

Crystal field Theory (CFT) ①

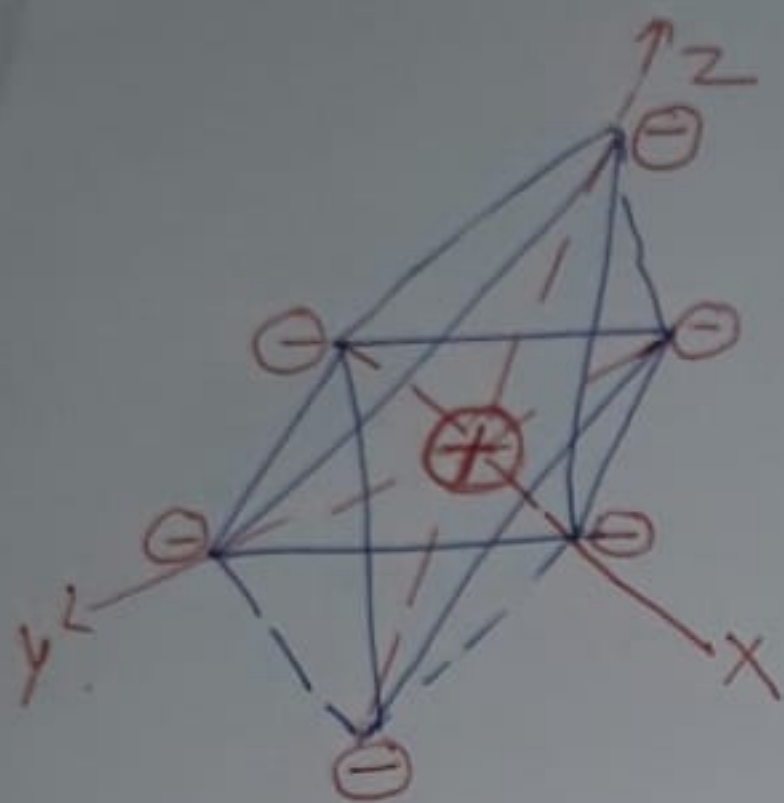
- Developed by Hans Bethe (1929) and John Van Vleck (1932)
- Importance: Gives the explanation for bonding and the properties of complexes.

- Assumptions of theory.

- ① Metal-ligand bond is ionic arising purely from electrostatic interactions b/w metal ion & ligand. If the ligand is anion, then M^+ is cation, the forces of attraction are due to opposite charges. If ligand is neutral molecule like H_2O , NH_3 etc the negative ends of dipole are attracted towards central metal cation.
- ② It treats each ligand as point of negative charge & the arrangement is such that repulsion is minimum.
- ③ It considers the effect of ligand on the relative energies of d-orbitals of central atom/ion. Acc to this theory, in transition metal-ion, all the five d-orbitals are of equal energy i.e. degenerate. The degeneracy is maintained if -ve charges present around central atom form spherically symmetrical field. But if the -ve field is due to ligands which have anions or polar molecules such as H_2O , NH_3 etc & then -ve end towards central atom. The field is unsymmetrical and degeneracy splits which will depend on the nature of crystal field of M^{2+} .

FT for Octahedral Complexes.

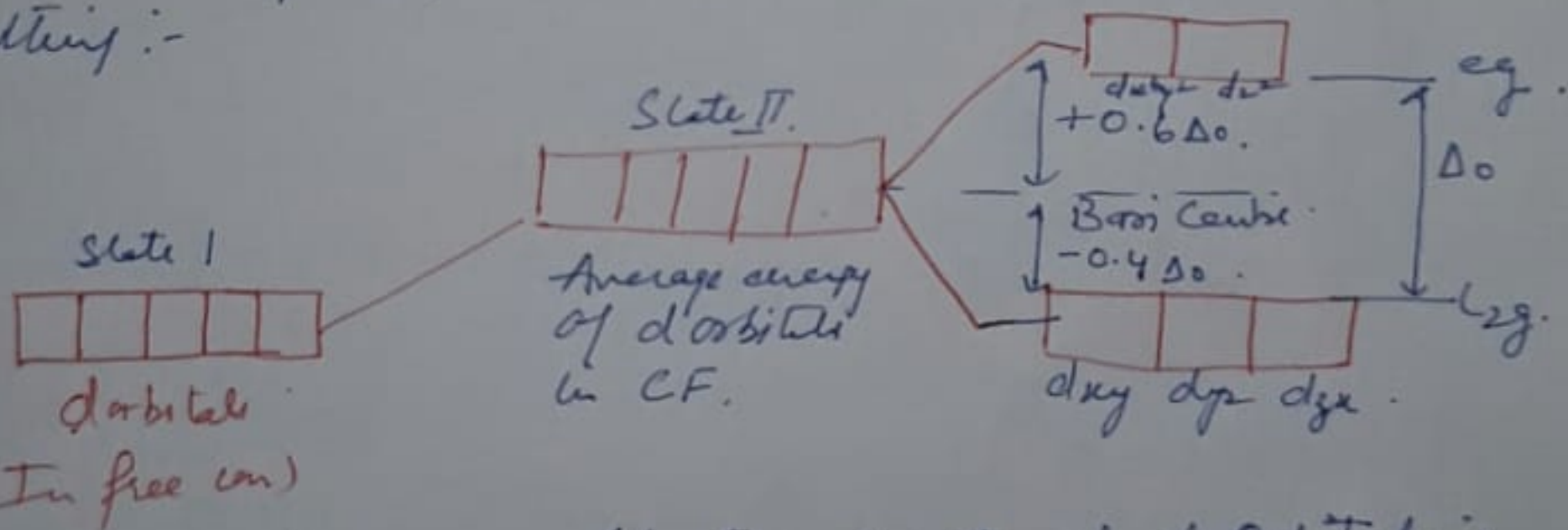
(2)



