Crystal Field Theory (CFT)

- This theory was applied mainly to ionic crystal and is therefore called Crystal Field Theory.

Postulates of CFT :

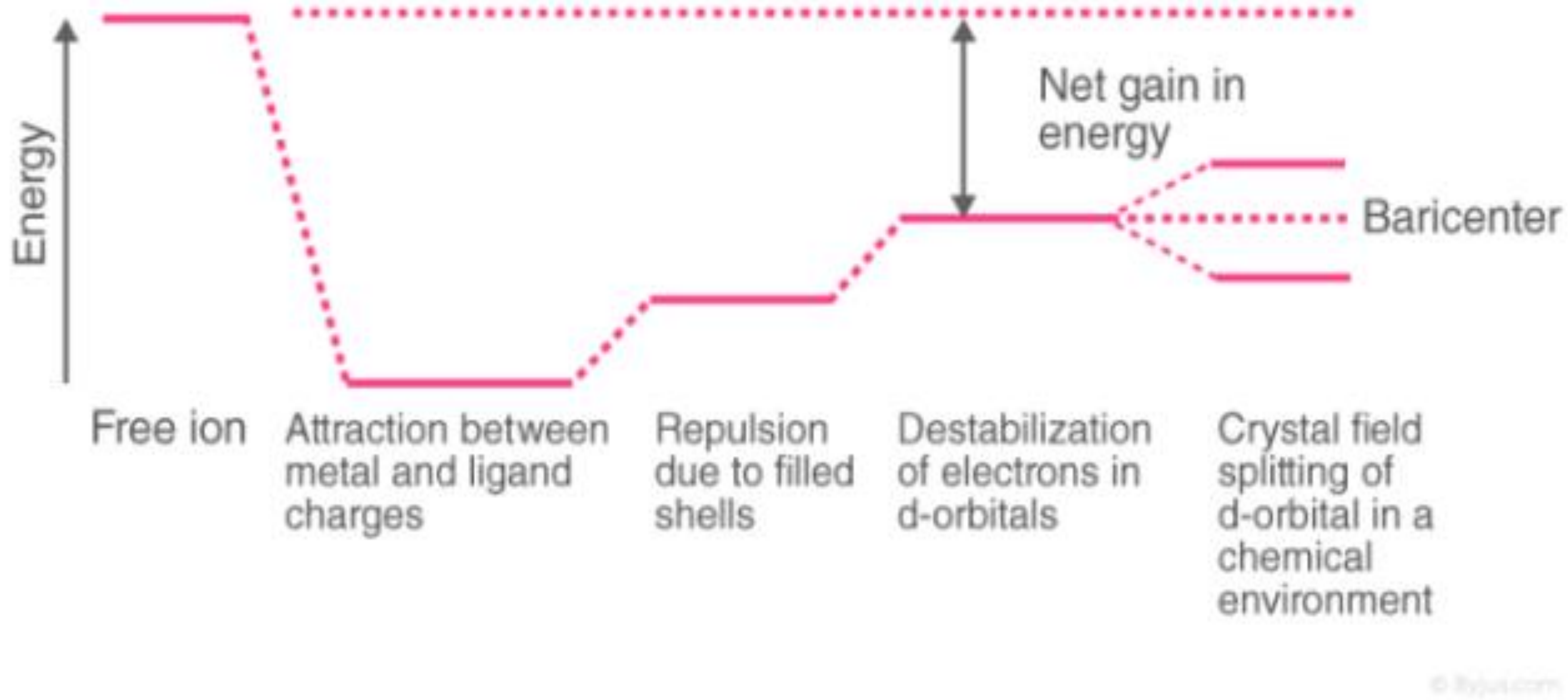
- A complex is a combination of a central metal ion surrounded by other ions (ligands) with electrical dipoles.It considers anions as point charges and neutral molecules as dipoles.
- The bonding between metal cations and ligands arises from the electrostatic attraction.

