

Theories of metal complexes

Crystal Field Theory

Inorganic & Physical Chemistry)

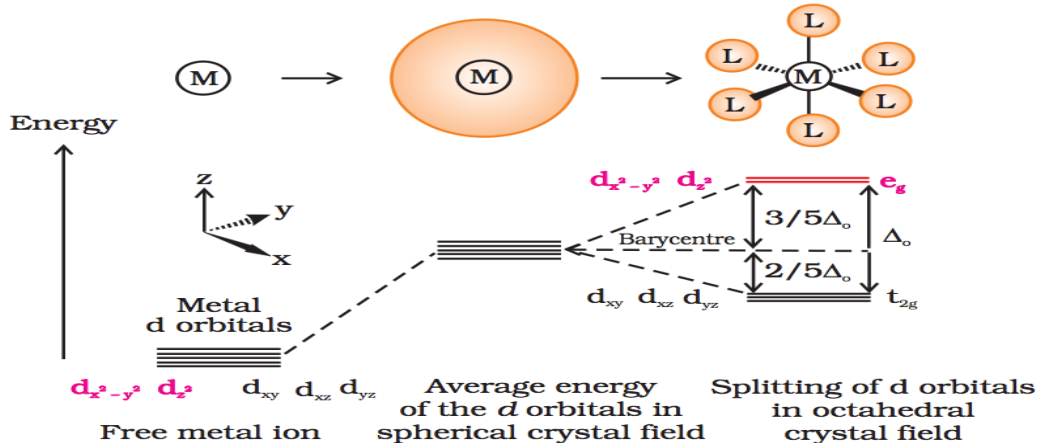
BY

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- ❑ *Introduction, Assumptions of CFT*
- ❑ *Crystal field splitting of 'd' orbital in octahedral, tetrahedral and square planar complexes.*
- ❑ *Crystal field stabilization energy (CFSE)*
- ❑ *Comparison of CFSE for O_h and T_d complexes*
- ❑ *Crystal field effects for weak and strong fields ligand*
- ❑ *Tetrahedral symmetry*
- ❑ *Factors affecting the Magnitude of $10 Dq$*
- ❑ *Spectrochemical series*
- ❑ *Jahn-Teller distortion*
- ❑ *Limitations of CFT.*

General Introduction

➤ *Three modern theories to study bonding & properties of coordination of complexes*

a) Valence Bond Theory

b) Crystal Field Theory

c) Molecular Orbital Theory

➤ *The VBT establishes a correlation between metal-ligand bonding, geometry of coordination compounds.*

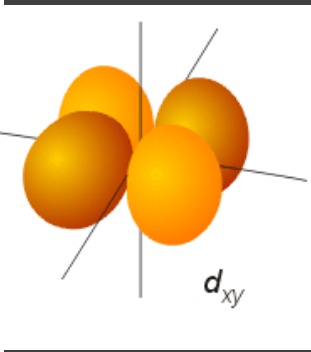
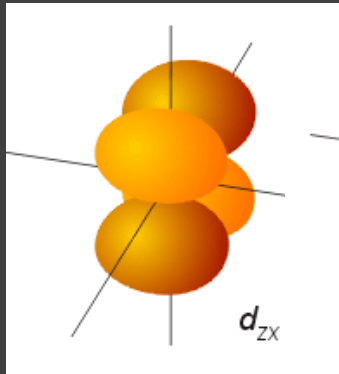
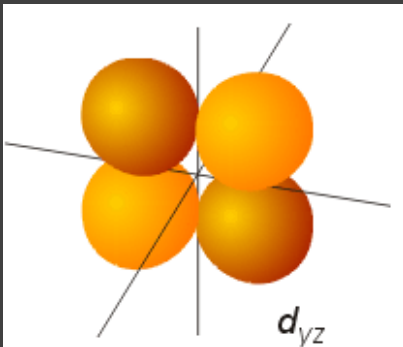
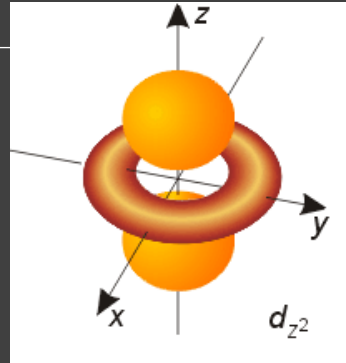
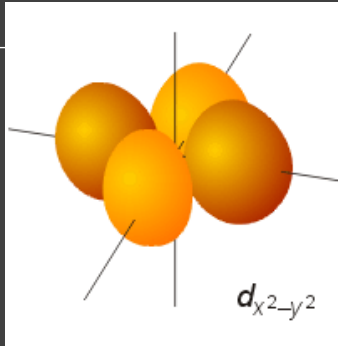
➤ *But still this theory have some drawbacks.*

Limitations of Valence Bond Theory

- ❑ **Doesn't account splitting of d-orbitals of metal**
- ❑ **Doesn't explain color of complexes**
- ❑ **Fails to explain magnetic Properties**
- ❑ **Unable to explain spectral properties**
- ❑ **Doesn't provide any idea about reactivity of complexes**
- ❑ **Fails to explain distorted octahedral and tetrahedral geometry.**
- ❑ **Fails to explain bonding in electron deficient complex**
- ❑ **It fails to explain excitation from 3d to 4p orbitals in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion.**
- ❑ **Doesn't provide relative energies of different structures.**

