CRYSTAL FIELD THEORY

Hans Bethe (1929) and Van Vleck (1935)

Failures of VBT

1. Tetrahedral or Square planar ??

2. Distortions in complexes – No

3. Colour of Complexes (optical spectra) ??

4. Temperature dependence of Magnetic Properties

VBT   (1930's)   L. Pauling

CFT   (1930's)   Bethe & V. Vleck

Application of CFT to chemical problems – 1950's

Main assumptions in CFT

- Interaction between Metal ion and Ligand is <u>electrostatic</u>

- Ligands are tretated as negative <u>point charges</u>

(Real life is different)

Geometry of Metal d orbitals

— interaction with Ligands

— crucial to understand crystal field effects in Transition Metal (d - block) complexes.

Three p - orbitals

Nodal plane

z

x y

p_x

Nodal plane

z

x y

p_y

Nodal plane

z

x y

p_z

Five d - orbitals

z

x y

d_{xy}

(a)

z

x y

d_{yz}

(b)

z

x y

d_{xz}

(c)

z

x y

$d_{x^2-y^2}$

(d)

z

x y

d_{z^2}

(e)

z

x y

f_{xyz}

(f)

d_{xy}, d_{xz}, d_{yz} — t_{2g} set
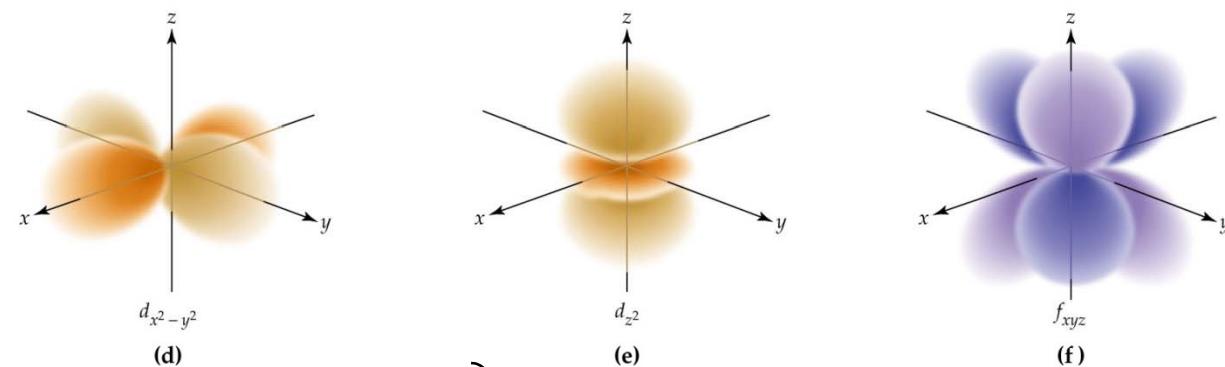
d_{z^2}, $d_{x^2-y^2}$ — e_g set

In octahedral field
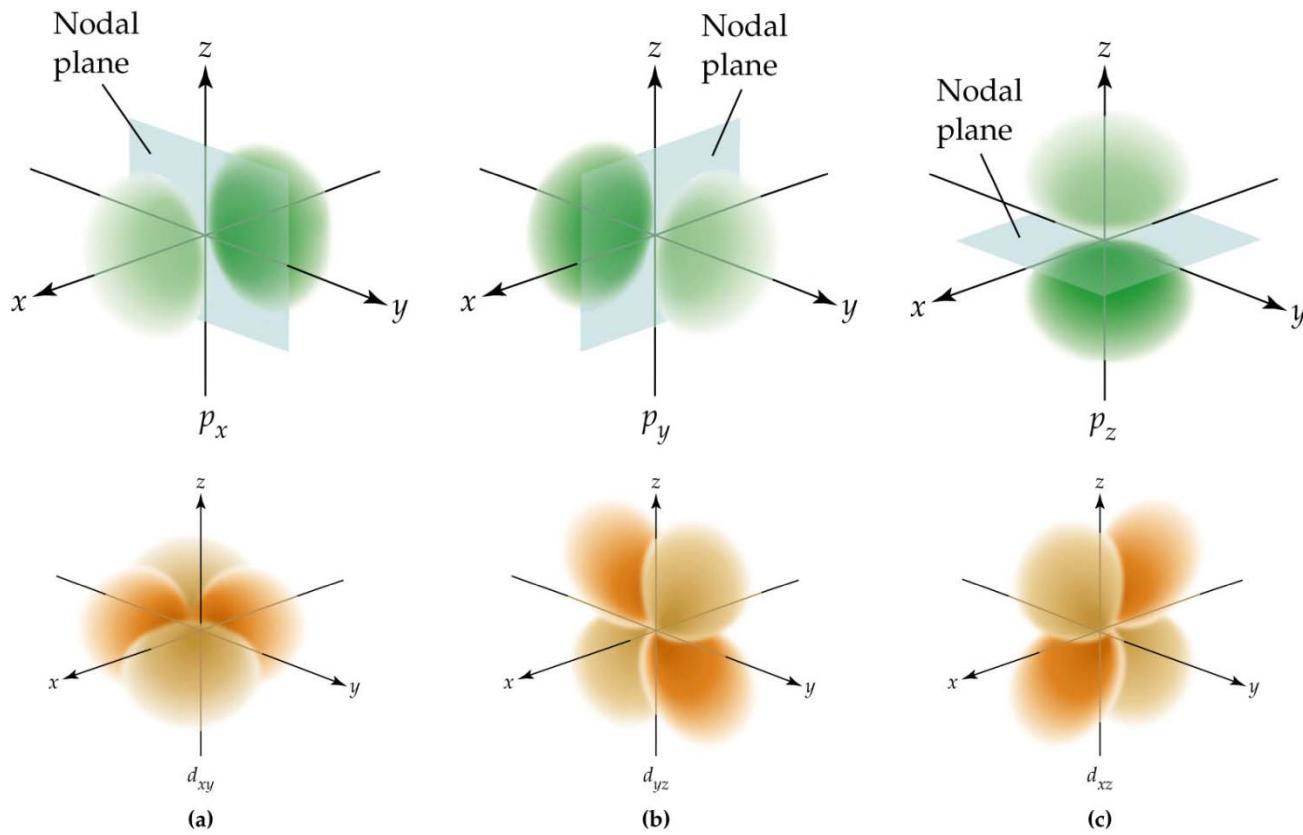
CFT (simple point charges)

