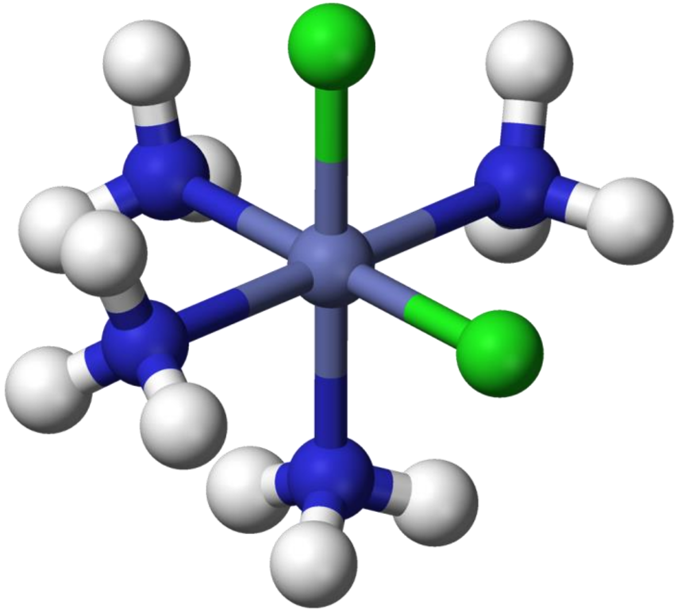
Coordination Chemistry



UGC NET Coaching

Postgraduate Department of Chemistry

St. Mary’s College, Manarcaud

Reference

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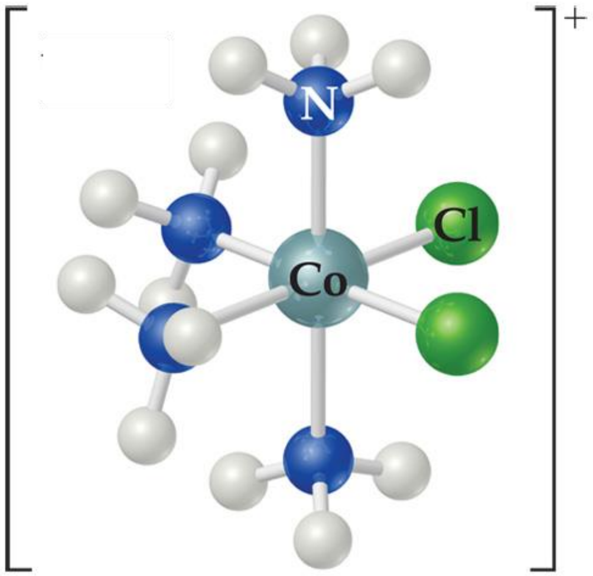
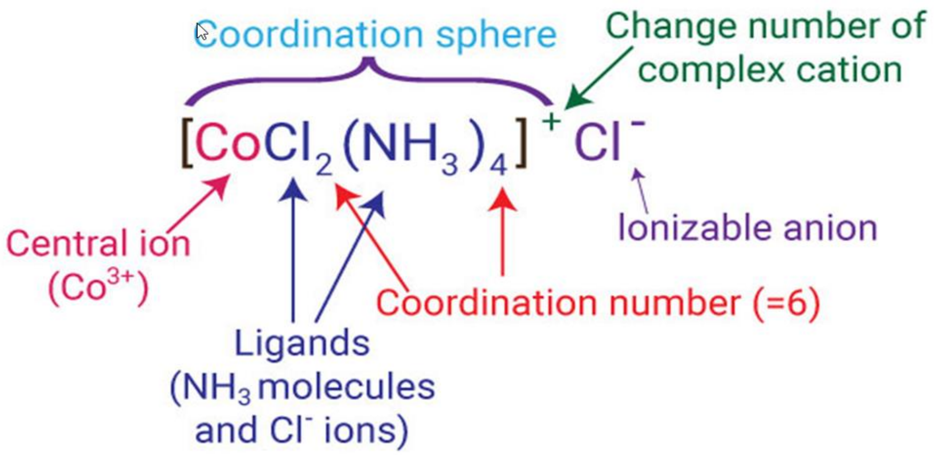
Werner’s Theory



Co(III) oxidation state

Coordination Number is 6



- Suggested in 1893 that metal ions have ***primary*** and ***secondary*** valences.
  - Primary valence equal the metal’s oxidation number-Its non directional & ionizable
  - **Secondary valence is the number of atoms directly bonded to the metal (coordination number)- Its directional and non ionizable**