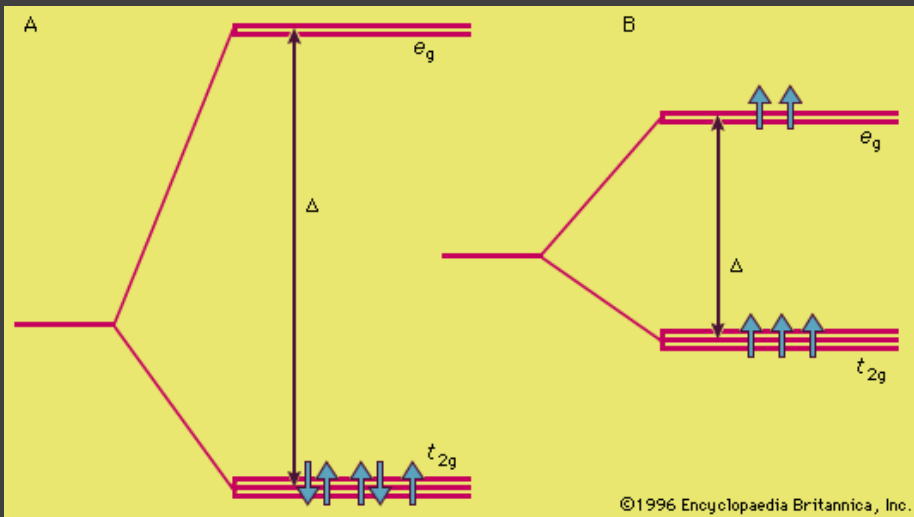
Shape of d Orbitals

d Orbitals



Ponits to remember

Crystal Field Theory



*Developed by
H. Bethe & V. Bleck
(1935)*

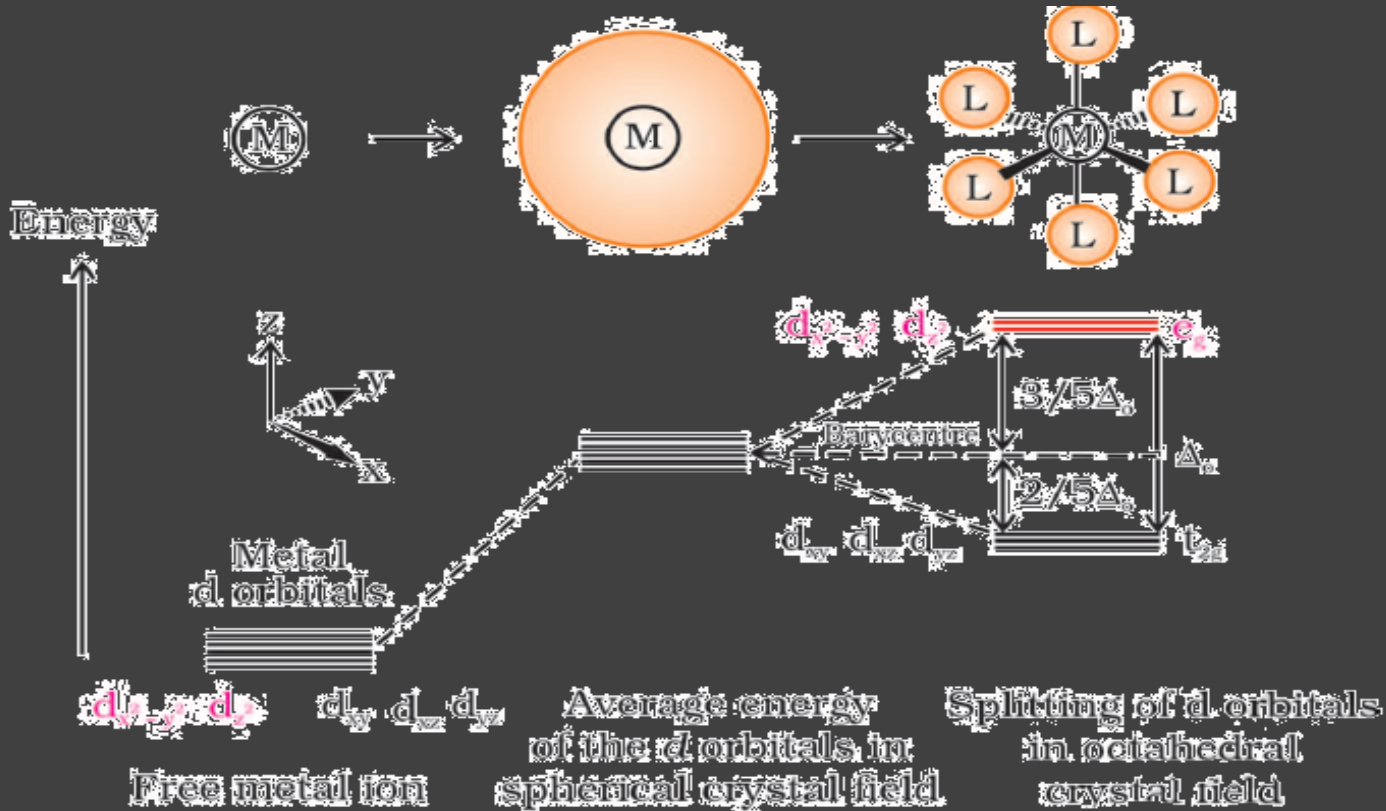


- *This is Purely electrostatic approach*
- *Explains colors & Magnetic properties of solid ionic crystals.*

Central assumption of CFT

Metal-ligand connections are electrostatic interactions between a **central metal ion** and a set of negatively charged **ligands** (or **ligand dipoles**) arranged around metal ion.

