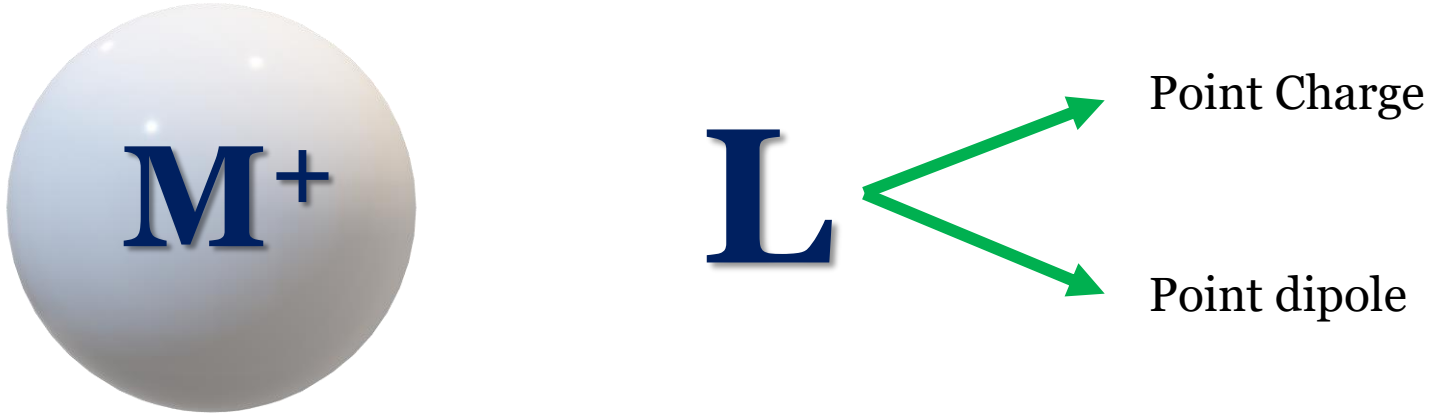
Crystal Field Theory

Tony Francis
Assistant Professor
Postgraduate Department of Chemistry
St. Mary's College, Manarcaud

Crystal field theory

- Proposed in 1929 by Hans Bethe
- Later it was modified by J H Van Vleck in 1935
- Pure Crystal field theory assumes that the only interaction between the metal ion and the ligands is an electrostatic or ionic one with the ligands being regarded as negative point charges



Postulates of CFT

- This theory considers a complex as a combination of a central ion surrounded by ions or molecules called as ligands. It regards these ligands as point charges (Cl^-, Br^- etc) or as point dipoles (H_2O, NH_3 etc).

- All d orbitals of the central metal ion have the same energy. They are said to be degenerate. The degeneracy is destroyed by the approach of the ligands during the formation of a complex. And d orbitals split into different energy levels.

- The bonding between the metal cation and ligands arises due to the electrostatic attraction between the nucleus of the metal cation and the partial negative charge present in the ligands. Thus the bond between the metal and ligand is purely ionic in nature.

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

Interactions in CFT

- Attractive Interactions
- Repulsive interactions

The repulsive interactions are the cause of crystal field splitting.

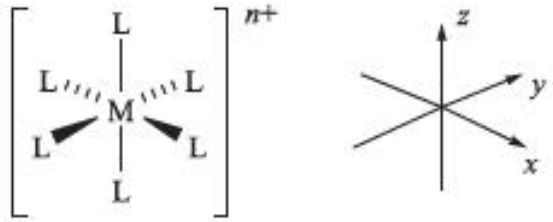
The splitting of d-orbitals and its consequences are considered as the backbone or heart of CFT

To have a fine grip on CFT one should have a clear idea on the shape and distribution of d- orbitals in space.

The five d-orbitals are- d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}.

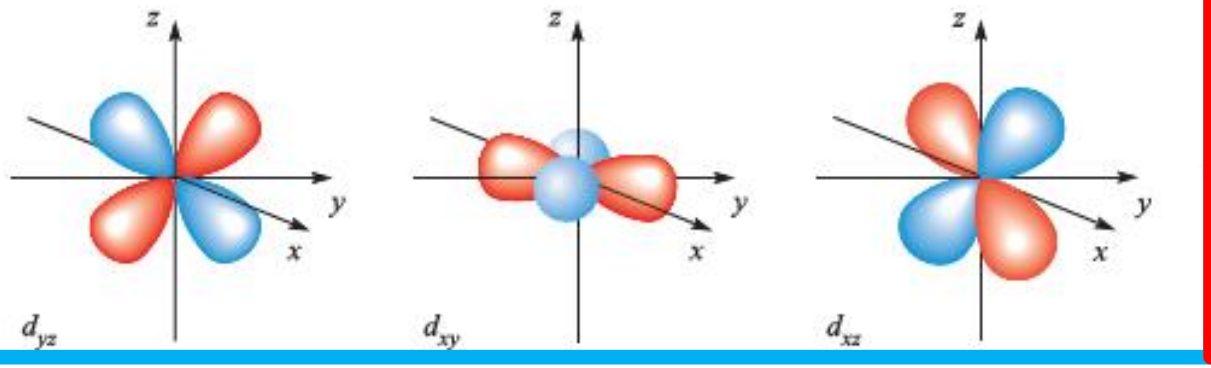
The tt means triply degenerate while the ee means doubly degenerate (degenerate means have the same energy).

