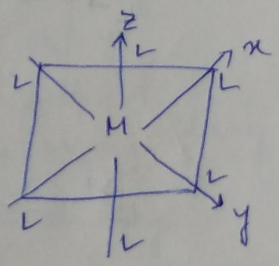
Crystal Field Theory.

Important features of CFT :

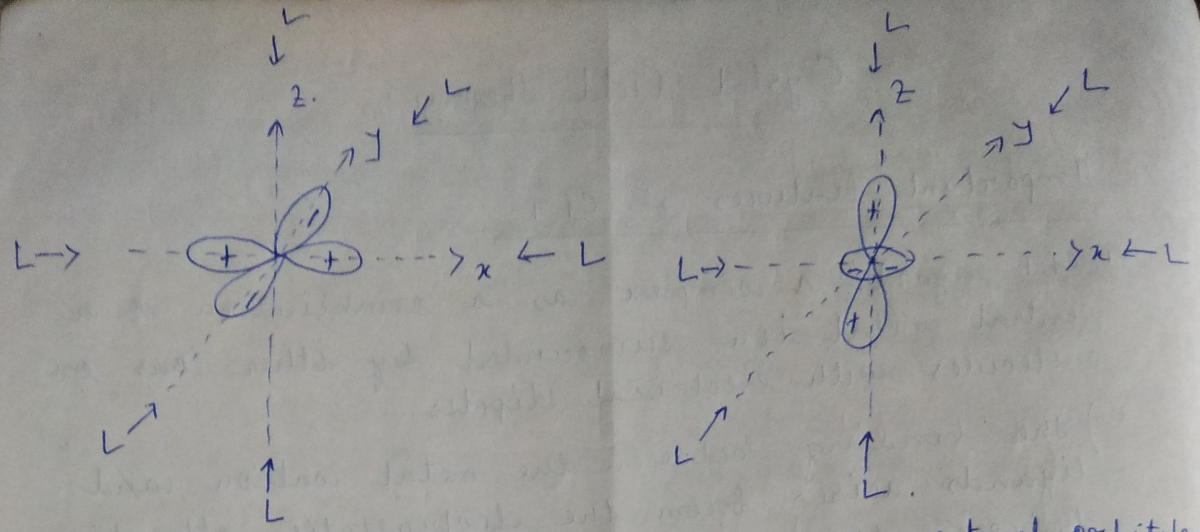
i) CFT regards a complex as a combination of a central metal ion surrounded by other ions or molecules with electrical dipoles.

ii) The bonding between the metal cation and ligands arises from the electrostatic attraction between the nucleus of the metal cation and the partial negative charges invariably present on the ligand.

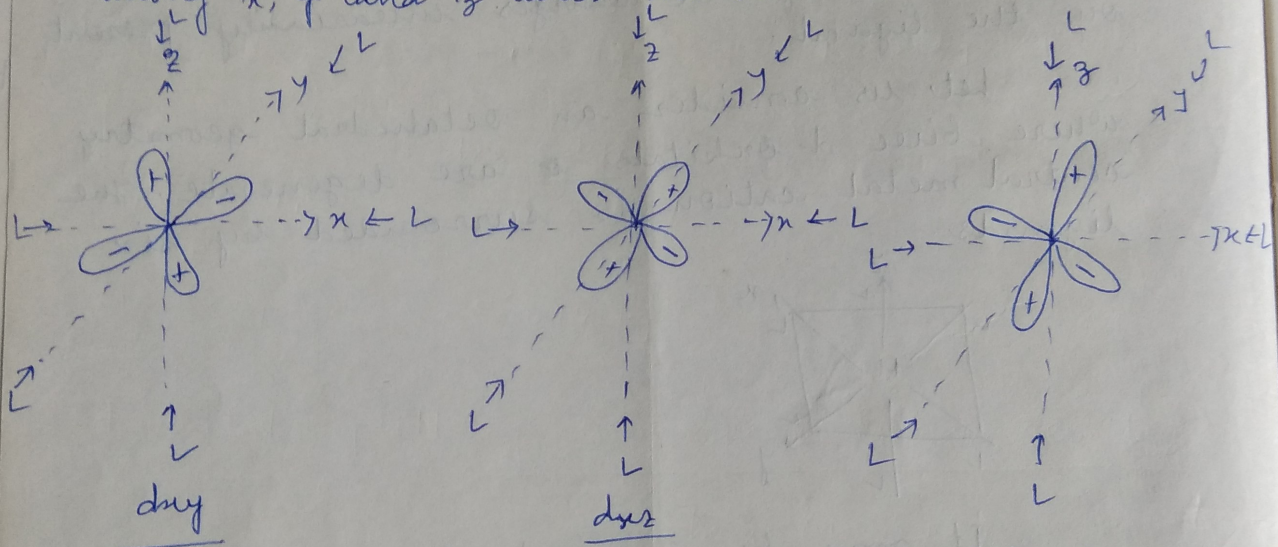
Let us consider an octahedral geometry where five d-orbitals are degenerate. The central metal cation is surrounded by six ligands.



It may be supposed that all the ligands on each of the axis are allowed to approach to the central metal cation M^{n+} from the end of the axis. In this process the electrons in d-orbitals are repelled by the negative charges of the ligands. This repulsion will raise the energy of all the five d-orbitals. If all the ligands are allowed to approach at an equal distance from the metal ion, the energy of the all orbitals remain degenerate. This is a hypothetical situation. Since the lobes of e_g orbitals lies directly in the path of approaching ligands; so these orbitals experience greater energy than those in t_{2g} set orbitals which are directed in space between the path of approaching ligands.