Crystal Field Splitting of d-orbitals in Octahedral Complexes



d orbital splitting in an octahedral crystal field

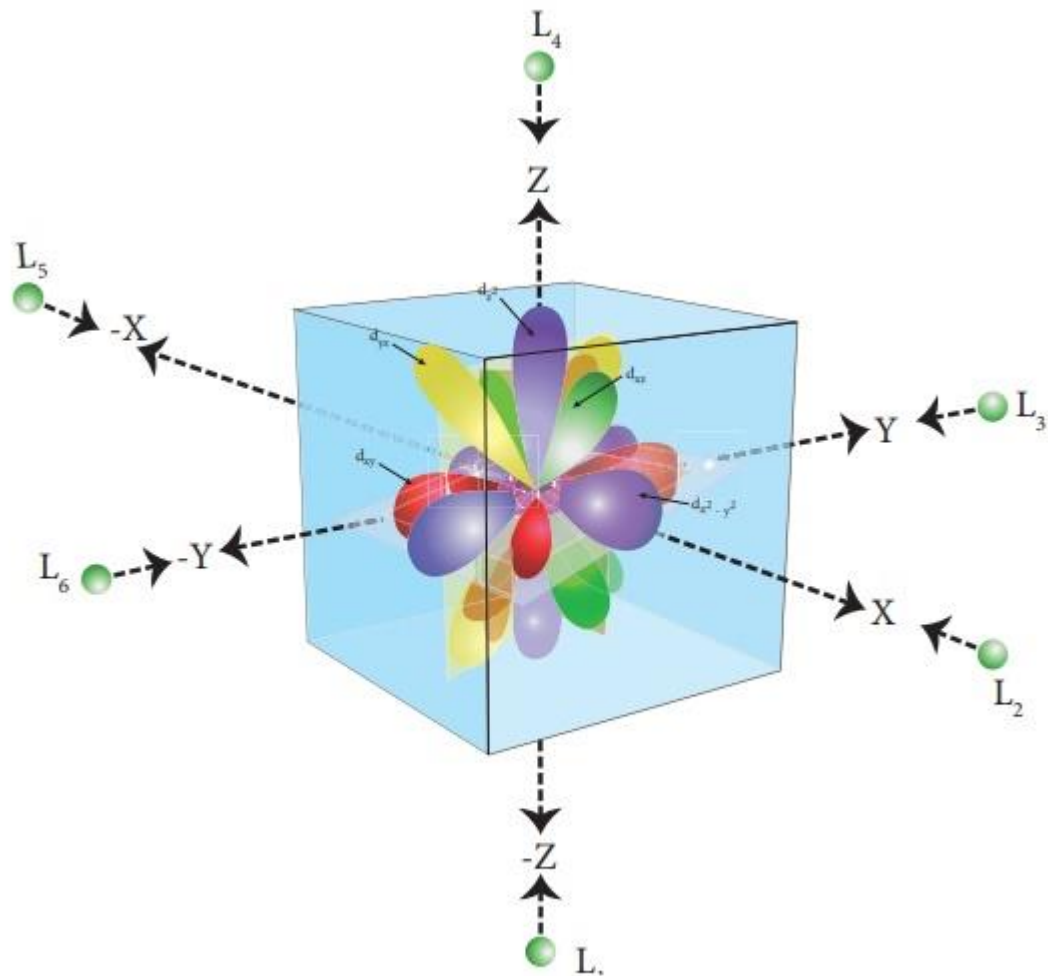
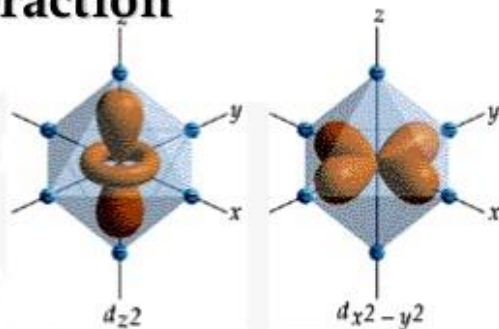


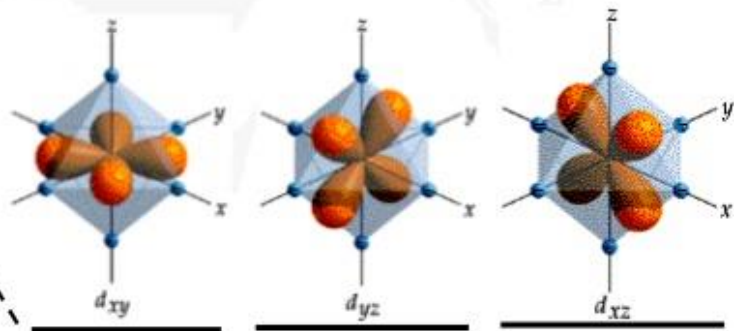
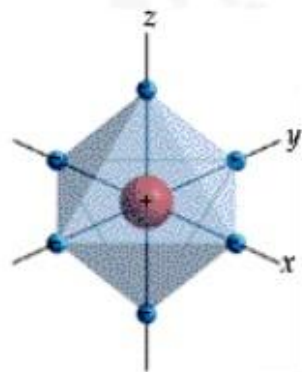
Figure 5.9 octahedral ligand field

d-Orbitals and Ligand Interaction (Octahedral Field)

Ligands
approach
metal



d-orbitals pointing directly at axis are affected most by electrostatic interaction



