UNIT 5 - PAPER 2

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UNIT 5 - PAPER 2
CFT THEORY

1. Weak Crystal Field
2. Strong Crystal Field
3. Correlation Diagram
4. J.T Theorem

UNIT - 5 | PAPER - 2

CRYSTAL FIELD THEORY (CFT)

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THEORIES FOR METAL - LIGAND BONDING IN COMPLEXES

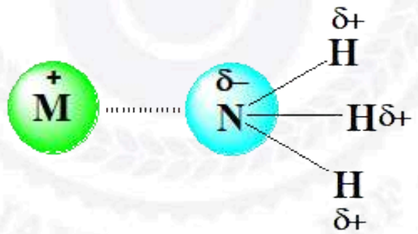
There are three theories to explain the nature of bonding in transition metal complexes

1. Valence Bond Theory (VBT)
2. Crystal Field Theory (CFT)
3. Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT)

CRYSTAL FIELD THEORY (CFT)

- Considers the bond between metal and ligand is ionic arising purely due to electrostatic interaction. Hence the theory is called as crystal field theory.
- If the ligand is anion then the metal has to be a cation and the force of attraction is due to opposite charges.

- If the ligand is neutral molecules like H_2O, NH_3 etc then the negative end of their dipoles are attached to the metal ion.



- Considers each ligands as point of negative charges.
- Metal – Ligand bond is not covalent i.e. there is no overlapping of orbitals.

The five d-orbitals in a free metal ion are degenerate i.e. same energy. When a complex is formed, the electrostatic field of the ligands destroy the degeneracy of these orbitals i.e. these orbitals now have different energies.

d-orbital degenerate

SHAPES OF D-ORBITALS

- In fact there are six d-orbitals with each having four lobes. These orbitals are d_{xy}, d_{yz}, d_{xz} (Non-axial d-orbitals i.e. lie in between axis) and $d_{x^2-y^2}$, $d_{z^2-x^2}$, $d_{z^2-y^2}$ (Axial d-orbitals i.e. lie along the axis).

- But there are only five independent d-orbitals d_{xy}, d_{yz}, d_{xz} (Non-axial d-orbitals) and $d_{x^2-y^2}$, d_{z^2} (Axial d-orbitals).

- The d_{z^2} is regarded as the linear combination of the $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals.

SHAPES OF D-ORBITALS

- d- orbitals are present in the d-subshell for which
  $n = 3, l = 2$ and $m_l = -2, -1, 0, +1, +2$

- There are five orientations leads to five different orbitals
  $m_l = (2l + 1) = (2 \times 2 + 1) = 5$

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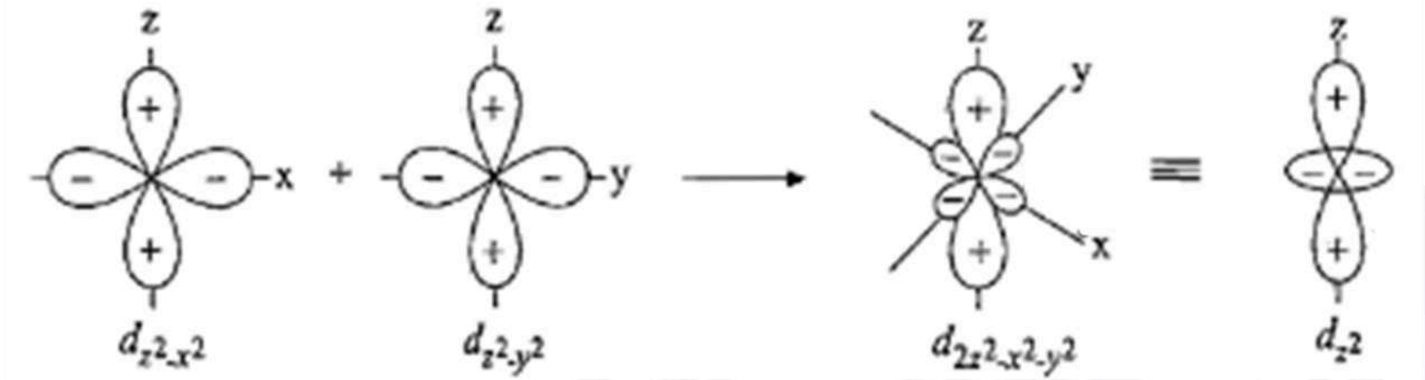

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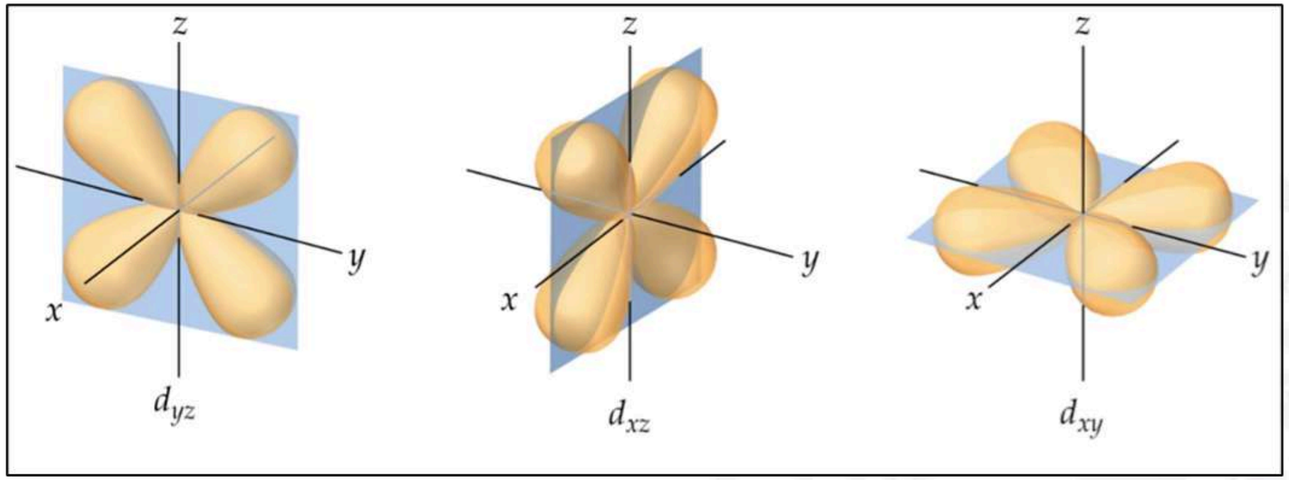
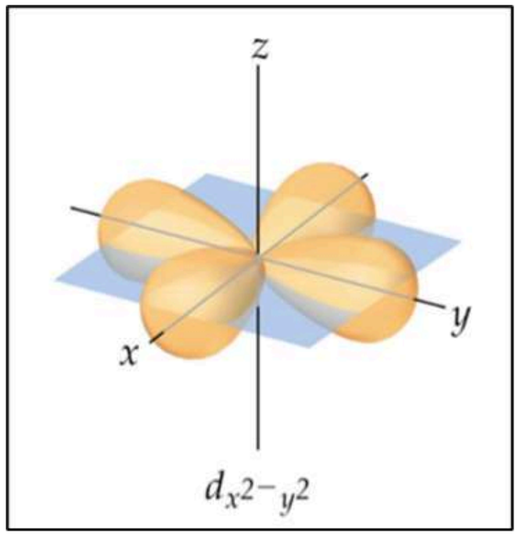


Non-axial d-orbitals

Lobes = 4

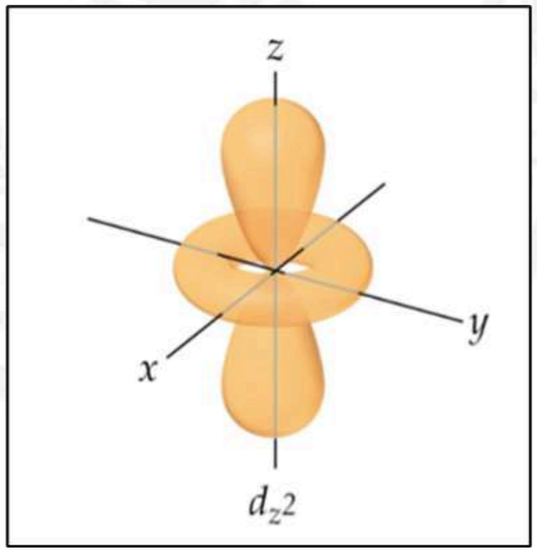
Gerade (i)



Axial d-orbitals

Lobes = 4

Gerade (i)



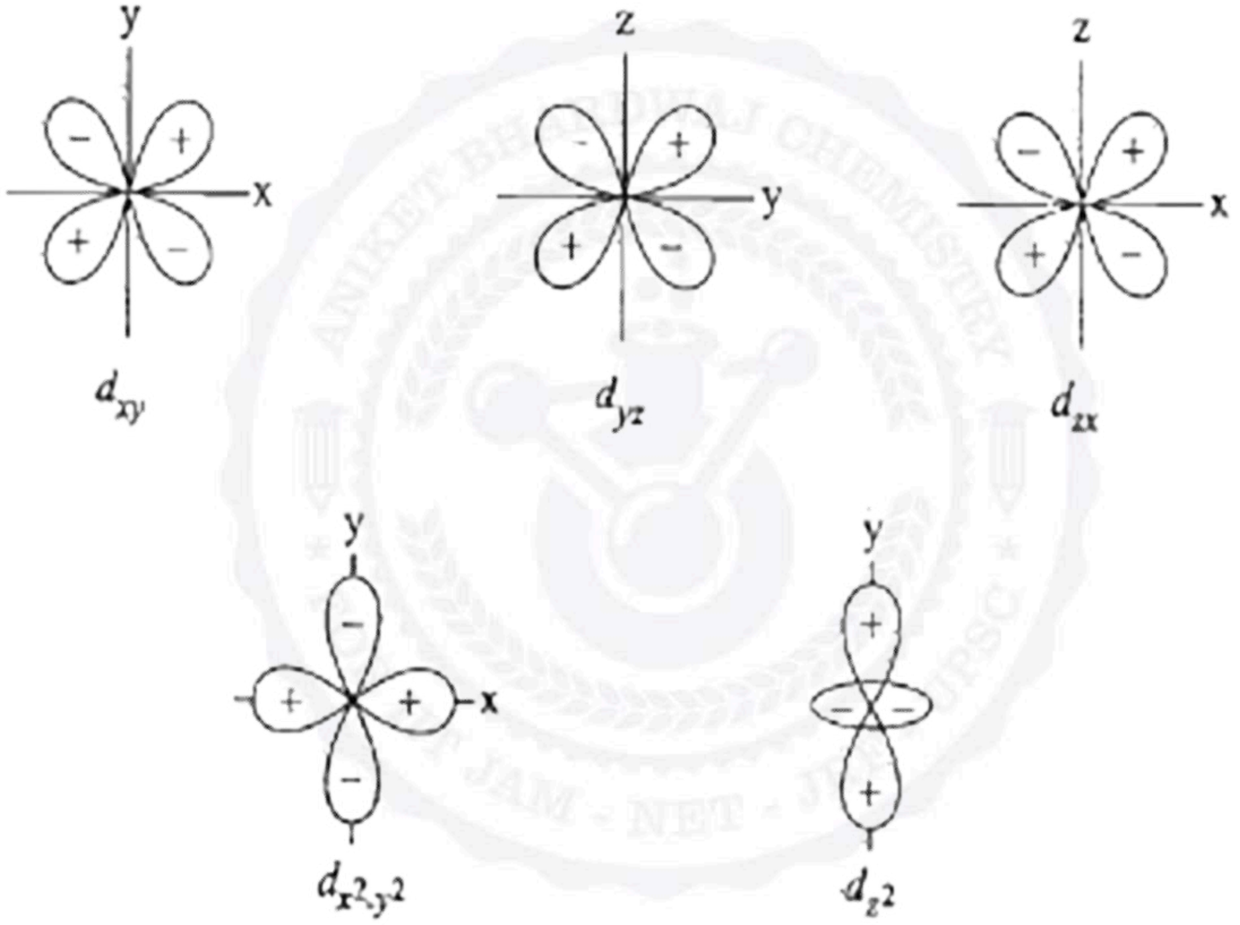
Axial d-orbitals

$d_{z^2} = d_{z^2-x^2} + d_{z^2-y^2}$

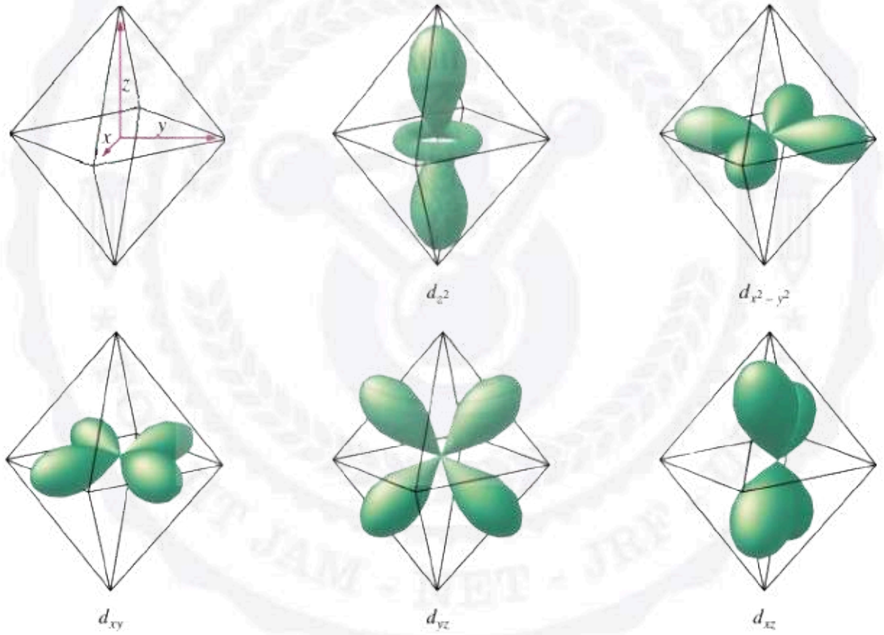
Lobes = 8

Gerade (i)

All the five d-orbitals are gerade because the opposite lobes have inversion centre (centre of inversion) with respect to phase of wave functions.



d_{xy}: lobes lie in-between the x and the y axes.
d_{xz}: lobes lie in-between the x and the z axes.
d_{yz}: lobes lie in-between the y and the z axes.
$d_{x\,2\,-y\,2}$: lobes lie on the x and y axes.
d_{z2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes



- d-orbitals lying in the direction of the ligands are raised in energy more than those lying away from the ligands because of the repulsion between the d-electrons and the ligands.

CRYSTAL FIELD SPLITTING D-ORBITALS IN OCTAHEDRAL COMPLEX

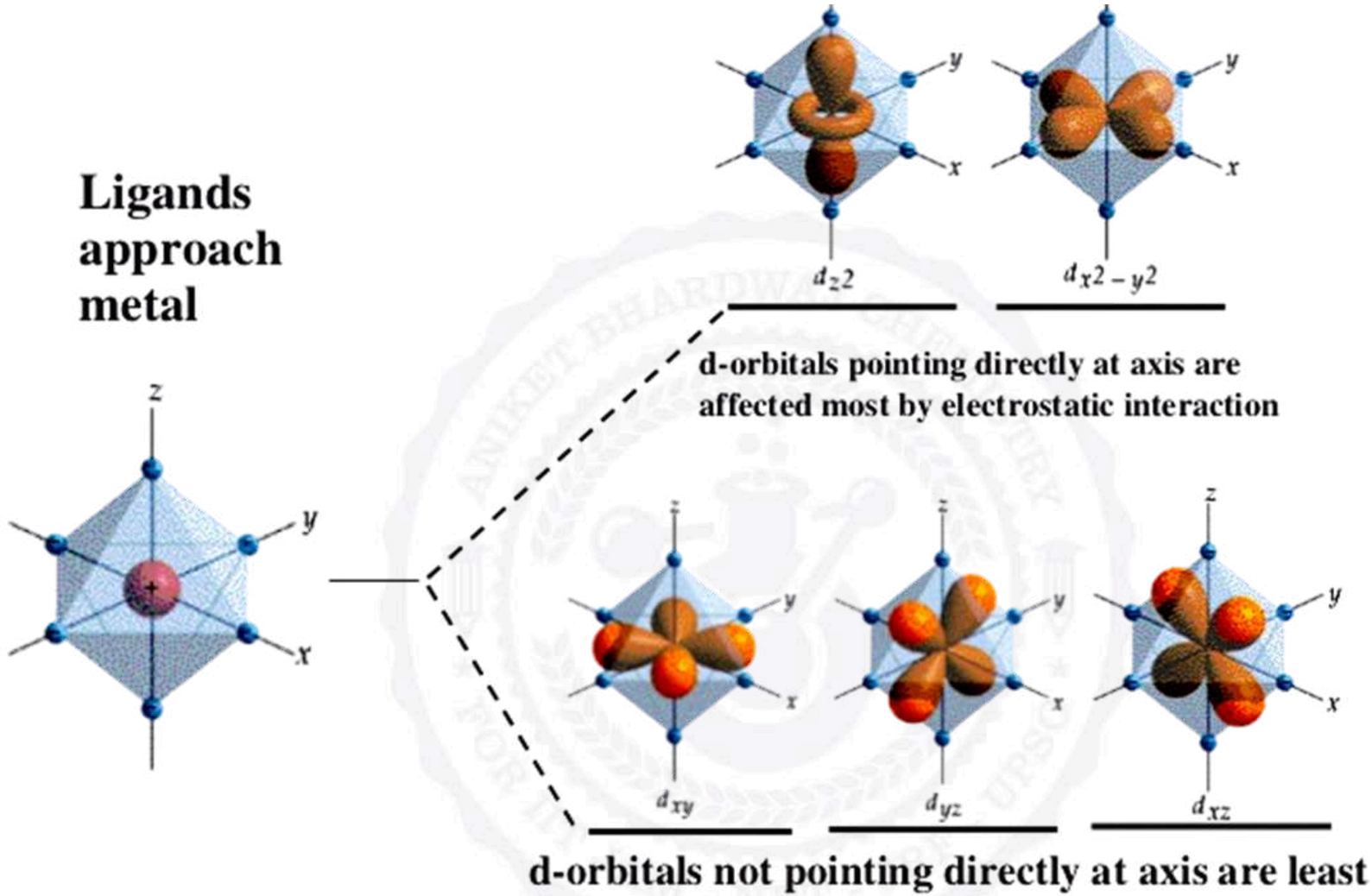
- In octahedral complexes, the ligands approach along the axes.

- The d-orbitals where electron density is oriented along the axes, $d_{x^2-y^2}$, d_{z^2} are repelled much more by the ligands while the orbitals d_{xy}, d_{yz}, d_{xz} having electron density oriented in between the axes are repelled lesser by the ligands.

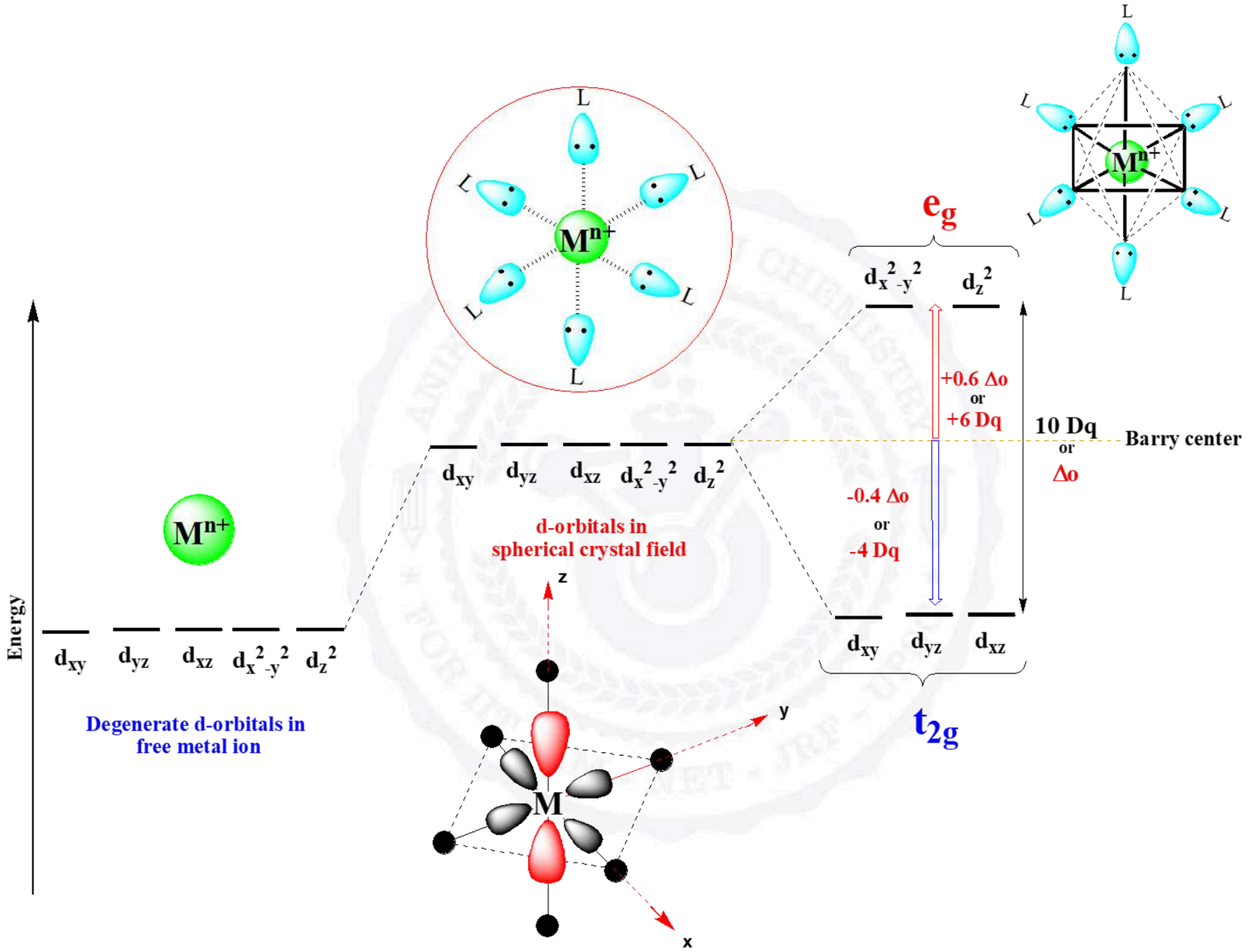
- Two sets of orbitals e_g (doubly degenerate set) and t_{2g} (triply degenerate) are formed due the repulsion between metals and ligands orbitals.

- The energy gap between e_g and t_{2g} is called crystal field splitting energy and it is denoted by Δo or Δoct or 10Dq,
  where Δ represent Crystal field splitting energy,
  "o" in Δo is for octahedral.

E_g / e_g and T_{2g} / t_{2g} = Mulliken symbol



➢ **Because the overall energy is maintained, the energy of the three t_{2g} orbitals are lowered or stabilised by 0.4 Δo and the energy of the two e_g orbitals are raised or repelled by 0.6Δo with respect to hypothetical the spherical crystal field or Bary Centre.**



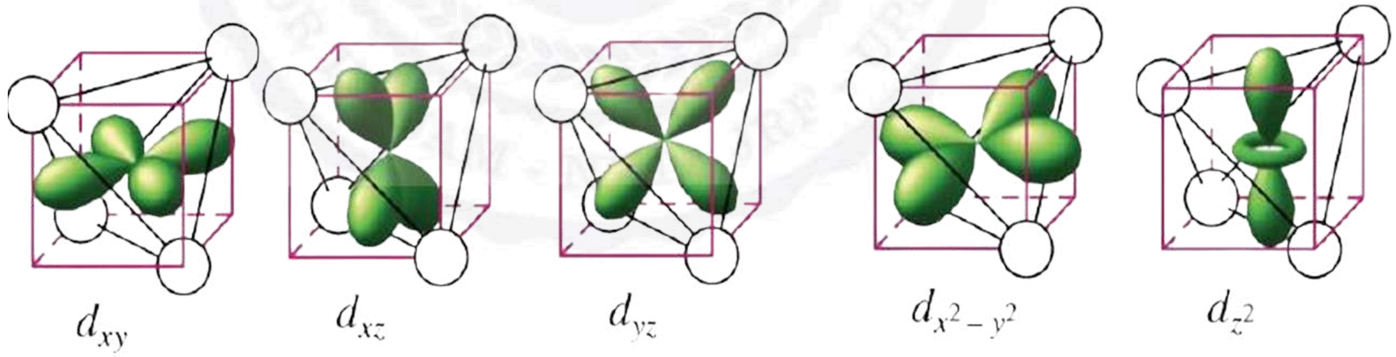
CRYSTAL FIELD SPLITTING D-ORBITALS IN OCTAHEDRAL COMPLEX

- In a tetrahedral complex, there are four ligands attached to the central metal.

- These ligands do not point directly to any of the d-orbitals of the metal but more closer to t_2 set of orbitals (d_{xy}, d_{yz}, d_{zx}) than e orbitals ($d_{x^2-y^2}$, d_{z^2}) and therefore, t_2 set of orbitals get repelled more than e orbitals.

- The g subscript is not used with t_2 and e sets because the tetrahedral complexes have no inversion center.

- It can simply be stated that the d-orbital splitting diagram in tetrahedral complexes is just inverse of octahedral complexes.



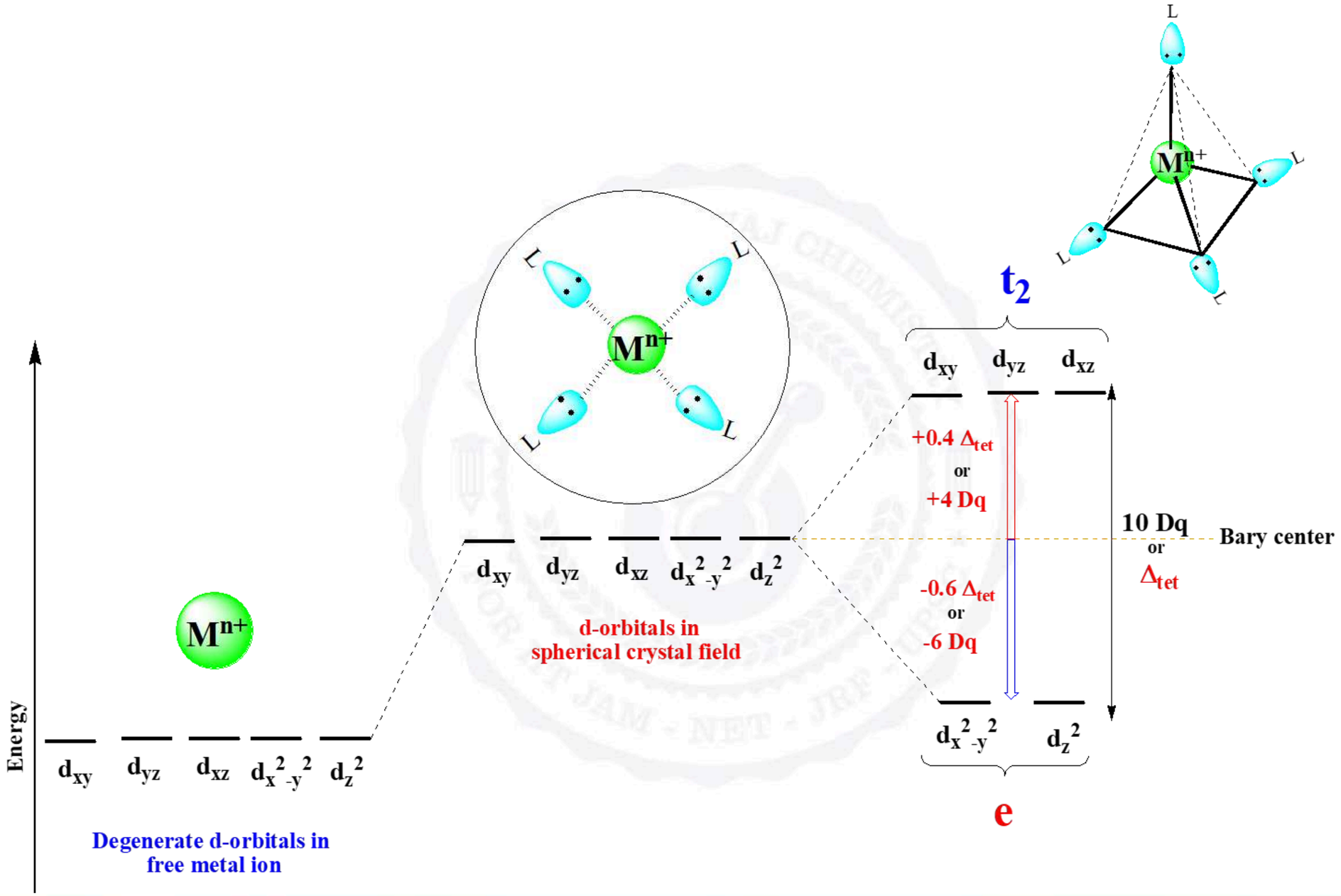
Tetrahedral (T_d) lacks a center of inversion

CRYSTAL FIELD SPLITTING D-ORBITALS IN OCTAHEDRAL COMPLEX

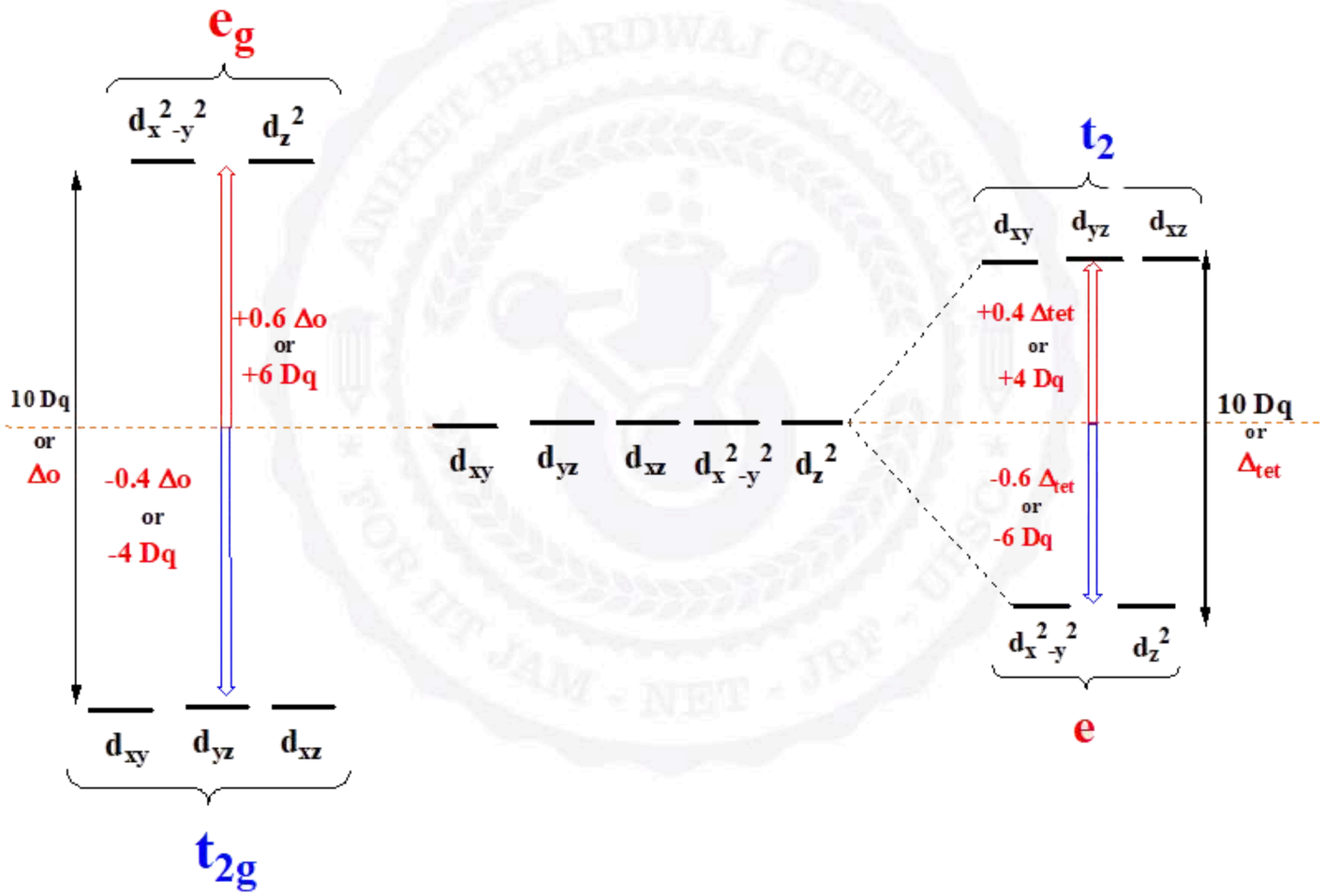
- Because the overall energy is maintained, the energy of the two e orbitals are lowered or stabilised by 0.6 Δt and the energy of the three t_2 orbitals are raised or repelled by 0.4 Δt with respect to hypothetical the spherical crystal field or Bary Centre.

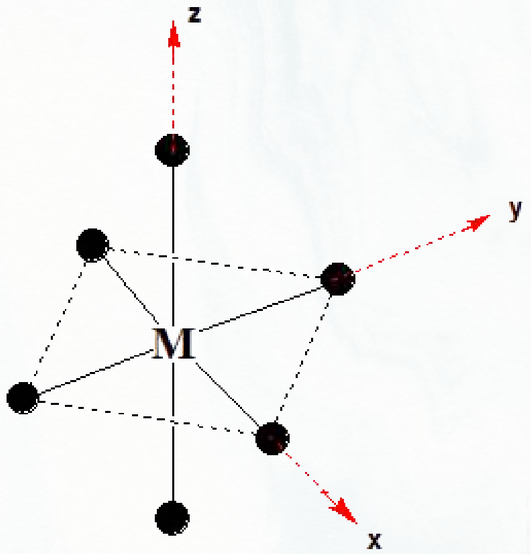
- The energy gap between t_2 and e is called crystal field splitting energy and it is denoted by Δt or Δtet or 10Dq,

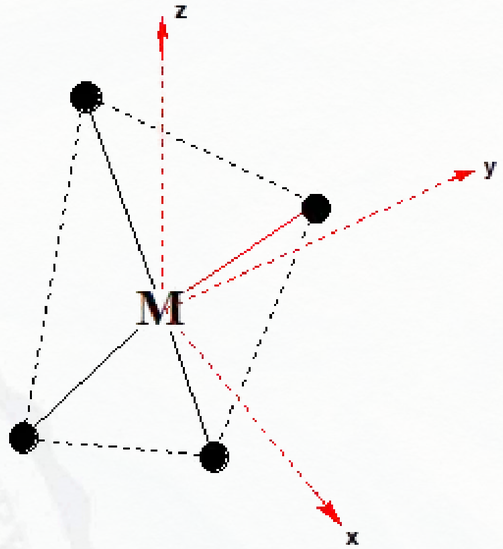
  where Δ represent Crystal field splitting energy,
  "t" in Δt is for tetrahedral.



COMPARISON OF CRYSTAL FIELD SPLITTING OF D-ORBITALS IN OCTAHEDRAL AND TETRAHEDRAL COMPLEX







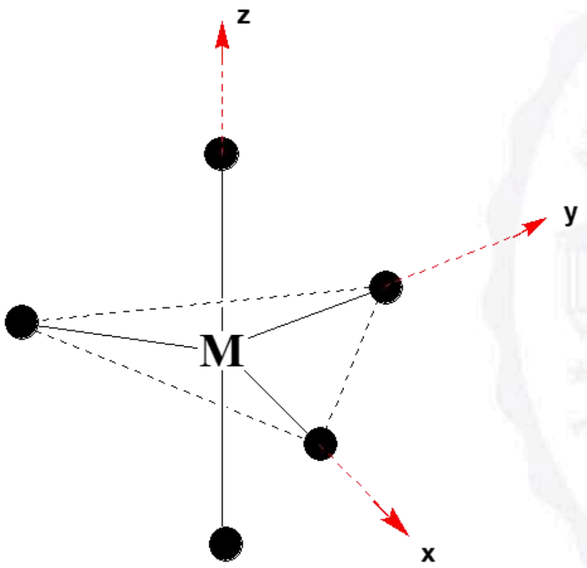
- The splitting of energy levels in a tetrahedral field is less compare to an octahedral field of ligands due to the poor orbital overlap between the metal and the ligand orbitals.

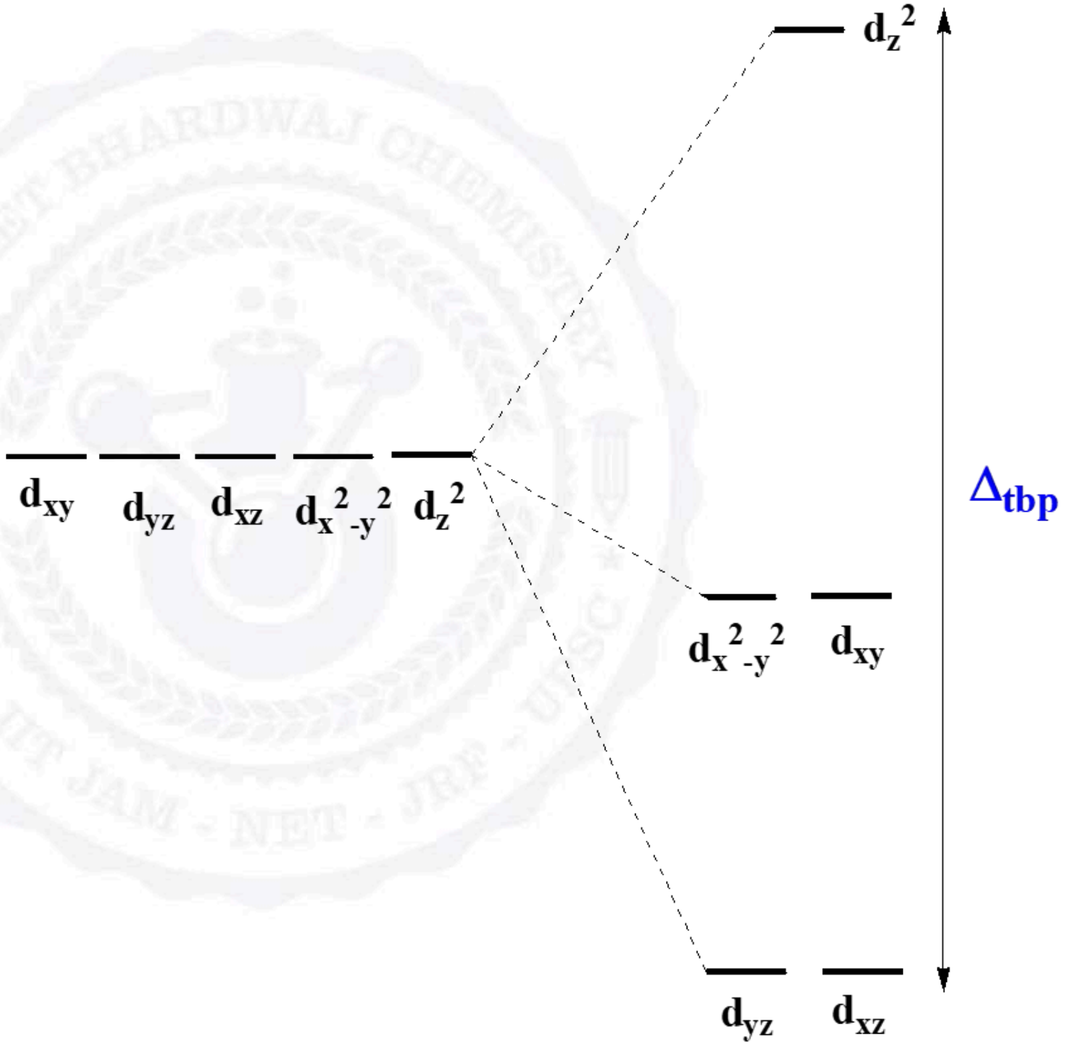
- For most purposes the relationship may be represented as $\Delta t = 4/9\ \Delta o$ because
  (i) The number of ligands in Td are 2/3 compared to octahedral complex.
  (ii) The ligands in Td complex repel t_2 orbitals 2/3 times less than the octahedral complex.

