# NG ECRETS: CE OF ARBON

# luction

he realm of time
on dating, where
story to unravel the
t. Let us look within
acts and fossils and
e year of its
hnique offers us a
age of organic
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n us as we embark
e through time
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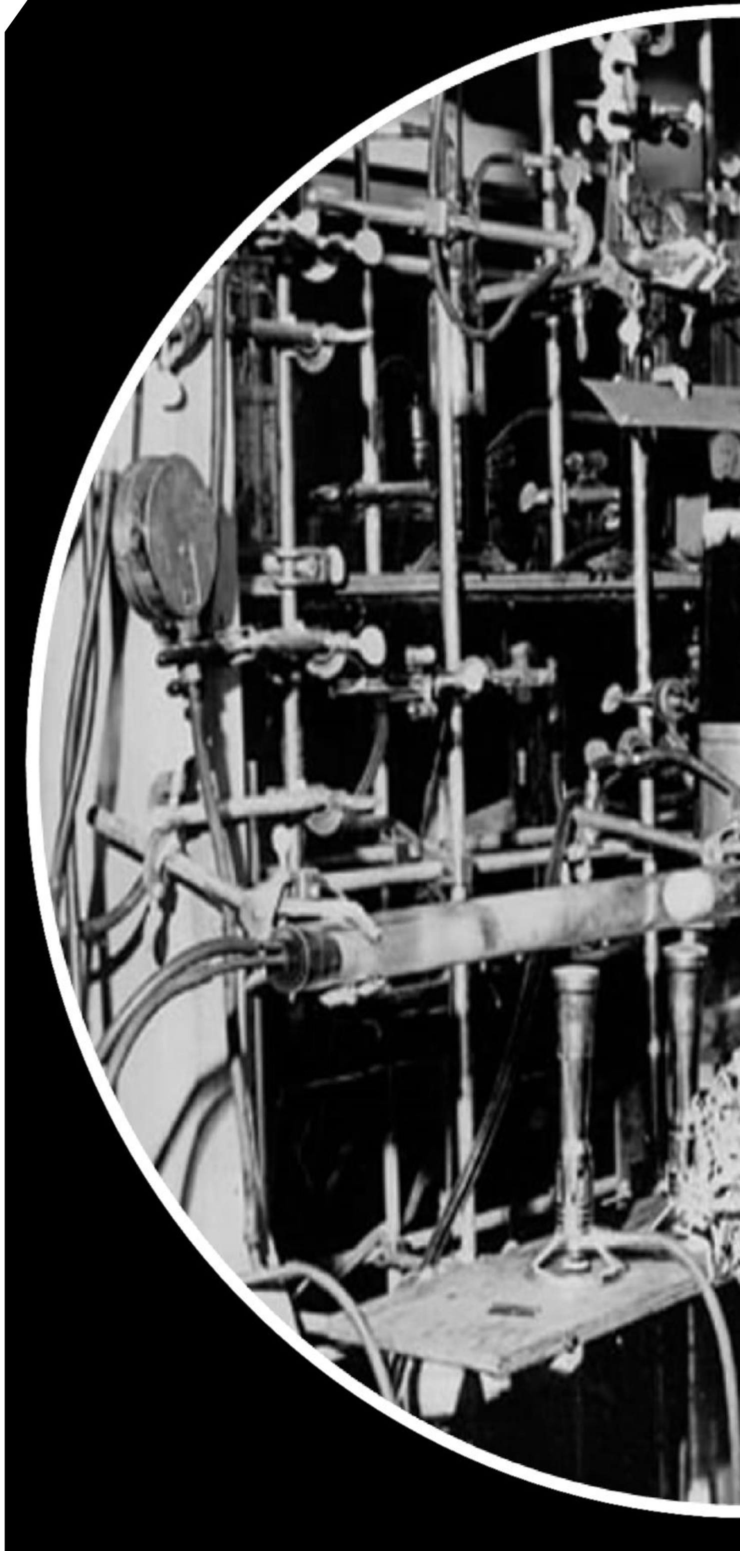
ting' and

# Tracing Time: Th
# Evolution

Radiocarbon Dating being the necessa
archeology and geology has a fascinati
spanning over more than 70 years. It al
when Dr. Martin Kamon & Dr. Samuel
Berkeley Radiation Laboratory synthes
cyclotron accelerator, they soon discov
life was far longer than expected; it wa
Serge Alexander Korff, who showed tha
carbon forms naturally in the upper atr
World War II, Dr Willard F. Libby then a
of Dr Korff's research and conceived th

ng on developing ‘Radiocarbon Dating’.
lished a paper where he proposed that
tain radiocarbon (14C) along with
along with some collaborators began
gas collected from sewage, after
it, the sample was found to contain $^{14}$C.
ng with Dr. James Arnold tested the
nalyzing the samples collected from the
lings that were dated back to 2625 BC ±
analyzing the samples they were dated
rs. These results were published in the
cember 1949. In 1960 Dr. Willard F.



# Behind

Radiocarbon dating is a radiometric
is measuring the decay of a certain ty
found in once living organism to det
was last alive. This dating technique
natural process of radioactive decay.
carbon $^{14}C$ is being produced natura
the lower stratosphere and the uppe
when the solar cosmic rays interacts
in the atmosphere, this megavolt ene
leads to release of a thermal neutron
the $^{14}N$ atom present in atmosphere
radioactive $^{14}C$.

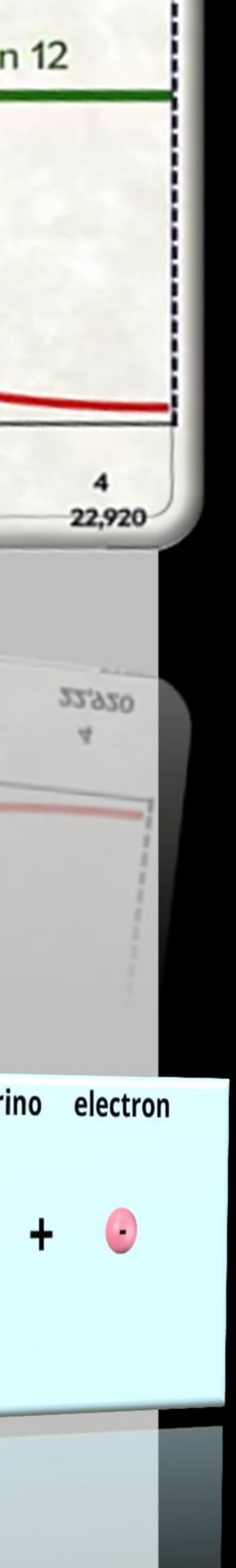
$$^{0}n + {}^{14}N_7 \rightarrow 14C_6 + p+$$

nospheric Oxygen and forms
oxide and finally to carbon
ch is radioactive.

$\rightarrow {}^{14}CO + O$

$O_2 \rightarrow 2\ {}^{14}CO_2$

ctive carbon dioxide thus
sily diffuses in the atmosphere,
in the ocean and is taken up by
other living organisms by
again, these plants are eaten up
als in this way the radiocarbon is



will have some portion of $^{14}C$ as of in the biosphere. Onc ceases to exchange carbon with the environment; hence i proportion of normal and radioactive carbon during its de The ratio of $^{14}C$ to $^{12}C$ is approximately 1.25 parts of $^{14}C$ $^{12}C$.

As time passes by this $^{14}C$ undergoes radioactive decay re significant amount is gone; as the rate of $^{14}C$ decay and th $^{12}C$ is known, by undergoing certain calculations the time the sample can be predicted- as older the sample, the less the sample.

The Radioactive (β) Decay Equation of $^{14}C$ is :

$$^{14}C \rightarrow {}^{14}N + e^{-}(\beta) + \bar{\nu}_e$$

(where $\bar{\nu}_e$ is electron antineutrino & $e^-$ is the β radiation)

Calculations showed that the half-life ($t_{1/2}$) of $^{14}C$ is 5700 after this much times half of the total concentration will b (t) is 11,400 years and one eighth life (t) is 17,100 y

# Limitatio

This method cannot be employed to date Samples older than 60,000 years because radiocarbons in such species are negligibly found.

Conventional radiocarbon dating requires 10-100 grams of sample from an object, which makes it difficult for very rare substance or <10 gram objects.

It can only date organi material since radiocarbon is found i organic biomass only.

materials like wood,
provides
y and environmental changes.

ucial in dating events such as
d the spread of agriculture

or Mass Spectrometry (AMS)
y of radiocarbon dating and
le size. Even tiny traces of
be dated accurately.
ns fundamental in archaeology,
interpret cultural and
en combined with other
ues to refine our
making it indispensable in

# Conclusion

**In essence, radiocarbon dating is a transformative tool that has reshaped our understanding of the past. By analyzing carbon isotopes, it provides precise dating for organic materials, aiding in the reconstruction of ancient lifeways and environmental dynamics. Its interdisciplinary applications extend beyond archaeology, offering insights into climate variability and ecological shifts. As we continue to refine our methods, radiocarbon dating remains a cornerstone of archaeological research, guiding us through the annals of time and enriching our understanding of human history.**

# *Bibliography*

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(YouTube)

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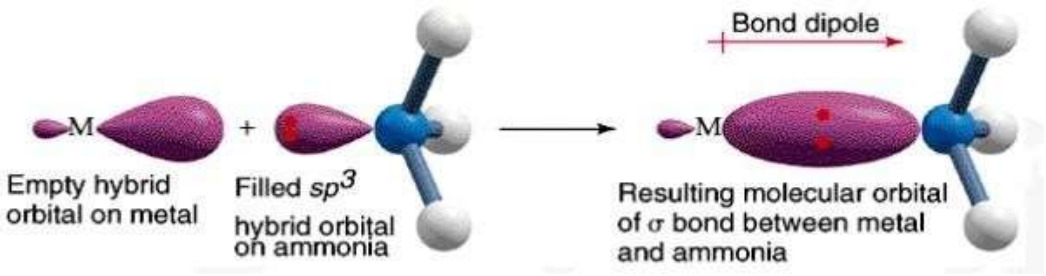
Koye

# CRYSTAL FIELD
# THEORY

## Origin & History:

- Advanced by Bethe and Van Velck and originally applied to explain the colour and magnetic properties of some ionic crystal.
- It is a hypothetical model where ligands are considered as point –ve charge (for negatively charged ligand) and dipoles (for neutral molecule) where as metals are considered as point +ve charge.
- Electric field generated by the ligands influences the distribution of electrons in the metal ions i.e. d-orbital splitting.
- \The bonding between the metal cation and the ligand is believed to be due to electrostatic attraction between the nucleus of the metal ion and the negative or partial negative charge invariably present on the ligands.