Q1.The primary and secondary valency of Pt in $[Pt(en)_2Cl_2]Cl_2$ are

a) 4,4 b) 4,6

c) 6,6 d) 4,2

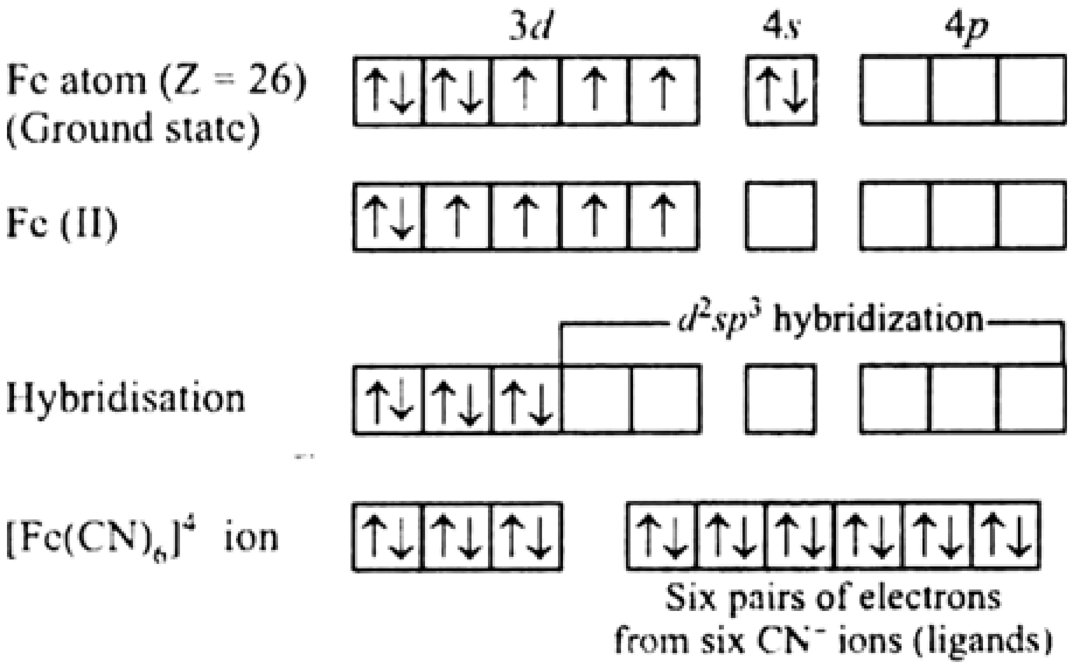
Q2. Coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively

a) 3,0 b)3,3

c) 6,3 d)4,2

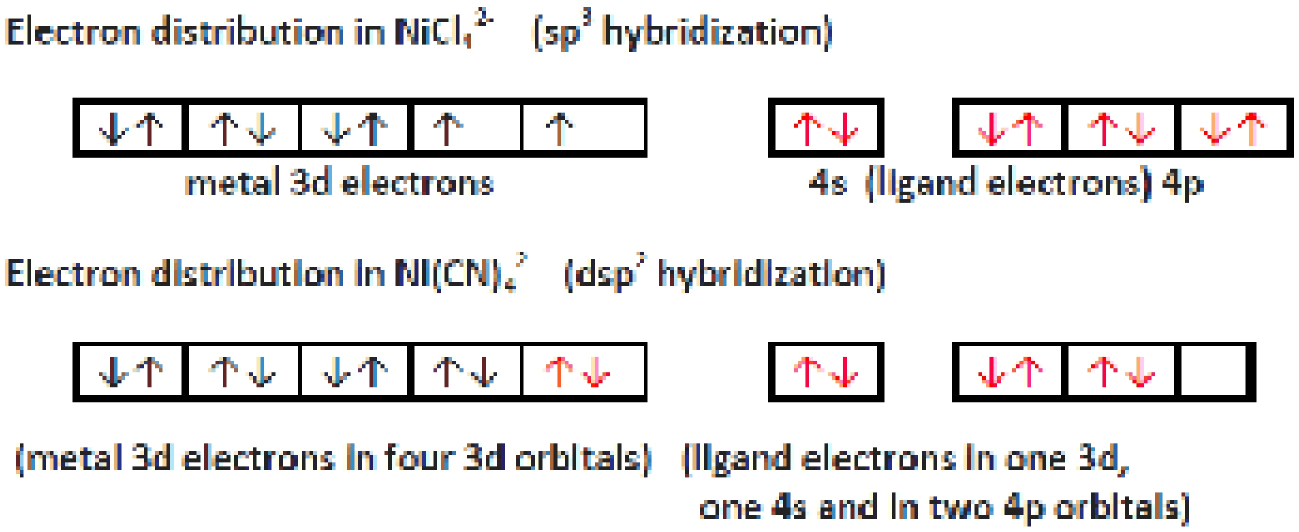
Valance Bond Theory

- This model utilizes hybridization of metal valance orbitals to account for the observed structures and magnetic properties of the complexes.
- The *(n-1)d*, *ns* and *np* orbitals undergo hybridization to give hybridized orbitals.
- Here an empty hybrid orbital on the metal centre accept a pair of electrons from a ligand to form a σ- bond.
- From VBT we get geometry, hybridization, magnetic properties etc.