Therefore,

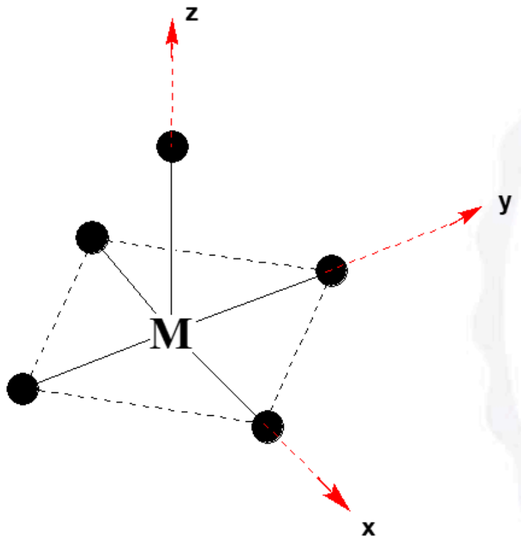
$$\Delta t = 2/3 \times 2/3 \times \Delta o$$
$$= 4/9\ \Delta o$$

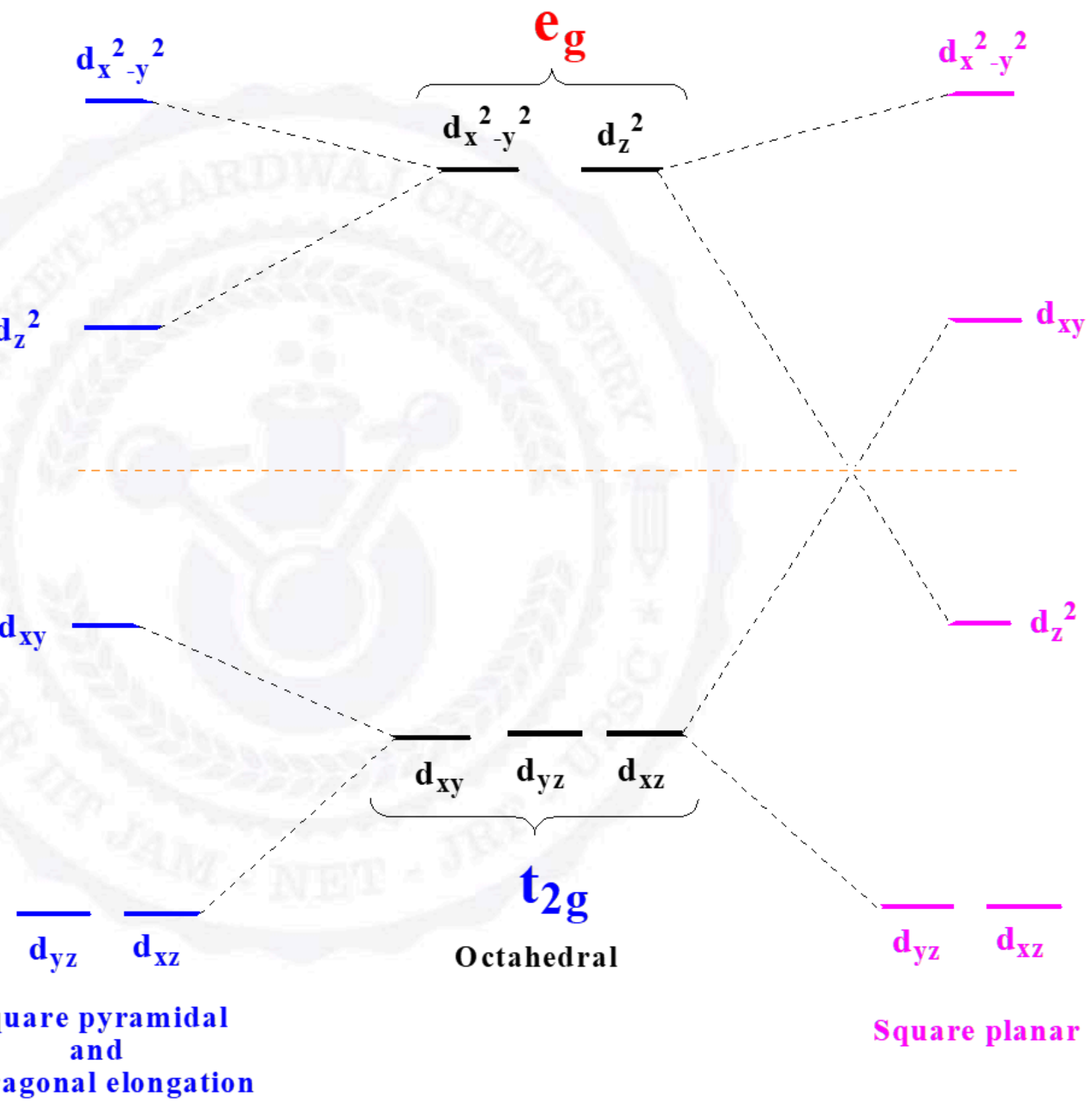
CRYSTAL FIELD SPLITTING OF D-ORBITALS IN TRIGONAL BIPYRAMIDAL COMPLEX





CRYSTAL FIELD SPLITTING OF D-ORBITALS IN SQUARE PYRAMIDAL COMPLEX





CRYSTAL FIELD SPLITTING OF D-ORBITALS IN SQUARE PLANAR COMPLEX

- The removal of a pair of ligands from the z-axis of an octahedron leaves four ligands in the x-y plane.

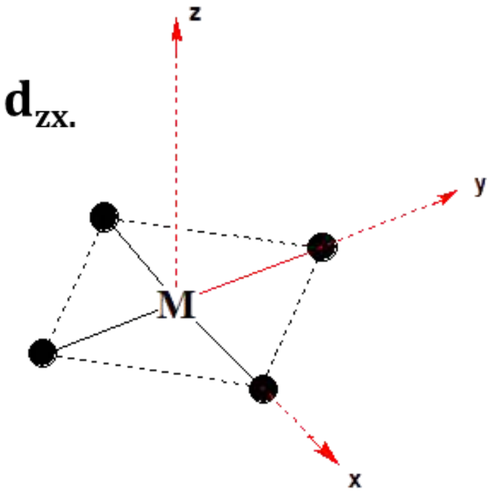
- Therefore, the crystal field splitting diagram for square planar geometry can be derived from the octahedral diagram.

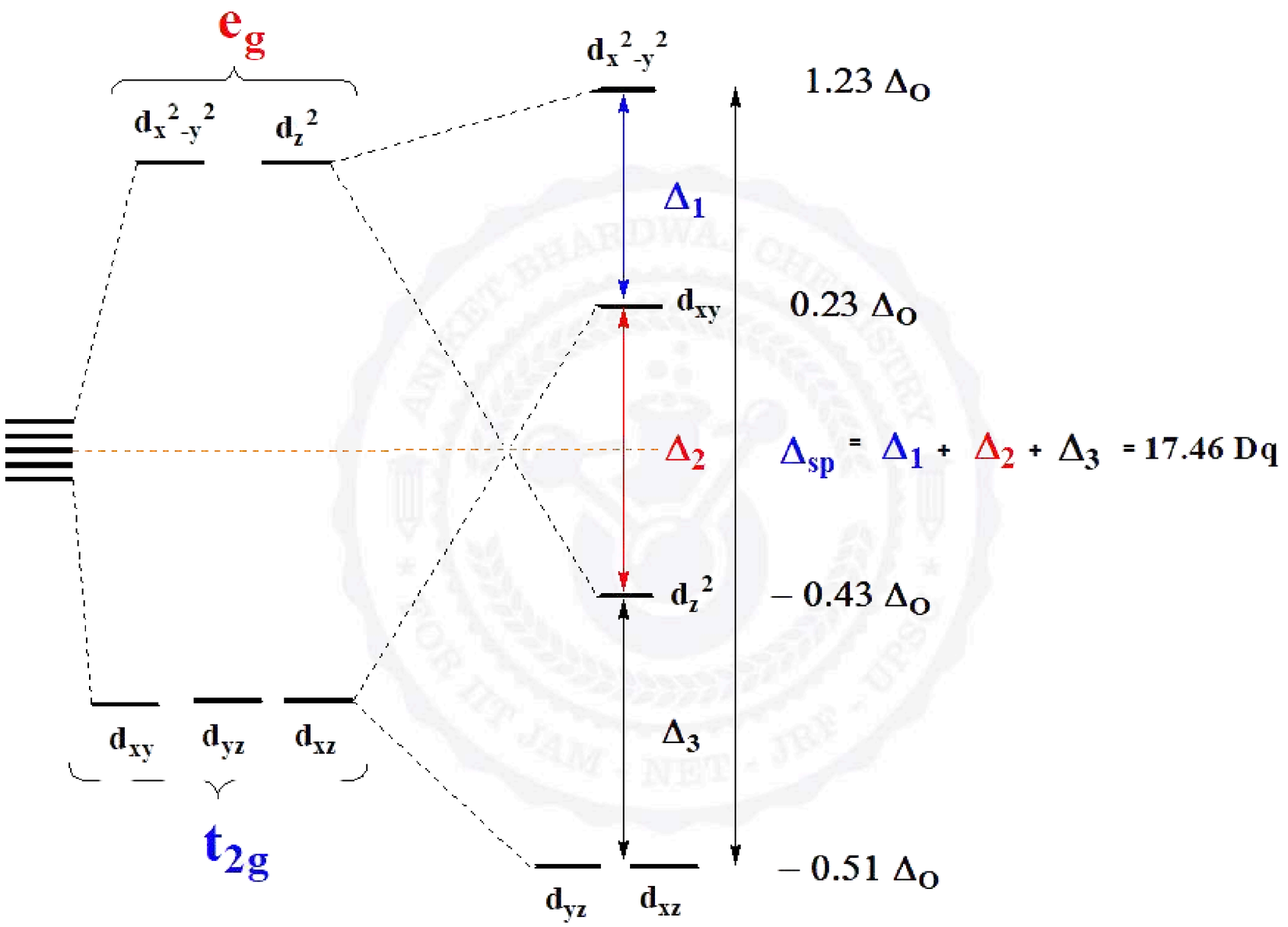
- The removal of the two ligands stabilizes the d_{z^2} level, leaving the $d_{x^2-y^2}$ level as the most destabilized.

- d_{xy} orbital is closer to ligands hence its energy also increases than the d_{yz}, d_{zx}.

- The spectroscopic results showed that

$$\Delta_{sp} = 1.74 \times \Delta_o \quad (\text{i.e. } \Delta_{sp} > \Delta_o)$$





MAGNITUDE OF CFSE (Δ) WILL DEPEND ON :

Number of factors that affect the extent to which metal d-orbitals are split by ligands. The most important factors are listed below

Metal factors

(1) Oxidation state

(2) Number of d-electrons

(3) Nature of metal ion

(4) Spin pairing energy

Ligand factors

(1) Ligand character

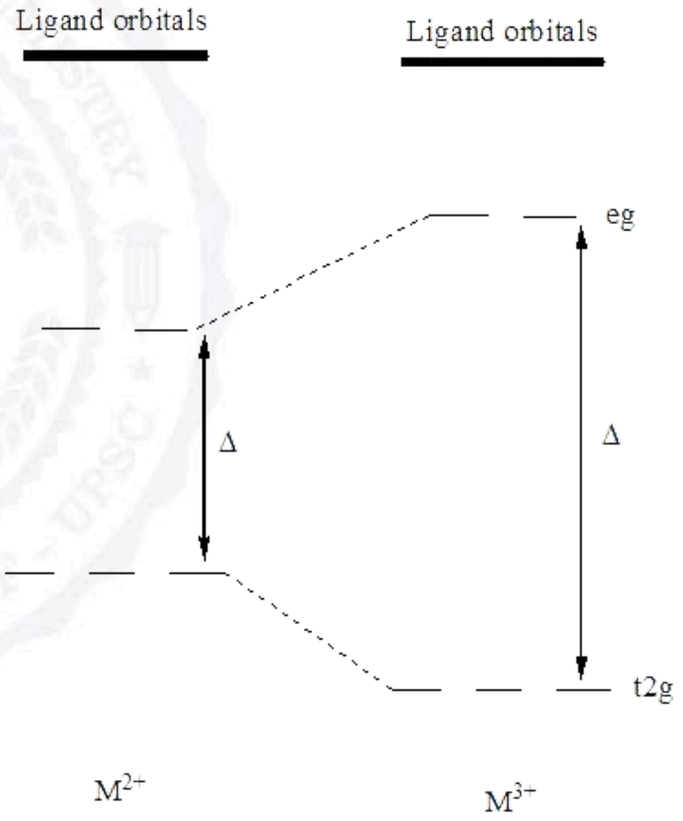
(2) Number and Geometry of the Ligands

1. OXIDATION STATE

Higher the oxidation state of metal ion causes the ligands to approach more closely to it and therefore, the ligands causes more splitting of metal d-orbitals.

$[Co(H_2O)_6]^{2+}$ $\Delta o = 9200\ cm^{-1}$

$[Co(H_2O)_6]^{3+}$ $\Delta o = 20760\ cm^{-1}$



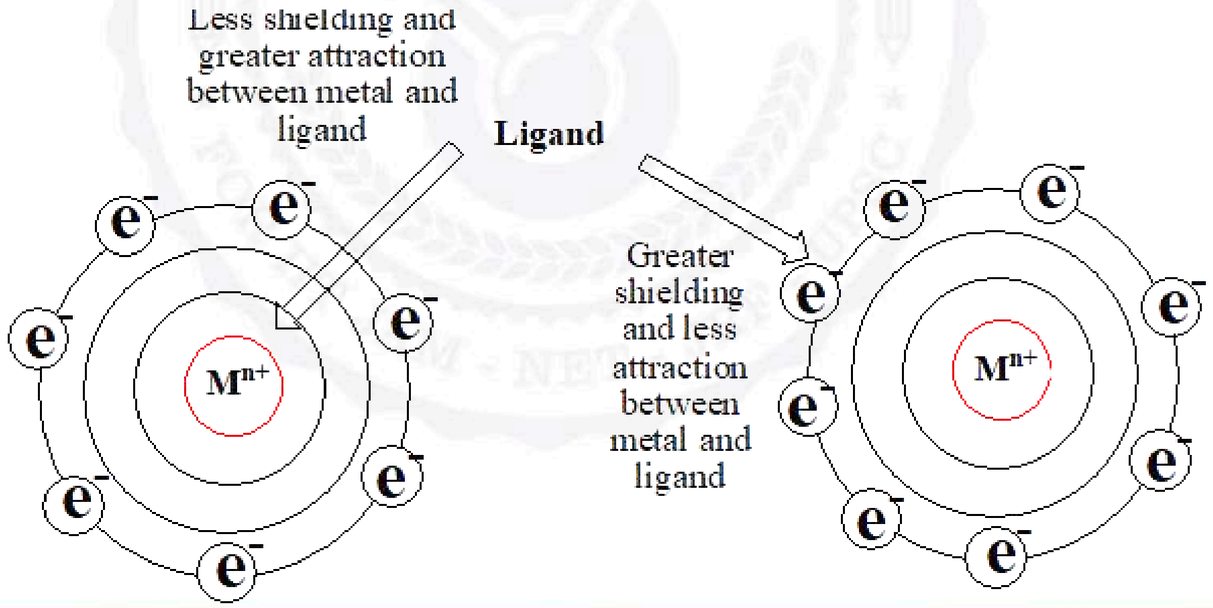
2. NUMBER OF D-ELECTRONS

For a given series of transition metal, complexes having metal cation with same oxidation state but with different number of electrons in d-orbitals, the magnitude of Δ decreases with increase in number of d-electrons.

$$\Delta \ \alpha \ \frac{1}{\text{Number of d-electrons}}$$

$[Co(H_2O)_6]^{2+}$ $\Delta o = 9200\ cm^{-1}\ (3d^7)$

$[Ni(H_2O)_6]^{2+}$ $\Delta o = 8500\ cm^{-1}\ (3d^8)$



3. NATURE OF METAL ION

In complexes having the metal cation with same oxidation state, same number of d-electrons and the magnitude Δ for analogues complexes within a given group increases about 30% to 50% from 3d to 4d and same amount from 4d to 5d.

(i) On moving 3d to 4d and 4d to 5d, the size of d-orbitalsincreases and electron density decreases therefore, ligands can approach metal with larger d-orbital more closely.

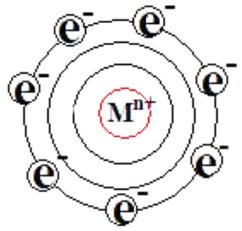
(ii) There is less steric hindrance around metal.

$[Co(NH_3)_6]^{3+}$ $\Delta o = 2300\ cm^{-1}$

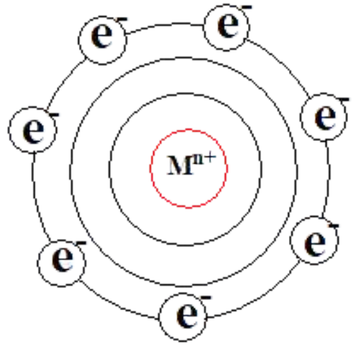
$[Rh(NH_3)_6]^{3+}$ $\Delta o = 34100\ cm^{-1}$

$[Ir(NH_3)_6]^{3+}$ $\Delta o = 41200\ cm^{-1}$

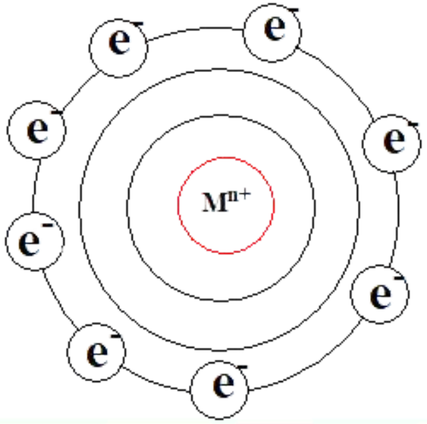
3d



4d



5d



4. SPIN PAIRING ENERGY

Metal ion with higher pairing energy will have lower Δ, whereas metal ion with lower pairing energy will have higher Δ.

Metal factor summary affecting magnitude of CFSE (Δ)

(1) $\Delta \alpha$ Oxidation state of Metal ion

(2) $\Delta \alpha \frac{1}{\text{Number of d-electrons}}$

(3) $\Delta \alpha$ Principal quantum number (n)

(4) $\Delta \alpha \frac{\text{Low Pairing energy}}{\text{High Pairing energy}}$

SPIN PAIRING ENERGY (P)

Energy required to put two electrons in the same orbital

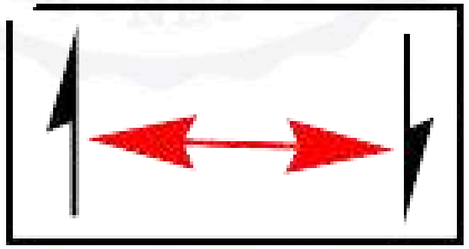
The electron pairing energy has two terms

1. Coulombic repulsion
2. Loss of exchange energy on pairing

1. **Coulombic repulsion** is caused by repulsion of electrons and it decreases down the group.

$$3d > 4d > 5d$$

Coulombic repulsion contribute to the destabilizing energy



SPIN PAIRING ENERGY (P)

(2) Loss of exchange energy on pairing contributes to the stabilizing energy associated with two electrons having parallel spin.

Mathematically, exchange energy can be calculated using the following equation

$$E_{exchange} = \frac{n(n-1)}{2}$$

n = number of pairs of parallel spin electrons

How to calculate the loss of exchange energy for metal ion.

For example, consider Fe^{2+} (d^6) and Mn^{2+} (d^5) in this case Fe prefers low spin whereas Mn prefer high spin and this is explained by considering the loss of exchange energy.

Fe^{2+} (d^6)

Degenerate

High spin

$$E_{exchange} = \frac{n(n-1)}{2}$$

$$= \frac{5(5-1)}{2}$$

$$= 10$$

Low spin

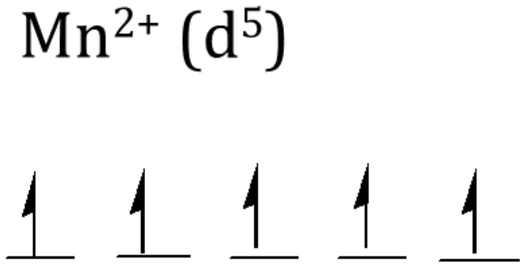
$$E_{exchange} = \frac{n(n-1)}{2}$$

$$= \left(\frac{3(3-1)}{2}\right) \times 2$$

$$= 6$$

Loss of exchange energy = 10 - 6 = 4

Mn^{2+} (d^5)



Degenerate

High spin

$$E_{exchange} = \frac{n(n-1)}{2}$$

$$= \frac{5(5-1)}{2}$$

$$= 10$$

Low spin

$$E_{exchange} = \frac{n(n-1)}{2}$$

$$= \left(\frac{3(3-1)}{2}\right) + \left(\frac{2(2-1)}{2}\right)$$

$$= 3 + 1 = 4$$

Loss of exchange energy = 10 - 4 = 6

From the above calculation reveals that Mn^{2+} (d^5) has greater loss of exchange energy hence it has higher pairing energy therefore it prefers high spin instead of low spin.

1. LIGAND CHARACTER

The ligands are classified as weak and strong field ligands.

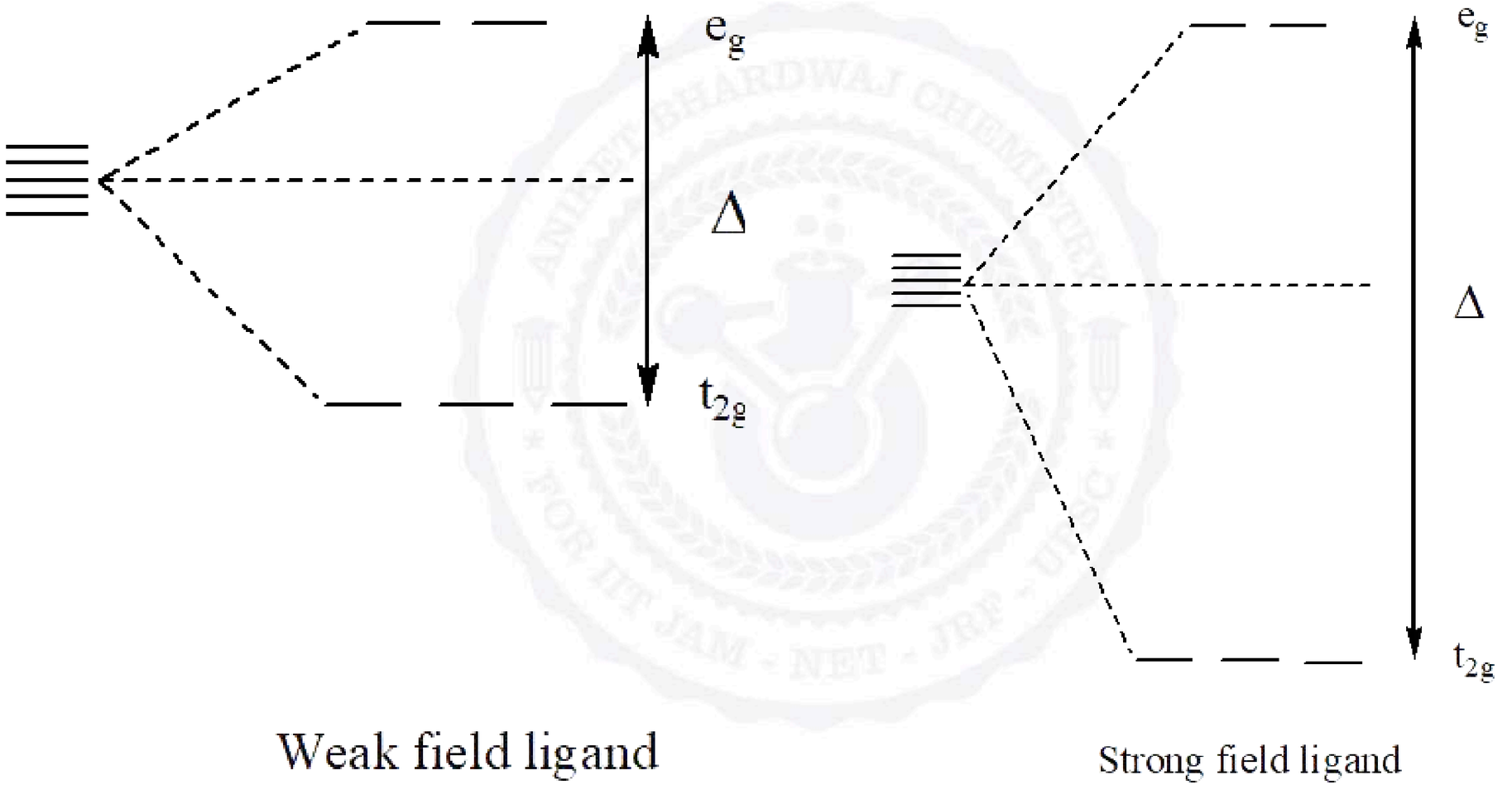
Ligand which cause a small degree of splitting of d-orbital are called weak field ligands.

Ligand which cause large splitting of d-orbital are called strong field ligands.

The common ligands have been arranged in order of their increasing crystal field splitting power to cause splitting of d-orbitals from study of their effects on spectra of transition metal ions. This order usually called as Spectrochemical series.

$I^- < Br^- < SCN^- < Cl^- < N_3^- < F^- <$ Urea, $OH^- <$ Ox, $O^{2-} < H_2O <$ $NCS^- <$ Py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO$

X = Weak field
O = Middle
N = Strong
C = Very strong



Weak field ligand

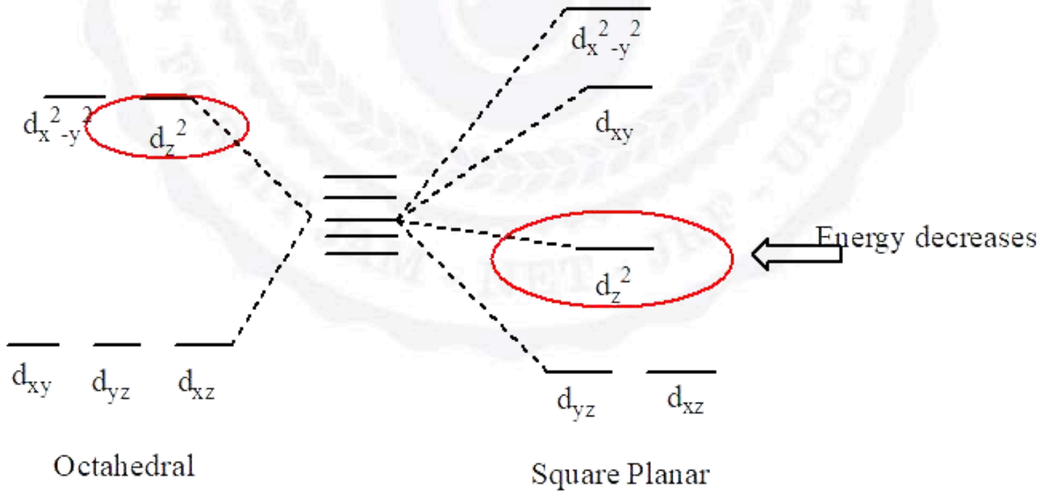
Strong field ligand

NUMBER AND GEOMETRY OF THE LIGANDS

The magnitude of crystal field splitting increases with increase of the number of ligands. Hence, the crystal field splitting will follow the order

$$\Delta_{sp} > \Delta_{oct} > \Delta_{tet}$$

Though the number of ligands in square planar complex is smaller than octahedral, the magnitude of splitting is greater for square planar than octahedral because of the fact that square planar complex are formed by much strong ligands and also the two electrons in dz2 orbital are stabilized.

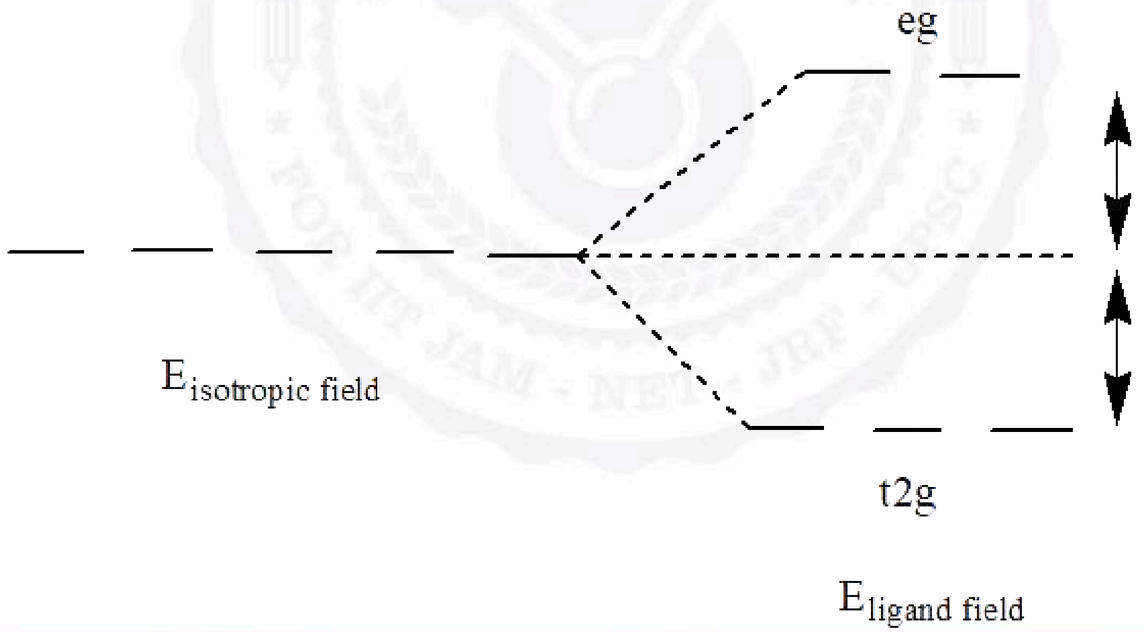


CRYSTAL FIELD STABILIZATION ENERGY

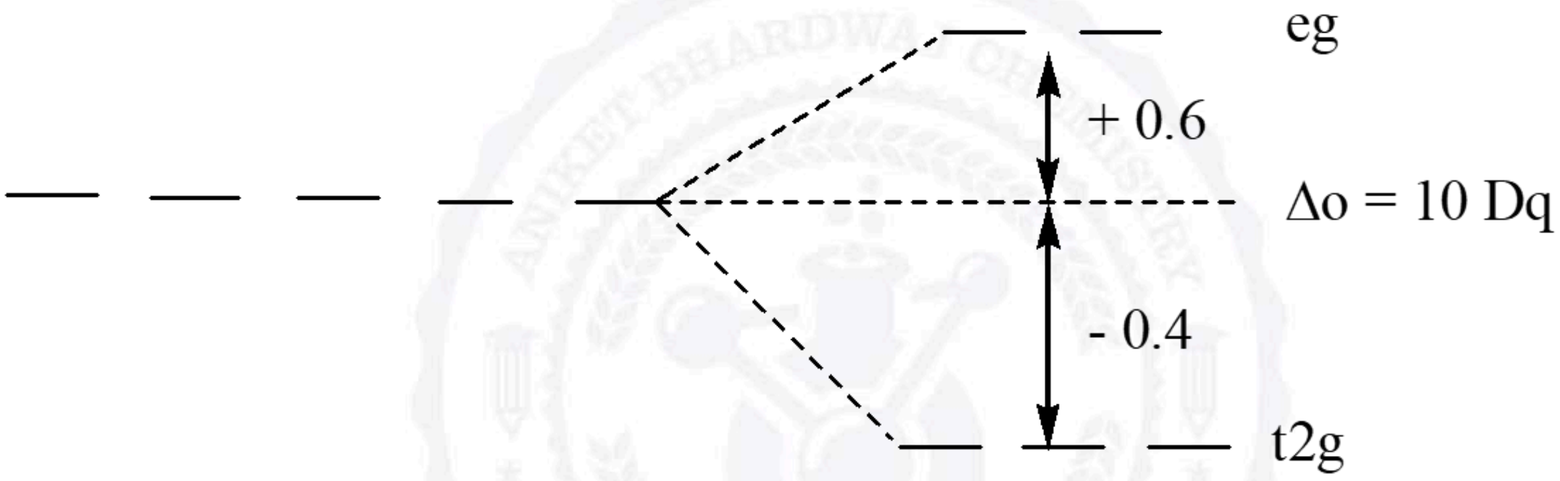
Crystal Field Stabilization Energy is defined as the difference in the energy of the electron configuration in the ligand field to the energy of the electronic configuration in the isotropic field.

$$\mathbf{CFSE = E_{ligand\ field} - E_{isotropic\ field}}$$

$E_{isotropic\ field}$ = Number of electrons in degenerate d-orbital + Pairing energy



CRYSTAL FIELD STABILIZATION ENERGY OF OCTAHEDRAL COMPLEXES WILL BE CALCULATED USING



$$\mathbf{CFSE = [-0.4\ n\ t_{2g} + 0.6\ n\ e_g]\ \Delta o + mP}$$

n = number of electron present in t_{2g} and e_g orbital respectively

m = number of pair of electrons

CRYSTAL FIELD STABILIZATION ENERGY OF TETRAHEDRAL COMPLEXES WILL BE CALCULATED USING

$$\mathbf{CFSE = [-0.6\ n\ e + 0.4\ n\ t_2]\ \Delta t}$$

n = number of electron present in e and t_2 orbital respectively

$$\text{w.k.t} \quad \Delta t = \frac{4}{9}\ \Delta o$$

$$\text{CFSE} = [-0.6\ n\ e + 0.4\ n\ t_2] \quad x \quad \frac{4}{9}\ \Delta o$$

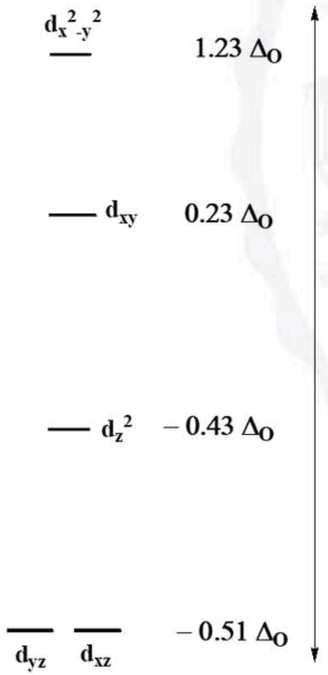
Crystal Field Stabilization Energy of Tetrahedral complexes simplified form in terms of Octahedral

$$\text{CFSE} = [-0.27\ n\ e + 0.18\ n\ t_2]\ \Delta o$$

CRYSTAL FIELD STABILIZATION ENERGY OF SQUARE PLANAR COMPLEXES WILL BE CALCULATED USING

CFSE = (-0.51) (# e) + (-0.42) (# e) + (0.23) (# e) + (1.23) (# e) Δsp

e = number of electron present in each orbital respectively



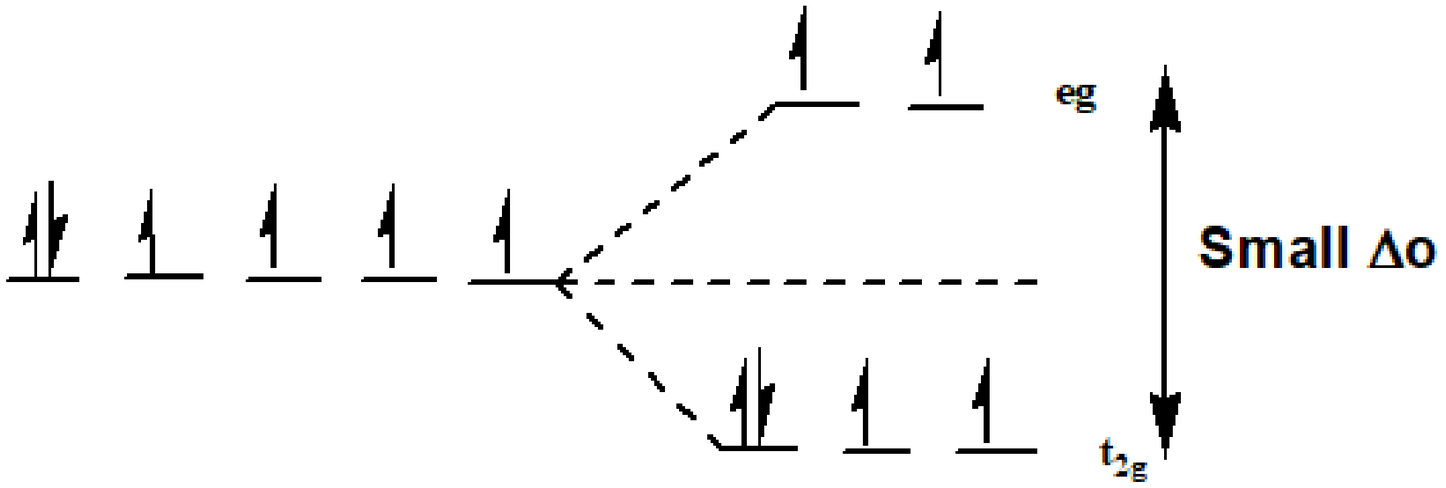
w.k.t $\Delta sp = 1.74\ \Delta o$

CFSE = (-0.51) (# e) + (-0.42) (# e) + (0.23) (# e) + (1.23) (# e) X 1.74 Δo

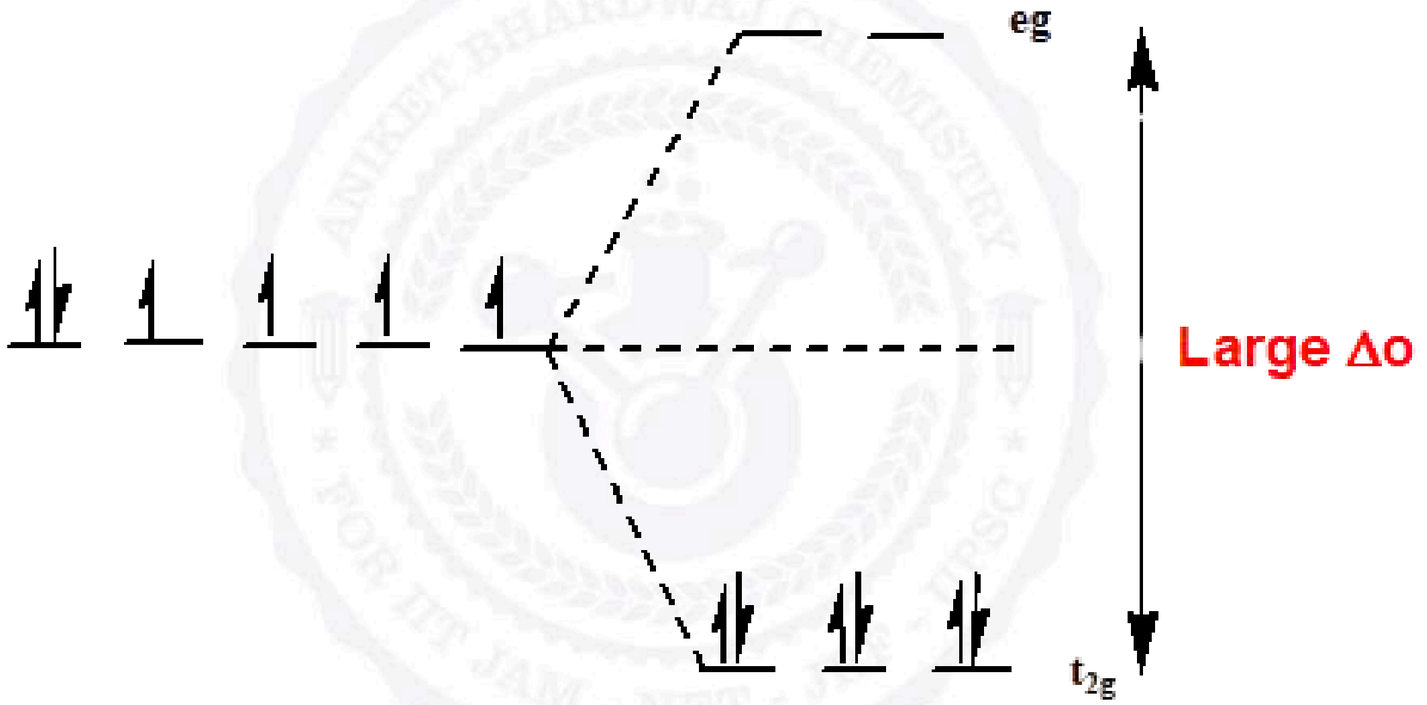
DISTRIBUTION OF D-ELECTRONS IN OCTAHEDRAL COMPLEX

The distribution of d-electrons in t2g and eg orbitals takes place according to Hund's rule of maximum multiplicity i.e. pairing of electrons will occur only when each of five orbital is singly filled.

