CRYSTAL FIELD THEORY developed by Hans Bethe & John Hasbrouck Van Vleck

CFT describes the breaking of orbital degeneracy in transition metal complex due to the fnce of ligands

⇒ It describes qualitatively the strength of Metal–Ligand bonds.

↓

Based on strength of M→L, the energy of the system is altered

↓

Leads to change in Magnetic properties & color.

In Simple words, this theory explains the effect of the electrical field of neighboring ions on the energies of the valence orbitals of an Ion in a crystal

Acc. to CFT, the attraction b/w the central metal & ligand in a complex is purely electrostatic.

Important features of CFT:

1. Central metal cation is surrounded by ligands which contains one or more lone pairs of electrons.

2. The Ionic ligands (eg. F^-, Cl^-, CN^- etc) are considered as negative pt. charges or point charges

Neutral ligands (CH_2O, NH_3 etc) are considered as point dipoles or simple dipoles and the negative end of ligand dipole is oriented towards the metal cation.

f↑ reaction b/w positive charge of metal & non-bonding le⁻ of the ligand. positive change of metal & the ligand

3. Acc; to CFT, no overlapping of orbitals or mixing of orbitals takes place.

4. The bonding b/w the metal cation & ligand is not covalent, but it is purely electrostatic or Columbic attraction b/w cations & anions.

↓

Complex form^n takes place due to this electrostatic attractions of metal cation which is centrally situated centrally and attracts -vely charged ligands or dipole molecules.

Description of d-orbitals:

dxy   dyz   dxz

dx²-y²   dz²
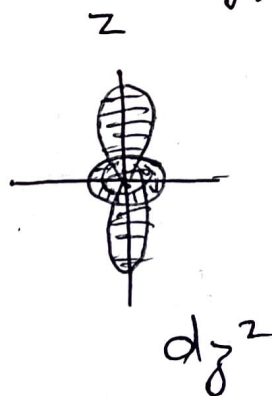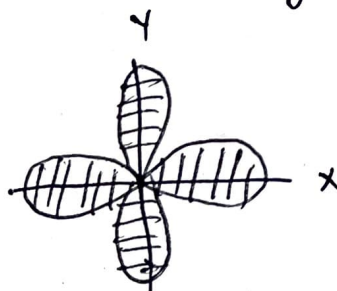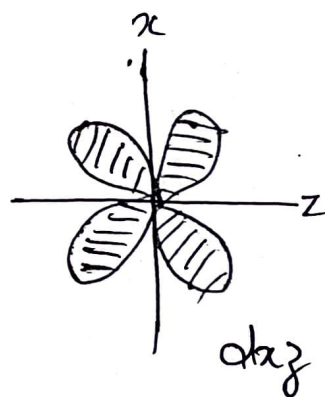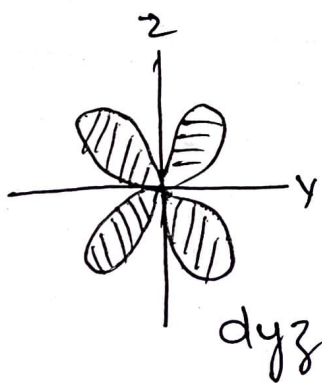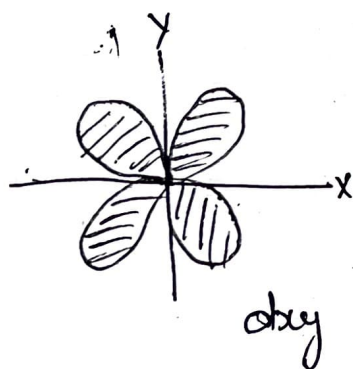
- d_{xy}: lobes lies in b/w x & y axes
- d_{yz}: " " " y & z axes
- d_{xz}: " " " x & z axes
- $d_{x^2-y^2}$: lobes lie on the or along x & y axes
- d_{z^2}: Lobes → two on z-axis
  → Donut shape ring which lies on xy plane area

Depending upon orientation of the lobes, the 5 d-orbitals are grped into two sets:

1. e_g set of orbitals (d_{z^2} & $d_{x^2-y^2}$)
   → consists two orbitals
   → lobes are along the axes
   → known as axial orbitals
   → Acc. to group theory, e refers to doubly degenerate set. also known as e_g orbitals when

2. t_{2g} set of orbitals (d_{xy}, d_{yz}, d_{xz})
   → includes three orbitals
   → d_{xy}, d_{yz}, d_{xz}
   → lobes lie b/w the axes
   → non-axial orbitals known as t_{2g} orbitals
   → Acc. to grp theory, t refers to triply degenerate set.

<u>Crystal field splitting of d-orbitels in octahedral complexes</u>
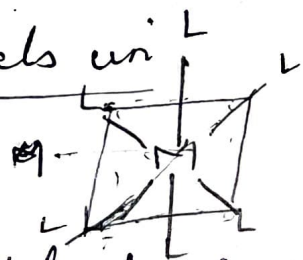
In a single metal ion, all 5 d-orbitals have same energy.
↓
when ligand approaches the metal ions,
↓
The e⁻s in d-orbitals of metal cation are repelled by -ve pt. charge or by -ve end of the dipole ligands.
↓
this repulsion will raise the energy of the 5 d-orbitals
↓

↓

If all the ligands approaching the central cation are at equal distance from each of the d-orbitals

↓↓

the energy will raise (of all d-orbitals) by same amt.

