Bonding IN Coordination compounds: crystal field theory

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UNIT-I Chemistry of coordination compounds

Theories put forward to explain bonding in coordinati compounds:-

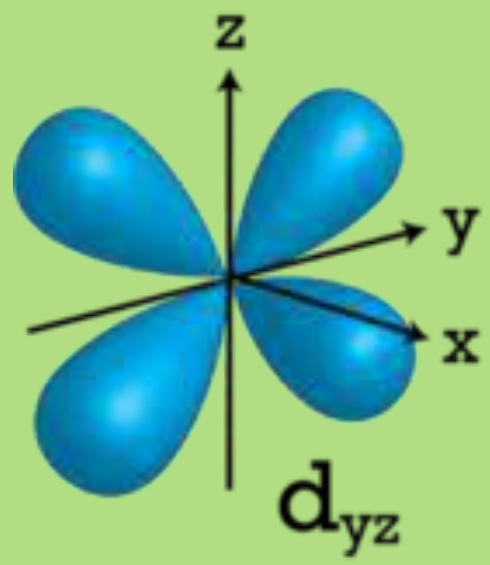
- **Valence Bond Theory**
- **Crystal Field Theory**
- **Molecular Orbital Theory**

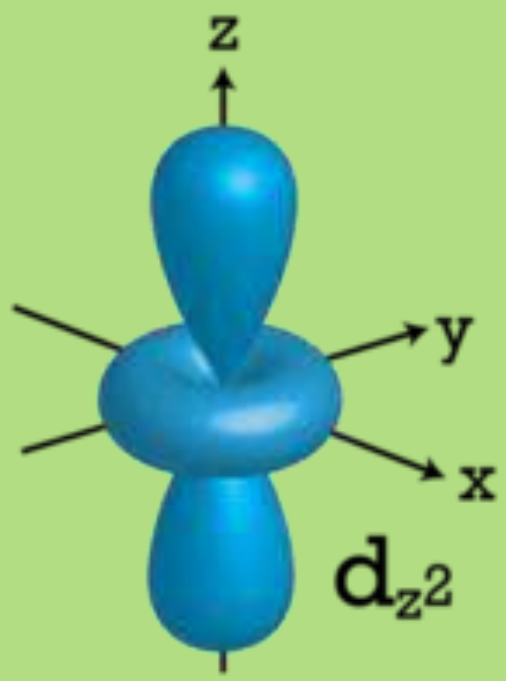
Basic assumptions of Crystal Field Theory (CFT)

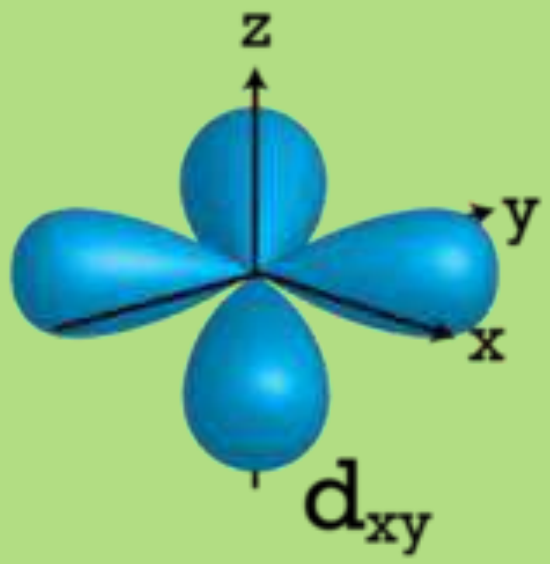
- ligands are considered as point negative charges
- metal electrons are considered to maintain their wave mechanical identity i.e. they occupy suitable orbitals

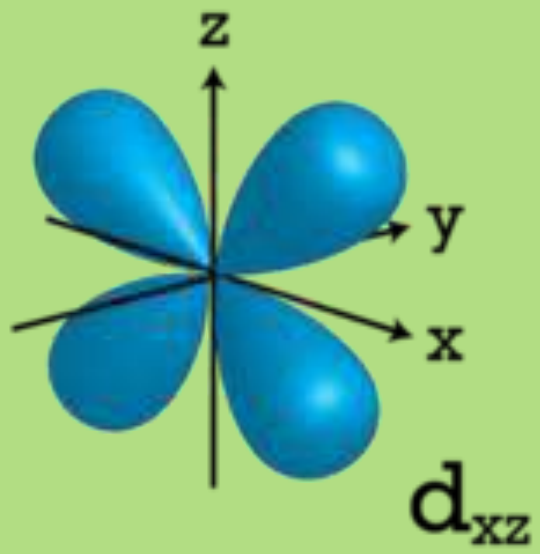
- Pure electrostatic interaction is considered between the ligands and the metal

