Crystal Field Theory

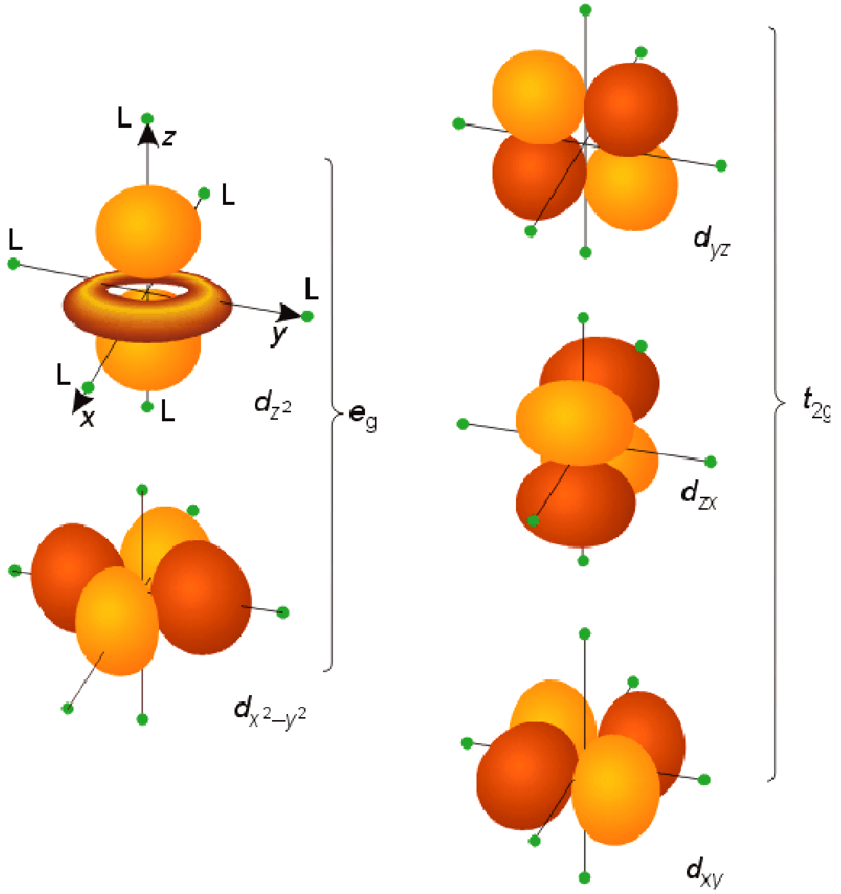
(Text : JD Lee; pp.204-222)

- This theory (**CFT**) largely replaced **VB Theory** for interpreting the chemistry of coordination compounds.
- It was proposed by the physicist Hans Bethe in 1929.
- Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications are often referred to as **Ligand Field Theory**.
- For a review on the evolution of bonding models see:

C. J. Ballhausen, *J. Chem. Ed.* **1979** *56* 194-197, 215-218, 357-361.

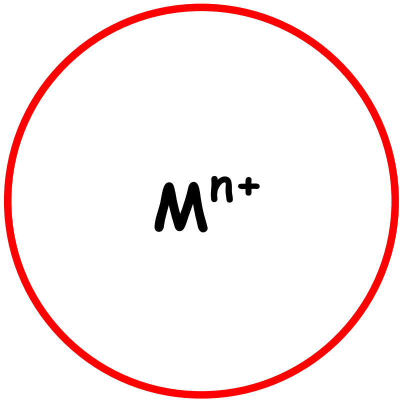
CFT-Assumptions

- The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges
- If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral : ion-dipole interaction
- The electrons on the metal are under repulsive from those on the ligands
- The electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands

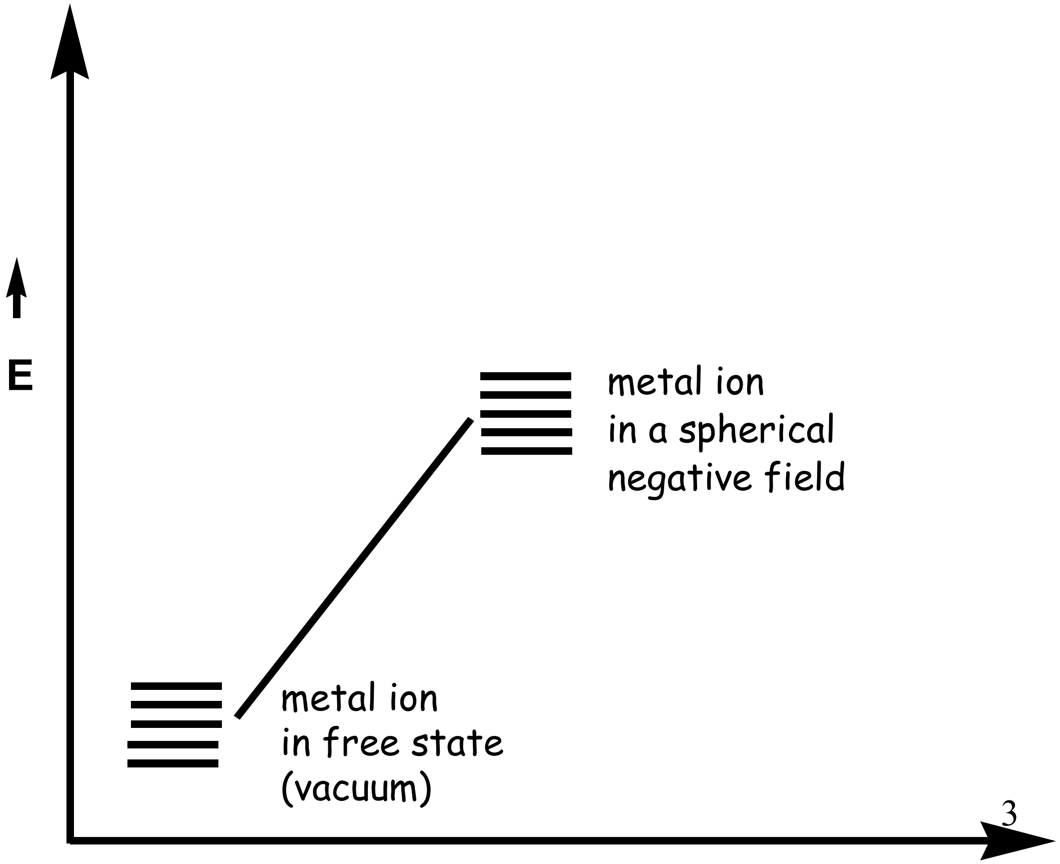


Symmetric Field

- The 5d orbitals in an isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these 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.