Electrostatic potential:

$$(E) \; \alpha \; \frac{q_1 q_2}{r^2}$$

Alkali Metals K^+, Na^+

(spherical charge dist.)

Low charge and large radius

   → low interaction potential

   → few coordination compounds

Transition metal ions

   — d – orbitals

   (not spherically symmetric)

# Splitting of d – orbitals in an Octahedral Field

Free ion M^{n+}

ML_6 $[Fe(H_2O)_6]^{2+}$ etc

Spherical field

Degenerate (same energy) set of five d orbitals

e^-

M

Increases the energy of all five d orbitals (no splitting)

● ligand

t_{2g} (d_{xy}, d_{xz}, d_{yz})

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

shaded

e_g orbitals are directly facing the ligands – more repulsion
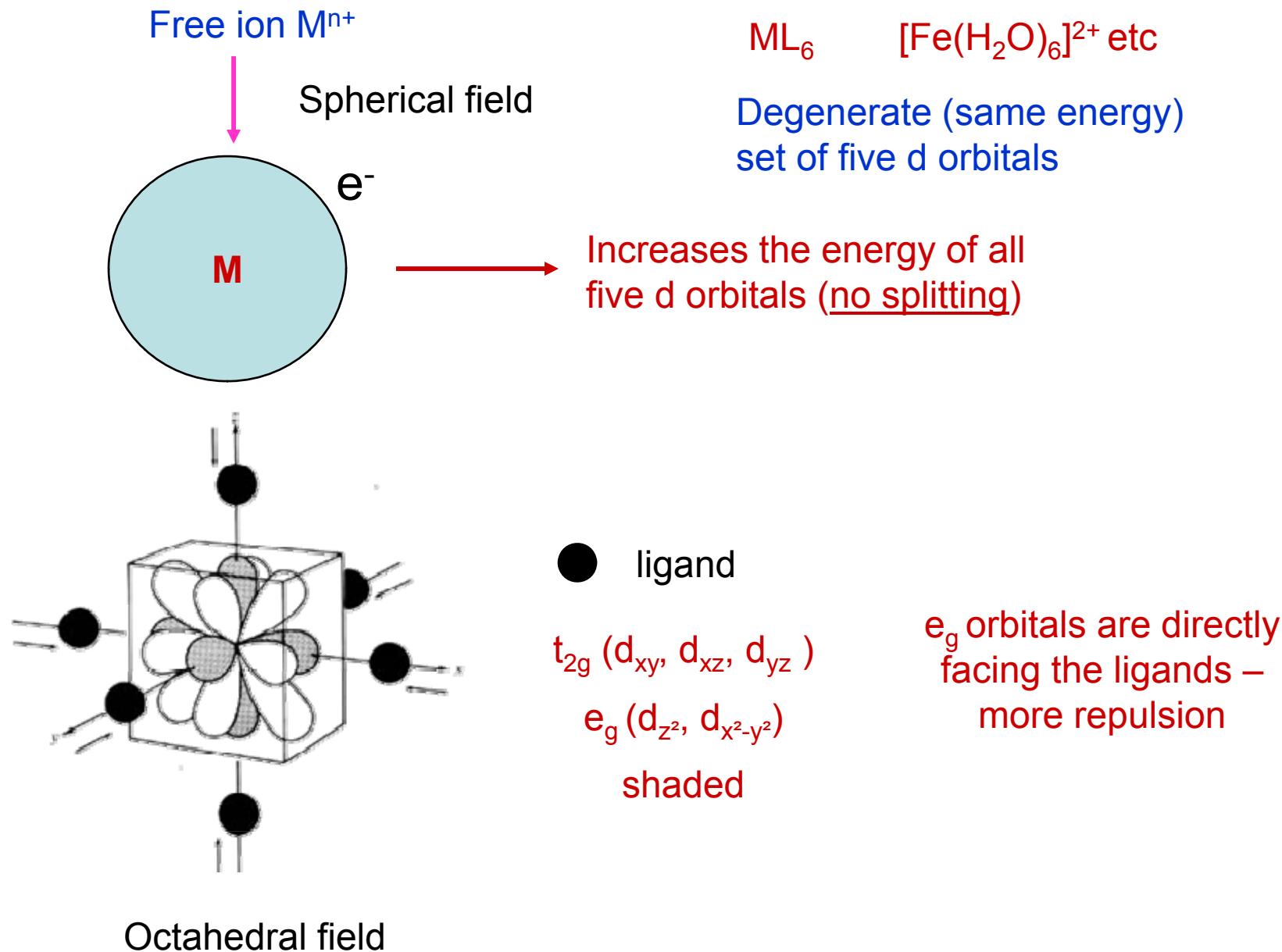
Octahedral field