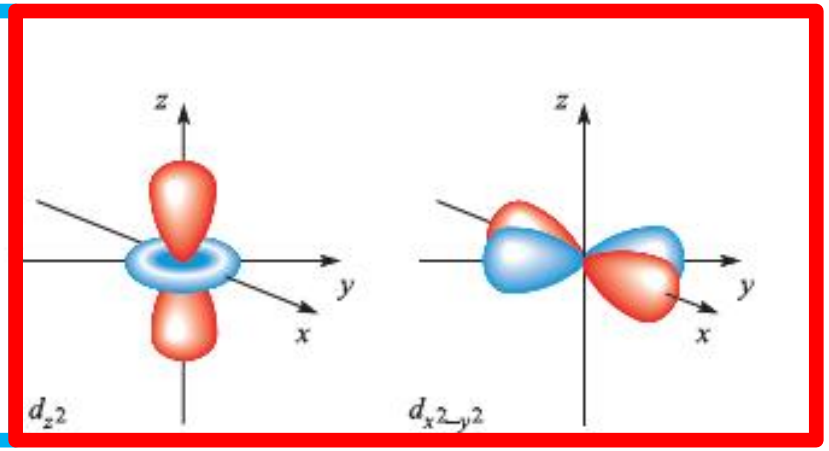
The t means triply degenerate while the e means doubly degenerate (degenerate means have the same energy).



(a)