Inner Orbital Complex- d^2sp^3

Outer Orbital Complex- sp^3d^2



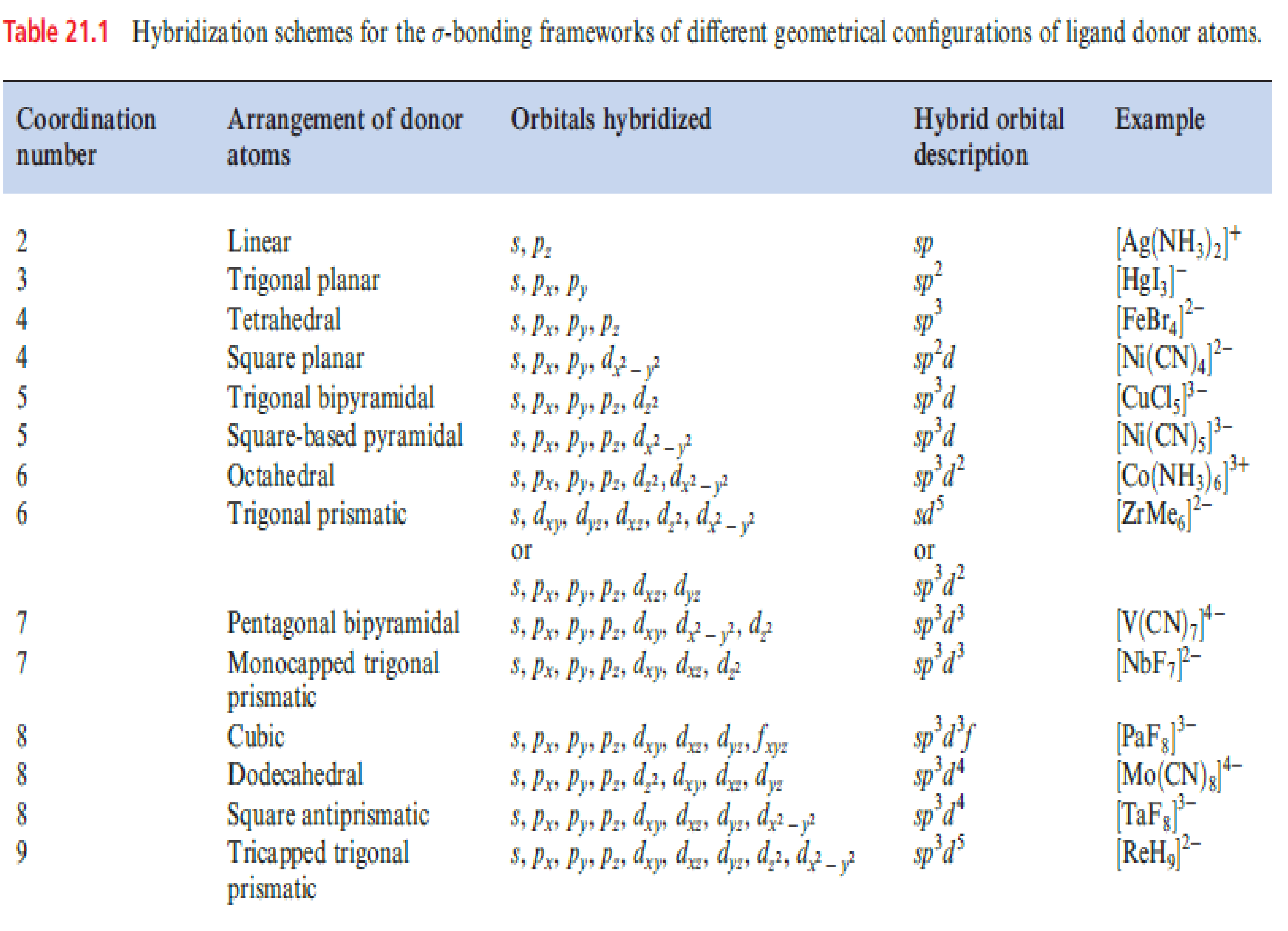


Table 21.1 Hybridization schemes for the σ-bonding frameworks of different geometrical configurations of ligand donor atoms.