Metal-Ligand Bonding:

# Introduction to Crystal Field Theory

## Crystal Field Theory Overview

Crystal Field Theory is a model used to describe the electronic structure of transition metal complexes. It focuses on the interactions between the d-orbitals of the metal and the ligand field. This theory helps explain the color, magnetism, and reactivity of transition metal complexes.

## Ligand Field Effects

The ligands cause a splitting of the d-orbitals of the metal, leading to the formation of energy sub-levels. This splitting depends on the geometry and nature of the ligands, affecting the properties and electronic configurations of the metal complex.

## Crystal Field Stabilization Energy

Crystal Field Stabilization Energy (CFSE) quantifies the stability of different electron configurations within a crystal field. The energy difference between the high and low-energy orbitals influences the reactivity and stability of the metal complex.

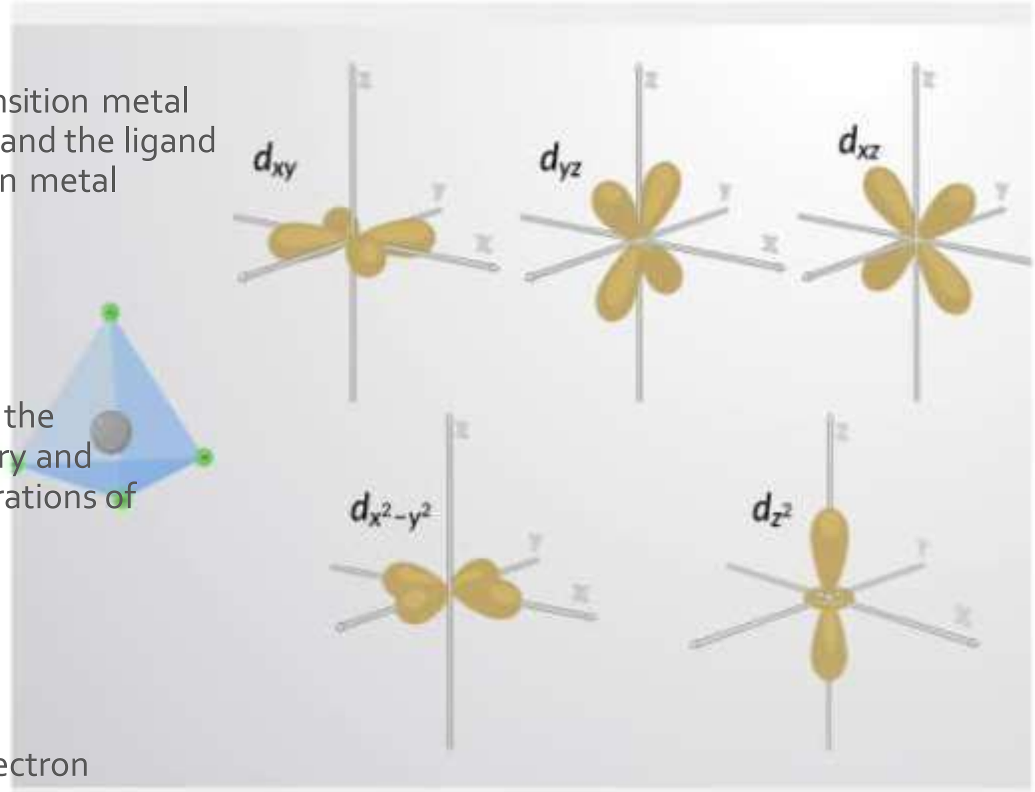


fig : orbital diagrams

# Challenges of Valence Bond Theory

## > Complex Molecules

Preference of geometry of complex compounds cannot be predicted.

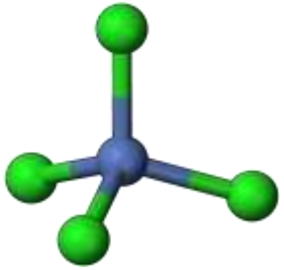
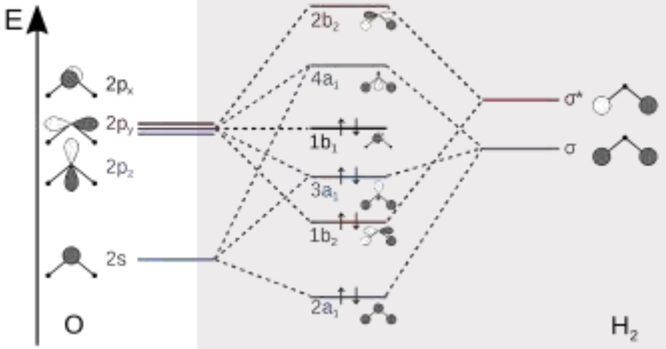


Fig:$[Ni(Cl)_4]^{2-}$



## >Symmetry Adapted LCAO

The application of Symmetry Adapted Linear Combinations of Atomic Orbitals (LCAO) in Valence Bond Theory is often computationally intensive, limiting its practicality in studying large molecules.

## > Coloured Complexes

Colouration of complex compounds cannot be explained.

| Coordinaton entity | Wavelength of light absorbed (nm) | Colour of light absorbed | | Colour of coordination entity | |
|---|---|---|---|---|---|
| $[CoCl(NH_3)_5]^{2+}$ | 535 | Yellow | 🟨 | Violet | 🟪 |
| $[Co(NH_3)_5(H_2O)]^{3+}$ | 500 | Blue Green | 🟩 | Red | 🟥 |
| $[Co(NH_3)_6]^{3+}$ | 475 | Blue | 🟦 | Yellow Orange | 🟧 |
| $[Co(CN)_6]^{3-}$ | 310 | Ultraviolet | Not in visible region | Pale Yellow | 🟨 |
| $[Cu(H_2O)_4]^{2+}$ | 600 | Red | 🟥 | Blue | 🟦 |
| $[Ti(H_2O)_6]^{3+}$ | 498 | Blue Green | 🟩 | Violet | 🟪 |

## >Magnetic Momentum

Observed Magnetic moment is different from spin only magnetic moment in many cases.This deviation cannot be explained.

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

$\mu_s$=1.73 B.M $\mu_{obs}$=2.4 B.M

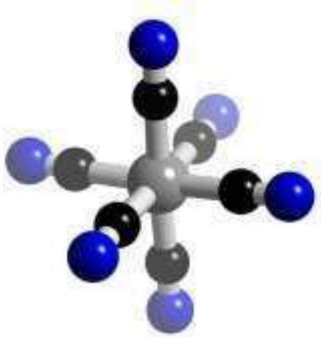
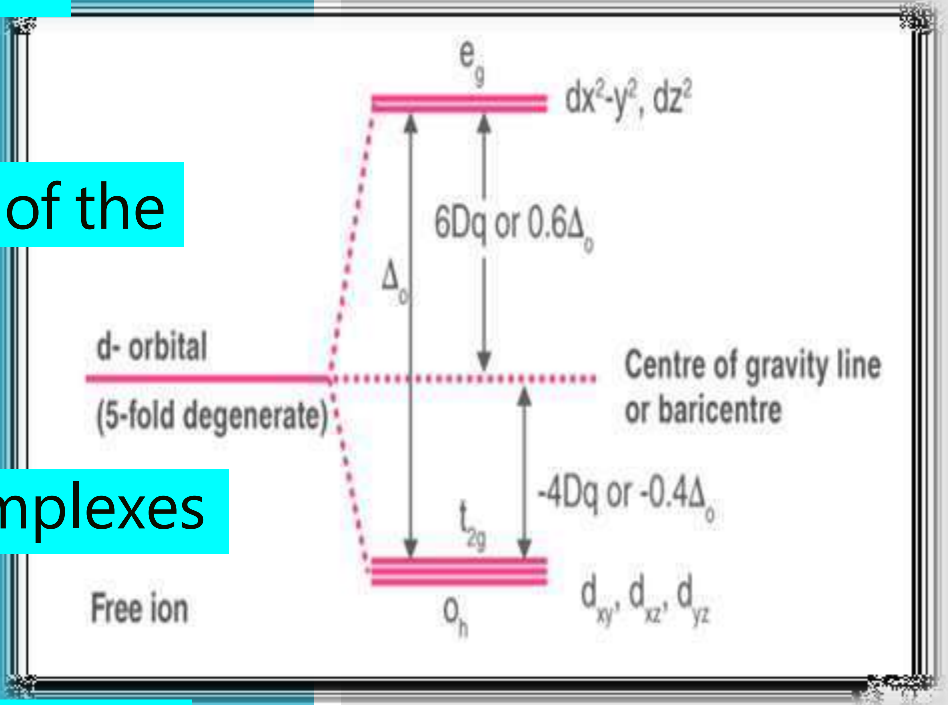


Fig:$[Fe(CN)_6]^{3-}$

# Superiority of Crystal Field Theory over Valence Bond Theory

## MODIFICATIONS OF CRYSTAL FIELD THEORY

- Magnetic properties of complexes and variation with temperature are explained by crystal field theory.
- Crystal field theory gives the quantitative measure of the stability of complexes. It predicts the geometry of complexes.
- Kinetic and thermodynamic properties of some complexes are explained by crystal field theory.
- Crystal field theory explains d-d transitions and colour of complexes.

