

CML 101: Inorganic Chemistry

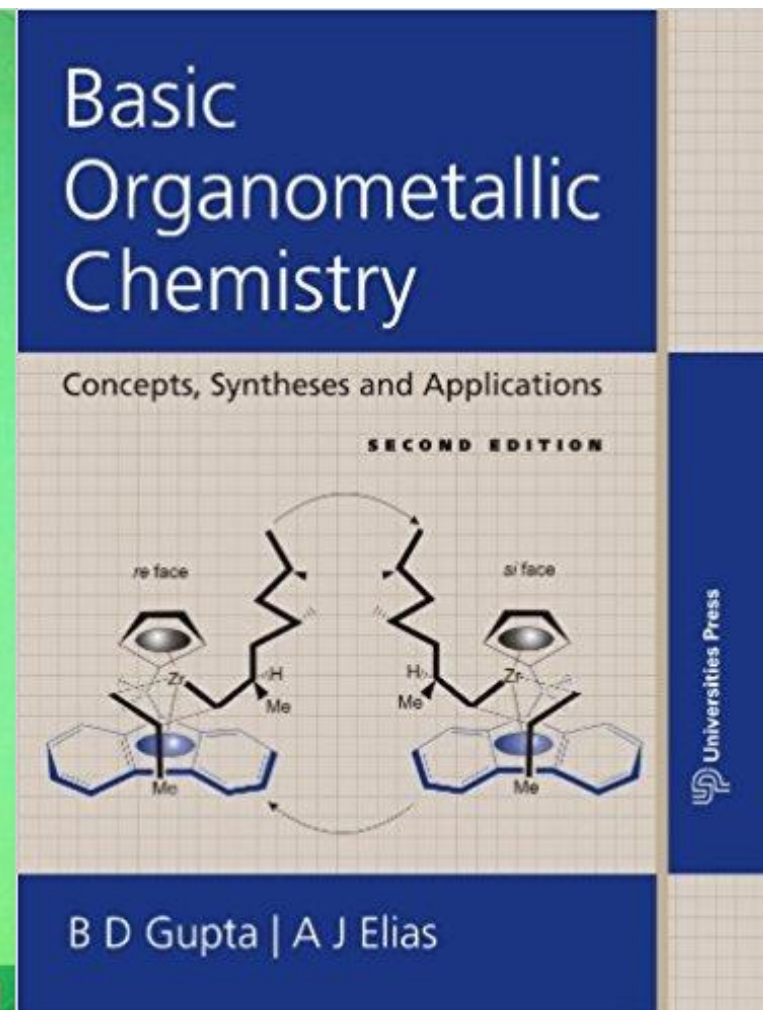
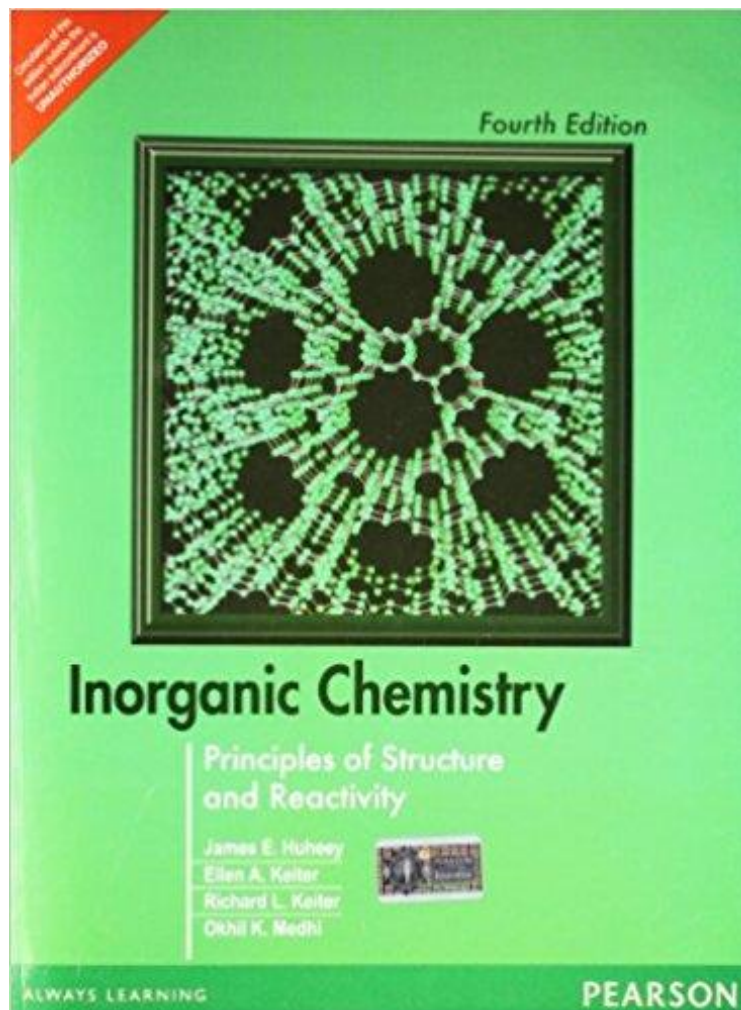
Reference Books

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Email: subrata@iitd.ac.in

- 12 + 2 Lectures
- 4 Tutorials
- Lecture slides will be available as pdf files from Impartus.