The complex having small value of Δo, no pairing of electrons will takes place i.e. Arrangement of d-electron remains as in free metal ion.

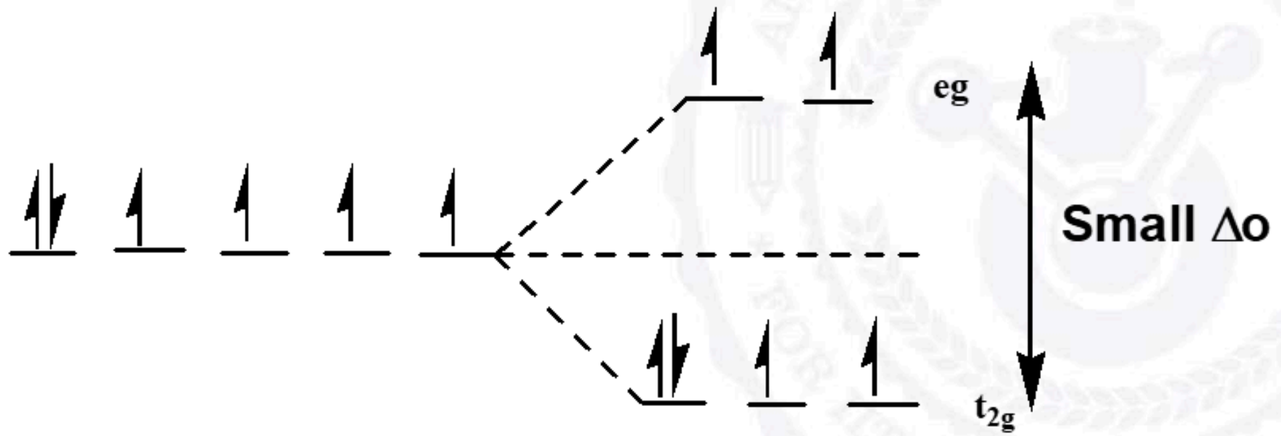


The complex having high value of Δo,the distribution of electrons does not obey Hund's rule.



WEAK FIELD OR HIGH SPIN OR SPIN FREE COMPLEXES

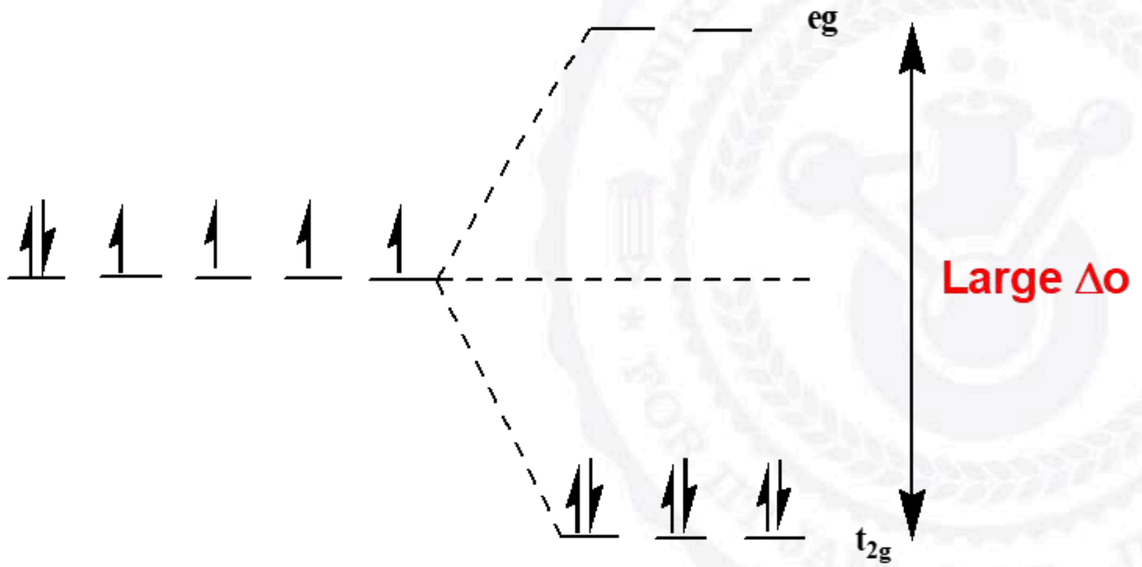
In weak field octahedral complex the value of Δo small and no pairing of d-electrons. These complexes have maximum number of unpaired electrons are called high spin or spin free complexes.



Four unpaired electrons hence high spin complex

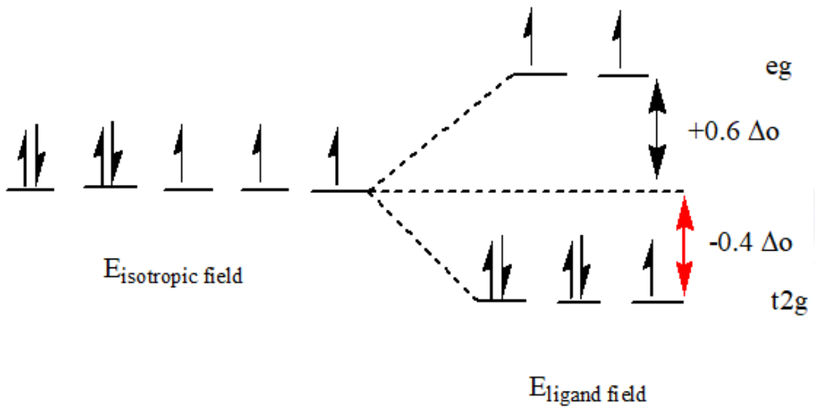
STRONG FIELD OR LOW SPIN OR SPIN PAIRED COMPLEXES

In strong field octahedral complex the value of Δo is large and pairing of d-electrons. These complexes have maximum number of paired electrons are called low spin or spin paired complexes.



Three paired electrons
hence high spin complex

What is CFSE for a high spin d^7 octahedral complex



$E_{isotropic\ field} = 7 \times 0 + 2P = 2P$

$E_{ligand\ field} = (-0.4 \times 5 + 0.6 \times 2)\ \Delta o + 2P = -0.8\ \Delta o + 2P$

So, the CFSE is

$CFSE = E_{ligand\ field} - E_{isotropic\ field}$

$= -0.8\ \Delta o + 2P - 2P$

$CFSE = -0.8\ \Delta o$

Octahedral CFSEs for d^n configuration with pairing energy P

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{oct}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{oct}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{oct}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{oct} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}^6 e_g^4$	0		

Table has been taken from Inorganic Chemistry by Catherine E. Housecraft and Alan G. Sharpe, 4th Edition

Tetrahedral CFSEs for d^n configuration

# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6\ \Delta_t$	6	$-0.6\ \Delta_t$
2	$-1.2\ \Delta_t$	7	$-1.2\ \Delta_t$
3	$-0.8\ \Delta_t$	8	$-0.8\ \Delta_t$
4	$-0.4\ \Delta_t$	9	$-0.4\ \Delta_t$
5	zero	10	zero

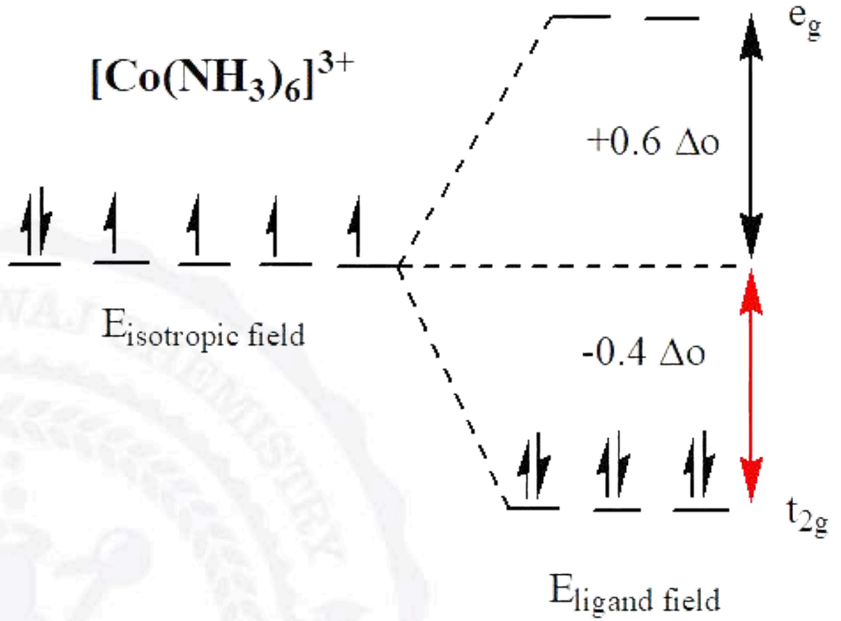
PAIRING ENERGY

IF ΔO > P, FAVORS LOW SPIN COMPLEXES

IF ΔO < P, FAVORS HIGH SPIN COMPLEXES

IF ΔO = P, HIGH AND LOW SPIN COMPLEXES EQUALLY EXISTS

Calculate the CFSE of $[Co(NH_3)_6]^{3+}$ complex whose $\Delta o = 23000\ cm^{-1}$ and $P = 21000\ cm^{-1}$



$\Delta o = 23000\ cm^{-1}$

$P = 21000\ cm^{-1}$

Since

$\Delta o > P$

⇓

Favors low spin complex

$CFSE = (-0.4 \times nt_{2g} + 0.6 \times ne_g)\ \Delta o + m \times P$

$CFSE = (-0.4 \times 6 + 0.6 \times 0)\ \Delta o + 2 \times P$

$= (-2.4)\ 23000 + 2 \times 21000$

$= -55000 + 42000$

$CFSE = -13200\ cm^{-1}$

FOR COMPLEXES THE HIGH SPIN AND LOW SPIN WILL BE DECIDED ON THE BASIS OF LIGAND FIELD STRENGTH

FOR WEAK FIELD LIGANDS PAIRING ENERGY WILL NOT BE CONSIDERED WITH CFSE

WHEREAS FOR STRONG FIELD LIGANDS PAIRING ENERGY WILL BE CONSIDERED ALONG WITH CFSE

Consider for example two complexes $[Co(H_2O)_6]^{2+}$ and $[Co(CN)_6]^{4-}$

Here in the above complexes we need to decide for which complex we need to add pairing energy along with CFSE will be decided by ligand field strength.

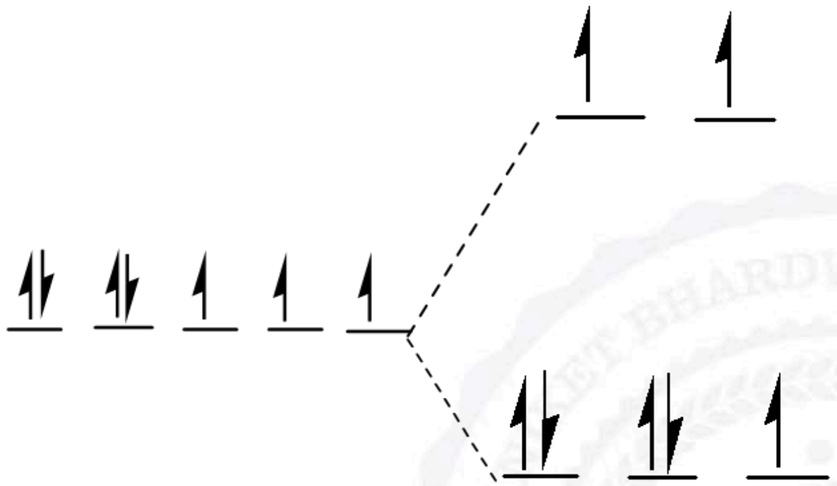
$[Co(H_2O)_6]^{2+}$ ⇓ Co^{2+}

$[Co(CN)_6]^{4-}$ ⇓ Co^{2+}

In both complexes Cobalt is in +2 oxidation state hence both will have same pairing energy. Hence ligand field strength will be considered.

⇓ H_2O
Weak ligand

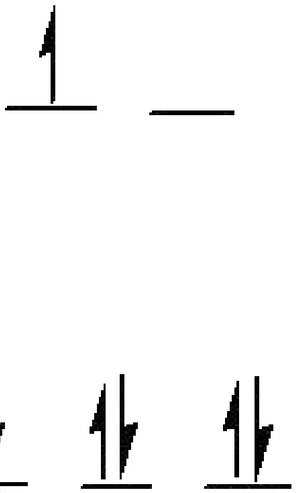
⇓ CN^-
Strong ligand



High spin

$$CFSE = (-0.4 \times 5 + 0.6 \times 2)\,\Delta o$$
$$= -2.0 + 1.2\,\Delta o$$
$$= -0.8\,\Delta o$$

H_2O
Weak ligand



Low spin

$$CFSE = (-0.4 \times 6 + 0.6 \times 1)\,\Delta o + 1P$$
$$= -2.4 + 0.6\,\Delta o + 1P$$
$$= -1.8\,\Delta o + P$$

CN^-
Strong ligand

Given CFSE of $[Co(H_2O)_6]^{2+}$ complex is 7360 cm^{-1}. Calculate the value of Δo in KJ/mol.

$$CFSE = (-0.4 \times 5 + 0.6 \times 2)\,\Delta o$$

$$= -2.0 + 1.2\,\Delta o$$

$$= -0.8\,\Delta o$$

$$\mathbf{CFSE = -0.8\,\Delta o}$$

$$\frac{7360}{0.8} = \Delta o$$

$$\boxed{\Delta o = 9200\ cm^{-1}}$$

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

High spin

1 KJ = 83.7 cm^{-1}

$$\Delta o = \frac{9200}{83.7}$$

$$\boxed{\Delta o = 109.91\ KJ/mol}$$

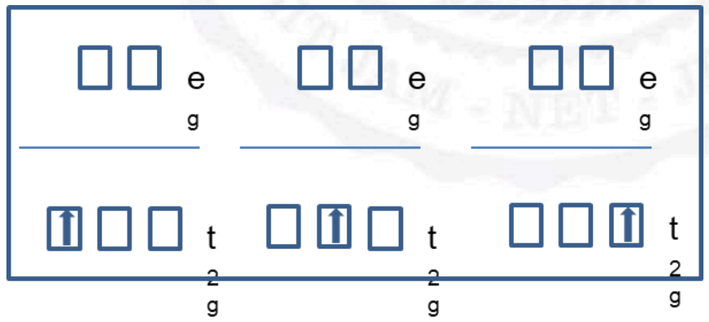
TETRAGONAL DISTORTION OR JAHN-TELLER DISTORTION

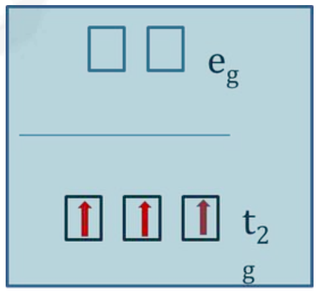
A complex will be regular octahedron when the electronic rearrangement in t_{2g} and e_g orbital is symmetric. It is because of the fact that symmetrically arranged electrons will repel all the six ligands equally.

When either t_{2g} or e_g orbital are asymmetrically filled i.e. electronically degenerate, the regular octahedral geometry is not stable but it transforms into a distorted octahedral geometry.

Electronic Degeneracy : t_{2g}^1
Here there are three different ways by which the single electron can occupy the t_{2g} orbitals. There are three possible electronic configurations which are of the same energy. **Electronic degeneracy is present.**

Electronic Degeneracy : t_{2g}^3
Here there is only one way by which the three electron can occupy the t_{2g} orbitals. So there is **no electronic degeneracy**





JAHN-TELLER DISTORTION THEOREM

States that any non linear molecule in an electronically degenerate state is unstable and the molecule becomes distorted in such a way as to remove degeneracy, lower its symmetry and the energy.

Jahn-Teller distortion α Z - component

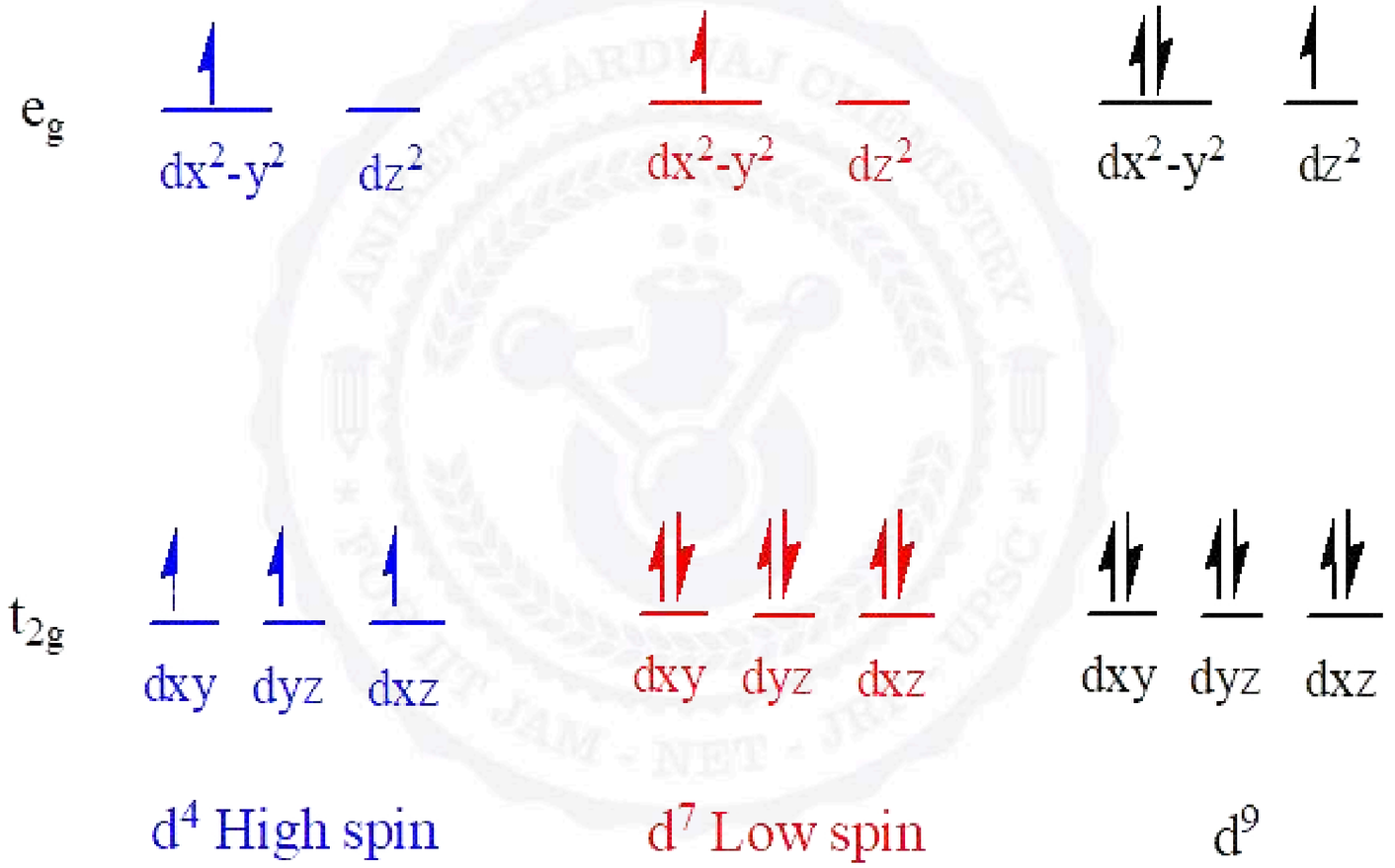
Order of Jahn-Teller distortion

Octahedral > Square planar ~ Trigonal bipyramidal > Tetrahedral

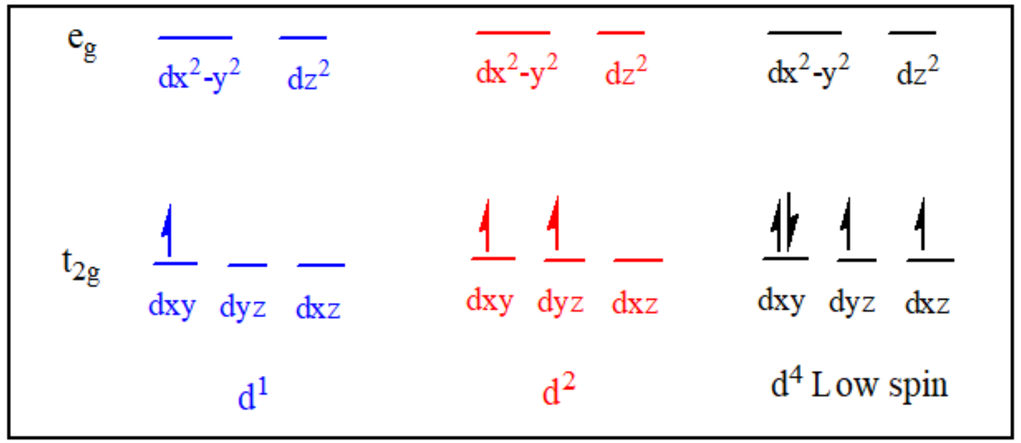
Practically, distortion in the regular octahedral geometry is observed when eg orbitals which point directly at ligands, are asymmetrically filled.

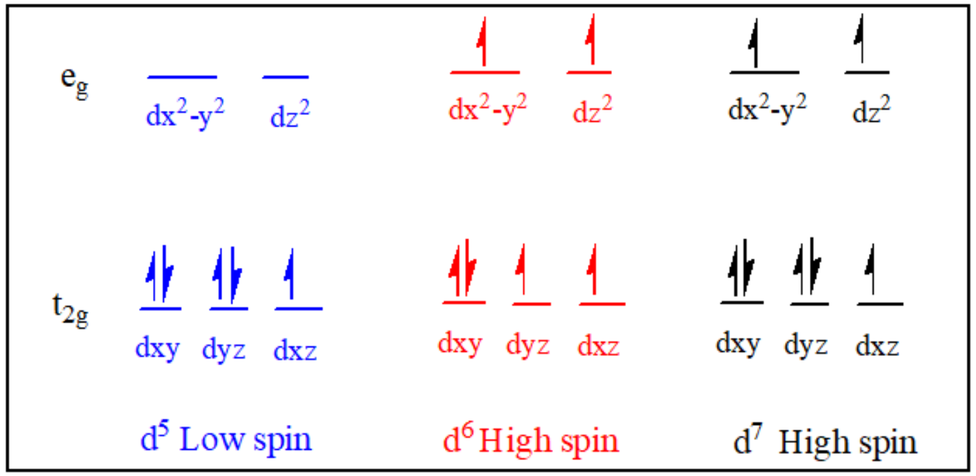
The t2g orbitals do not point directly at ligands, asymmetrical filling of electrons in them does not give any observable distortion.

Considerable distortions are usually observed in high spin d^4, low spin d^7 and d^9 configurations in the octahedral environment.



CONFIGURATIONS SHOWING WEAK JAHN-TELLER DISTORTION

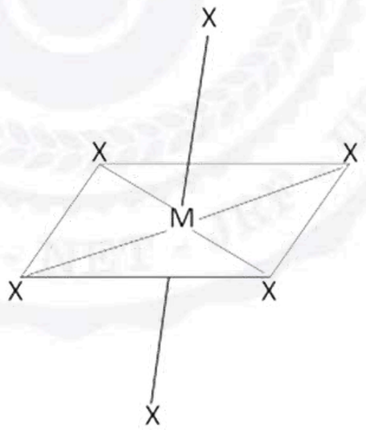




Z-OUT & Z-IN JAHN-TELLER DISTORTION

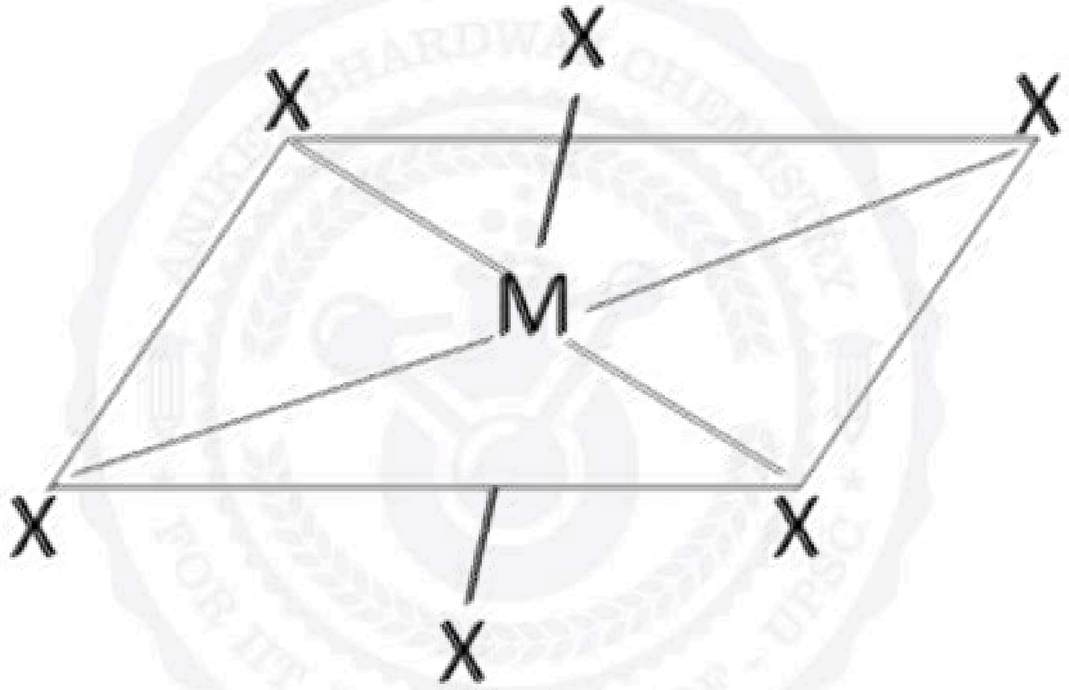
The degeneracy of orbitals can be removed by lowering the symmetry of molecule. This can be achieved by either elongation of bonds along the z-axis (Z-out distortion) or by shortening the bonds along the z-axis (Z-in distortion). Thus an octahedrally symmetrical molecule is distorted to tetragonal geometry.

Z-out Jahn-Teller distortion: In this case, the energies of d-orbitals with z factor (d_z^2, d_{xz}, d_{yz}) are lowered since the bonds along the z-axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in eg level.

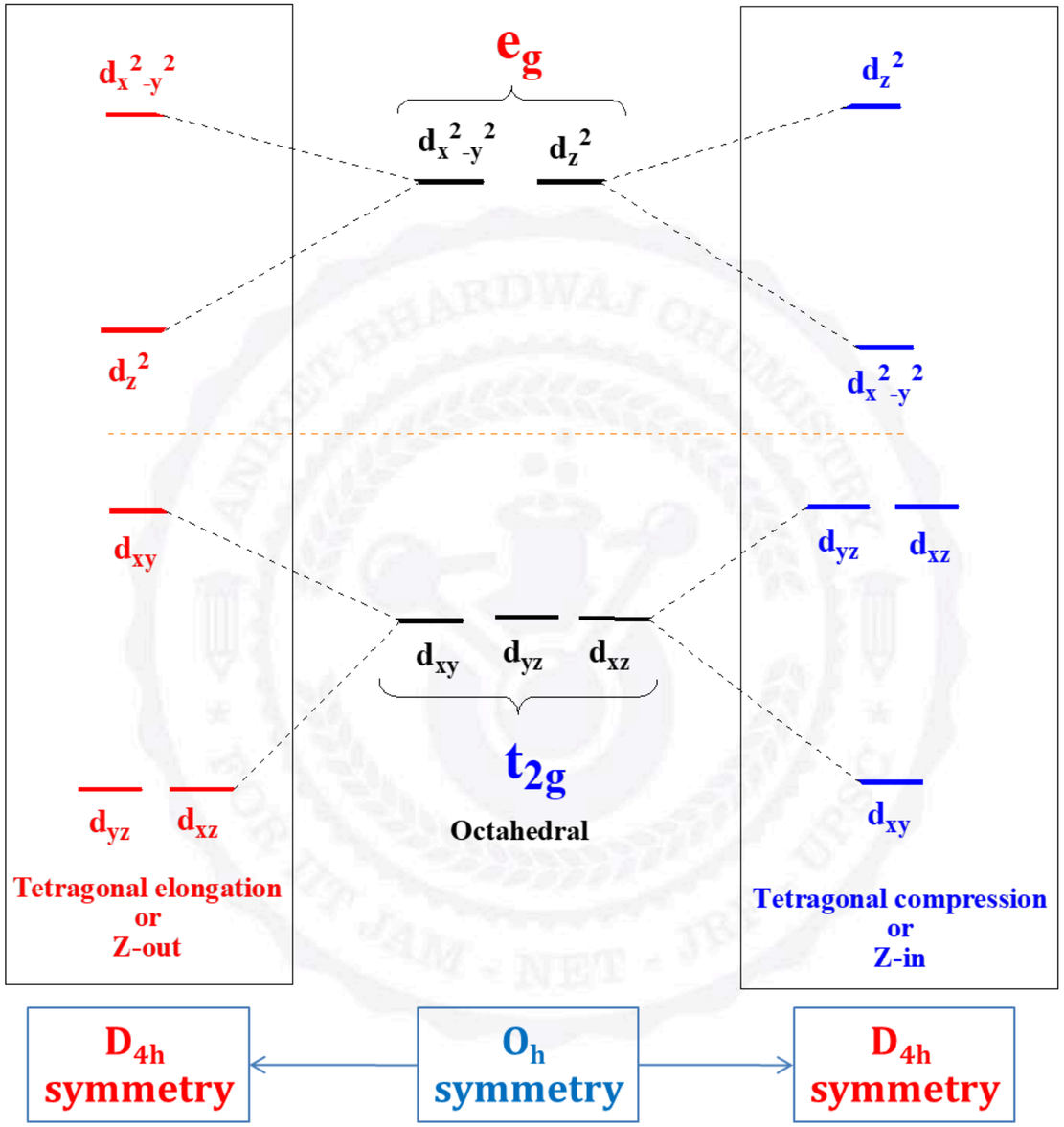


Z-out distortion or Tetragonal elongation

Z-in Jahn-Teller distortion: In this case the energies of orbitals with z factor are increased since the bonds along the z-axis are shortened.



Z-in distortion or Tetragonal elongation



STATIC & DYNAMIC JAHN-TELLER DISTORTIONS

Static Jahn-Teller distortion: Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. It is observed when the degeneracy occurs in e_g orbitals. Hence, the distortion is strong and permanent.

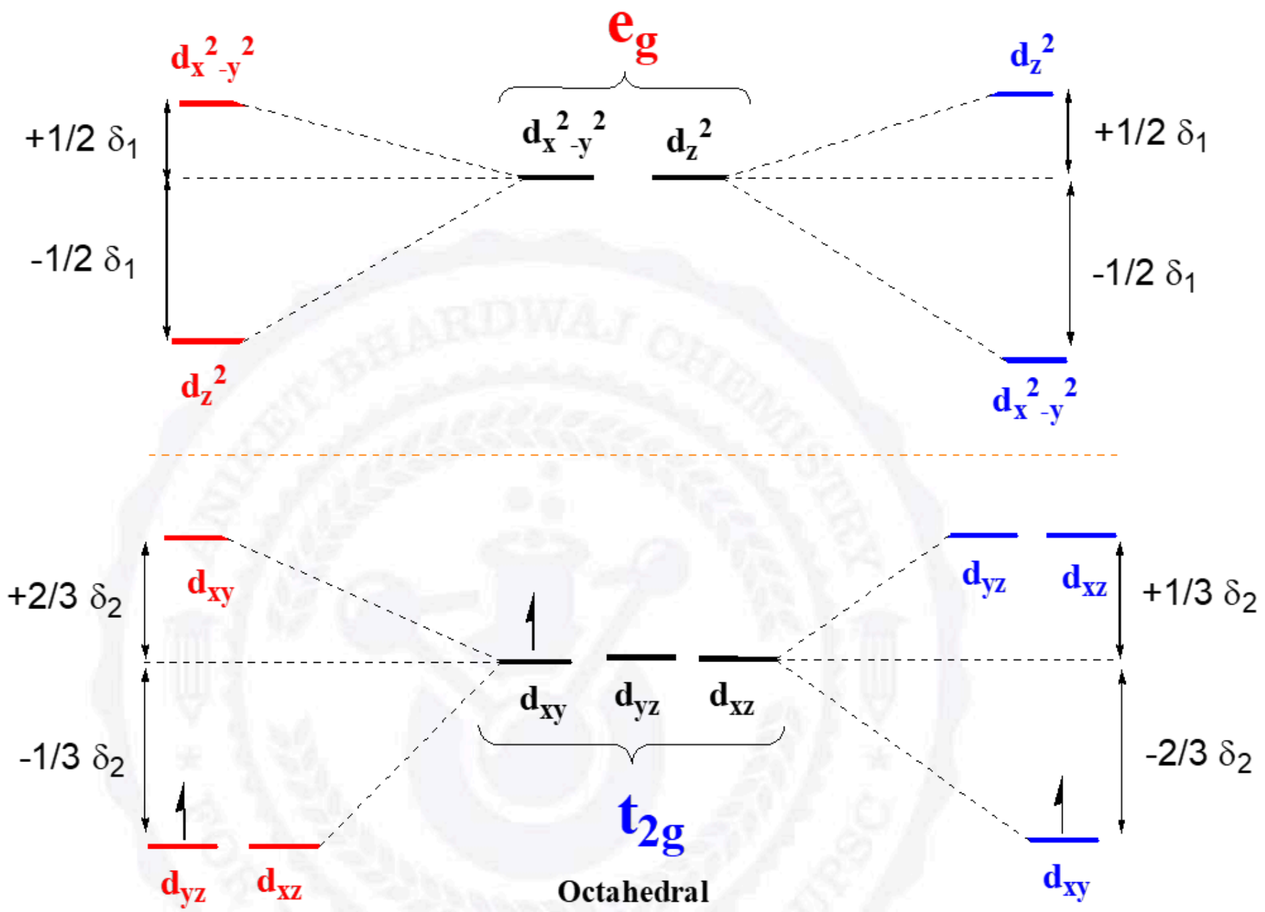
Dynamic Jahn-Teller distortion: In some molecules, the distortion is not seen either due to random movements of bonds or else the distortion is so weak. However, the distortion can be seen by freezing the molecule at lower temperatures. This condition is referred to as dynamic Jahn-Teller distortion.

For example, $[Fe(H_2O)_6]^{2+}$ complex ion shows dynamic Jahn-Teller distortion and appears octahedral. In this case, the distortion is small since the degeneracy occurs in t_{2g} orbitals.

Fe2+ in the above complex is a high spin d^6 system with $t_{2g}^4 e_g^2$ configuration.

d^1 configuration undergoes Z-in Jahn-Teller distortion

Since JTSE for Z-in is greater than Z-out & also in Z-out case results in electronic degenerate state



Tetragonal elongation or Z-out

JTSE = -1/3 x 1

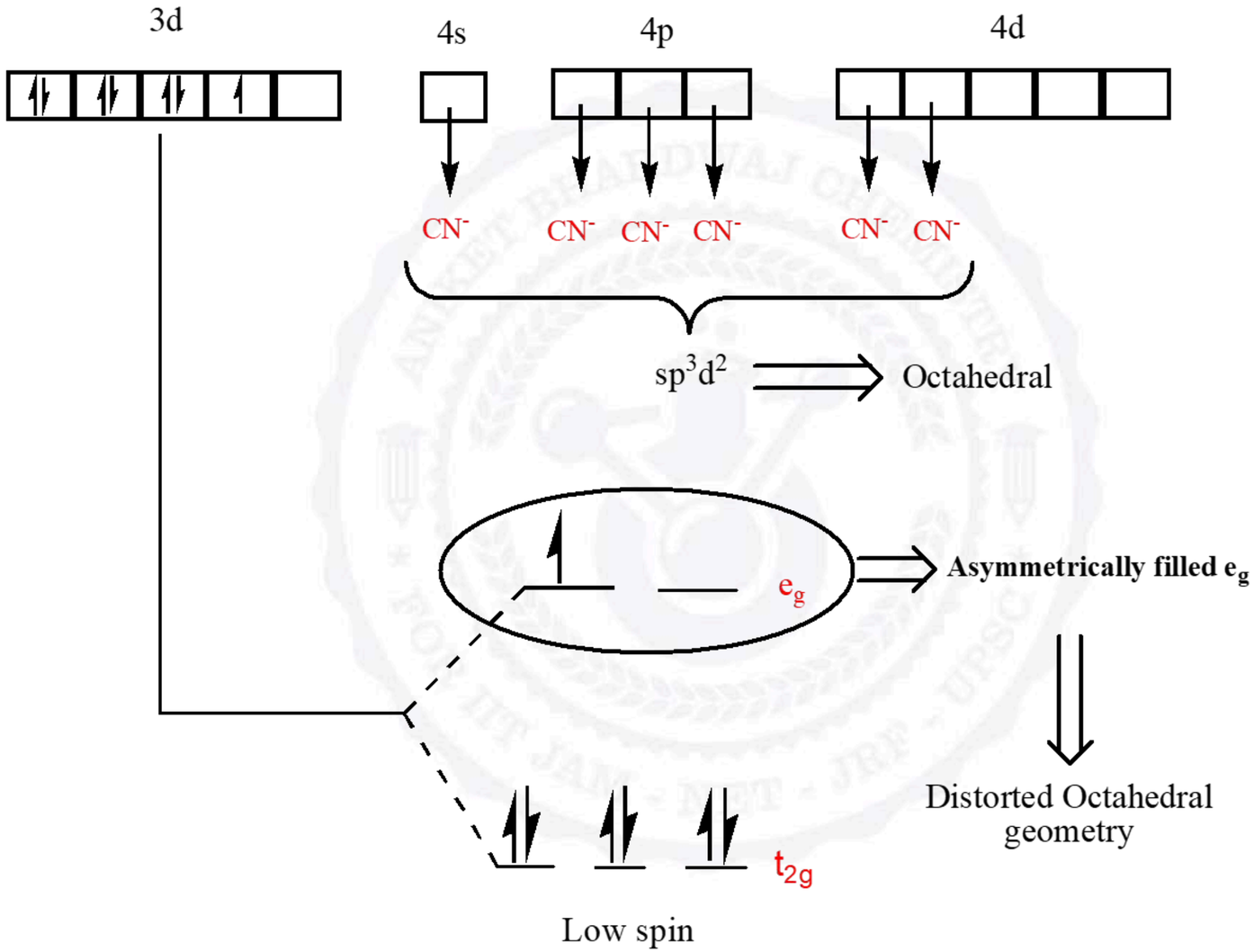
JTSE = -0.33

Tetragonal compression or Z-in

JTSE = -2/3 x 1

JTSE = -0.67

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



CONSEQUENCES OF JAHN-TELLER DISTORTIONS

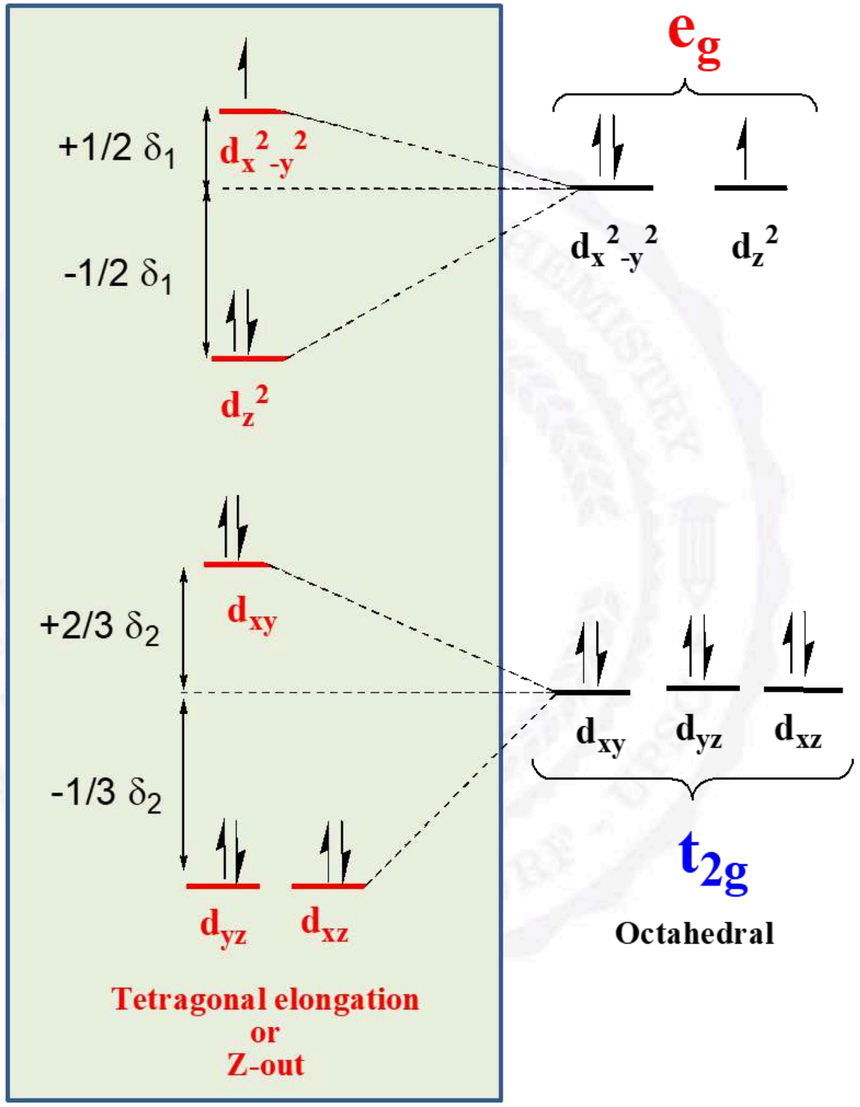
1) Stability of Cu^{2+} complexes

For a given ligand, the relative stability of complexes with dipositive ion of the first transition series follows the order

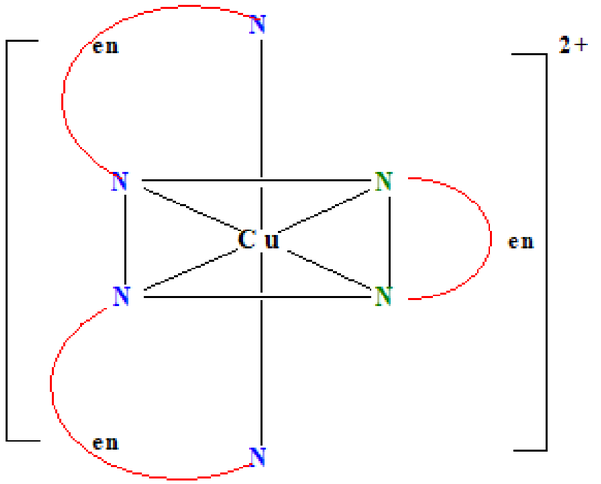
$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

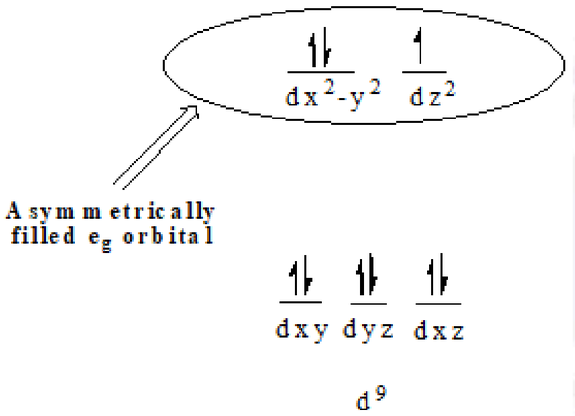
This series is called **Irving-Willian series**. The extra stability of Cu(II) complexes is due to Jahn-Teller distortion. During distortion two electrons are lowered in energy while one is raised.