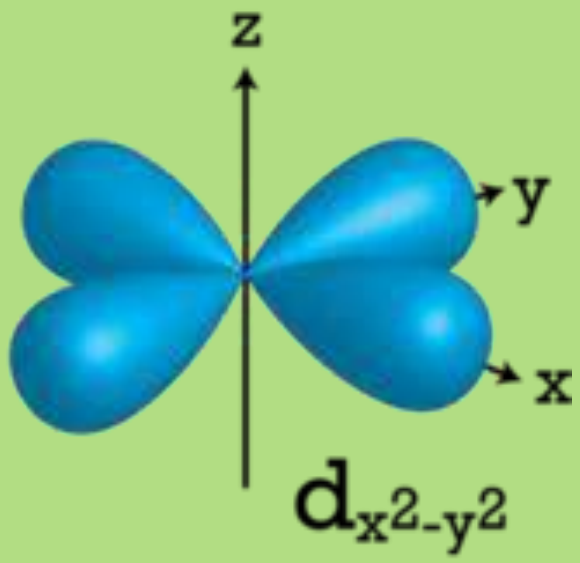
The d orbitals











Spherically Symmetric Field

If a spherically symmetric field of negative charges is placed around the metal, the d orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals

Octahedral Field

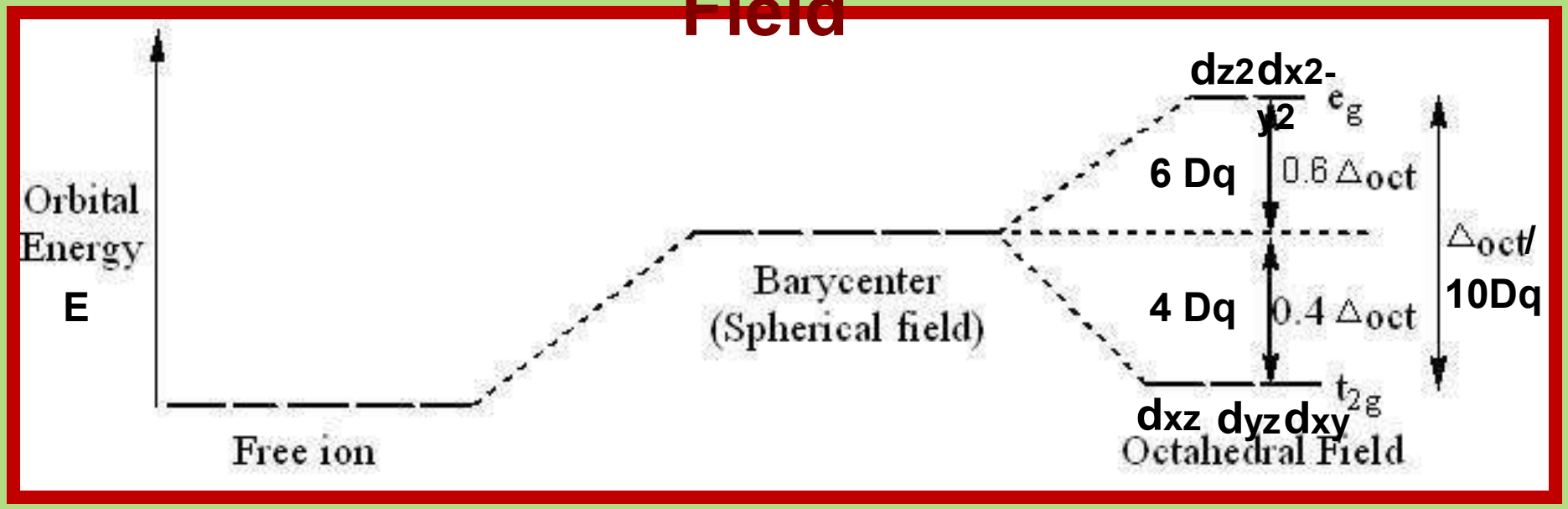
If rather than a spherical field, ligands are arranged around the metal in an octahedral field, the degeneracy of the d orbitals is removed

- **The splitting of d orbital energies and its consequences are at the heart of the Crystal Field Theory**

- The ligands approach the central metal in an octahedral field along the three cartesian axes
- The orbitals which lie along these axes (i.e. d_{x2-y2}, d_{z2}) will be destabilized more than the orbitals which lie in-between the axes (i.e. d_{xy}, d_{xz}, d_{yz}). The splitting of the d orbitals also conserve the barycenter.