d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

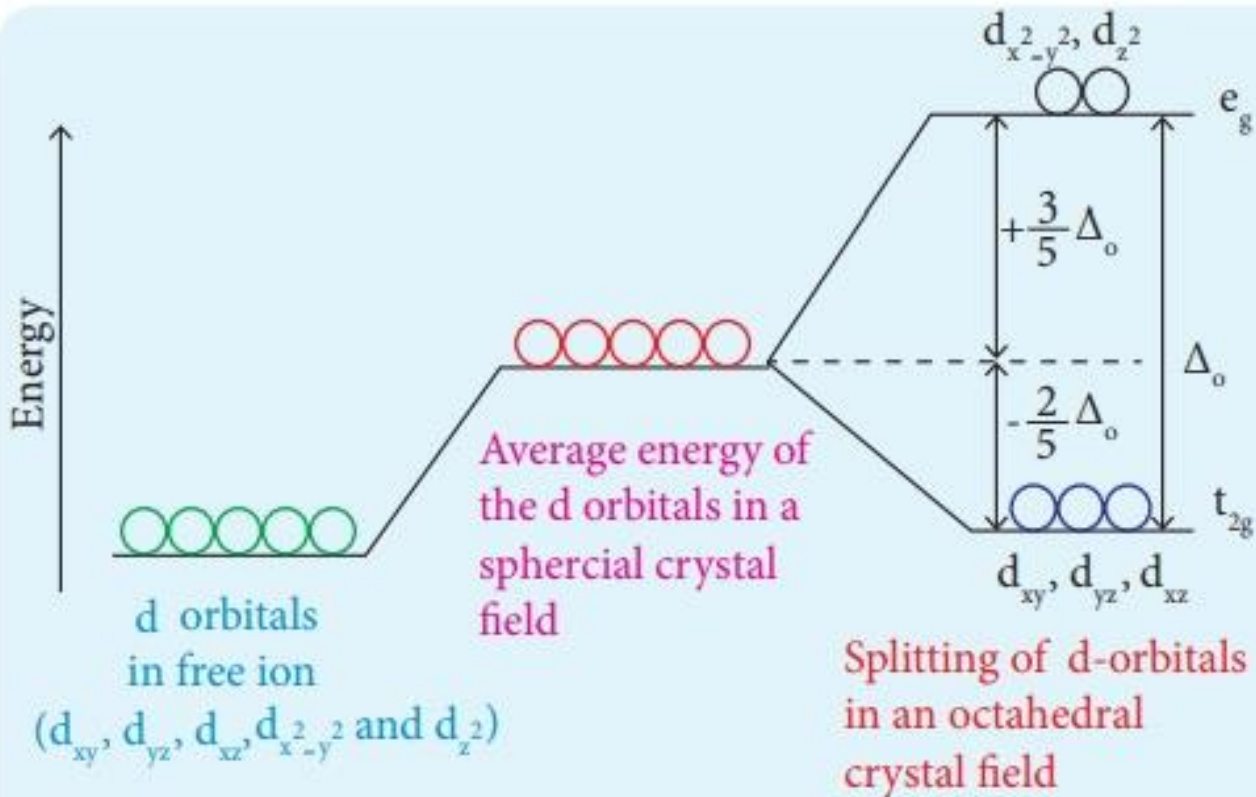
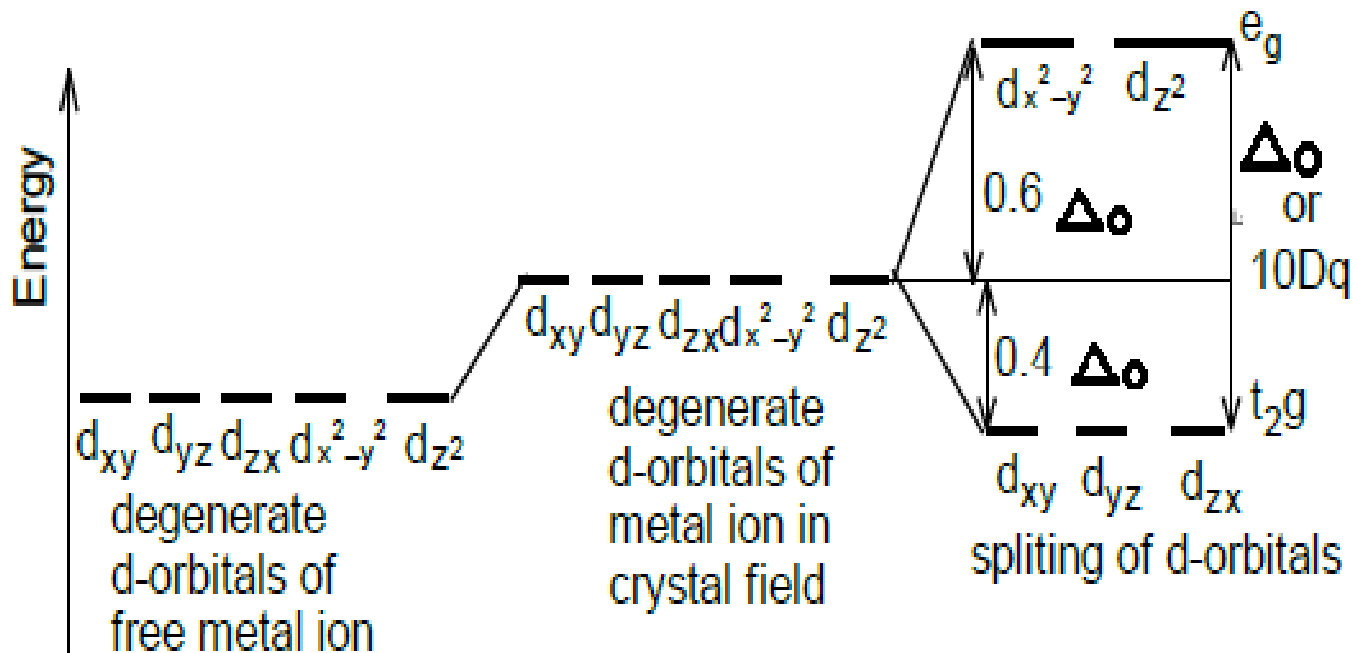


Figure: 5.10 - Crystal field splitting in octahedral field



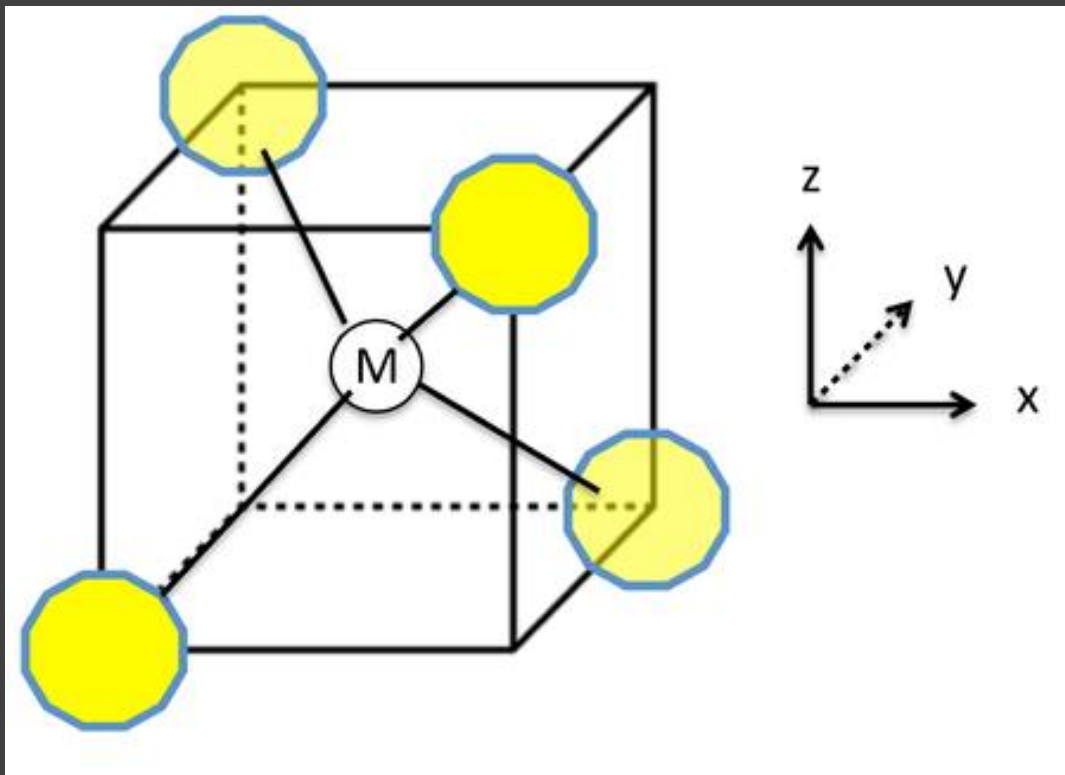
splitting of d-orbitals in octahedral crystal field,