Splitting of t_{2g} and e_g sets

g = gerade

u = ungerade

E

Barycentre

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

6 Dq $\frac{3}{5}\Delta_o$

Δ_o or 10 Dq$_o$

4 Dq $-\frac{2}{5}\Delta_o$

t_{2g} d_{xy} d_{xz} d_{yz}

Free ion   Spherical field   Octahedral field
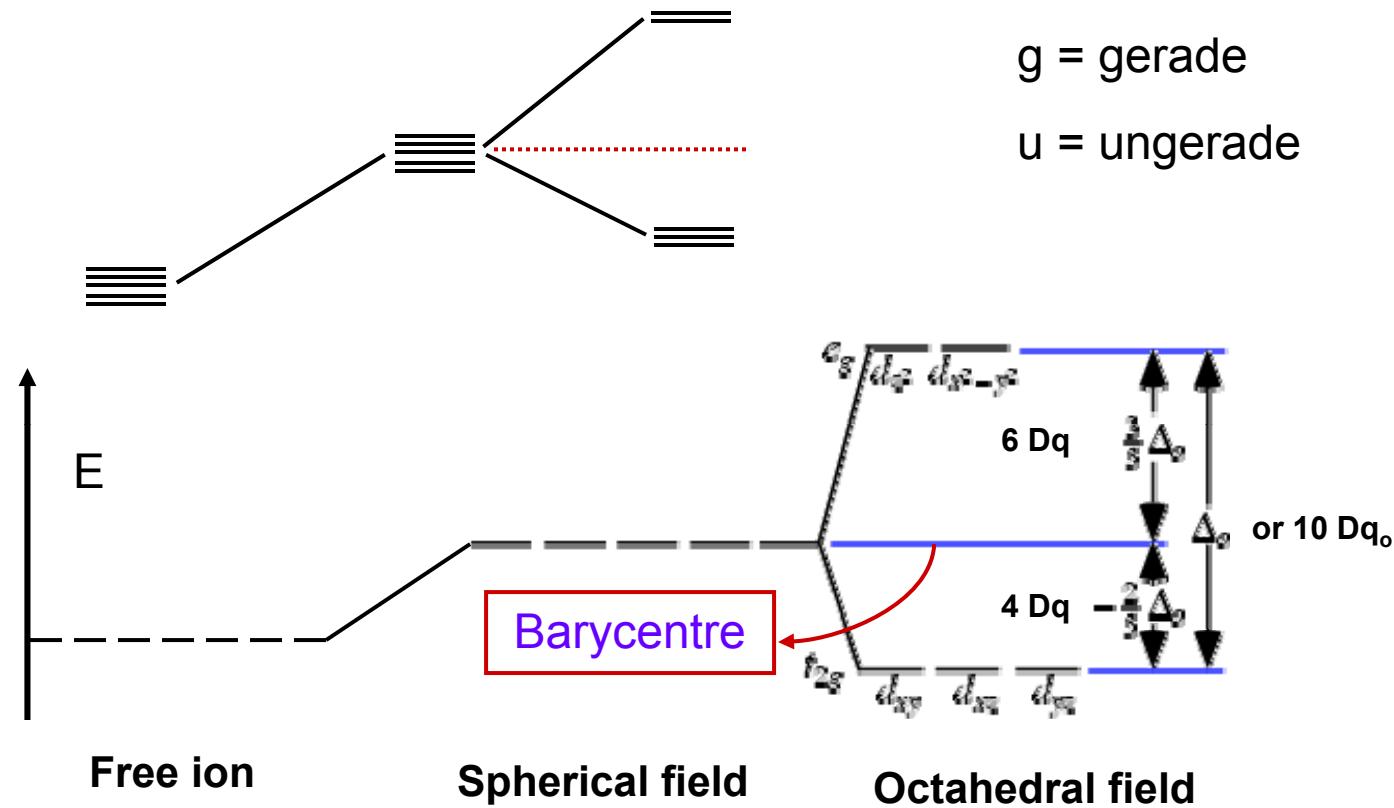
C. F. Splitting of d – orbitals in an octahedral field = Δ_o or 10 Dq$_o$

octahedral
t_{2g} triply degenerate set of orbitals and centrosymmetric

e_g doubly degenerate and possess a centre of symmetry

C. F. Splitting in Tetrahedral Complexes

ML_4; $Ni(CO)_4$

Remove four corner from a cube

↓

Tetrahedron

Ligands do not point directly any of the d – orbitals of the metal

closer to the dxy, dyz, dxz (raised in energy)