t_{2g}

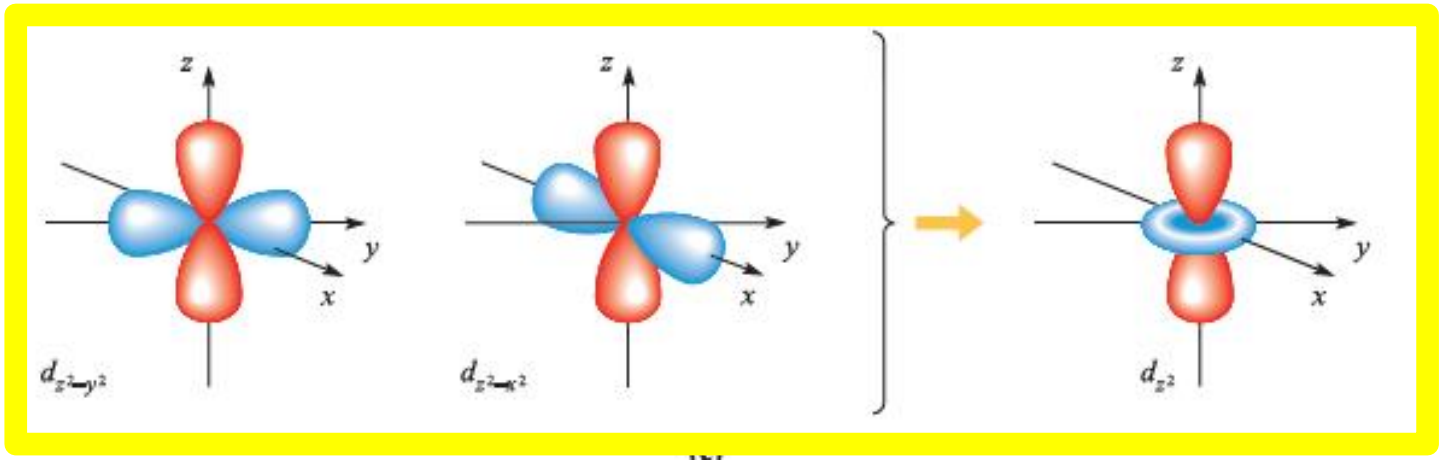




e_g

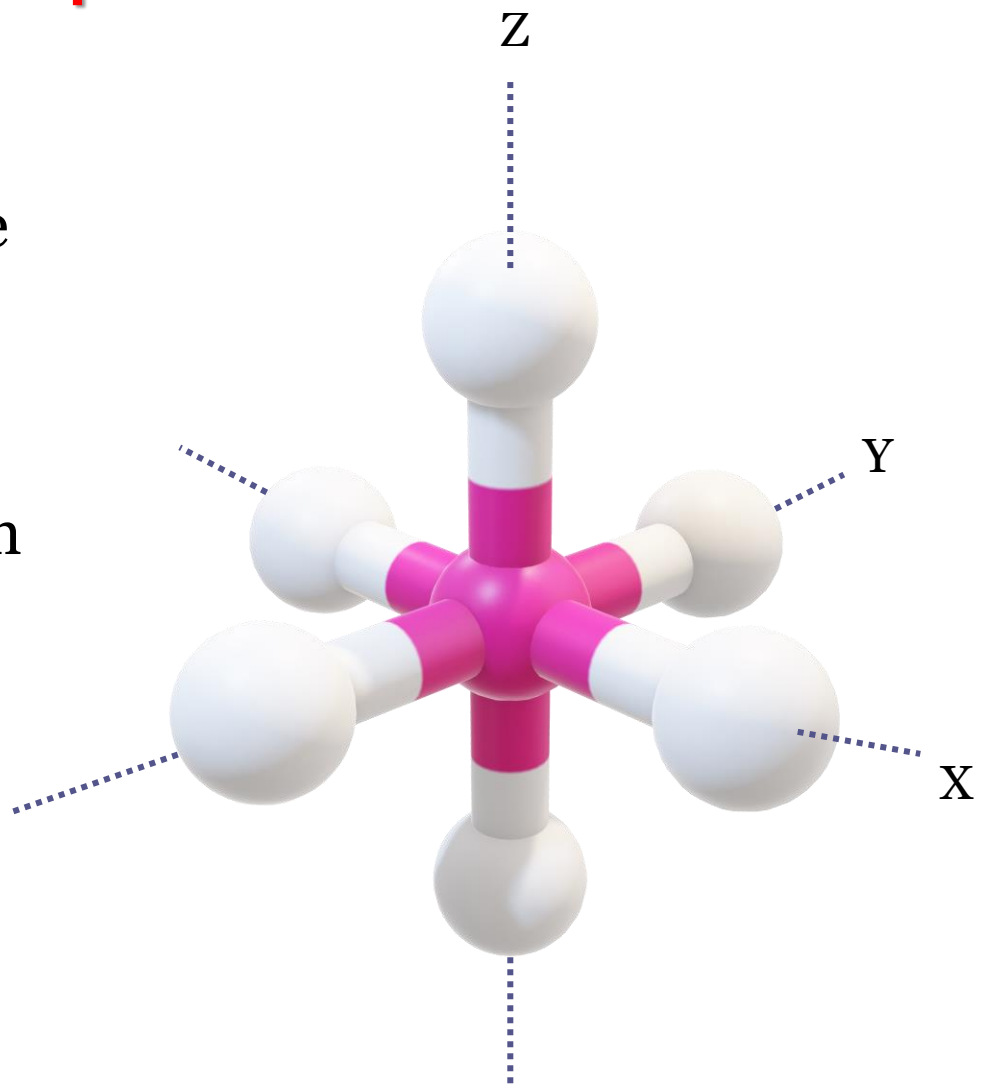
Orbitals in between the axis

Orbitals along the axis

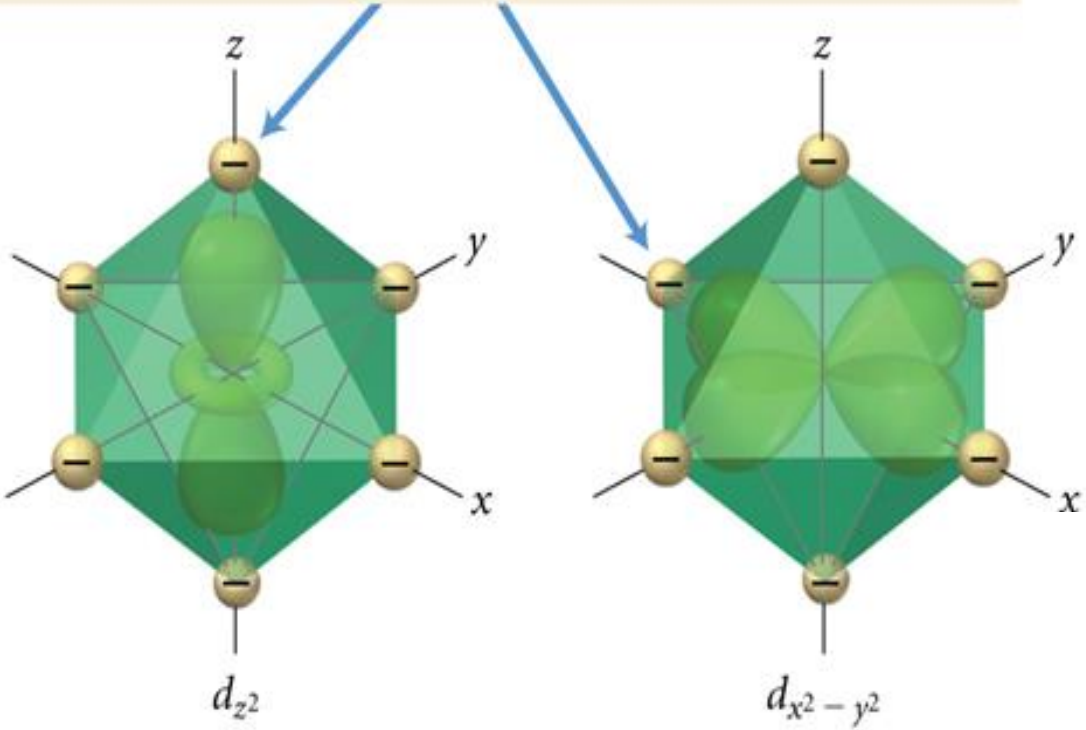


Splitting of d orbitals in Octahedral Complexes

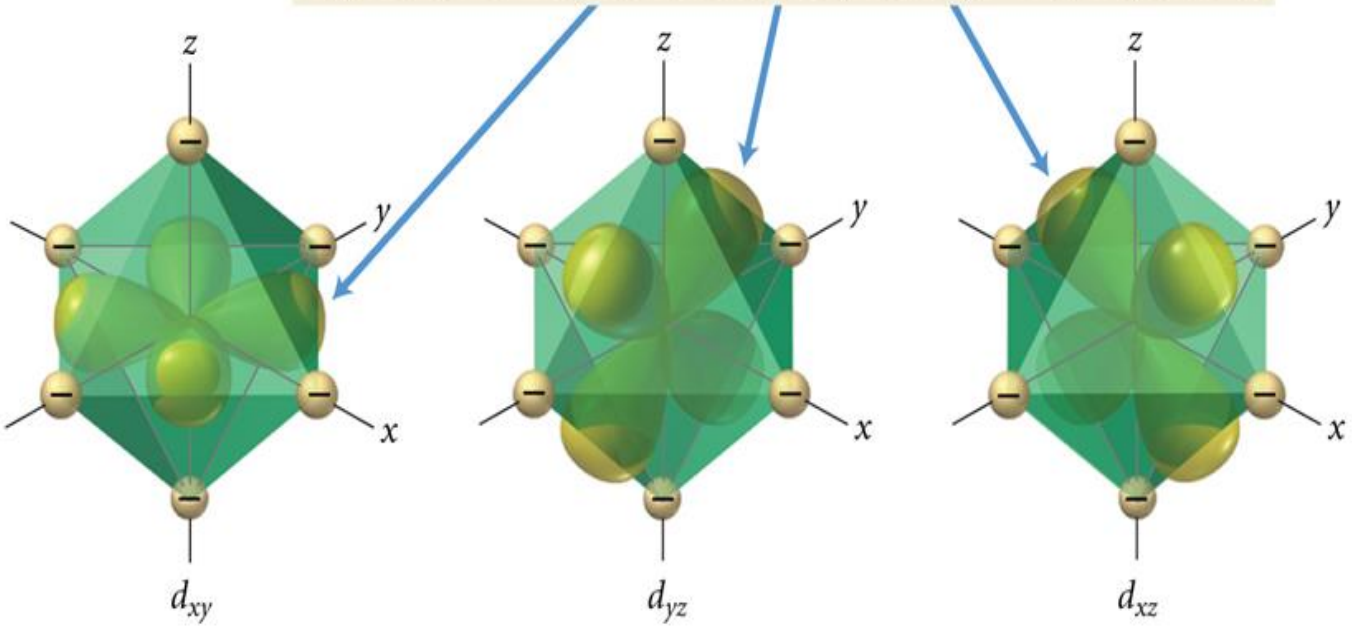
- In Oh Complex the approach directions of the ligand are along the axis.
- That is the six ligands are positioned along the axes of a Cartesian coordinate system with the metal ion at the origin.
- So the d-orbitals along the axis (dx^2-y^2 and dz^2) will be more strongly repelled than orbitals with lobes directed in between the axis(dxy, dyz and dxz)