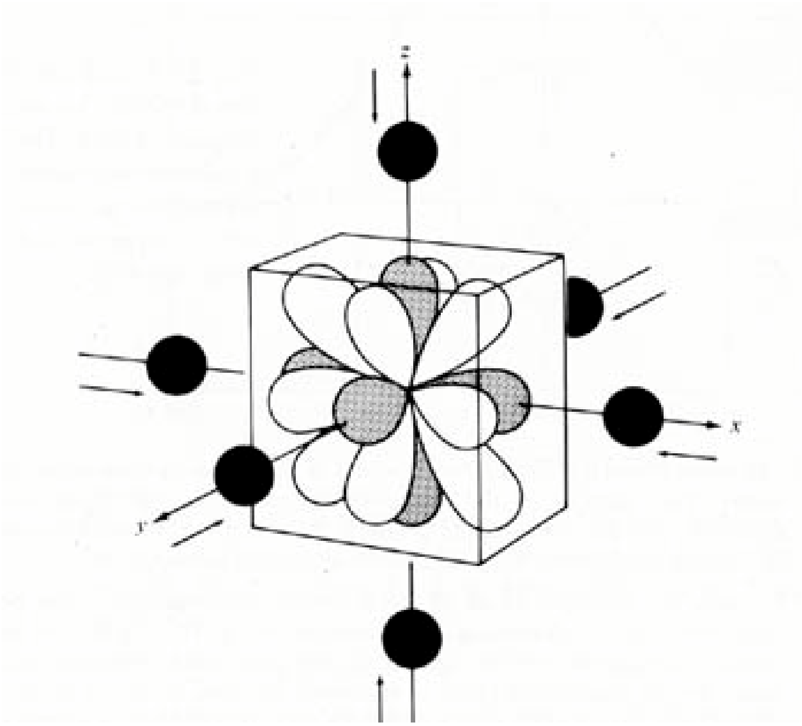


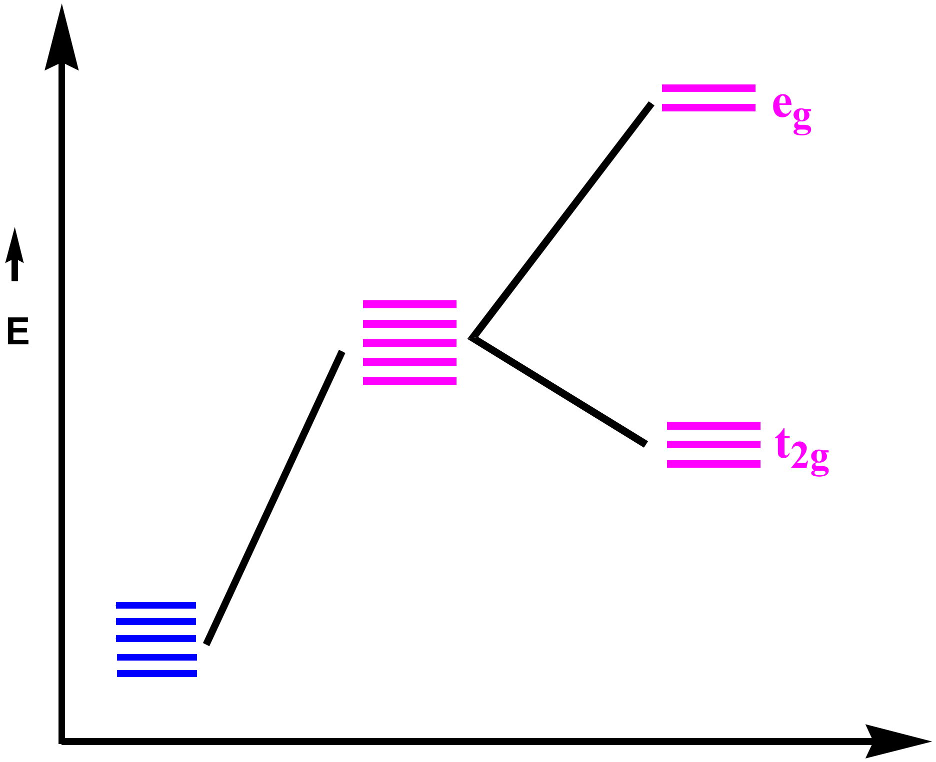
spherical negative field



Octahedral Field

- If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.





- Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.

- The orbitals which lie along these axes (i.e. x^2-y^2, z^2) will be destabilized more that the orbitals which lie in-between the axes (i.e. xy, xz, yz).

CFT-Octahedral Complexes

- For the Oh point group, the x^2-y^2, z^2 orbitals belong to the E_g irreducible representation and xy, xz, yz belong to the T_{2g} representation.
- The extent to which these two sets of orbitals are split is denoted by Δ_0 or alternatively 10Dq. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

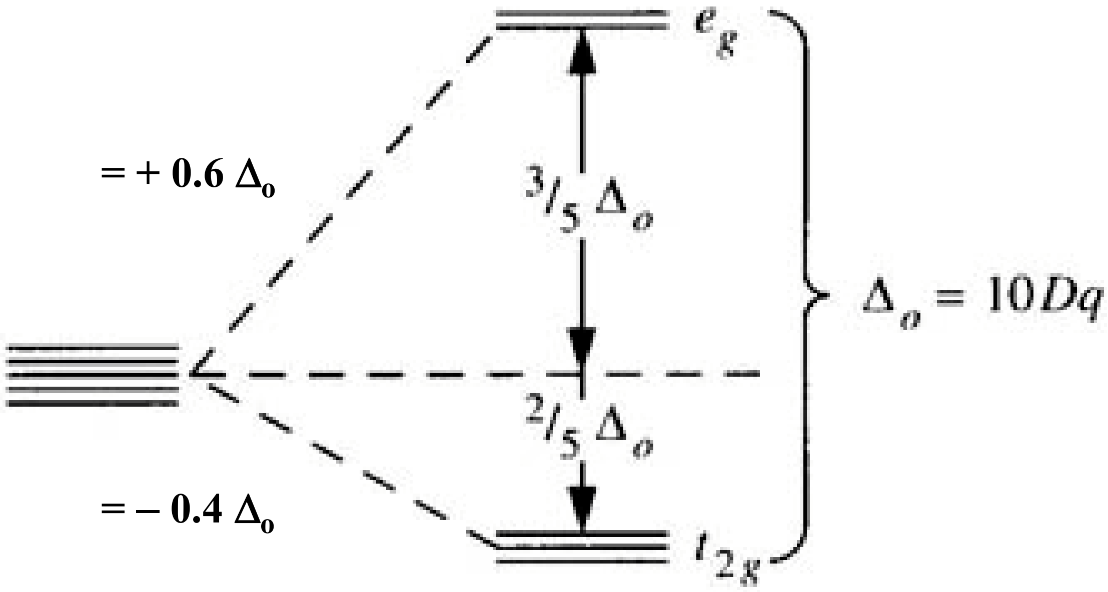
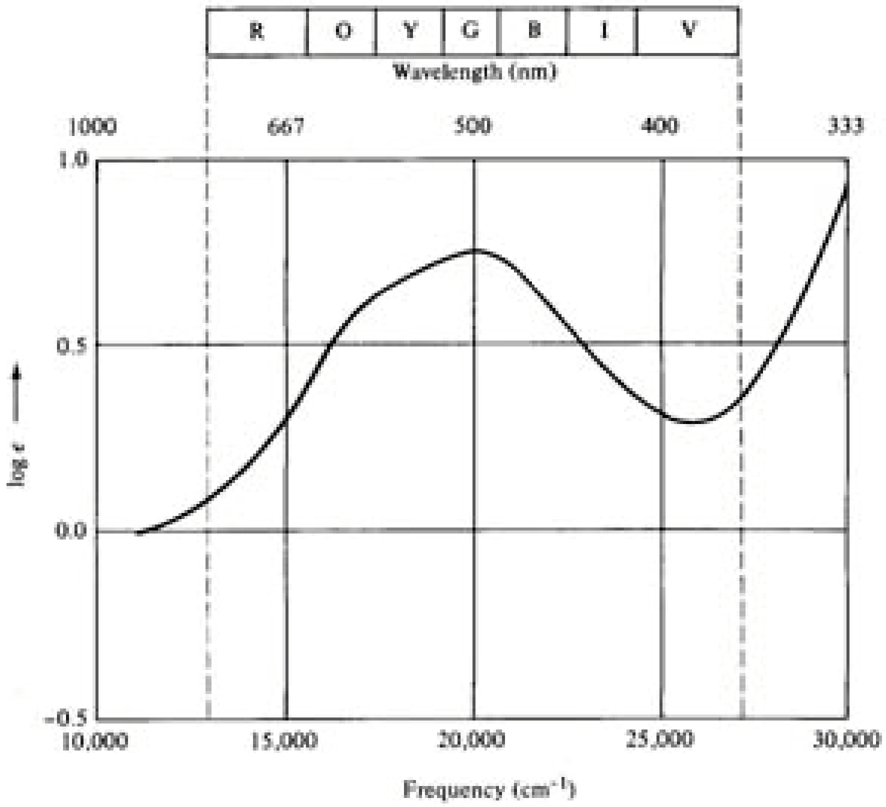