- The set of three lower energy degenerate orbitals (d_{xy}, d_{xz}, d_{yz}) are termed as t_{2g} (triplet) and the set of two higher energy orbitals (d_{x2-y2}, d_{z2})are termed as e_g (doublet)

Splitting of d orbitals in an Octahedral Field



For d^1, CFSE = 1 × 0.4 = 0.4 Δo
For d^2, CFSE = 2 × 0.4 = 0.8 Δo
For d^3, CFSE = 3 × 0.4 = 1.2 Δ

For d^8, CFSE = (6 × 0.4) – (2 × 0.6) = 1.2 Δo
For d^9, CFSE = (6 × 0.4) – (3 × 0.6) = 0.6 Δo
For d^{10}, CFSE = (6 × 0.4) – (4 × 0.6) = 0.0 Δo

For d^4–d^7, CFSE = two possibilities

Crystal Field Stabilization Energy (CFSE)

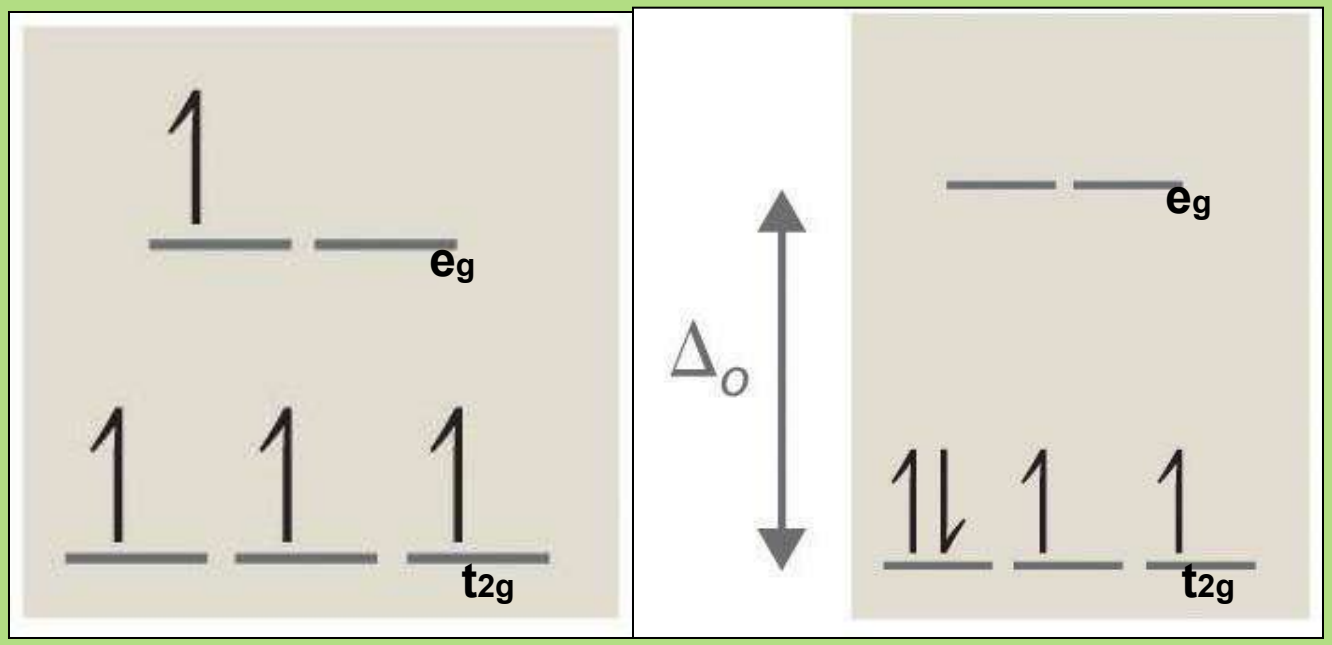
- The extent by which the energy of the electrons are lowered in a field in comparison to a hypothetical spherical field of the ligands at the same distance is called crystal field stabilization energy.