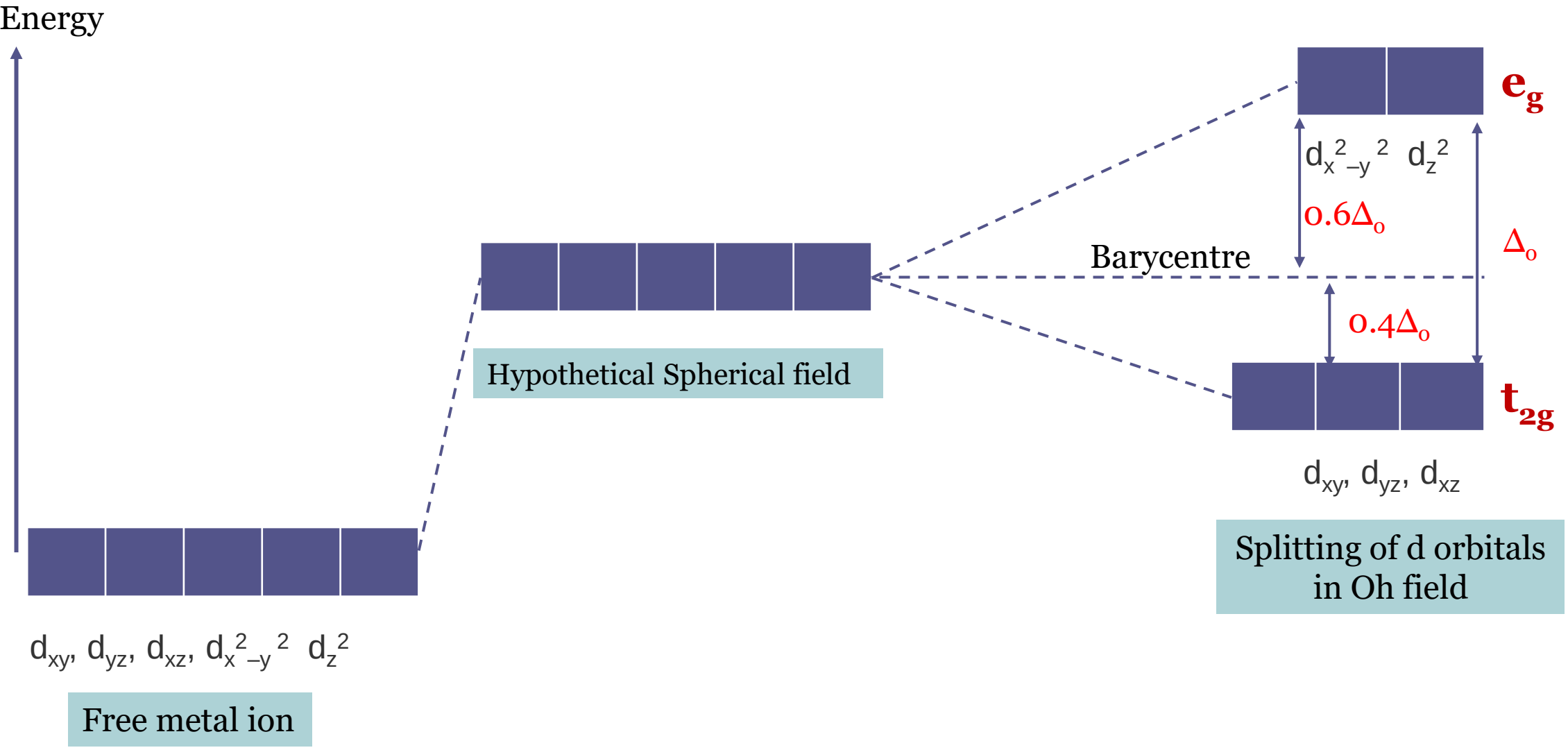
Ligands overlap with orbital lobes, resulting in strong repulsions.