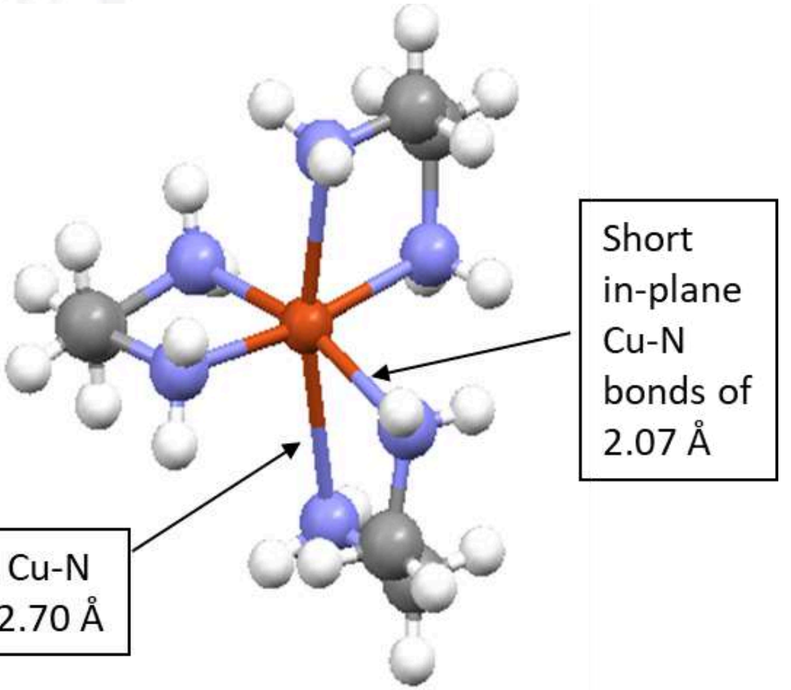
Cu^{2+} complexes



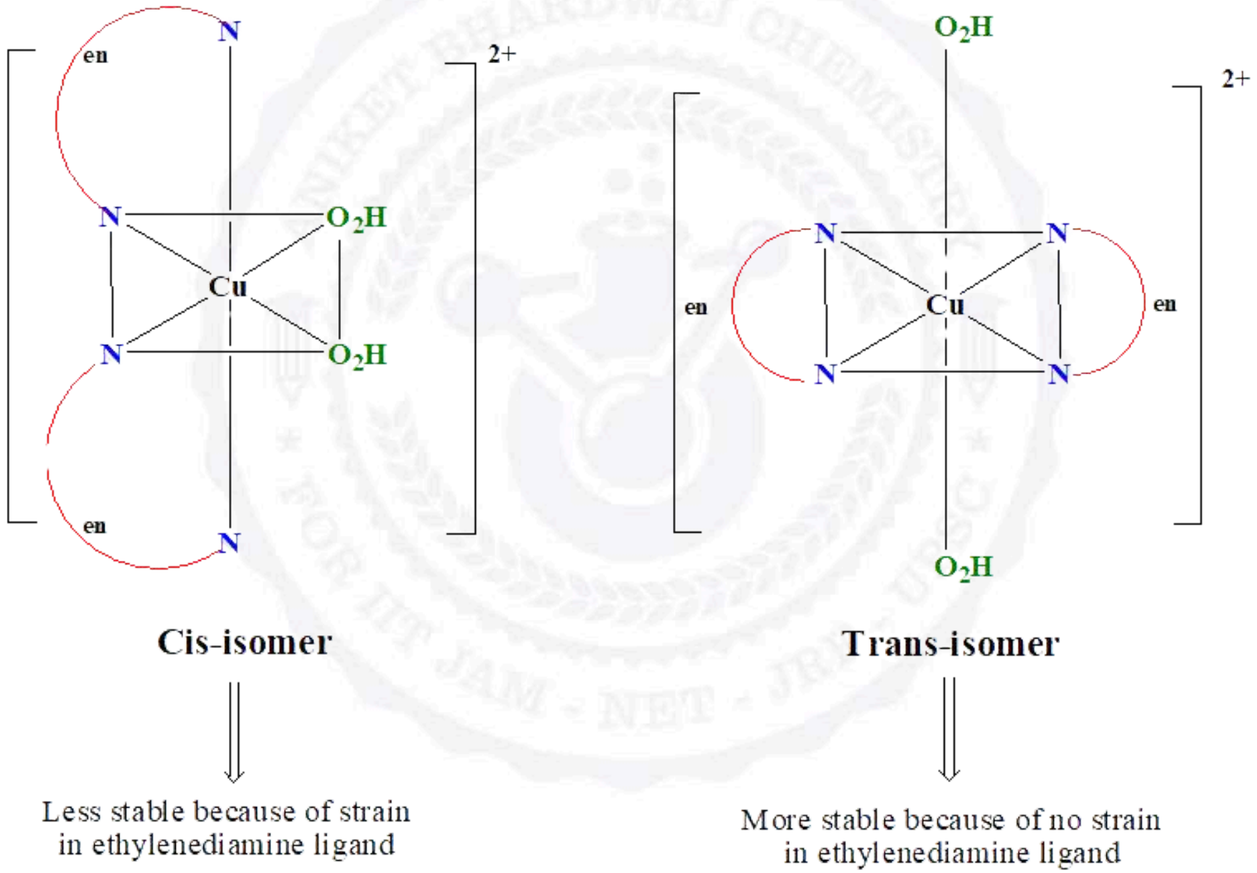
2) The complex $[Cu(en)_3]^{2+}$ is unstable due to Jahn-Teller distortion. It causes strain into ethylenediamine molecule attached along z-axis.







Similar manner trans-$[Cu(en)_2(H_2O)_2]^{2+}$ is more stable than cis-$[Cu(en)_2(H_2O)_2]^{2+}$ due to Jahn-Teller distortion. It causes strain into ethylenediamine molecule attached along z-axis in cis-isomer.



Cis-isomer

⇓

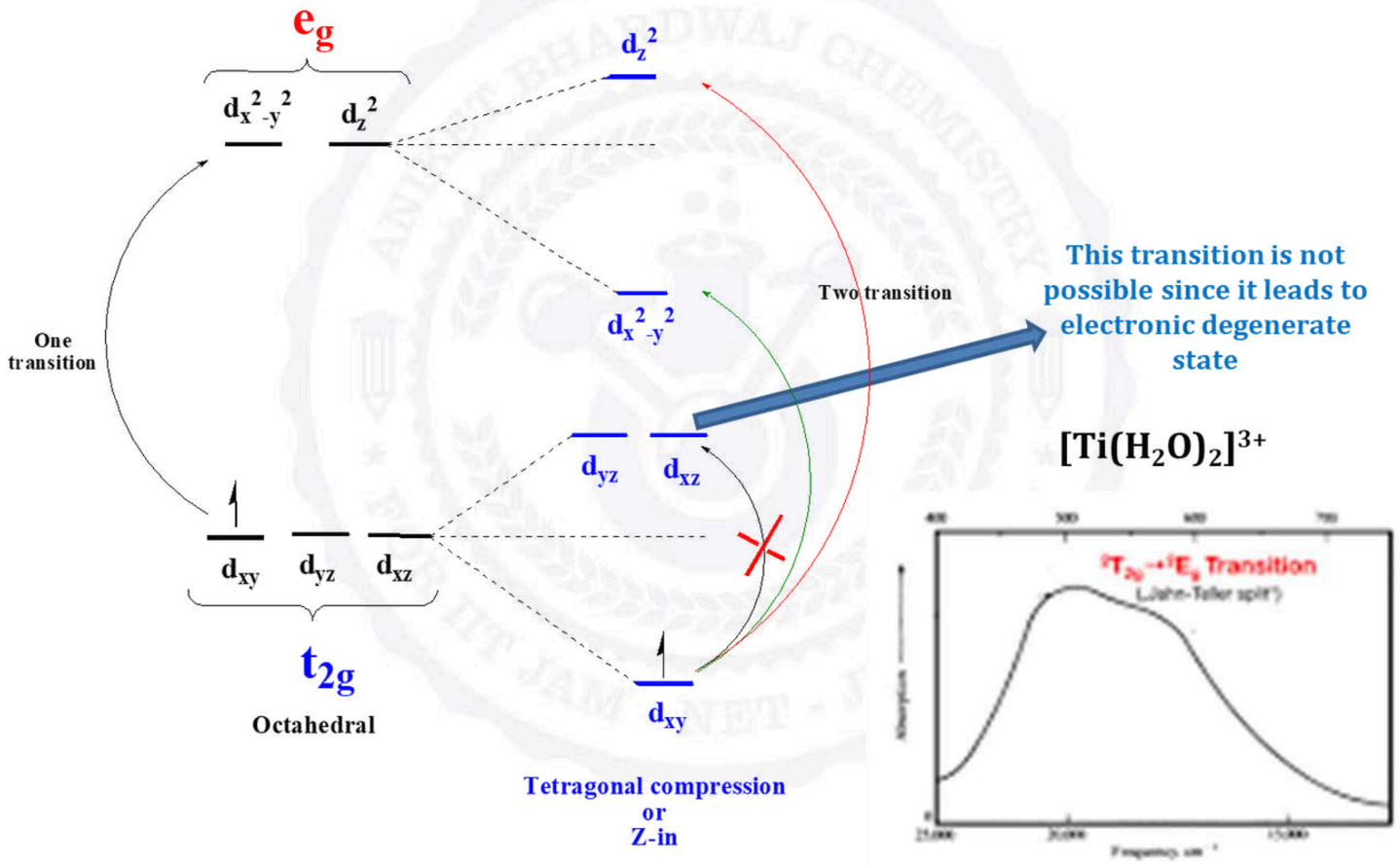
Less stable because of strain in ethylenediamine ligand

Trans-isomer

⇓

More stable because of no strain in ethylenediamine ligand

3) Splitting of absorption bands in the electronic spectra of complexes due to Jahn-Teller distortion.



4) Disproportionation of Au (II) salts

Au (II) ion is less stable and undergoes disproportionation to Au (I) & Au (III) even though Cu (II) & Ag (II) are comparatively stable.

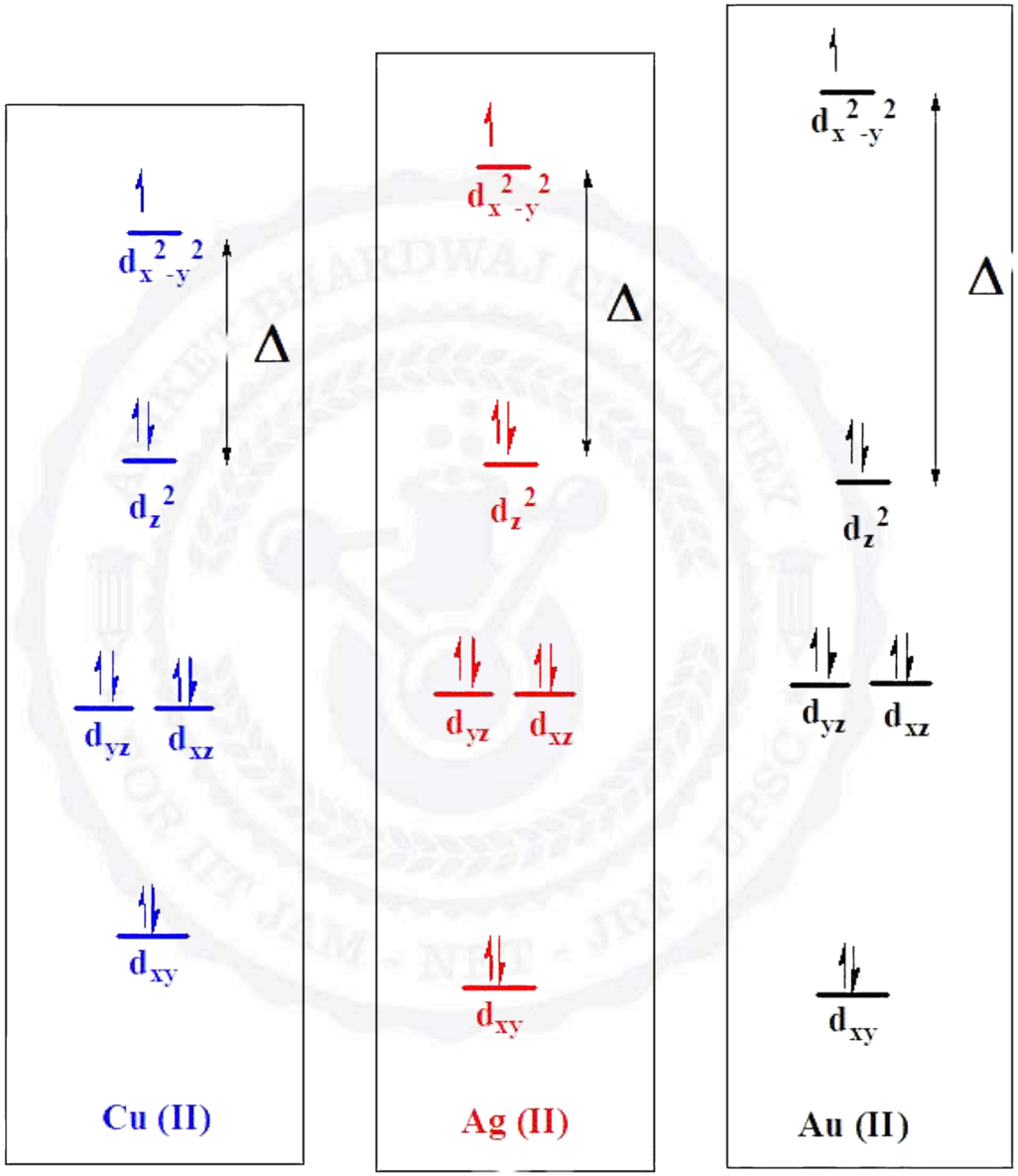
One may expect same stability since all are d9 system & undergoes Jahn-Teller distortion.

However, the Δ value increases down the group. Hence, Au (II) ion reaches maximum and causes high destabilization of last electron in $d_{x^2-y^2}$.

Therefore,
Au (II) either undergo

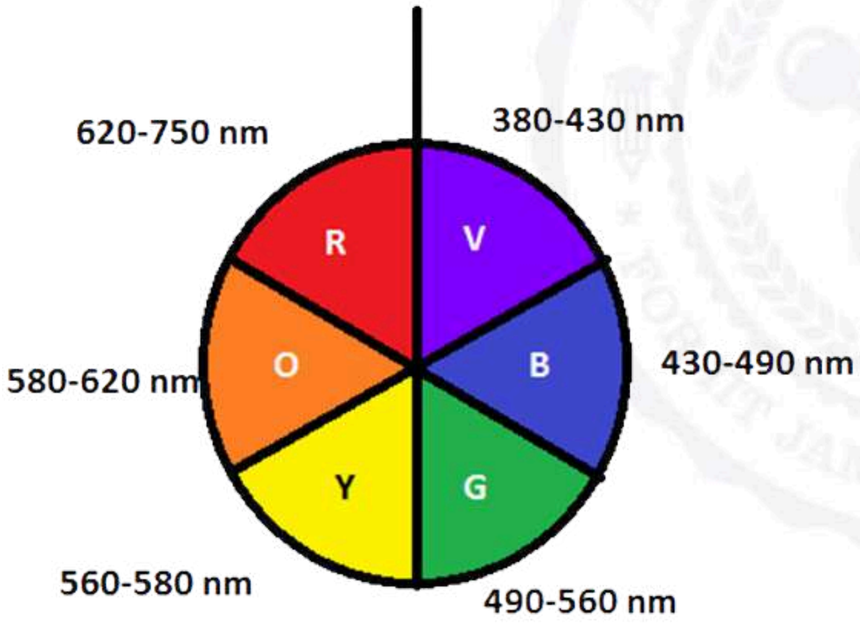
oxidation to Au (III) – d8 system

(or) reduction to Au (I)- d10 system.



COLOROF TRANSITION METAL COMPLEX AND CFT

Colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition. For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δo.



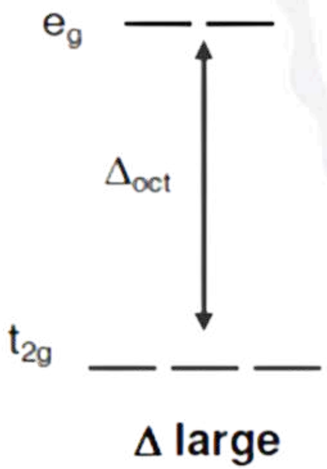
Colour of light absorbed	Approx. λ ranges / nm	Colour of light transmitted
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow

COLOR DEPENDS ON OXIDATION STATE

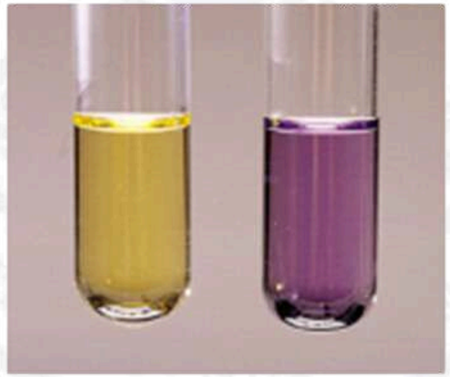
Different oxidation states of one metal can produce different colors

$[V(H_2O)_6]^{3+}$
V(III) = d^2 ion

violet light absorbed
complex appears yellow

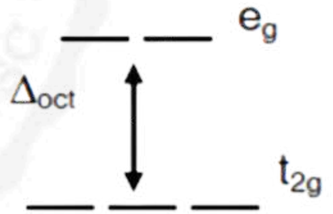


Δ large



$[V(H_2O)_6]^{2+}$
V(II) = d^3 ion

yellow light absorbed
complex appears violet

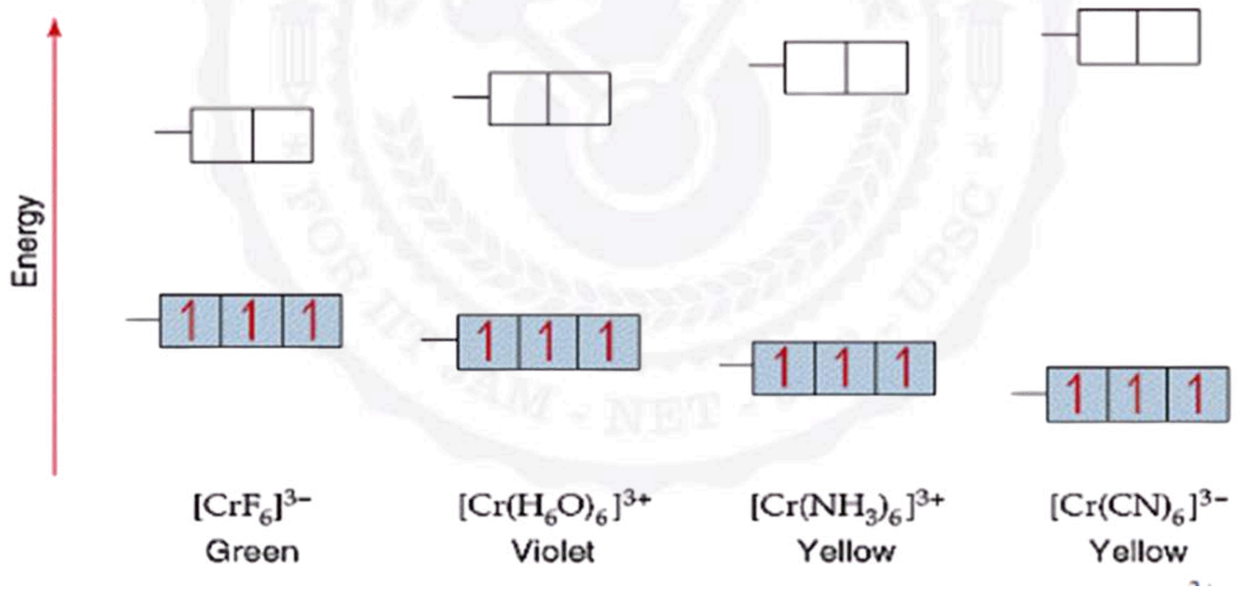


Δ small

COLOR DEPENDS ON LIGAND FIELD

The specific ligands coordinated to the metal center also influence the color of coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δo.

Increasing ligand field strength



SELECTION RULE

1. Laporte Selection Rule

Allowed transitions are those which occur between gerade to ungerade
or
ungerade to gerade orbitals

Allowed

g u & u g

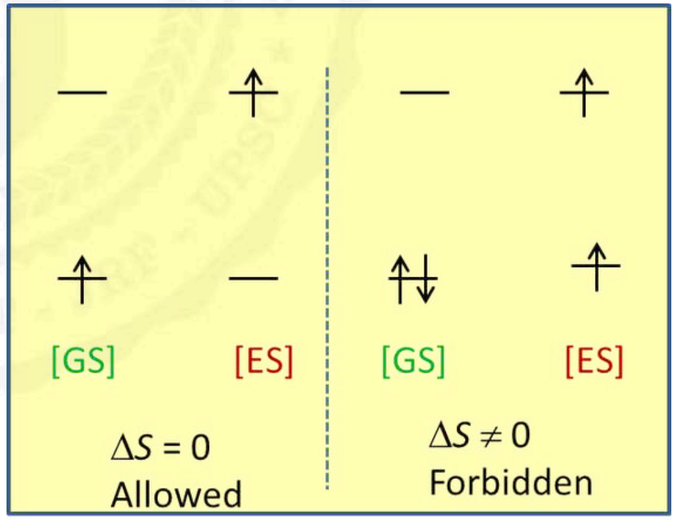
Not allowed (FORBIDDEN)

g g & u u

Azimuthal quantum number can change only by ± 1 ($\Delta l = \pm 1$)

2. Spin Selection Rule

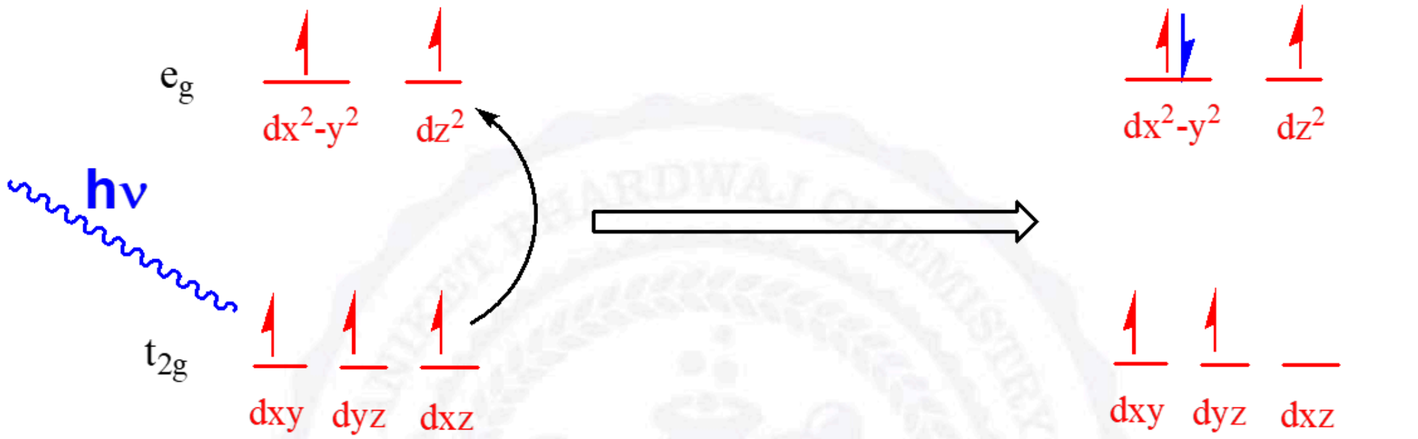
During an electronic transition, the electron should not change its spin
According to this rule, any transition for which
$\Delta S = 0$ is allowed
and
$\Delta S \neq 0$ is forbidden



CLASSIFICATION OF INTENSITIES OF ELECTRONIC TRANSITIONS

Transition type	Example	Typical values of ε /dm3cm-1mol-1
Spin forbidden, Laporte forbidden (partly allowed by spin–orbit coupling)	$[Mn(H_2O)_6]^{2+}$	< 1
Spin allowed (octahedral complex), LaportE forbidden (partly allowed by vibronic coupling and d-p mixing)	$[Co(H_2O)_6]^{2+}$	1 - 10
Spin allowed (tetrahedral complex), Laporte allowed (but still retain some original character)	$[CoCl_4]^{2-}$	10 - 1000
Spin allowed, Laporte allowed e.g. charge transfer bands	$KMnO_4$	1000 - 50000

$$[Mn(H_2O)_6]^{2+} \longrightarrow Mn^{2+} \longrightarrow d^5$$



S = 5/2

Spin multiplicity = (2S+1)

= (2 (5/2)+1)

= 6

S = 3/2

Spin multiplicity = (2S+1)

= (2 (3/2)+1)

= 4

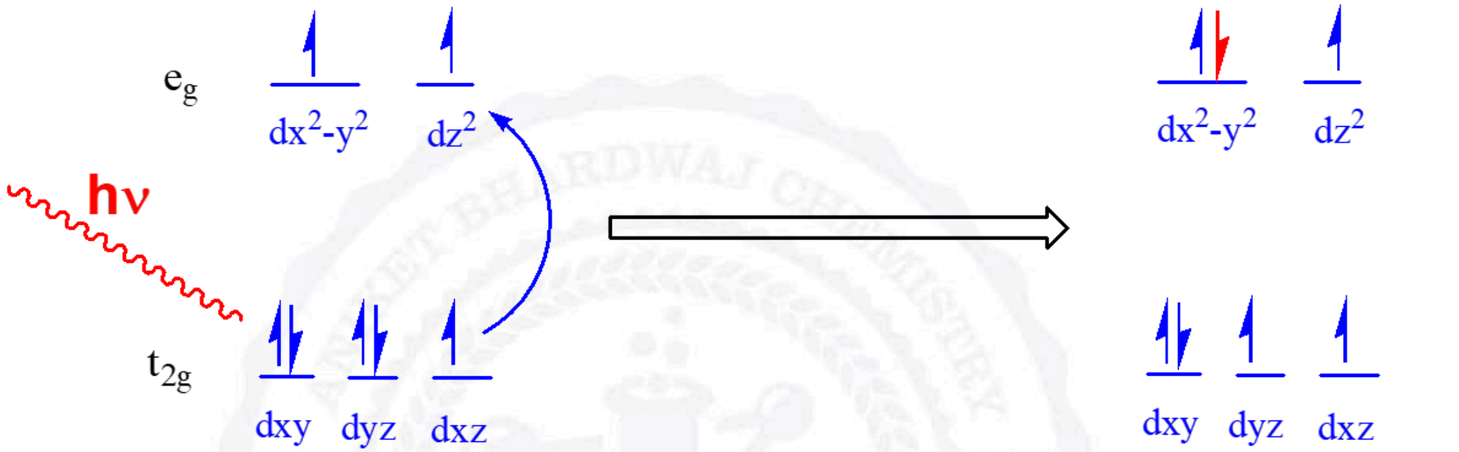
ΔS = 6 - 4 = 2

Due to spin–orbit coupling above transition is partly allowed . Hence, light pink color is observed

ΔS ≠ 0 ⟹ **Spin Forbidden**

g → g ⟹ **Laporte Forbidden**

$$[Co(H_2O)_6]^{2+} \longrightarrow Co^{2+} \longrightarrow d^7$$



S = 3/2

Spin multiplicity = (2S+1)

= (2 (3/2)+1)

= 4

S = 3/2

Spin multiplicity = (2S+1)

= (2 (3/2)+1)

= 4

ΔS = 4 - 4 = 0

Due to vibronic coupling and d-p mixing above transition is partly allowed .

ΔS = 0 ⟹ **Spin Allowed**

g → g ⟹ **Laporte Forbidden**

MAGNETIC PROPERTIES OF METAL COMPLEXES BY CFT

Magnetism is caused by moving charged electrical particles (Faraday, 1830s). These particles can be the current of electrons through an electric wire, or the movement of charged particles (protons and electrons) within an atom. These charged particles move much like planets in a solar system:

Nucleus spin around its own axis, causing a very weak magnetic field.

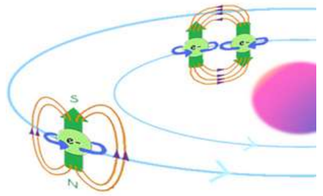
Electrons orbit around the nucleus, causing a weak magnetic field.

Electrons spin around their own axis, causing a significant magnetic field .

Spinning electrons generate the bulk of the magnetism in an atom. Within each orbit, electrons with opposite spins pair together, resulting in no net magnetic field. Therefore only unpaired electrons lead to magnetic moment

The spin-only formula (μ_s)

$$\mu_s = \sqrt{n(n+2)}$$



In the presence of weak field ligand, the complex has small value of Δo. Hence,no pairing of electrons will takes place i.e. Number of unpaired electrons are more and magnetic moments is greater.

$[CoF_6]^{3-} \longrightarrow Co^{3+} \longrightarrow d^6$

e_g : dx^2-y^2 (↑), dz^2 (↑)

t_{2g} : dxy (↑↓), dyz (↑), dxz (↑)

n = 4

$\mu_s = \sqrt{n(n+2)}$

$= \sqrt{4(4+2)}$

$= \sqrt{4(6)} = \sqrt{24}$

$\mu_s = 4.90$ BM

Since F- is weak field ligand no pairing of electrons will takes place.
Hence, it is paramagnetic.

While in the presence of strong field ligand, the complex has large value of Δo. Pairing of electrons will takes place i.e. Number of unpaired electrons are less and magnetic moment is lesser.

$[Co(CN)_6]^{3-} \longrightarrow Co^{3+} \longrightarrow d^6$

e_g : dx^2-y^2 (↑↓), dz^2 (↑↓)

t_{2g} : dxy (↑↓), dyz (↑↓), dxz (↑↓)

n = 0

$\mu_s = \sqrt{n(n+2)}$

$\mu_s = 0$ BM

Since CN- is strong field ligand pairing of electrons will takes place.
Hence, it is diamagnetic.

Spin only formula

$$\mu_s = \sqrt{n(n+2)}$$

Used when seperation energy levels are large

$$\mu_{eff} = g\sqrt{J(J+1)}$$

$$g = 3/2 + \left(\frac{S(S+1) - L(L+1)}{2J(J+1)}\right)$$

Van-Vleck formula used when seperation energy levels are small

$$\mu_{eff} = \mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

Spin-orbit coupling equation applies only to ions having A or E ground term

$$\mu_{eff} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta o}\right)$$

λ = Spin-orbit coupling constant

α = 4 for A ground term

α = 2 for E ground term

The orbital contribution is possible only when an orbital will transform into an equivalent orbitals by rotation. The t_{2g} orbitals can be transformed into each other by rotating about an axis by 90°.

The configuration with t_{2g}^3 and t_{2g}^6 have no orbital contribution

In Octahedral complexes the following configurations make orbital contributions

$$d^1(t_{2g}^1 e_g^0),\ d^2(t_{2g}^2 e_g^0),\ d^6\text{HS}(t_{2g}^4 e_g^2),\ d^7\text{HS}(t_{2g}^5 e_g^2),\ d^4\text{LS}(t_{2g}^4 e_g^0),\ d^5\text{LS}(t_{2g}^5 e_g^0)$$

In Tetrahedral complexes the following configurations make orbital contributions

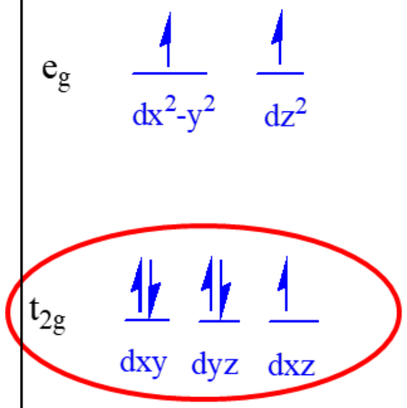
$$d^3(e^2 t_2^1),\ d^4(e^2 t_2^2),\ d^8(e^4 t_2^4) \text{ and } d^9(e^4 t_2^5)$$

MAGNETIC PROPERTIES: SPIN ONLY AND EFFECTIVE

The spin-only formula (μ_s) applies reasonably well to metal ions from the first row of transition metals: (units = μ_B,, Bohr-magnetons)

Metal ion	d^n configuration	μ_s(calculated)	μ_{eff} (observed)
Ca^{2+}, Sc^{3+}	d^0	0	0
Ti^{3+}	d^1	1.73	1.7-1.8
V^{3+}	d^2	2.83	2.8-3.1
V^{2+}, Cr^{3+}	d^3	3.87	3.7-3.9
Cr^{2+}, Mn^{3+}	d^4	4.90	4.8-4.9
Mn^{2+}, Fe^{3+}	d^5	5.92	5.7-6.0
Fe^{2+}, Co^{3+}	d^6	4.90	5.0-5.6
Co^{2+}	d^7	3.87	4.3-5.2
Ni^{2+}	d^8	2.83	2.9-3.9
Cu^{2+}	d^9	1.73	1.9-2.1
Zn^{2+}, Ga^{3+}	d^{10}	0	0

$[Co(H_2O)_6]^{2+} \longrightarrow Co^{2+} \longrightarrow d^7$



$n = 3$

$\mu_s = \sqrt{n(n+2)}$

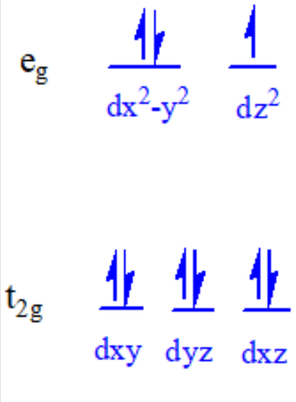
$= \sqrt{3(3+2)}$

$= \sqrt{3(5)} = \sqrt{15}$

$\mu_s = 3.87$ BM

make orbital contributions to magnetic moment

$Cu^{2+} \longrightarrow d^9$



$n = 1$

$\mu_s = \sqrt{n(n+2)}$

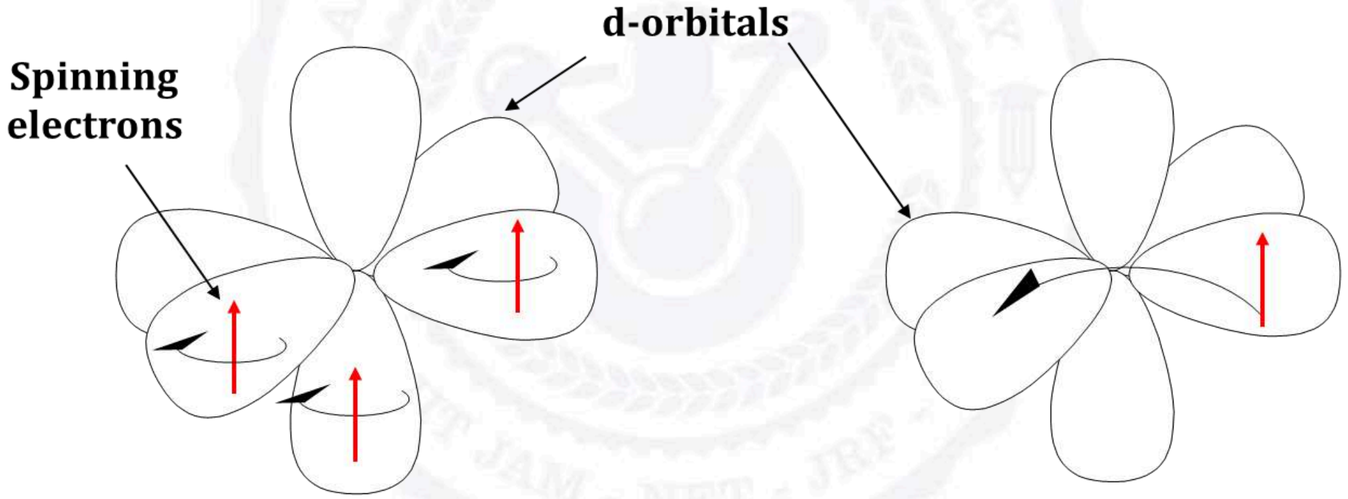
$= \sqrt{1(1+2)}$

$= \sqrt{1(3)}$

$\mu_s = 1.73$ BM

SPIN AND ORBITAL CONTRIBUTIONS TO μ_{eff}

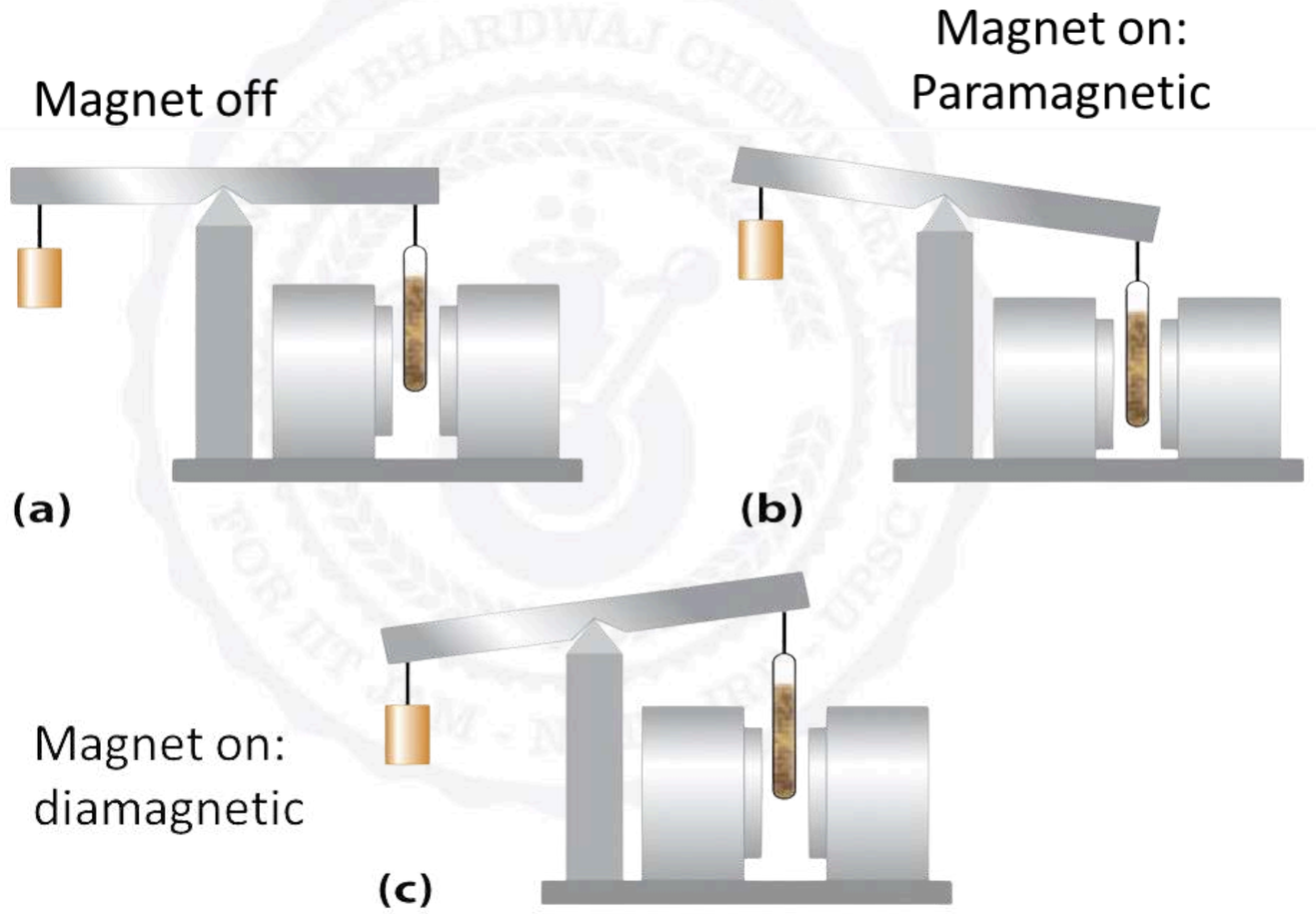
For the first-row d-block metal ions the main contribution to magnetic susceptibility is from electron spin. However, there is also an orbital contribution (especially for the second and third row TM) from the motion of unpaired electrons from one d-orbital to another. This motion constitutes an electric current, and so creates a magnetic field.