Represent ligand by \ominus and metal ion by \oplus
 here the -ve charges lie along x, y and z axis and the metal ion is at the Origin.
 As the ligand approach M^{2+} repulsion occurs b/w ligand & d Orbitals \therefore by raising their energy relative to that of free ion.

Mean Value of Energy of d Orbitals is taken as zero. (Barycentre) - $d_{x^2-y^2}$ & d_{z^2} have lobes along axes \therefore they point towards the ligands and lobes of d_{xy} , d_{yz} , d_{zx} lie b/w the axes hence they lie b/w ligands. So the energy of t_{2g} are lower than those of (eg) orbitals.

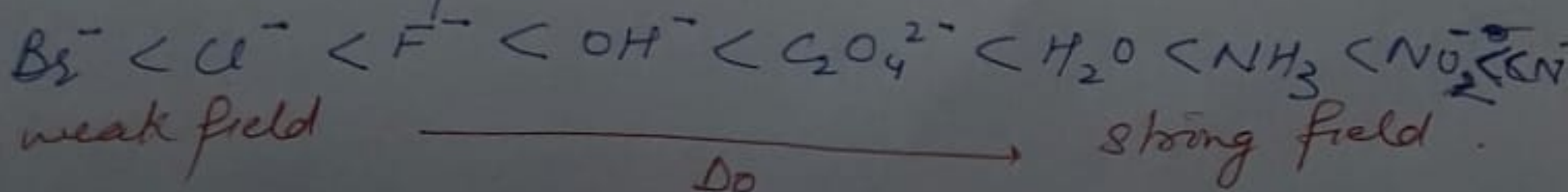
splitting:-



The difference in energy b/w the 2 sets of d Orbitals is called CFSE. (Crystal field Stabilization Energy). Δ_0 .
 eg orbitals are $+0.6\Delta_0$ above average energy level.
 t_{2g} " are $-0.4\Delta_0$ below " " " " " "

For any M^{2+} , the magnitude of Δ_0 depends on nature of ligand.

This arrangement of ligands in order of CFSE Values is known as spectrochemical Series.



Δ_0

Explanation of properties of Complexes & CFT.

High spin state stable if Δ_0 is small. (~~for~~ No pairing)
Low spin state stable if Δ_0 is large (pairing)
सहायक diff pairing Δ_{011} , if pair then low spin.

Δ_0 comparison \bar{c} P (Pairing)

- (i) If $\Delta_0 < P =$ No pairing. eg weak field.
 so $4^{th} e'$ will enter eg then for $4e'$ the configuration is $t_{2g}^3 e_g^1$.
- (ii) If $\Delta_0 > P =$ (will not go up) Pairing occurs upto d^6 in t_{2g} .
 eg (strong field)

Remember (सहायक diff. \rightarrow Pairing \rightarrow low spin)
eg strong field ligands)
So max we go to RHS more will be the pairing.

(2) Magnetism: - Strong field ligands cause low spin state to be more and stable. & the weak field ligands cause high spin state to be more stable.