- The interaction between the electrons of cation and those of the ligand is entirely repulsive .These repulsive forces are responsible for causing the splitting of d orbitals of the metal cations.

- In the free metal ion , all the metal d orbitals have the same energy (i.e, degenerate).However when complex is formed the ligands destroy degeneracy of these orbitals i.e, orbitals now have different energies and the metal d orbitals splits into t_{2g} set (d_{xy},d_{xz},d_{yz}) and e_g set (d_{x2-y2},d_z^2).

Crystal Field Splitting

A summary of the interactions is given below.



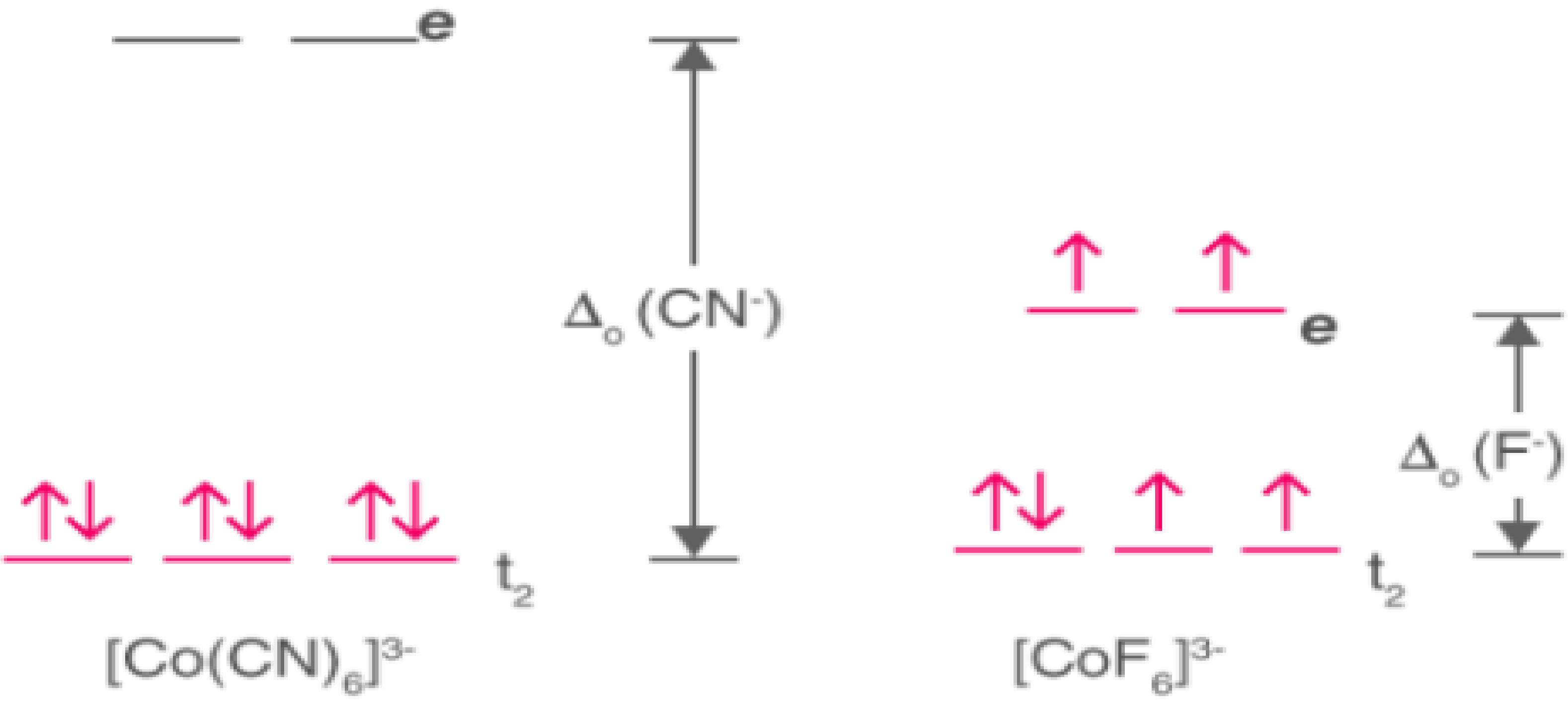
Crystal Field Splitting

High Spin & Low Spin Complex

- The high spin complex ions are those complex ions which contains greater number of unpaired electrons,