$\Delta_{tet} = 4/9\ \Delta_{oct}$

E →

dxy dxz dyz t_{2g}

dx^2-y^2 dz^2 e_g $\Delta_t = \frac{4}{9}\Delta_o$

Tetrahedral crystal field

Isolated atom or ion

t_2 $\mathbf{d_{xy}}$ $\mathbf{d_{yz}}$ $\mathbf{d_{xz}}$

Δ_{tet}

e $\mathbf{d_{x2-y2}}$ $\mathbf{d_{z2}}$

e_g $\mathbf{d_{x2-y2}}$ $\mathbf{d_{z2}}$

Δ_{oct}

t_{2g} $\mathbf{d_{xy}}$ $\mathbf{d_{yz}}$ $\mathbf{d_{xz}}$

Tetrahedral field   free-ion   Octahedral field
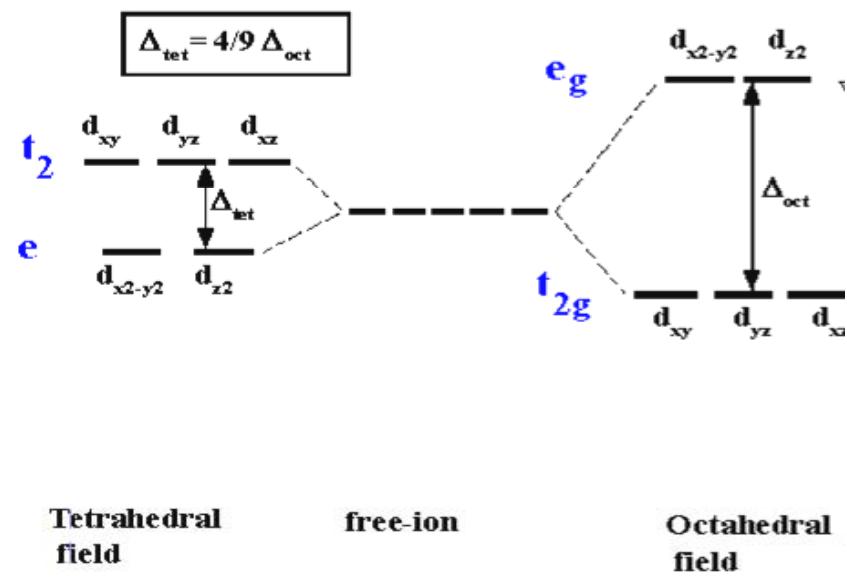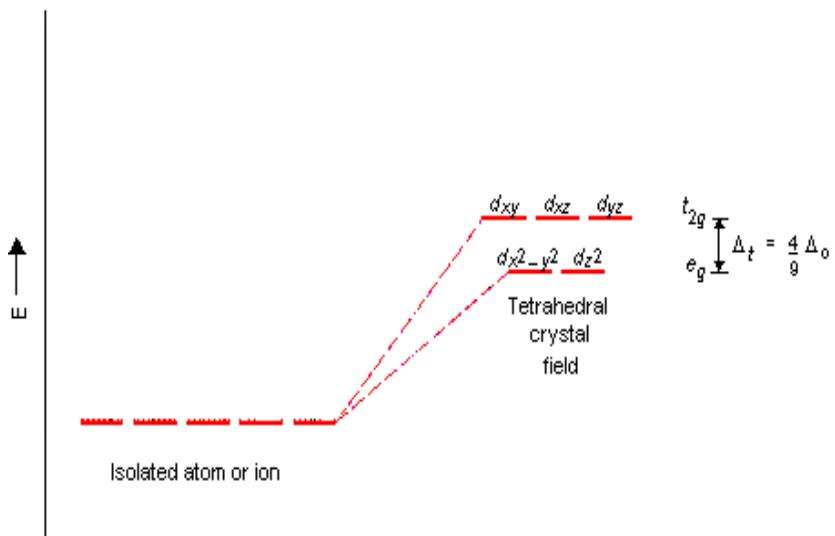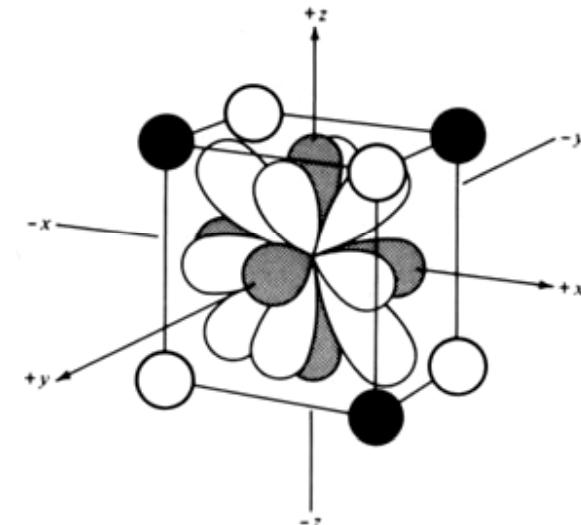
Crystal field stabilization energy: CFSE