Six ligands approaching with the e_g - set of orbitals along x, y and z axes in octahedral complex.



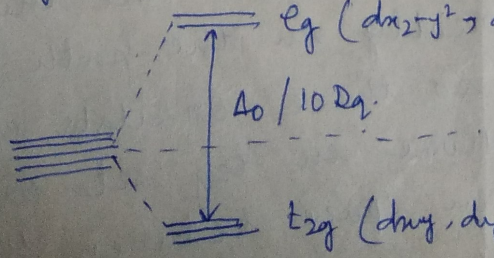
d_{xy} d_{xz}

Ligand approaching with the t_{2g} set of orbital along x y z axes in the octahedral complex.

Therefore the energy of e_g set orbital is greater than that of the t_{2g} - set orbitals. Hence under influence of the approaching ligands, the free d-orbitals which are originally degenerated in the free metal ion, now split up into two levels.

i) e_g levels which is of higher energy and

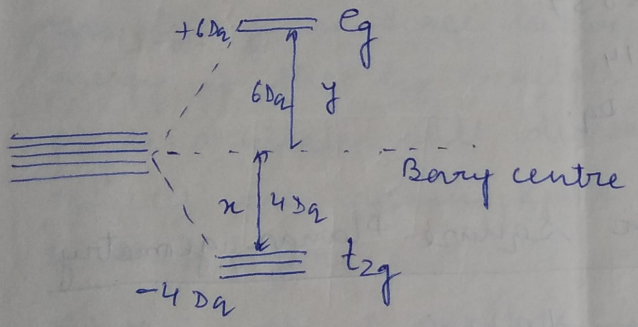
ii) t_{2g} levels which is of lower energy.



Thus the degeneracy of five d-orbitals are removed into two sets of energy levels. The seperation of five degenerated d-orbitals into two sets having different energy is called crystal field splitting or energy level splitting.

The energy gap between t_{2g} set and e_g set orbital is denoted by Δ_o which is equal to $10\,Dq$. This Δ_o or $10\,Dq$ is called crystal field ~~splitting~~ splitting energy ~~(CFSE)~~.

With the help of simple geometry it can be shown that the energy of e_g set is $6\,Dq$ higher than the hypothetical degenerated d orbitals and for t_{2g} is $4\,Dq$ less than the hypothetical degenerated d-orbitals.



Let $x + y = 10\,Dq$.

$5E = 2(E+y) + 3(E-x)$

$3x = 2y$.

$\frac{x}{y} = \frac{2}{3}$

$\frac{x+y}{y} = \frac{5}{3}$.

$\therefore x = 4\,Dq$.

$y = 6\,Dq$.

$\frac{10}{y} = \frac{5}{3}$ or $y = 6\,Dq$.

$x = 10 - 6 = 4\,Dq$.

From ~~octa~~ octahedral geometry if two ligands on the z-axis are completely removed, then we get the square planar geometry. The energies of dx^2-y^2 and dxy orbital will raise and the energies of dz^2, dxz, dyz will fall.

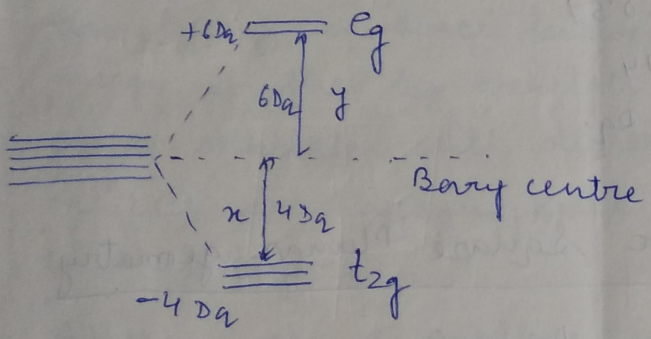
Now due to removal of ligands from z-axis

i) For each ligand removed dz^2 will have energy lower by $5.14\,Dq$ for each ligand.

Thus the degeneracy of five d-orbitals are removed into two sets of energy levels. The seperation of five degenerated d-orbitals into two sets having different energy is called crystal field splitting or energy level splitting.

The energy gap between t_{2g}-s and e_g set orbital is denoted by Δ_o which is equal to 10 Dq. This Δ_o or 10 Dq is called crystal field ~~splitting~~ splitting energy ~~CFSE~~.

With the help of simple geometry it can be shown that the energy of e_g set is 6 Dq higher than the hypothetical degenerated 'd' orbitals and for t_{2g} is 4 Dq less than the hypothetical degenerated d-orbitals.



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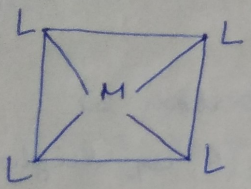
Now due to removal of ligands from z-axis

i) For each ligand removed dz^2 will have energy lower by 5.14 Dq for each ligand.

ii) For each ligand removed d_{yz} and d_{zx} will have lower energy by 0.57 Dq ~~for each ligand~~.

iii) For each ligand removed d_{xy} and $d_{x^2-y^2}$ will have increased energy by 3.14 Dq for each ligand.

Square planar geometry



d_{z^2}

$E = +6 - 2 \times 5.14$

$= 6 - 10.28$

$= -4.28$ Dq.

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

$= 6 + 2 \times 3.14$

$= 6 + 6.28$

$= 12.28$ Dq.

d_{xy}

$= -4 + 2 \times 3.14$

$= -4 + 6.28$

$= +2.28$ Dq.

d_{xz}, d_{yz}.

$= -4 - 2 \times 0.57$

$= -4 - 1.14$

$= -5.14$ Dq.

d-orbital Splitting in Square-Planar geometry