- The low spin complex ions are those complex ions which contains lesser number of unpaired electrons.
- High spin complexes are expected with weak field ligands due to less spin pairing.
- Low spin complexes are expected with strong field ligands due to maximum spin pairing.
- For High Spin Complex ions , crystal field splitting energy (Δ) is small .
- For Low Spin Complex ions , crystal field splitting energy (Δ) is large .

- **High spin –** Maximum number of unpaired electrons.
- **Low spin –** Minimum number of unpaired electrons.
- **Example:** $[Co(CN)_6]^{3-}$ & $[CoF_6]^{3-}$

High Spin & Low Spin Complex



High Spin and Low Spin Complex

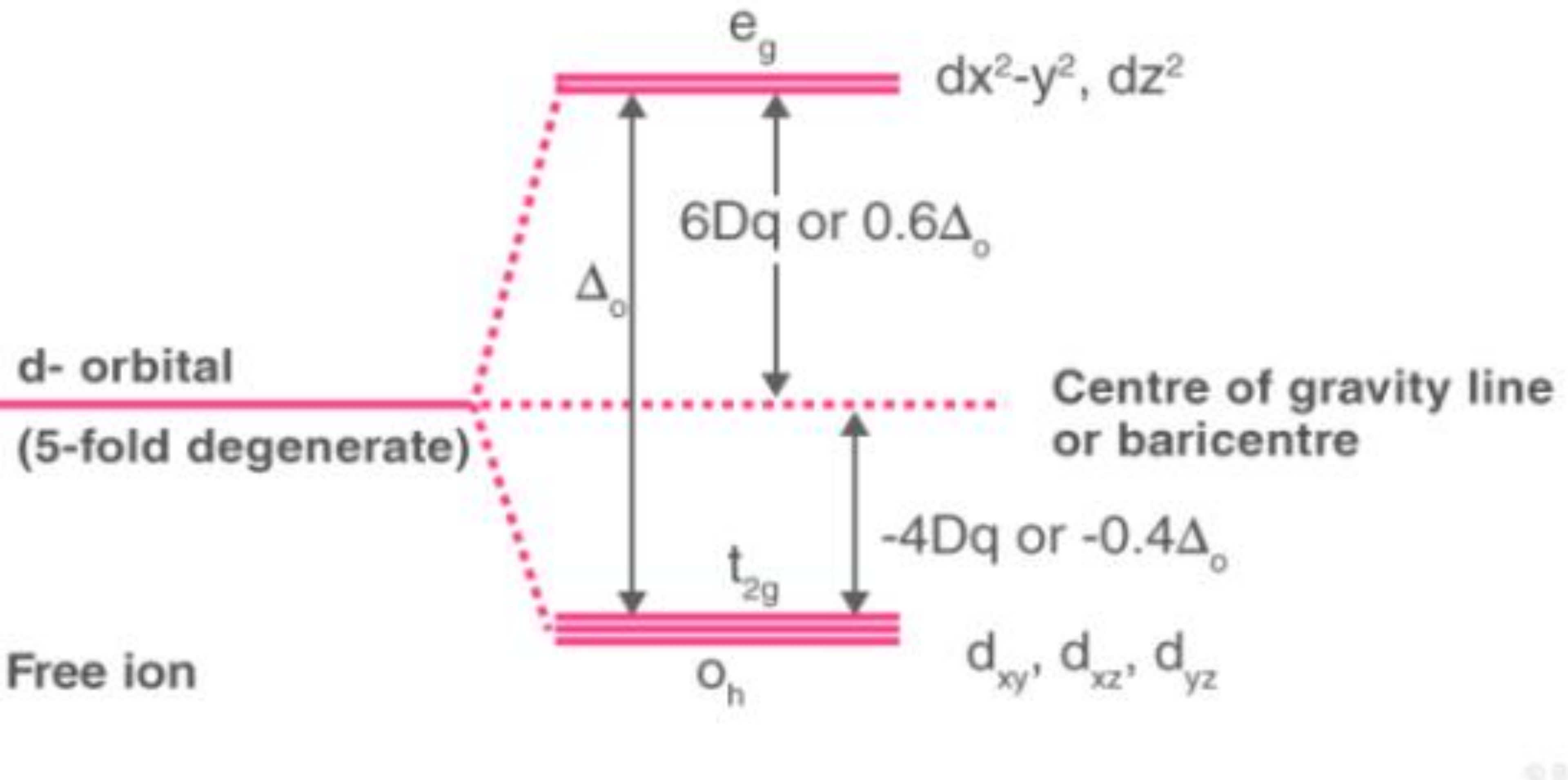
- $[Co(CN)_6]^{3-}$ – Low spin complex
- $[CoF_6]^{3-}$ – High spin complex