Spin contribution – electrons are spinning creating an electric current and hence a magnetic field

Orbital contribution - electrons move from one orbital to another creating a current and hence a magnetic field

GOUY BALANCE USED TO MEASURE THE MAGNETICSUSCEPTIBILITIES



CRYSTAL FIELD THEORY TO EXPLAIN OBSERVED PROPERTIES OF COMPLEXES: VARIATION OF SOME PHYSICAL PROPERTIES ACROSS A PERIOD:

1. Lattice energy of transition metal ions in a complex
2. Ionic radii of transition metal ions in a complex
3. Enthalpy of hydration of transition metal ions
4. Site preference of Spinels and Inverse spinels

Lattice Energy: Energy released when one mole of an ionic solid is formed from isolated gaseous ions.

Calculated theoretically using the Born- Lande Equation

$$U_o = \frac{A N Z^+ Z^- e^2}{4\pi\varepsilon_o r_o}\left(1-\frac{1}{n}\right)$$

Where

A = Madelung constant (related to the geomet

N = Avogadro's number

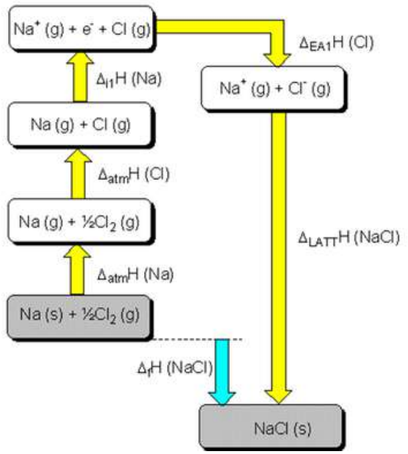
Z= Charge on the M+ and M- ions

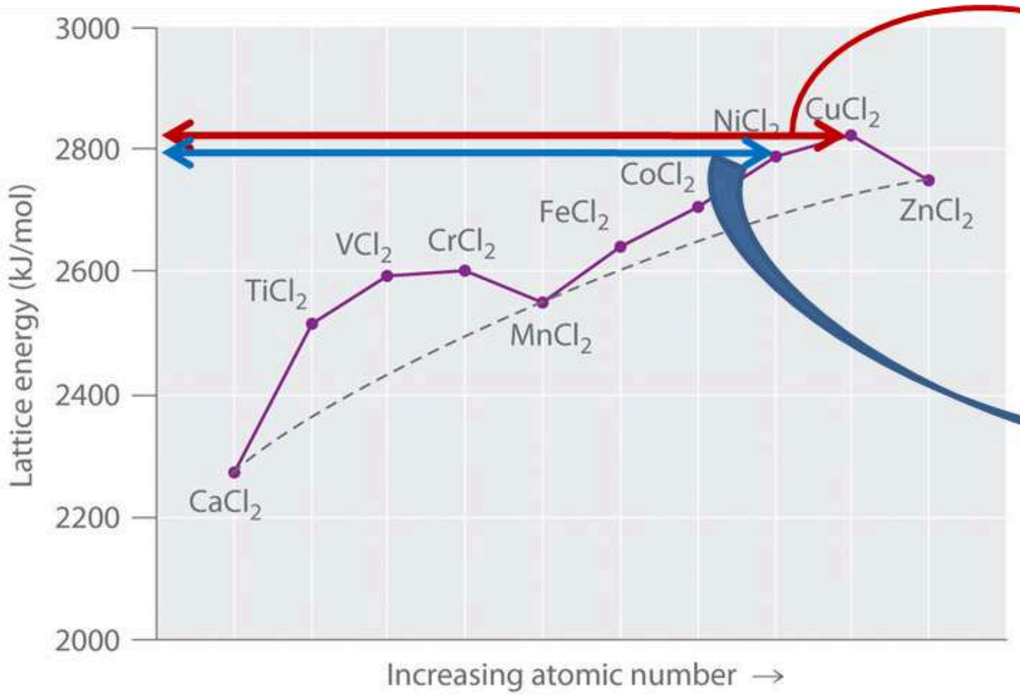
ε_0= permittivity of free space

r_0 = distance to the closest ion

n= Born exponent (a number between 5 and 12)

Experimentally determined using the Born- Haber cycle





$LE_{obs} = LE_{cal} + CFSE + JTSE$

$LE_{obs} = LE_{cal} + CFSE$

•According to the Born – Lande Equation one can expect a smooth increase in lattice energies as we go from left to right due to decrease in ionic radius of the metal ions.

•As anticipated a smooth curve is not seen: instead a double hump shaped curve is obtained
•Ca^{2+} (d^0), Mn^{2+}(d^5 HS) and Zn^{2+} (d^{10}) which in common have CFSE =0 lie almost on the expected line.

•Ions such as V^{2+} which show high CFSE in a weak field situation with high lattice energy values show significant deviation from the calculated lattice energies.

For d^0 → CFSE = 0

For d^1-d^3 → CFSE increases

For d^4-d^5 → CFSE decreases

For d^5 → CFSE = 0

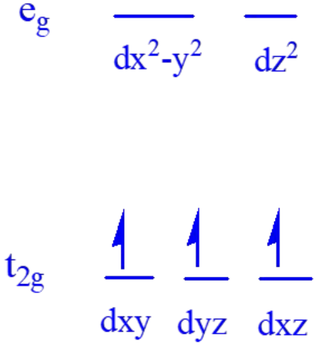
For d^6-d^8 → CFSE increases

For d^9-d^{10} → CFSE decreases

For d^{10} → CFSE = 0

Lattice energy α CFSE

$V^{2+} \longrightarrow d^3$



CFSE = (-0.4 x 3 + 0.6 x 0) Δo

= -1.2 Δo

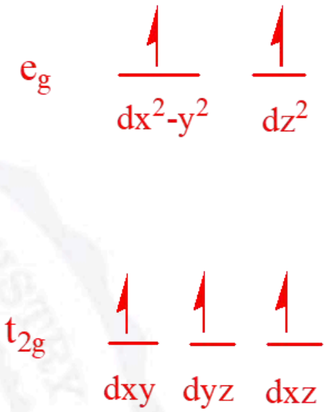
$Fe^{2+} \longrightarrow d^6$

CFSE = (-0.4 x 4 + 0.6 x 2) Δo

= -1.6 + 1.2 Δo

= -0.4 Δo

$Mn^{2+} \longrightarrow d^5$



CFSE = (-0.4 x 3 + 0.6 x 2) Δo

= -1.2 + 1.2 Δo = 0

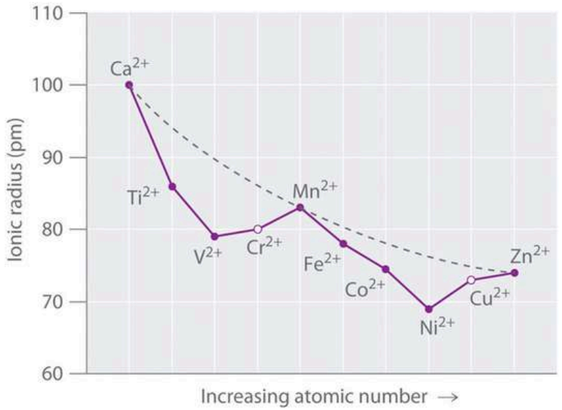
IONIC RADII

One can expect decrease the ionic radii of the M^{2+} ions smoothly from Ca^{2+} to Zn^{2+} due to the increase in nuclear charge

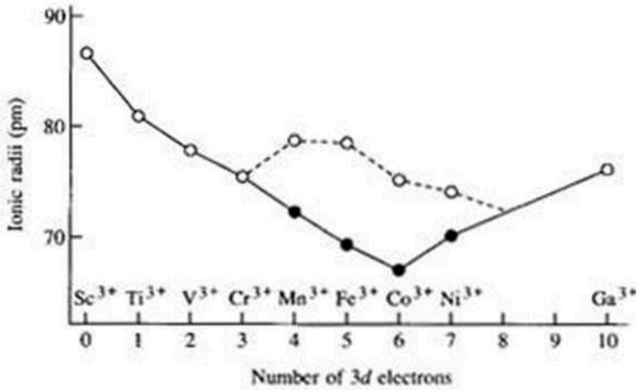
But the plot shown below (left) for weak field ligands indicate that the expected regular decrease is absent expect for Ca^{2+}, Mn^{2+} and Zn^{2+}

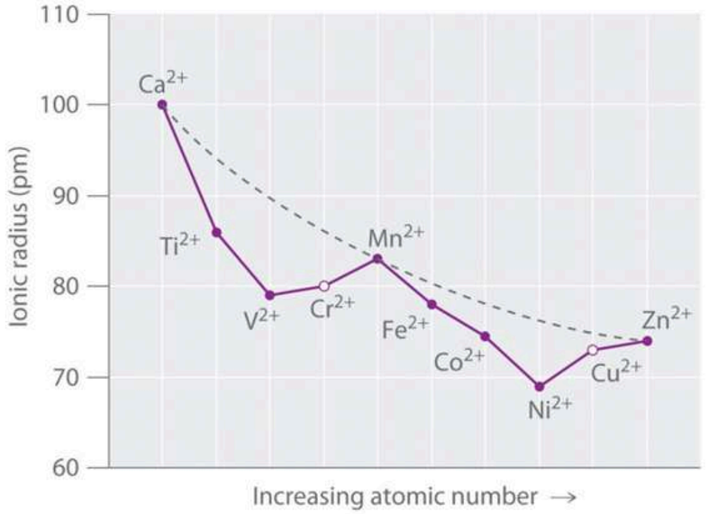
For strong field ligands like CN- a different trend in variation is observed with a steady decrease till d^6 (t_{2g}^6)

Weak field ligand



M^{3+} ionic radii





Why does the ionic radii decreases and then increases?

Ti^{2+} (d^2) electron occupy only t_{2g}
V^{2+} (d^3) electrons occupy only t_{2g}
Cr^{2+} (d^4HS) electrons start occupying the e_g orbitals. As the e_g orbitals point directly towards the ligands, the repulsion between the metal electrons and ligand electrons will be higher than normal leading to the eventual increase in the ionic radius.

In the case of strong field ligand such as cyanide there will be a steady decrease in ionic radii till t_{2g}^6 is reached.

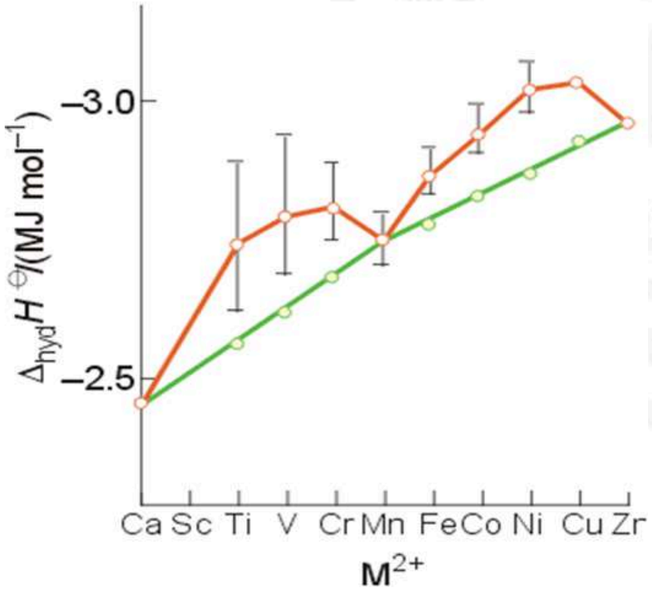
The same tend is observed also for M^{3+} transition metal complexes

Enthalpy of hydration of transition metal ions

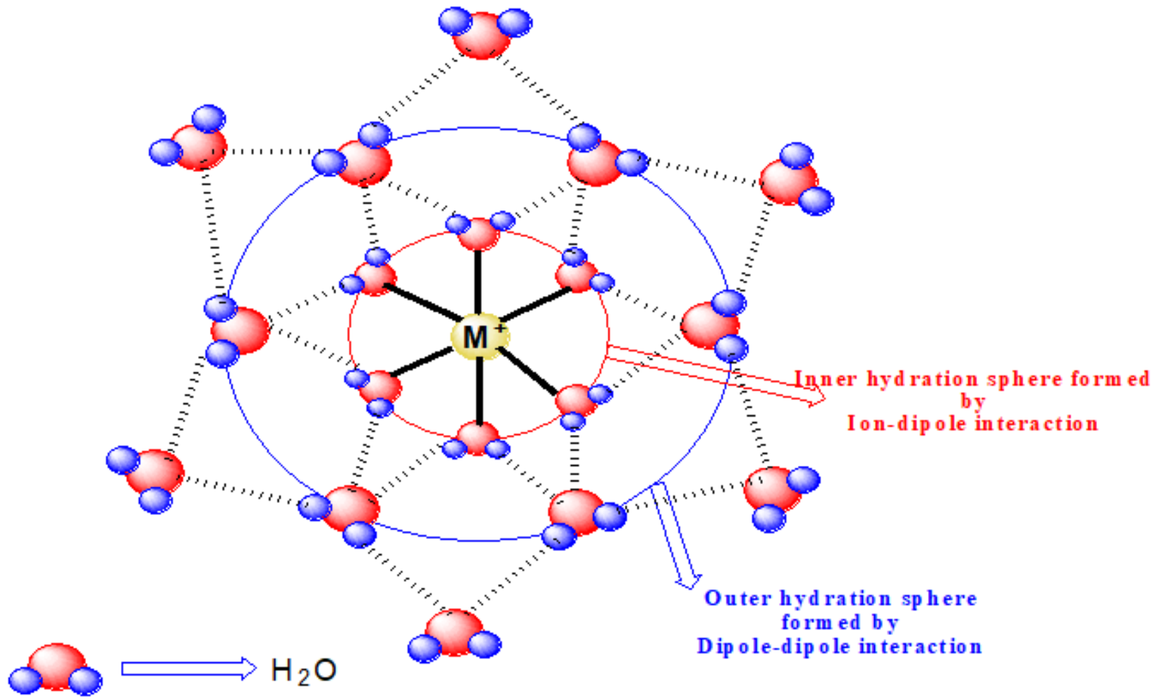
The amount of energy released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution in the process.

$$M_{(g)}^{2+} + \text{excess } H_2O \qquad [M(H_2O)_6]^{2+}$$

Higher the charge on the ions and smaller the size, more exothermic will be the hydration energy. So it is expected to increase smoothly on going from left to right of the transition metals (**green line in the graph**)



The heats of hydration show two "humps" consistent with the expected CFSE for the metal ions. The values for d5 and d10 are the same as expected with a CFSE equal to 0.



In the case of alkali and alkaline metal ions the enthalpy of hydration

$\Delta_{hyd}H = E_{Inner} + E_{Outer}$

In the case of transition metal ions the enthalpy of hydration due to formation of octahedral complex

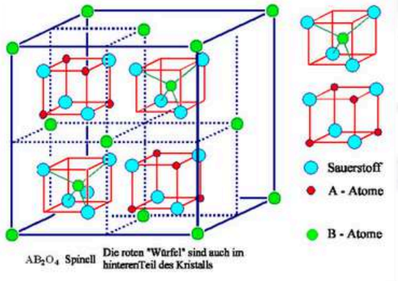
$\Delta_{hyd}H = E_{Inner} + E_{Outer} + CFSE$

Site preference of Spinels and Inverse Spinels

Spinels are a class of crystalline solids of the general formula AB_2O_4 ($A^{II}B^{III}{}_2O_4$) where

A = Main group (Group IIA) Or transition metal ion in the +2 oxidation state	B= main group (Group IIIA) Or transition metal ion in the +3 oxidation state

The weak field oxide ions provide a cubic close-packed lattice.
In one unit cell of AB_2O_4 there are 8 tetrahedral and 4 octahedral holes



If A and B of AB_2O_4 are both s or p block elements (e.g. $MgAl_2O_4$) it always show Spinel structure.

$Mn_3O_4 = Mn^{II}Mn^{III}_2O_4$

O^{2-} = a weak field ligand

$Mn^{2+} = d^5$ HS : CFSE = 0

$Mn^{3+} = d^4$ HS : CFSE = $-0.6\ \Delta_o$

Mn^{2+} by exchanging positions with Mn^{3+} in an octahedral hole is not going to gain any extra crystal field stabilization energy. While Mn^{3+} by being in the octahedral hole will have CFSE.

Therefore Mn_3O_4 will be Normal Spinel

$Fe_3O_4 = Fe^{II}Fe^{III}_2O_4$

O^{2-} = a weak field ligand

$Fe^{2+} = d^6$ HS : CFSE = $-0.4\ \Delta_o$

$Fe^{3+} = d^5$ HS: CFSE = 0

Fe^{2+} by exchanging positions with Fe^{3+} to an octahedral hole is going to gain extra crystal field stabilization energy. While Fe^{3+} by being in the octahedral hole will not have any CFSE.

Therefore Fe_3O_4 will be Inverse Spinel

$$Mn_3O_4 \longrightarrow \overset{(II)}{Mn}\overset{(III)}{Mn_2}O_4$$

O^{2-} behaves as a weak ligand.

Octahedral	Tetrahedral
$Mn^{2+}(d^5)\ t_{2g}^3\ e_g^2$	$e^2\ t_2^3$
$CFSE = [-0.4 \times 3 + 0.6 \times 2]\Delta_o$ $= 0$	$CFSE = [-0.27 \times 2 + 0.18 \times 3]\Delta_o$ $= 0$

Octahedral	Tetrahedral
$Mn^{3+}(d^4)\ t_{2g}^3\ e_g^1$	$e^2\ t_2^2$
$CFSE = [-0.4 \times 3 + 0.6 \times 1]\Delta_o$ $= -0.6\Delta_o$	$CFSE = [-0.27 \times 2 + 0.18 \times 2]\Delta_o$ $= -0.18\Delta_0$

$$Fe_3O_4 \longrightarrow \overset{(II)}{Fe}\overset{(III)}{Fe_2}O_4$$

O^{2-} behaves as a weak ligand.

Octahedral	Tetrahedral
$Fe^{2+}(d^6)\ t_{2g}^4\ e_g^2$	$e^3\ t_2^3$
$CFSE = [-0.4 \times 4 + 0.6 \times 2]\Delta_o$ $= -0.4\Delta_o$	$CFSE = [-0.27 \times 3 + 0.18 \times 3]\Delta_o$ $= -0.27\Delta_o$

Octahedral	Tetrahedral
$Fe^{3+}(d^5)\ t_{2g}^3\ e_g^2$	$e^2\ t_2^3$
$CFSE = [-0.4 \times 3 + 0.6 \times 2]\Delta_o$ $= 0$	$CFSE = [-0.27 \times 2 + 0.18 \times 3]\Delta_o$ $= 0$

Co_3O_4 always form Normal spinel

$$Co_3O_4 \longrightarrow \overset{(II)}{Co}\overset{(III)}{Co_2}O_4$$

Co^{3+} is low spin in the field produced by oxide ions.

Octahedral	Tetrahedral
$Co^{3+}(d^6)\ t_{2g}^6\ e_g^0$	$e^3\ t_2^3$
$CFSE = [-0.6 \times 4 + 0.6 \times 0]\Delta_o$ $= -2.4\Delta_o$	$CFSE = [-0.27 \times 3 + 0.18 \times 3]\Delta_o$ $= [-0.81 + 0.54]\Delta_o$ $= -0.27\Delta_o$

Octahedral	Tetrahedral
$Co^{2+}(d^7)\ t_{2g}^5\ e_g^2$	$e^4\ t_2^3$
$CFSE = [-0.4 \times 5 + 0.6 \times 2]\Delta_o$ $= -0.8\Delta_o$	$CFSE = [-0.27 \times 4 + 0.18 \times 3]\Delta_o$ $= -0.54\Delta_o$

ADVANTAGES OF CRYSTAL FIELD THEORY

1. Explains colors of complexes.
2. Explains magnetic properties of complexes (without knowing hybridization) and temperature dependence of magnetic moments.
3. Classifies ligands as weak and strong.
4. Explains anomalies in physical properties of metal complexes.
5. Explains distortion in shape observed for some metal complexes.

DISADVANTAGES OF CRYSTAL FIELD THEORY

1. Evidences for the presence of covalent bonding (orbital overlap) in metal complexeshave been disregarded.
2. Cannot predict shape of complexes (since not based on hybridization).
3. Charge Transfer spectra not explained by CFT alone.

UNIT - 5 | PAPER - 2

VALENCE BOND THEORY (VBT)

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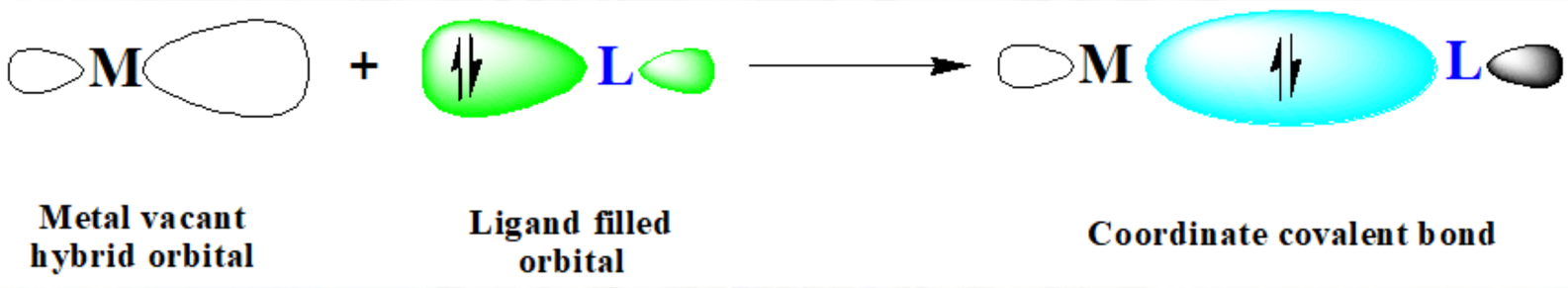
THEORIES FOR METAL - LIGAND BONDING IN COMPLEXES

There are three theories to explain the nature of bonding in transition metal complexes

1. Valence Bond Theory (VBT)
2. Crystal Field Theory (CFT)
3. Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT)

VALENCE BOND THEORY (VBT)

- The central metal ion or atom provides vacant hybrid orbitals of equivalent energy.
- The bonding in metal complexes arises when a filled ligand orbital overlaps with vacant hybrid orbital of metal ion or atom to form a coordinate covalent bond.



- The magnetic moment (i.e. number of unpaired electrons) and the coordination number of the metal cation or atom decide the hybridization and geometry of the complex.

The ligands are classified into two categories
(i) Strong ligands like CN-, CO etc.
(ii) Weak ligands like F-, Cl-, oxygen containing ligands.

Strong ligands have tendency to pair up the d-electrons of metal ion or atom. Other the other hand, weak ligands do not have the tendency to pair up the d-electrons.

The bond formed between metal and strong ligands is considered to be covalent whereas with weak ligands it forms ionic bond.

In Octahedral complexes, the metal ion is either d^2sp^3 or sp^3d^2 hybridized. The d-orbitals involved in d^2sp^3 hybridization belong to the inner shell i.e. (n-1) d-orbital and these complexes are called as inner orbital complexes and are more stable. The d-orbitals involved in sp^3d^2 hybridization belong to the outer most shell i.e. n d-orbital and these complexes are called as outer orbital complexes and are less stable.

The complexes having one or more unpaired electrons are paramagnetic and the complexes having only paired electrons are diamagnetic.

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} \quad \text{BM}$$

n = Number of unpaired electrons

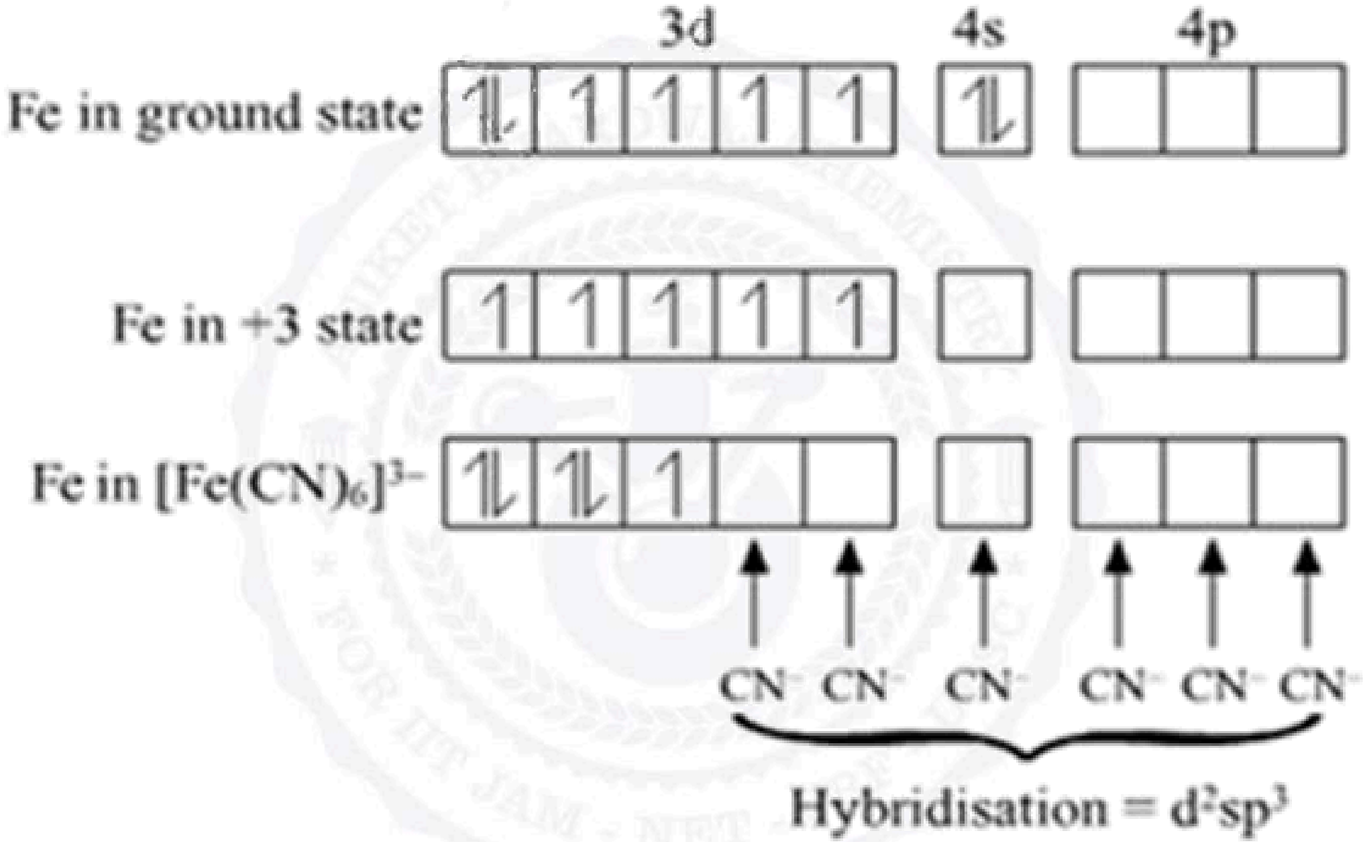
Coordination number	Type of hybridization	Geometry
2	sp	Linear
4	sp^3	Tetrahedral
4	dsp^2	Square planar
6	d^2sp^3	Octahedral (Inner orbital)
6	sp^3d^2	Octahedral (Outer orbital)

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} \quad \text{BM}$$

n = Number of unpaired electrons

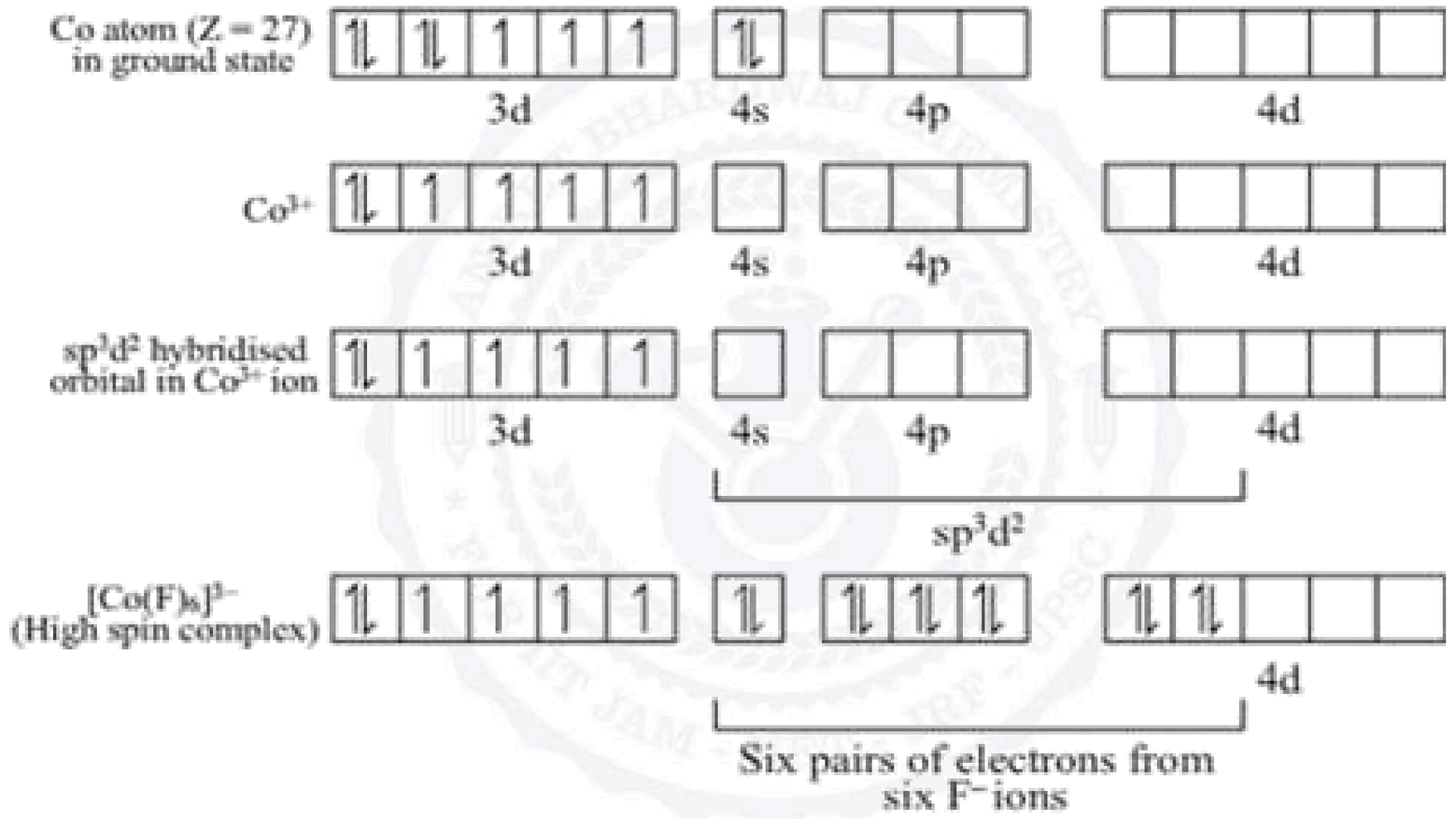
Coordination number	Type of hybridization	Geometry
2	sp	Linear
4	sp^3	Tetrahedral
4	dsp^2	Square planar
6	d^2sp^3	Octahedral (Inner orbital)
6	sp^3d^2	Octahedral (Outer orbital)

$[Fe(CN)_6]^{3-}$ complex



Inner orbital paramagnetic octahedral complex

$[Co(F)_6]^{3-}$ complex



Outer orbital paramagnetic octahedral complex

LIMITATIONS OF VBT

- It could not explain the nature of ligands i.e. which ligand is strong and weak.
- It could not explain why the pairing of electrons occurs in the presence of strong ligands.
- It could not explain the effect of temperature on magnetic moment and also it could not explain why the experimental value of magnetic moment is greater than the calculated in some complexes.
- It could not explain the distortion in some octahedral complexes.
- It fails to explain the color and electronic spectra of complexes.
- It fails to explain reaction rates and mechanism of reactions of complexes.
- It fails to explain why some complexes are high spin and others are low spin.

UNIT - 5 | PAPER - 2

LIGAND FIELD THEORY (LFT)

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INTRODUCTION

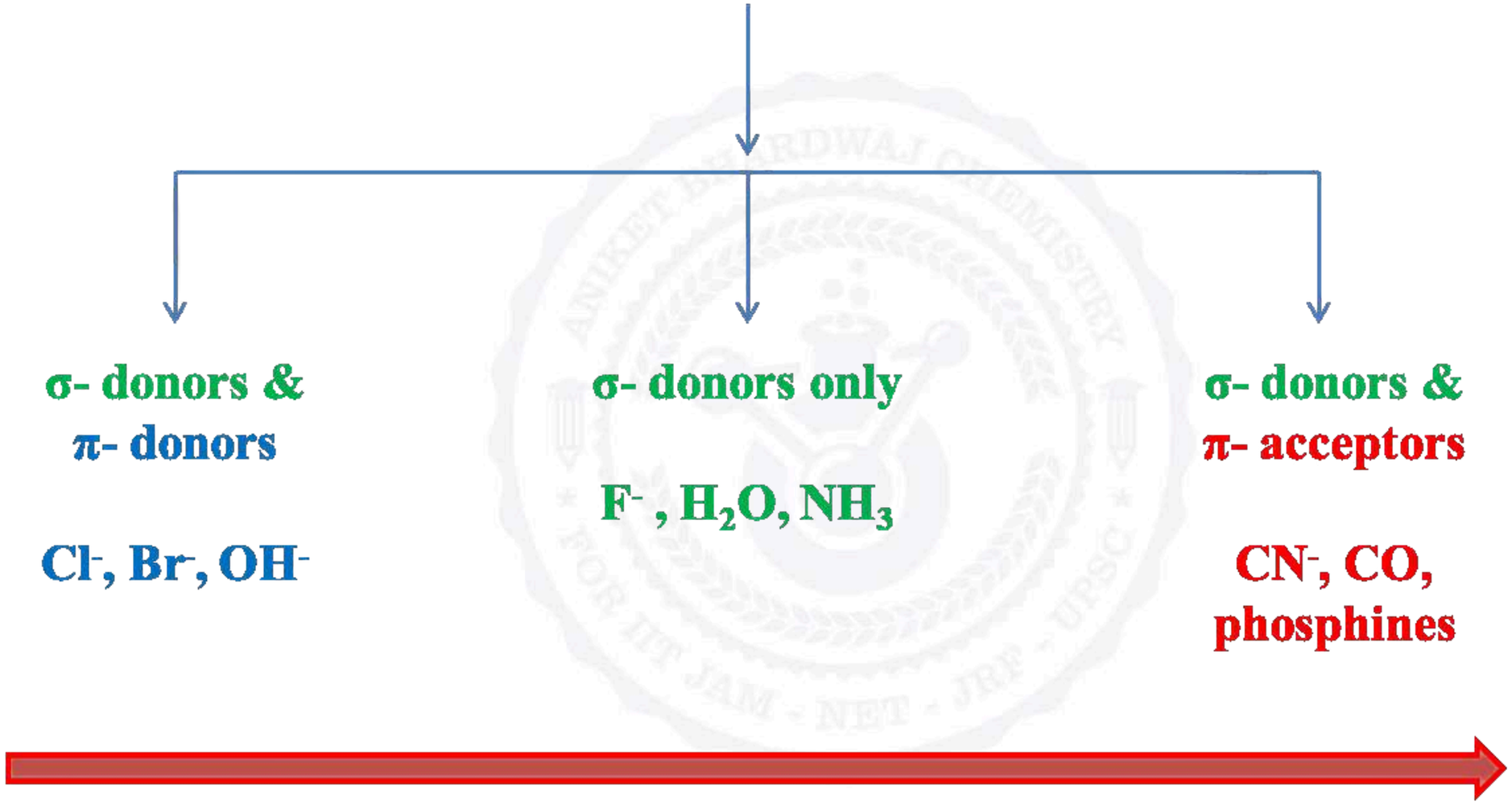
The physical measurements such as electron spin resonance (ESR), nuclear magnetic resonance (NMR), nuclear quadrpole resonance (NQR) and Racah parameters calculations from electronic spectra give evidence in favor of covalent bonding in coordination compounds.

Crystal field theory (CFT) only includes ionic interactions whereas Molecular orbital theory (MOT) developed and applied only to non metal compounds.

But ligand field theory combines both to explain bonding in transition metal coordination compounds.

According to LFT, the covalent bonds between metal and ligands are formed by the linear combination of the metal atomic orbitals (AOs) and ligand group orbitals (LGOs).

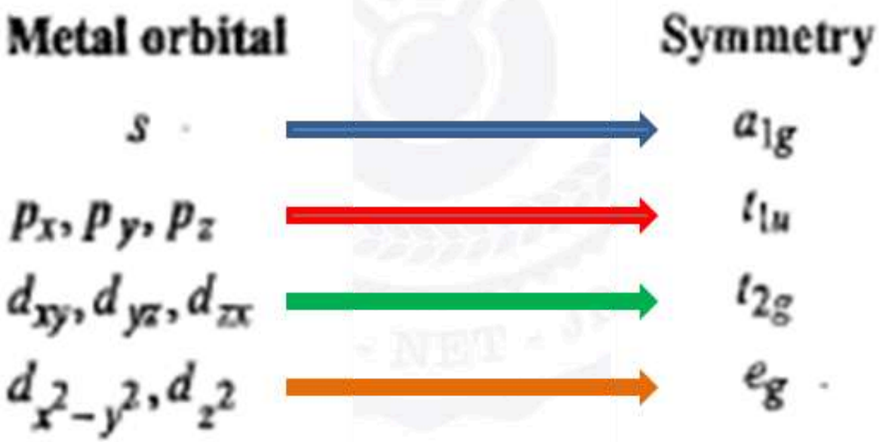
The symmetries of LGOs must match the symmetries of the metal AOs for positive overlapping.