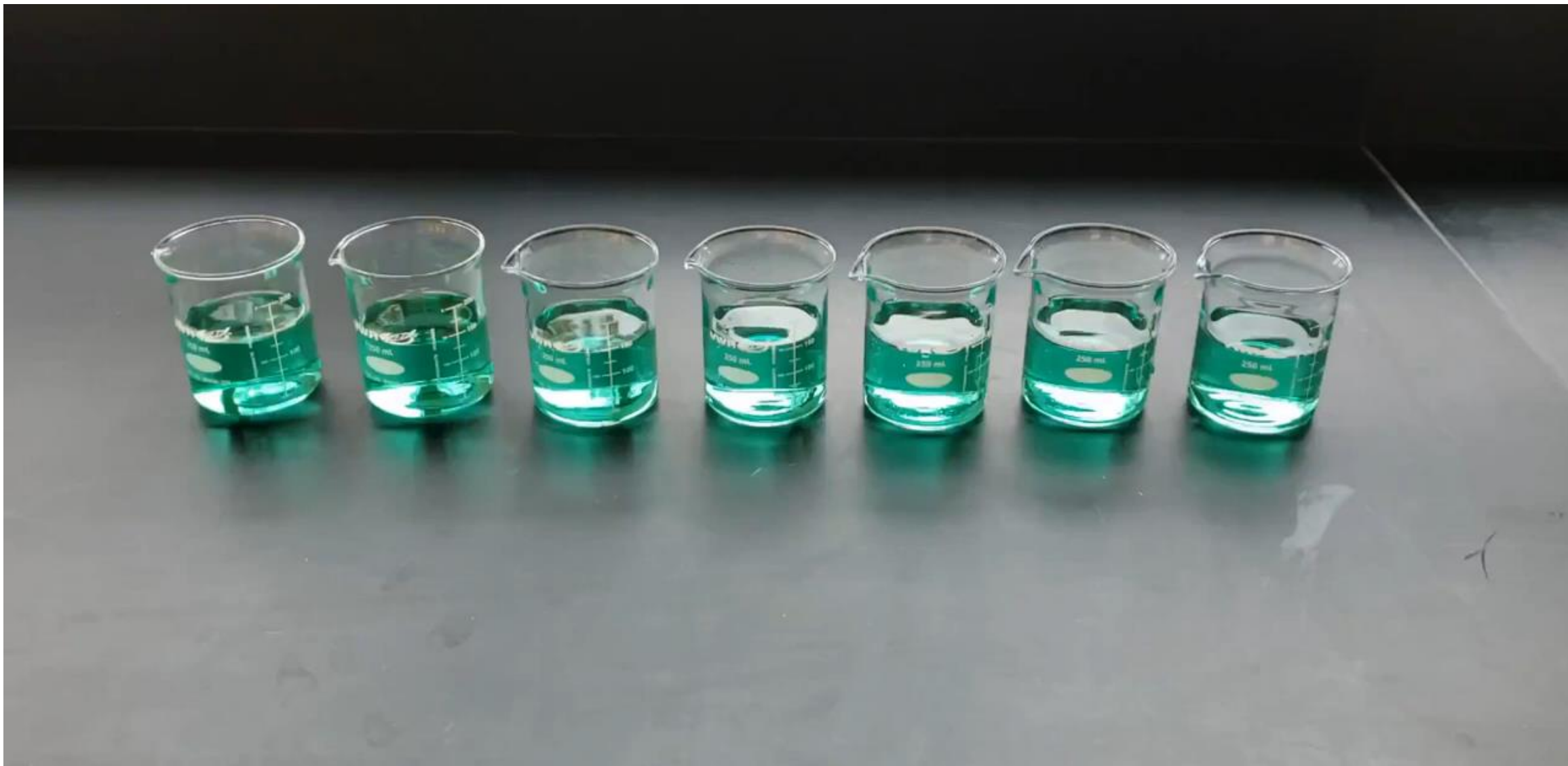


I kindly acknowledge Prof. Elias and Prof. Paria for the slide materials

Syllabus

- Applications of crystal field theory
- Stability of organometallic compounds;
- Metal carbonyls: structure and bonding;
- Important reactions of organometallic compounds; Homogeneous catalysis;
- An overview of metals in biology; Functions of metalloproteins.

NB: What ever the topic is covered will be in your exam. You don't have to worry about the syllabus.



https://www.youtube.com/watch?v=w3UgDC9nkf0&t=68s&ab_channel=JackWiley

Background requirement: +2 level CBSE/ICSE and JEE advanced syllabus level

9.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

- (i) It involves a number of assumptions.
- (ii) It does not give quantitative interpretation of magnetic data.
- (iii) It does not explain the colour exhibited by coordination compounds.
- (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- (v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- (vi) It does not distinguish between weak and strong ligands.

9.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards



Coordination Compounds are the backbone of modern inorganic chemistry and chemical industry.

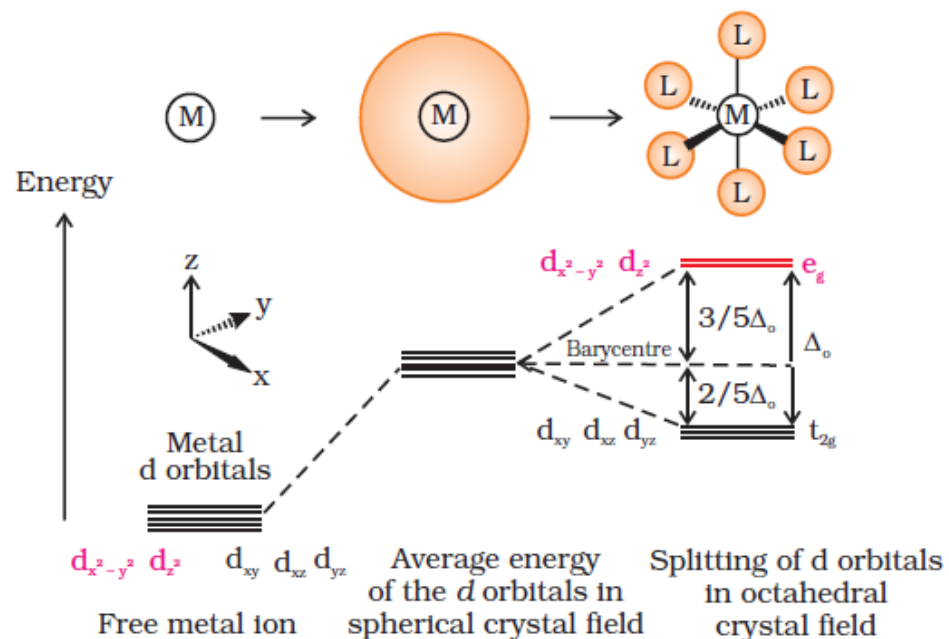
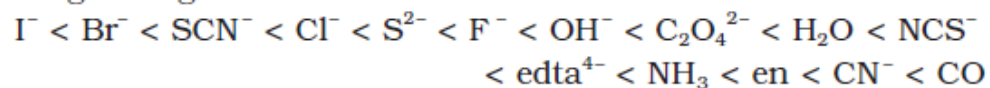


Fig.9.8: d orbital splitting in an octahedral crystal field

degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by Δ_o (the subscript o is for octahedral) (Fig.9.8). Thus, the energy of the two e_g orbitals will increase by $(3/5) \Delta_o$ and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.

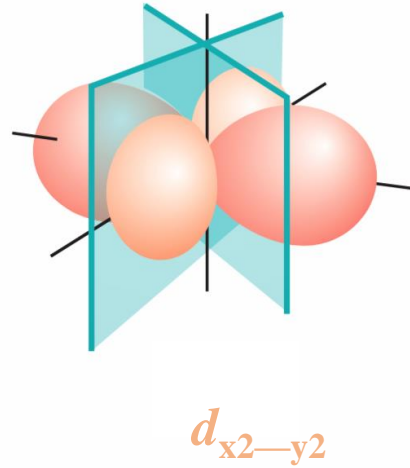
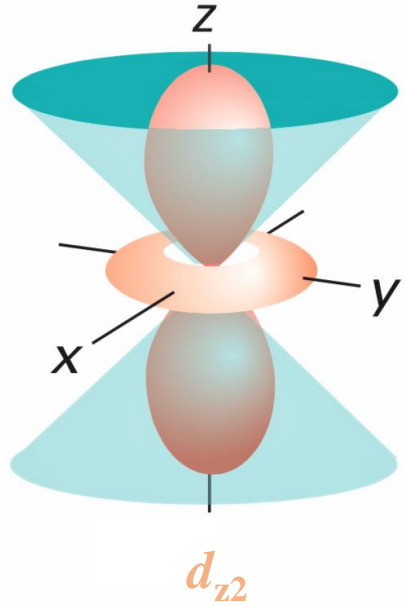
The crystal field splitting, Δ_o , depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In

general, ligands can be arranged in a series in the order of increasing field strength as given below:

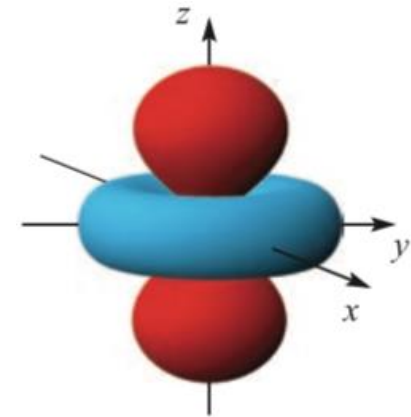
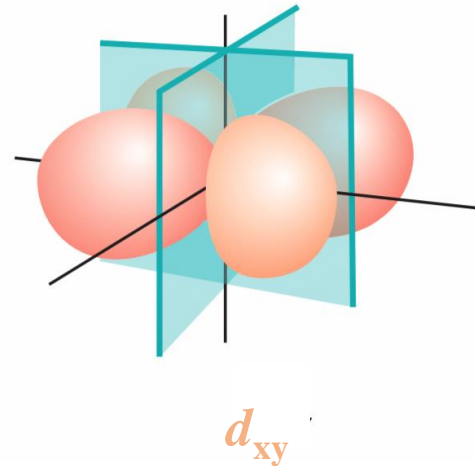
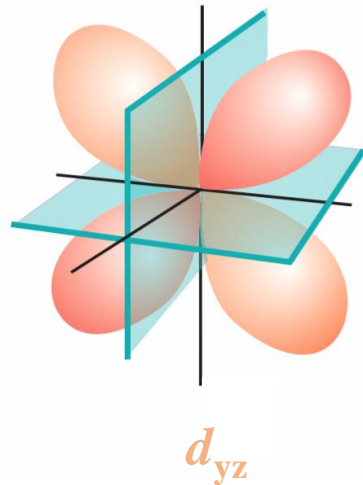
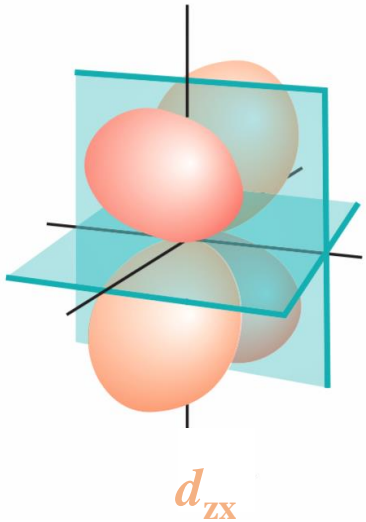
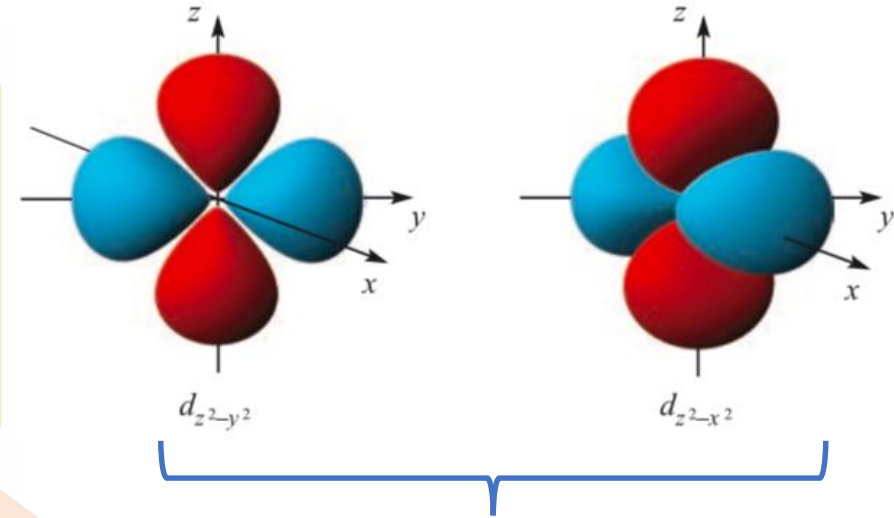


Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the d orbitals of metal ion in octahedral coordination entities. Obviously

The conventional representation of a set of five degenerate d -orbitals



The formation of a d_{z^2} orbital from a linear combination of $d_{z^2-y^2}$ and $d_{z^2-x^2}$ orbitals.



Theories of bonding in transition metal complexes – in a nutshell

Theories of bonding were proposed and used to explain the observed properties of transition metal complexes such as color, magnetism, shape of complexes

Valence bond theory

- Based on the concept of hybridization sp^3 , dsp^2 , dsp^3 , d^2sp^3 & sp^3d^2 : Predicts shapes of complexes very efficiently
- Can determine magnetic moment if hybridization is known and vice versa
- Does not explain color of complexes, distortion of shape of complexes
- Does not predict strength of ligands or temperature dependence of magnetic moments

Crystal Field theory

- Basic assumptions: Ligands and metal are point charges and the attraction between them is purely electrostatic in nature
- Considers how the energies of the five metal d orbitals change in the presence of a ligand field (removing /lifting of the degeneracy).
- Provides explanation to color, arranges ligands according to their strength, explains distortion of complexes and anomalies in their physical properties
- **VBT and CFT should not be MIXED**: A common mistake done by many students

Molecular Orbital Theory

- A larger picture where both metal orbitals and *ligand group orbitals* are made to form bonding, non bonding and antibonding orbitals.
- CFT splitting is included in this picture; also orbital overlap: π bonding
- Explains color, magnetism and energetics (does not predict shape)



Linus Pauling; Nobel 1954,1962



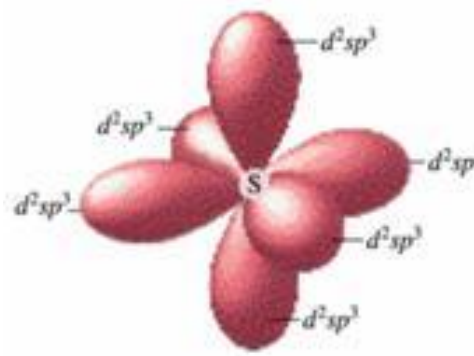
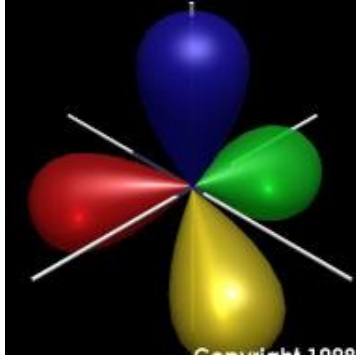
Hans Bethe, Nobel 1967



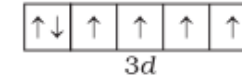
Mulliken & Hund, Nobel 1966(Mulliken)

Theories of bonding in transition metal complexes

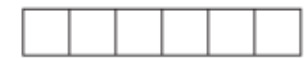
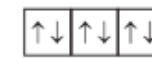
Valence bond theory



Orbitals of Co^{3+} ion

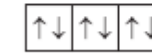


d^2sp^3 hybridised orbitals of Co^{3+}



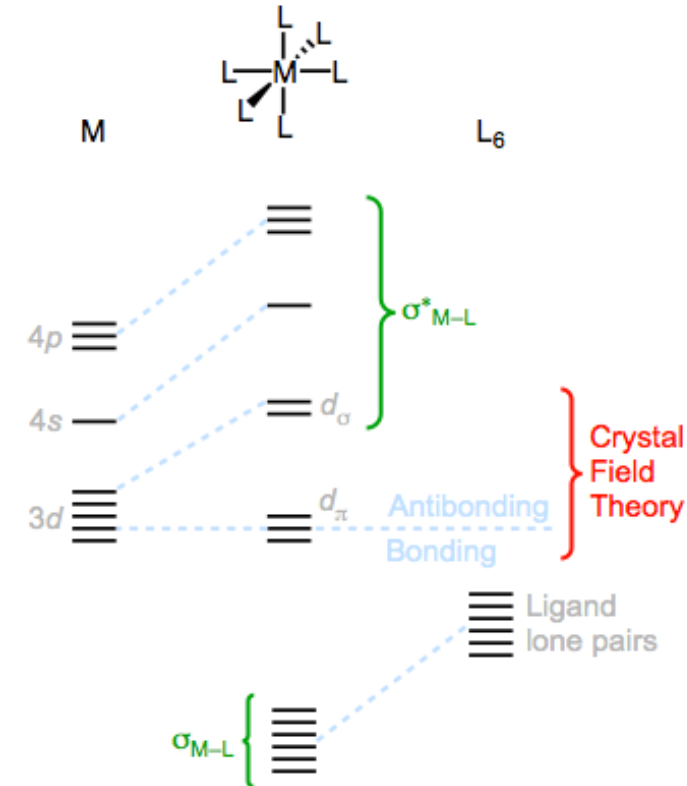
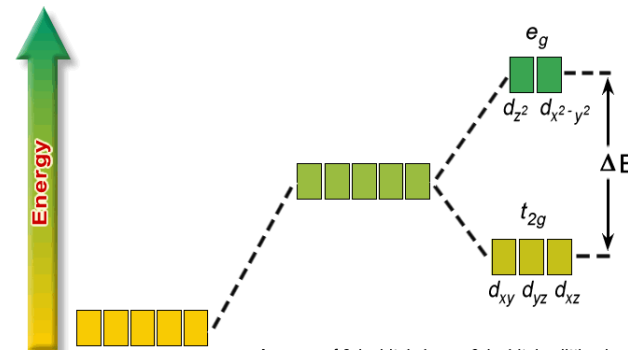
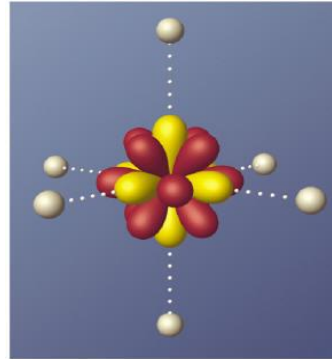
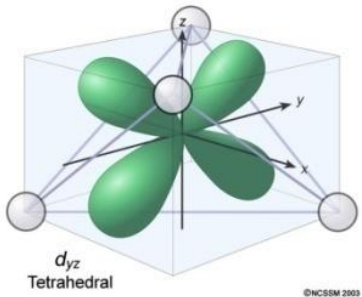
d^2sp^3 hybrid

