



# *Inorganic Chemistry*

**Programme Code- MSCCH-17/18/19**

**Course Code-CHE-501**

**Unit- 6 Crystal Field Theory (CFT)**

Presented by-

Dr. Charu C. Pant

Department of Chemistry

Uttarakhand Open University, Haldwani

## ❖ *CRYSTAL FIELD THEORY (CFT)*

In view of the weaknesses of Valence Bond Theory (VBT), an alternative bonding model was applied to transition metal complexes. This is known as crystal field theory (CFT). Brethe and Van Vlick have been proposed a theory to explain the bonding in the ionic crystals, which is called as Crystal Field Theory (CFT). Initially this theory was propound for the ionic crystals but in 1952 Vage has been proposed this theory for the metal-ligand bonding in the complex compounds, which is known as CFT of the Coordination Chemistry.

## ❖ POSTULATES OF CFT

1. According to the CFT, central metal ion (CMI) of the complexes being surrounded by the number of ligands.
2. According to this theory, ligands can be of the two types which are given below:
  - a. Negative ligands also known as point dipole.
  - b. Neutral ligands also known as point dipole.
3. According to CFT there does not occur any type of the overlapping between the orbitals of the ligand and CMI i.e. metal ligand bonding having zero % covalency.

4. According to CFT always there occur an electro static interaction between the +ve charge nucleus of the CMI and –ve charge of the ligand i.e. metal- ligand bonding having 100% ionic character. Complexes are thus presumed to form when CMI electrically attract ligand which may be either anions or dipolar molecules.

If the complex containing neutral ligand then the –ve pole of neutral ligand (point dipole) will be oriented toward the CMI.

# 1. CFT FOR THE OCTAHEDRAL COMPLEXES

CFT of octahedral complexes can be defined in the following steps:-

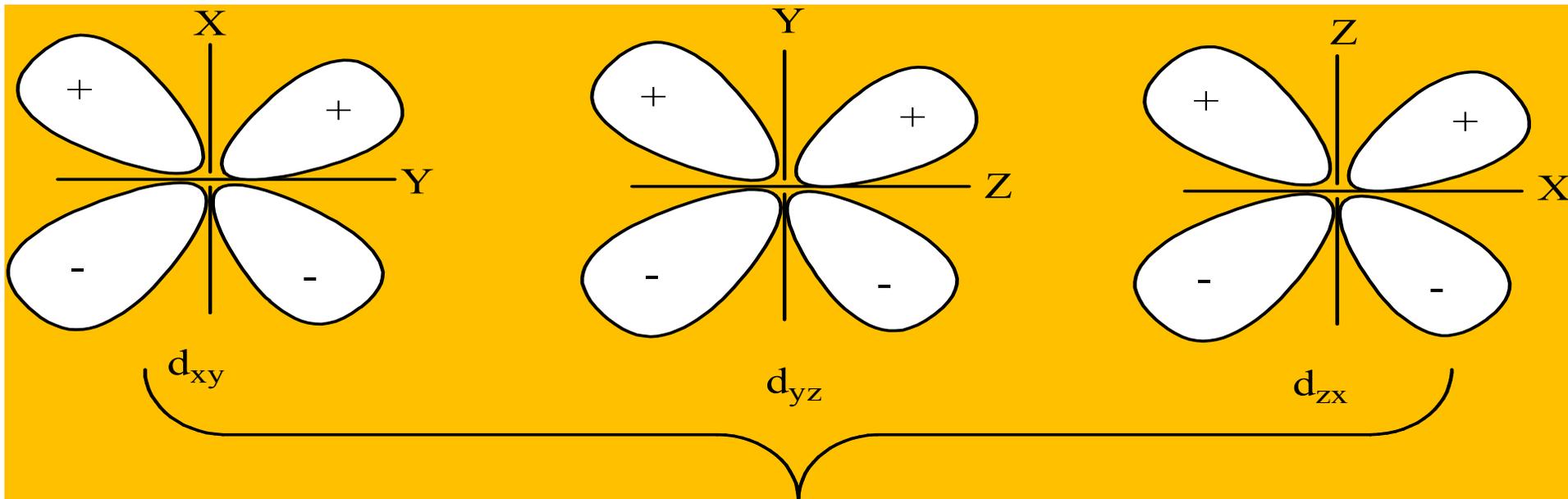
## **Step I- Shape of 5- d orbital's of CMI:**

Five d- orbitals of the CMI can be divided into two different set of orbital's which are

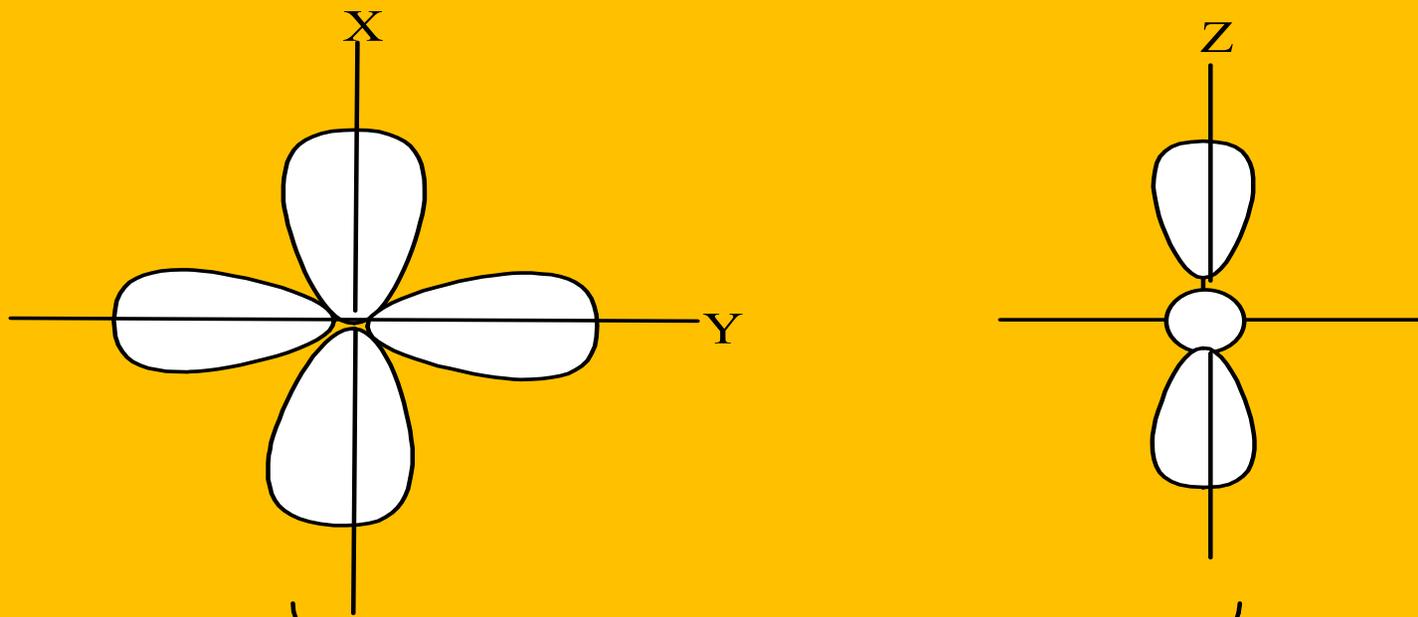
given below:-

### **a. $t_{2g}$ set (Non-axial set of d-orbital):**

$d_{xy}$   $d_{yz}$  &  $d_{zx}$  orbital's are known as  $t_{2g}$  set of orbital's. All these orbital being present between the axis due to which they are also known as Non-axial set of d- orbitals