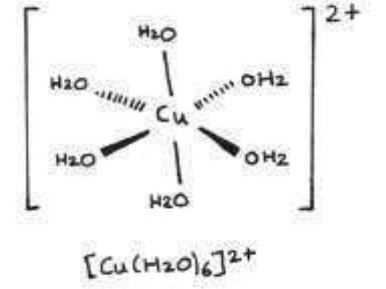


# POSTULATES OF CRYSTAL FIELD THEORY

1. In crystal field theory, we assume that the metal ion is surrounded by an electric field created by the ligands surrounding the metal ion.
2. The forces of attraction between the central metal ion and the ligand are considered purely electrostatic. The metal ion is targeted by the negative end of the dipole of the neutral molecule ligand.
3. The transition metal ion is a positive charge ion equal to the oxidation state.
4. The transition metal atom is surrounded by a specific number of ligands, which may be negative ions or neutral molecules having lone pairs of electrons.
5. Ligands act as point charges that are responsible for generating an electric field. This electric field changes the energy of the orbitals on the metal atom or ions.
6. The repulsive force between the central metal ion and ligand is responsible for the electrons of the metal ion occupying the d-orbitals as far as possible from the direction of approach of the ligand.
7. There is no interaction between metal orbital and ligand orbitals.
8. In an isolated metal atom or ion, all the orbitals have the same energy, which means all the d-orbitals are degenerate.
9. If the central metal atom or ion is surrounded by the spherical symmetrical field of negative charges, the d-orbitals degenerate. However, the energy of orbitals is raised due to the repulsion between the field and the electron on the metal atom or ion.
10. The d-orbitals are affected differently in most transition metal complexes, and their degeneration is lost due to the field produced by the unsymmetrical ligand.

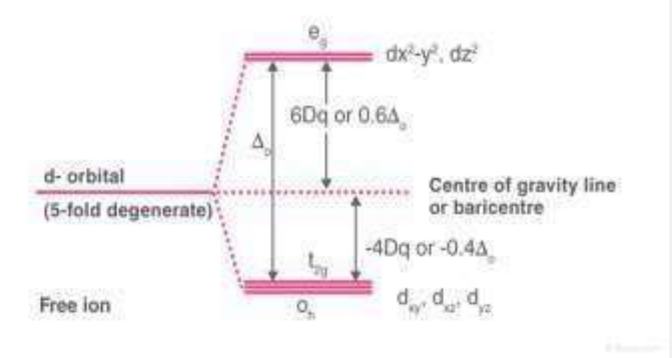
# SPLITTING OF d-ORBITALS IN DIFFERENT COMPLEXES

## 1.Octahedral complex:

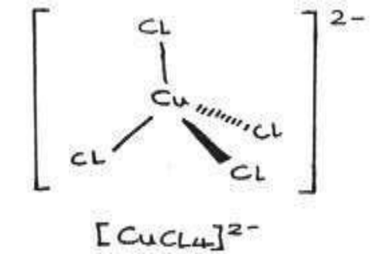


$[Cu(H_2O)_6]^{2+}$

The splitting of the d orbitals in an octahedral field takes place in such a way that $d_{x^2y^2}$ , $d_{z^2}$ experience a rise in energy from Bary center and form the eg level, while $d_{xy}$, $d_{yz}$and $d_{zx}$ experience a lowering of energy and form the $t_{2g}$ level.

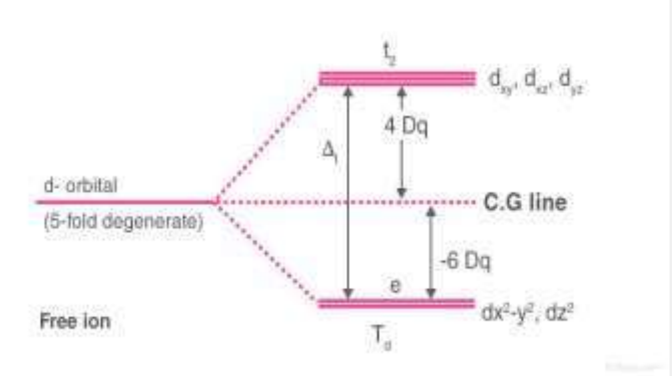


## 2.Tetrahedral complex:

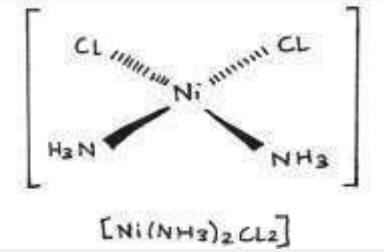


$[CuCl_4]^{2-}$

The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as $t_2$ and e. The electrons in $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are less repelled by the ligands than the electrons present in $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals. As a result, the energy of $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbital sets are raised while that of the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are lowered.

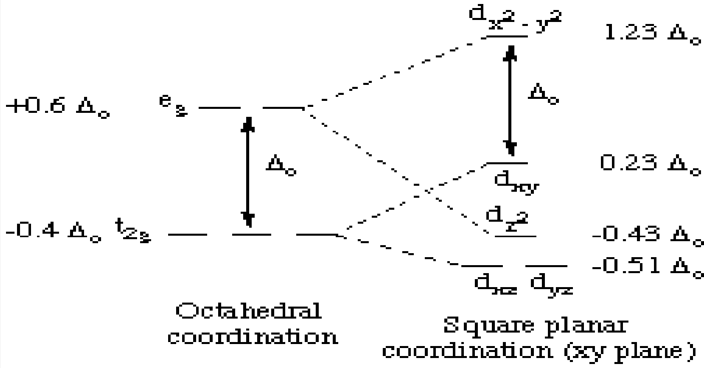


## 3.Square Planar complex:

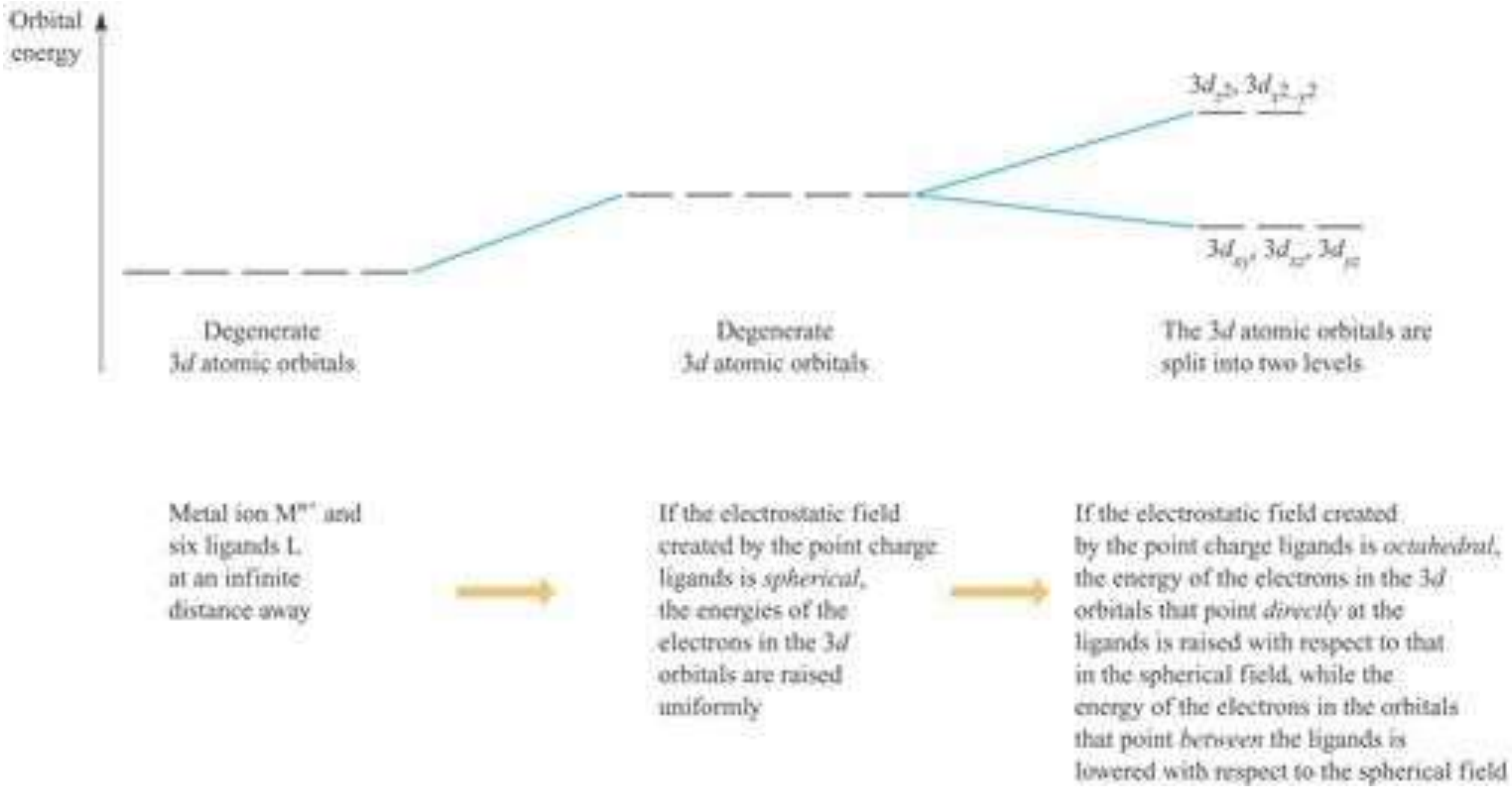


$[Ni(NH_3)_2Cl_2]$

A square planar complex also has a coordination number of 4. The structure of the complex differs from tetrahedral because the ligands form a simple square on the x and y axes.Since there are no ligands along the z-axis in a square planar complex, the repulsion of electrons in the $d_{xz}dxz$, $d_{yz}dyz$, and the $d_{z_2}dz2$ orbitals are considerably lower than that of the octahedral complex. The $dx2-y2$ orbital has the most energy, followed by the $dxy$ orbital, which is followed by the remaining orbitals. This pattern of orbital splitting remains constant throughout all geometries. Whichever orbitals come in direct contact with the ligand fields will have higher energies than orbitals that slide past the ligand field and have more of indirect contact with the ligand fields.