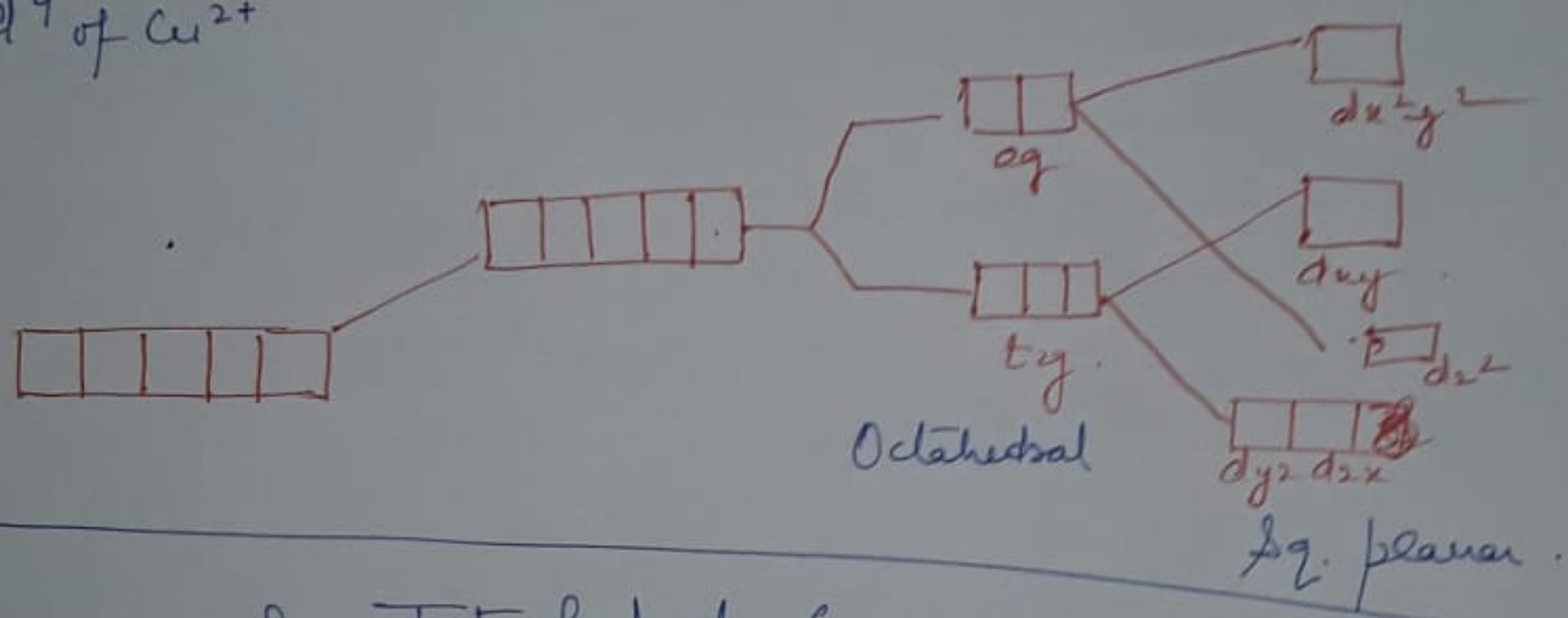
(3) Colour: - Transition metal complex absorb visible light which excites e' from lower d orbitals to higher $d \bar{c}$ higher energies. for eg.
 $[Ti(H_2O)_6]^{3+}$ Ti III has only one $3d e'$
It has energy 240 kJ/mole greater than Δ_0 value and is sufficient to excite e' from t_{2g} to e_g orbital. So green yellow colour absorbed so the colour is purple.

Drawbacks: The energy of splitting caused by certain ligand is not according to expectation.
(1) Expected that ammine ligand should have greater splitting effect but this is not so.
(2) OH^- is below H_2O & NH_3 yet it produces greater splitting.

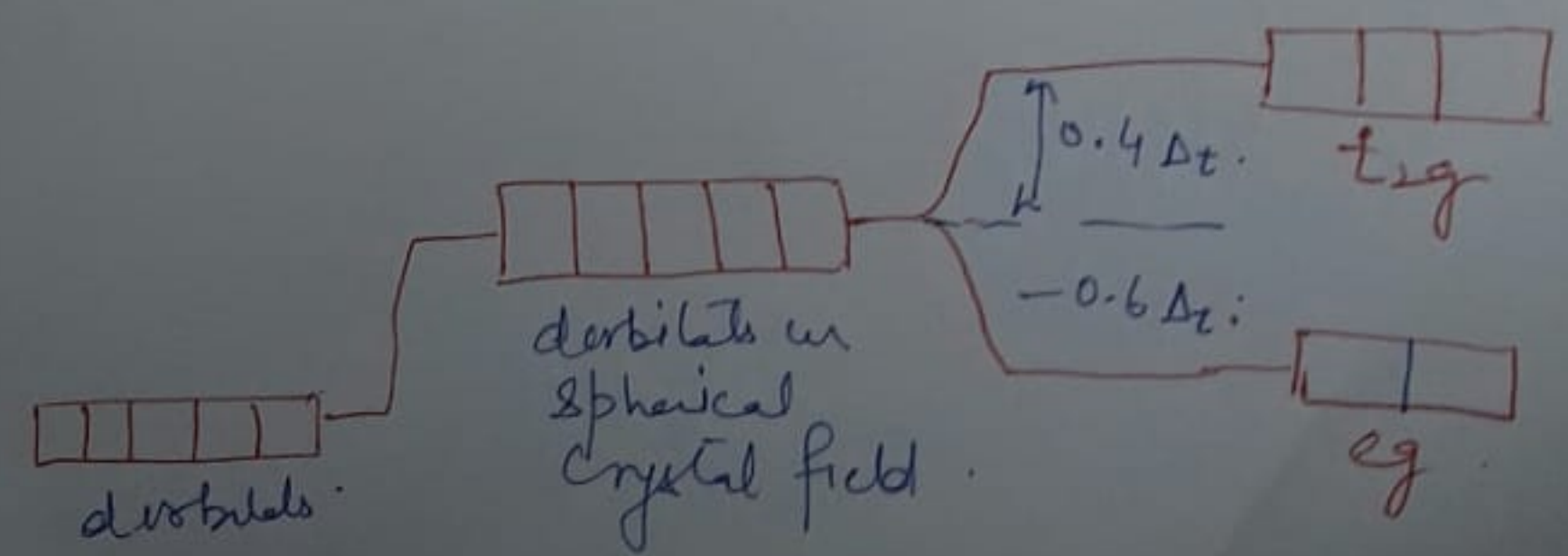
CT for Square planar (remove -ve charges from 2 axis).
 So d_{z^2} , d_{xz} and d_{yz} orbitals become more stable. So;