Pairing Energy

- The electron-pairing energy is composed of two terms. One is the inherent coulombic repulsion that must be overcome when forcing two electrons to occupy the same orbitals. The second factor is the loss of exchange energy , that occurs when electrons with parallel spins are forced to have anti parallel spins

High spin and Low Spin Complexes

d^4 system

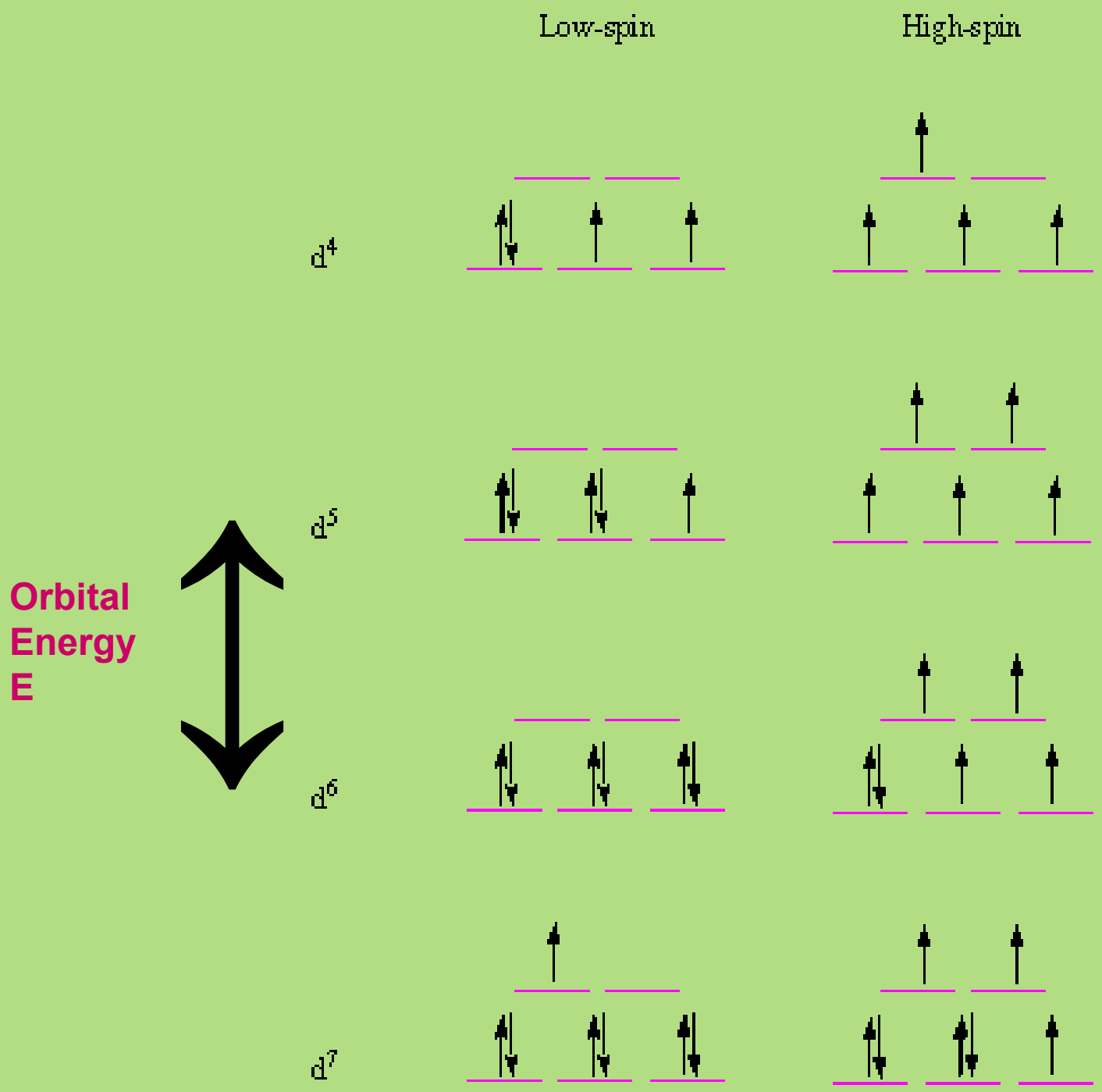


high spin

low spin

Δo < P

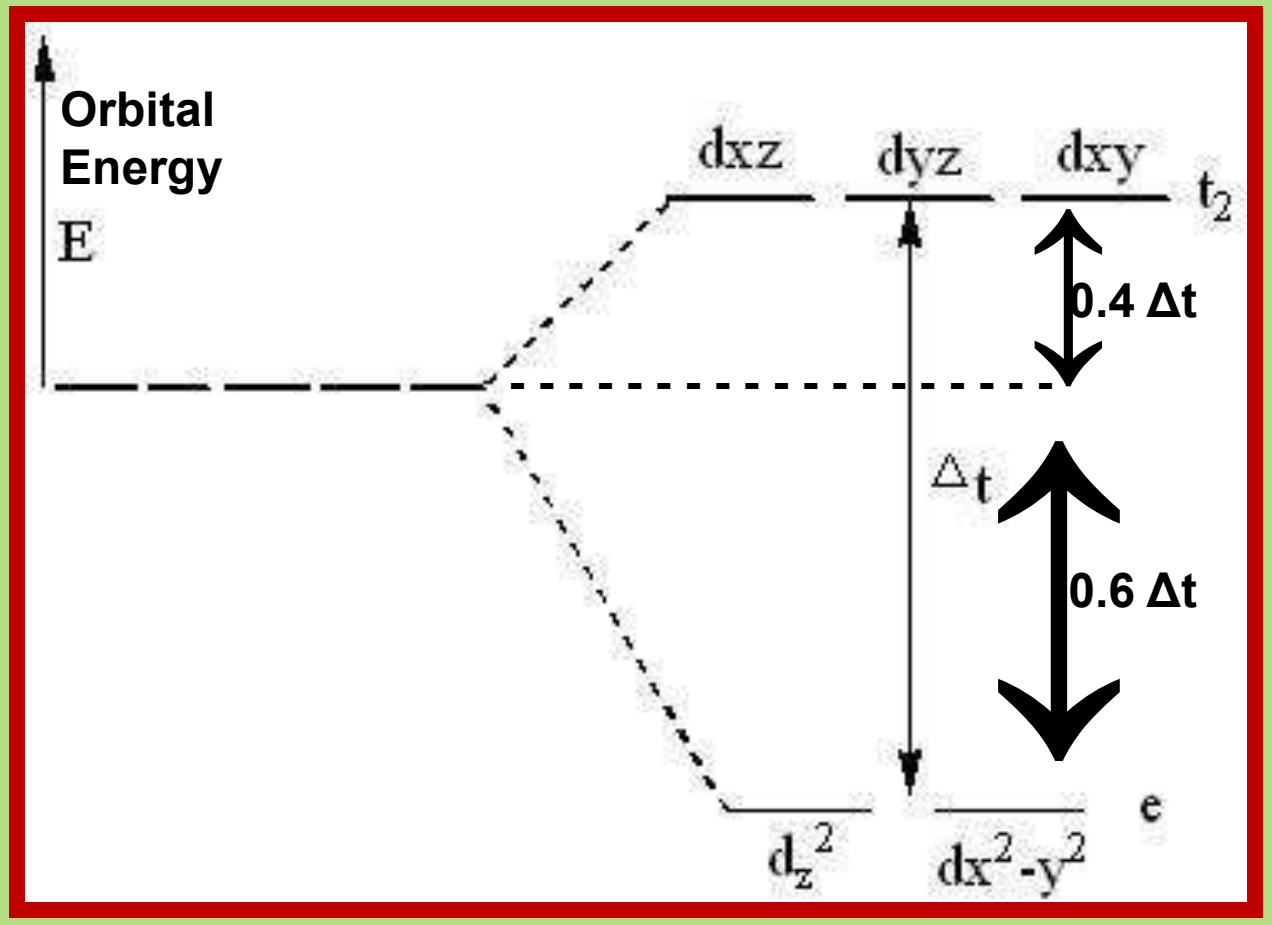
Δo > P


Low-spin
High-spin
d4
d5
d6
d7
Orbital
Energy
E

CFSE in High Spin and Low Spin Octahedral Complex