Coordination number	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[Ag(NH_3)_2]^+$
3	Trigonal planar	s, p_x, p_y	sp^2	$[HgI_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[FeBr_4]^{2-}$
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	sp^2d	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d	$[CuCl_5]^{3-}$
5	Square-based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d	$[Ni(CN)_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2	$[Co(NH_3)_6]^{3+}$
6	Trigonal prismatic	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yz}$	sd^5 or sp^3d^2	$[ZrMe_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^3	$[V(CN)_7]^{4-}$
7	Monocapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3	$[NbF_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	sp^3d^3f	$[PaF_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$	sp^3d^4	$[Mo(CN)_8]^{4-}$
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	sp^3d^4	$[TaF_8]^{3-}$
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5	$[ReH_9]^{2-}$

- Magnetic moment is given by

$$\mu = \sqrt{n(n+2} \text{ BM}$$

Where n is the number of unpaired electrons. Magnetic Moment is measured in Bohr Magnetons (BM)

- Presence of Unpaired electrons- **Paramagnetic**

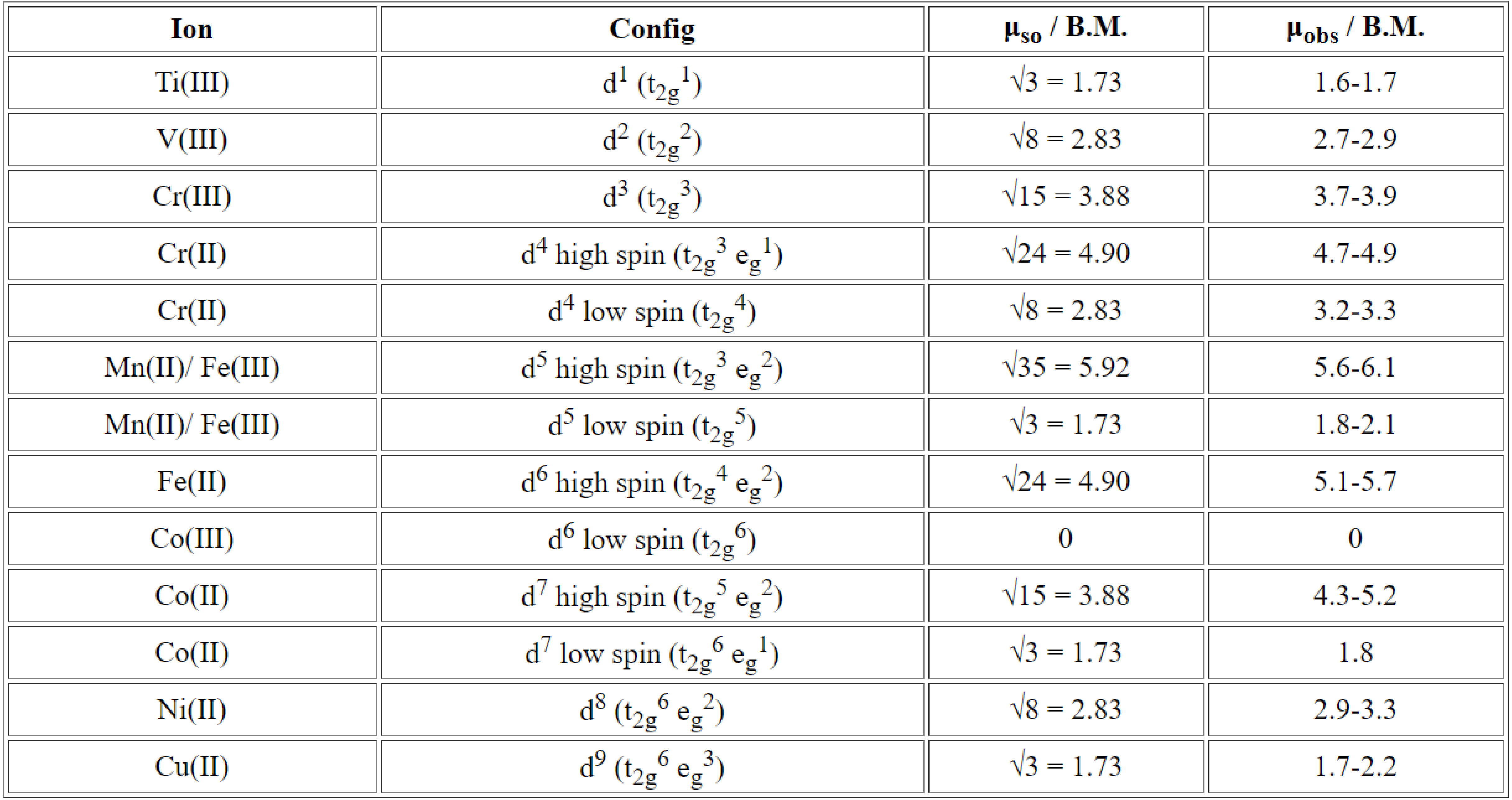
  No Unpaired electrons- **Diamagnetic**