# Energetics:

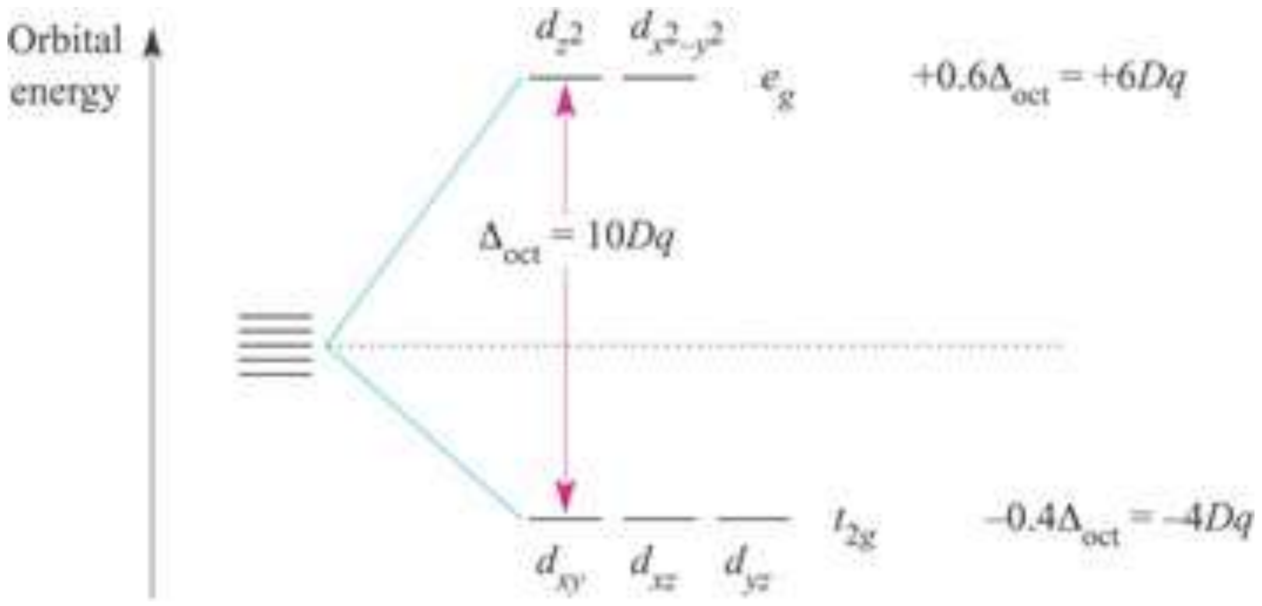


Metal ion $M^{n+}$ and six ligands L at an infinite distance away

If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the 3*d* orbitals are raised uniformly

If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the 3*d* orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands is lowered with respect to the spherical field

# continuation



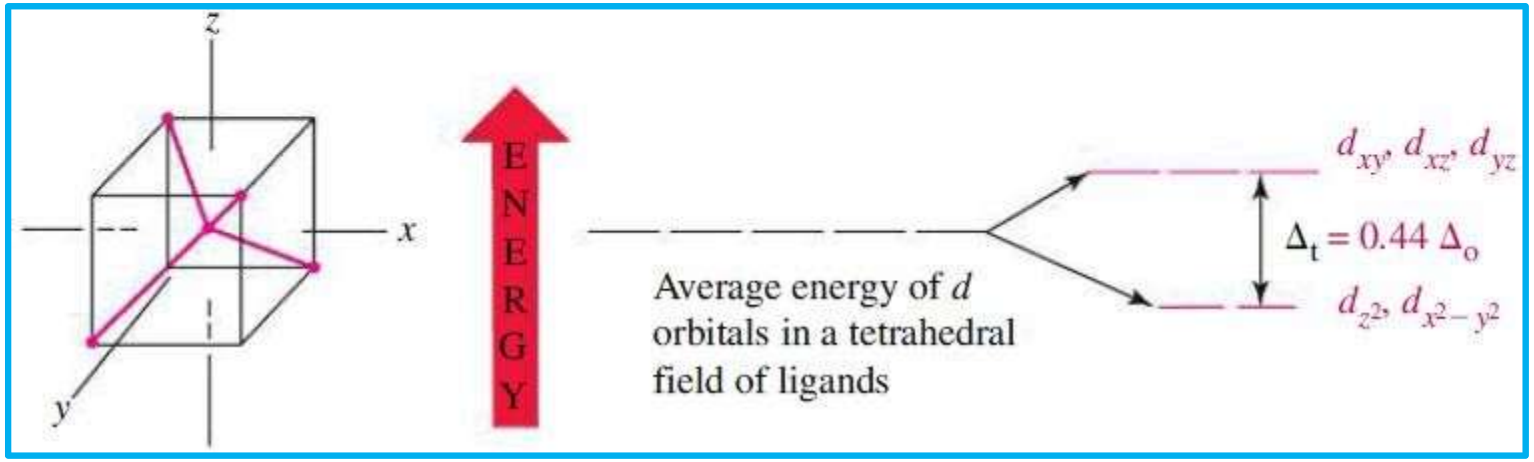
$t_{2g}$ : $d_{xy}$ , $d_{yz}$ , $d_{zx}$

$e_g$ : $d_{z^2}$ , $d_{x^2-y^2}$

- For strong ligand field: crystal field splitting high; Δ(oct) > Pairing Energy (P); results low spin metal complexes

- For weak ligand field: crystal field splitting low; Δ(oct) < Pairing Energy (P); results high spin metal complexes

# CF Splitting: Tetrahedral Field



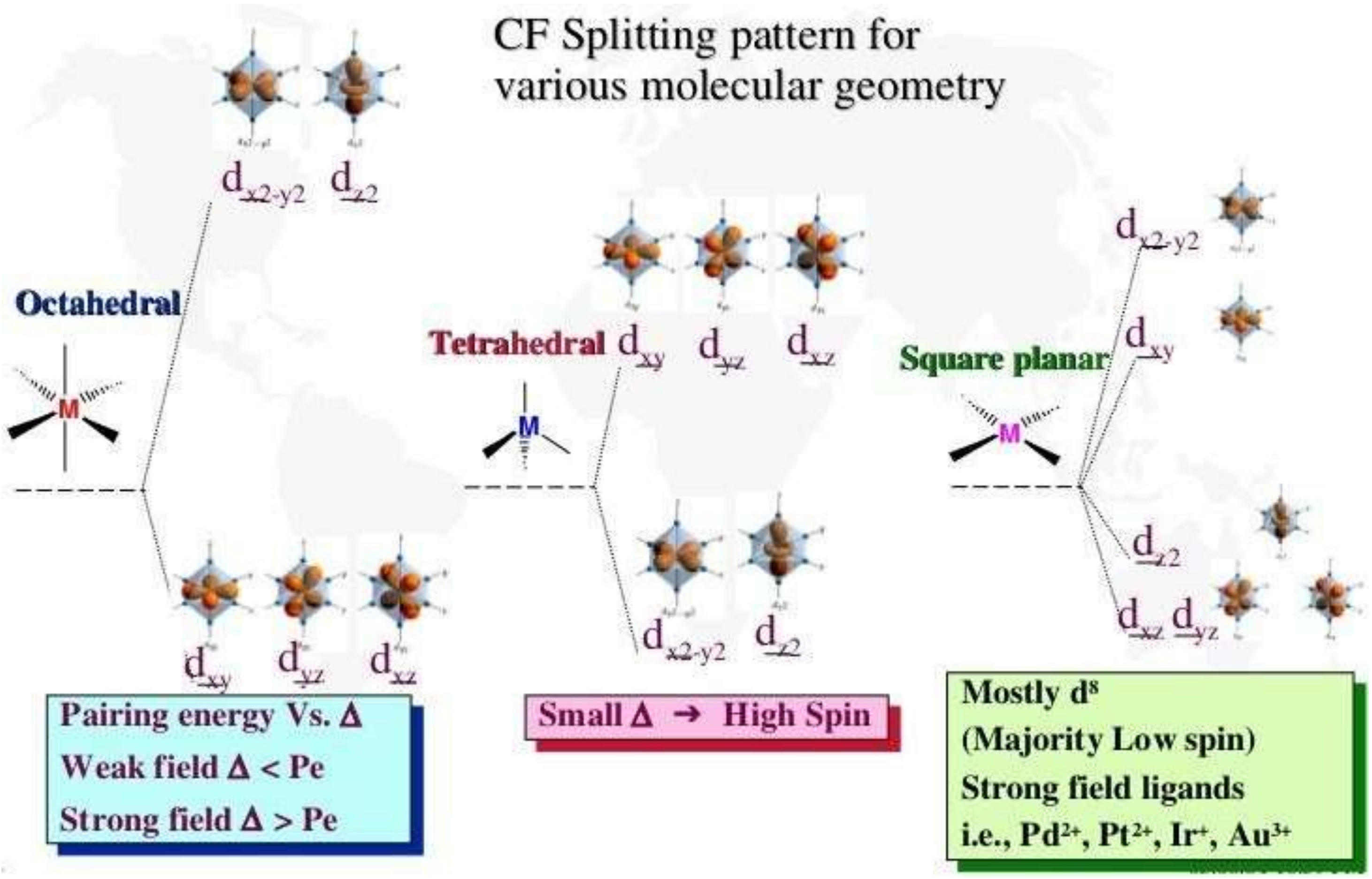
- Suppose a tetrahedral molecule is present inside the cube and metal ion is seated at the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

- It has no center of symmetry. So there is no question of mentioning ‘g’ or ‘u’ terms.

