Crystal field theory

- Dr. SHASHI KUMAR SINGH
L.S. College.

by Bethe and Van Vleck

Two Main limitations of Valence bond theory
(i) Fail to explain Spectra or Colour of compounds
(ii) Couldnot explain tem. depend Magnetic moment

Then Crystal field theory come.

The main points of C.F.T.

(1) ligands are treated as point charge
As we know there are three types of ligands
(i) Negative ligands, example — Cl^-, Br^-, I^-, F^-, CN^-, OH^- etc.
(ii) Neutral ligands — $\cdot \rightarrow NH_3$, H_2O, organic ligands i.e. Ethylenediamine, EDTA etc.
(iii) Positive ligands — NO^+, CH_3 etc

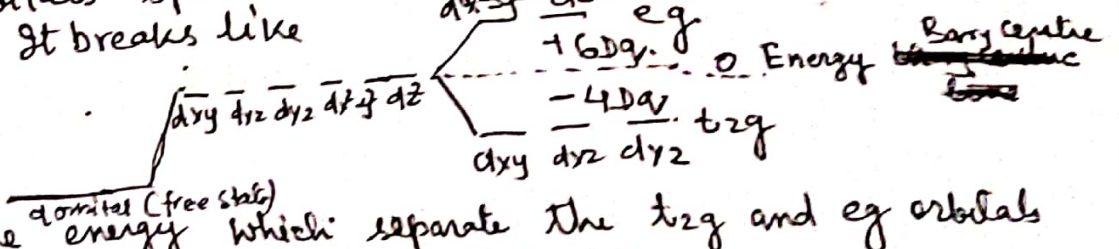
Neutral ligands have dipole moment as for example

$$NH_3 \quad H-\overset{\delta-}{N}-\overset{\delta+}{H} \quad = \quad M \leftarrow \overset{\delta-}{N}H_3$$

So, the force exist between Metal and ligands are purely electrostatic i.e. ion-ion interaction or ion-dipole interaction takes place

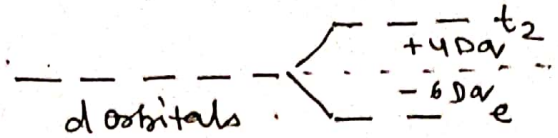
(ii) There is no interaction between Metal orbital and ligands orbitals.

(iii) When metal is in free state all d-orbitals are degenarate, means all d-orbitals ~~are~~ ~~deg~~ have equivalent energy. As Metal comes with ligands field the degeneracy of d-orbitals destroy.
d-orbitals split into t_{2g} and e_g. In octahedral field
— It breaks like

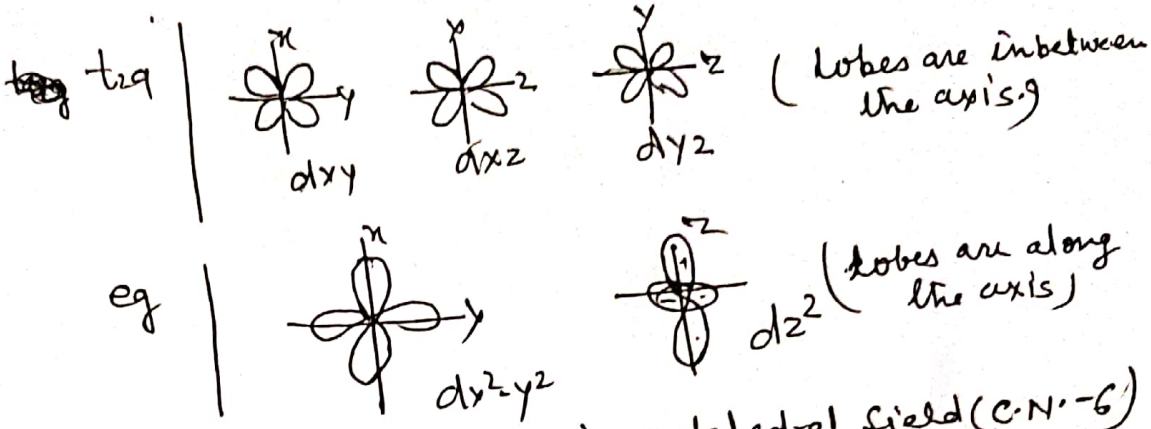


The energy which separate the t_{2g} and eg orbitals is termed as crystal field splitting energy and denoted as Δ_o or Dq. The value is taken as above figure. Even one electron which present in d orbitals cause this separation and stablize by $-4Dq$ or $-0.4\Delta_o$.

For tetrahedral field this will split like

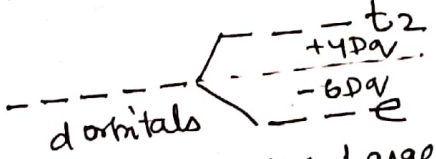


In octahedral field ligands inter through along the axis. As we know the shape of d-orbitals are



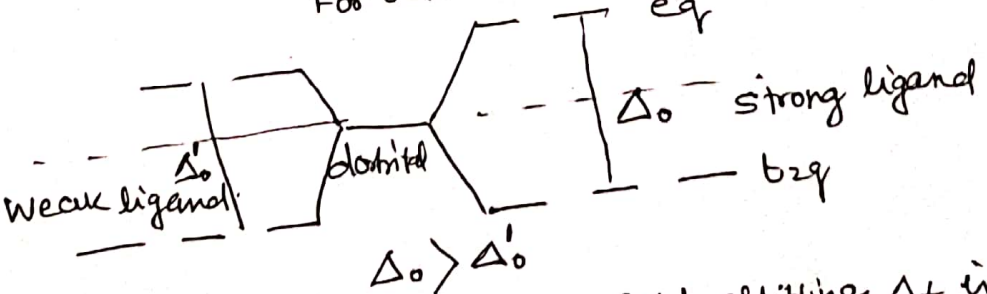
As ligands inter along the axis in octahedral field (C.N.-6) The energy raises of eg orbitals i.e. $d_{x^2-y^2}$ and d_{z^2}.

But for tetrahedral field ligands inter through near in between axis so, The separation will just opposite.



The ligands which causes large splitting is known as STRONG LIGAND and which causes less is calles WEAK LIGAND

For octahedral field



The magnitude of the crystal field splitting Δ_t in tetrahedral is considerably less than in octahedral fields.

There are two main reason for this

(i) only four ligands instead of six, so the ligand field is only two thirds the size. hence the ligand field is also two thirds the size.

(ii) the direction of the orbitals does not coincide with direction of the ligands. This reduces the crystal field splitting by roughly a further two third.

(contd.)