Crystal Field Splitting in Octahedral Complex

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.
- Hence, they have higher energy than average energy in the spherical crystal field.
- On the other hand, d_{xy}, $d_{yz,}$ and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.
- Thus, the repulsions in octahedral coordination compound yield two energy levels:

- t_{2g}– set of three orbitals (d_{xy} , d_{yz} and d_{xz}) with lower energy
- e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy

Crystal Field Spitting In Octahedral Complex



Crystal Field Splitting in Octahedral Complex

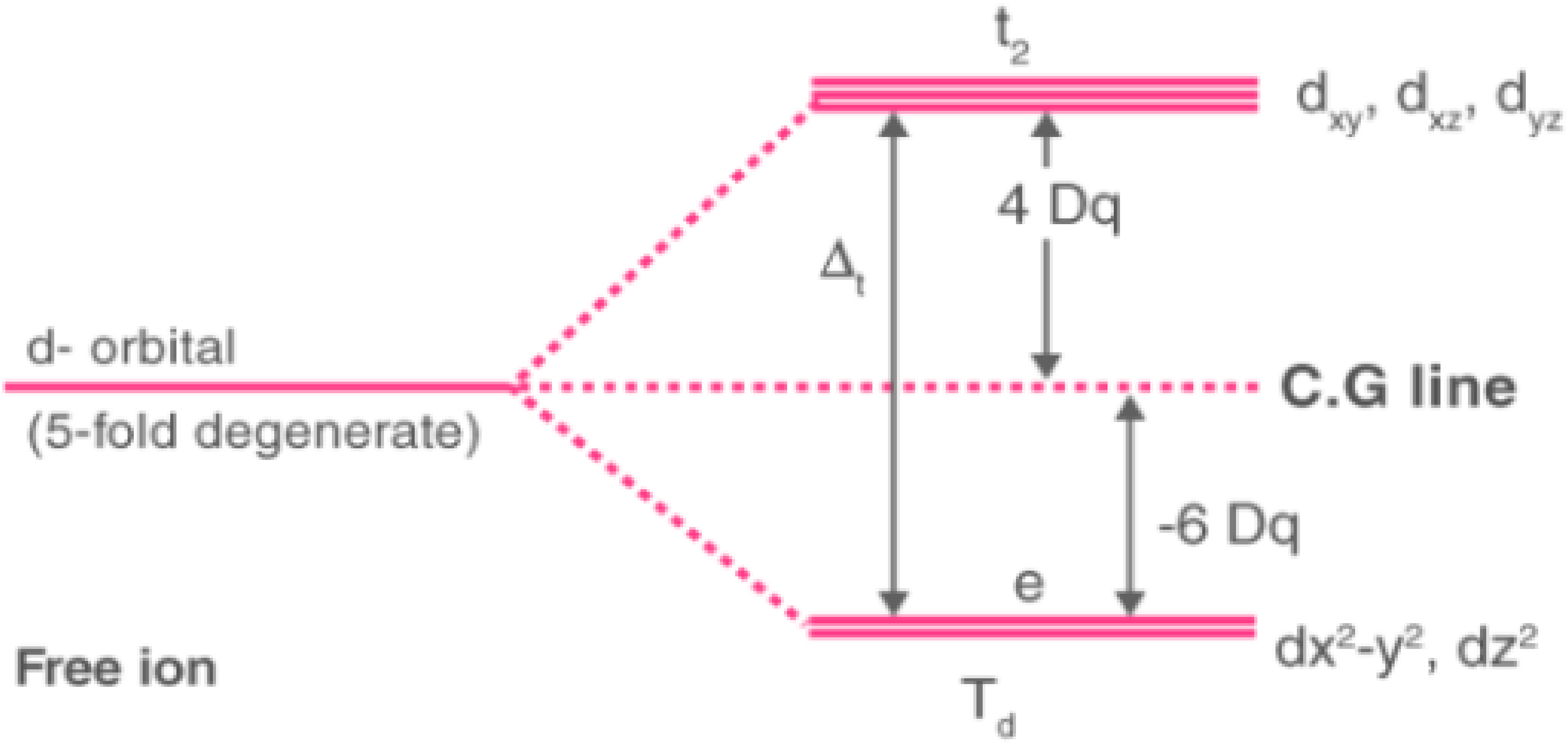
Crystal Field Spitting In Octahedral Complex