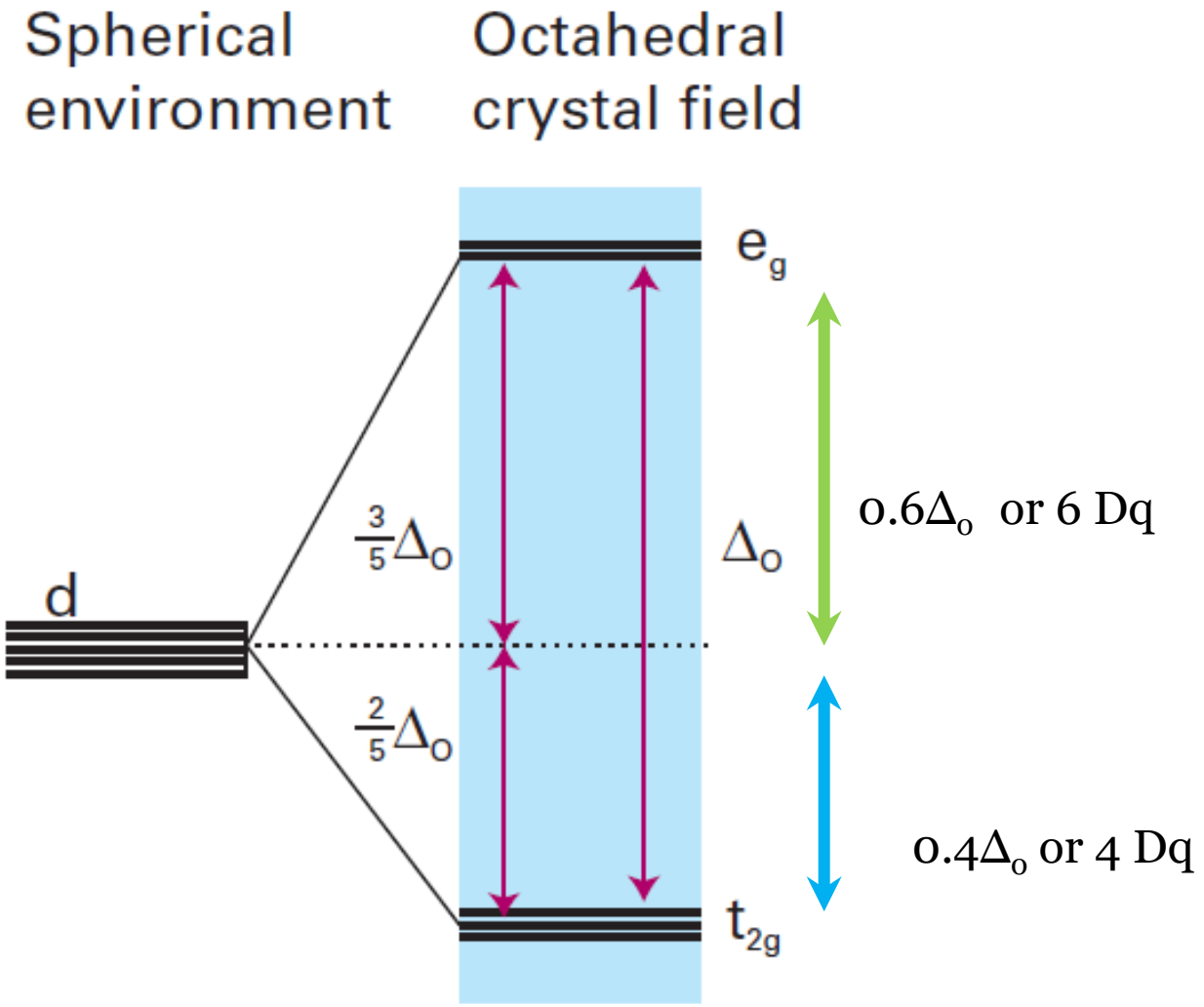


Ligands come in between orbital lobes, resulting in weak repulsions.



Splitting of the five d orbitals by an Oh field





- This splitting of degenerate d orbitals into two sets having different energy is called Crystal field splitting.
- The extent to which the eg and t2g orbitals are separated in an Oh complex is denoted by Δ_o or 10 Dq are called crystal field splitting energy.
- The centre of gravity or barycentre of the orbitals remain constant.
- Here the two eg orbitals will be repelled by 0.6 Δo while the three t2g orbitals are stabilized to an extent of 0.4Δo with respect to the barycentre.

Crystal field stabilisation energy (CFSE)

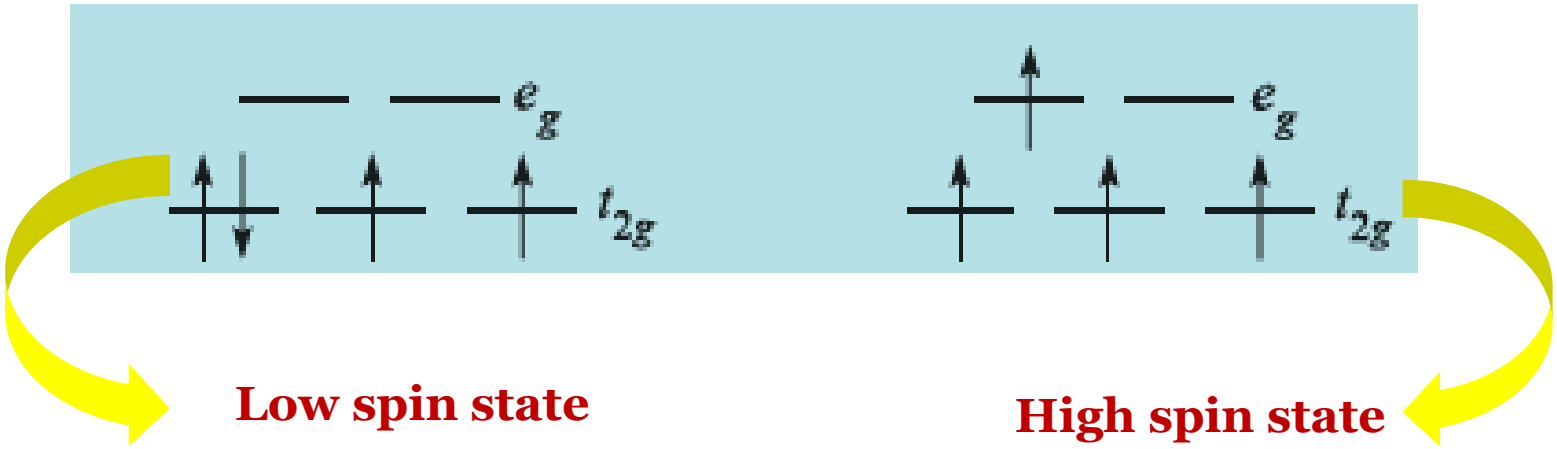
- In a d^1 case , the electron occupies a t2g orbital, which has an energy of $-0.4\Delta_o$ relative to the barycentre of the d orbitals.

