

Two Main limitations of Valence bond theory

- ① Fail to explain spectra or colour of compounds
- ② Could not explain temp. depend Magnetism

Then Crystal field theory came.

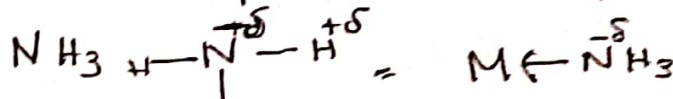
The main points of C.F.T.

① Ligands are treated as point charge

As we know there are three types of ligands

- ① Negative ligands, example - Cl^- , Br^- , I^- , F^- , CN^- , OH^- etc.
- ② Neutral ligands - $\rightarrow \text{NH}_3$, H_2O , organic ligands i.e. ethylenediamine, EDTA etc.
- ③ Positive ligands - VO^+ , CH_3 etc.

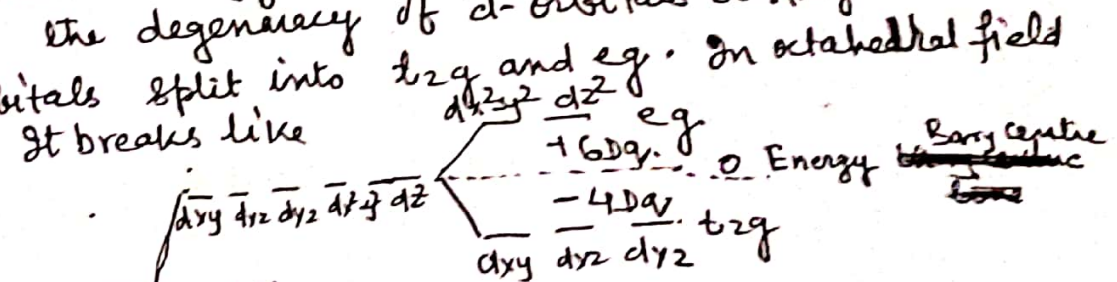
Neutral ligands have dipole moment as for example



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

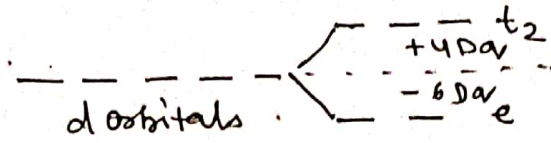
② There is no interaction between Metal orbital and ligands orbitals.

③ When metal is in free state all d-orbitals are degenerate, means all d-orbitals ~~are~~ ~~do~~ 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

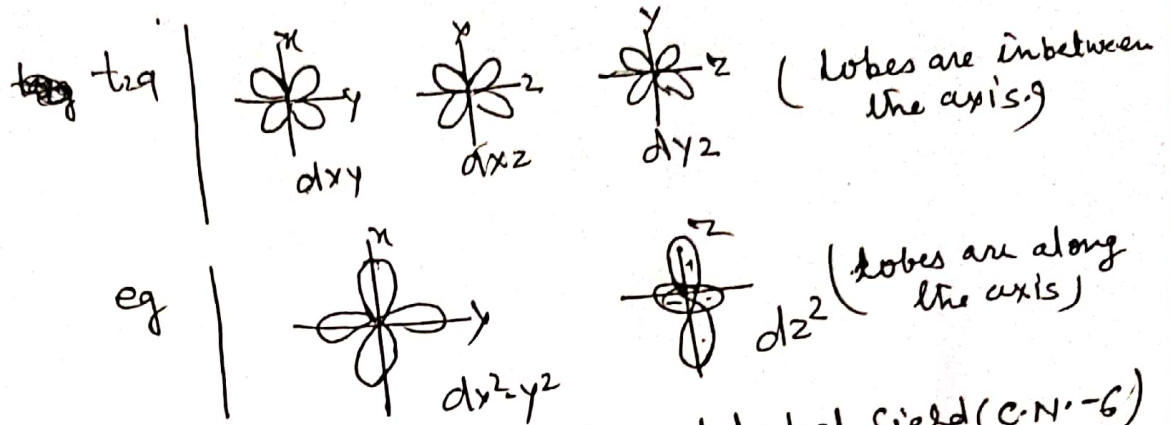


The ^{d-orbital (free state)} energy which separate the t_{2g} and e_g orbitals is termed as crystal field splitting energy and denoted as Δ_o or $10Dq$. The value is taken as above figure. Even one electron which present in d orbitals cause this separation and stabilize by $-4Dq$ or $-0.4 \Delta_o$.

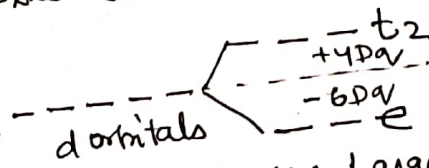
For tetrahedral field this will split like (2)



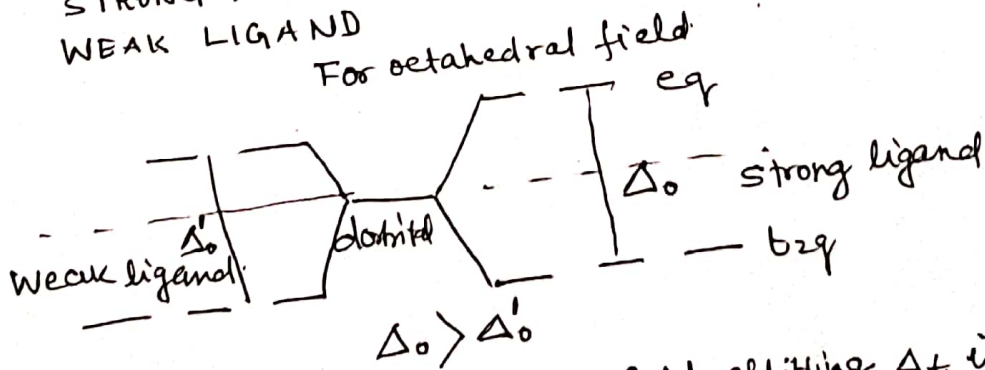
In octahedral field ligands enter through along the axis. As we know the shape of d-orbitals are



As ligands enter along the axis in octahedral field (C.N. = 6) the energy raises of eg orbitals i.e. dx^2-y^2 and d_{z^2} . But for tetrahedral field ligands enter through near in between axis so, the Δ separation will just opposite.



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



- 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.)