- **Mostly, Td Complexes are Paramagnetic &**

  Sp complexes are Diamagnetic

- **3d,4d,5d transition metals with d^8configuration and strong field ligands are usually square-planar**

Comparison of calculated spin-only magnetic moments with experimentally observed data for some octahedral complexes



Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	√3 = 1.73	1.6-1.7
V(III)	d^2 (t_{2g}^2)	√8 = 2.83	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin (t_{2g}^3 e_g^1)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin (t_{2g}^3 e_g^2)	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1
Fe(II)	d^6 high spin (t_{2g}^4 e_g^2)	√24 = 4.90	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin (t_{2g}^5 e_g^2)	√15 = 3.88	4.3-5.2
Co(II)	d^7 low spin (t_{2g}^6 e_g^1)	√3 = 1.73	1.8
Ni(II)	d^8 (t_{2g}^6 e_g^2)	√8 = 2.83	2.9-3.3
Cu(II)	d^9 (t_{2g}^6 e_g^3)	√3 = 1.73	1.7-2.2

Q_3 Among $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$

(a) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic

(b) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

(c) $Ni(CO)_4$ is diamagnetic and $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$ are paramagnetic

(d) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

Q_4 Which is true for $[Ni(en)_2]^{2+}$,Z(Ni) = 28 ?

(a) Paramagnetism, dsp^2, square planar, CN of Ni = 2

(b) Diamagnetism, dsp^2, square planar, CN of Ni = 4

(c) Diamagnetism, sp^3, tetrahedral, CN of Ni = 4

(d) Paramagnetism, sp^3, square planar, CN of Ni = 44

Q5 $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$ have similarity but not in

a) Magnetic moment b) CN and ON

c) Geometry d) Both a and c

Q6. The number of unpaired electrons present in the complexes; $[Ni(CN)_4]^{2-}$ and $[PtCl_4]^{2-}$ respectively are:

A. 2 in both the cases B. 0 in both

B. C. 0 in first and 2 in second D. 2 in first and 0 in second

Crystal field theory

- Proposed in 1929 by Hans Bethe
- Pure Crystal field theory assumes that the only interaction between the metal ion and the ligands is an electrostatic or ionic one with the ligands being regarded as negative point charges

M^+

L

Point Charge

Point Dipole

- In CFT we consider two main interaction

1) Attractive interaction- Bonding Interaction

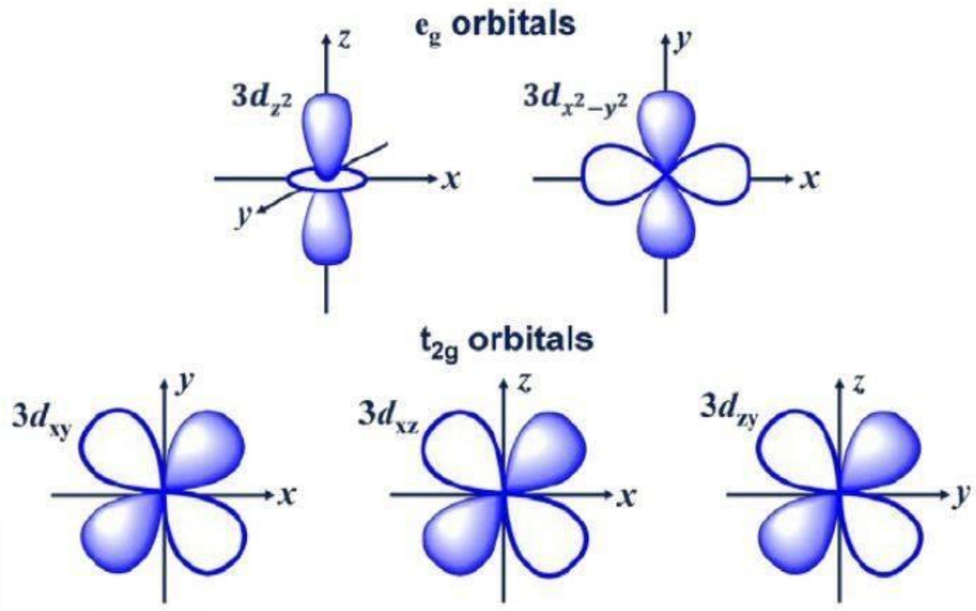
2) Repulsive interaction – Cause of Crystal field splitting