No. of d electrons	Electronic Configuration and CFSE	
	High Spin Complexes	Low Spin Complexes
d1	$t_{2g}1e_g0$ 0.4 Δo	$t_{2g}1e_g$ 0 0.4 Δo
d2	$t_{2g}2e_g0$ 0.8 Δo	$t_{2g}2e_g0$ 0.8 Δo
d3	$t_{2g}3e_g0$ 1.2 Δo	$t_{2g}3e_g0$ 1.2 Δo
d4	$t_{2g}3e_g1$ 0.6 Δo	$t_{2g}4e_g0$ 1.6 Δo - p
d5	$t_{2g}3e_g2$ 0.0 Δo	$t_{2g}5e_g0$ 2.0 Δo - 2p
d6	$t_{2g}4e_g2$ 0.4 Δo	$t_{2g}6e_g0$ 2. 4 Δo -2p
d7	$t_{2g}5e_g2$ 0.8 Δo	$t_{2g}6e_g1$ 1.8 Δo -p
d8	$t_{2g}6e_g2$ 1.2 Δo	$t_{2g}6e_g2$ 1.2 Δo
d9	$t_{2g}6e_g3$ 0.6 Δo	$t_{2g}6eg3$ 0.6 Δo
d10	$t_{2g}6e_g4$ 0.0 Δo	$t_{2g}6e_g4$ 0.0 Δo