- The two ‘e’ ($d_{x2-y2}$ and $d_{z2}$) orbitals point to the center of the face of the cube while the three ‘$t_2$’ ($d_{xy}$, $d_{yz}$ and $d_{zx}$) orbitals point to the center of the edges of the cube.

- Thus, the $t_2$ orbitals are nearer to the direction of approach of the ligands than the e orbitals. (The ligands do not directly approach any of the metal d orbitals)

# CF Splitting: Octahedral Vs. Tetrahedral Vs. Square Planar

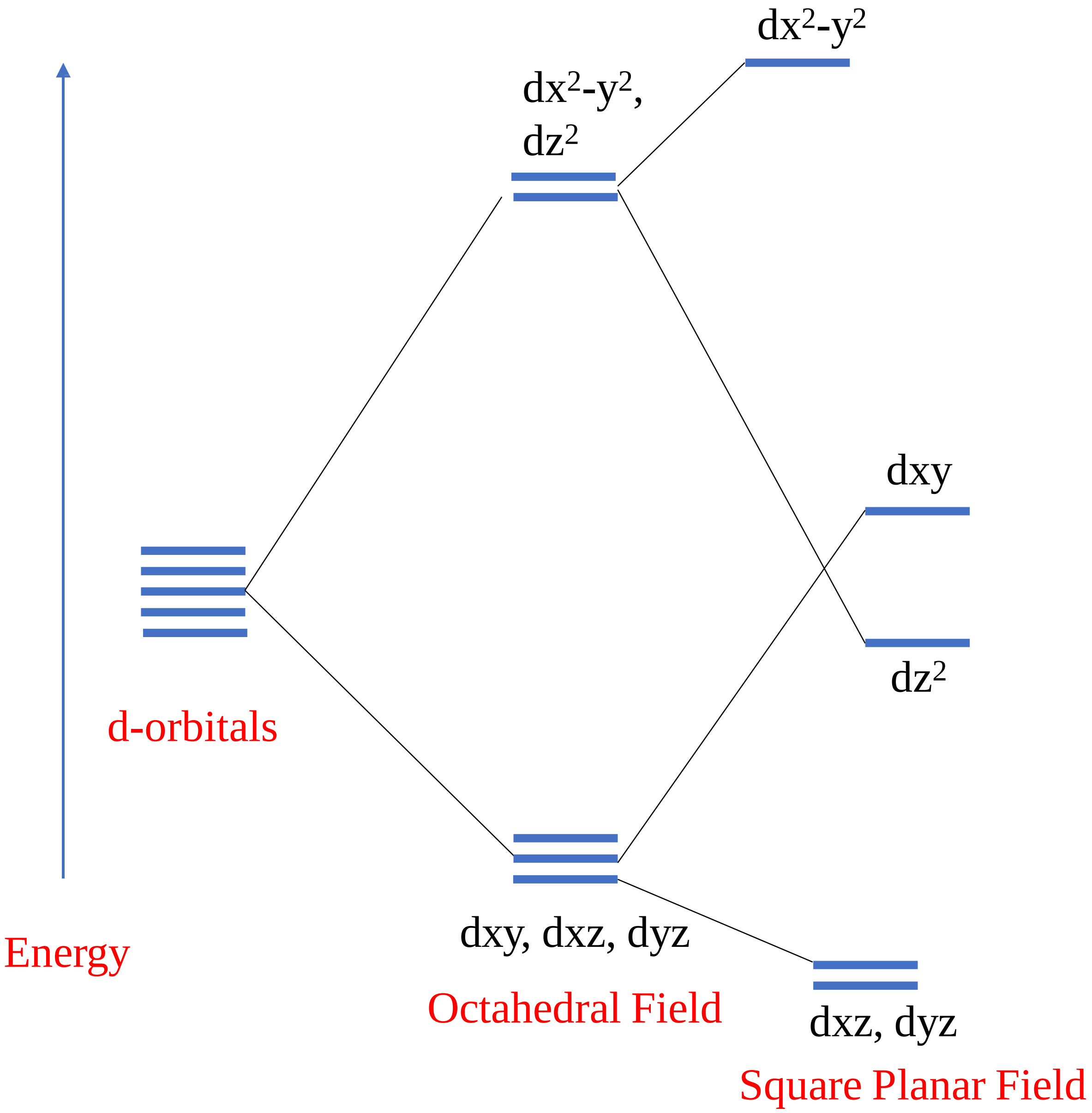

CF Splitting pattern for various molecular geometry

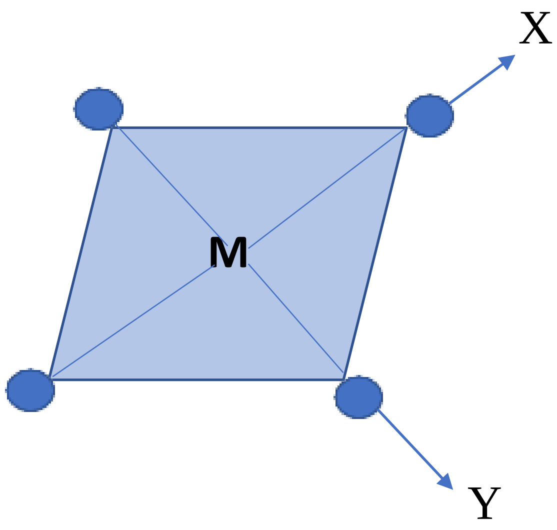
Pairing energy Vs. Δ
Weak field Δ < Pe
Strong field Δ > Pe

Small Δ ➔ High Spin

Mostly $d^8$
(Majority Low spin)
Strong field ligands
i.e., $Pd^{2+}$, $Pt^{2+}$, $Ir^{+}$, $Au^{3+}$

# CF Splitting: Square Planar Field





- Ligands along the Z axis are removed from an octahedral complex to get a square planar complex.

# Factors affecting the value of Δ in CFT:

- In the context of Crystal Field Theory (CFT), "delta" (often denoted as Δ) refers to the energy difference between the d orbitals in a transition metal complex. This energy difference arises due to the interaction between the metal ion's d orbitals and the surrounding ligands. The magnitude of this energy difference, Δ, plays a crucial role in determining various properties of transition metal complexes, such as their color, magnetic behavior, and reactivity.
- **Several factors influence the value of Δ in CFT:**
- Steric Effects: Steric effects, which refer to the spatial arrangement and bulkiness of ligands, can also influence Δ. Bulky ligands may hinder effective orbital overlap, resulting in smaller Δ values compared to complexes with smaller or less bulky ligands.

- Nature of the Metal Ion: The identity of the central metal ion significantly affects the magnitude of Δ. For instance, transition metals with a higher oxidation state typically have larger Δ values compared to those with lower oxidation states. This is because higher oxidation states lead to a greater charge on the metal ion, resulting in stronger electrostatic interactions with the ligands.
- a)Oxidation state of metal:
- Δ --→ Fe2+ < Fe3+
- with increase in the oxidation state of metal ,
- Δ value increases.

b) Position of metal in a group:

Δ --→ CO3+ < Rh3+ < Ir3+

down the group the spatial distribution of d o orb increases from 3d to 4d to 5d ,effective nuclear charge increases , electrostatic repulsion increases so Δ value increases

- Nature of the Ligands: The ligands surrounding the central metal ion also play a crucial role in determining Δ. Ligands can be classified as either strong-field ligands or weak-field ligands based on their ability to cause splitting of the d orbitals. Strong-field ligands (e.g., CN^-, CO, NH3) cause larger splitting (larger Δ), whereas weak-field ligands (e.g., F^-, Cl^-, H2O) cause smaller splitting (smaller Δ). This distinction arises from the different extent of overlap between the ligand orbitals and the d orbitals of the metal ion.

I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < OH2 < NCS^- < NC^- < NH3 < en < bpy < NO2^- < CN^- < CO

Example: Δ --→ **[CoF6]3– < Co [(H2O) 6] 3+**

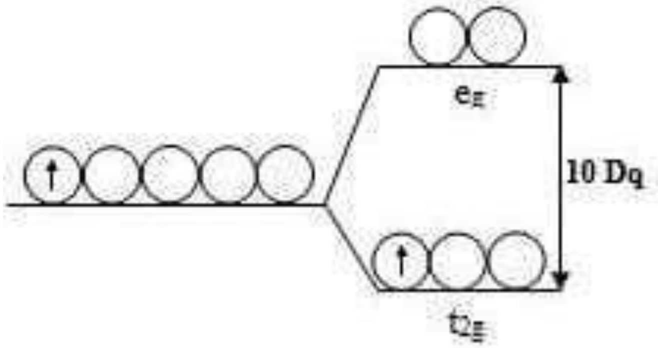
## Crystal Field Stabilisation Energy (CFSE):

- CFSE stands for "Crystal Field Stabilization Energy," and it's a concept in Crystal Field Theory (CFT). In CFT, the interaction between metal ions and ligands is described in terms of electrostatic forces. When ligands approach a metal ion, they create a region of negative charge around the metal ion due to their lone pairs of electrons. This interaction splits the d orbitals of the metal ion into two sets: one set of higher energy orbitals and one set of lower energy orbitals.
- CFSE refers to the energy difference between these two sets of d orbitals. Specifically, it's the energy required to pair up electrons in the lower energy orbitals, thus stabilizing the system. The magnitude of CFSE depends on factors such as the oxidation state of the metal ion, the nature of the ligands, and the geometry of the complex. In octahedral complexes, for example, the CFSE is typically higher than in tetrahedral complexes due to differences in orbital splitting.