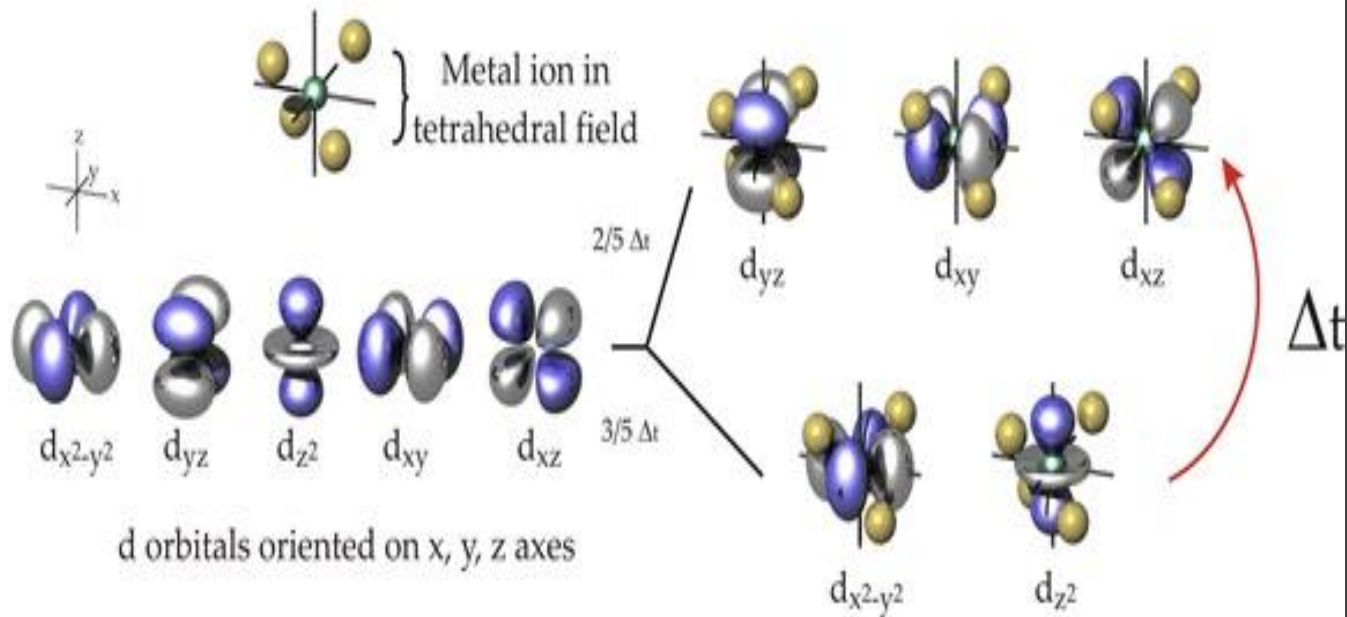
where $0.6\Delta_o = 6 Dq$ & $0.4\Delta_o = 4Dq$

Examples-Co(III) complexes, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

Crystal Field Splitting of d-orbitals in Tetrahedral Complexes

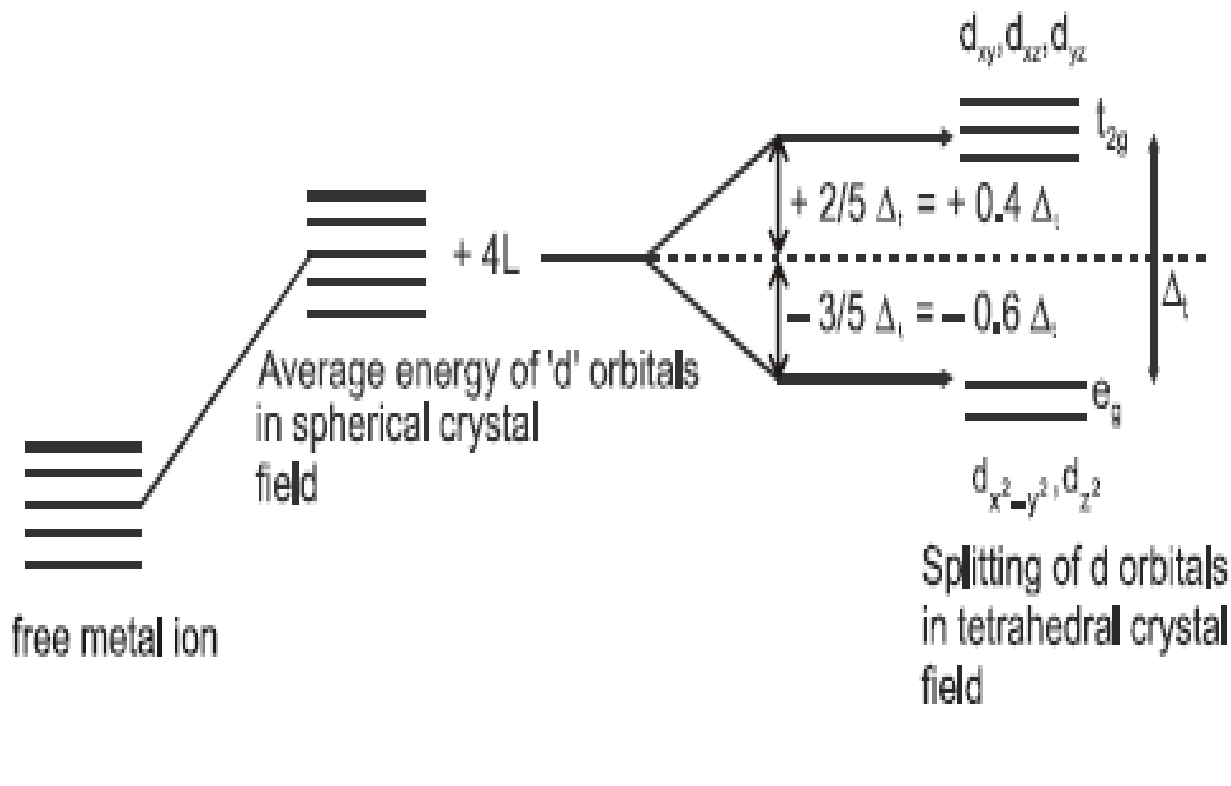
Cubic arrangement where alternate corners are vacant





d Orbital Splitting in a Tetrahedral Field

Energy



- The energy separation between t_2 & e orbitals in tetrahedral complexes is less than octahedral complexes.
- If the central metal ion, ligands & distances between them are all same in **Td & Oh** complexes, we get