- Here we can say that the complex is said to be stabilized to the extent of $0.4\Delta_o$ compared to the hypothetical spherical field.
- This quantity is termed as crystal field stabilization energy (CFSE)
- For d^2 case give $t2g^2$ and has a CFSE of $0.8\Delta_o$

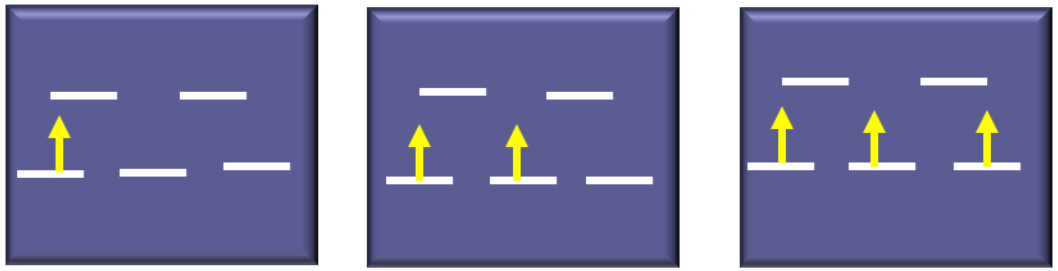
- For d^3 case give $t2g^3$ and has a CFSE of $1.2\Delta_o$

For high-spin : Δ < P
For low-spin: Δ > P

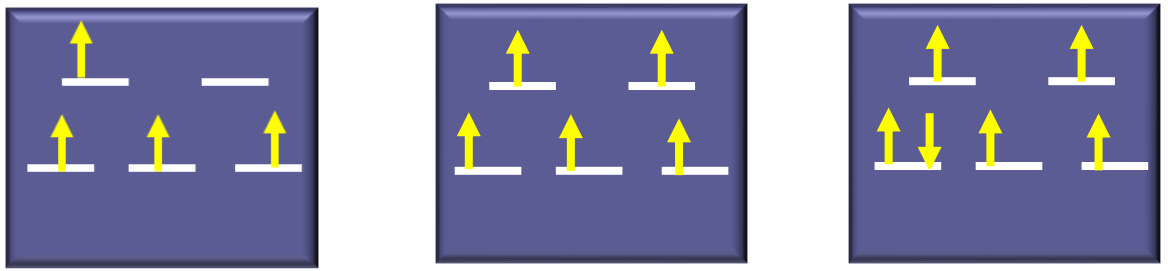
Strong ligand field = large Δ= low spin
Weak ligand field = small Δ = high spin



Complexes with weak field ligand (High Spin)

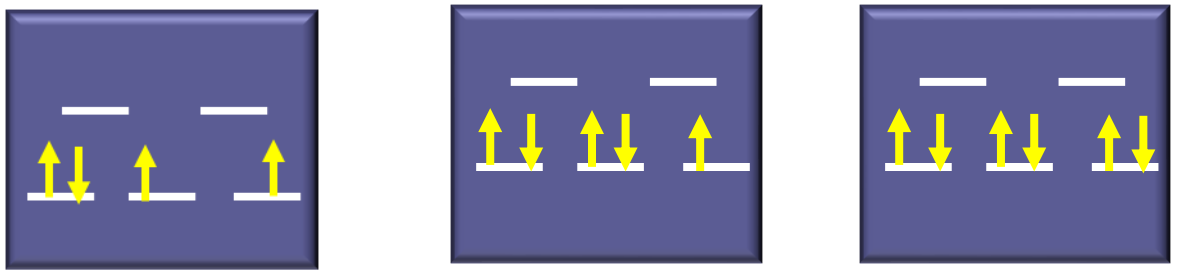


d^1 d^2 d^3



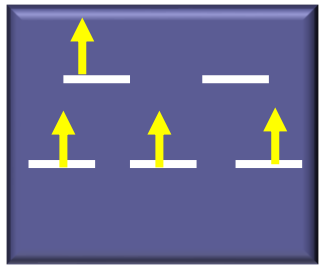
d^4 d^5 d^6

Complexes with strong field ligand (Low Spin)