Illustration of CFSE

$[Ti(H_2O)_6]^{3+}$: a d^1 complex and the e^- occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. The purple colour is a result of the absorption of light which results in the promotion of this t_{2g} electron into the e_g level. $t_{2g}^1e_g^0 \rightarrow t_{2g}^0e_g^1$



The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

(1000 cm^{-1} = 11.96 kJ/mol or
2.86 kcal/mol or
0.124 eV.)

Typical Δ_0 values are of the same order of magnitude as the energy of a chemical bond.

•What happens for more than 1 electron in d orbitals?

•The electron-electron interactions must be taken into account.

•For d^1-d^3 systems: Hund's rule predicts that the electrons will not pair and occupy the t_{2g}set.

•For d^4-d^7 systems (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation)**.

•Therefore, there are two important parameters to consider: **The Pairing energy (P),** and **the e_g - t_{2g} Splitting (referred to as Δ_0, 10Dq or CFSE)**

•For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE.**

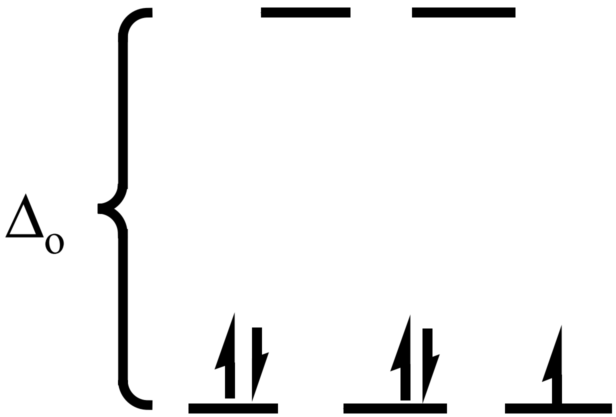
For an octahedral complex, CFSE

$$\boxed{= -0.4 \text{ x } n(t_{2g}) + 0.6 \text{ x } n(e_g)\ \Delta_o}$$

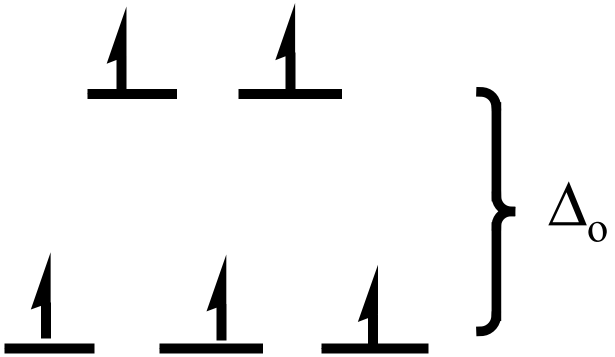
Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e P > CFSE)

d^5 system



Case I results in LS complex



Case II results in HS complex

CFSE vs Pairing Energy

Complex	**Config.**	**Δ_o, cm□1**	**P, cm^{-1}**	**spin-state**
$[Fe(OH_2)_6]^{2+}$	d^6	10,400	17,600	high-spin
$[Fe(CN)_6]^{4-}$	d^6	32,850	17,600	low-spin
$[CoF_6]^{3-}$	d^7	13,000	21,000	high-spin
$[Co(NH_3)_6]^{3-}$	d^7	23,000	21,000	low-spin