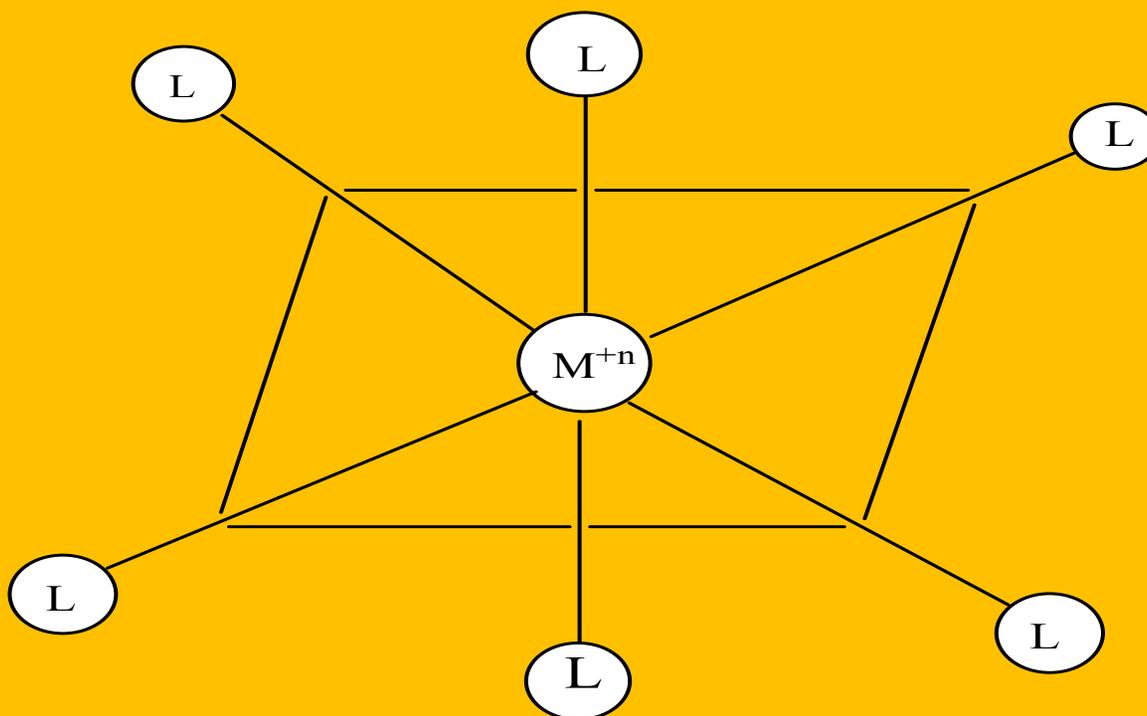
**$t_{2g}$  -orbitals (Non-axil)**



**$e_g$  - set of orbital's**

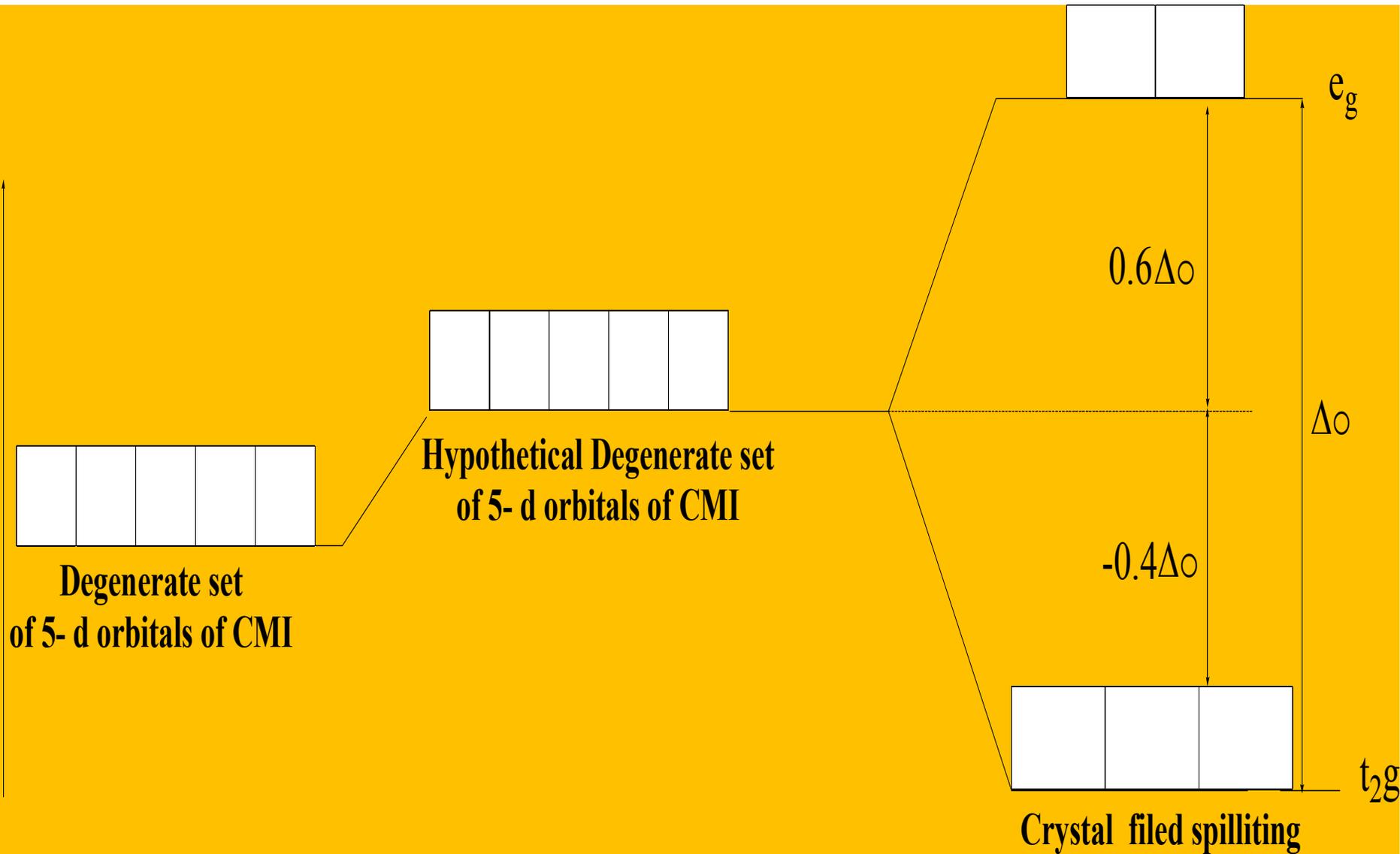
## Step II- Orientation of 6 ligands around the CMI in the octahedral complexes

In the octahedral complexes all the six ligands being oriented toward the CMI from the six opposite corners of the three cartesian axis, which can be represented:-



### **Step III- Crystal field splitting of the 5-d orbital's of CMI:**

When the CMI being present in the isolated form then all the five-d orbital's of the CMI having same energy and they are combindly known as degenerates of 5- d orbital's but if the ligand comes in the environment of CMI the hypothetically energy of all the 5-d orbitals is slightly increased due to the repulsion between the -ve charge of the ligand and 5- d orbital's finally when the 6 ligands comes in the octahedral environment around the CMI to constrict the octahedral complex then 5- d orbital's of the CMI into lower energy  $t_{2g}$  set and higher energy  $e_g$ - set of orbital's, which is called as crystal field splitting in the octahedral complexes. The energy difference b/w the spillited set of orbitals is known as crystal field splitting energy difference ( $\Delta_o$ ).

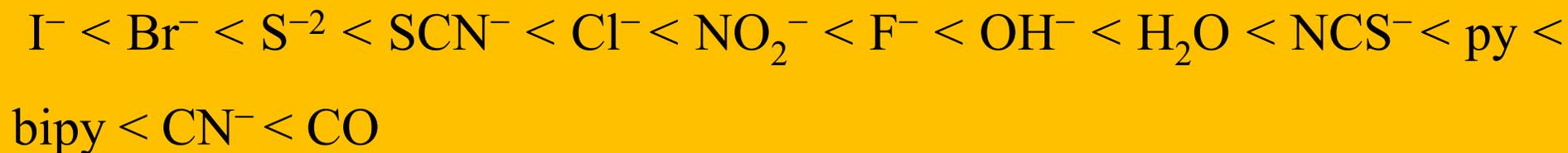


## **Step IV-Distribution of $d^n$ configuration of the CMI in the splitted set of d-orbitals:**

To define the distribution of  $d^n$  configuration of CMI in the **splitted** set of d-orbitals at first we have to define the strength of ligand i.e. spectrochemical series.

**Spectrochemical Series:** According to the concept of CFT those ligands which having the more splitting power are known as stronger ligands while on the other hand those ligands which having the less spitting power are known as weak ligands. After arranging the various ligands in order of their uncrossing or decreasing splitting power the arrangement which is obtained is known as spectro chemical series.