SIGMA BONDING IN OCTAHEDRAL COMPLEXES

In octahedral complexes, the ligands approach the metal cation along x-, y- and z-axes. Therefore, LGOs will overlap with metal orbitals orienting along the axes to form sigma bonds.

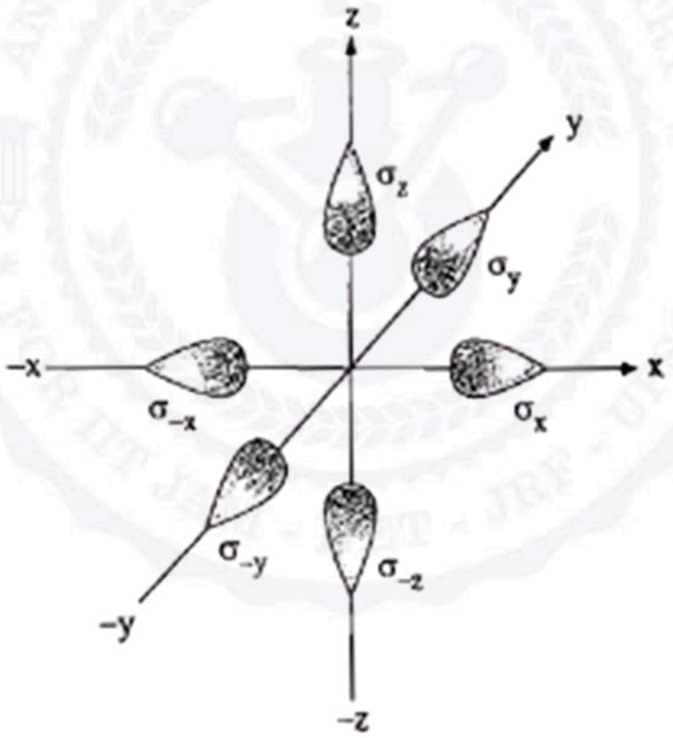
The metal ion has one ns, three np and five (n-1) d-rbitals with following symmetries.

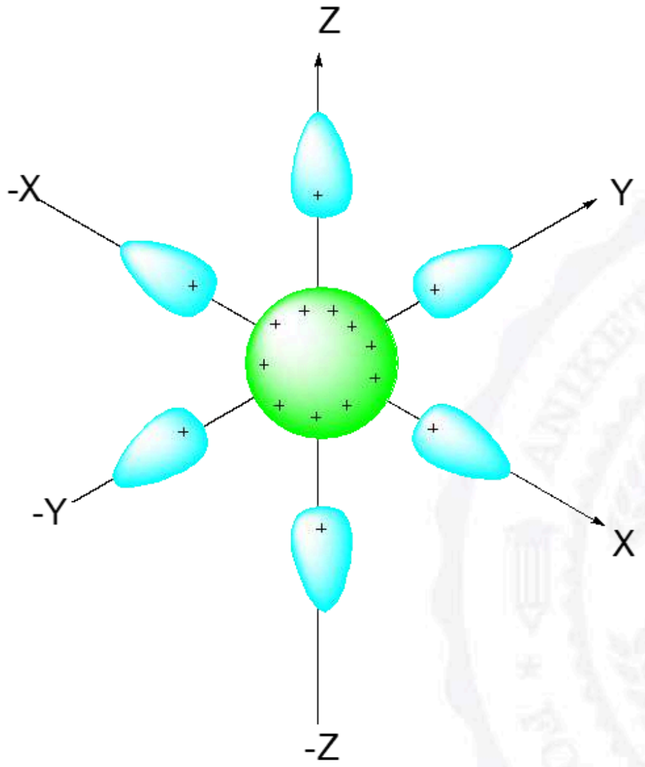


Since a_{1g} orbital is spherical in shape therefore, it can overlap with LGOs on all axes.

The t_{1u} and e_g point along the axes can form sigma bonds overlapping with LGOs.

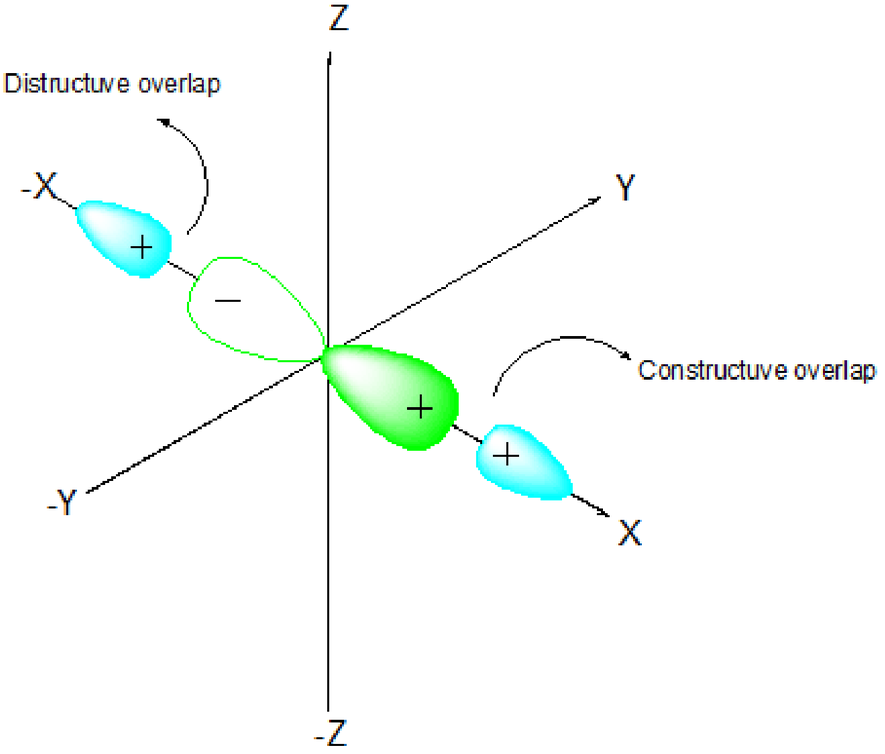
The t_{2g} orbitals lie in between the axes, hence these orbitals are not capable to overlap with LGOs to form sigma bonds.





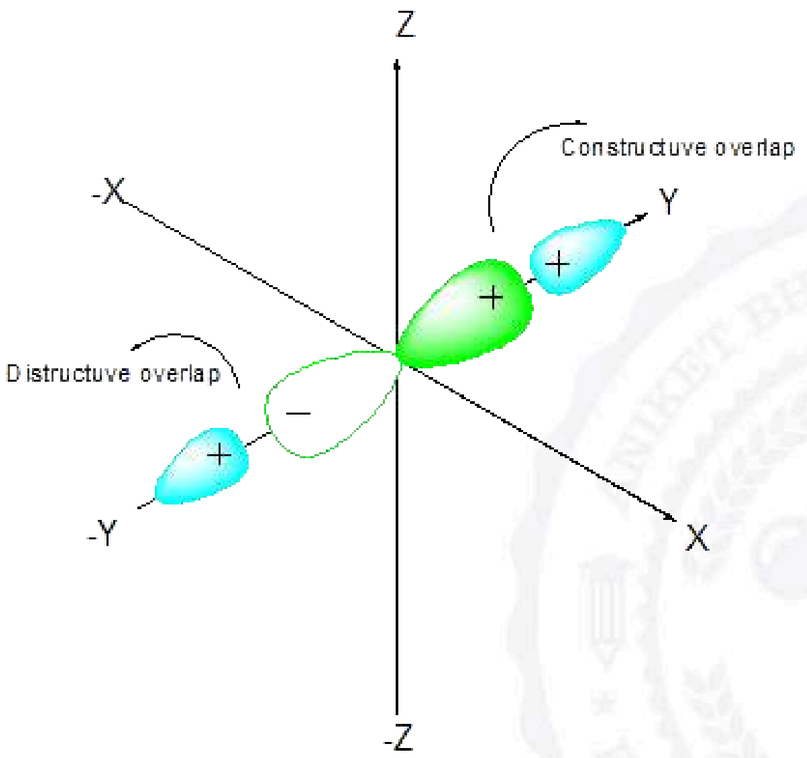
S – orbital of metal overlap with LGOs with a_{1g} symmetry

$$\Sigma_{a_{1g}} = \frac{1}{\sqrt{6}} (\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})] \quad a_{1g}$$



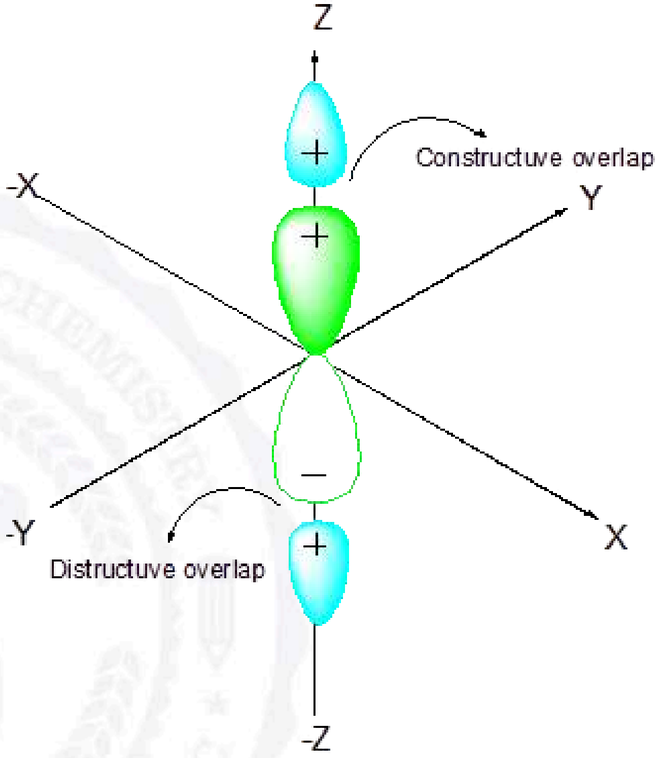
p_x – orbital of metal overlap with LGOs with t_{1u} symmetry

$$\Sigma_x = \frac{!}{\sqrt{2}} (\sigma_x - \sigma_{-x})$$



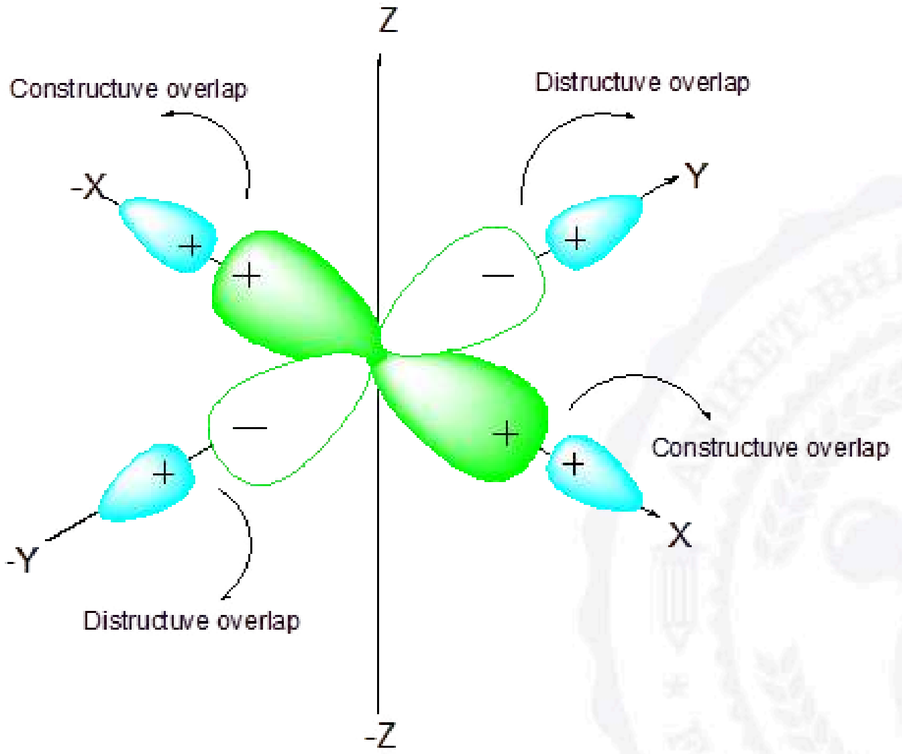
p_y – orbital of metal overlap with LGOs with t_{1u} symmetry

$$\Sigma_y = \frac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$$



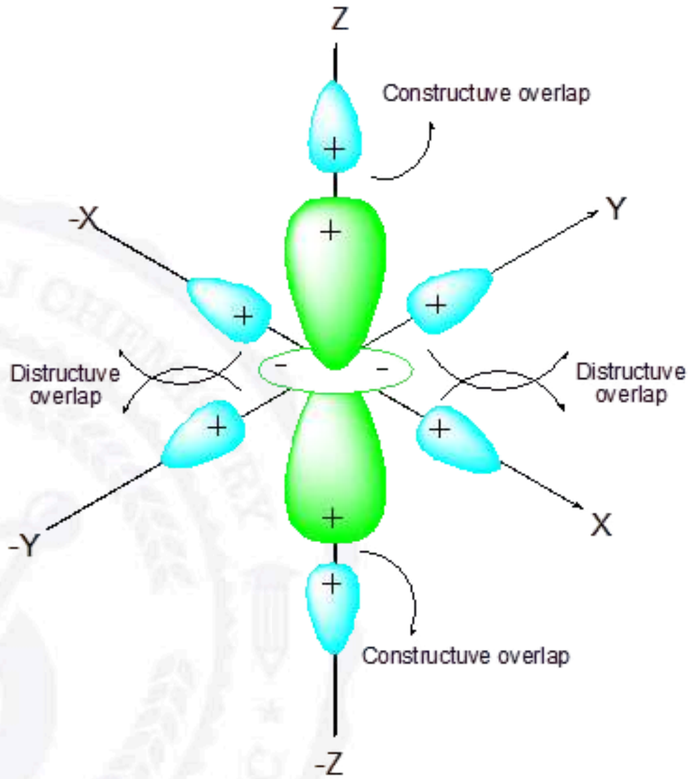
p_z – orbital of metal overlap with LGOs with t_{1u} symmetry

$$\Sigma_z = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$$



$d_{x^2-y^2}$ – orbital of metal overlap with LGOs with e_g symmetry

$$\Sigma_{x^2-y^2} = \frac{1}{2}(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$



d_{z^2} – orbital of metal overlap with LGOs with e_g symmetry

$$\Sigma_{z^2} = \frac{1}{2\sqrt{3}}(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$$

s – orbital of metal overlap with LGOs with a_{1g} symmetry to give
One bonding a_{1g} and one anti-bonding a_{1g}* molecular orbitals

Three degenerate p_x , p_y , p_z – orbitals of metal overlap with LGOs with t_{1u} symmetry to give
three degenerate bonding t_{1u} and three degenerate anti-bonding t_{1u}* molecular orbitals

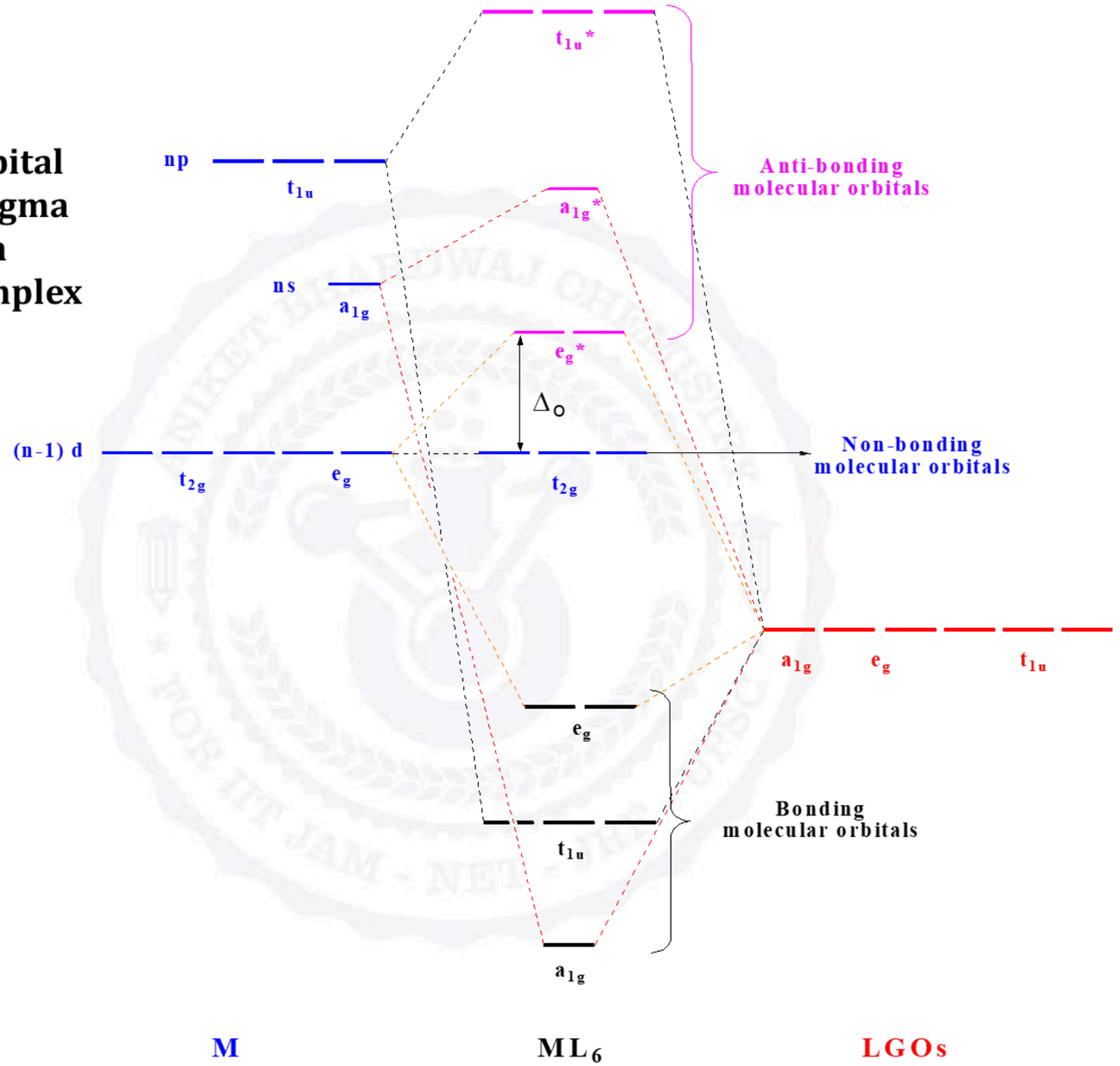
Doubly degenerate e_g set of orbitals of metal overlap with LGOs with e_g symmetry to give
two degenerate bonding e_g and two degenerate anti-bonding e_g* molecular orbitals

Therefore, there are six bonding and six anti-bonding molecular orbitals along with three degenerte metal t_{2g} orbitals as non bonding orbitals.

In an octahedral complex, there are total of 12 + d^n electrons to be placed in molecular orbitals.

d^n = Number of metal d-electrons

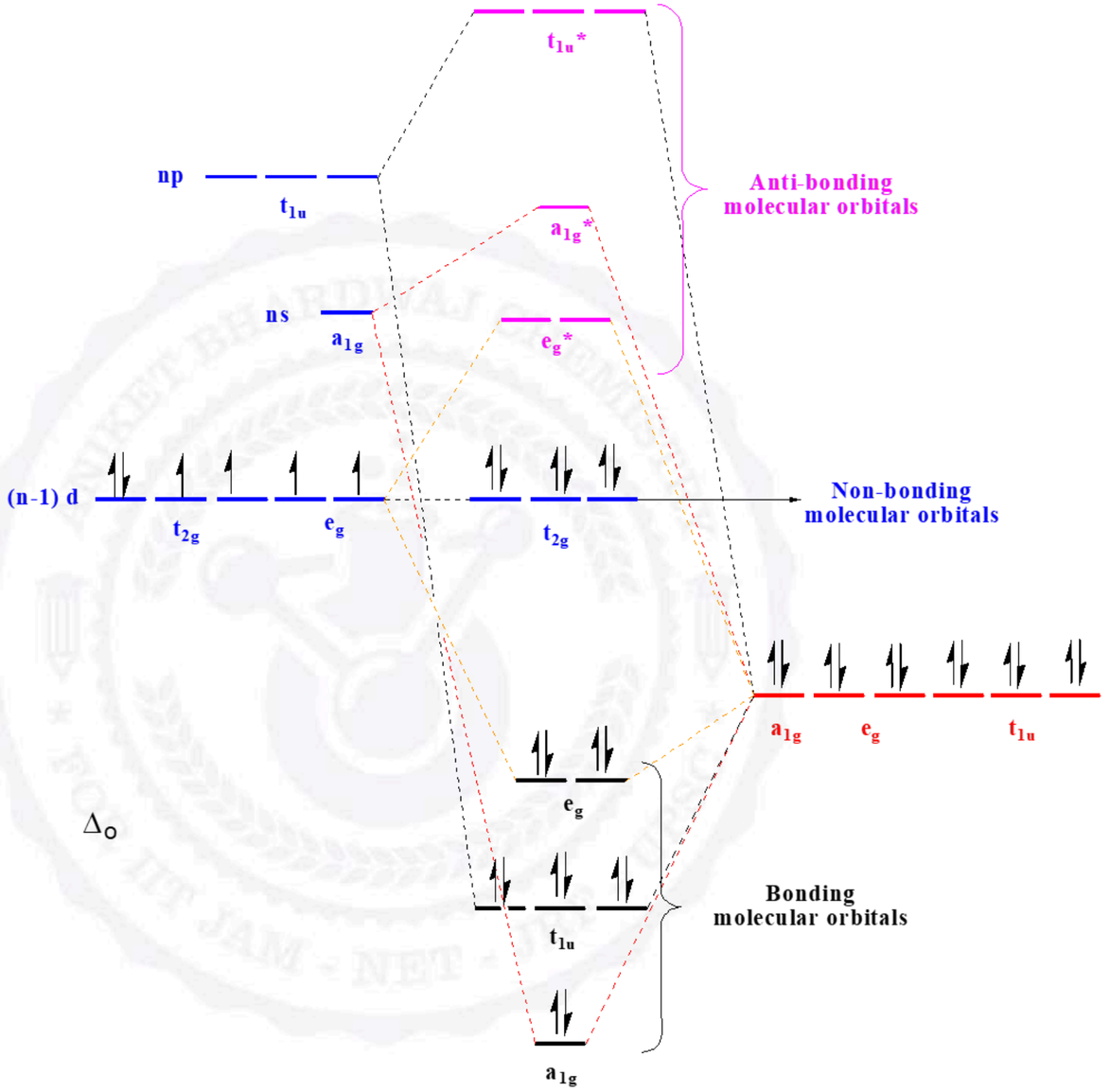
Molecular orbital diagram for sigma bonding in octahedral complex



$[Co(NH_3)_6]^{3+}$

Co^{3+} - d^6

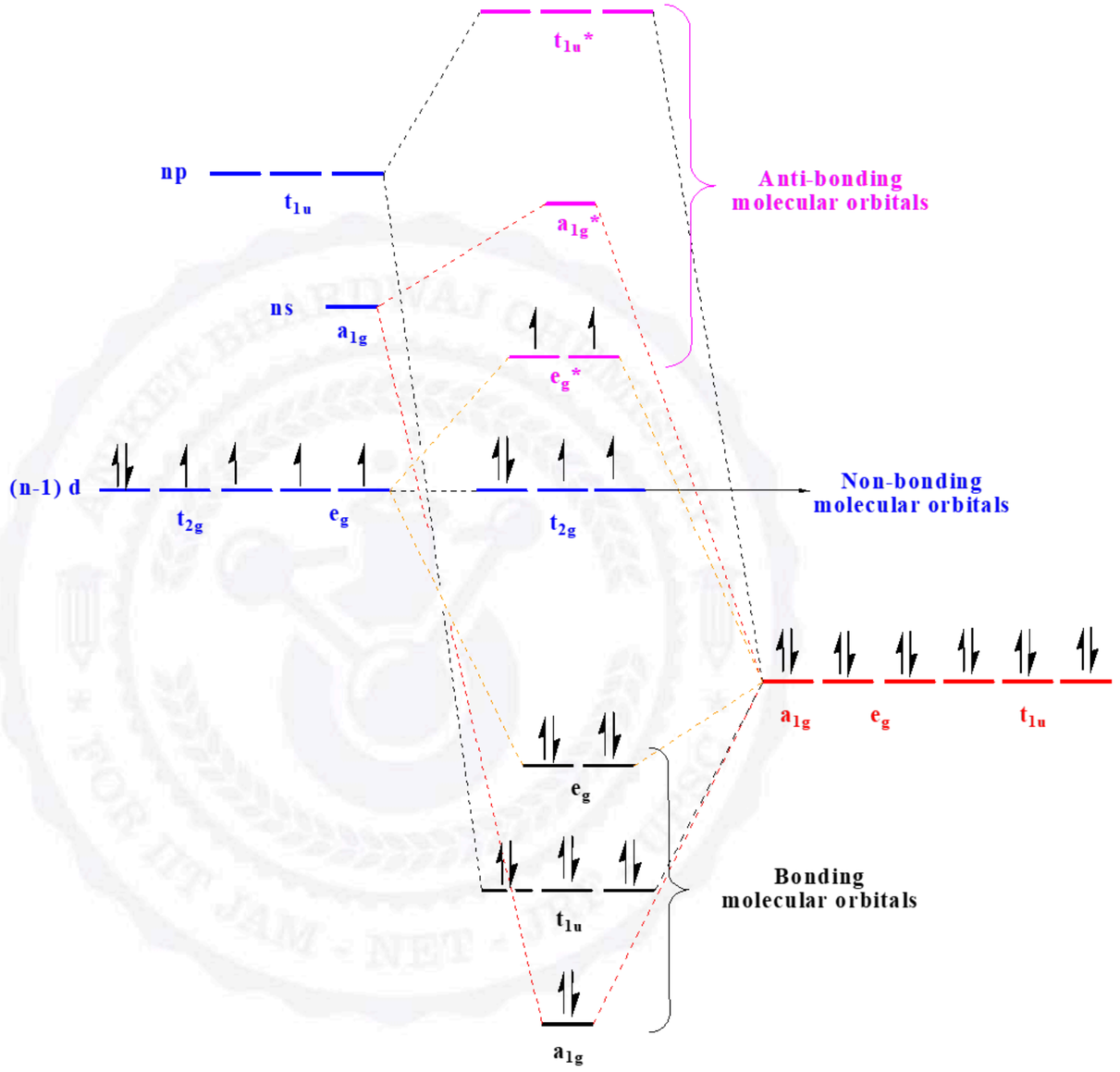
12 + 6 = 18 electrons to be placed in molecular orbitals and it is low spin complex since Δ_o is large



$[Co(F)_6]^{3-}$

Co^{3+} - d^6

12 + 6 = 18 electrons to be placed in molecular orbitals and it is high spin complex since Δ_o is small



PI - BONDING IN OCTAHEDRAL COMPLEXES

In addition to metal ligand sigma interactions, many ligands which have orbitals with π-symmetry with respect to octahedral axes are capable of forming π-bonding interaction with the metal ion.

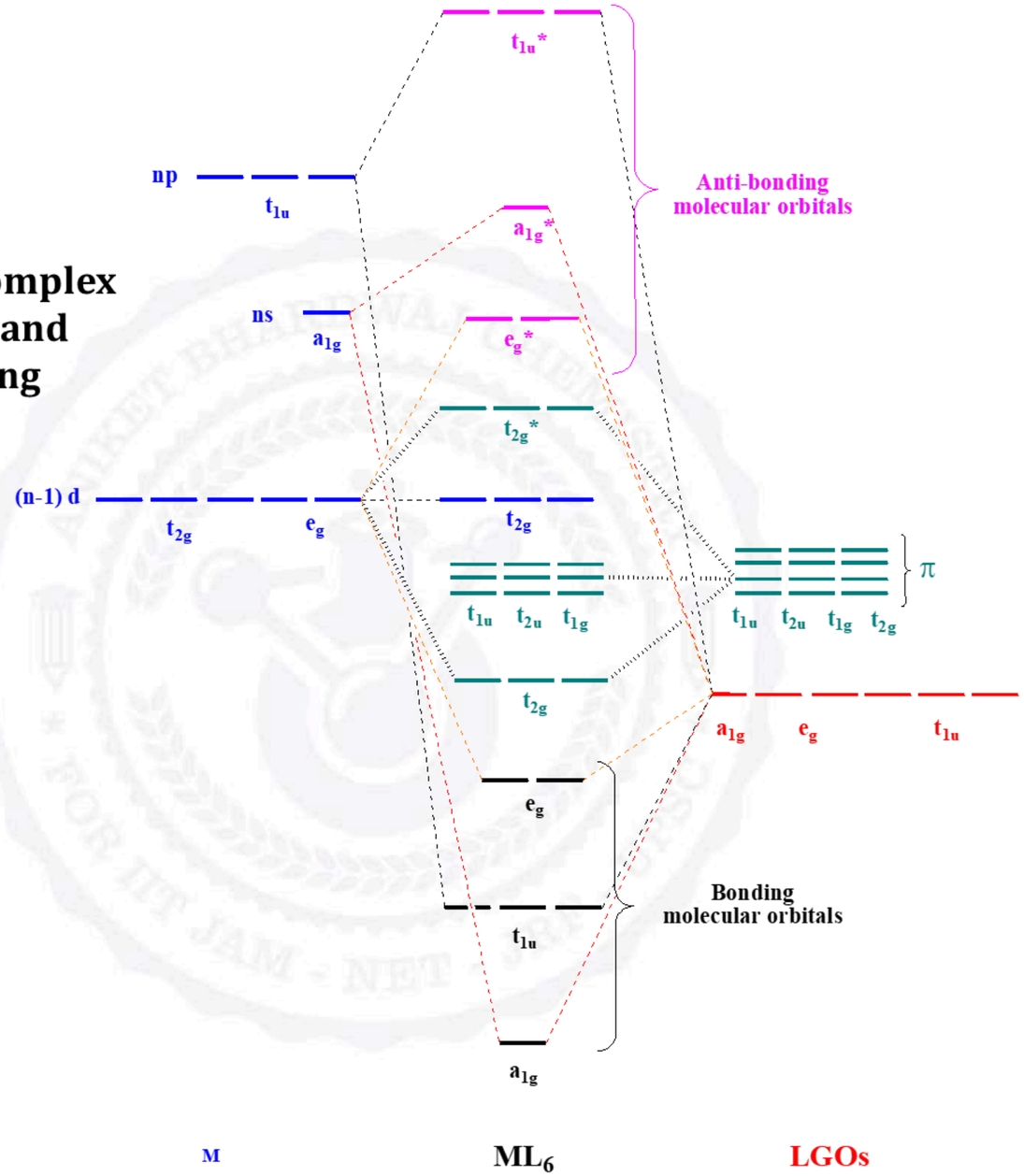
In octahedral complex there are 12 ligand group orbitals capable of π-interactions. These LGOs belongs to four symmetry classes: t_{1g}, t_{2g}, t_{1u} and t_{2u}.

Metal ion in octahedral complex has t_{1u} and t_{2g} symmetry orbitals for π-bonding. The t_{1g} and t_{2u} ligand group orbitals are non bonding because there are no metal orbitals of these symmetries.

Since t_{1u} symmetry orbitals already involved in sigma bonding hence these orbitals are unavailable for π-bonding.

Therefore, t_{2g} LGOs and metal orbital of same symmetry can form three degenerate bonding t_{2g} and three degenerate anti-bonding t_{2g}^* molecular orbitals.

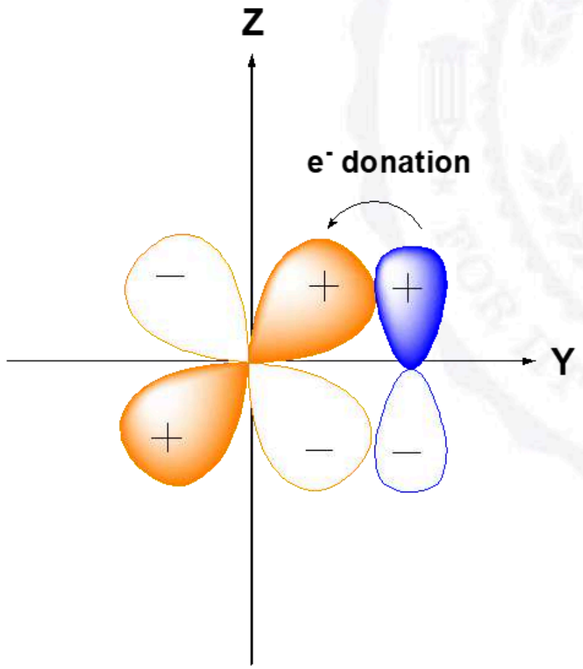
MOT for Oh complex with sigma and Pi - bonding



In octahedral complexes the LGOs corresponding to t_{2g} symmetry may form four types of π- interactions

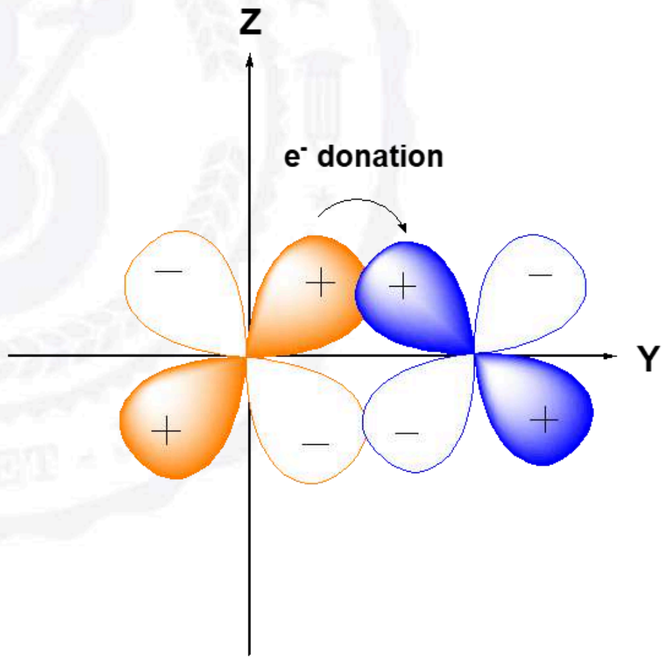
(i) dπ – pπ = are formed by donation of electrons from pπ orbitals of ligands to empty dπ orbitals of the metal.

Example: F^-, Cl^-, Br^-, I^-



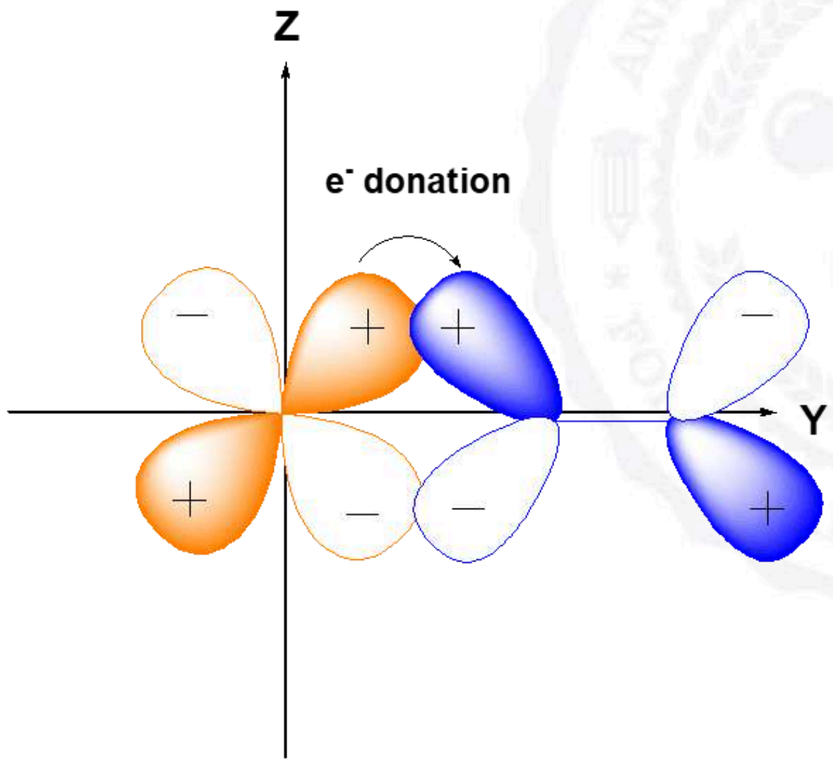
(ii) dπ - d π = formed by overlap of filled d-orbital with empty d-orbital of ligands.

Example: R_3P, R_2S



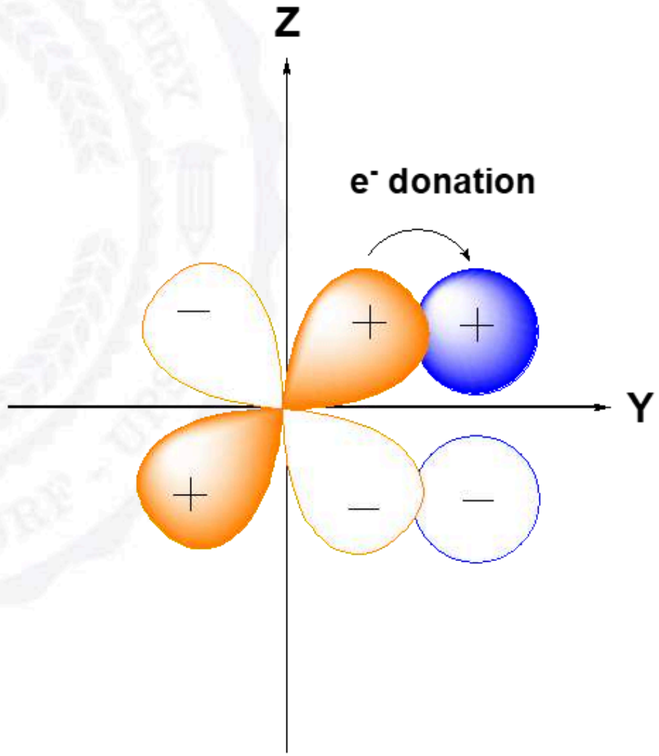
(iii) dπ – π* = formed when filled d-orbital of metal overlap with the empty π* anti-bonding of the ligands.