Splitting of d orbitals in a Tetrahedral Field



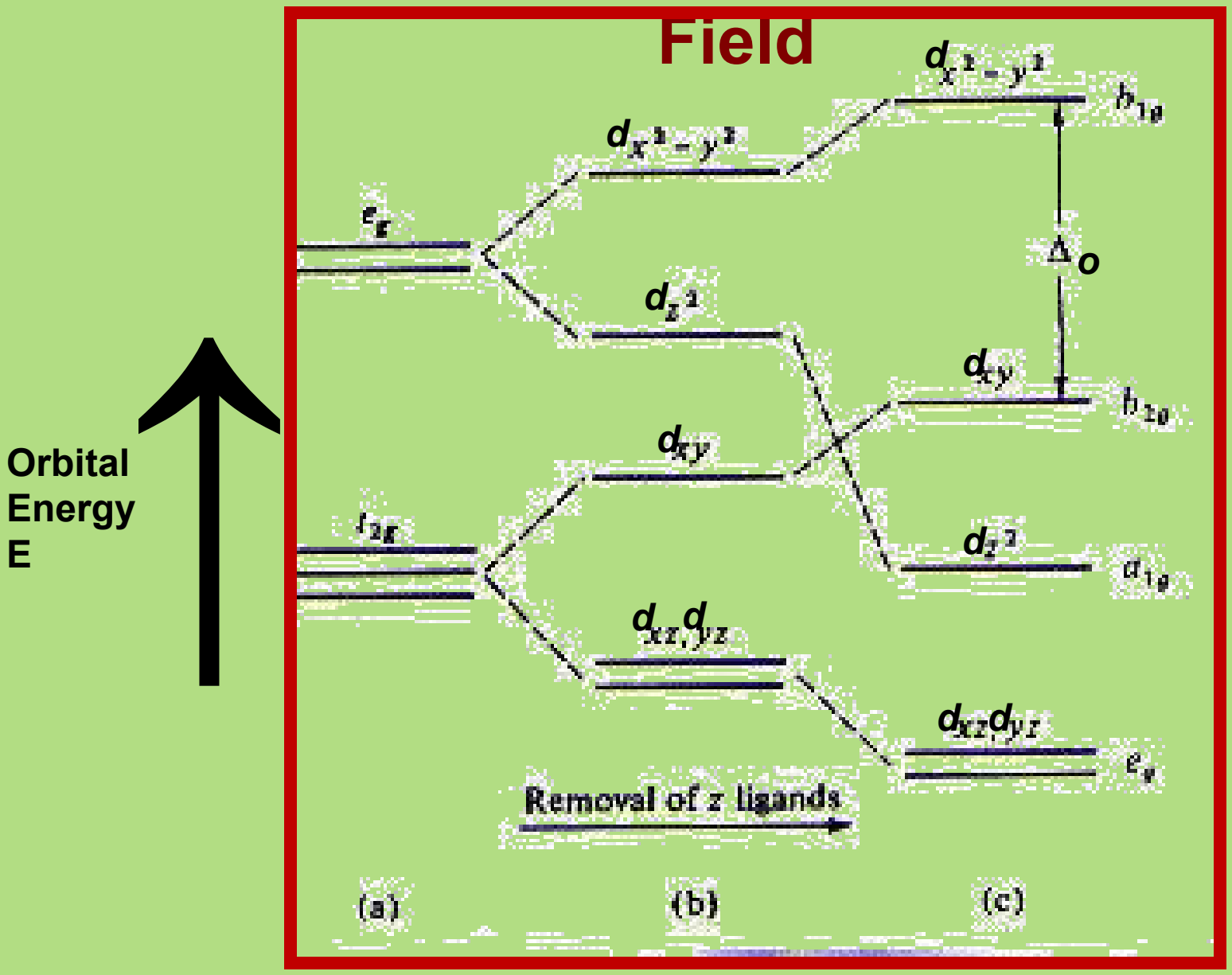
$\Delta t = 4/9\ \Delta o$

- There are only 4 ligands in the tetrahedral complex
- The direction of ligand approach in tetrahedral complex does not coincide with the direction of d-orbitals
- Tetrahedral splitting is seldom large enough to result in pairing of the electrons. As a result, low-spin tetrahedral complexes are not common.