Arrangement of certain ligands in order of their increasing splitting power according to spectro chemical series can be given as:



The ligands interact weakly: - weak field ligands e.g.  $I^-$ ,  $Br^-$ ,  $S^{-2}$ ,  $SCN^-$ ,  $Cl^-$

The ligands interact strongly: - strong field ligands e.g.  $NO_2^-$ ,  $CN^-$ ,  $CO$

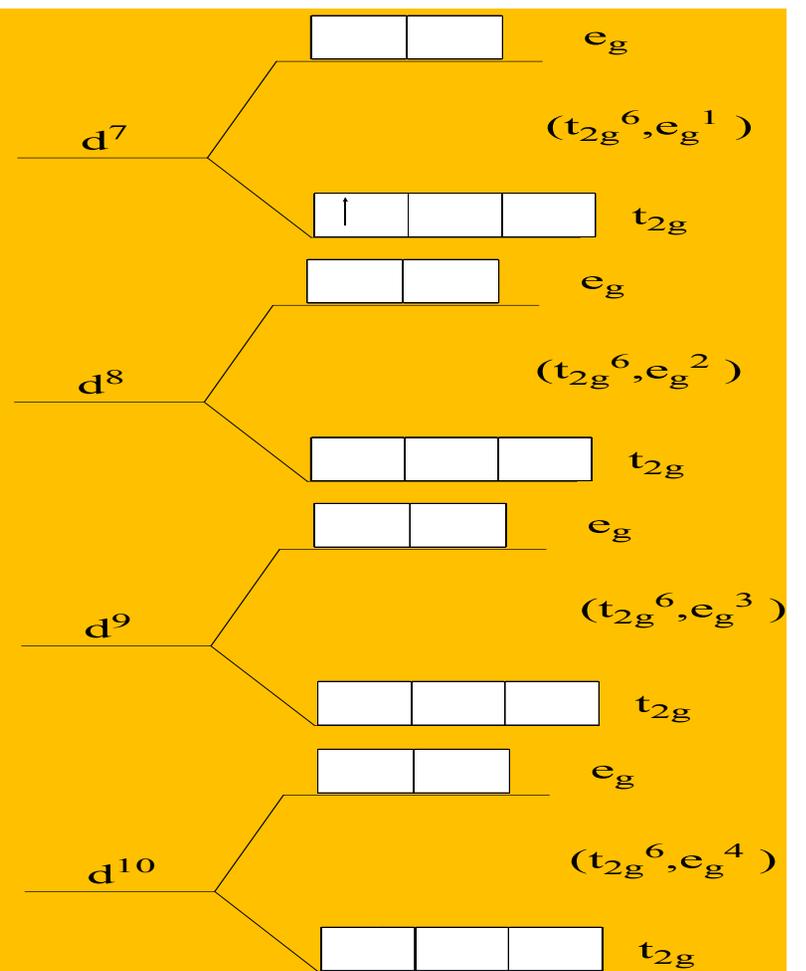
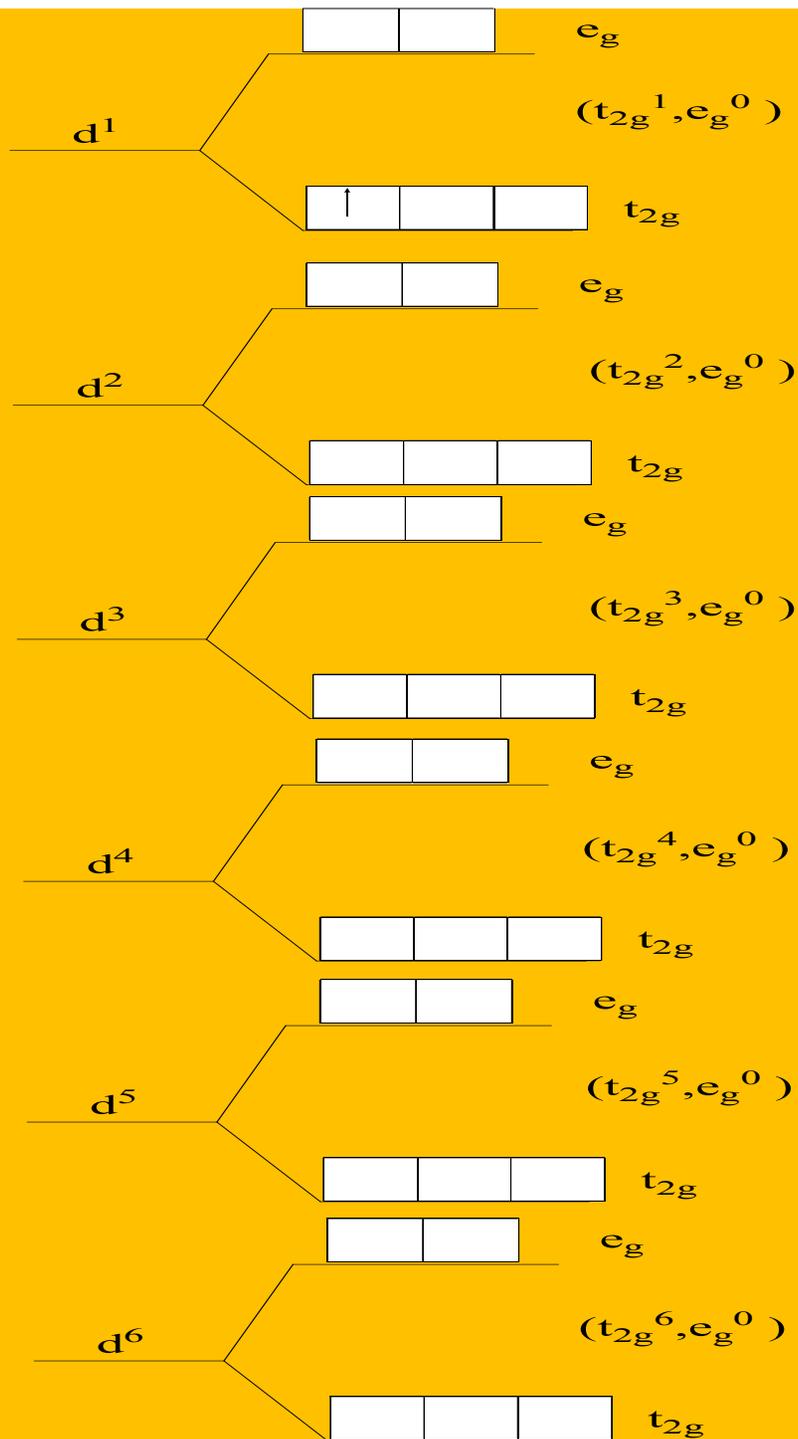
Similarly, if metal ions are different with same ligand,  $\Delta_o$  are different.

Metals with more positive charge and from 2<sup>nd</sup> and 3<sup>rd</sup> transition series interact more (higher splitting).

Now distribution of  $d^n$  configuration of the CMI can be given under the two conditions:-

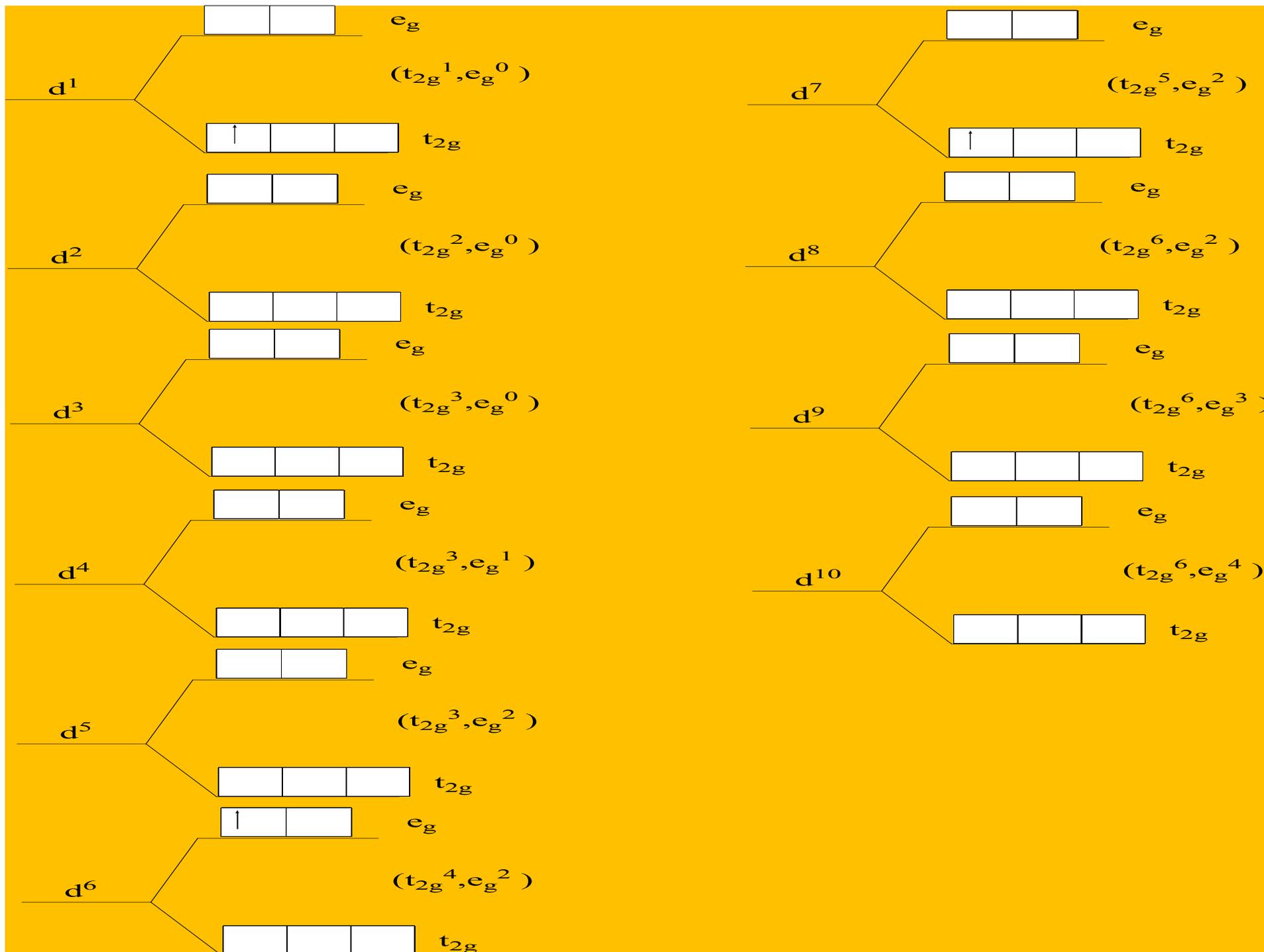
• If  $\Delta_0 > P$  i.e. under the strong field octahedral condition:

