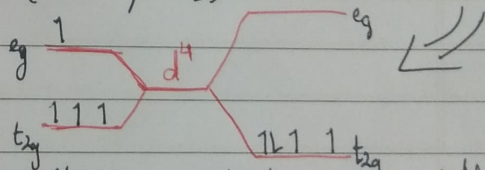
For WFL,

$$\mu_s = \sqrt{4(4+2)} = \sqrt{24} \text{ B.M.} = 2\sqrt{6}$$

For SFL,

$$\mu_s = \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.} = 2\sqrt{2}$$

Eg:- For d^4 configuration:-



If $\Delta_o > P$:- then the next e^- will pair up in the lower energy orbitals instead of going up to higher energy orbitals (huge gap)

* $P \rightarrow$ Pairing energy required to pair the $e^-(s)$

If $\Delta_o < P$:- then the next e^- will go to the higher energy orbital instead of pairing in lower energy orbitals. (low gap)