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

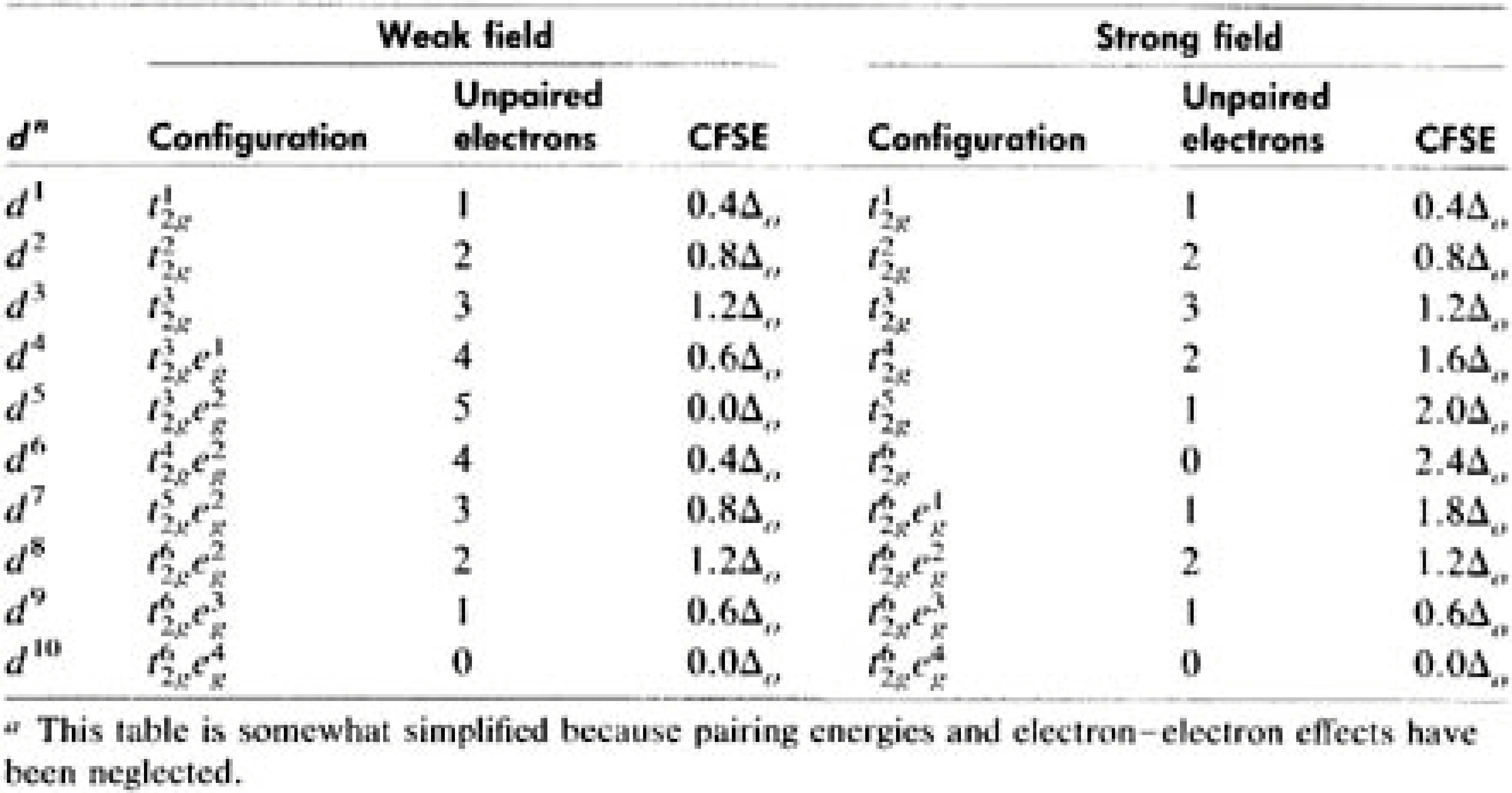
Ligands which cause a small splitting are ***Weak field ligands*** (CFSE in the range 7000 - 30000 cm^{-1}) and those cause a large splitting are ***Strong field ligands*** (CFSE typically > 30000 cm^{-1})

Spectrochemical Series

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

$[CrCl_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[Cr(H_2O)_6]^{3+}$	17830	213
$[Cr(NH_3)_6]^{3+}$	21680	314
$[Cr(CN)_6]^{3-}$	26280	314

$[Co(NH_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[Rh(NH_3)_6]^{3+}$	34000	213
$[Ir(NH_3)_6]^{3+}$	41000	314

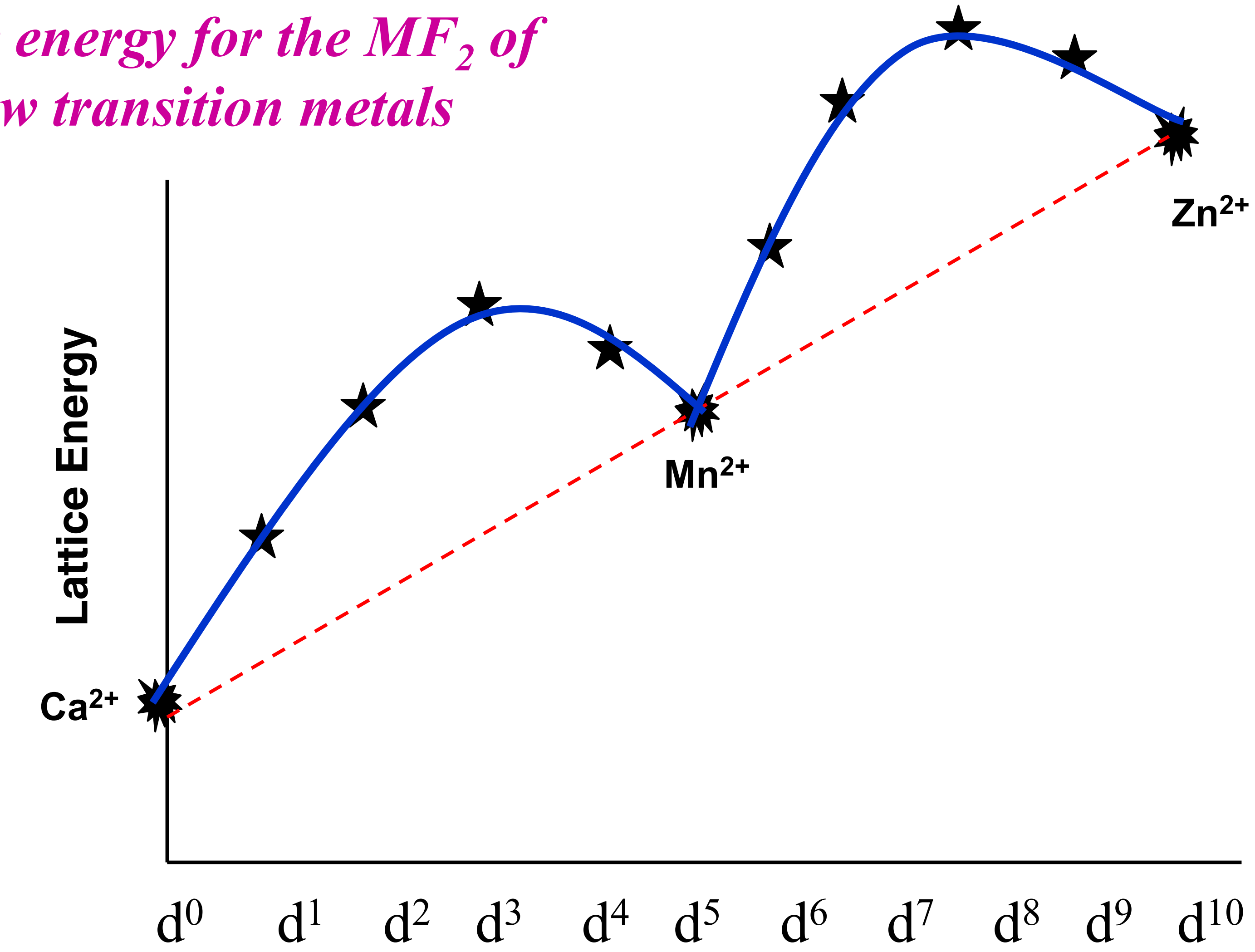


	Weak field			Strong field		
d^n	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$0.4\Delta_o$	t_{2g}^1	1	$0.4\Delta_o$
d^2	t_{2g}^2	2	$0.8\Delta_o$	t_{2g}^2	2	$0.8\Delta_o$
d^3	t_{2g}^3	3	$1.2\Delta_o$	t_{2g}^3	3	$1.2\Delta_o$
d^4	$t_{2g}^3e_g^1$	4	$0.6\Delta_o$	t_{2g}^4	2	$1.6\Delta_o$
d^5	$t_{2g}^3e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$2.0\Delta_o$
d^6	$t_{2g}^4e_g^2$	4	$0.4\Delta_o$	t_{2g}^6	0	$2.4\Delta_o$
d^7	$t_{2g}^5e_g^2$	3	$0.8\Delta_o$	$t_{2g}^6e_g^1$	1	$1.8\Delta_o$
d^8	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$
d^9	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$
d^{10}	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$

[a] This table is somewhat simplified because pairing energies and electron–electron effects have been neglected.