CFSE in Tetrahedral Complexes

No. of d electrons	Electronic Configuration and CFSE
d1	$e^1 t_2^0$ 0.6 Δt
d2	$e^2 t_2^0$ 1.2 Δt
d3	$e^2 t_2^1$ 0.8 Δt
d4	$e^2 t_2^2$ 0.4 Δt
d5	$e^2 t_2^3$ 0.0 Δt
d6	$e^3 t_2^3$ 0.6 Δt
d7	$e^4 t_2^3$ 1.2 Δt
d8	$e^4 t_2^4$ 0.8 Δt
d9	$e^4 t_2^5$ 0.4 Δt
d10	$e^4 t_2^6$ 0.0 Δt

Splitting of d orbitals in a Square Planar Field



Factors Affecting The Magnitude of Δ

1. Higher oxidation states of the metal atom correspond to larger Δ

Δ =10,200 cm for $[Co(NH_3)_6]^{III}$ and 22,870 cm for $[Co(NH_3)_6]^{III}$

Δ =32,200 cm for $[Fe(CN)_6]^{II}$ and 35,000 cm for $[Fe(CN)_6]^{III}$

2. In groups, heavier analogues have larger Δ

For hexaammine complexes $[M(NH_3)_6]^{III}$:

Δ = 22,870 cm (Co)

34,100 cm (Rh)

41,200 cm Ir)

3. Geometry of the metal coordination unit affects Δ greatly

Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6

Δ = 10,200 cm for $[Co(NH_3)_6]^{III}$

5,900 cm for $[Co(NH_3)_4]^{III}$

4. Nature of the ligands

For $[Co^{III}L_6]$, Δ in cm : 13,100 (F^-); 20,760 (H_2O); 22,870 (NH_3)

For $[Cr^{III}L_6]$, Δ in cm : 15,060 (F^-); 17,400 (H_2O); 26,600 (CN^-)

Spectrochemical Series

- **An arrangement of ligands according to their ability to increase Δ for a given metal center**

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- < urea, OH^- < ox, O^{2-} < H_2O < NCS^- < py, NH_3 < en < bpy, phen < NO_2^- < CH_3^-, C_6H_5^- < CN^- \leq CO$

Use of CFSE- Spinels and Inverse Spinels

- **Spinel is the name given to the mineral $MgAl_2O_4$.**

It has a common structural arrangement shared by many oxides of the transition metals with formula **AB_2O_4**.

- **Normal Spinel- The oxygens form a cubic close packed array. The Mg(II) (A-type) sit in tetrahedral sites. The Al(III) (B-type) sit in octahedral sites i.e. $[M(II)][M(III)M(III)]_{oh}O_4$ eg. Co_3O_4, Mn_3O_4**

- **Inverse Spinel- This is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites i.e. $B(AB)O_4$ i.e. $[M(III)]_{tet}[M(II)M(III)]_{oh}O_4$ eg. Fe_3O_4**

- If M^{3+} ion has a higher CFSE in an octahedral field compared to M^{2+} ion, normal spinel will result.