$[\text{Co}(\text{NH}_3)_6]^{3+}$
(inner orbital or low spin complex)

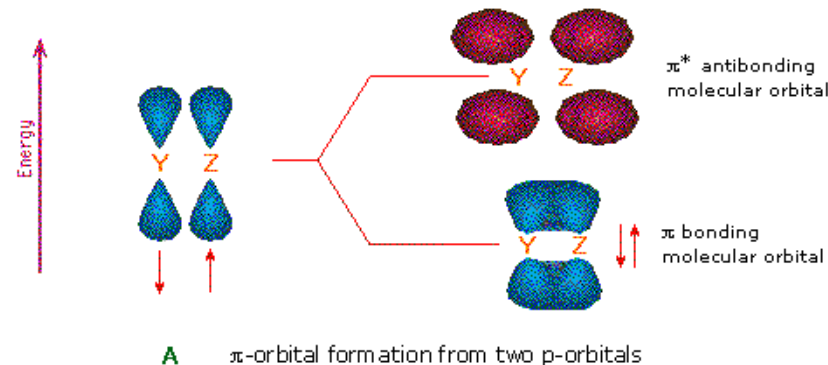


Six pairs of electrons from six NH_3 molecules

Crystal field theory

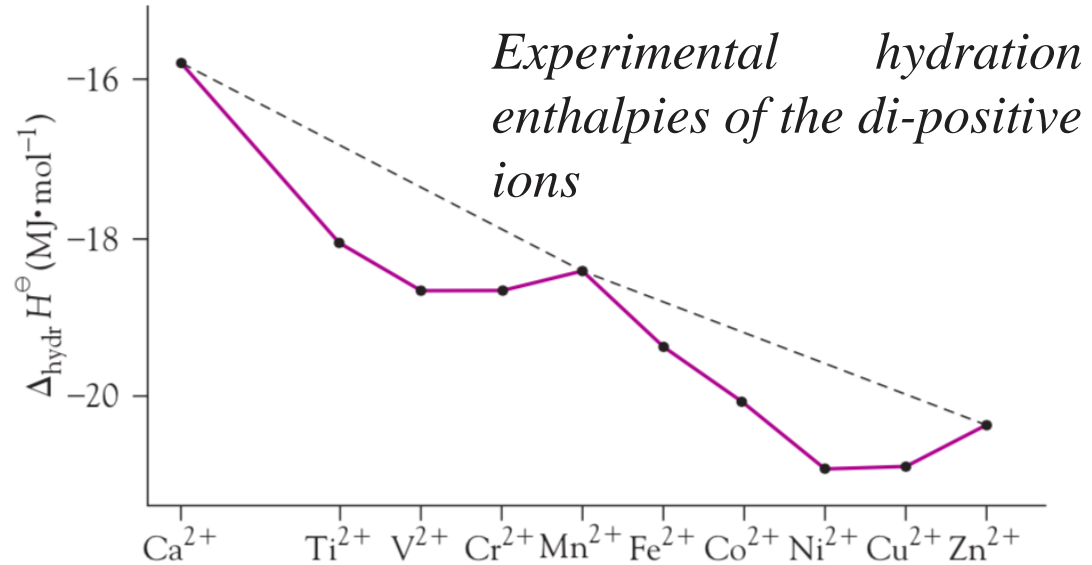


Molecular orbital Theory

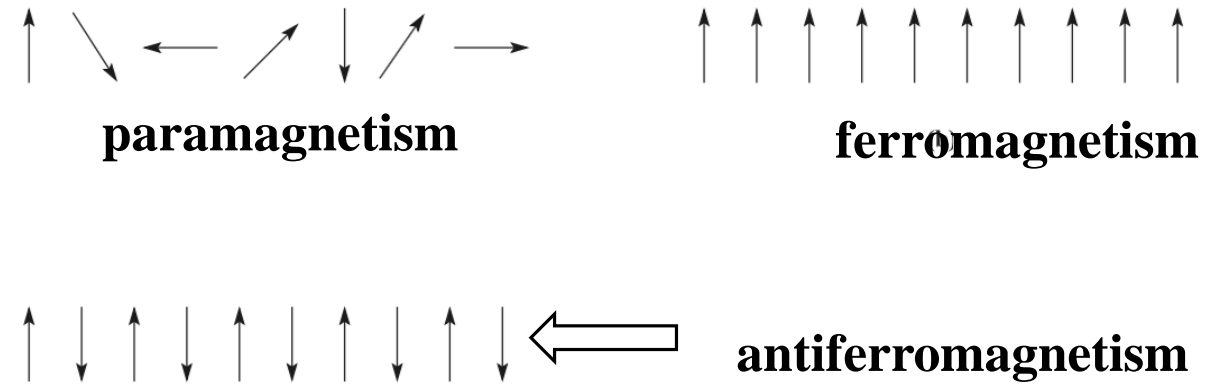


Importance of understanding bonding of transition metal complexes

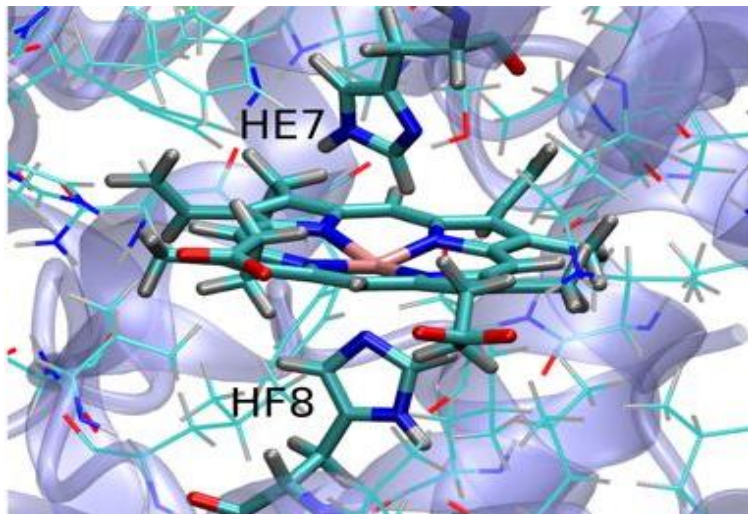
Physical properties of metal complexes



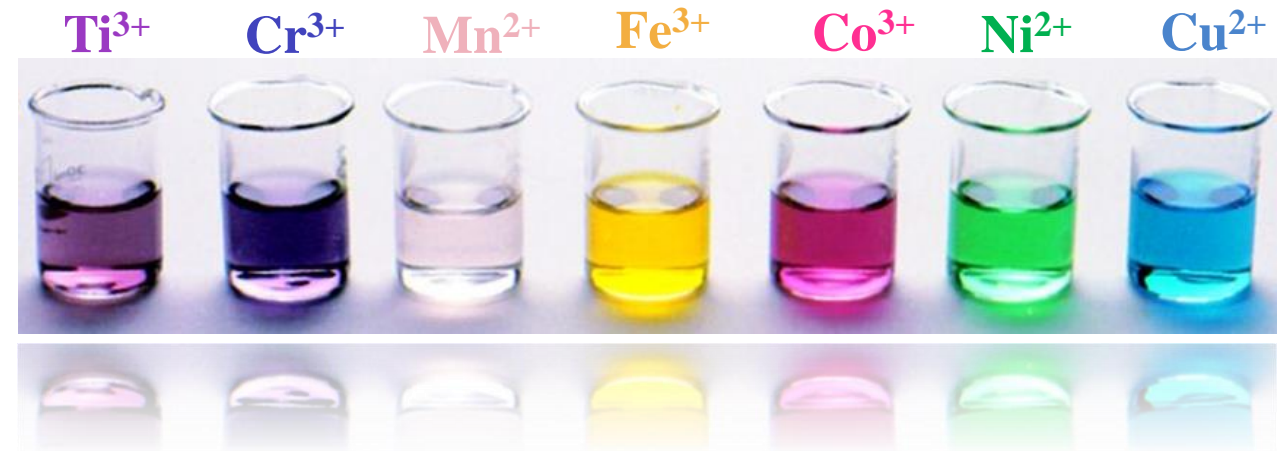
Magnetic properties of metal complexes



Structure and reactivity of metalloenzymes



Color of transition metal complexes



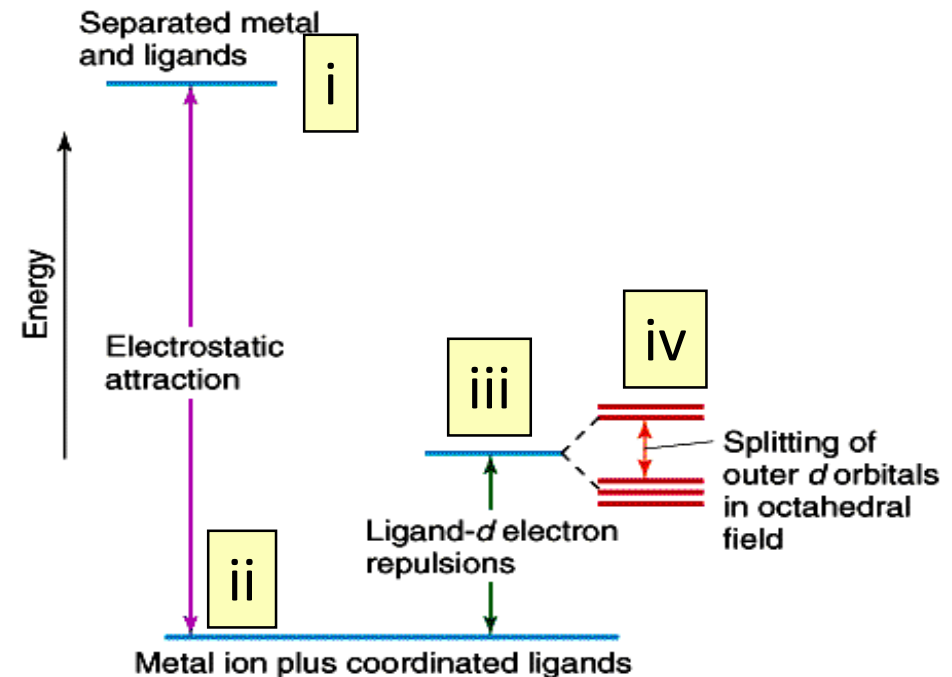
Aqueous solution of different divalent/trivalent first-row transition metal ions

Energetics involved in the CFT model

Basic Assumptions of Crystal Field theory (concept borrowed from solid state physics)

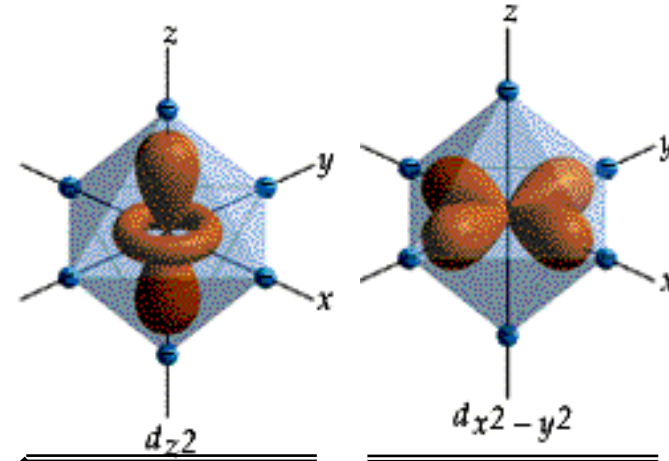