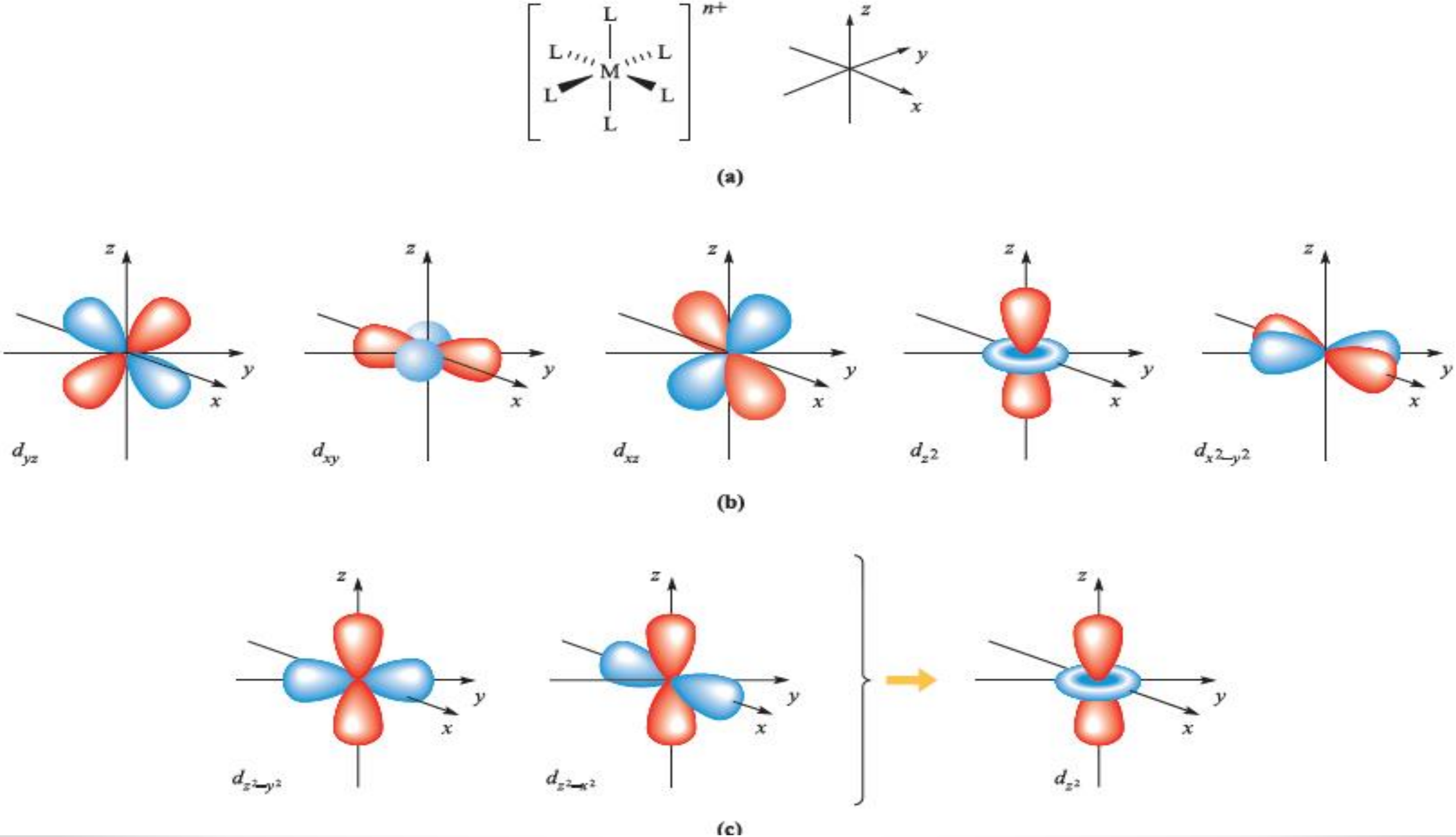
Splitting of d-orbitals and its consequences are considered as the backbone of CFT

Shape of d-orbitals

- The five d orbitals are not identical and the orbitals may be divided into two set.

1) Orbitals along the axis – d_{Z2},$d_{x2\text{-}y2}$- e_g or dγ
2) Orbitals in between the axis- dxy, dxz, dyx- t2g or dε