Applications of CFT

Lattice energy for the MF_2 of first row transition metals



F = weak field ligand

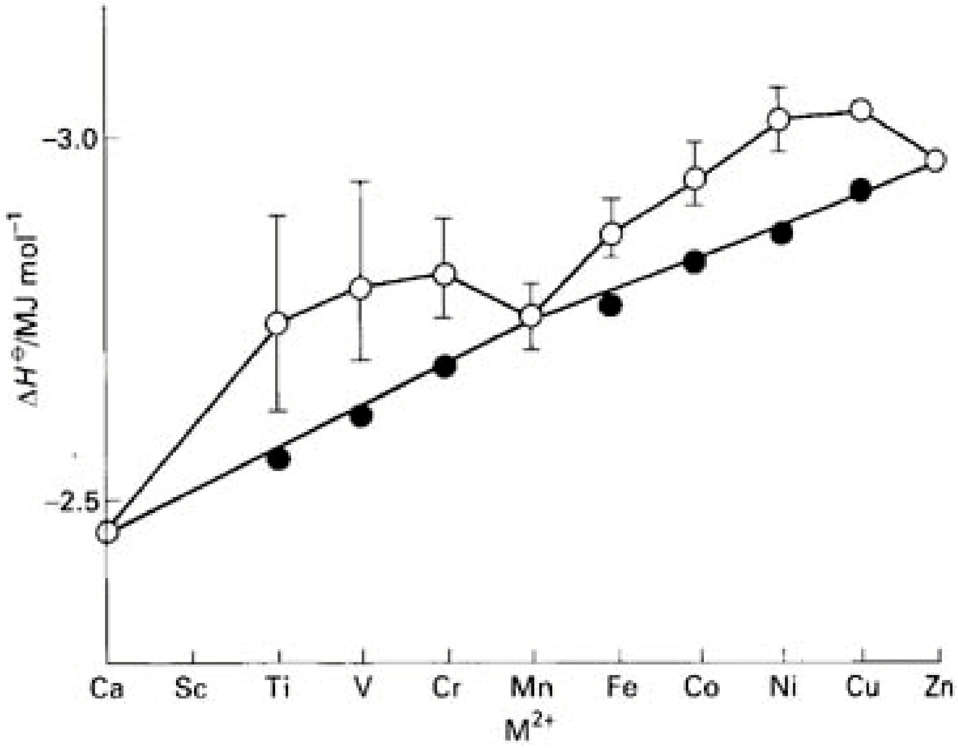
Applications of CFT

Hydration Enthalpy. Let us look at the variation of enthalpy of M^{2+} ions

$M^{2+}(g) + 6\ H_2O(l) =$

$[M(O_2H)_6]^{2+}(aq)$

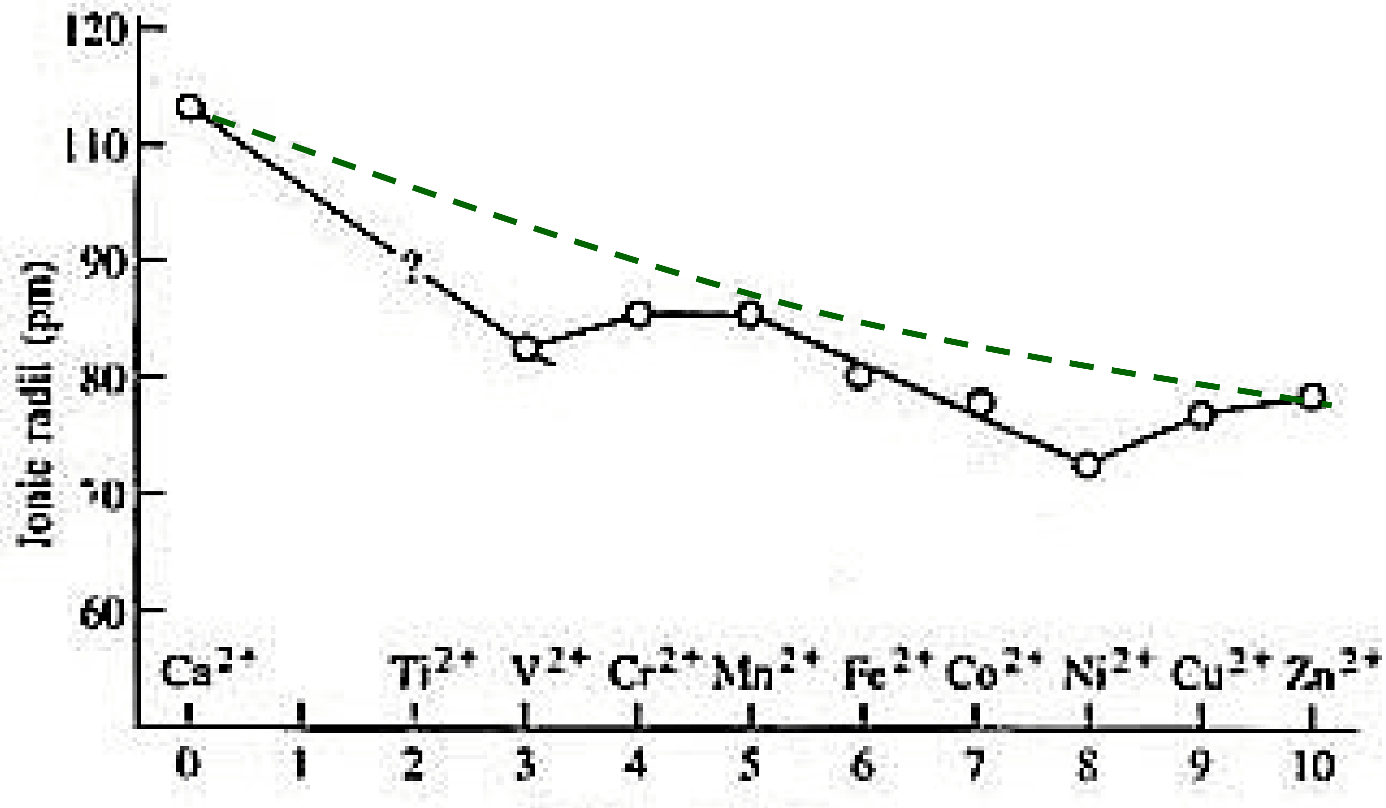
$Ca^{2+,}$ Mn^{2+}, and Zn^{2+} have d^o, d^5, and d^{10}, hence CFSE is 0. Other metal ions deviate from the expected line due to extra CFSE



H_2O = weak field ligand

Applications of CFT

Ionic Radii. For a given oxidation state, the ionic radius decreases steadily on going from left to right in a transition series (dotted line).