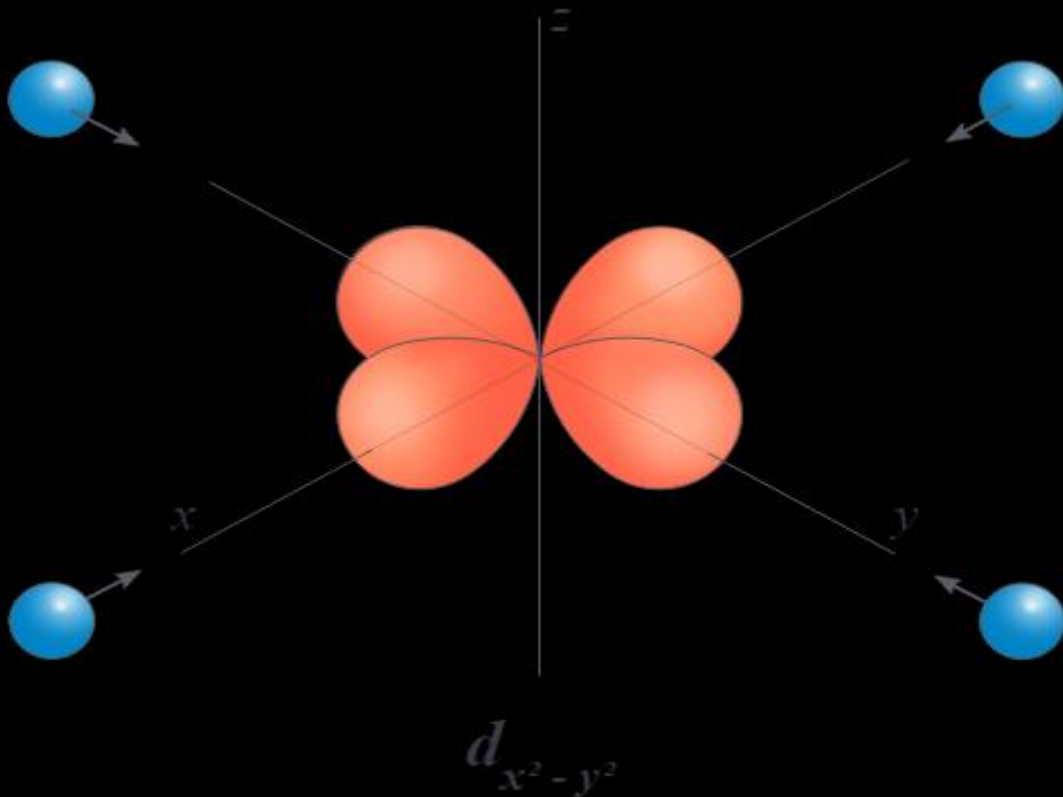
$$\Delta_t = 4/9 \Delta_o \text{ (i.e. } 0.45 \Delta_o \text{)}.$$

- As **10Dq** value is **low** in **Td symmetry** crystal field favors the **formation of Oh complexes** rather Td complexes.
- Td complexes are formed only when both t_2 & e are symmetrical i.e. empty, half filled, completely filled.

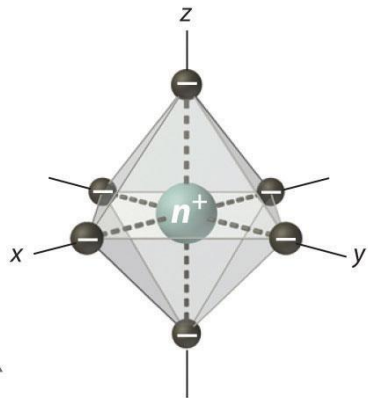
□ *Examples- d^0 , d^1 , d^2 , d^5 , d^7 , & d^{10}*

- d^0 - $[\text{TiCl}_4]$
- d^5 - $[\text{FeCl}_4]^-$
- d^{10} - $[\text{ZnCl}_4]^{2-}$

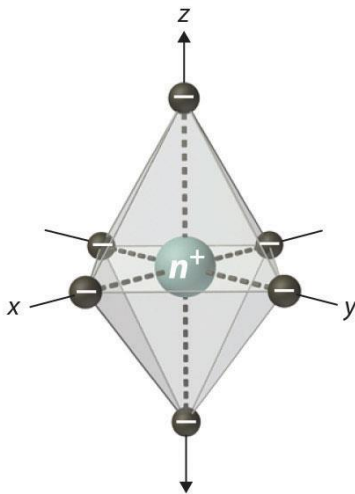
Splitting of d-orbitals in Square planar complexes



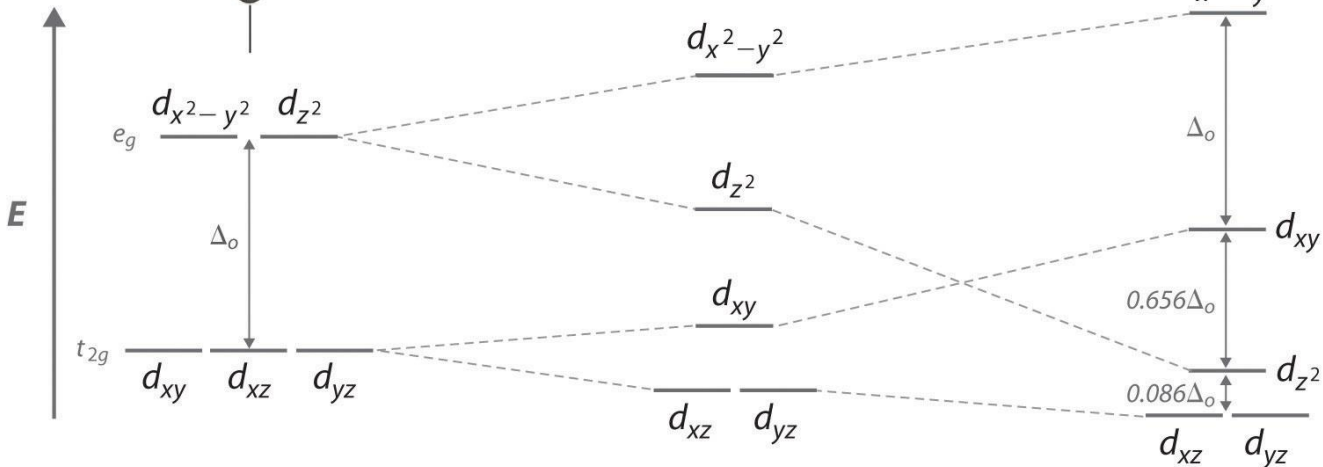
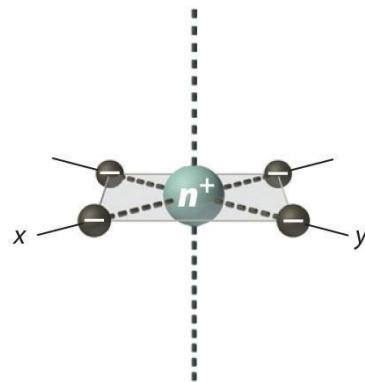
Octahedral