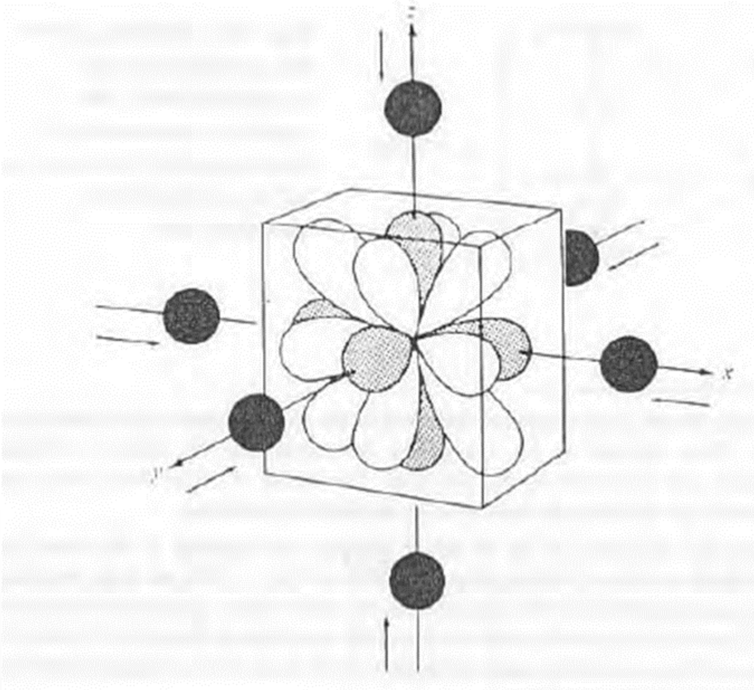


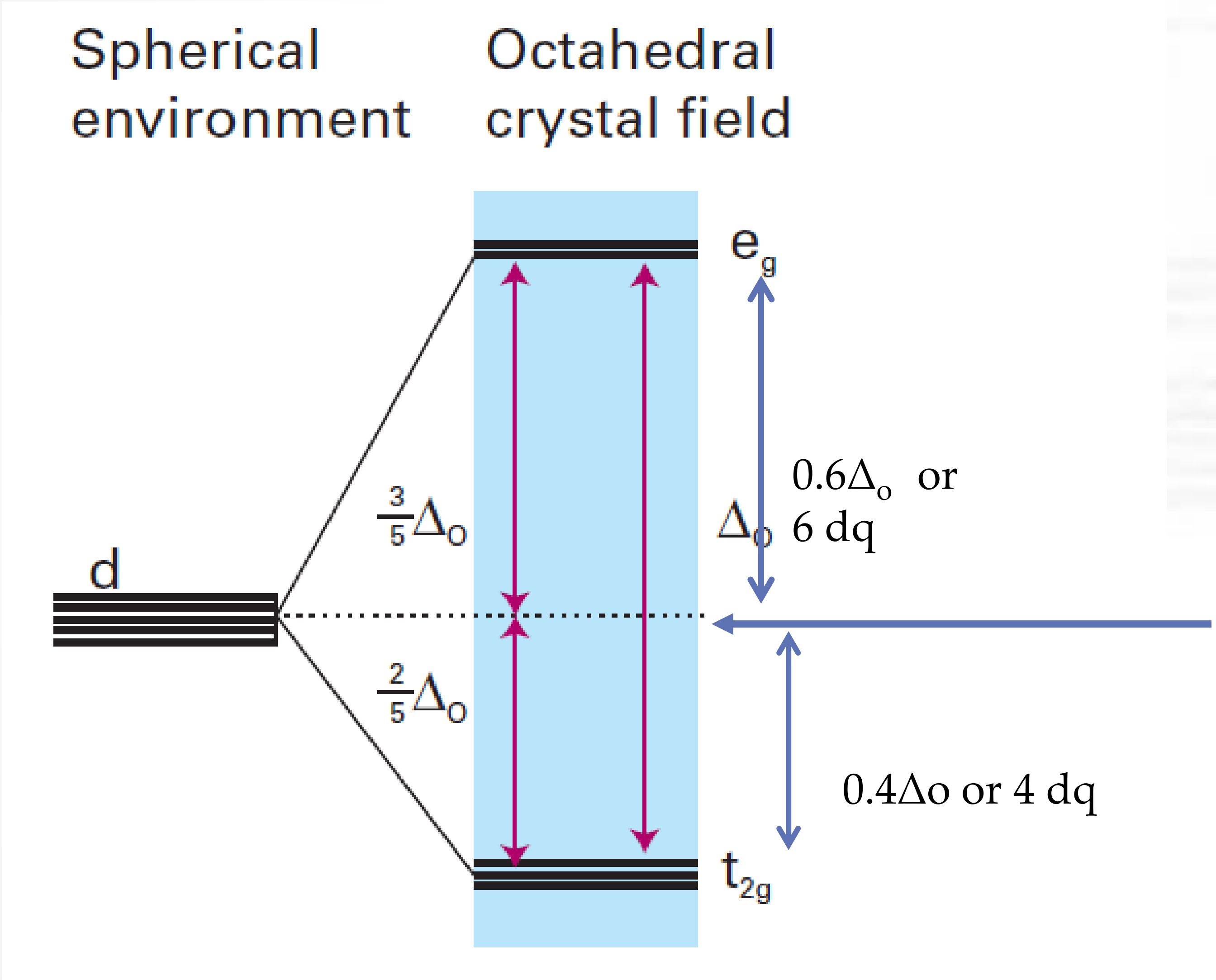


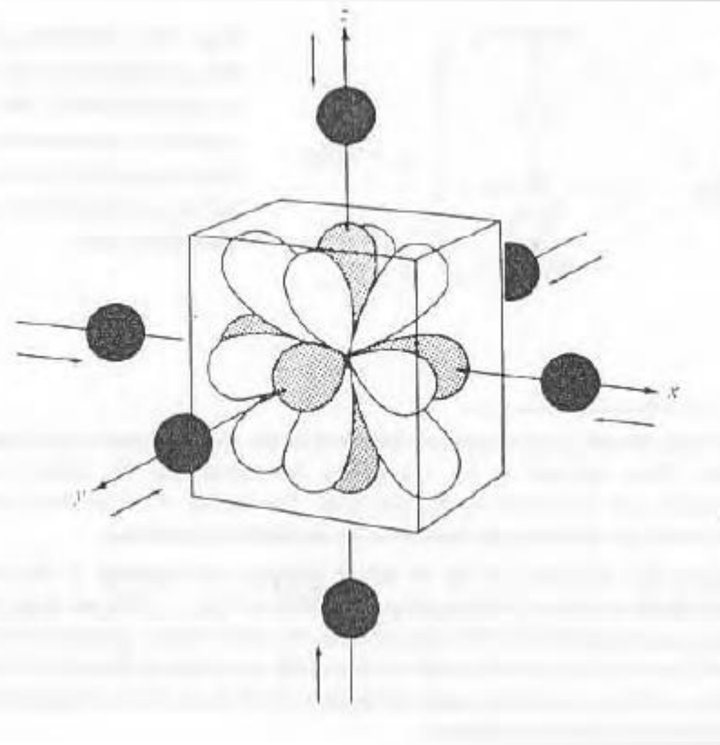
L
L
L
M
L
L
L
n+
z
y
x
(a)
z
y
x
d_{yz}
d_{xy}
d_{xz}
d_{z^2}
$d_{x^2-y^2}$
(b)
$d_{z^2-y^2}$
$d_{z^2-x^2}$
d_{z^2}
(c)

Octahedral symmetry

- In an Oh complex, six ligands are symmetrically positioned along the axes of cartesian coordinate system with the metal ion at the origin.