- This splitting of degenerate level in the presence of ligand is known as crystal field splitting.
- The difference between the energy of t_{2g} and e_g level is denoted by "Δ_o" (subscript o stands for octahedral).
- Some ligands tend to produce strong fields thereby causing large crystal field splitting
- whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

Crystal Field Splitting in Td Complex

- The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field .
- The electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbitals set are raised while the energy $d_{x^2-y^2}$ and d_{z^2} orbitals set are lowered.
- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.

Crystal Field Splitting in Tetrahedral Complex



Crystal Field Splitting in Tetrahedral Complex

Crystal Field Splitting in Tetrahedral Complex

- Thus, the repulsions in tetrahedral coordination compound yield two energy levels:
- ***t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy***
- ***e – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with lower energy***
- The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be -6Dq and the destabilizing effect of t_2 set will be +4Dq

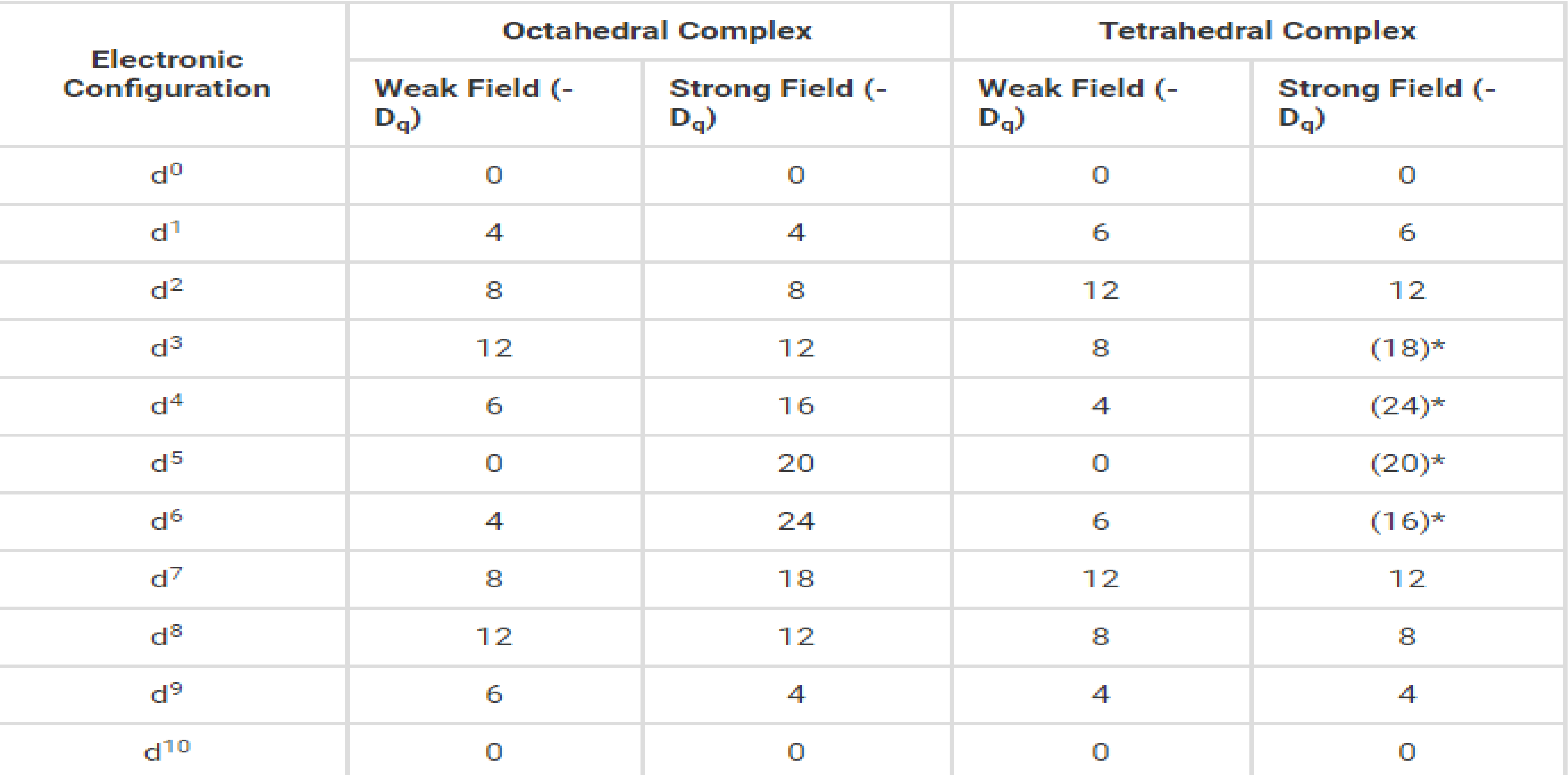
Crystal Field Stabilization Energy (CFSE)

- The stability gained by a d^n ion due to the splitting of its d orbitals by a crystal field and preferential occupation of lowest energy d orbitals is called it’s Crystal Field Stabilization Energy (CFSE).
- The energy difference between the eg and t_{2g} levels is given by $10D_q$. It states that each electron that goes into the lower t_{2g} level stabilizes the system by an amount of $-4D_q$ and the electron that goes into e_g level destabilizes the system by $+6D_q$. That is the t_{2g} is lowered by $4D_q$ and the e_g level is raised by $+6D_q$.

- For example, the net change in energy for d^5 and d^{10} systems will be zero as shown below.
- **d^5 :- $3(-4D_q) + 2(+6D_q) = -12D_q + 12D_q = 0$**
  d^{10} :- $6(-4D_q) + 4(+6D_q) = -24D_q + 24D_q = 0$