Tetrahedral Field- Considerations

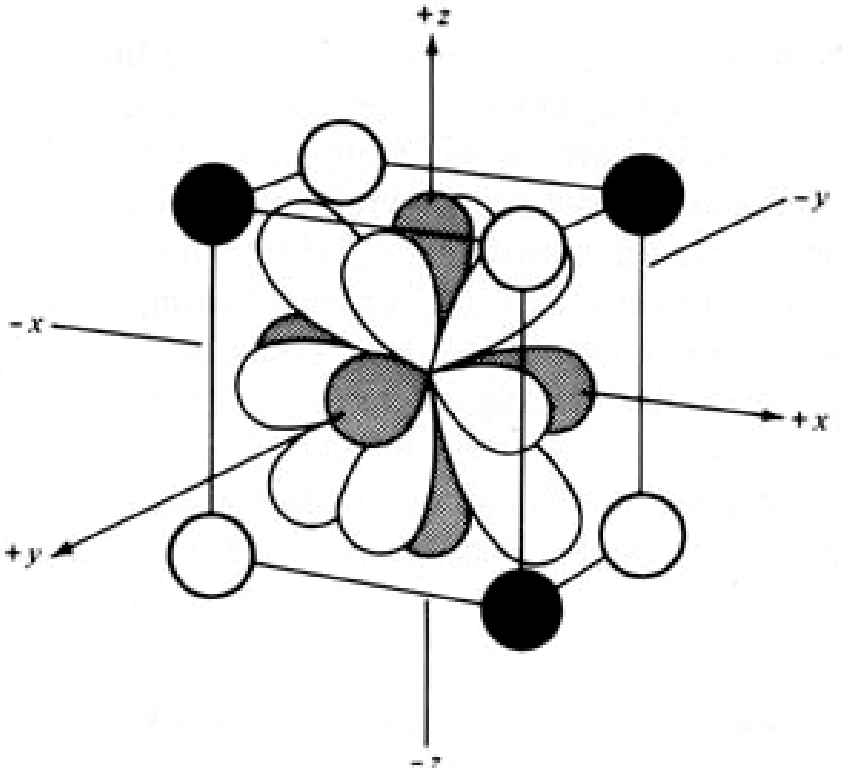
Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two ‘e’ orbitals point to the center of the face of the cube while the three ‘t_2’ orbitals point to the center of the edges of the cube.

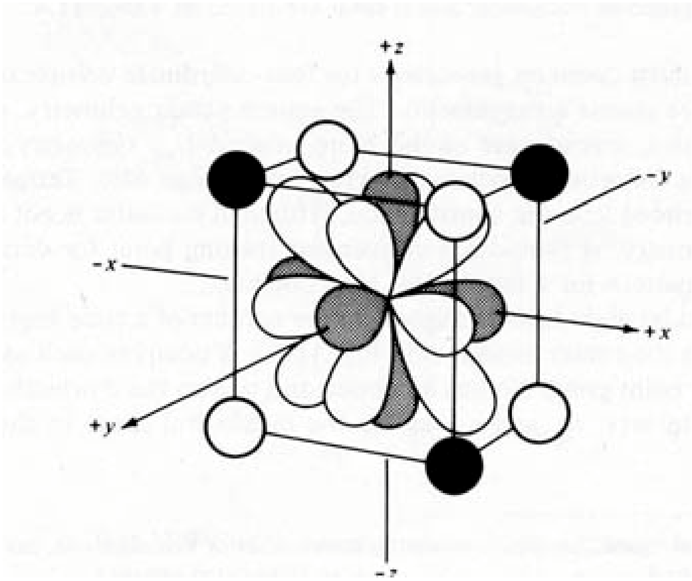
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedra angle, i.e. **$109^{o}28' / 2 = 54^{o}44'$**. But the angl between the t_2-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. **$109^{o}28$ $/ 3 = 35^{o}16'$**.

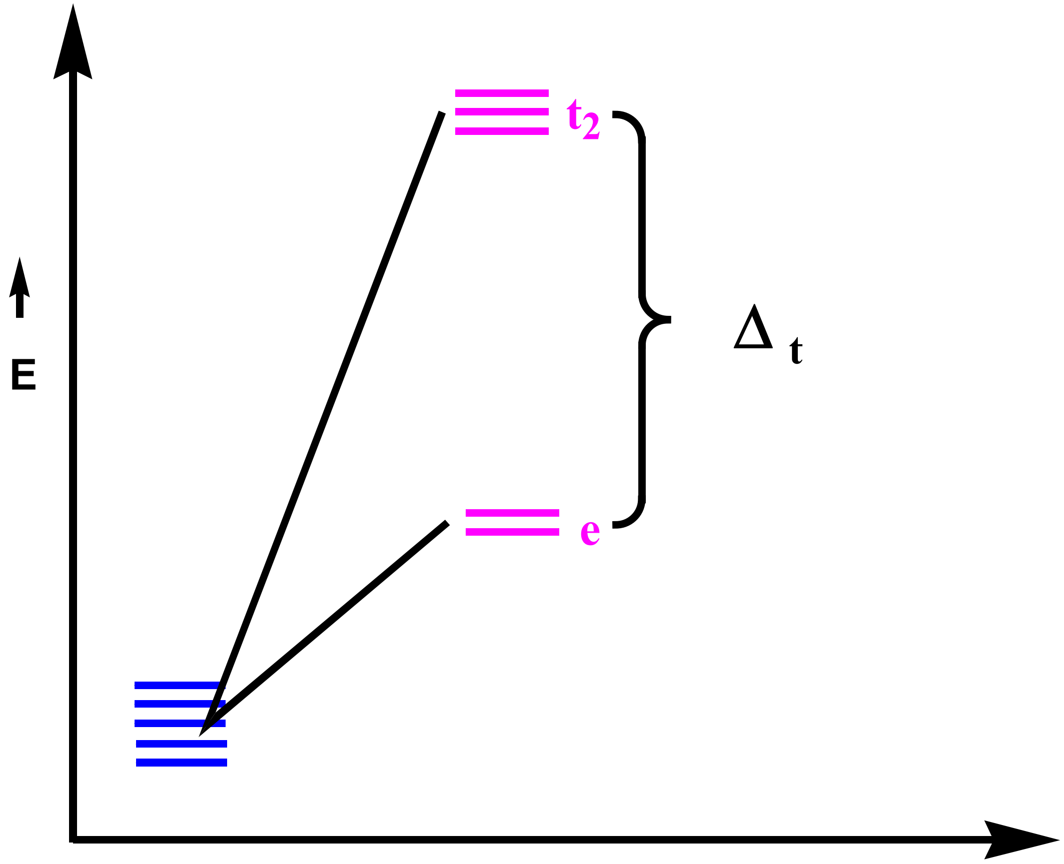
Thus the t_2 orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t_2 orbitals have higher energy compared to e-orbitals



Tetrahedral Field





$\Delta_t < \Delta_o$

$\Delta_t = 4/9\ \Delta_o$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9 of Δ_o

As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the paring energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Spinels - Use of CFSE

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.