If the octahedral complex containing stronger ligand than value of  $\Delta_0$  being greater than the mean pairily energy ( $p$ ), under such condition destitution of the  $d^n$  configuration of CMI in the splitted set of d-orbitals can be given as:



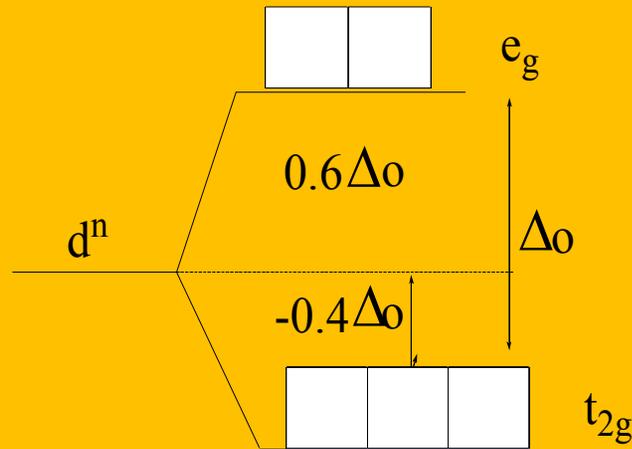
• If  $\Delta_0 < P$  i.e. under the weak field octahedral condition:

If the octahedral complex containing weak ligand then value of  $\Delta_0$  being less than mean pairing energy (P), under such conditions distribution of the  $d^n$  configuration of the CMI in the splitted set of d orbital's can be given as:



**Step V: Crystal field stabilization energy in the octahedral complexes:**

Crystal field splitting of the  $d^n$  configuration in the octahedral complexes can be given as:



Total no of  $e^-$  in  $e_g$  set =  $q$  ( $1 \rightarrow 4$ )

Suppose total number of  $e^-$  in  $t_{2g}$  set =  $P$  ( $1 \rightarrow 6$ )

Then decrease in energy of  $d^n$  configuration by entrance of 1  $e^-$  in  $t_{2g}$  set =  $-0.4 \Delta_o$

So decrease in energy of  $d^n$  configuration by entrance of  $p$   $e^-$  in  $t_{2g}$  set =  $(-4P)$ .

Increase in energy of  $d^n$  configuration by entrance of 1  $e^-$  in  $e_g$  set =  $0.6 \Delta_o$

So increase in energy of  $d^n$  configuration by enter of  $q$   $e^-$  in  $e_g$  set =  $(0.6\Delta_o) q$

$$\begin{aligned}\text{Thus total energy change of } d^n \text{ configuration} &= (-0.4\Delta_o) P + (0.6\Delta_o) q \\ &= (-0.4p + 6q) \Delta_o\end{aligned}$$

This total amount of the energy change for the  $d^n$  configuration is known as crystal field stabilization energy (CFSE) for the  $d^n$  configuration of CMI in the octahedral complexes.

Thus

$$\text{CFSE} = (-0.4p + 0.6q) \Delta_o$$

$$\text{CFSE} = (-0.4 p + 0.6q) \Delta_o + nP$$

If the value of mean pairing energy being  $P$  and no of pairs in the  $t_{2g}$  or  $e_g$  orbitals being  $n$  then  $nP$  amount of energy will also increases the energy of  $d^n$  configuration. Thus the net energy

$$\text{CFSE} = (-0.4 p + 0.6q) \Delta_0 + nP$$

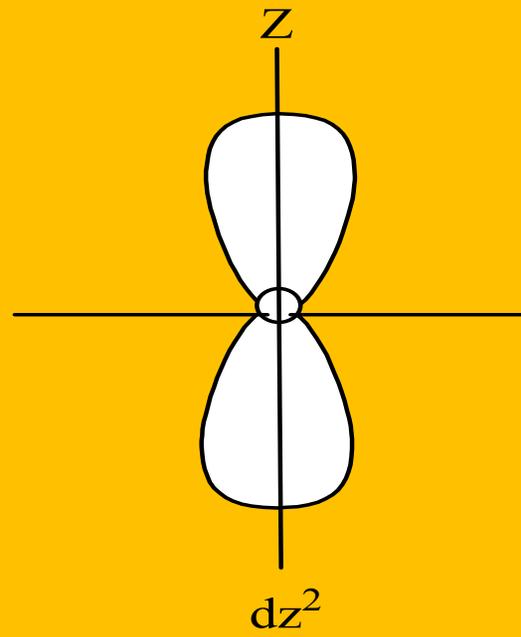
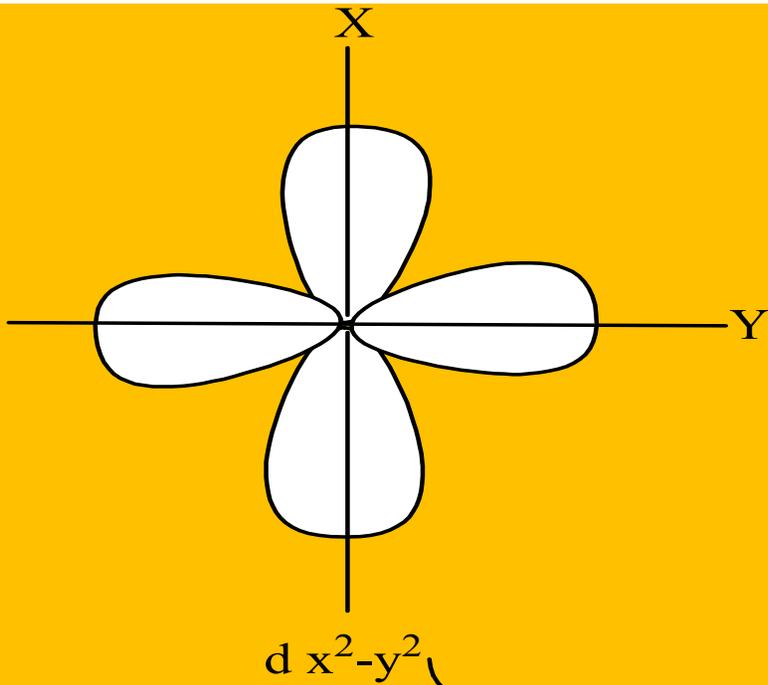
## 2. CFT FOR THE TETRAHEDRAL COMPLEXES:

CFT tetrahedral complexes can be explained under the five different steps, which are given below:

**Step I Shape of 5- d orbitals:** All the 5-d orbitals of the CMI can be levied into 2 different set of orbitals, which are given below.

• **‘e’- set:**  $dx^2 - y^2$  and  $dz^2$  orbital are combindly known as ‘e’ set of axed set orbital’s.

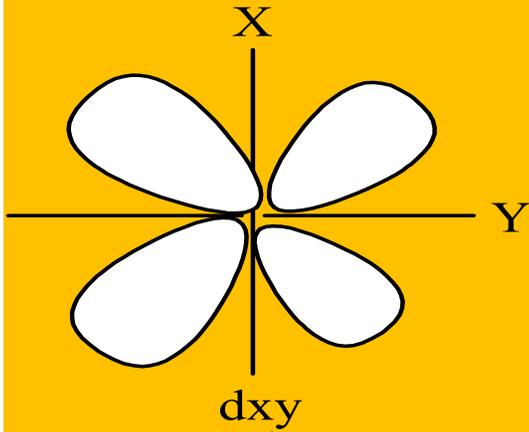
•  **$t_2$  set:**  $d_{xy}$ ,  $dyz$  &  $dzx$  orbitals are cmbindly known as ‘ $t_2$ ’ – set or non axial set of orbitals.