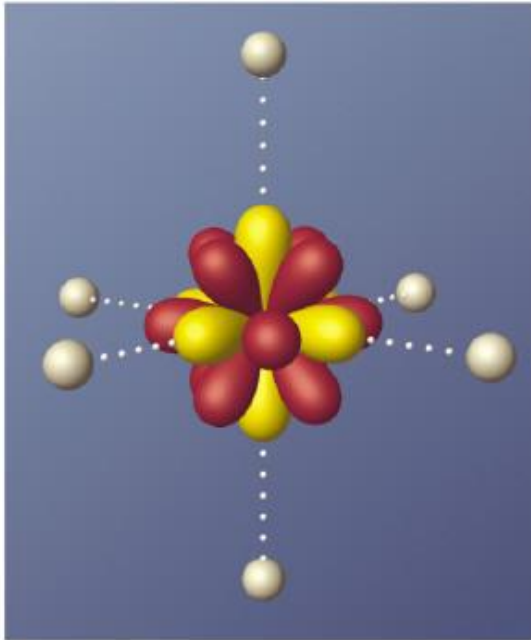
- *The ligands and the metal are considered as point charges*
- *The attraction between the metal and the ligands is purely electrostatic*
- *Properties of the metal complexes are explained based on changes happening to the **d orbitals of the metal only***

- Separated metal and ligands at high energy
- Electrostatic attraction between metal and ligands leading to stabilization (**heart of CFT**)
- Destabilization due to ligand electrons- metal d electrons repulsion in a **spherical** field
- Further splitting of the 5 d orbitals to 2 sets due to an **octahedral** field.

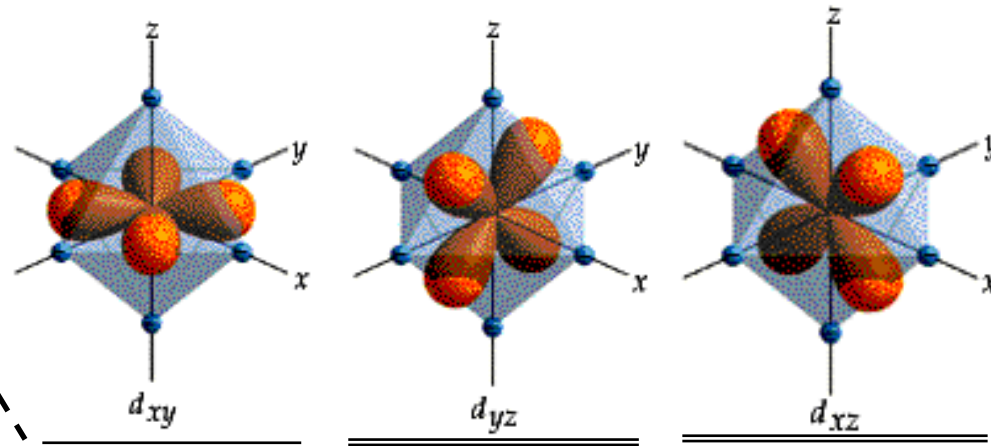


Orbitals affected when ligands approach a metal in an octahedral arrangement

Electrons in d_{z^2} and $d_{x^2-y^2}$ orbitals are concentrated close to the ligands, along the axes, resulting strong repulsions.