- Example:

(d1,Octahedral)

1) $d^1$



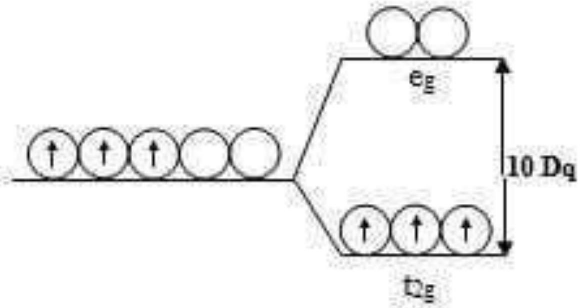
$C.F.S.E. = x(-4Dq) + y(+6Dq) + P$

$C.F.S.E. = 1 \times (-4Dq) + 0 \times (+6Dq) + 0$

$= -4Dq$

(d3,Octahedral)

3) $d^3$



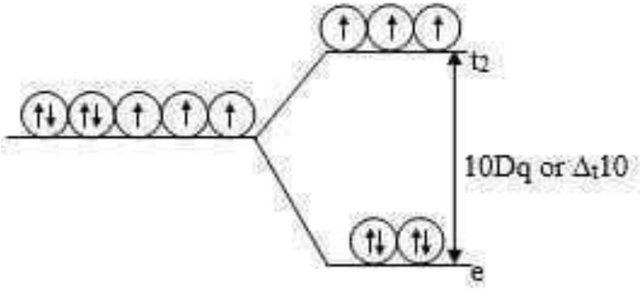
$C.F.S.E. = x(-4Dq) + y(+6Dq) + P$

$C.F.S.E. = 3 \times (-4Dq) + 0 \times (+6Dq) + 0$

$= -12Dq$

(d7,Tetrahedral)

7) $d^7$



$C.F.S.E. = x(-6Dq) + y(+4Dq) + P$

$C.F.S.E = 4 \times (-6Dq) + 3 \times (+4Dq) + 2P$

$= -24Dq + 12Dq + 2P$

$= -12Dq + 2P$

# HIGH SPIN AND LOW SPIN STATE

High spin and low spin refer to the ways electrons can be distributed within the d orbitals of transition metal ions in coordination complexes.

**1.******High Spin******:** In a high spin configuration, electrons occupy degenerate (equal-energy) orbitals before pairing up. This means that electrons will occupy each orbital singly before pairing up with another electron in the same orbital. This configuration maximizes the number of unpaired electrons and thus maximizes the total electron spin, leading to a higher overall spin state. High spin configurations are favored when the energy required to pair electrons is greater than the energy difference between the d orbitals.

**2.******Low Spin******:** In a low spin configuration, electrons preferentially pair up in the d orbitals before occupying higher energy orbitals. This results in fewer unpaired electrons and a lower overall spin state. Low spin configurations are favored when the energy required to pair electrons is less than the energy difference between the d orbitals.

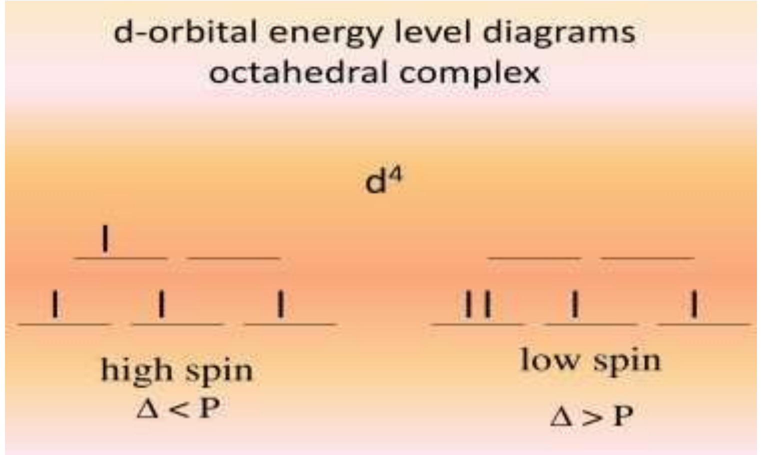
The choice between high spin and low spin configurations depends on various factors, including the nature of the ligands surrounding the metal ion, the metal ion's oxidation state, and the crystal field splitting energy of the complex.

# EXAMPLE

I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < OH2 < NCS^- < NC^- < NH3 < en < bpy < NO2^- < CN^- < CO

| $[Mn(H_2O)_6]^{3+}$ | $[Co(NH_3)_6]^{3+}$ | $[Cr(OH_2)_6]^{3+}$ |
|---|---|---|
| (d5,Octahedral) | (d6,octahedral) | (d4,octahedral) |
| (High Spin) | (Low spin) | (High spin) |

Mathematically we can show that $[Cr(OH_2)_6]^{3+}$ is a High Spin complex. If given **p=23500cm^- & Δo=13900cm^-**



H.S CFSE= -0.6 **Δo**

**=** -0.6x139000 cm^-

= -8340 cm^-

L.S CFSE= -1.6 **Δo +** P

=(-1.6x13900 + 23500)cm^-

= +1260 cm^-

**High Spin state is more stable than low low spin state as CFSE is (-) ve for H.S while that is (+) ve in L.S state.**

- **$[NiCl_4]^{2-}$** **$[CoCl_4]^{2-}$**

(d8 ,Tetrahedral) (d7, Tetrahedral)

(High Spin) (High Spin)

*Tetrahedral complexes are always High Spin.

**$[Ni(CN)_4]^{2-}$** **$[NiF6]2-$**

**(d8**, Square Planar) **(**d6,Octahedral)

(Low Spin) (Low Spin)

*Here Ni is in higher oxidation state(Ni+4),
so it is the L.S complex despite having a weaker field ligand (F-).

## Jahn-Teller Distortion (JT):

### JT Theorem:

Any non linear molecule in a degenerate electronic state will undergo distortion to remove degeneracy and to lower energy.

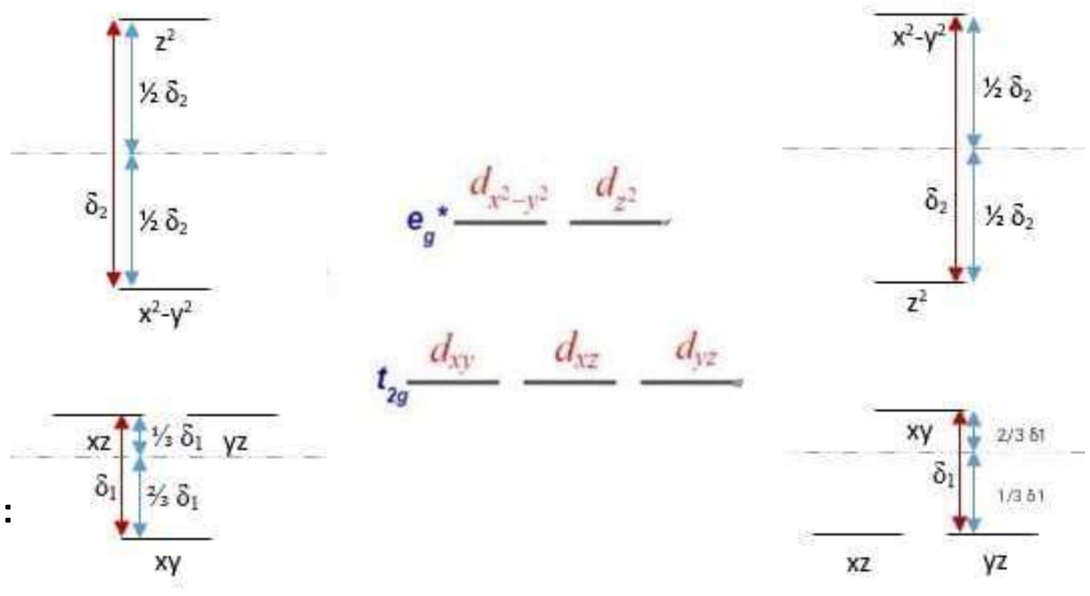
### In Octahedral Field:

eg orbitals are more sensitive than t2g orbitals towards JT Distortion as eg orbitals have their lobes projected towards the ligand.

### In Tetrahedral Field:

t2 orbitals are more sensitive towards JT Distortion than e orbitals.

Example:



**z-in**

**z-out**

1) **[Ti(H2O)6]3+** **(d1)** distorted or perfect oh?