e. g. d^1 (Ti^{3+}) complex $[Ti(H_2O)_6]^{3+}$

$t_{2g}^1 e_g^0$

CFSE = -4Dq or $-0.4\Delta_o$

d² — -8 Dq or -0.8 Δº $t_{2g}^2 e_g^0$

d³ — -12 Dq or -1.2 Δo $t_{2g}^3 e_g^0$

d⁴ — d⁹ pairing energies
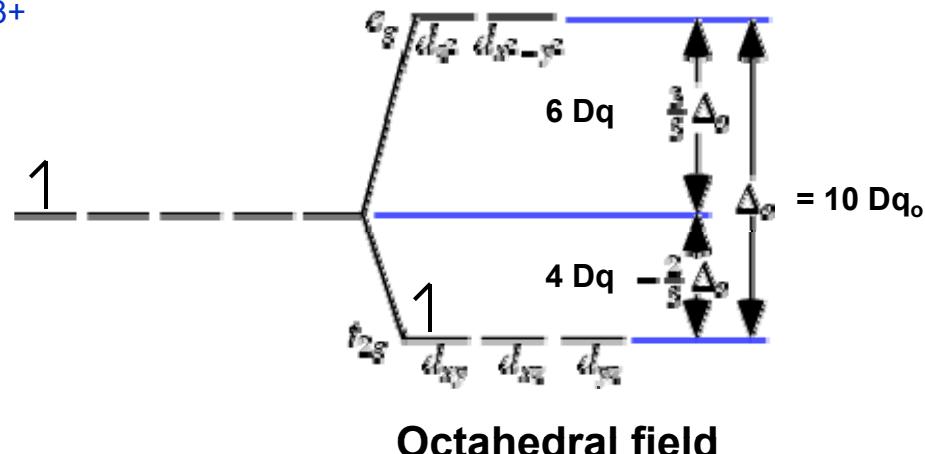
Experimentally obtained — Δ_o or 10 Dq_o

$[Ti(H_2O)_6]^{3+}$ in solutin

(purple in colour)

$\Delta_o = h\upsilon = h\bar{\upsilon}c$

Δ_o = 243 kJ/mole

6 Dq

Δ_o = 10 Dq_o

4 Dq

Octahedral field
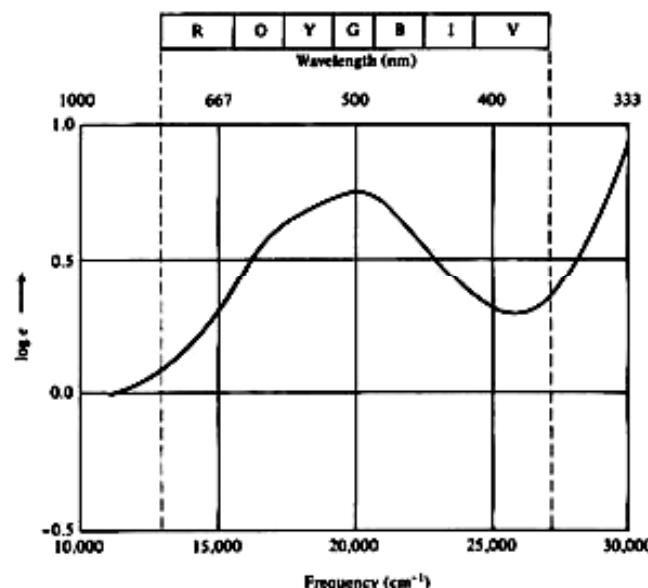
Absorption spectra (in the visible region)

Δ_o Crystal Field Splitting

P   Pairing Energies

$\downarrow$

Low Spin & High Spin

Factors affecting Δ_o

Factors affecting   P

Case (i)

$t_{2g}^3 e_g^1$

CFCE = -12 Dq + 6 Dq = -6 Dq

High Spin Complex
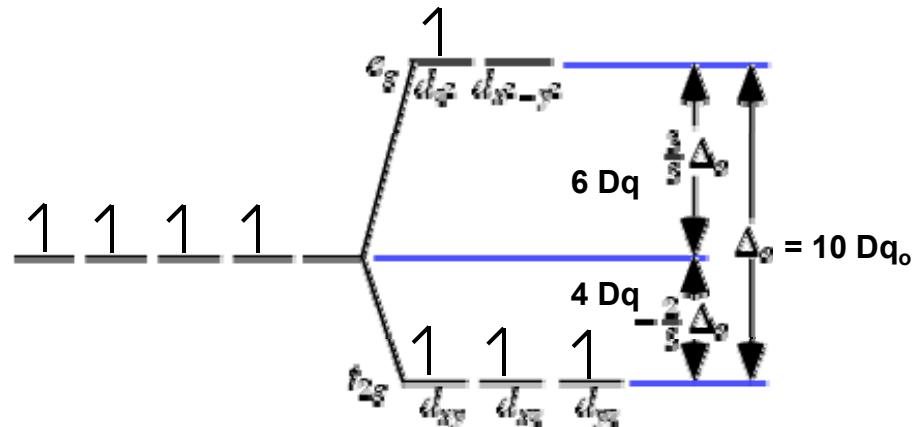
Case (ii)