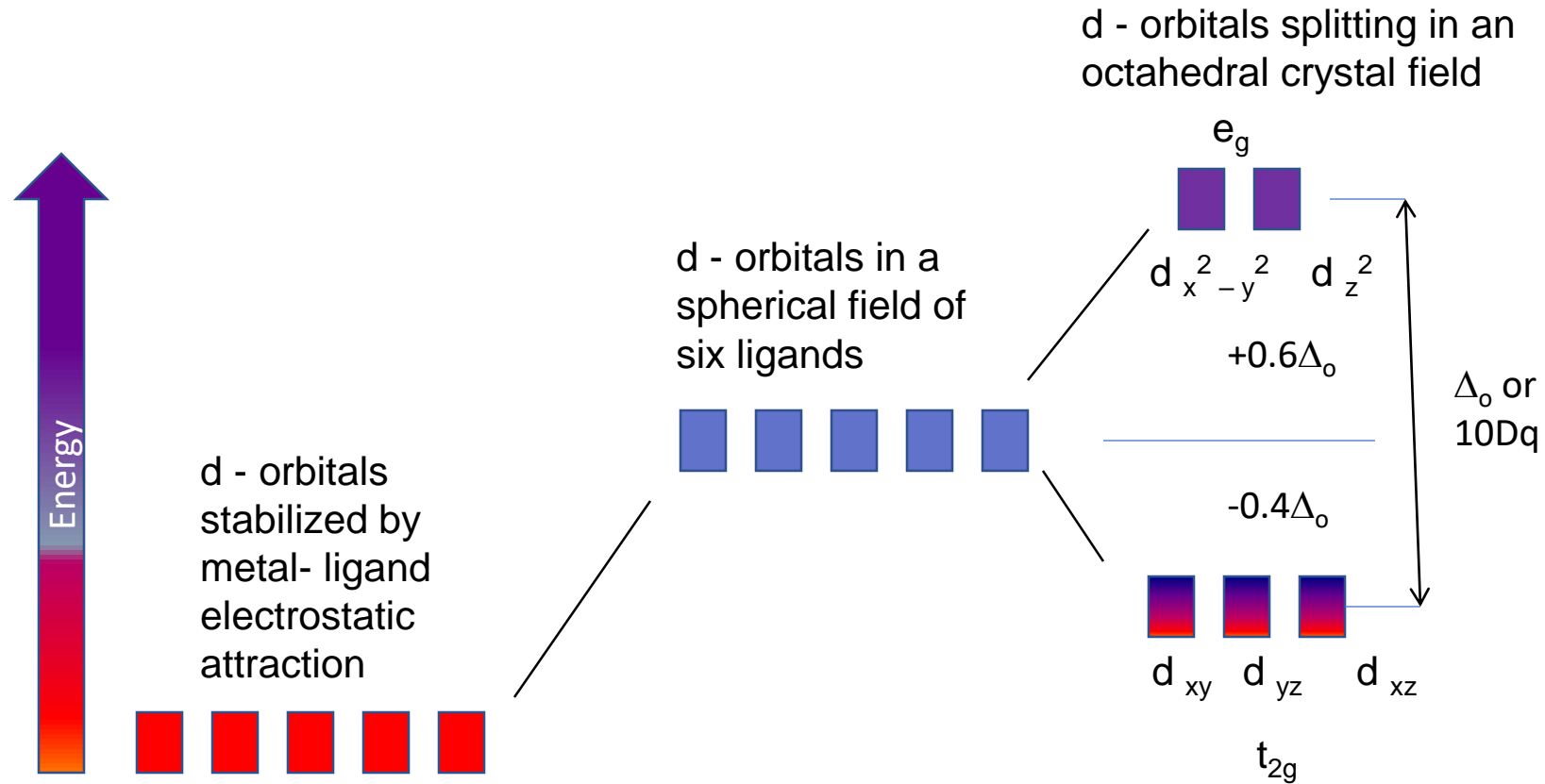


d-orbitals having lobes pointing directly at x, y and z axis are repelled most by electron-electron repulsion



d-orbitals not pointing directly at x, y and z axis are stabilized to maintain the overall energy same

Splitting of the d-orbitals in an octahedral field



t_{2g} : triply degenerate set of orbitals :

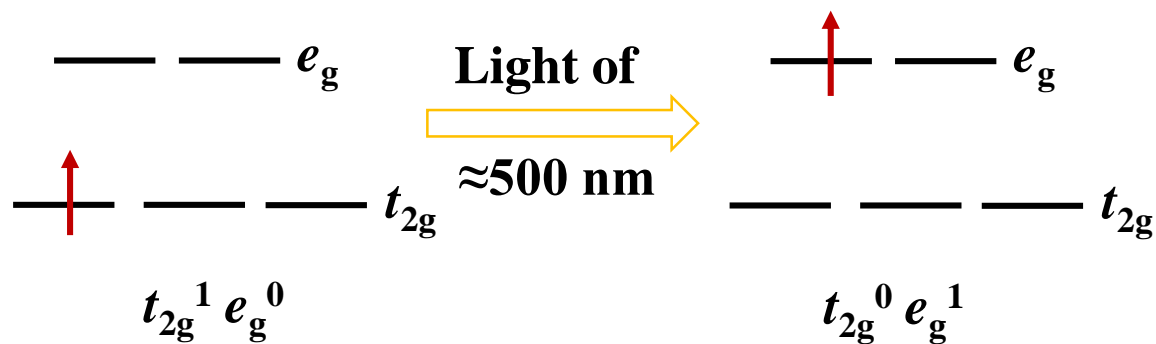
E_g : doubly degenerate set of orbitals

G = gerade: symmetric with respect to the centre of inversion

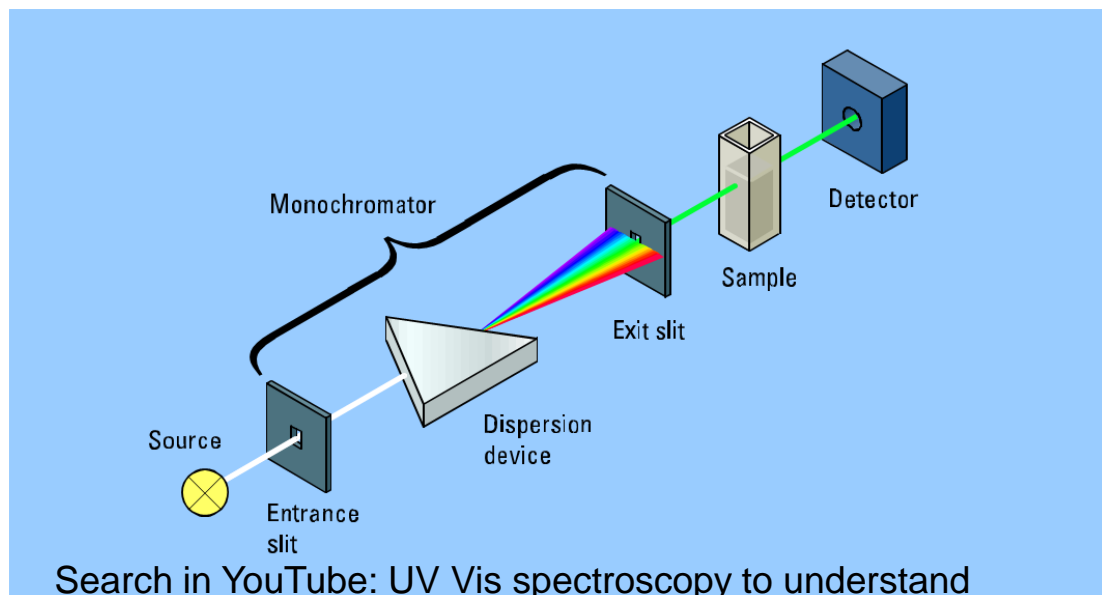
U = ungerade: antisymmetric w. r. t the centre of inversion

Barycenter: A point between objects where they balance each other

Δ_O is an experimental quantity and can be evaluated from electronic absorption spectroscopic data

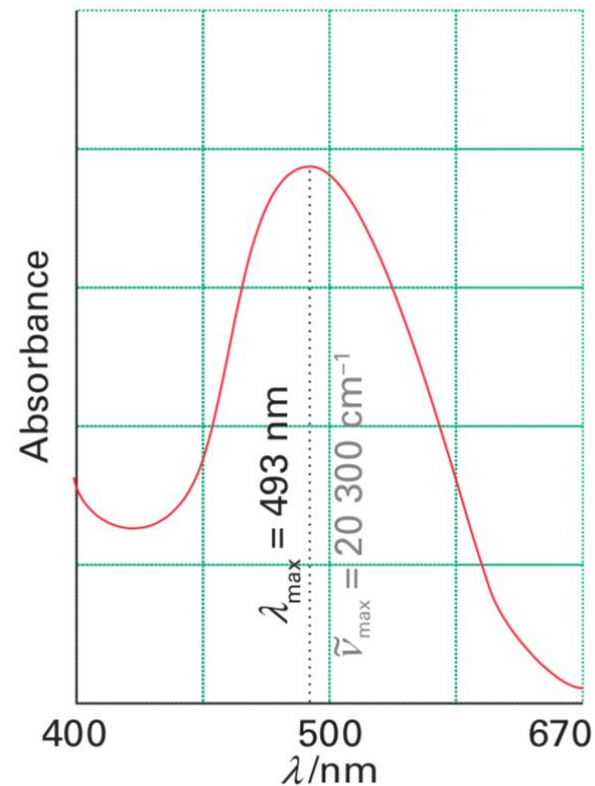


- Corresponding to an energy change of 243 kJ mol^{-1} corresponds to Δ_O ($1 \text{ cm}^{-1} = 11.96 \times 10^{-3} \text{ kJ/mole}$)



Search in YouTube: UV Vis spectroscopy to understand more about it.