In the **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. $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie $B(AB)O_4$.

i.e. $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

Spinels - Use of CFSE

There are several transition metal oxides which have the formula AB_2O_4 and crystallize in spinel or inverse spinel structure. E.g. $FeCr_2O_4$, $ZnAl_2O_4$, Co_3O_4, Mn_3O_4, Fe_3O_4, $NiFe_2O_4$ etc.

CFSE is highly useful to determine whether a structure would be normal or inverse

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

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

normal $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$; **inverse** $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

Spinels - Use of CFSE

Example: Mn_3O_4 (oxygen weak field ligand)

Mn^{2+}; $d^5 = t_{2g}^{\ 3}e_g^{\ 2}$; no CFSE

Mn^{3+}; $d^4 = t_{2g}^{\ 3}e_g^{\ 1}$; $0.6\ \Delta_o$

Structure: **Normal** Spinel

Example: Fe_3O_4 (oxygen weak field ligand)

Fe^{2+}; $d^6 = t_{2g}^{\ 4}e_g^{\ 2}$; $0.4\ \Delta_o$

Fe^{3+}; $d^5 = t_{2g}^{\ 3}e_g^{\ 2}$; no CFSE

Structure: **Inverse** Spinel

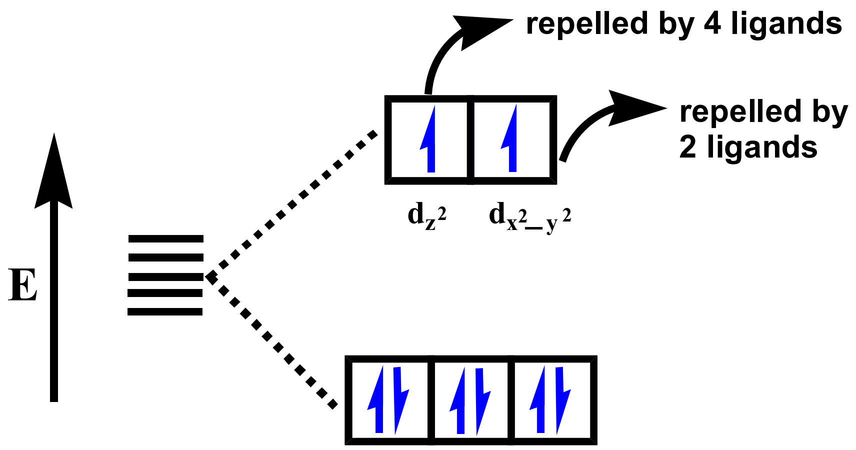
How about $MnCr_2O_4$ and $FeCr_2O_4$? Work out.

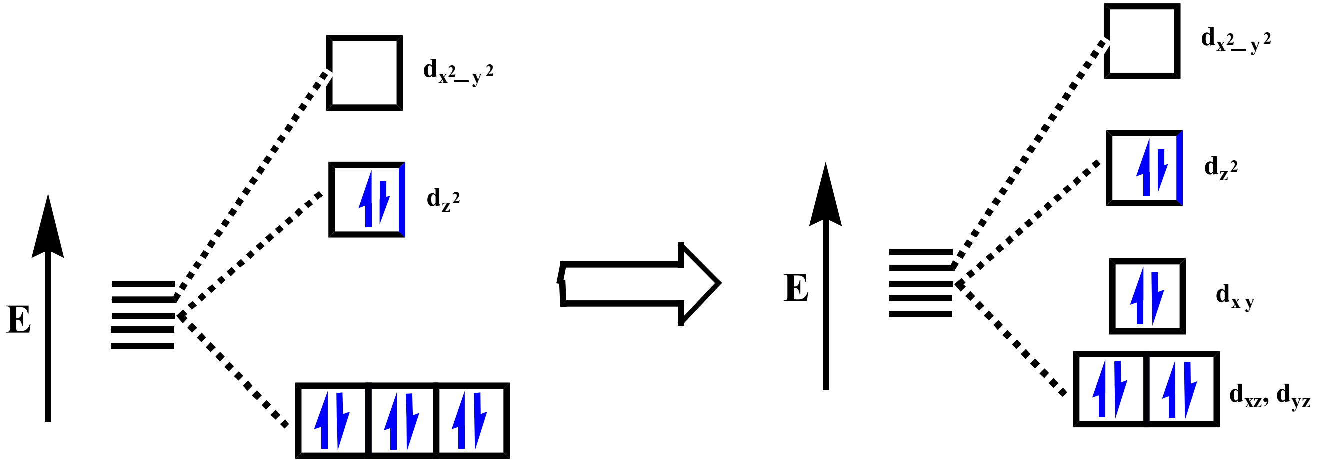
Tip: If A^{2+} is d^6, d^7, d^8, or d^9 ion and B^{3+} is Fe^{3+}, AB_2O_4 is INVERSE

Special case of d^8 Octahedral

Examples:

Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}



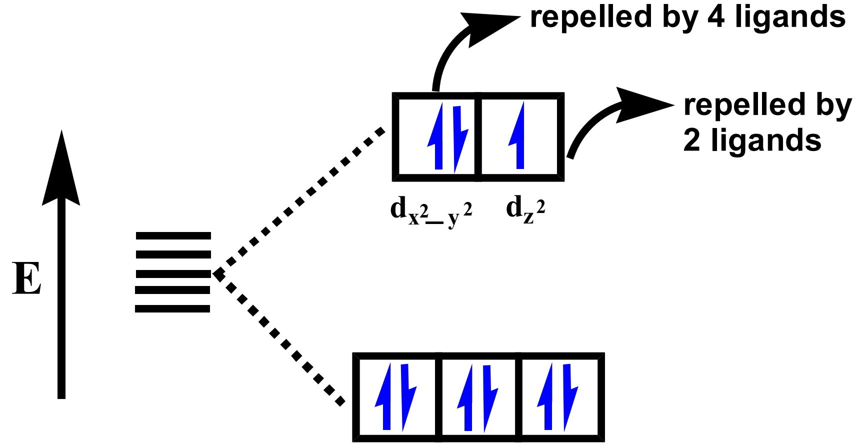


Square-planar complex is formed ; attempts to form octahedral complexes become impossible

Special case II
Jahn-Teller Distortion

If bot the e_g orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other . **Result:** Distorted octahedron



Consider e_g configuration: $(d_{z^2})^1\ d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the z axis.