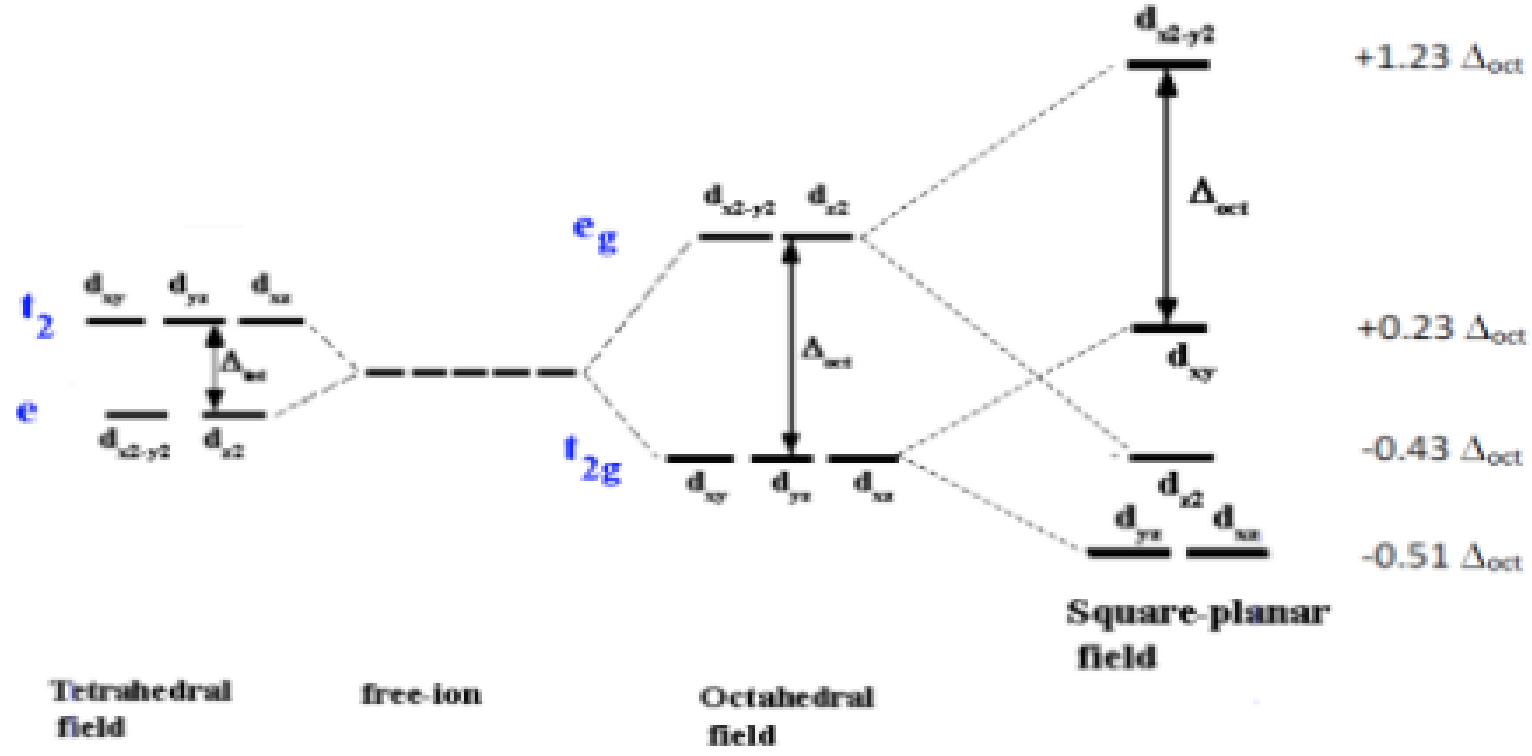
Crystal Field Stabilization Energy Table

The crystal field stabilization energies for some octahedral and tetrahedral complexes of 3d metal ions are tabulated below.



Electronic Configuration	Octahedral Complex		Tetrahedral Complex	
	Weak Field (-D_q)	Strong Field (-D_q)	Weak Field (-D_q)	Strong Field (-D_q)
d^0	0	0	0	0
d^1	4	4	6	6
d^2	8	8	12	12
d^3	12	12	8	(18)*
d^4	6	16	4	(24)*
d^5	0	20	0	(20)*
d^6	4	24	6	(16)*
d^7	8	18	12	12
d^8	12	12	8	8
d^9	6	4	4	4
d^{10}	0	0	0	0

Crystal Field Splitting in Square Planar Complex



Relation

- $\Delta_t = 4/9\Delta_o$
- $\Delta sp=1.3\ \Delta o$
- $\Delta_t < \Delta_o < \Delta_{sp}$