Example: CO, CN^-

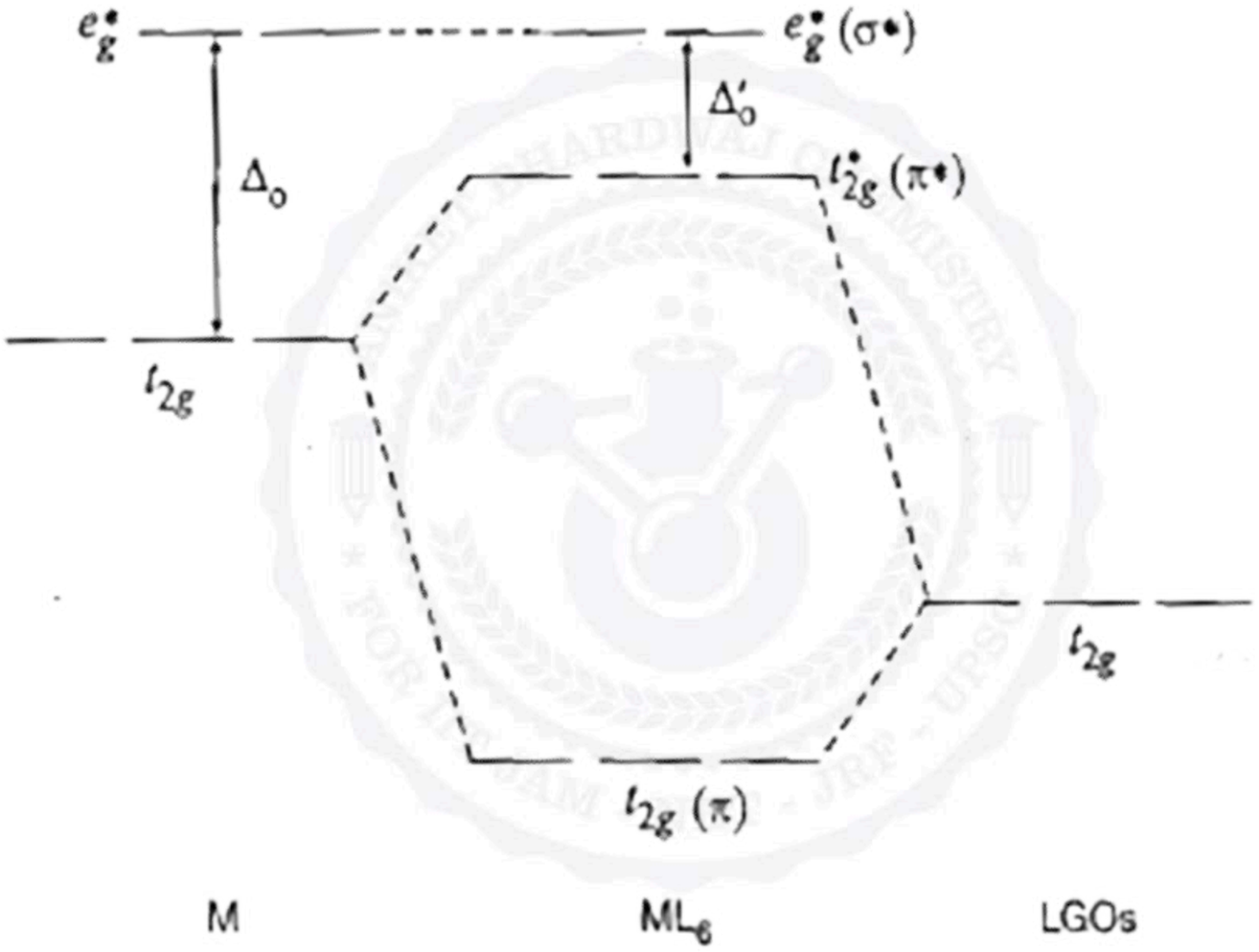


(iv) dπ – σ* = formed when filled d-orbital of metal overlap with the empty σ* anti-bonding of the ligands.

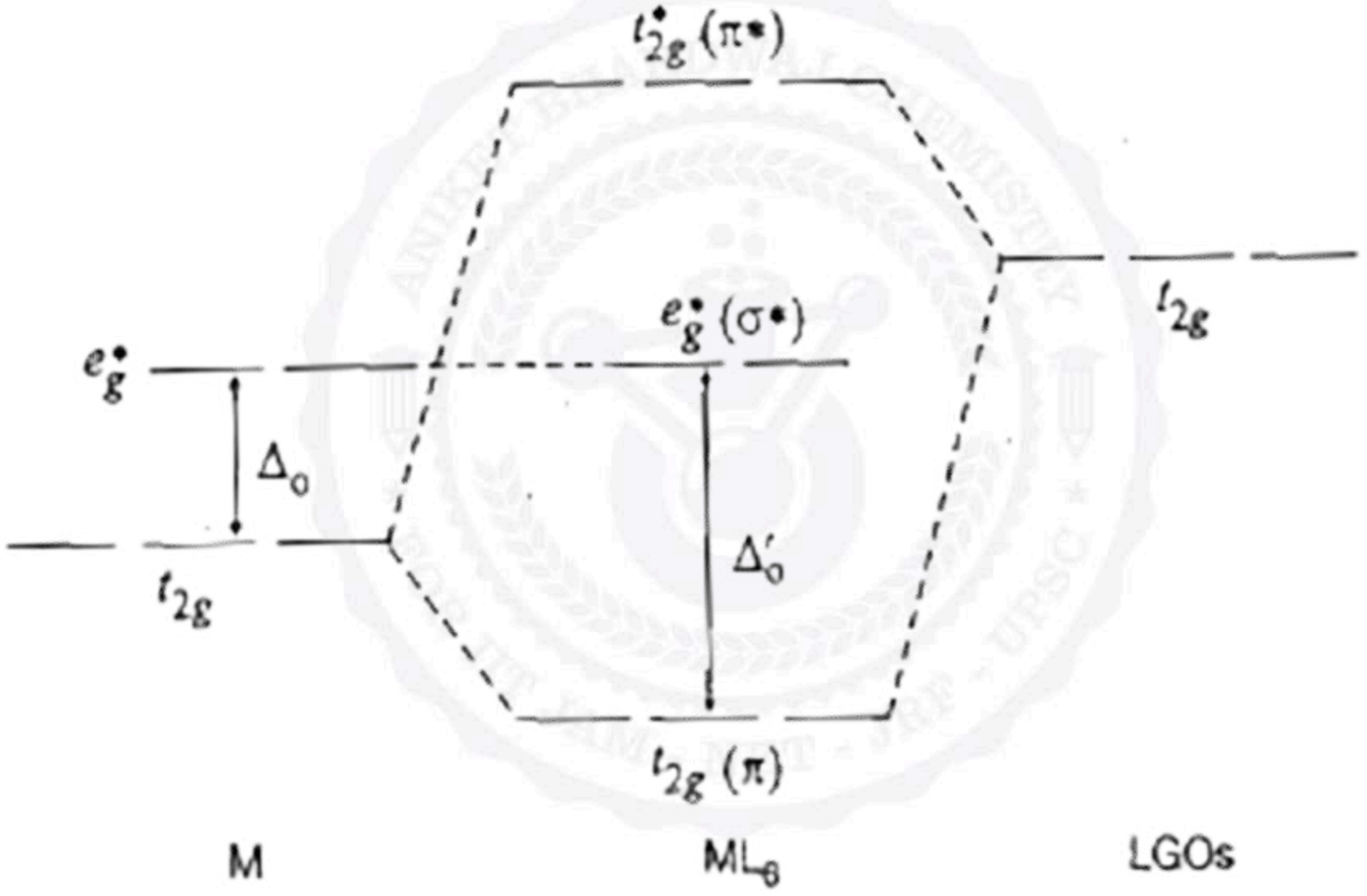
Example: H_2, alkene



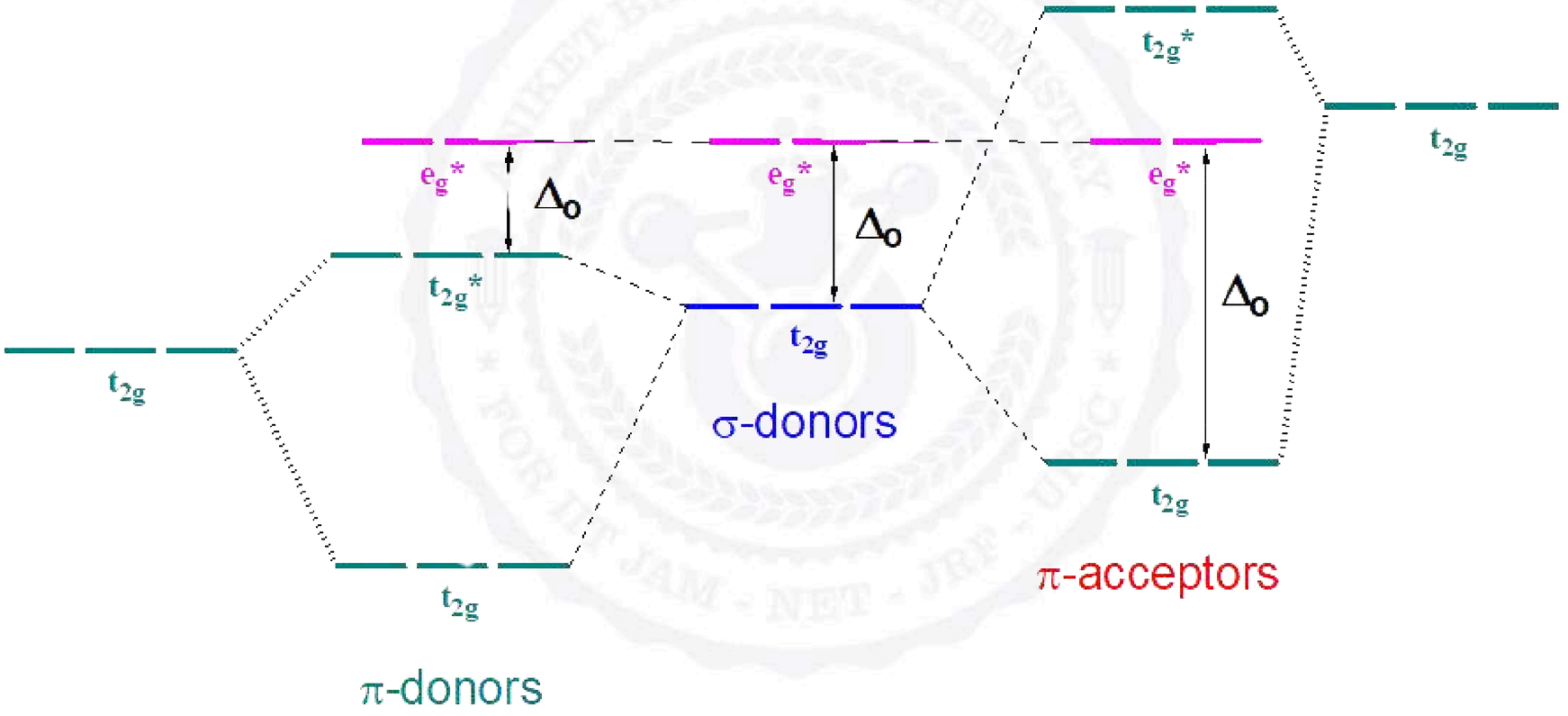
Molecular orbital diagram for pi bonding in octahedral complex with pi-donor ligands



Molecular orbital diagram for pi bonding in octahedral complex with pi-acceptor ligands



Comparison of Molecular orbital diagram for pi bonding in octahedral complex with Pi-donor, sigma-donor and pi-acceptor ligands



SIGMA BONDING IN TETRAHEDRAL COMPLEXES

For a tetrahedral ML_4 complex, the metal s and p-orbitals have a_1 and t_2 symmetries respectively.

The d_{xy}, d_{xz} & d_{yz} orbitals have t_2 and d_z^2 & $d_{x^2-y^2}$ have e symmetry.

Both p-orbitals and d_{xy}, d_{xz} & d_{yz} orbitals have same symmetry i.e. t_2.

It is due to the fact that the p-orbitals hybridized with s-orbitals for sp^3 hybridization and d_{xy}, d_{xz} & d_{yz} orbitals hybridized with s-orbitals form sd^3 hybridization. Both sp^3 and sd^3 have tetrahedral geometry.

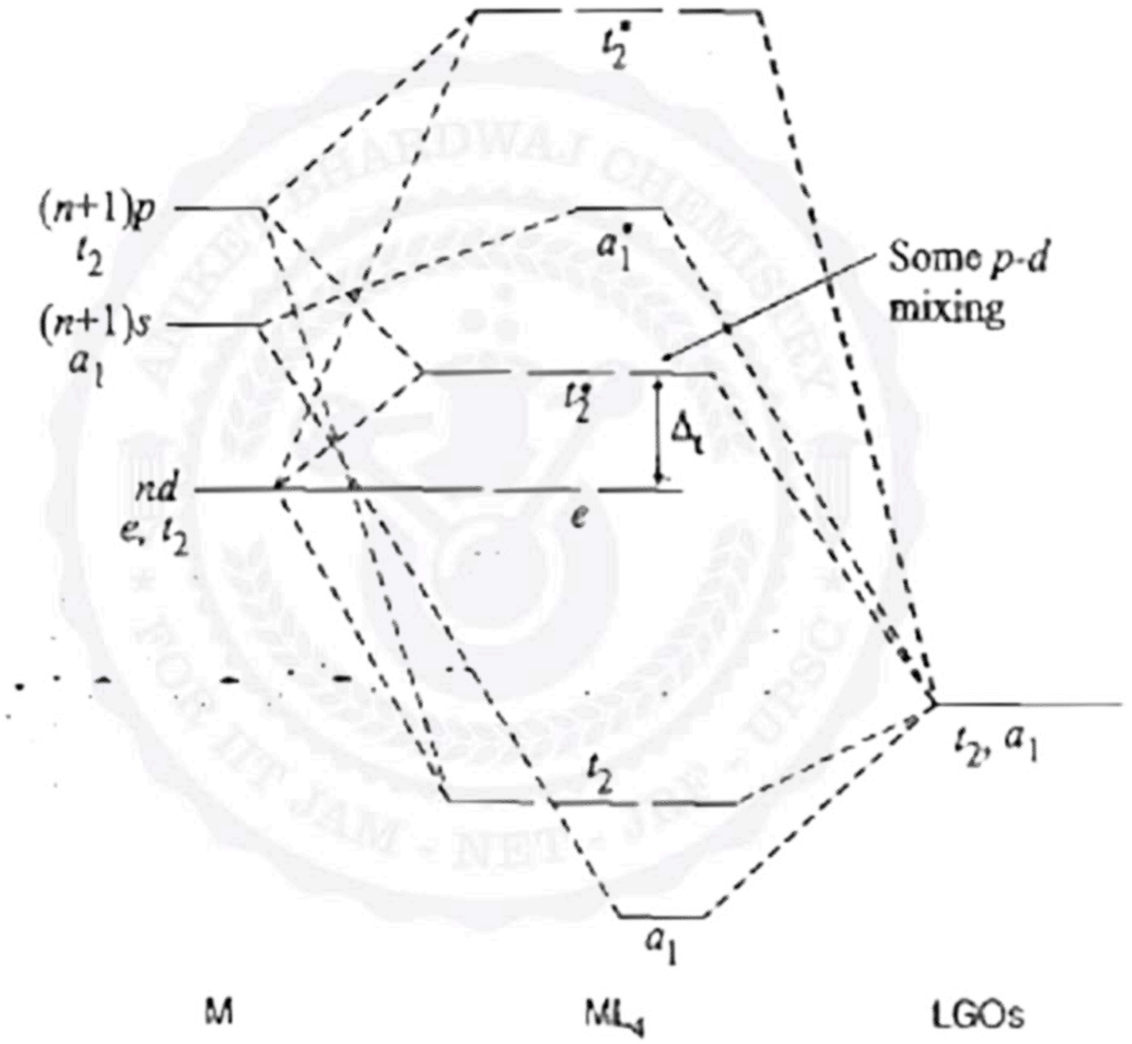
Of the four LGOs, one has a_1 and three have t_2 symmetries.

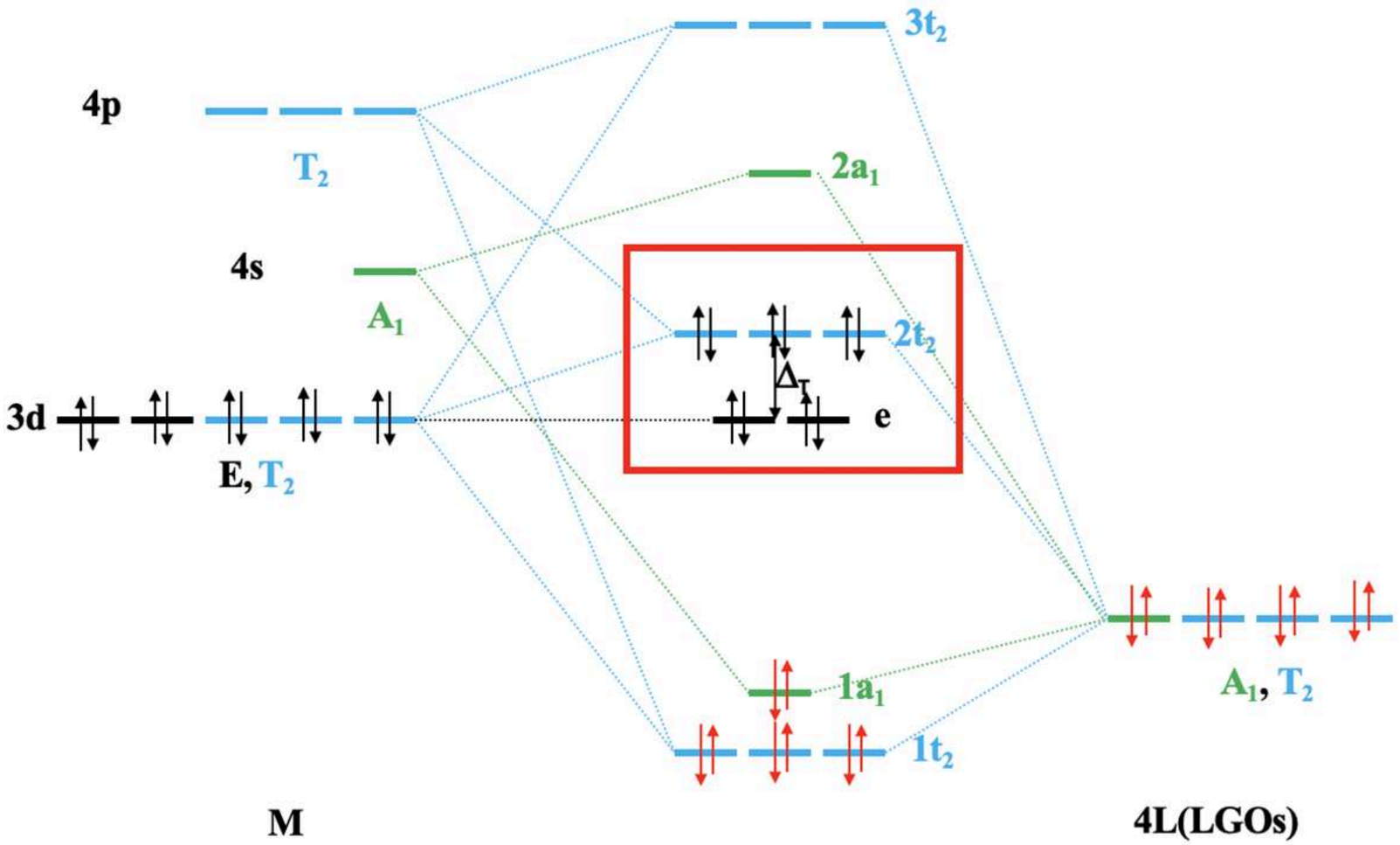
The a_1 symmetry LGO interact with a_1 orbital of metal to give one bonding and one antibonding MO.

t_2 LGOs interact with both sets of metal orbitals (p and d_{xy}, d_{xz} & d_{yz}) to give one bonding and two antibonding Mos.

In tetrahedral complex, the metal e set of orbitals remain as non bonding.

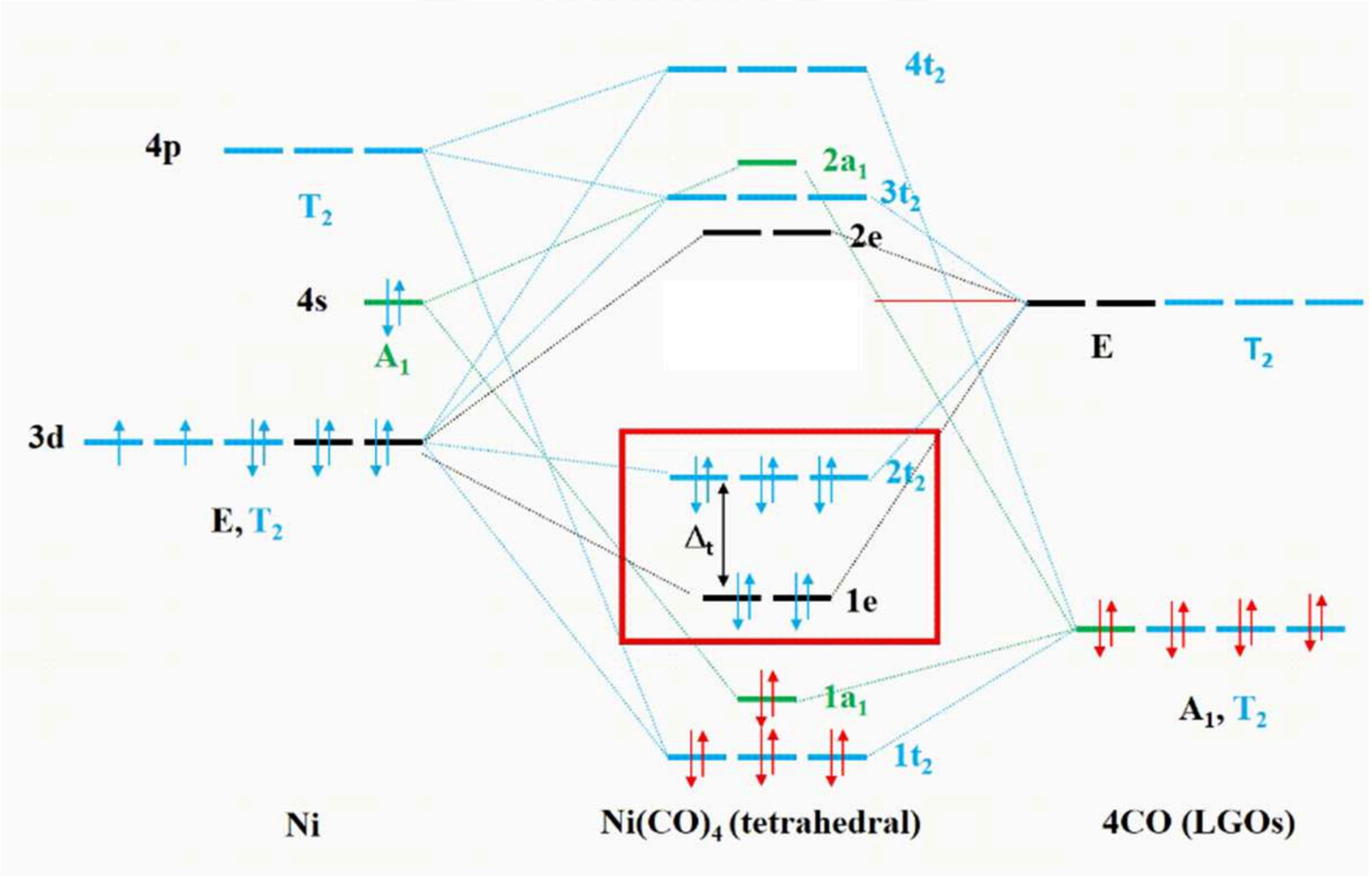
Molecular orbital diagram for sigma bonding in tetrahedral complex



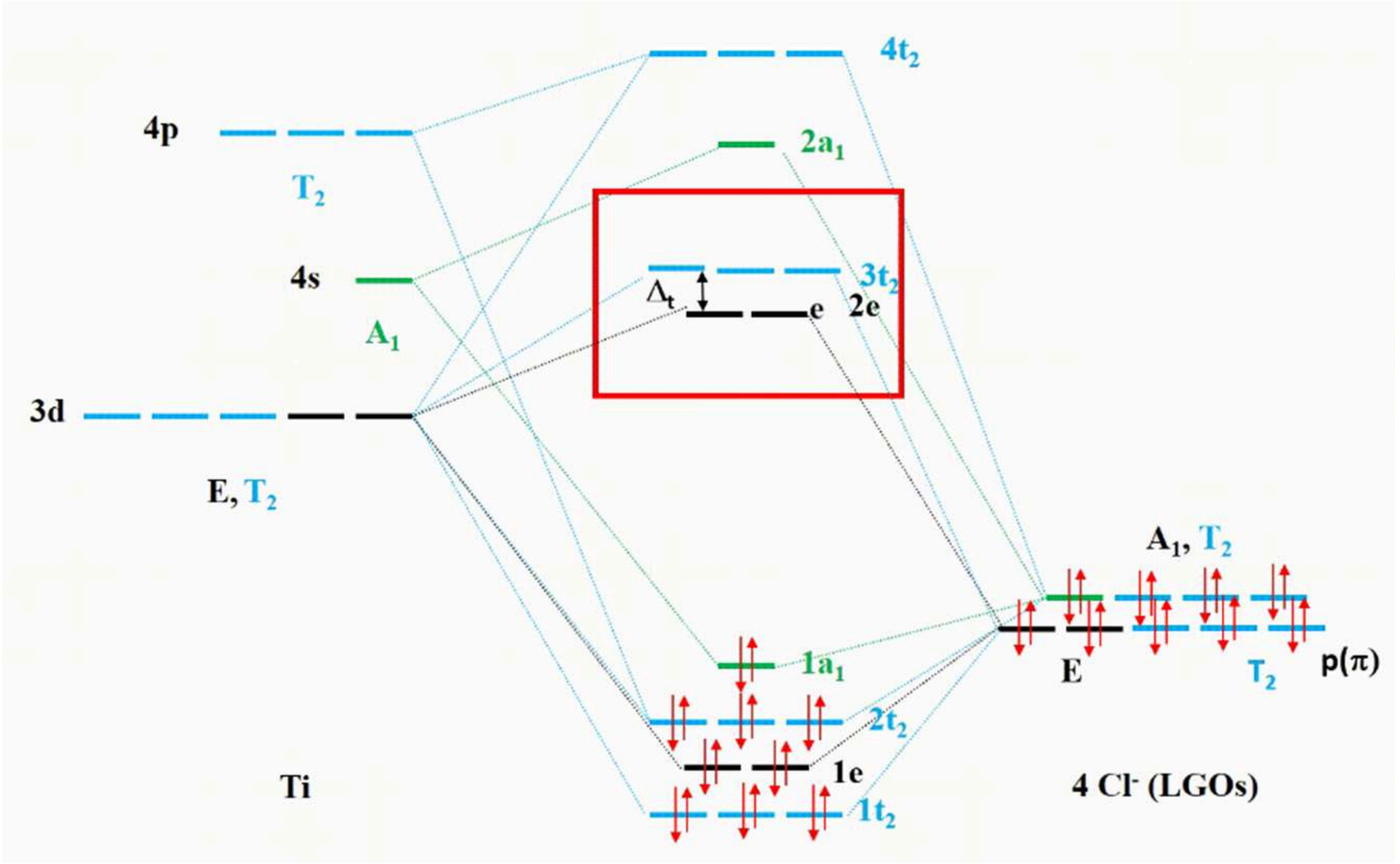


Molecular orbital diagram for pi bonding in tetrahedral complex with pi-acceptor ligand

In tetrahedral complex there are 08 ligand group orbitals capable of π-interactions. These LGOs belongs to three symmetry classes: e, t_1 and t_2.



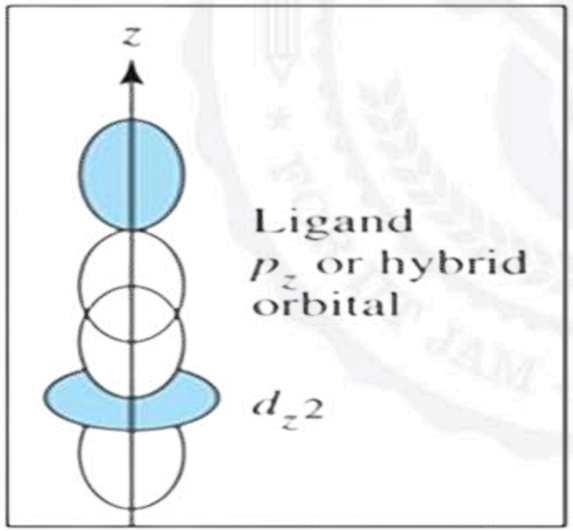
Molecular orbital diagram for pi bonding in tetrahedral complex with pi-donor ligand

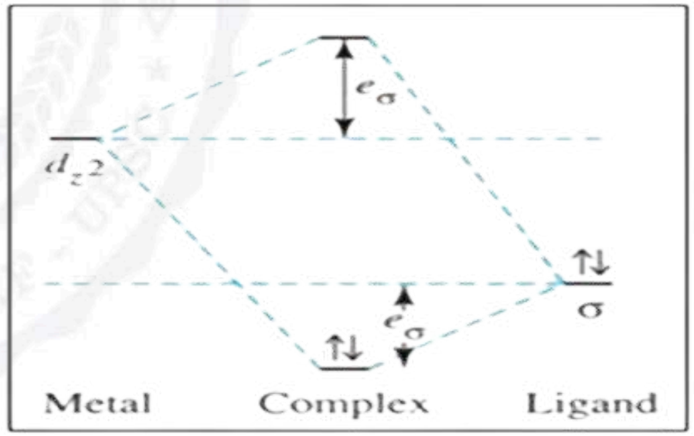


ANGULAR OVERLAP METHOD (AOM)

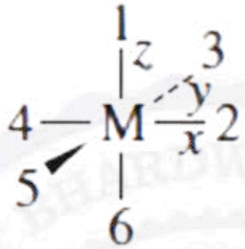
This theory estimates the bonding strength and energies according to the ability of frontiers orbitals from ligands to overlap with the valence d-orbitals of metal.

The main consideration for orbital interactions is the direction / positions of d-orbitals and ligand orbitals in space. That is overlap depends strongly on the angles of the orbitals.





Octahedral Positions

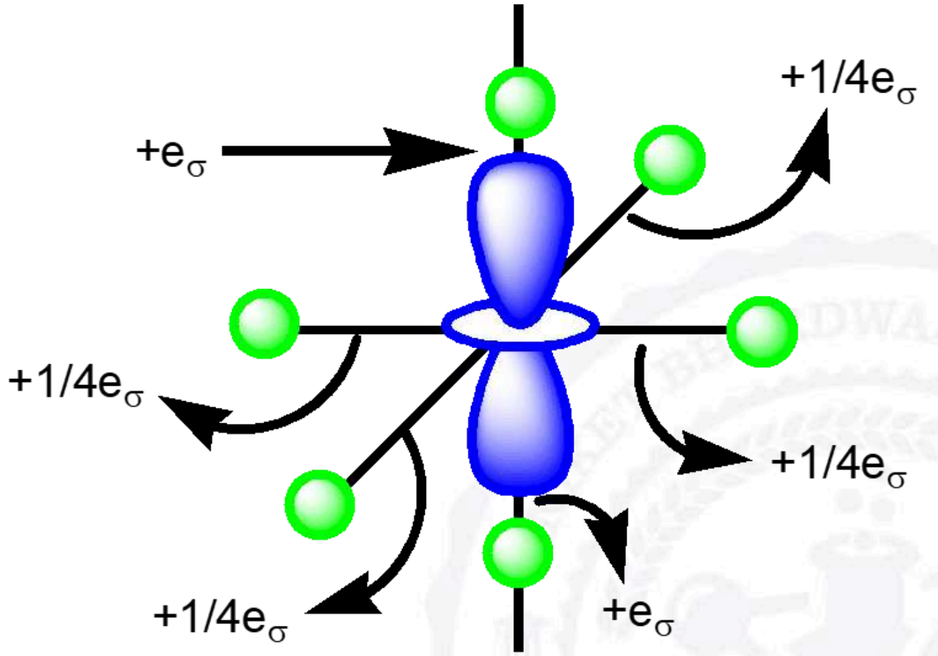


Ligand Positions for Coordination Geometries

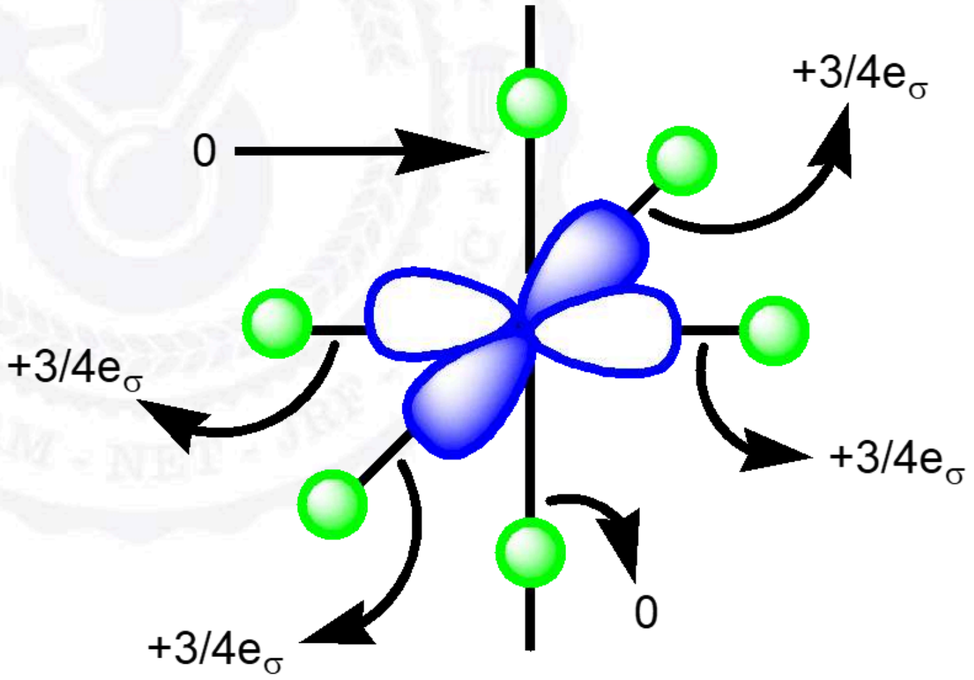
CN	Shape	Positions
6	Octahedral	1, 2, 3, 4, 5, 6

Sigma Interactions (in units of e_σ) Metal *d* Orbital

Ligand Position	z^2	x^2-y^2	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0



Remember for an octahedral complex in the sigma only case the d_z^2 and $d_{x^2-y^2}$ orbitals interact with ligands.



Example: $[M(NH_3)_6]^{3+}$

a) Only sigma interactions are possible with NH_3 ligands

b) Lone pair of electrons can be thought of as isolated in N p_z orbital

c) Metal d-orbitals

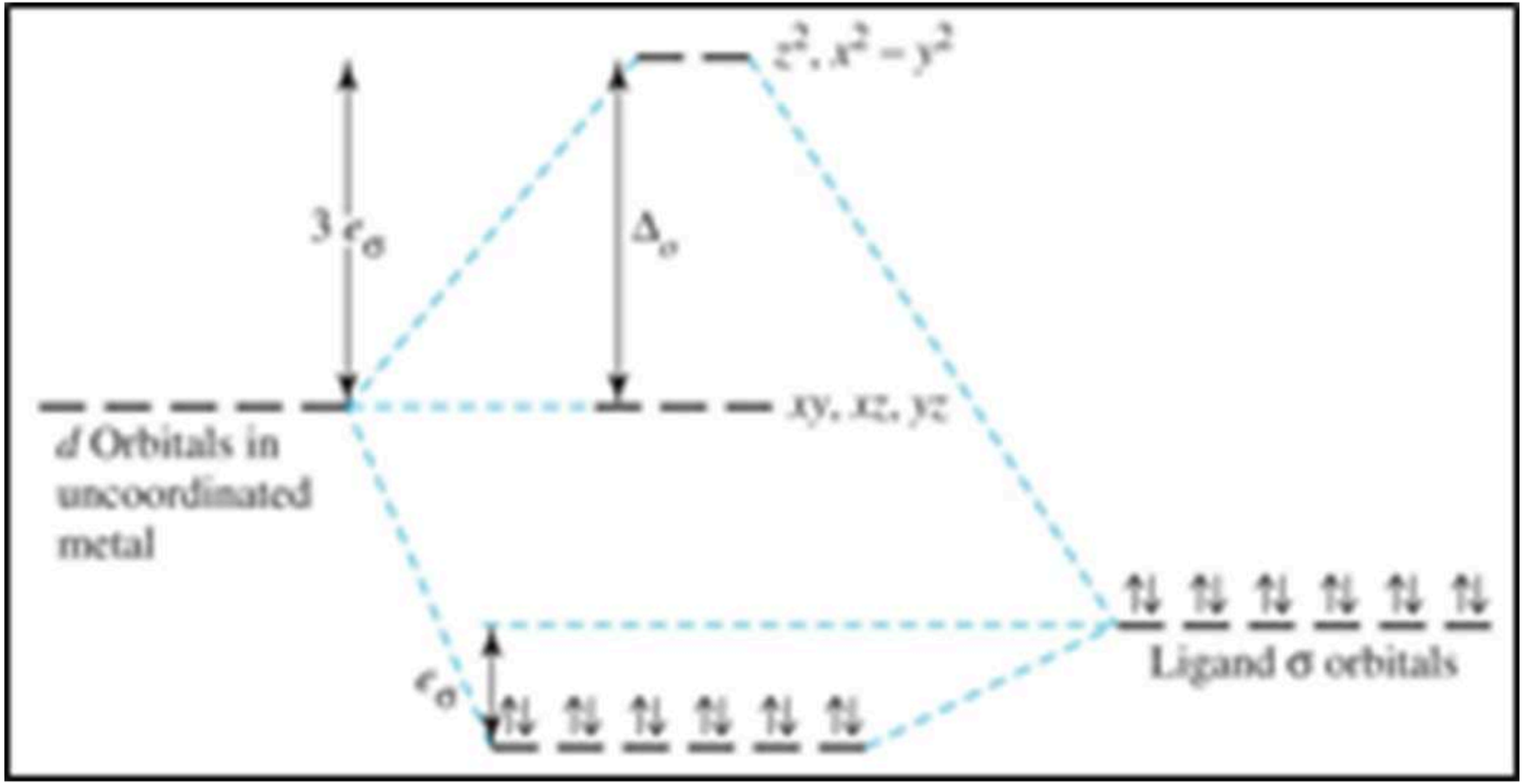
- **i) Add the values of interactions down the column**
- **ii) d_z^2 = (2 x 1) + (4 X 1/4) = $3e_\sigma$**
- **iii) $d_{x^2-y^2}$ = (2 x 0) + (4 X 3/4) = $3e_\sigma$**
- **iv) d_{xy}, d_{xz}, d_{yz}, = 0 (no interactions with the ligands)**

d) Ligand orbitals

- **i) Total interactions with the metal d-orbitals across the row**
- **ii) Ligand #1 & #6 = (1 x 1) + 0 = $1e_\sigma$**
- **iii) Ligand #2, #3, #4 & #5 = (1 x 1/4) + (1 X 3/4) = $1e_\sigma$**

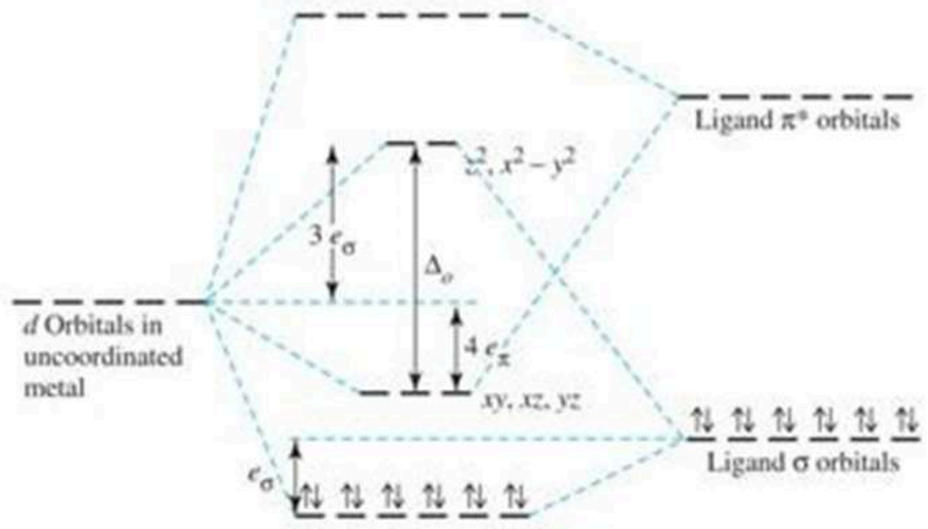
e) Result

- **i) Same pattern as LFT**
- **ii) 2 d-orbitals energy are raised**
- **iii) 3 d-orbitals energy are unchanged.**



Pi-acceptor interactions in octahedral complex

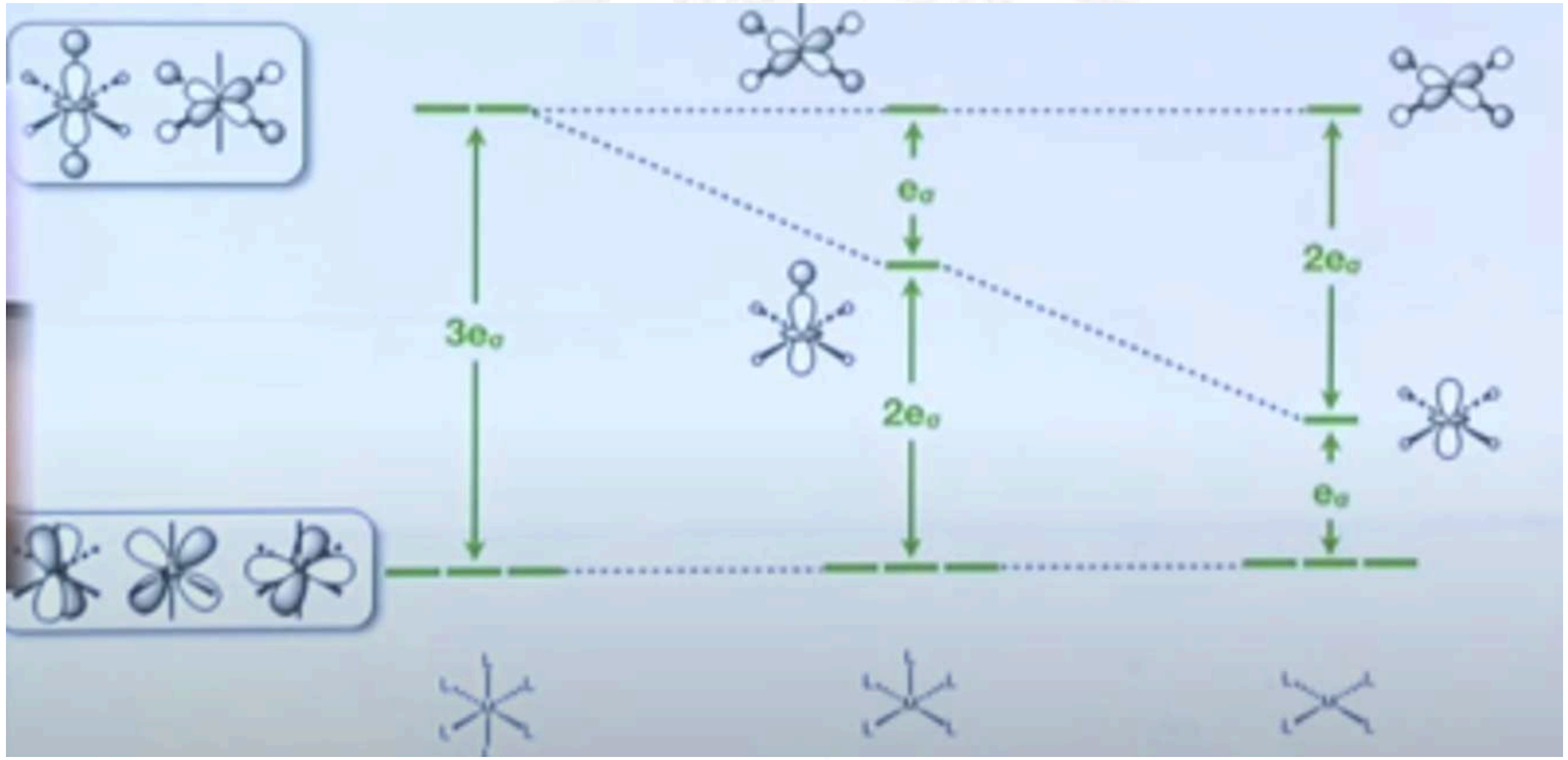
a) pi-acceptor has empty p or pi MOs
b) Strongest overlap is between dxy and π*
c) π* is higher in energy than the dxy. Hence, it becomes stabilized.
d) d_{xy}, d_{xz}, d_{yz} all are stabilized by $-4e_\pi$
e) d_z^2 and $d_{x^2-y^2}$ are unaffected.
f) $e_\pi < e_\sigma$
g) $3e_\sigma + 4e_\pi = \Delta o$



Pi Interactions (all in units of e_π)
Metal *d* Orbital

Ligand Position	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1

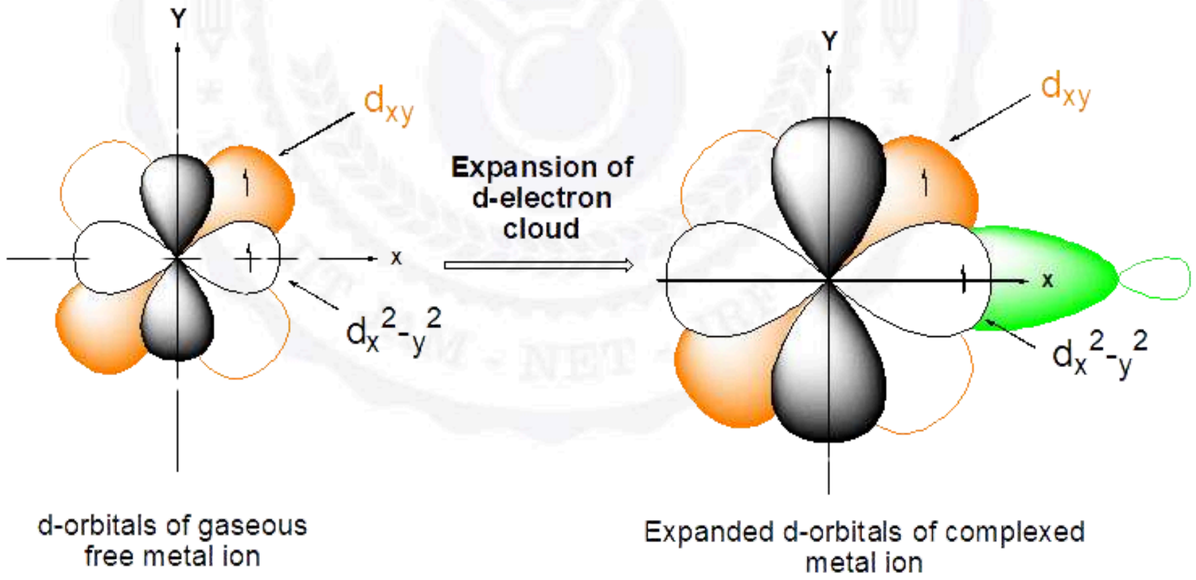
The usefulness of the AOM is that it gives a good approximation of the energies of the metal d orbitals n different coordination geometries.