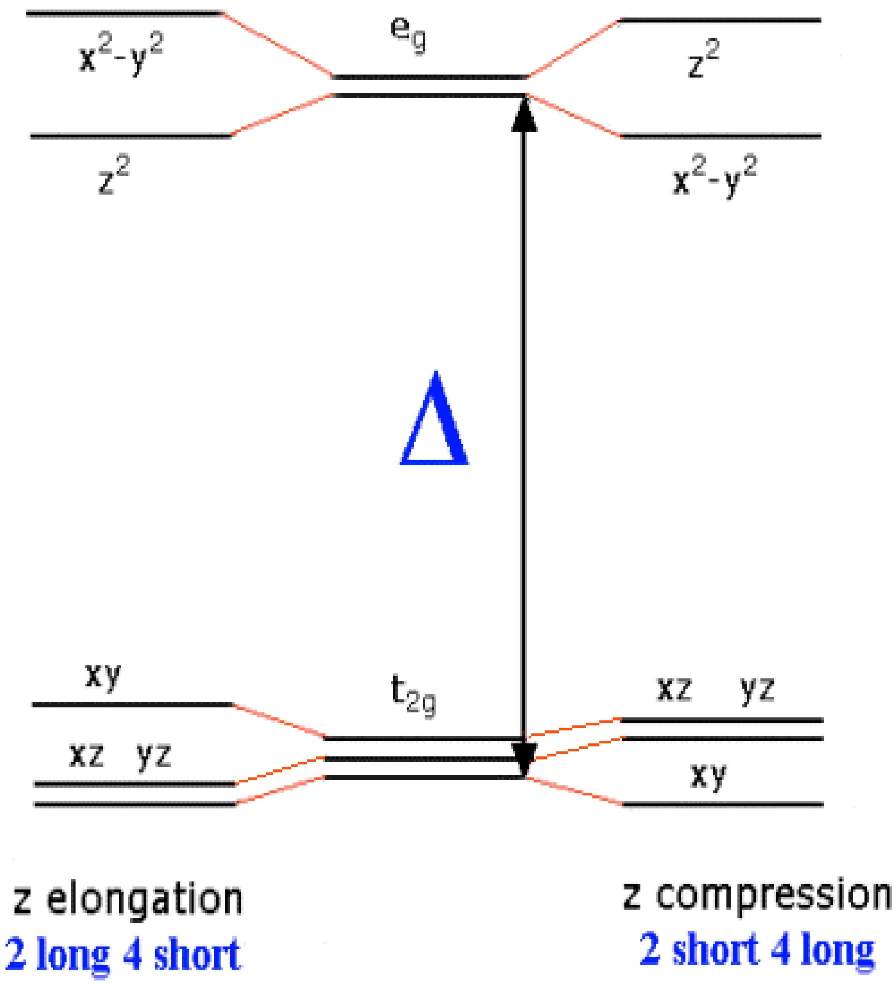
Consider e_g configuration: $(d_{z^2})^2\ d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.

The Jahn-Teller Theorem was published in 1937 and states:

> "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"

The e_g point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



Some examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240pm 2 Br at 318pm
$CuCl_2.2H_2O$	2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm
$CsCuCl_3$	4 Cl at 230pm 2 Cl at 265pm
CuF_2	4 F at 193pm 2 F at 227pm
$CuSO_4.4NH_3.H_2O$	4 N at 205pm 1 O at 259pm 1 O at 337pm
K_2CuF_4	4 F at 191pm 2 F at 237pm
CrF_2	4 F at 200pm 2 F at 243pm
$KCrF_3$	4 F at 214pm 2 F at 200pm
MnF_3	2 F at 209pm 2 F at 191pm 2 F at 179pm

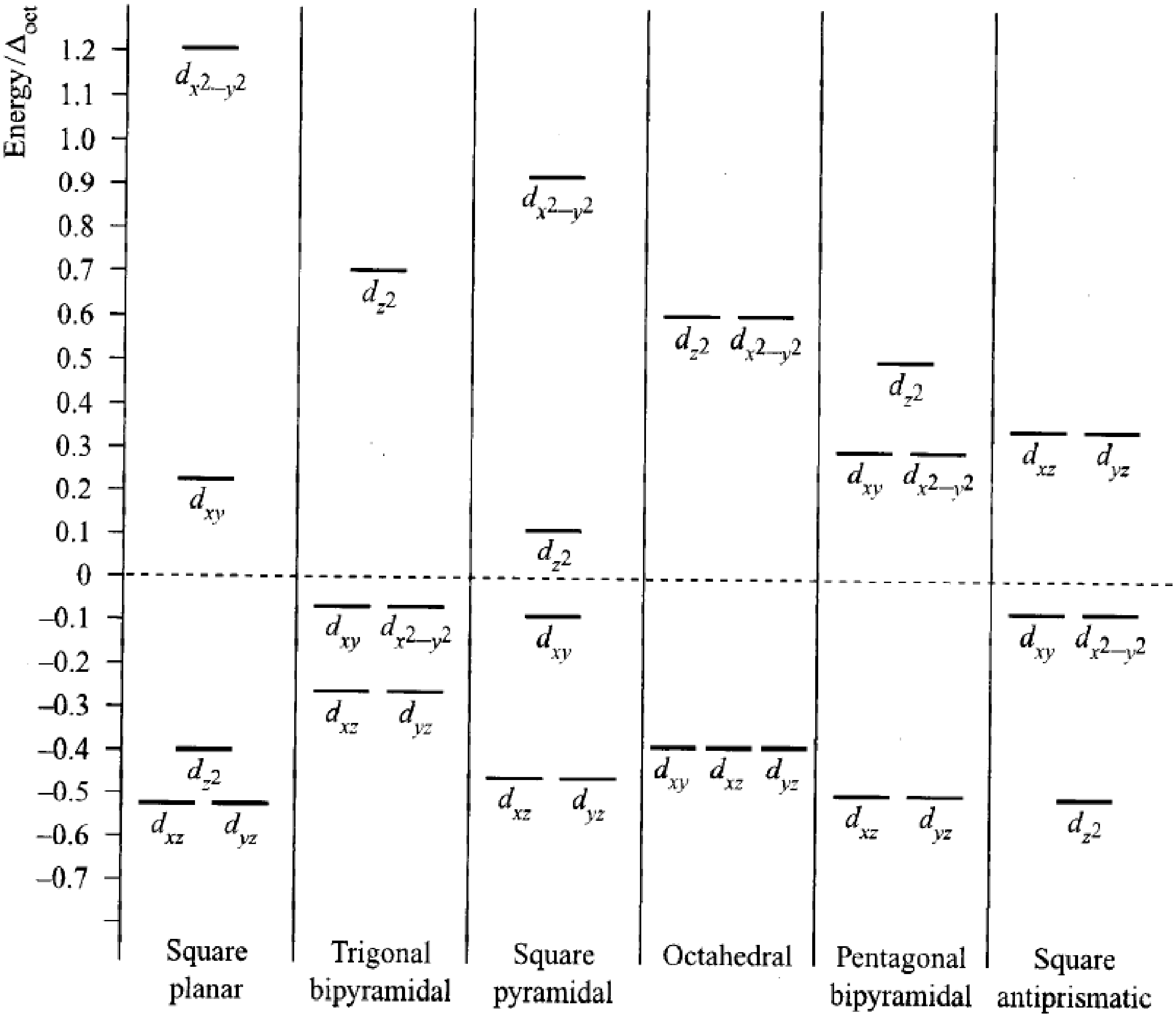


Figure 2 Crystal field splittings of d orbitals