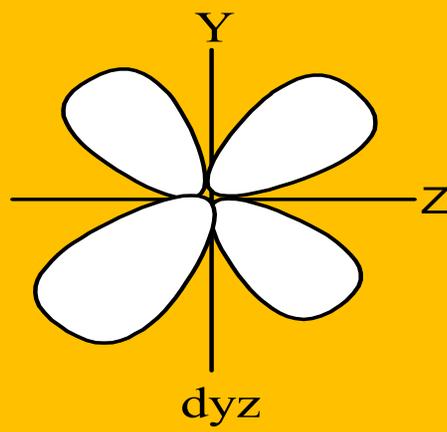
$d_{x^2-y^2}$

$d_{z^2}$

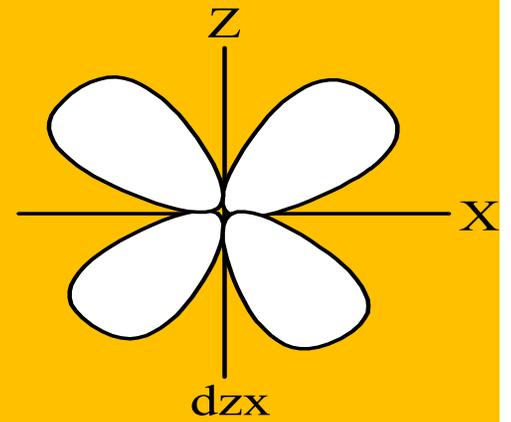
**e -set**



$d_{xy}$



$d_{yz}$

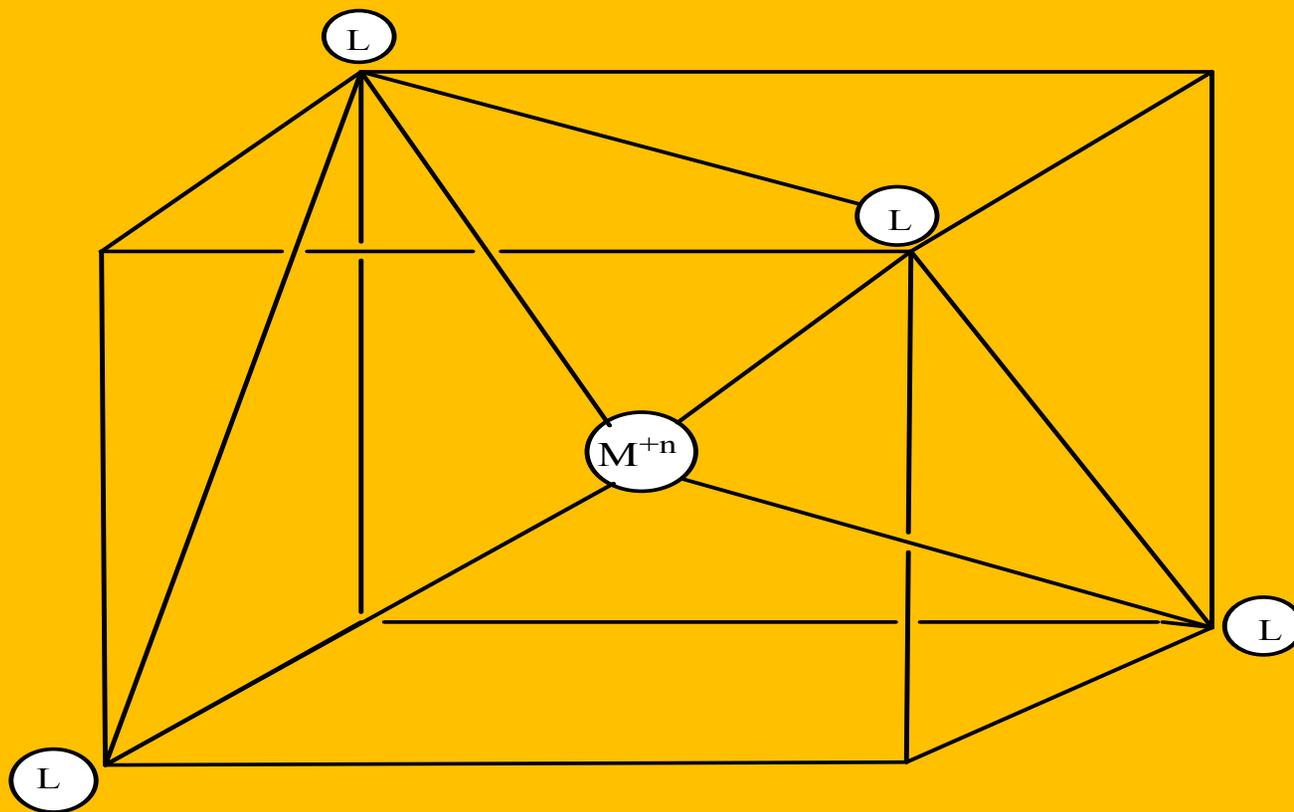


$d_{zx}$

**$t_2$  -set**

## Step II- Orientation of 4- ligands around the CMI in the tetrahedral complexes:

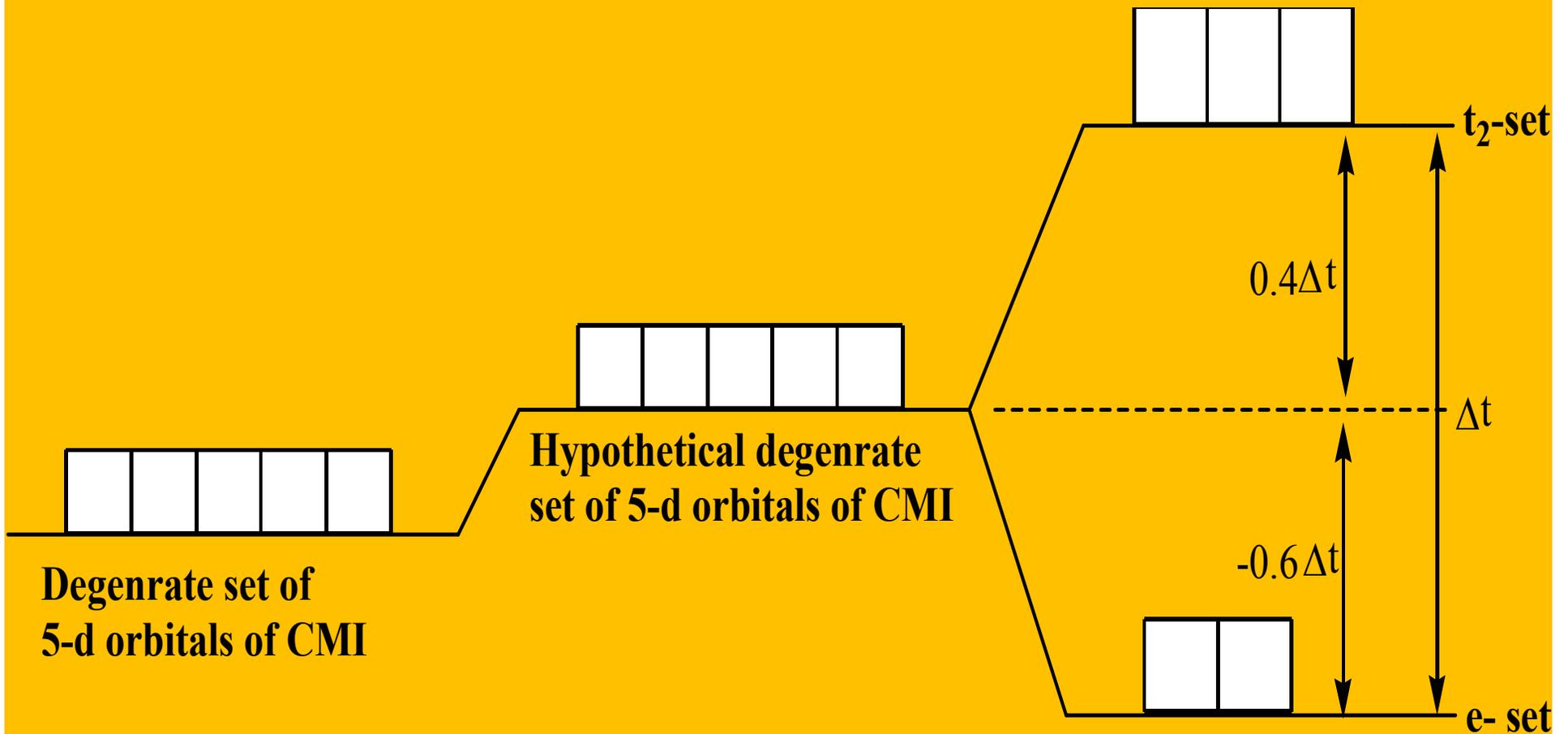
In the tetrahedral complexes all the 4- ligands being oriented toward the CMI from the non axial position, that can be represented as:-