EVIDENCE FOR METAL--LIGAND COVALENT BONDING

In metal complexes, there is evidence for sharing of electrons between metal and ligand.

In metal complexes, due to formation of M-L bond d-electron cloud of metal ion expands leading to decrease in interelectronic repulsion and that the effective size of the metal orbitals has increased. This is the nephelauxetic effect.



For complexes with a common metal ion, it is found that the nephelauxetic effect of ligands varies according to a series independent of metal ion:

$$F^- < H_2O < NH_3 < en < [ox]^{2-} < [NCS]^- < Cl^- < [CN]^- < Br^- < I^-$$

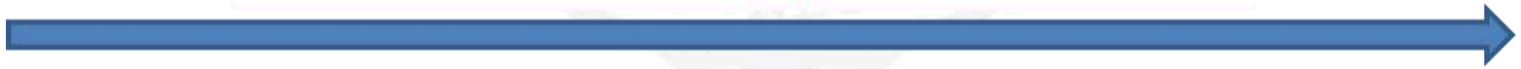
increasing nephelauxetic effect

Increase in covalent character
Increase in size
Increase in soft character

A nephelauxetic series for metal ions (independent of ligands) is as follows:

$$Mn(II) < Ni(II) \approx Co(II) < Mo(II) < Re(IV) < Fe(III) < Ir(III) < Co(III) < Mn(IV)$$

increasing nephelauxetic effect



Increase in covalent character
Decrease in size

The nephelauxetic effect can be parameterized and the values shown in the table were used to estimate the reduction in electron-electron repulsion upon formation of complex.

Metal ion	*k*	Ligands	*h*
Co(III)	0.35	6 Br^-	2.3
Rh(III)	0.28	6 Cl^-	2.0
Co(II)	0.24	6 $[CN]^-$	2.0
Fe(III)	0.24	3 en	1.5
Cr(III)	0.21	6 NH_3	1.4
Ni(II)	0.12	6 H_2O	1.0
Mn(II)	0.07	6 F^-	0.8

$$\frac{B_o - B}{B_o} \approx h_{ligands} \times k_{metal\ ion}$$

B = Interelectronic repulsion in the complex is the Racah parameter

B_o = Interelectronic repulsion in the gaseous M^{n+} ion.

Nephelauxetic effect α $h_{ligands}$ α $k_{metal\ ion}$

Estimate the reduction in the interelectronic repulsion in going from the gaseous Fe^{3+} ion to $[FeF_6]^{3-}$.

$$\frac{B_o - B}{B_o} \approx h_{ligands} \times k_{metal\ ion}$$

$$\approx 0.8 \times \mathbf{0.24}$$

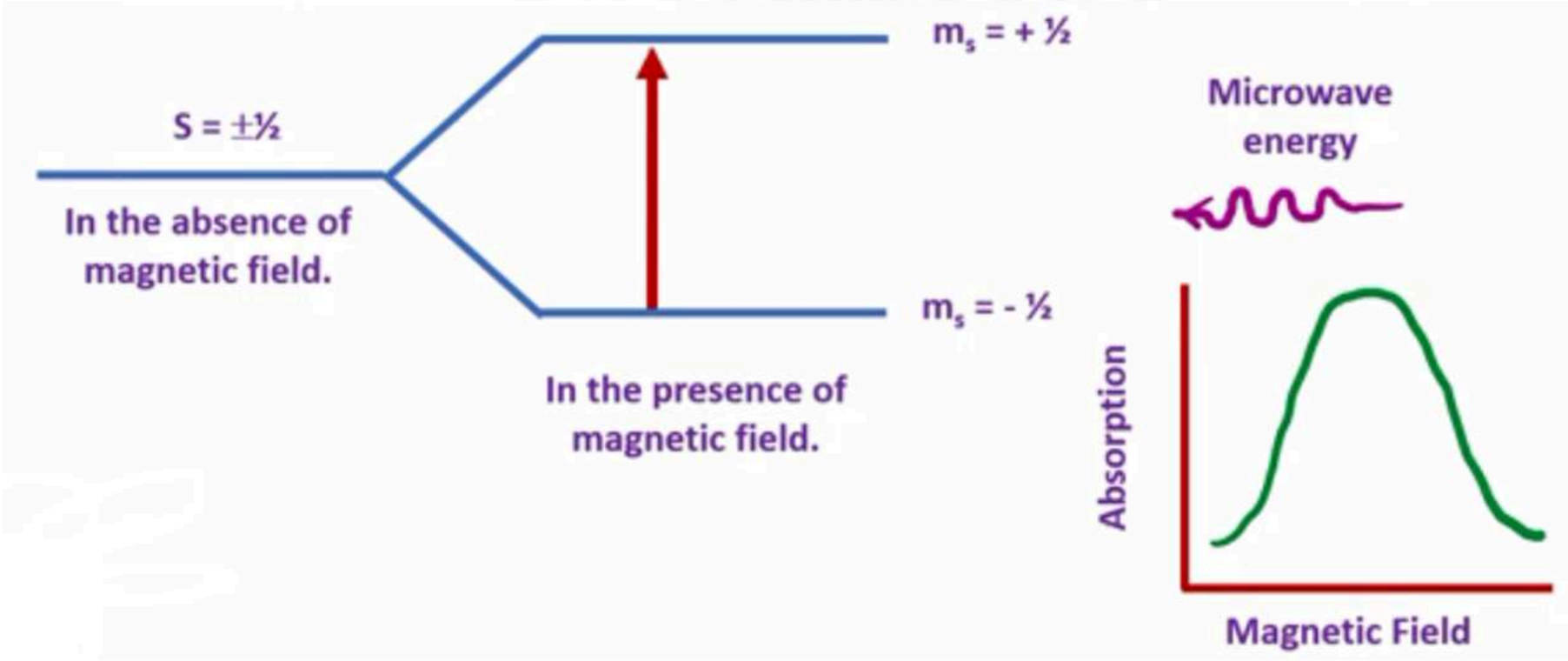
$$\approx 0.192 \approx 19\ \%$$

Reduction in the interelectronic repulsion

Therefore, the reduction in the interelectronic repulsion in going from the gaseous Fe^{3+} ion to $[FeF_6]^{3-}$ is 19 %.

EVIDENCE FOR METAL-LIGAND COVALENT BONDING

Electron Spin Resonance (ESR) spectroscopy a branch of absorption spectroscopy in which molecule having unpaired electrons absorb microwave radiation.



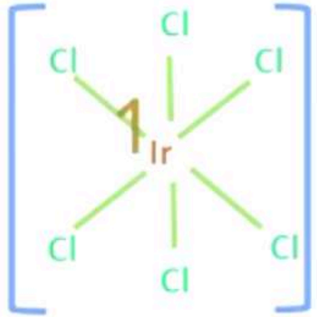
If a metal ion carrying an unpaired electron is linked to a ligand containing nuclei with nuclear spin quantum number I ≠ 0, then hyperfine splitting is observed showing that the orbital occupied by the electron has both metal and ligand character, i.e. there is metal-ligand covalent bonding.

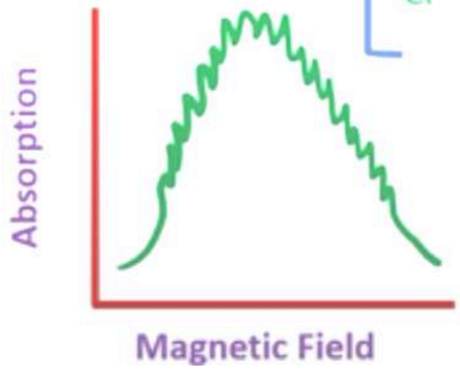
$[Ir(Cl)_6]^{2-}$

Ir^{+4} 

Ir = $5d^7 6s^2$ (Outer electrons)

X + (-6) = -2
X = +4





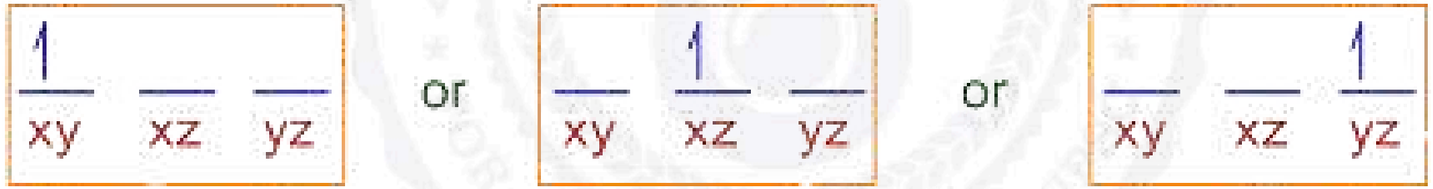
UNIT - 5-4 | PAPER - 2

J.T THEOREM

WHAT IS ELECTRONICALLY DEGENERATE STATE?

An electronically degenerate state represents the availability of more than one degenerate orbitals for an electron. In this condition the degenerate orbitals are said to be asymmetrically occupied.

E.g. In octahedral symmetry, the d^1 configuration is said to be electronically degenerate since three t_{2g} orbitals with same energy are available for the electron to occupy. In this condition, the degenerate orbitals are also said to be asymmetrically occupied by electrons.



Electronically degenerate state of d^1 configuration.

The lone electron may occupy any of the degenerate t_{2g} orbitals.

Whereas the d^3 configuration in octahedral geometry is non-degenerate and symmetric. It is not possible to put two electrons in one orbital, which is against of Hund's rule of maximum multiplicity.

Only one arragement for d^3 configuration is possible according to Hund's rule.

In the electronically degenerate state, the orbitals are said to be asymmetrically occupied and hence get more energy. Therefore, the system tries to get rid of extra energy by lowering the overall symmetry of the molecule i.e., undergoing distortion, which is otherwise known as **Jahn Teller distortion (effect).**

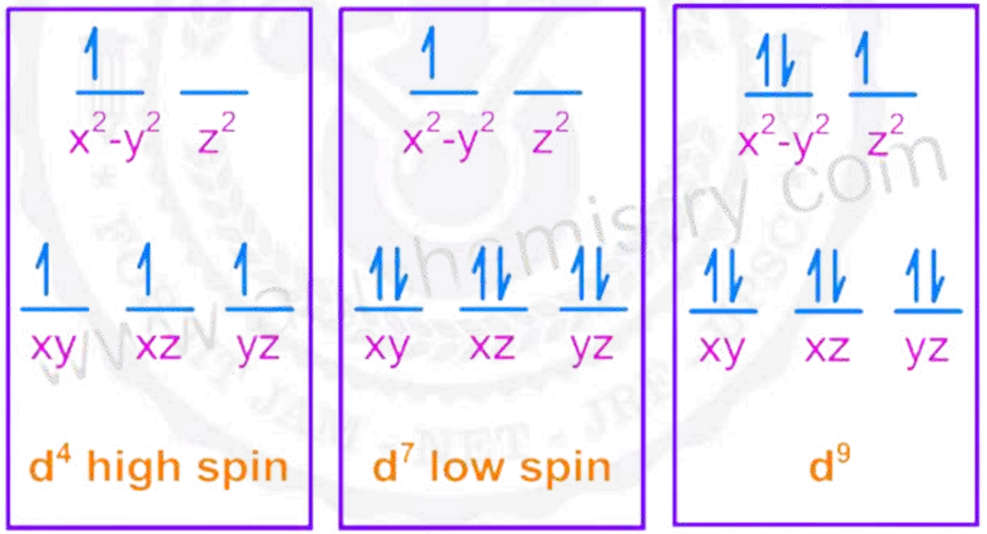
E.g. In case of octahedral d^9 configuration, the last electron may occupy either d_z2 or d_x2-_y2 orbitals of e_g set. If it occupies d_z2 orbital, most of the electron density will be concentrated between the metal and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four on xy plane. This asymmetric distribution of the electron density may increase the overall energy of the system. To get rid of this, the complex suffers elongation of bonds on z-axis and thus lowers the symmetry.

Conversely, occupation of the d_x2-_y2 orbital would lead to elongation of bonds along the x and y axes.

*The Jahn Teller effect is mostly observed in octahedral environments. Theoretically, the electronic degeneracy in octahedral symmetry is possible in all the configurations except d^3, d^8, d^{10}, high spin d^5 and low spin d^6 configurations.

However, considerable distortions are usually observed in **high spin d^4, low spin d^7, and d^9** configurations in the octahedral environment. It is because the Jahn Teller distortion is usually significant for asymmetrically occupied e_g orbitals since they are directed towards the ligands and the energy gain is considerably more.

Configurations with significant JT distortions



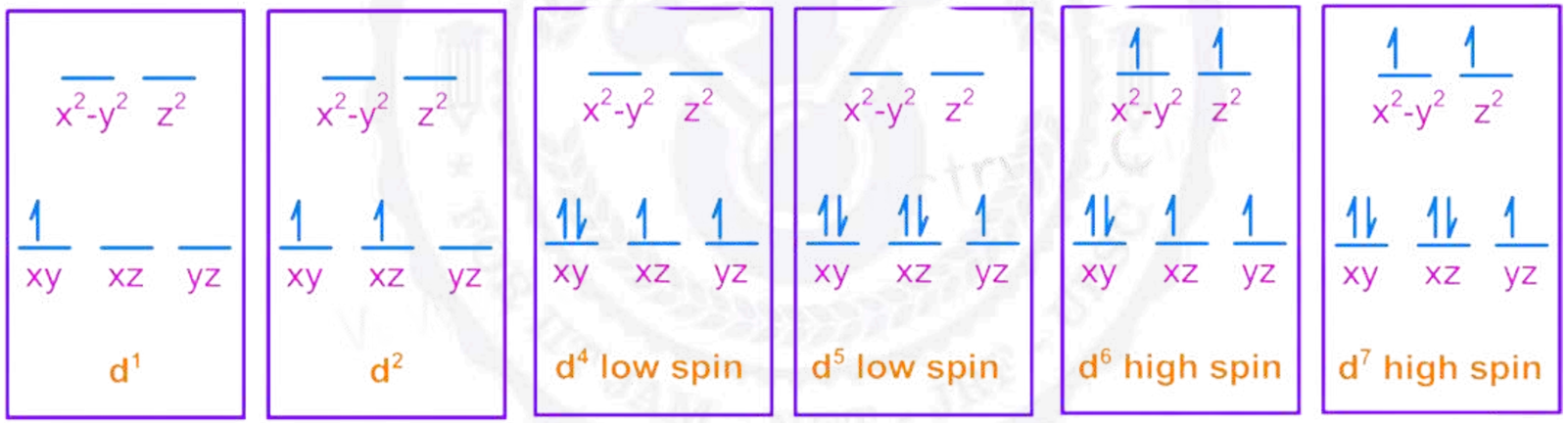
Cr(II) Mn(III) | Co(II) Ni(III) | Cu(II) Ag(II)

*In case of unevenly occupied t_{2g} orbitals, the Jahn Teller distortion is very weak since the t_{2g} set does not point directly at the ligands and therefore the energy gain is much less.

E.g. d^1; d^2; low spin d^4 & d^5; high spin d^7 & d^7 configurations.

Because of same reason, the *tetrahedral complexes also do not exhibit Jahn-Teller distortion*. Again, in this case also the ligands are not pointing towards the orbitals directly and hence there is less stabilization to be gained upon distortion.

Configurations showing weak JT distortions



Sc(II) Ti(III) V(IV)

Ti(II) V(III) Cr(IV)

Cr(II) Mn(III)

Fe(III)

Fe(II)

Co(II) Ni(III)

The degeneracy of orbitals can be removed by lowering the symmetry of molecule. This can be achieved by either elongation of bonds along the z-axis (Z-out distortion) or by shortening the bonds along the z-axis (Z-in distortion). Thus an octahedrally symmetrical molecule is distorted to tetragonal geometry.

Z-out Jahn-Teller distortion: In this case, the energies of d-orbitals with z factor (i.e., d_{z^2}, d_{xz}, d_{yz}) are *lowered* since the bonds along the z-axis are elongated. This is the most preferred distortion and occurs in most of the cases, especially when the degeneracy occurs in e_g level.

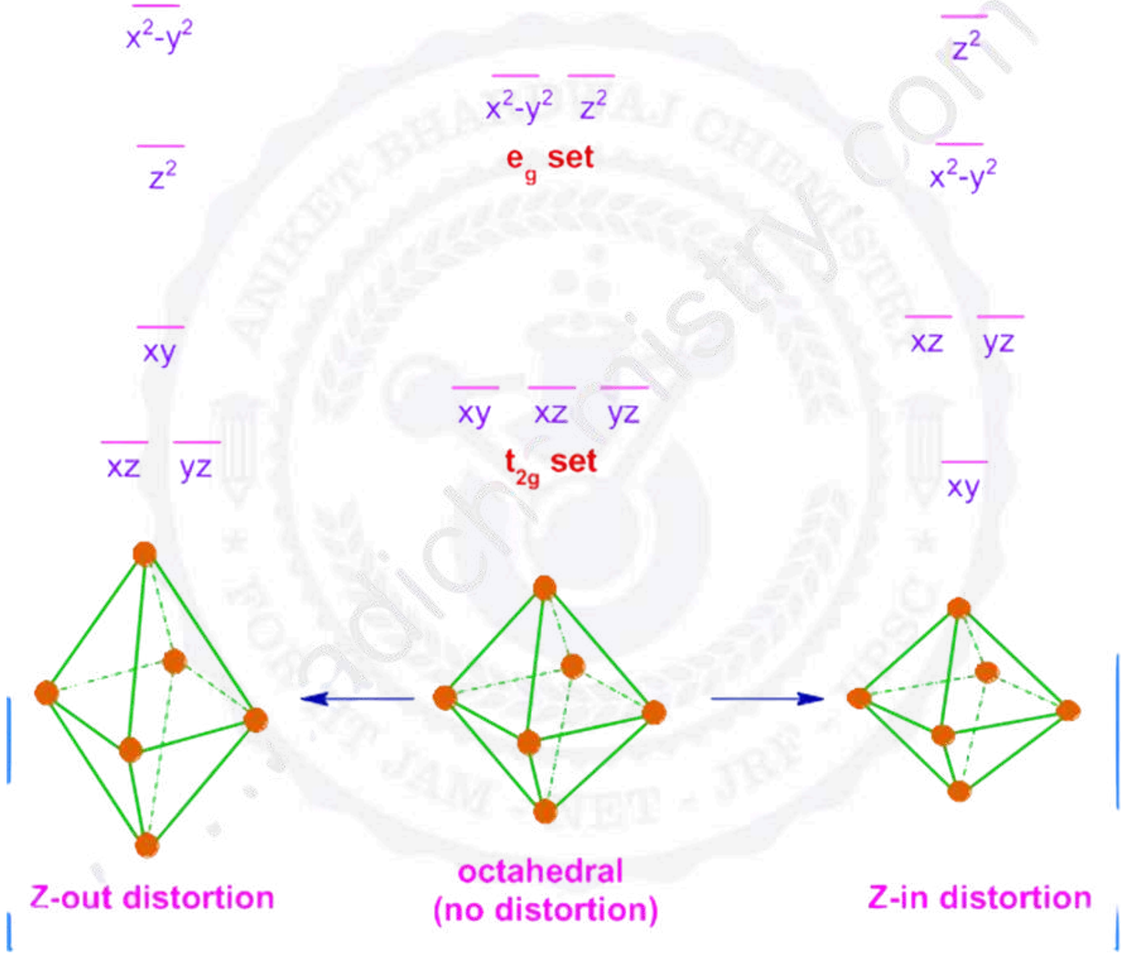
E.g. Usually the octahedral d^2, d^4 high spin, d^7 low spin, d^8 low spin & d^9 configurations show the z-out distortion.

Theoretically it is not possible to predict the type of distortion that occurs when the degeneracy occurs in e_g level. However it is observed that z-out distortion is more preferred.

Z-in Jahn-Teller distortion: In this case the energies of orbitals with z factor are *increased* since the bonds along the z-axis are shortened. This type of distortion is observed in case of octahedral d^1 configuration. The only electron will now occupy the d_{xy} orbital with lower energy.

E.g. The octahedral d^1 configurations like Ti(III) in $[Ti(H_2O)_6]^{3+}$ can show z-in distortion (theoretically?). In this case, the z-out distortion do not remove the degeneracy since even after distortion there are still two degenerate orbitals i.e., d_{xz} and d_{yz} available for the electron to occupy. See the following diagram.

Also remember that the Jahn-Teller theorem does **NOT** predict how large a distortion should occur.



Static Jahn-Teller distortion: Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. It is observed when the degeneracy occurs in e_g orbitals. Hence the distortion is strong and permanent.

Dynamic Jahn-Teller distortion: In some molecules, the distortion is not seen either due to random movements of bonds which does not allow the measurement within a time frame or else the distortion is so weak as to be negligible. However, the distortion can be seen by freezing the molecule at lower temperatures. This condition is referred to as dynamic Jahn- Teller distortion.

E.g.

1). The complexes of the type $M_2PbCu(NO_2)_6$ show dynamic Jahn-Teller distortion. Here, M=

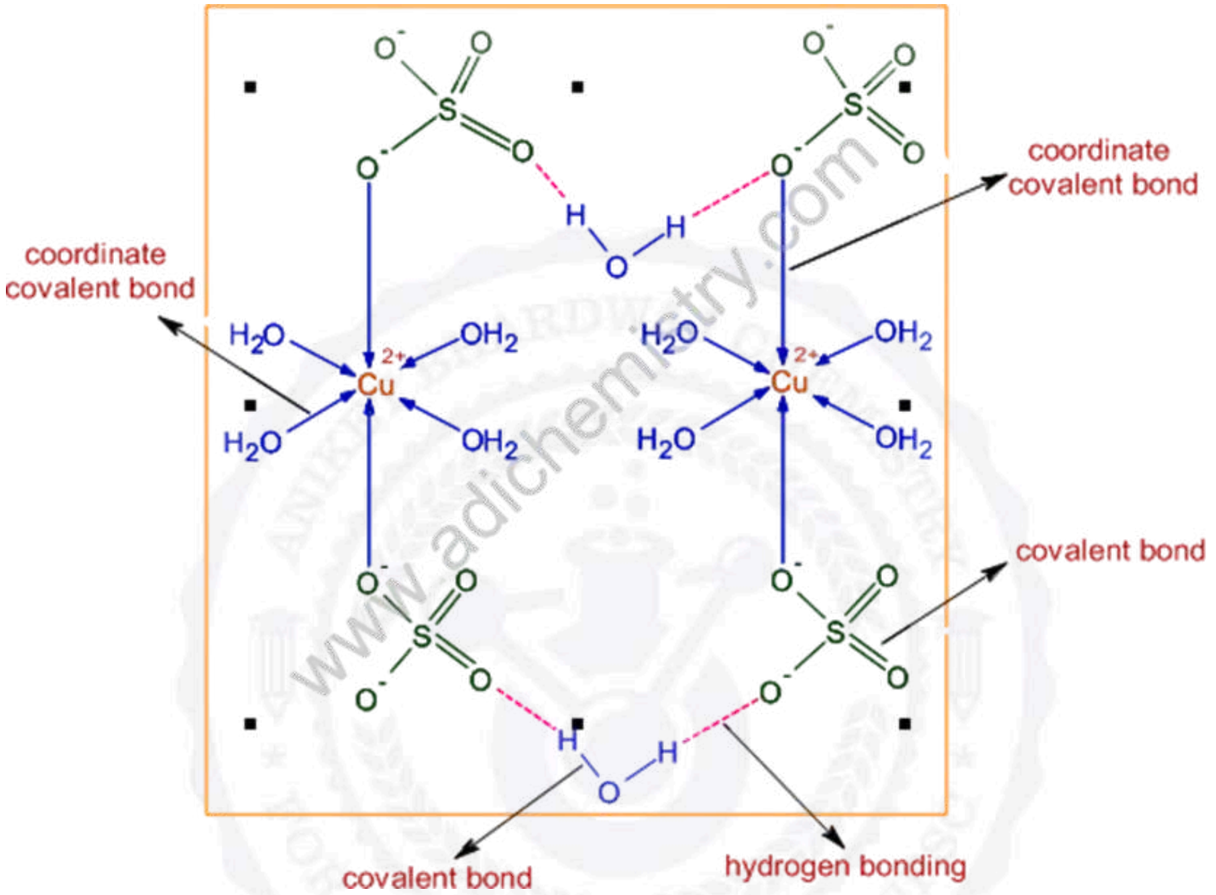
K, Rb, Cs, Tl;

They show tetragonal symmetry at lower temperatures due to static Jahn-Teller distortion. But at higher temperatures, these molecules appear octahedral due to the dynamic Jahn-Teller effect.

1. Jahn-Teller distortion in complexes formed by Cu(II) ions:

(a) Tetragonal structure of Cu(II) complexes: The Cu(II) ion is a d^9 system and expected to show Jahn-Teller distortion and depart considerably from octahedral geometry. The Cu(II) ion in the *aqueous medium* is surrounded by six water molecules in tetragonal geometry i.e., four of which are at the corners of square plane and are at shorter distances with stronger interactions, whereas, the remaining two are weakly interacting with the metal ion at distant axial positions.

(b) Structure of hydrated copper(II) sulphate, $CuSO_4.5H_2O$ and other Cu(II) complexes: In the *solid* $CuSO_4.5H_2O$, the copper ion is surrounded by four water molecules in square planar geometry. There are also weak interactions with the sulphate ions in the axial positions. The 5th water molecule is hydrogen bonded to the sulphate ion. That means the two water molecules on the axial positions are completely eliminated and substituted by sulphate ions while forming the solid.



Note: Due to interactions with these ligands, the d orbitals are split into different energy levels, which makes d-d transitions possible. It absorbs red color and transmits blue color during the d-d transition. But upon heating, all the water molecules are lost, which makes all the d orbitals degenerate again. Hence the anhydrous $CuSO_4$ is colorless.

(c) Extra stability of Cu^{2+} ions: The relative stabilities of complexes formed by high spin divalent first row transition metal ions is given by Irving-Williams series. The stability order is shown below:

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)

The extra stability of Cu(II) ion can be explained by taking into account of Jahn-Teller distortion of this d^9 ion.

(d) Other examples: Because of Jahn-Teller distortion:

* In the crystalline $KCuF_3$, the two Cu- F distances are at 1.96 A^0 and the remaining four Cu - F distances are at 2.07 A^0. It is a case of Z-compression.

* In $[Cu(hfacac)_2(bipy)]$, there are two short Cu-O bonds and two long Cu–O bonds. (where hfacac = hexafluoroacetylacetone anion; bipy = 2,2'-bipyridine). It is an example for Z-out distortion

* Cu(II) cannot form $[Cu(en)_3]^{2+}$ since JT distortion brings strain into the ethylene diamine molecule that is added along z-axis. Hence only $[Cu(en)_2(H_2O)_2]^{2+}$ is formed.

2) The splitting of absorption bands in the UV-VIS spectra of complexes due to Jahn-Teller distortion:

E.g. The absorption band in the electronic spectrum of aqueous Ti(III), a d^1 octahedral system, is not symmetric but rather shows a distinct broad shoulder. It is because of Jahn-Teller distortion.

The Jahn-Teller distortion is negligible in case of degenerate t_{2g} orbitals in the ground state. Hence no distortion in the ground state. But when the electron gets excited, the configuration now becomes $t_{2g}^{\sim} e_g^{*}$, which is again degenerate. Hence in the excited state, the Jahn Teller distortion is possible. Now the promotion of electron may occur to either of the two non degenerate e_g orbitals, the d_z2 and d_x2-y2. Thus, two transitions are possible. But a shoulder appears since the energy difference between two transitions is small.

3) Coordinatively labile nature of $[Cr(H_2O)_6]^{2-}$ & $[Co(NH_3)_6]^{2+}$:

The $[Cr(H_2O)_6]^{2+}$ undergoes substitution easily since the Cr(II) ion is a high spin d^4 system with one electron in the e_g orbital. Hence it is electronically degenerate and shows Jahn-Teller distortion. Hence the hydrated Cr(II) ion is coordinatively labile.

On the same lines, the easy substitution of $[Co(NH_3)_6]^{2+}$ by water molecules can be explained. In this case the Co(II) ion is coordinatively labile since it is a low spin octahedral d^7 ion which is degenerate in e_g set. Hence it undergoes J-T distortion and is labile.

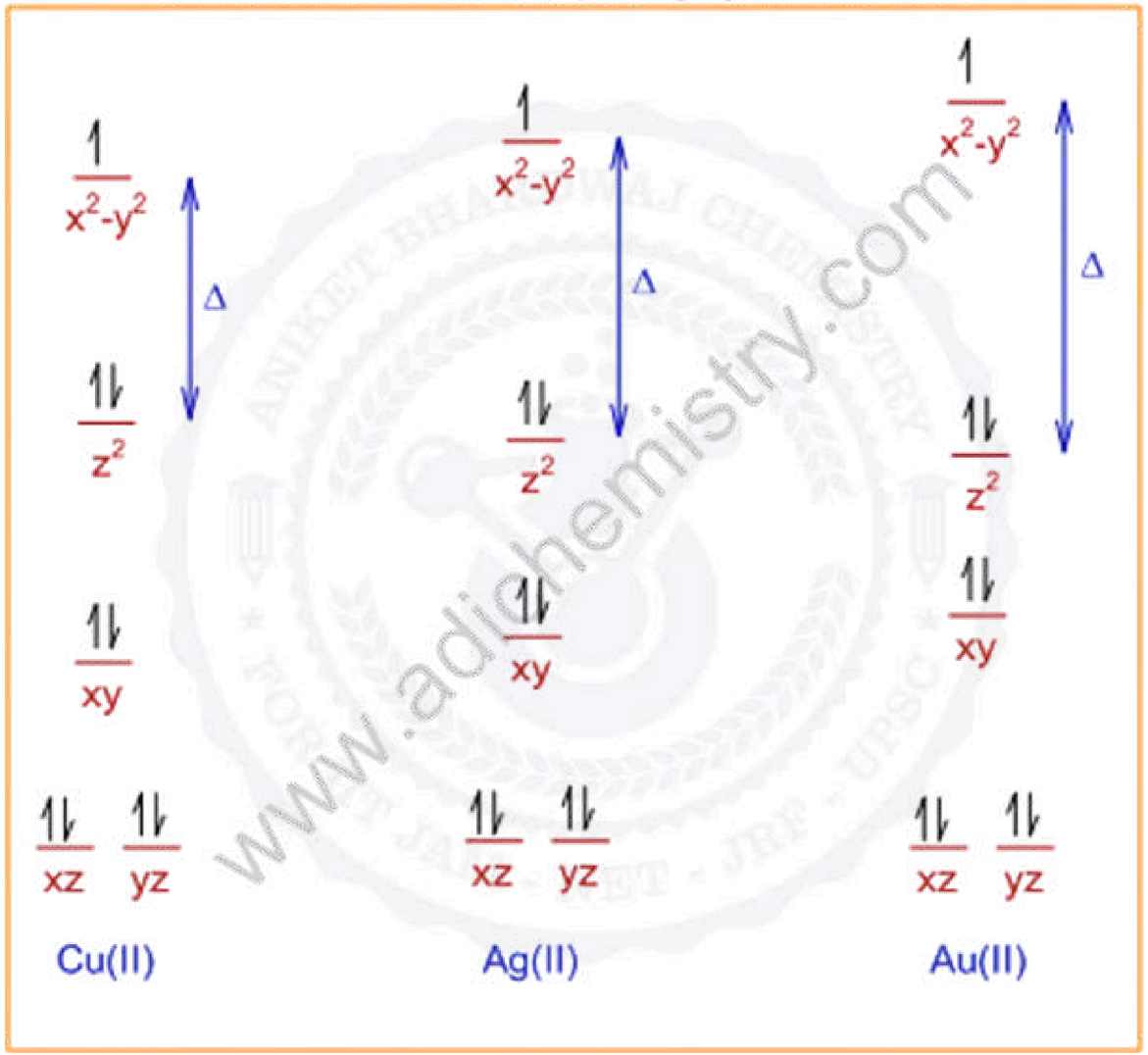
4) Disproportionation of Au(II) salts:

Au(II) ion is less stable and undergoes disproportionation to Au(I) and Au(III) even though the Cu(II) and Ag(II) ions are comparatively more stable. One may expect same stability since all are d^9 systems and undergo the Jahn-Teller distortion.

However, the Δ value increase down the group. Hence, in Au(II) ion, it reaches a maximum, which causes high destabilization of the last electron, which is now occupying the $d_{x^2-y^2}$. This makes Au(II) reactive, which may undergo either oxidation to Au(III), a d^8 system or reduction to Au(I), a d^{10} system.

The d^8 system, Au(III) is stable as the electron from the $d_{x^2-y^2}$ is removed. Mostly it prefers square planar geometry and more stable than both Au(II) and Au(I). The d^{10} system, Au(I) favors mostly linear geometry with coordination number = 2.

The Δ value increases from Cu(II) to Au(II). Therefore the last electron in Au(II) is highly destabilized.



Question-Why do the d^9 systems usually **not** undergo complete distortion to square planar geometry?

Answer: Usually, the d^9 systems are tetragonal with elongated bonds on z-axis and do not undergo complete distortion to square planar. It is because the last electron will be placed in highly destabilized $d_{x}2_{-y}2$ if they get square planar geometry. But the low spin d^8 complexes may undergo complete distortion to square planar geometry.

Question-1: Which metal complex ion is expected to be subject to a Jahn-telle distortion?

A) Cu^{2+}

B) Ni^{2+}

C) Ca^{2+}

D) Cr^{3+}

Answer: A

Question-2: Which of the following does not show octahedral geometry,

1) $[Cu(CN)_4]^{2+}$

2) XeF_4

3) $[NiCl_4]^{2}$

4) All

Answer: 4

Question-3: Strong Jahn-teller distortion is not observed for octahedral complexes of:

1) Cu^{2+}

2) Low spin Cr^{2+}

3) High spin Mn^{3+}

4) High spin Cr^{2+}

Answer: 2

Question-4: Which of the following shows strong Jahn teller distortion?

1) Fe^{3+}

2) High spin Co^{2+}

3) Ti^{2+}

4) Low spin Co^{2+}

Answer: 4

Question-5: Jahn teller effect is not observed in high spin complexes of:

A) Mn^{2+}

B) Cr^{2+}

C) Cu^{2+}

D) Fe^{3+}

Answer: A

Question-6: Which metal complex ion is expected to be subject to a Jahn teller distortion?

1) Low spin Co^{2+}

2) High spin Cr^{2+}

3) Ti^{2+}

4) All

Answer: 4

Question-7: Which of the following d-configuration shows strong distortion from octahedral geometry?

1) d^1

2) d^2

3) d^9

4) None

Answer: 3

Question-8: Why does the absorption spectrum of aqueous $[Ti(OH_2)_6]^{3+}$ exhibit a broad band with a shoulder?

1) Due to Jahn-Teller distortion in the ground state

2) Due to Compton effect

3) Due to jahn-Teller distortion in the excited state

4) Due to square planar geometry

Answer: 3

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