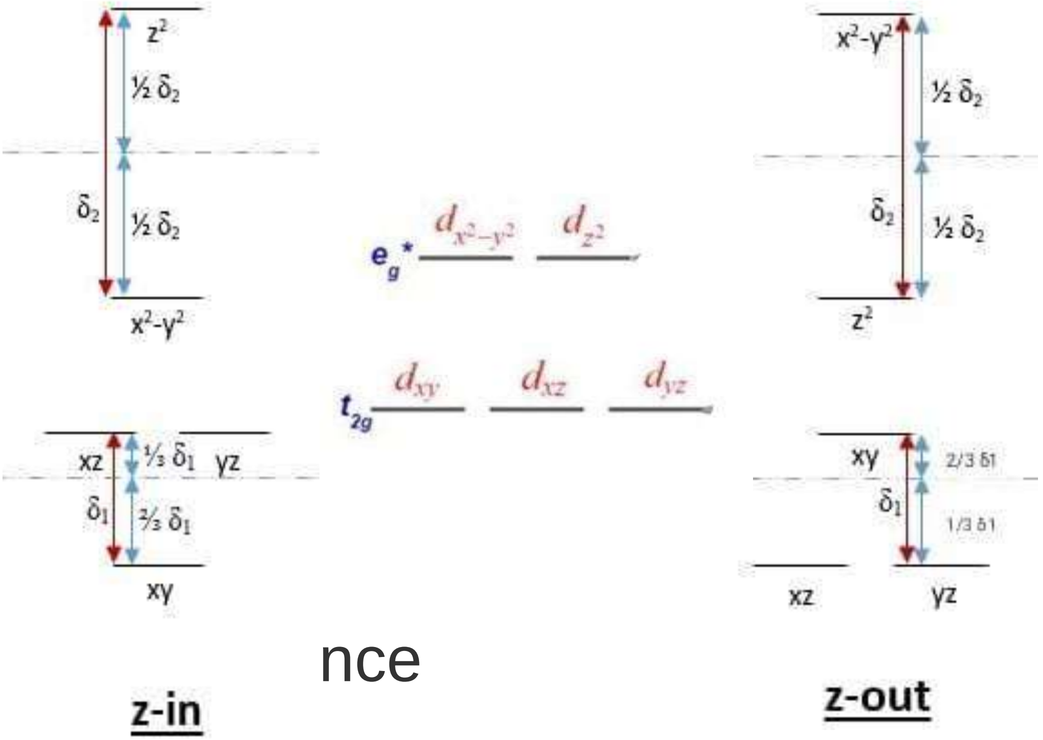
| Z-in( dxy1) | Z-out (dxz1 or dyz1) |
|---|---|
| **Add Stability** | **Add Stability** |
| =1x(-2/3δ1) | = 1x(-1/3δ1) |
| = -2/3 δ1 | = -1/3 δ1 |

Distorted,as it experiences addn stability through the distortion and it is **Z-in**.

**2) [V(H2O)6]3+** **(d2)** distorted or perfect oh?

| Z-in( dxy1 and dxz1or dyz1) | Z-out (dxz1 and dyz1) |
|---|---|
| **Add Stability** | **Add Stability** |
| = 1x(-2/3δ1) + 1x(+1/3δ1) | = 2x(-1/3 δ1) |
| = -1/3 δ1 | = - 2/3 δ1 |

So, Distorted and it is **Z-out**.



nce

## 3) $[Cr(OH_2)_6]^{3+}$ **(d3)** distorted or perfect oh?

Z-in( dxy1 and dxz1or dyz1) Z-out (dxz1 andyz1)

**Add Stability** **Add Stability**

= 1x(-2/3δ1) +2x(+1/3δ1) =2x (-1/3δ1)

**= 0** **= 0**

So, it is Perfect Octahedral , as it does any stability through the distortion.

*If unsymmetry in eg then extent of distortion in high.

*If unsymmetry in t2g then extent of distortion in low.

# Spinel structures and CFT

## Normal Spinal Structure.

**Spinel: $MgAl_2O_4$**

Both Mg(II) and Al(III) are $d^0$ system. So there will be no spatial preference on CFSE ground.

**So, $M^{2+}$ ion occupy tetrahedral holes and $M^{3+}$ ion occupy octahedral holes.**

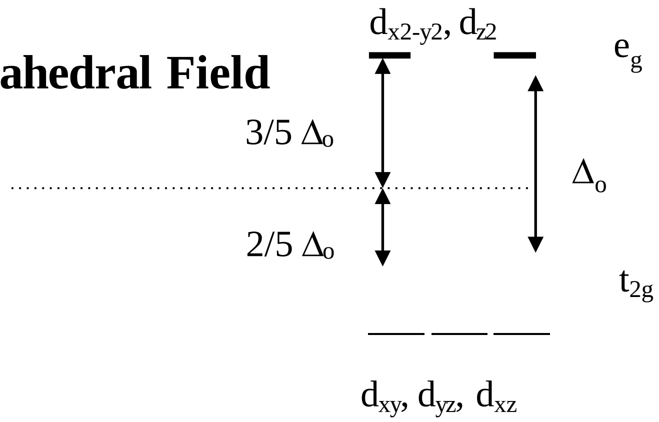
## Inverse Spinal Structure.

**Example: Magnetite: $(Fe^{3+})_T(Fe^{2+},Fe^{3+})_O(O^{2-})_4$**

$Fe_3O_4$ ($Fe^{2+}$, $2Fe^{3+}$, $2O^{2-}$)
Note the $O^{2-}$ is a weak field ligand. (Fe is H.S.)

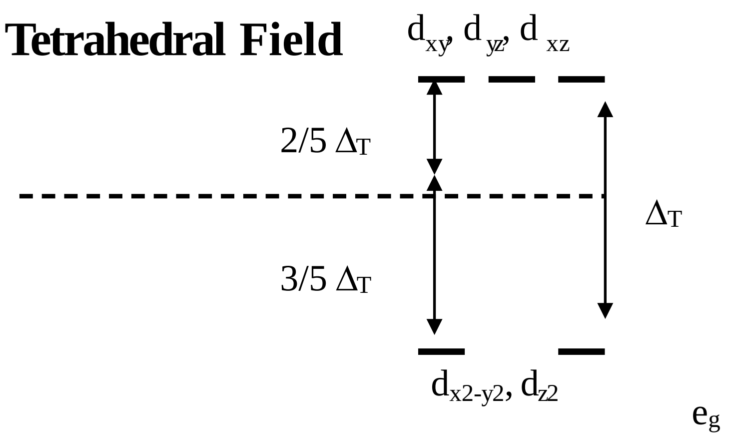
**$Fe^{3+}$ is $d^5$ and $Fe^{2+}$ is $d^6$.**

**Octahedral Field**



**OR**

**Tetrahedral Field**



Fe (II): CFSE(Oh)=-4 Dq
Fe(III): CFSE (Oh) = 0 Dq

→ **Inverse Spinal**

## $Mn_3O_4$ Spinel Structure:

Mn(II) $d^5$ system CFSE = 0 for both Oh and Td field under weak field.
Mn (III) $d^4$ system CFSE = -0.6 Dq (Oh) and -0.4Δt.

Inverted Spinel Structure

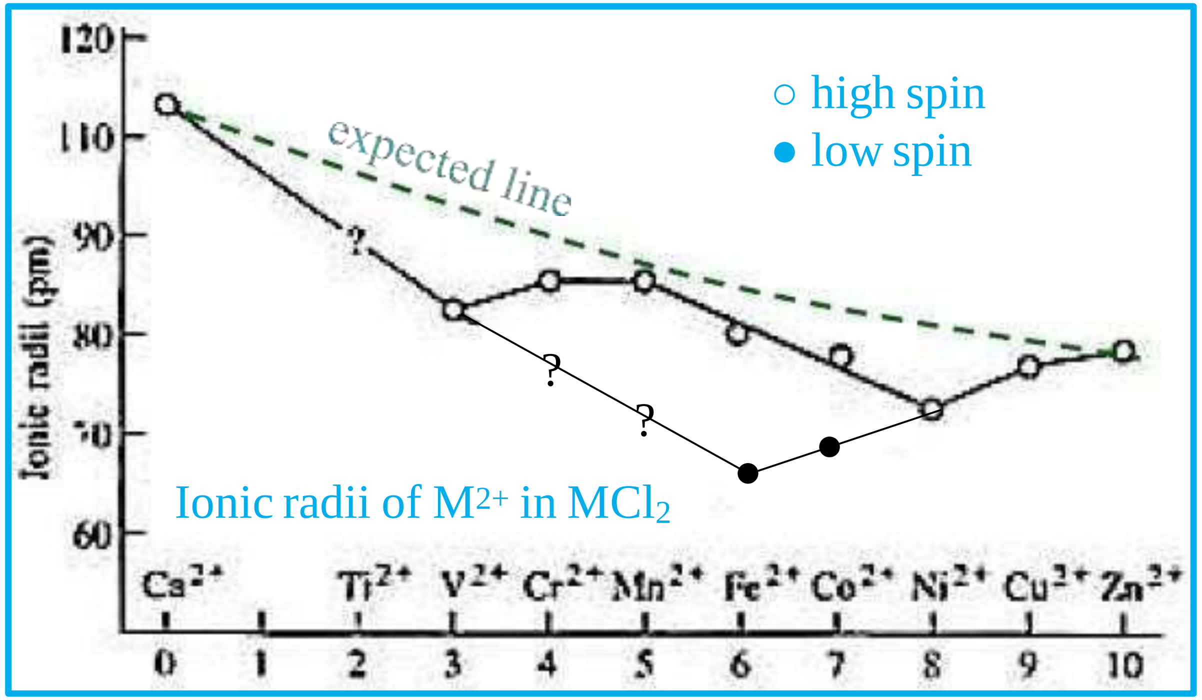
## $Co_3O_4$ Spinel Structure:

Co(II) $d^7$ system CFSE = -0.8Δo (Oh) and -1.2Δt (Td)
Co(III) $d^6$ system CFSE = -0.4 Dq (Oh) and -0.6Δt. (Td)
CFSE ($d^6$, low spin) = -24 Dq

- ❖ Because of very high CFSE of $d^6$ system in low spin situation, instead of having high spin environment provided by oxide ions Co(III) adopts low spin and occupy octahedral holes Spinel Structure.

Result : Normal Spinel Structure.