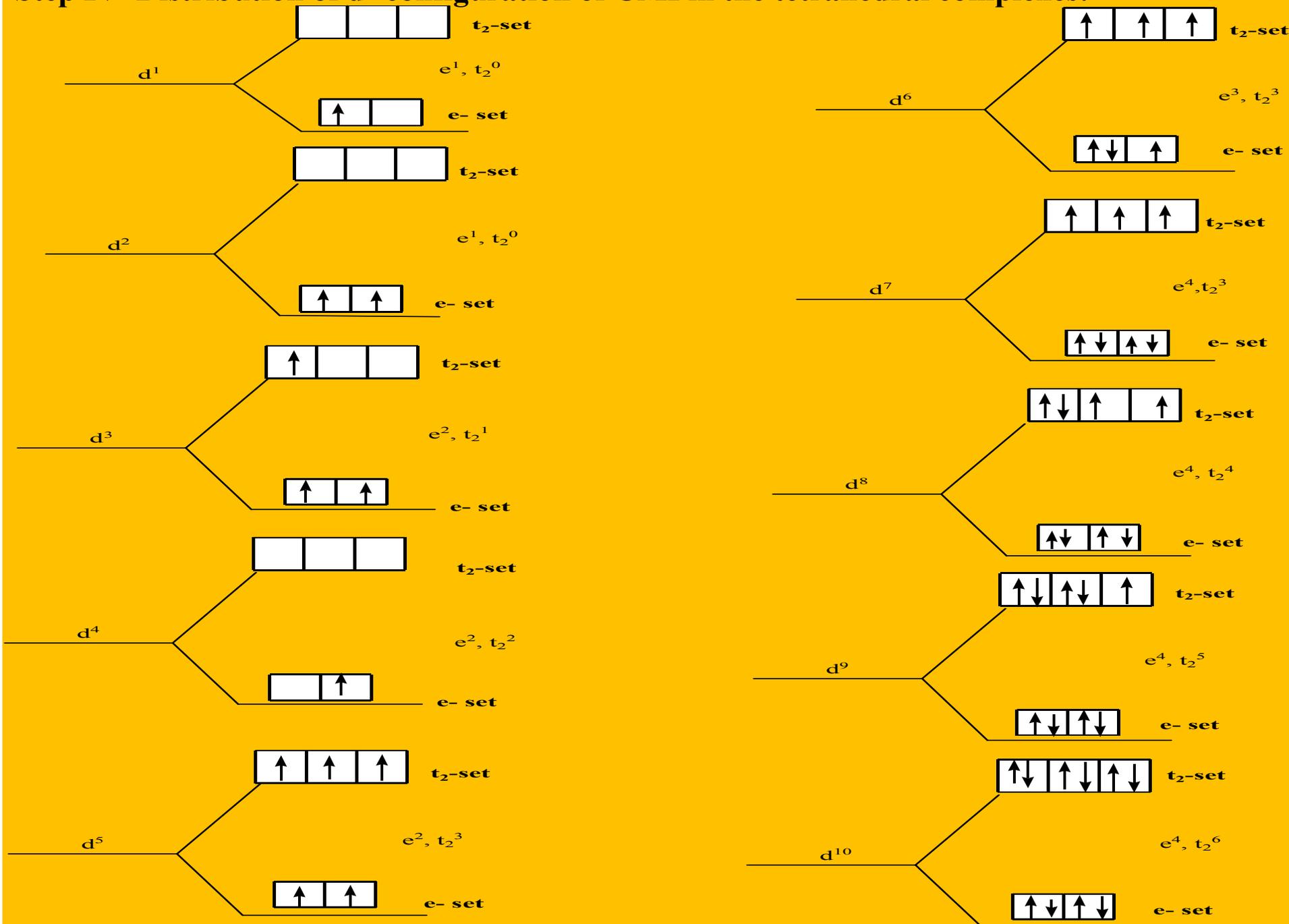
### **Step III- Crystal field splitting of the 5-d orbitals of CMI in tetrahedral complexes:**

When the CMI being present in the isolated form them, all the 5- d orbitals of the CMI having same energy and they are combindly known as degenerate set of 5- d orbitals of the CMI having same energy and they are combindly known as degenerate set of 5- d orbitals, but when the 4- ligands comes in the environment of CMI then there occur the partial hypothetic repulsion between the -ve charge of the ligands and all the 5- d orbitals due to which energy of all the 5-d orbitals of CMI is slightly increased then after that finally tetrahedral environment from the non axial position then there occur the splitting of all the 5 – d orbitals of CMI into lower energy e- set and higher energy t<sub>2</sub> set of orbitals which is known as crystal field splitting in the tetrahedral complexes.

The energy difference between the splitted set of d- orbital is known as crystal field splitting energy difference ( $\Delta t$ ).

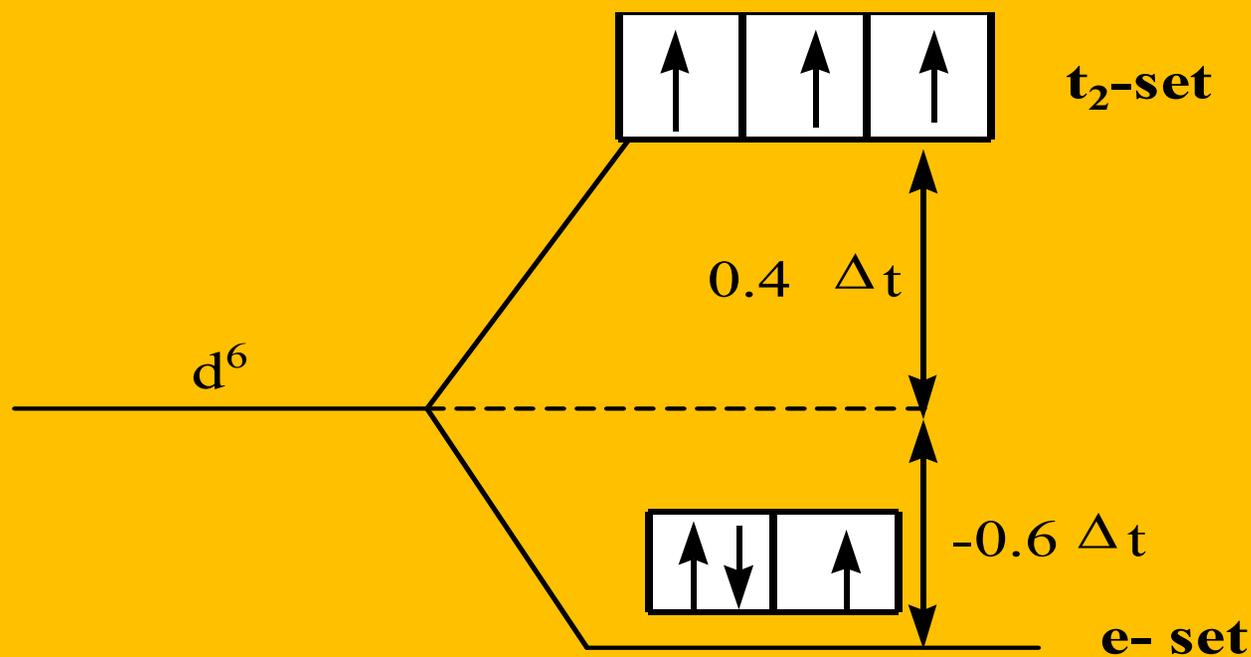


# Step IV- Distribution of $d^n$ configuration of CMI in the tetrahedral complexes:



## Step V- Crystal field stabilization energy in the tetrahedral complexes:→

Crystal field splitting diagram for the  $d^n$  configuration of CMI in the tetrahedral complexes can be represented as:-



Suppose no. of  $e^-$  in  $e$  set =  $q$  ( $1 \rightarrow 4$ )

No. of  $e^-$  in  $t_2$  set =  $p$  ( $1 \rightarrow 6$ )

Then decrease in energy of  $d^n$  configuration due to the entrance of  $(e^-$  in  $e$  set  $= -0.6 \Delta t$

So decrease in energy of  $d^n$  configuration due to the entrance of  $q e^-$  in  $e$  set  $= -0.6 \Delta t \times q$

Increase in energy of  $d^n$  configuration due to entrance of  $e^-$  in  $t_2$  set  $= 0.4 \Delta t$

So increase in energy of  $d^n$  configuration due to entrance of  $p e^-$  in  $t_2$  set  $= 0.4 \Delta t \times p$

Since net energy change of  $d^n$  configuration  $= (-0.6 \Delta t \times q + 0.4 \Delta t \times p)$   
 $= (-0.6 \times q + 0.4 \times p) \Delta t$

This net amount of the energy change for the  $d^n$  configuration is known as CFSE of the tetrahedral complexes.

$$\text{CFSE} = (-0.6q + 0.4P) \Delta t$$

Suppose the value of mean pairing energy is denoted by the symbol  $P$  and total no. of the pair in the splitted set of  $d$ - orbitals denoted by the symbol  $n$  then the  $nP$  amount of energy will also be involved is the CFSE formula. Thus