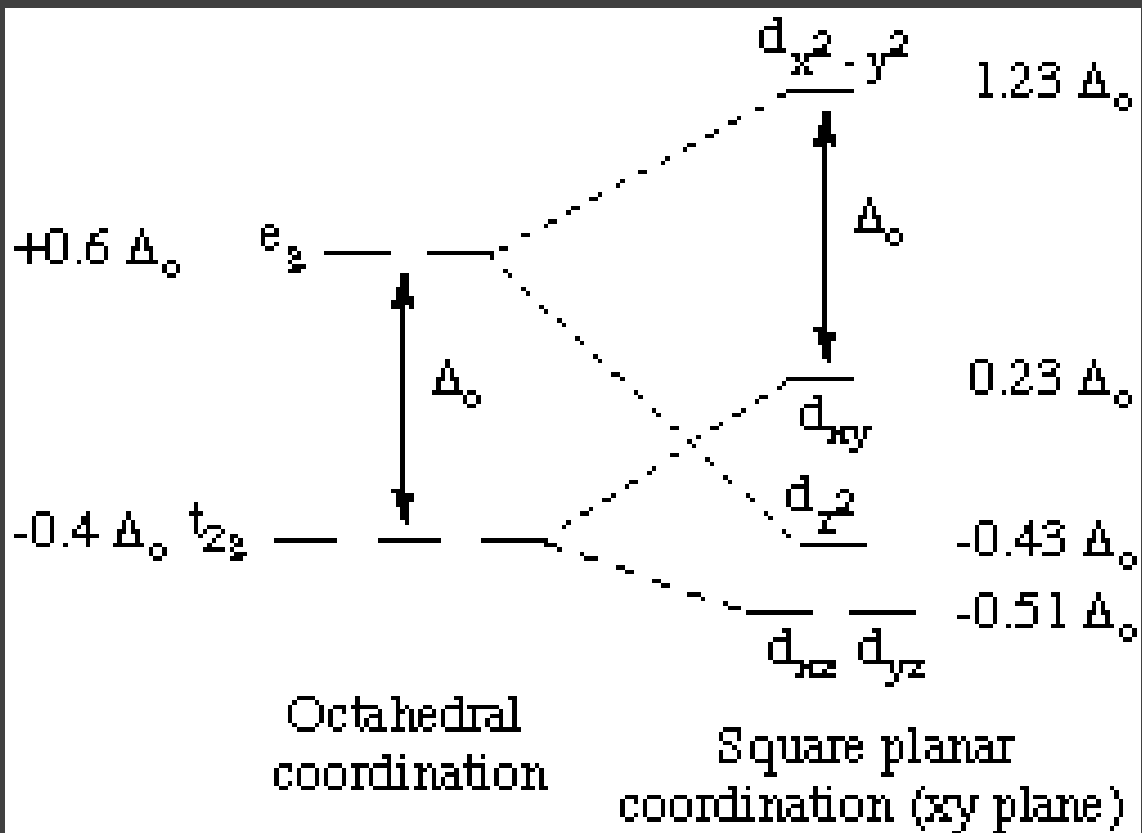


Tetragonal



Square planar





Examples: $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_4]^{2-}$ (Low spin complexes always)

High Spin & Low Spin Complexes (Strong & Weak field Complexes)

- ✧ **Weak Field Ligand:** The ligands which cause only a **small degree** of splitting of d-orbitals are called as-----
- ✧ **Strong Field Ligands:** The ligands which cause **large degree** of splitting of d-orbitals are called as-----
- ✧ **High Spin Complex:** Involves **weak field** ligand & Pairing energy is greater than the CFSE [$P > 10Dq$], **Paramagnetic & more reactive.**
- ✧ **Low Spin Complex:** Involves **Strong field** ligand & Pairing energy is lesser than the CFSE [$P < 10Dq$], **Stable & Diamagnetic**

* Example - High spin & low spin Octahedral Complexes
of Cobalt (III)

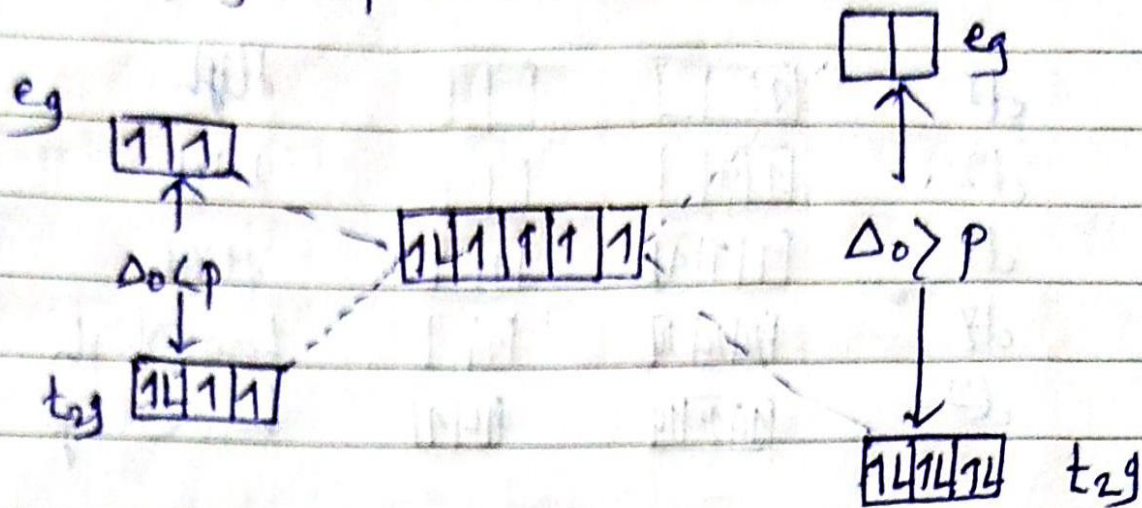
The E.C. of $\text{Co}^{\text{III}} (27) = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$

e.c. of $\text{Co}^{3+} (\text{III})$ is $= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$.