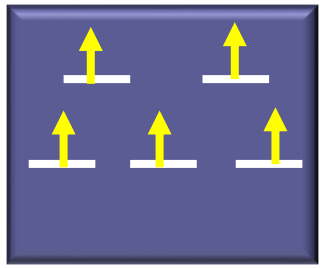


d^4 d^5 d^6

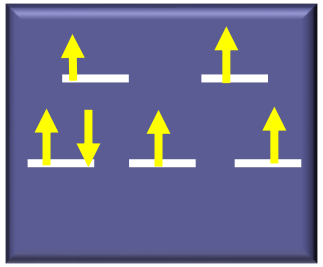
Complexes with weak field ligand (High Spin)



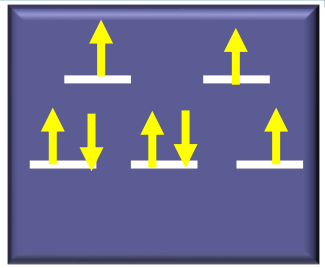
d^4



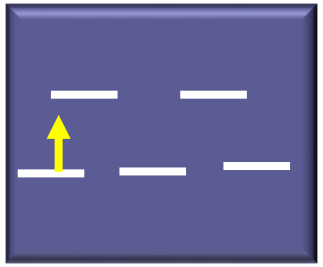
d^5



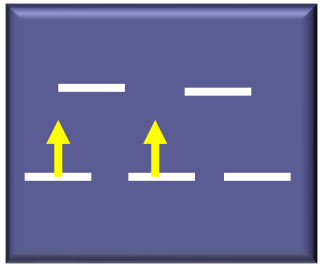
d^6



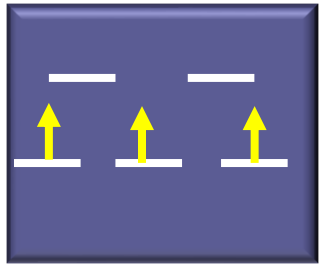
d^7



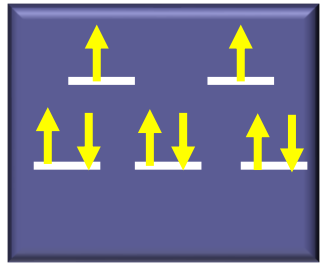
d^1



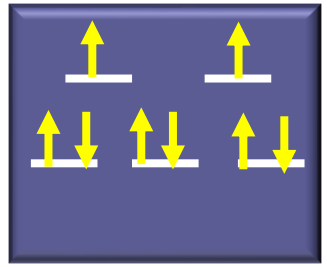
d^2



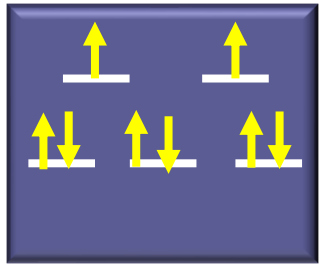
d^3



d^8

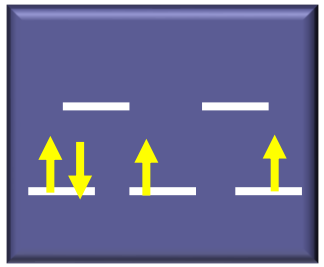


d^9

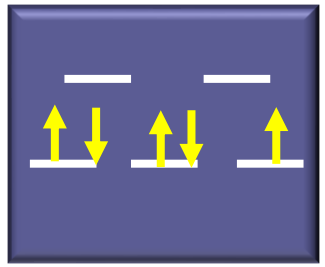


d^{10}

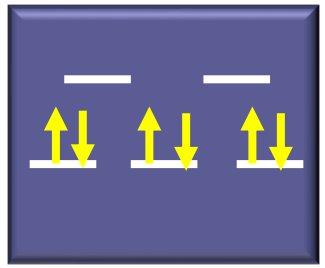
Complexes with strong field ligand (Low Spin)



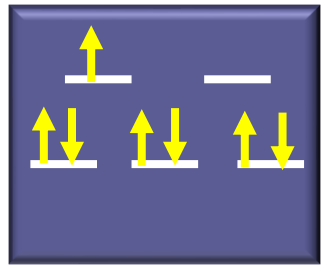
d^4



d^5



d^6



d^7