$t_{2g}^4 e_g^0$

CFCE = -4x4 Dq = -16 Dq + P

P = pairing energy for one pair

Low Spin Complex

$t_{2g}^4 e_g^0$
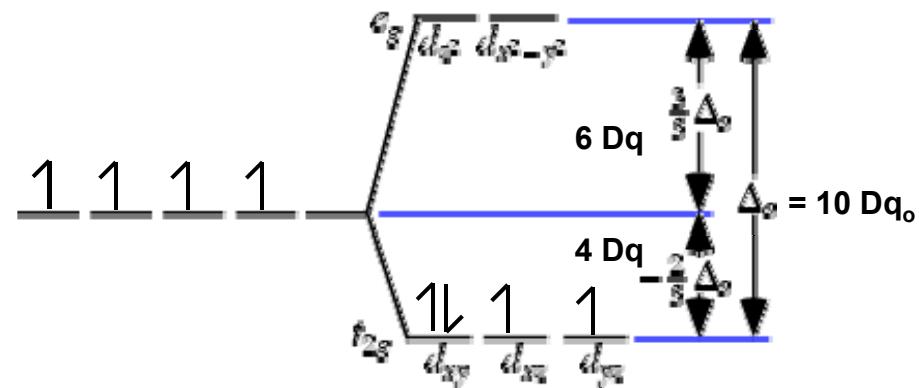
i.e. Low Spin Complex

If |CFSE of case (ii)| > |CFSE of case (i)|

If |-16 Dq + P | > | -6 Dq |

10 Dq > P then case (ii) will be possible

d^6 ion (Fe^{2+}, Co^{3+}); $[Fe(H_2O)_6]^{2+}$, $[CoF_6]^{3-}$
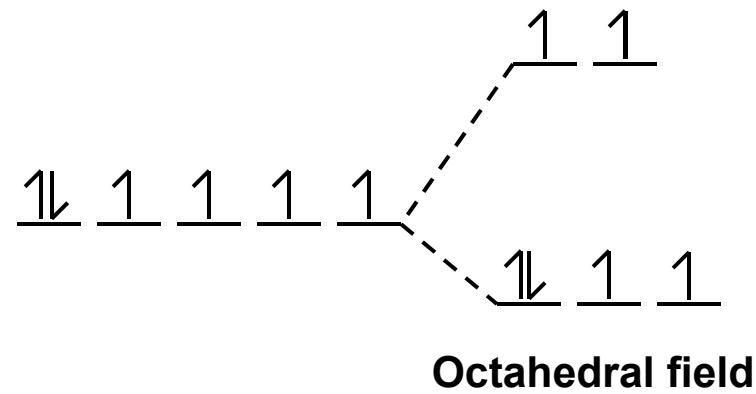
High Spin

4 unpaired e⁻

CFCE = -4x4 Dq + 2x6 Dq
= -4 Dq

Octahedral field

No pairing energy required
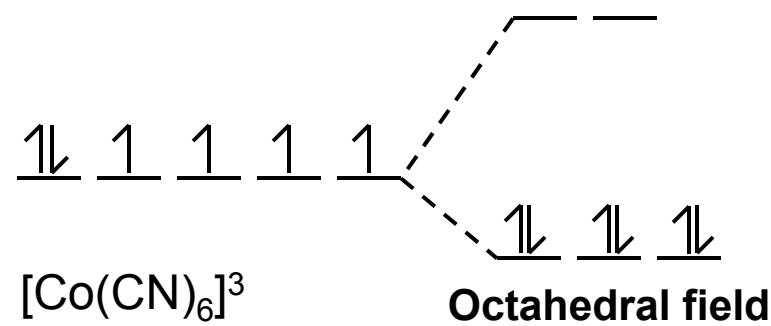
Low Spin

Diamagnetic

$[Co(CN)_6]^{3-}$ **Octahedral field**

CFCE = -6x4 Dq + 2P
= -24 Dq + 2P

2 extra pairs created

Factor affecting 10 Dq$_o$ (Δ_o)

1. Nature of Ligand

   weak field ligand (I$^-$) small Δ_o

   strong field ligand (CN$^-$) large Δ_o
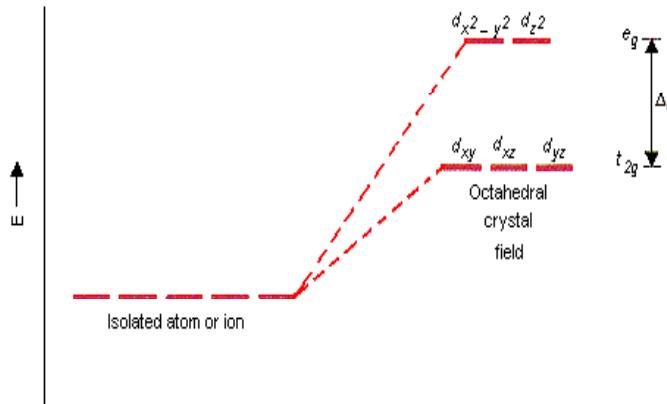
$$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4{}^{2-} < H_2O < NH_3 < en < bipy < phen < CN^- \sim CO$$