↓

i.e all the d-orbitals will still remain degenerate, although now will have higher energy than before.
(This is hypothetical situation)

As the lobes of e_g orbitals ($d_{x^2-y^2}$ & d_{z^2}) lie directly in the path of approaching ligands, so the e's in these orbitals experience greater force of attraction repulsion than t_{2g} orbitals (lobes are b/w the axes) i.e space b/w the path of approaching ligands).

↓

Therefore energy of e_g orbital is increased, while that of t_{2g} is decreased.
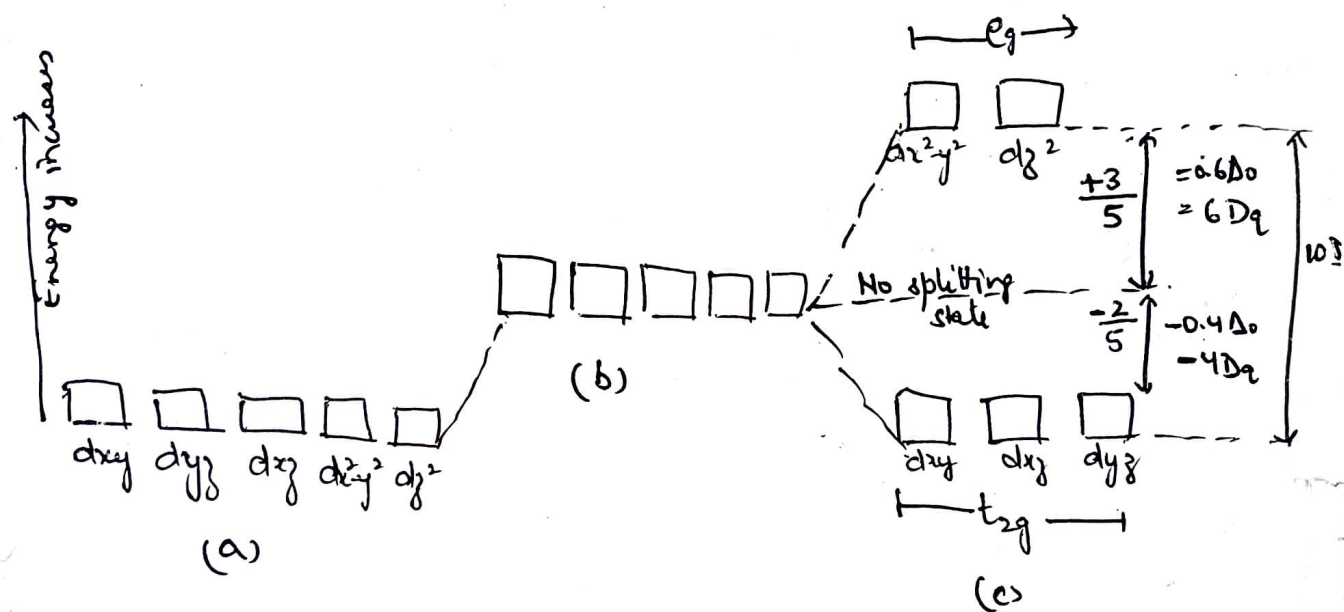∴ Greater is the repulsion, greater will be the increase in energy.

↓

There So, the 5 d-orbitals are now split into two levels viz., t_{2g} level which is triply degenerate and lower in energy and e_g which is doubly degenerate and hence is of higher energy

↓

∴ So, the degeneracy of 5 d-orbitals is removed under the influence of the ligands.

The sep^n of 5 d-orbitals of the metal ion into two sets with different energies is known as crystal field splitting or energy level splitting. The concept of crystal field splitting makes the basis of CFT.

The energy gap b/w t_{2g} & e_g → Δ_o or $10 Dq$
where O in Δ_o indicates an octahedral arrangement of ligands round the metal cation.

Δ_o → Crystal field splitting Energy (CFSE)

↑ Energy increases →

e_g →

$d_{x^2-y^2}$ d_{z^2}

$+\frac{3}{5}$ = 0.6Δ_o
        = 6 Dq

No splitting state

$-\frac{2}{5}$ $-0.4\Delta_o$
        $-4Dq$

10?

d_{xy} d_{yz} d_{zx} $d_{x^2-y^2}$ d_{z^2}

(a)

(b)

d_{xy} d_{xz} d_{yz}

t_{2g} →

(c)

a = Five degenerate d-orbitals of the metal cation free from ligand field

b = Hypothetical degenerate d-orbitals at a higher energy level.

c = splitting of d-orbitals into t_{2g} & e_g under the influence of six ligands in octahedral complexes.

1. t_{2g} set loses energy $= 0.4 \Delta_0$ $(4 Dq)$

e_g set gains energy $= 0.6 \Delta_0$ $(6 Dq)$

$+$ sign & $-ve$ sign indicates gain & loss of energy.