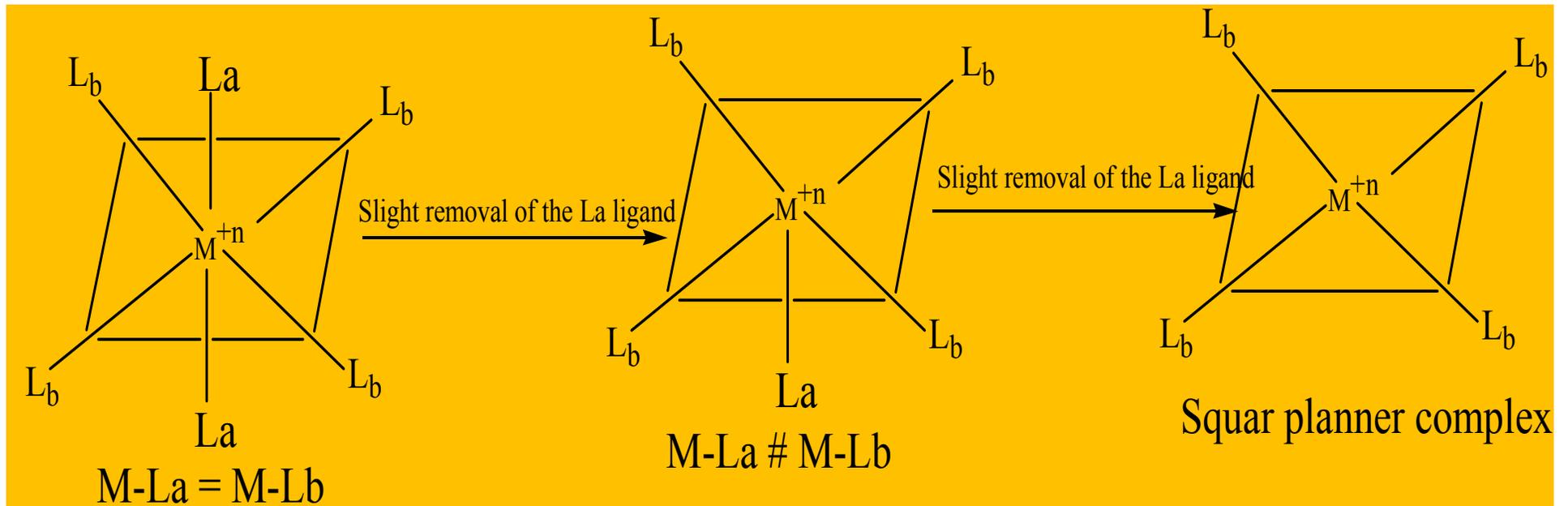
$$\text{CFSE} = (-.6q + .4P) + nP$$

### 3. CFT FOR THE SQUARE PLANNER COMPLEXES

CFT of the square planer complexes is arises from the CFT of octahedral complexes. The crystal field splitting diagram for the square planer complexes originated from the splitting diagram of octahedral complexes in the two steps which can be represented as:-

If two trans ligands in an octahedral  $ML_6$  complex (consider those along the z-axis) are moved either towards or away from the metal ion, the resulting is said to be tetragonally distorted. Ordinarily such distortions are not favored since they result in a net loss of bonding energy. In certain situations, however, such a distortion is favored because of a Jahn-Teller effect. A complex of general formula  $trans-Ma_2b_4$  also will have tetragonal symmetry.

For now, we will consider the limiting case of tetragonal elongation, a square planar  $ML_4$  complex, for the purpose of deriving its d-orbital splitting pattern. The crystal field diagram for the tetragonally distorted complex and the square-planar complexes is shown below. Removal of ligands from z-direction completely leads to the square-planar geometry. This geometry is favoured by metal ions having a d8 configuration in the presence of a strong field. This combination gives low-spin complexes where the first four orbitals are occupied and the high-energy  $dx^2-y^2$  orbital is unoccupied.

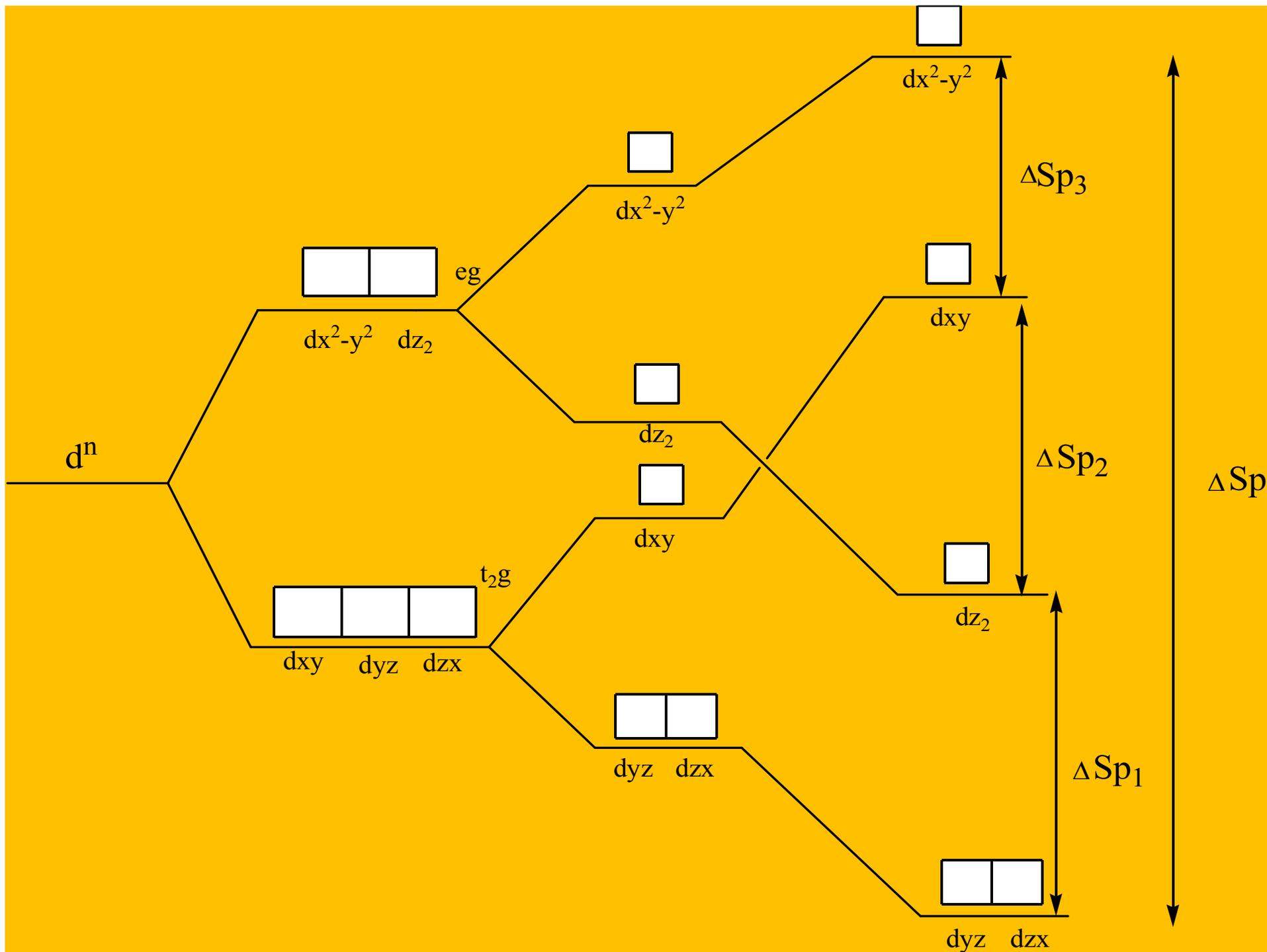


Pure octahedral complex

(Distorted octahedral)

### Crystal Field splitting for square planar complex:

Square planar complexes are similar to octahedral complexes. The difference is that square planar complexes have two ligands missing in the z axis. There is a very large energy gap between the  $x^2-y^2$  orbital and the lower four orbitals. Square planar complexes are favored by metal ions with  $d^8$  electron configurations. Since this configuration favours low-spin complexes in which the four lower-energy orbitals are filled and the high energy  $x^2-y^2$  orbital is empty. The crystal field splitting diagram of square planar complex is given as:



## ❖ FACTOR AFFECTING THE CRYSTAL FIELD PARAMETER

Some factors which can affect the value of  $\Delta$  (Crystal field splitting energy difference) are given below:

• **Nature of ligands:** With the increase in the strength of the ligands present in the complexes the  $\Delta$  value for the complexes is increases.

**Explanation:** With the increase in the strength of the ligand ability of the ligands to cause the closer approach with the CMA is increases by which the repulsion between the ligand and d orbitals as well as  $\Delta$ value is increases.