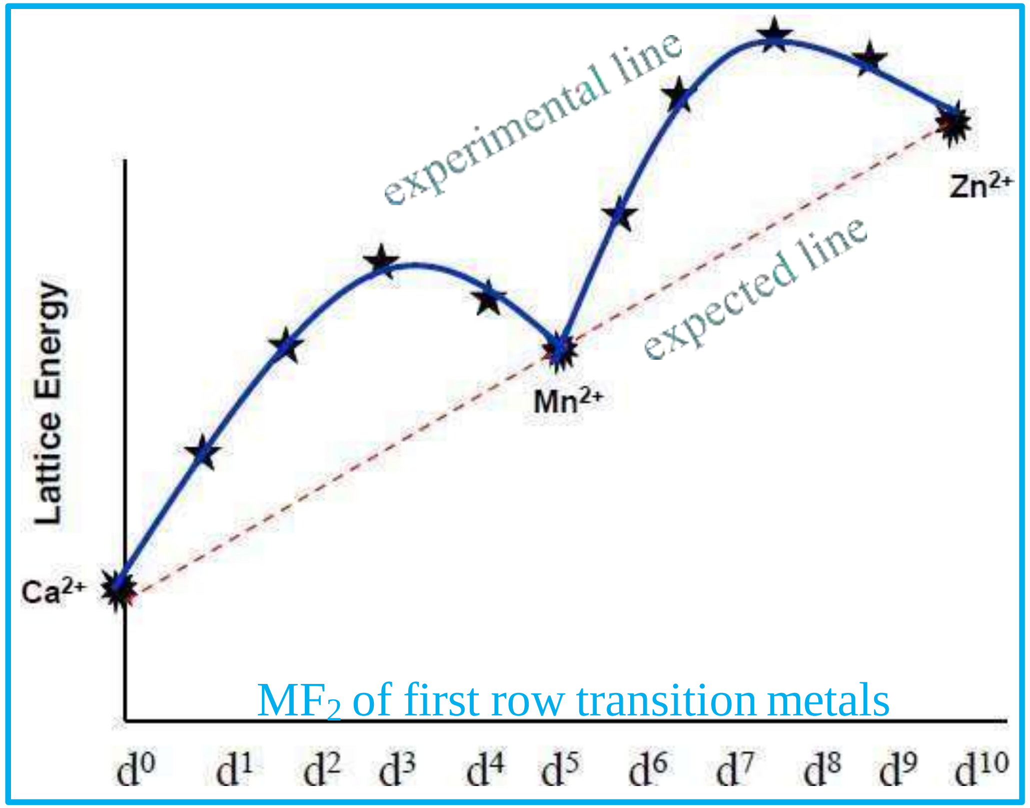
# Applications of Crystal Field Theory: Ionic Radii



- ❖ For a given oxidation state, the ionic radius is expected to decrease continuously across a transition series. Deviations from the expected line can be attributed to different electronic configurations (resulting from crystal field splitting).

- ❖ For weak field case, ionic radius starts to increase with $t_{2g}^3e_g^1$ configuration as the electron in the $e_g$ level experience repulsion with the ligands. For strong field case, ionic radius starts to increase with $t_{2g}^6e_g^1$ configuration.

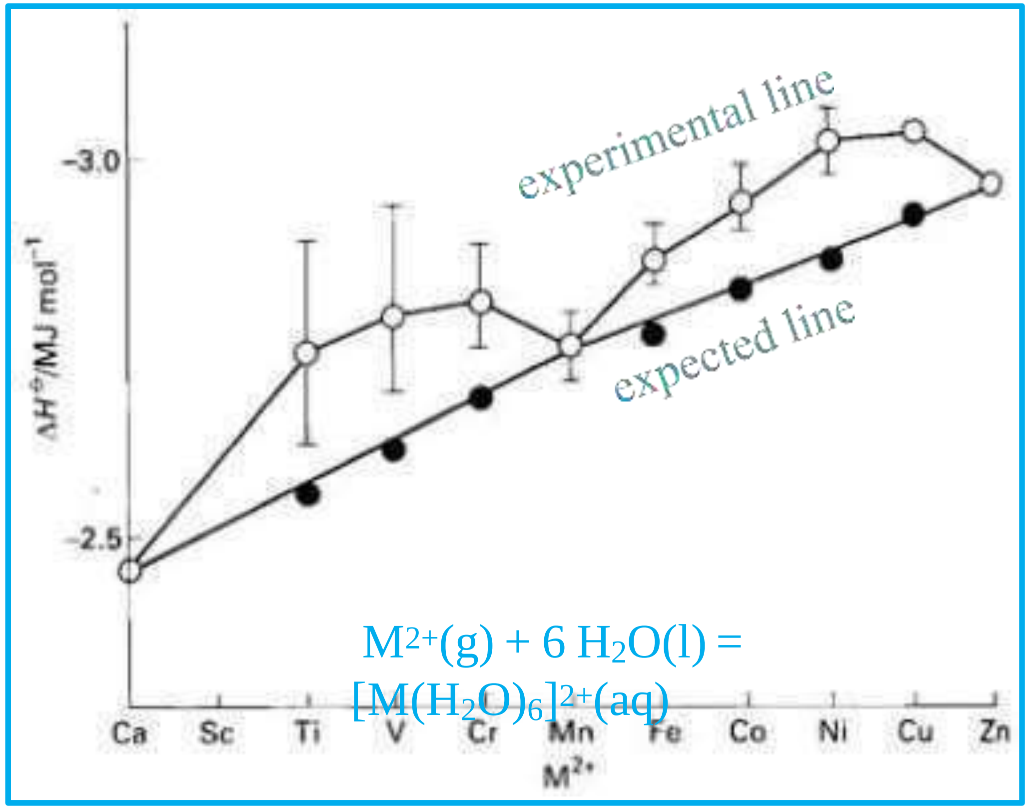
# Applications of Crystal Field Theory: Lattice Energy



- The lattice energy is expected to increase continuously across the transition series as the ionic radii of the metals decrease (lattice energy is proportional to $1/(r^+ + r^-)$. Deviations from expected line can be attributed to CFSE.

- $Ca^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ have $d^0$, $d^5$ and $d^{10}$, thus CFSE is 0. They follow the expected line. Other metal ions deviate from the expected line due to extra CFSE. CFSE increases from $d^1$ to $d^3$, decreases again to $d^5$, then rises to $d^8$.

# Applications of Crystal Field Theory: Enthalpy of Hydration/Formation



$M^{2+}(g) + 6\,H_2O(l) = [M(H_2O)_6]^{2+}(aq)$

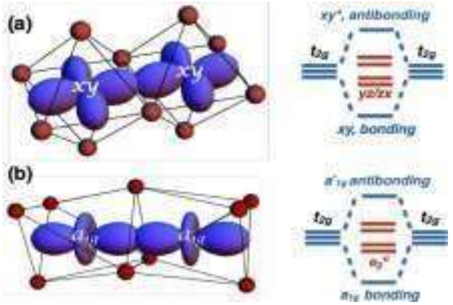
- Stronger electrostatic attraction energy between ions and water dipoles increases hydration enthalpy ($\Delta H$). $\Delta H$ is proportional to the charge but inversely proportional to the radius of the ion. $\Delta H$ should increase (become more negative) continuously across transition series due to decrease in ionic radii. But, experimental $\Delta H$ values show characteristic double-humped shape.

- The trend for hydration enthalpies corresponds with the one for the ionic radii.

# Challenges of Crystal Field Theory

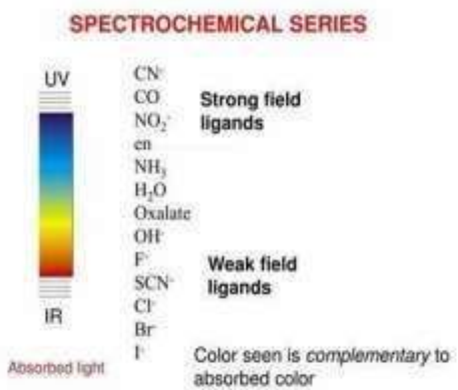
## > Covalent Bonding

Crystal field theory could not account for the covalent bonding found in some transition metal complexes.



## >Spectrochemical Series

It fails to explain the order of ligands in the spectrochemical series.This is because ligands are considered point charges,anionic ligands should have a stronger splitting effect.But anionic ligands are present at the bottom of spectrochemical series.



## > Exclusion of s and p orbitals

No contribution is considered for s and p orbitals,which is required in certain cases.This is a critical drawback because p-bonding is found in numerous compounds

## >Orbitals of Ligands

There is no discussion about the orbitals of the ligands in the transition metal.it fails to explain the properties related to ligand orbitals and their interaction with metal orbitals.

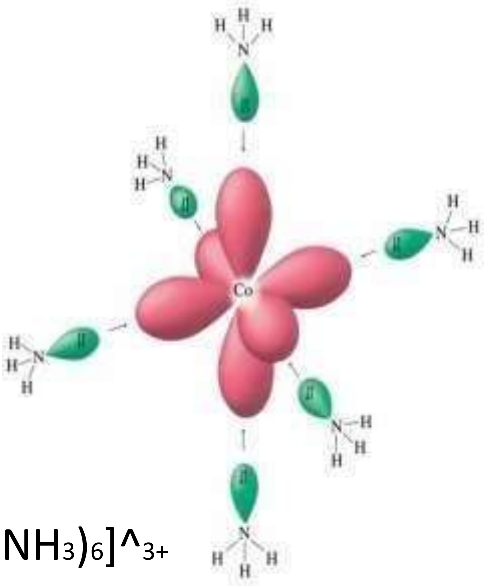


fig:$[Co(NH_3)_6]$^$^{3+}$

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5. And we would like to thank Dr.Sutanuva Mandal

# THANK YOU