Spectrochemical Series
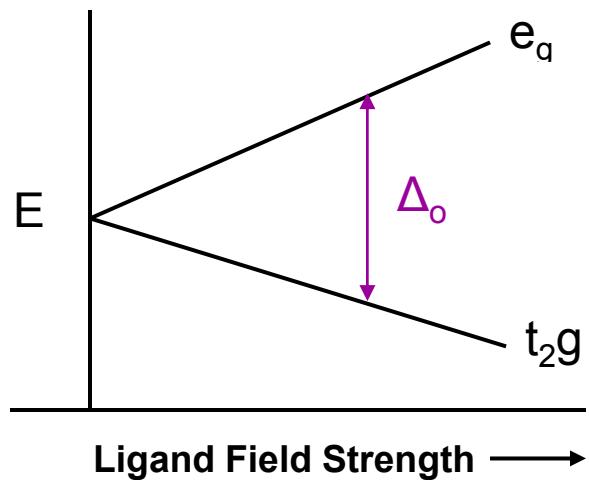
Anionic Ligands should show large splitting?

— Failures of CFT

Complex	Symmetry	Δ (cm^{-1})
1. $[CrF_6]^{2-}$	O_h	22000
2. $[CrF_6]^{3-}$	O_h	15060
3. $[Cr(en)_3]^{3+}$	O_h	22300
4. $[Cr(CN)_6]^{3-}$	O_h	26600
5. $[Fe(H_2O)_6]^{3+}$	O_h	14000
6. $[Fe(CN)_6]^{3-}$	O_h	35000
7. $[Co(NH_3)_6]^{3+}$	O_h	22870
8. $[Co(NH_3)_6]^{2+}$	O_h	10200
9. $[Co(NH_3)_4]^{2+}$	T_d	5900
10. $[Ir(NH_3)_6]^{3+}$	O_h	41200

Experimental (Δ) values

2. No. & Geometry of Ligands

$$\Delta_t \simeq \frac{4}{9} \Delta_o$$

Δ_t = splitting in a tetrahedral field

Δ_o = splitting in an octahedral field

$[Co(NH_3)_6]^{2+}$ — O_h 10200 cm^{-1} (Δ_o)

$[Co(NH_3)_4]^{2+}$ — O_h 5900 cm^{-1} (Δ_t)

3. Δ_o increases with oxidation state

$[Fe(H_2O)_6]^{2+}$ 9400 cm^{-1}

$[Fe(H_2O)_6]^{3+}$ 14000 cm^{-1}

4. Δ_o increases as the metal changes from 3d < 4d < 5d

Co	$[Co(NH_3)_6]^{3+}$	22870 cm^{-1}
Rh	$[Rh(NH_3)_6]^{3+}$	34000 cm^{-1}
Ir	$[Ir(NH_3)_6]^{3+}$	41200 cm^{-1}

5. Δ_o varies irregularly along the period

$[Cr(H_2O)_6]^{3+}$	17400 cm^{-1}
$[Fe(H_2O)_6]^{3+}$	14000 cm^{-1}
$[Co(H_2O)_6]^{3+}$	20760 cm^{-1}

<u>Factors affecting pairing energies (P)</u>

P = energy to cause pairing of electrons within a single orbital

I. Coulombic repulsion

Interelectronic repulsion between electrons occuping the same orbital decreases with size of orbital 3d > 4d > 5d

II. Loss of <u>excange energy</u> (basis on Hund's rule) on pairing

$$E_{exch} \; \alpha \; \underbrace{\frac{n(n-1)}{2}}_{\substack{\text{No. of pairs} \\ \text{of || spins} \\ \text{(same spins)}}} \qquad n = \text{No. of Parallel Spins}$$

d^6 (H. S) $\underline{\uparrow\downarrow} \; \underline{\uparrow} \; \underline{\uparrow} \; \underline{\uparrow} \; \underline{\uparrow}$ $n = 5$ $E_{exch} \; \alpha \; \dfrac{5(5-1)}{2} = 10$

d^6 (L. S) $\underline{\uparrow\downarrow} \; \underline{\uparrow\downarrow} \; \underline{\uparrow\downarrow} \; \underline{\quad} \; \underline{\quad}$