eg Complexes of
 d^8 ions Pt(II), Pd(II), Au(III), Rh(I), Ir(I), Ni(II)
 d^9 of Cu^{2+}

$d_{x^2-y^2}$ (towards the ligand)
 d_{xy} (lobes lie b/w ligand but are coplanar to them)
 d_{z^2} (Lobes point out of plane of complex)
 d_{xz}, d_{yz} (Lobes point out of plane least affected)



CFT for Tetrahedral (just reverse of Octahedral) i.e. t_{2g} has higher energy than e_g .
 eg. splitting is much smaller than that in Octahedral complexes.
 $\Delta_t = -\frac{4}{9} \Delta_o$. This energy is too small. So have high spin configurations.



eg. $CoCl_4^{2-}$, $MnBr_4^{2-}$, $FeCl_4^-$

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factors affecting Δ (orbital splitting energy).

(i) Oxidation state of metal ion:- Higher (OS) higher Δ value.

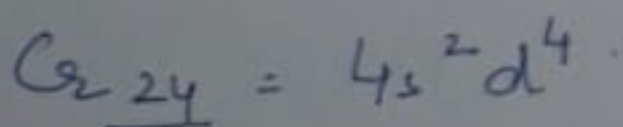
(ii) Nature of metal ion:- In d block as we move in same gp. 3d to 4d to 5d. Do 1st 2 have low spin complexes stability. 2nd & 3rd transition series have greater tendency to form low spin than 1st transition series.

(iii) Geometry of coordination entity:-

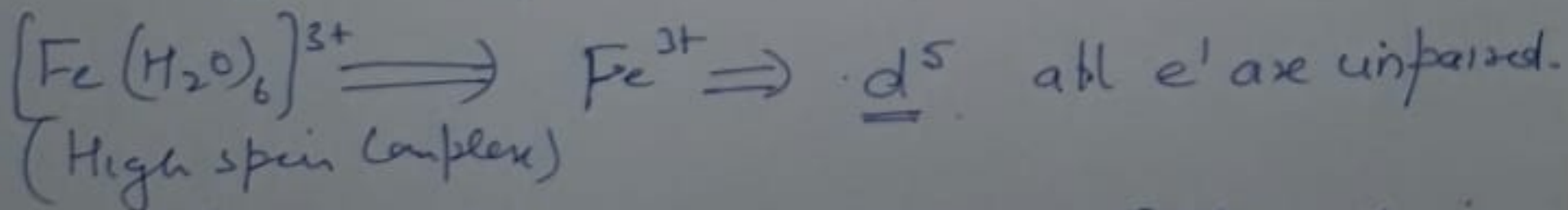
$$\Delta_t = -\frac{4}{9} \Delta_o \quad \Delta \text{ value of tetrahedral is } 50\% \text{ of octahedral.}$$

(iv) Nature of ligand: As shown in spectrochemical series.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At. No.	21	22	23	24	25	26	27	28	29	30



$\text{Cr}^{3+} = \underline{d^3}$ but if it d^4 to d^7 then several choices.



but $[\text{Fe}(\text{CN})_6]^{3-} \Rightarrow$ AS CN^- strong field so Δ_o is large \therefore ~~stop~~ pairing. hence low spin complex.

CN^- always gives low spin complexes for d^4, d^5, d^6, d^7