**Examples:**

a.  $[\text{Fe}(\text{CN})_6]^{-4}$  ion containing the stronger  $\text{CN}^-$  ligand while  $(\text{Fe} (\text{Cl})_6)^{-4}$  ion containing the weak  $\text{Cl}^-$  ligand due to which the value for (Fe

b.  $[\text{Co}(\text{F})_6]^{-3}$  ion containing the stronger  $\text{F}^-$  ligand while  $[\text{Co}(\text{Cl})_6]^{-3}$  ion containing the weak  $\text{Cl}^-$  ligand due to which the  $\Delta$  value for  $[\text{Co}(\text{Cl})_6]^{-3}$  ion is found to be less than  $[\text{Co}(\text{F})_6]^{-3}$  ion.

## 2. Nature of CMA:

a. **Same CMA with different charge:** If the complexes containing same CMA with the different charge then the complex with the higher +ve charge of the CMA will exhibit higher  $\Delta$  value.

**Explanation:** In the complexes containing different charge of the CMA then the complex with the higher +ve charge of the CMA exhibit higher value because the CMA with higher +ve charge can attract the ligand more closer toward itself by which the repulsion between the ligand and d-orbital of CMA as well as  $\Delta$  value is increases.

## **b. Different CMA with the different charge:**

If the complexes containing the different charge then the complex which containing higher +ve charge at the CMA exhibit higher  $\Delta$  value.

**Explanation:** If the complexes containing different CMA with the different charge then the complex which containing higher +ve charge of CMA exhibit the higher value because the CMA with the higher +ve charge can attract the ligand more closer toward itself due to which the repulsion between the ligand and d- orbital of CMA as well as  $\Delta$  value are increases.

- a.  $[\text{V}(\text{H}_2\text{O})_6]^{+2}$  ion containing lower +ve charge (+2) at the CMA while  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$  ion containing higher +ve charge (+3) at the CMA due to which  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$  ion will exhibit higher  $\Delta$  value.
- b.  $[\text{Fe}(\text{NH}_3)_6]^{+3}$  ion containing higher +ve charge of the CMA (+3) while  $[\text{Fe}(\text{NH}_3)_6]^{+2}$  ion containing lower +ve charge of the CMA (+2) due to which  $[\text{Fe}(\text{NH}_3)_6]^{+3}$  ion will exhibit higher  $\Delta$  value.

### **(C) Different CMA with same charge:**

If the complexes containing different CMA with the same charge then that complex which containing lower  $d^n$  configuration of CMA will exhibit higher  $\Delta$  value.

**Explanation:** This can be due to shielding effect.

**Example:**  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$  ion having  $3d^6$  configuration of CMA while  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  ion containing the  $3d^7$  configuration of CMA and both these complexes having same charge value, thus the former complex ion with lower  $d^n$  configuration will exhibit high  $\Delta$  value.

**(d) Principal quantum no of  $d^n$  configuration:**

With the increase in the Principal quantum number of  $d^n$  configuration of CMA, the value of  $\Delta$  is increases.

In other word the  $\Delta$  value for the complexes of II-transition series elements being 30% greater than the  $\Delta$  value for the complexes of I-transition series elements and the  $\Delta$  value for the complexes of III-transition series element being greater than the II-transition series elements.

**Example:**  $[\text{Fe}(\text{N})_6]^{-4}$  ion exhibit lower value than the  $[\text{Ru}(\text{N})]^{-4}$  ion because Ru having the higher Principal quantum number of  $d^n$  configuration in compare to Fe.

## ❖ APPLICATIONS OF THE CFT

The following properties of transition metal complexes can be explained on the basis of CFT.

1. According to the CFT if the splitted set d-orbitals of the CMI present in the complexes containing the unpaired  $e^-$  then the complex will be called as paramagnetic in nature while if the splitted set of d-orbitals of the CMI does not contain the unpaired  $e^-$  then the complex will be called as diamagnetic in nature.

### **Example:**

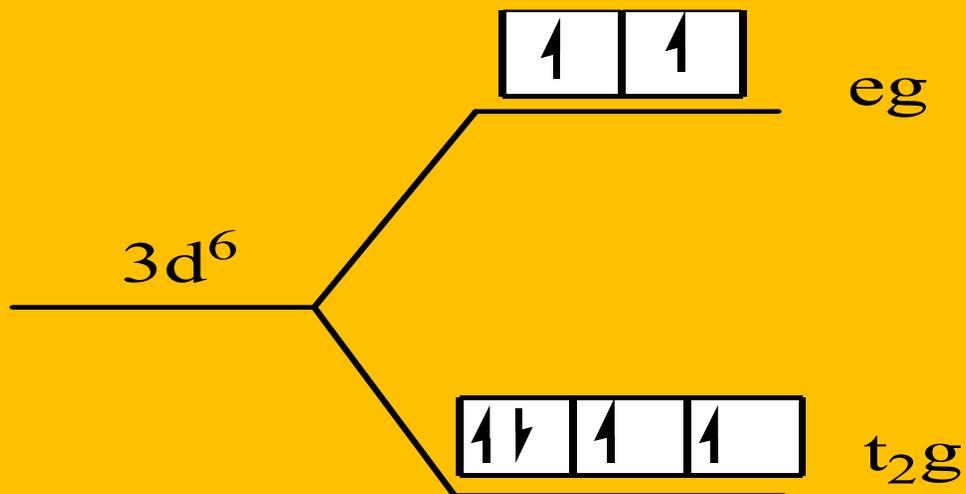
**(II)  $[\text{Co}(\text{F})_6]^{-3}$  ion**

Configuration of Co =  $3d^7, 4s^2$

Oxidation state of Co = +3

Configuration of  $\text{Co}^{+3}$  =  $3d^6$

According to CFT



Since the splitted set of d- orbital containing 4 unpaired  $e^-$  due to which the complex ion  $[Co (F)_6]^{-3}$  ion will be paramagnetic in nature and according to CFT.

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

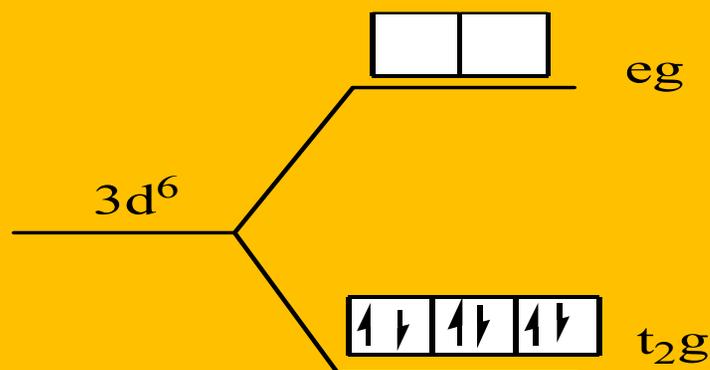
## (II) $[\text{Co}(\text{NH}_3)_6]^{+3}$ ion

Configuration of Co =  $3d^7 4s^2$

Oxidation State of Co = +3

Configuration of  $\text{Co}^{+3}$  =  $3d^6$

According to CFT



**2. Stability of the oxidation states:** With the help of CFT we can compare the stability of the different oxidation state exhibited by any particular transition metal element under the strong field and weak field condition by using the CFSE concept.

**Example:**  $\text{Co}(\text{III})$  is more stabilized than the  $\text{Co}(\text{II})$  under strong field condition  $\text{Co}(\text{II})$  is more stabilized than the  $\text{Co}(\text{III})$  under the weak field condition which can be explained by the CFSE concept of CFT.

**3. Colour of the complexes:** To define the colour of the complexes formed by the d- block element at first white light is passed from the sol<sup>n</sup> of complex compound then,

**(i.)** If whole of the white light is transmitted by the sample then the complex will be called as white in colour.

**(ii.)** If whole of the white light is absorb by the sample then the complex is called as black in colour.

**(iii.)** If some of the radiations of the white light are absorbed and some other radiation are transmitted, in such condition the complex can be coloured only if the absorbed radiations belong to the visible range (4000A<sup>0</sup> – 7000 A<sup>0</sup>)

When the complex absorbed the radiation of visible range then the actual colour of the complex will depend on the wavelength of that particular radiation which is absorbed by the complex compound:-

4000Å<sup>0</sup> 4350Å<sup>0</sup> 4800Å<sup>0</sup> 4900Å<sup>0</sup> 5000Å<sup>0</sup> 5600Å<sup>0</sup> 5800Å<sup>0</sup> 5900Å<sup>0</sup> 6050Å<sup>0</sup> 7000Å<sup>0</sup>

**Colour of absorption**

Voilet	Blue	Green blue	Blue Green	Green	Yellow green	Yellow	Orange	Red
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**Complementary colour**

Yellow Green	Yellow	Orange	Red	Purple	Voilet	Blue	Green	Blow Green
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## ❖ LIMITATIONS OF CFT

1. CFT considers the splitting of d- orbital but it does not consider the splitting of other orbitals in the ligand field environment.
2. CFT can't explain that how certain ligands having more splitting power/ability while certain other ligands having very low splitting ability.
3. According to the CFT metal ligand bond having 100% ionic character but from the various experiment it was proved that metal ligand bonds having certain extent of covalence with the ionic character.

THANK YOU