$(\uparrow) \, n = 3$ $E_{exch} \; \alpha \; \dfrac{3(3-1)}{2} = 3$

$(\downarrow) \, n = 3$ $E_{exch} \; \alpha \; \dfrac{3(3-1)}{2} = 3$

$\left. \right\} 6$
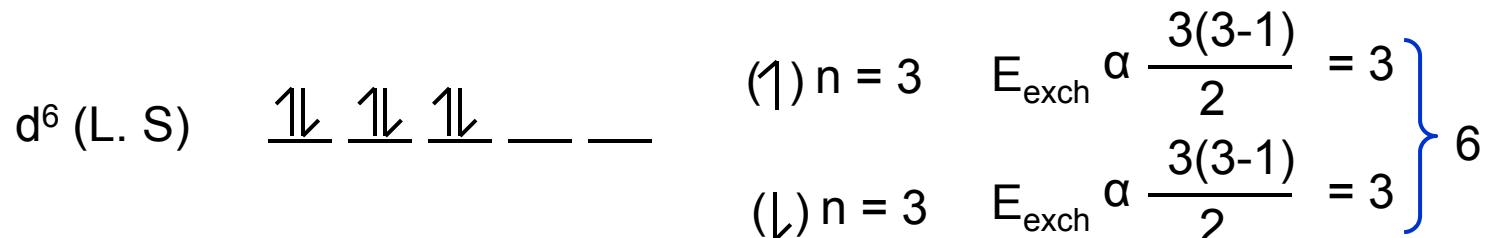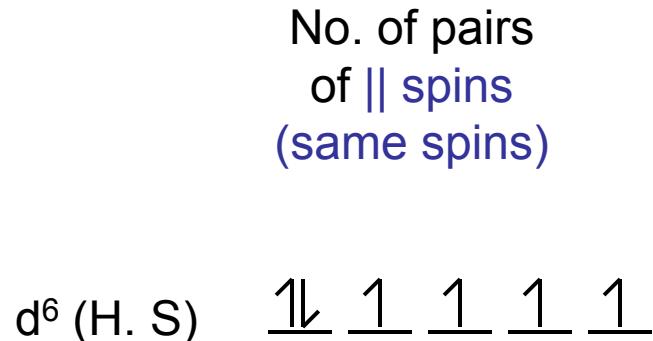
Why Fe^{2+} with weak ligands sometimes give low spin complexes Mn^{2+} does not

Fe^{2+} (d^6), Mn^{2+} (d^5)

$$\underline{1}\ \underline{1} \qquad\qquad\qquad \underline{}\ \underline{}$$

$$\underline{1\!\!\downarrow}\ \underline{1}\ \underline{1}\ \underline{1}\ \underline{1}$$

Fe^{2+}

$$\underline{1\!\!\downarrow}\ \underline{1}\ \underline{1} \qquad\qquad\qquad \underline{1\!\!\downarrow}\ \underline{1\!\!\downarrow}\ \underline{1\!\!\downarrow}$$

High Spin **Low Spin**

E_{exch} α $\dfrac{5(5-1)}{2}$ **High Spin** $\qquad$ E_{exch} α $2\left(\dfrac{3(3-1)}{2}\right)$ **Low Spin**

Loss in exchange energy α $(10 - 6) = 4$

$$\underline{1}\ \underline{1} \qquad\qquad\qquad \underline{}\ \underline{}$$

$$\underline{1}\ \underline{1}\ \underline{1}\ \underline{1}\ \underline{1}$$

Mn^{2+}

$$\underline{1}\ \underline{1}\ \underline{1} \qquad\qquad\qquad \underline{1\!\!\downarrow}\ \underline{1\!\!\downarrow}\ \underline{1}$$

High Spin **Low Spin**

Loss in exchange energy α $\left(\dfrac{5(5-1)}{2} - \dfrac{3(3-1)}{2} - \dfrac{2(2-1)}{2}\right)$

P is higher in Mn^{2+} $\qquad$ α $(10 - 4) = 6$

Temperature dependent paramagnetism

Consider a d^4 ion (Mn^3, Cr^{2+} etc)

$\mu = \sqrt{n(n+2)}$; n = 4

μ = 4.9 BM

CFSE = -12 Dq + 6 Dq

= - 6Dq

High Spin

$\mu = \sqrt{n(n+2)}$; n = 2

μ = 2.828 BM

CFSE = -16 Dq + P

Low Spin
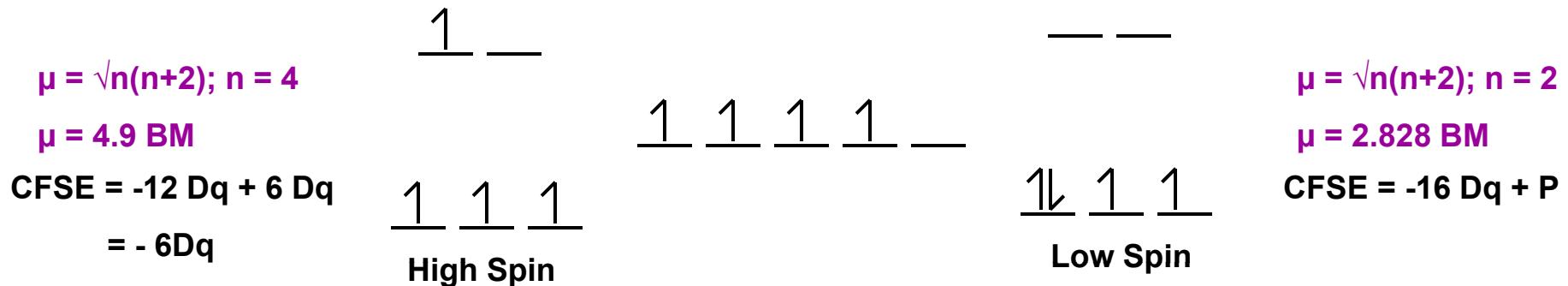
1. Measured magnetic moment = f (T) in black region

2. Lie between 2.828 to 4.9

- 6 Dq

- 16 Dq + P

High Spin

Low Spin