The optical absorption spectrum of $[\text{Ti}(\text{OH}_2)_6]^{3+}$.

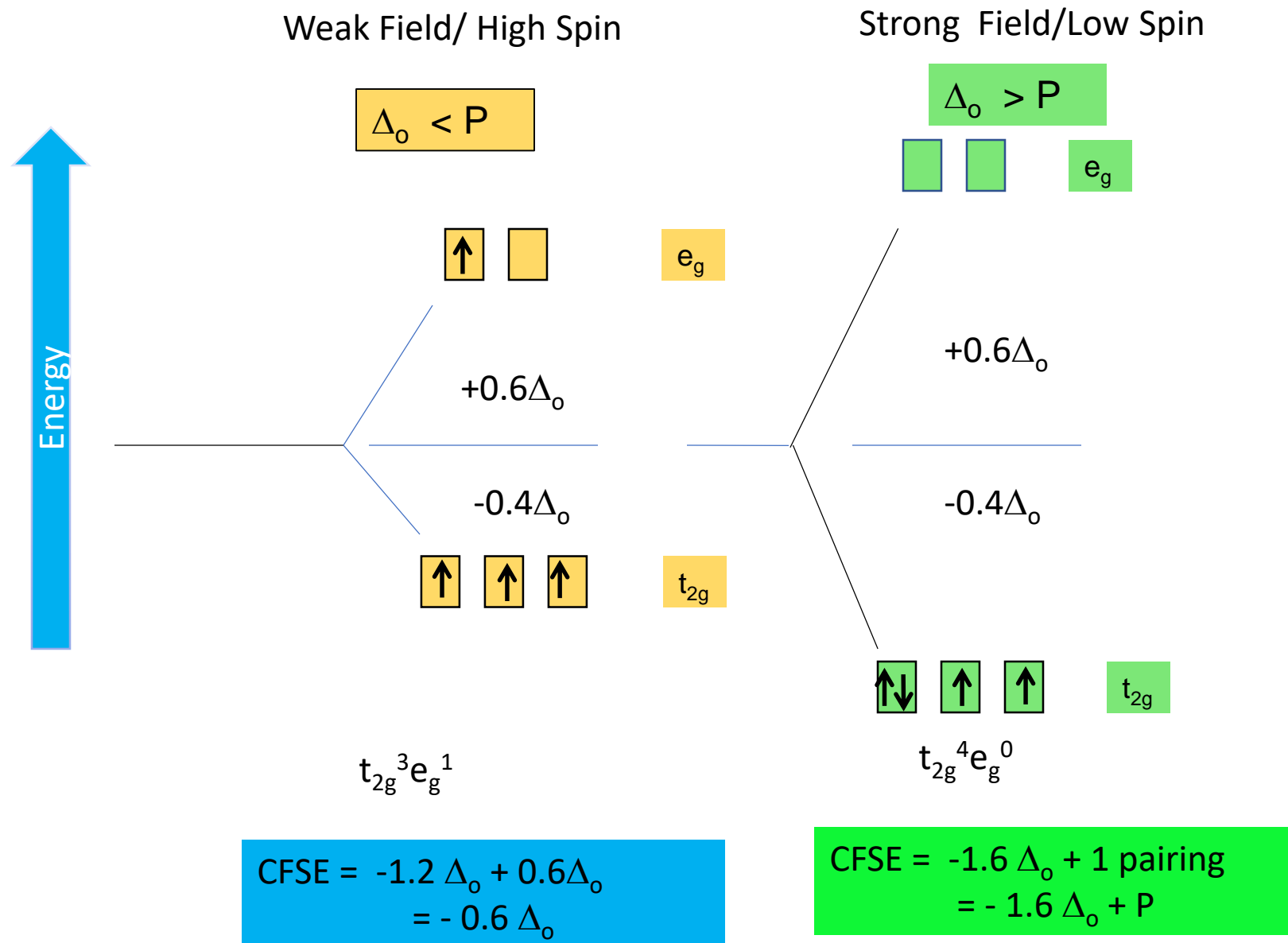


$$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \quad \Delta_O = 20,300 \text{ cm}^{-1} = 243 \text{ kJ/mol}$$

Since an electron in the t_{2g} set is stabilized by $-0.4 \Delta_O$
 $243 \times -0.4 = -97 \text{ KJ/mol}$

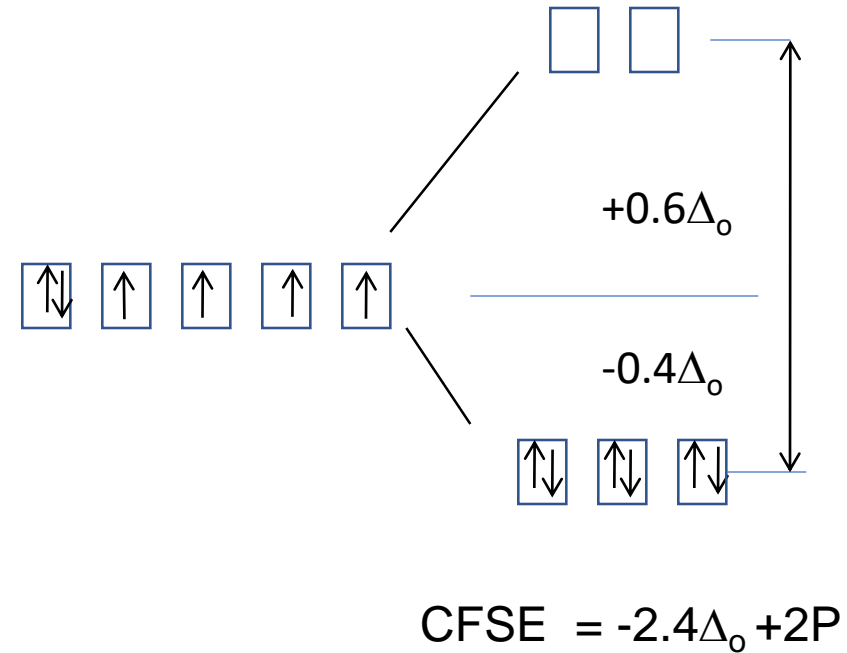
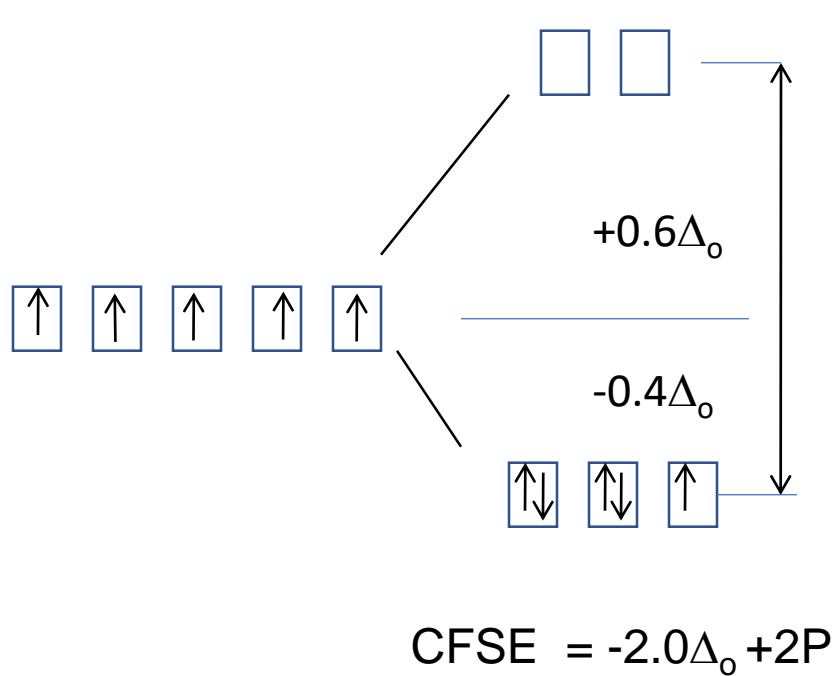
The complex is stabilized to the extent of 97 KJ/mol compared to a hypothetical spherical field due to the splitting of the d orbitals; This extra stabilization of the complex is called **crystal field stabilization energy (CFSE)**

Crystal Field Stabilization Energy : The d⁴ Case



The pairing energy is **not** an experimentally obtained value like Δ_o and is **same** for a metal ion irrespective of the ligands.