So, commonly it is referred to as d^6 case.

Now, consider splitting of 'd' orbital in strong & weak field.

$d^6 = Co^{3+}$:- splitting of 'd' orbitals,



Weak field case

High spin complex (a) spin free

strong field case

Low spin complex (a) spin paired

High-spin and low-spin complex ions of Mn^{2+} .

No field

Maximum number of unpaired electrons



Free Mn^{2+} ion

Weak-field ligand

High-spin complex

$E_{\text{pairing}} > \Delta$

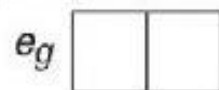


$[Mn(H_2O)_6]^{2+}$

Strong-field ligand

Low-spin complex

$E_{\text{pairing}} < \Delta$

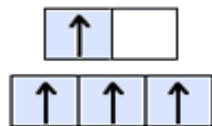


$[Mn(CN)_6]^{4-}$

High spin:
weak-field ligand

Low spin:
strong-field ligand

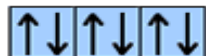
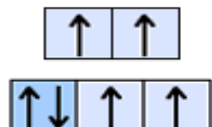
d^4



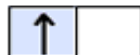
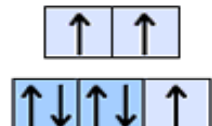
d^5



d^6



d^7



Crystal Field Stabilization energy (CFSE)/ Ligand Field stabilization energy (LFSE)

✿ Lowering in energy of a transition metal ion in a given ligand environment due to crystal field effects **known as ----**

OR Lowering in energy of metal ion caused by splitting of energy levels.

✿ The energy associated with the increased attraction leading to higher stability of the complex in presence of crystal field of ligands called as **CFSE**

✿ **Crystal Field Effect:** The splitting of d-orbitals of a metal ion due to electrostatic crystal field potential of ligands & consequences thereof are known as

$$\Delta_o(\text{CFSE}) = \left[-\frac{2}{5}(m)t_2g + \frac{3}{5}(n)eg \right] \Delta_o + lP$$

OR

$$\Delta_o(\text{CFSE}) = [-0.4(m)t_2g + 0.6(n)eg] \Delta_o + lP$$

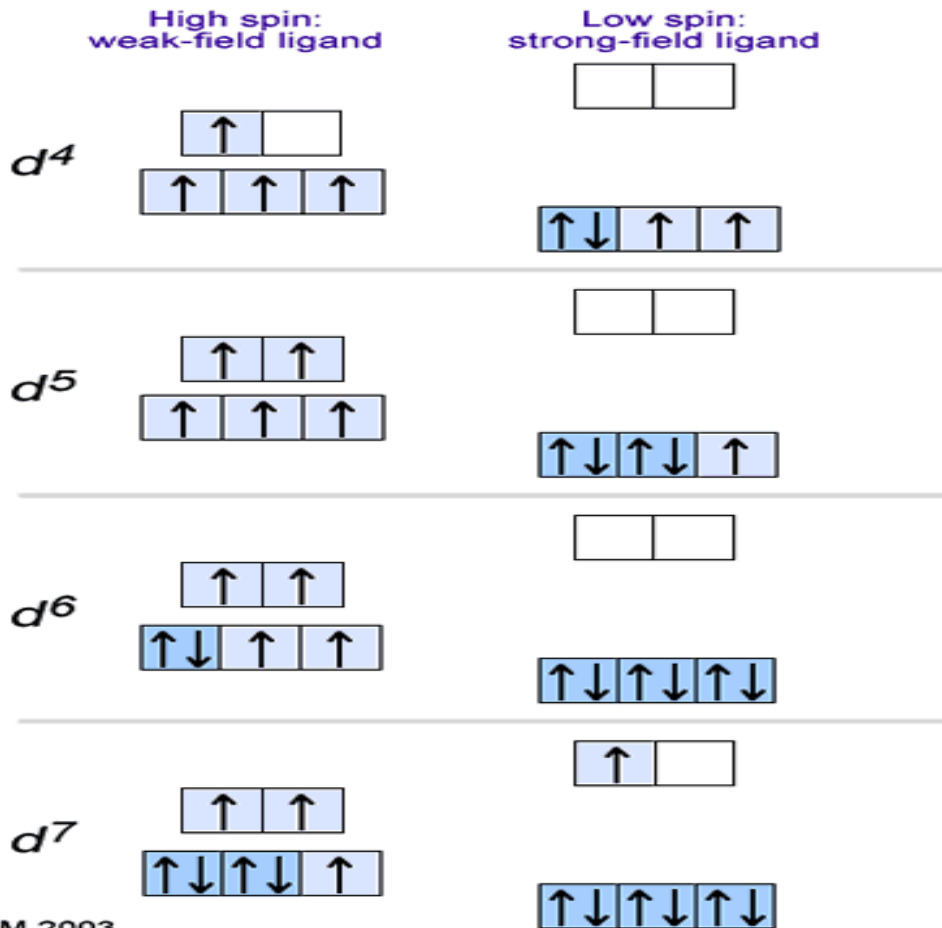
we know $\Delta_o = 10 Dq$ so that

$$\Delta_o(\text{CFSE}) = [-4(m)t_2g + 6(n)eg] \Delta_o + lP$$

$\Delta_o(\text{CFSE})$ = crystal field stabilisation energy for octahedral complex

Calculation of CFSE of different metal ion configurations

Calculation of CFSE of different metal ion configurations



Factors affecting to CFSE

Jahn-Teller Distortion



::::Thank You::::

::::Keep Learning::::