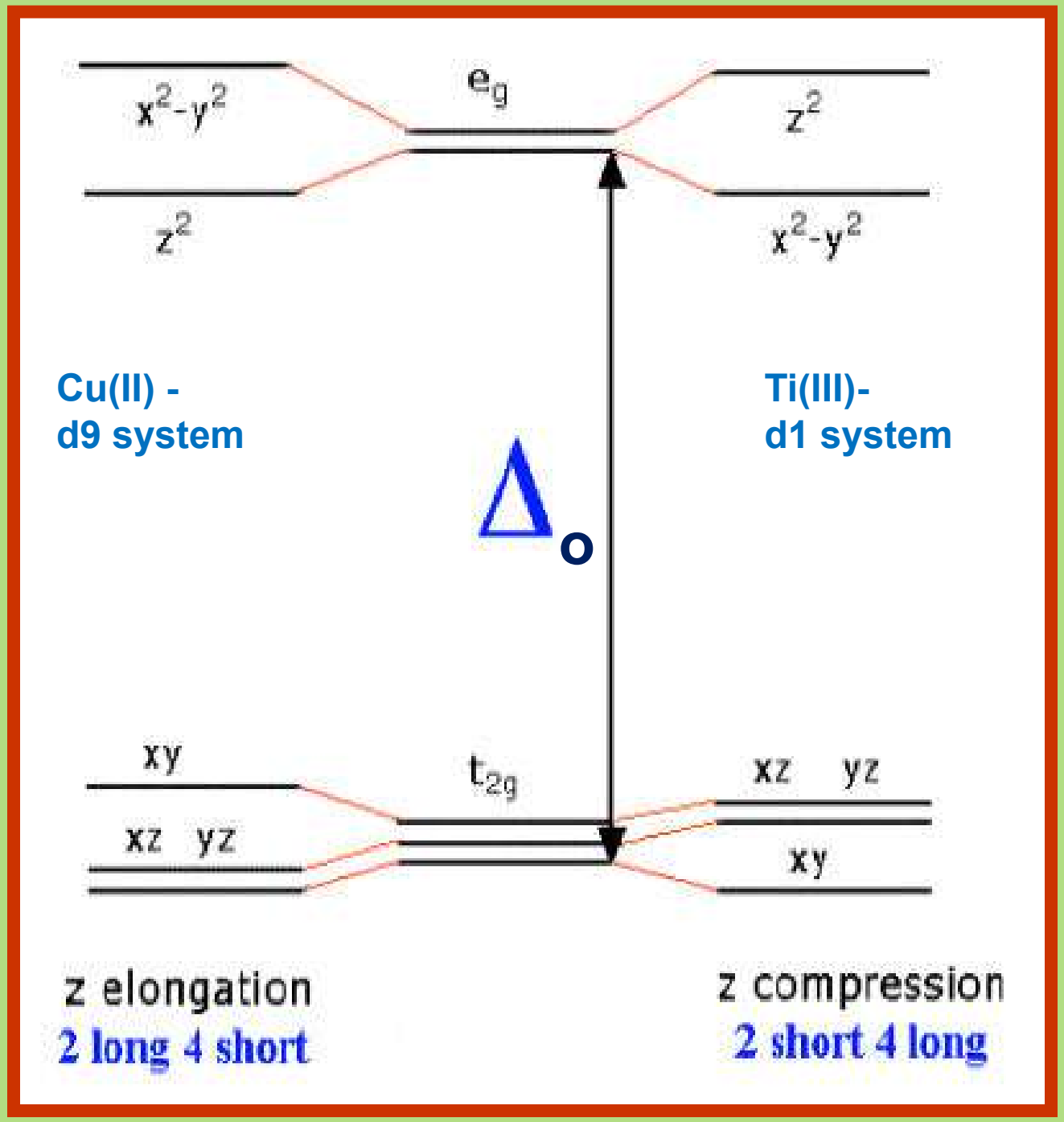
Mn_3O_4 (oxygen weak field ligand)
Mn^{2+}: $d^5 = t_{2g}^3 e_g^2$; no CFSE
Mn^{3+}: $d^4 = t_{2g}^3 e_g^1$; 0.6 Δo
Structure: Normal Spinel

- If M^{2+} ion has a higher CFSE in an octahedral field compared to M^{3+} ion, inverse spinel will result.

Fe_3O_4 (oxygen weak field ligand)
Fe^{2+}: $d^6 = t_{2g}^4 e_g^2$; 0.4 Δo
Fe^{3+}: $d^5 = t_{2g}^3 e_g^2$; no CFSE
Structure: Inverse Spinel

Jahn-Teller Distorsion

Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy


e_g
x^2-y^2
z^2
z^2
x^2-y^2
Cu(II) -
d9 system
Ti(III)-
d1 system
Δ_o
t_{2g}
xy
xz yz
xz yz
xy
z elongation
2 long 4 short
z compression
2 short 4 long

Dynamic Jahn-Teller Distorsion

When the distortion of the structure oscillates very quickly at random among the available symmetry axes of the complex; such that the oscillation is more rapid than any physical measurements can follow, a time average symmetry is indicated. This is Dynamic Jahn-Teller Distorsion.

eg. $[Cu(H_2O)_6]^{2+}$ in the host crystal $[Zn(H_20)_6]SiF_6$

Conclusion

- it permits the qualitative and quantitative interpretation of electronic spectra

- the theory explains the variation of magnetic moment with temperature

Thank You