The d^5 and d^6 low spin cases and the correct way to determine pairing energy contribution

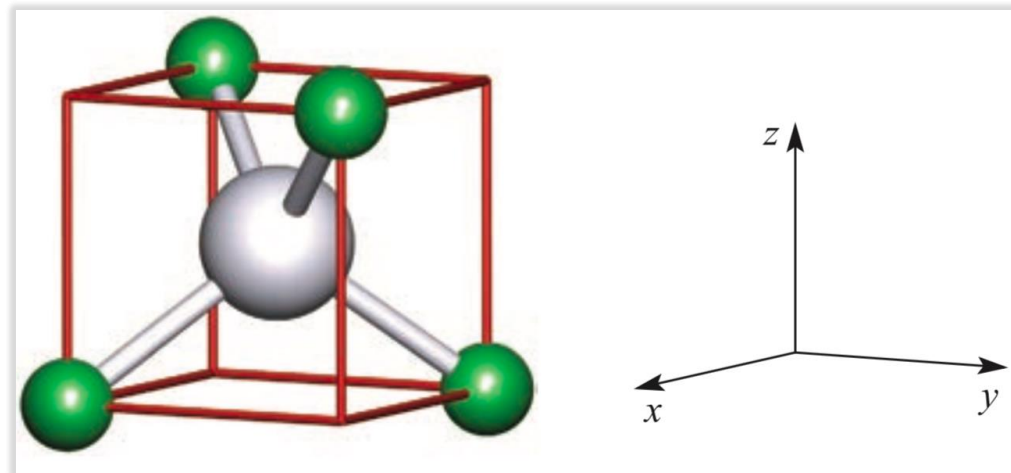


$$CFSE = -2.4\Delta_o + 3P$$

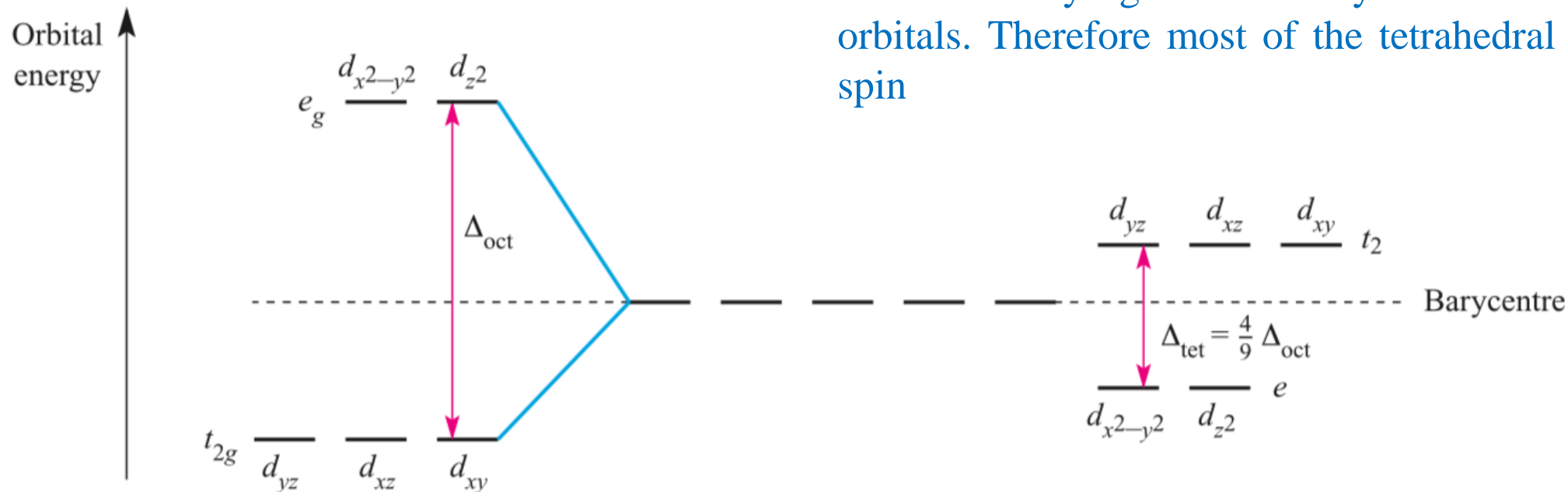


Always compare the extent of pairing with the situation before the splitting of five d orbitals occurred

Tetrahedral crystal field

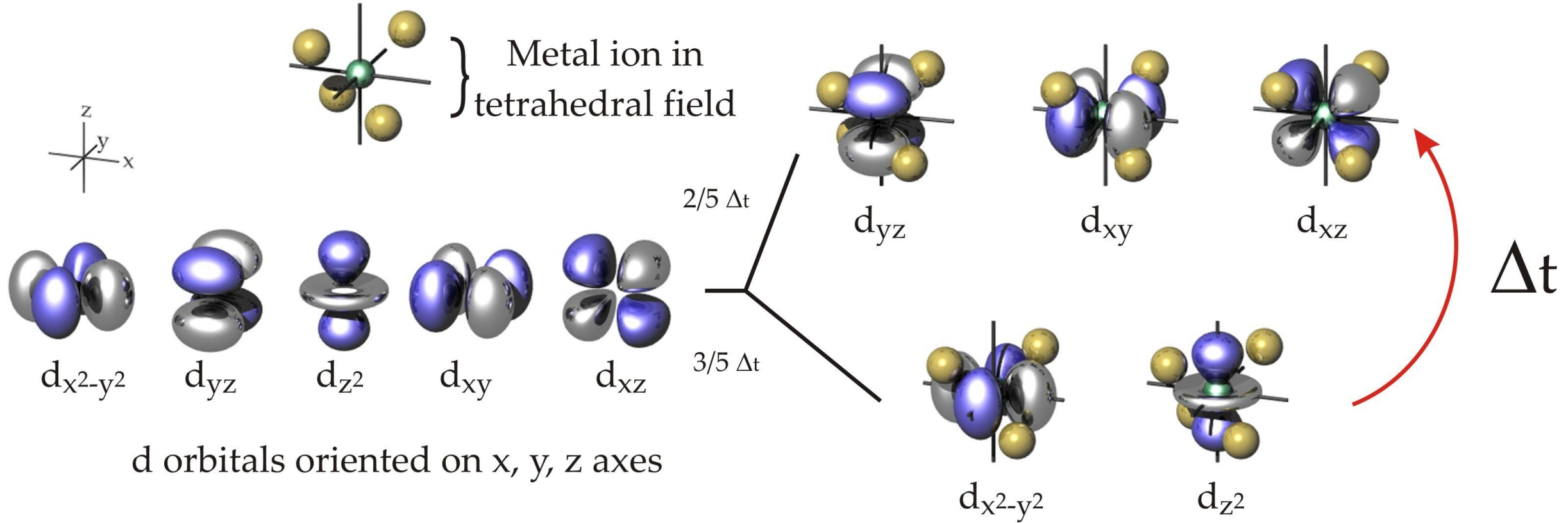


- In a tetrahedral complex, none of the metal d orbitals points exactly at the ligands, but the d_{xy} , d_{yz} and d_{xz} orbitals come nearer to doing so than the d_{z^2} and $d_{x^2-y^2}$ orbitals.
- The splitting of the d orbitals is therefore inverted compared with that for a regular octahedral structure, and the energy difference (Δ_t) is smaller.
- The crystal field splitting in a tetrahedral field is intrinsically smaller than that in octahedral field because there are only two-thirds as many ligands and they have less direct effect on the d orbitals. Therefore most of the tetrahedral complexes are high spin



$$\Delta_t = \frac{4}{9} \Delta_o \approx \frac{1}{2} \Delta_o$$

Position of the d-orbitals in tetrahedral crystal field



d Orbital Splitting in a Tetrahedral Field