- Here not all the orbitals will be affected to the same extent.
- The orbitals lying along the axis will be strongly repelled than the orbitals with lobes directed between the axis
- Under the influence of an octahedral field the d orbitals split into two groups of different energy with eg set at a higher energy than the t2g set

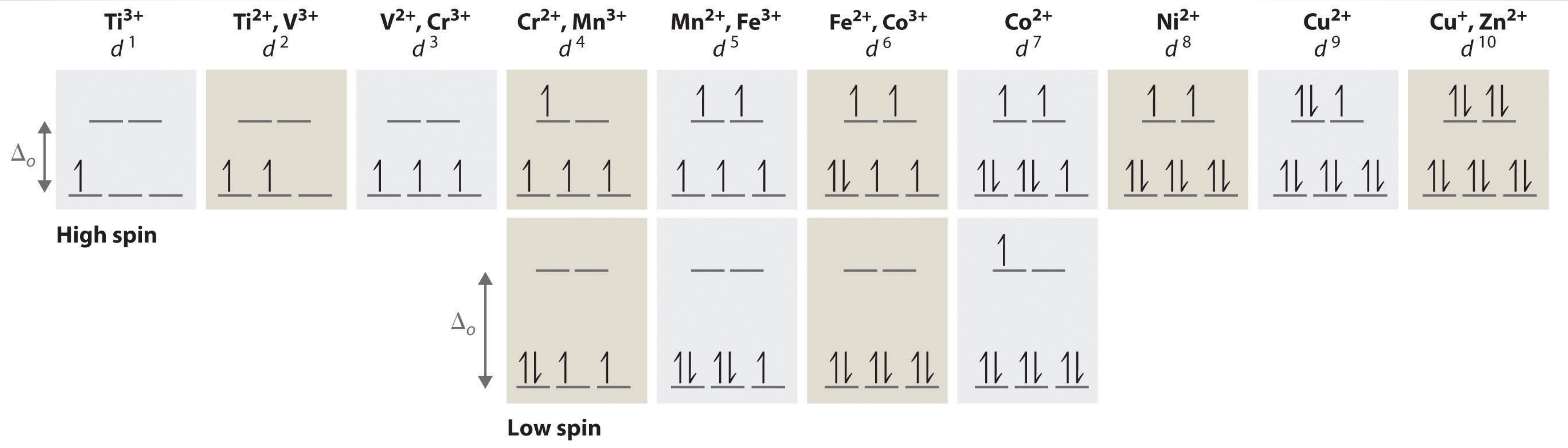




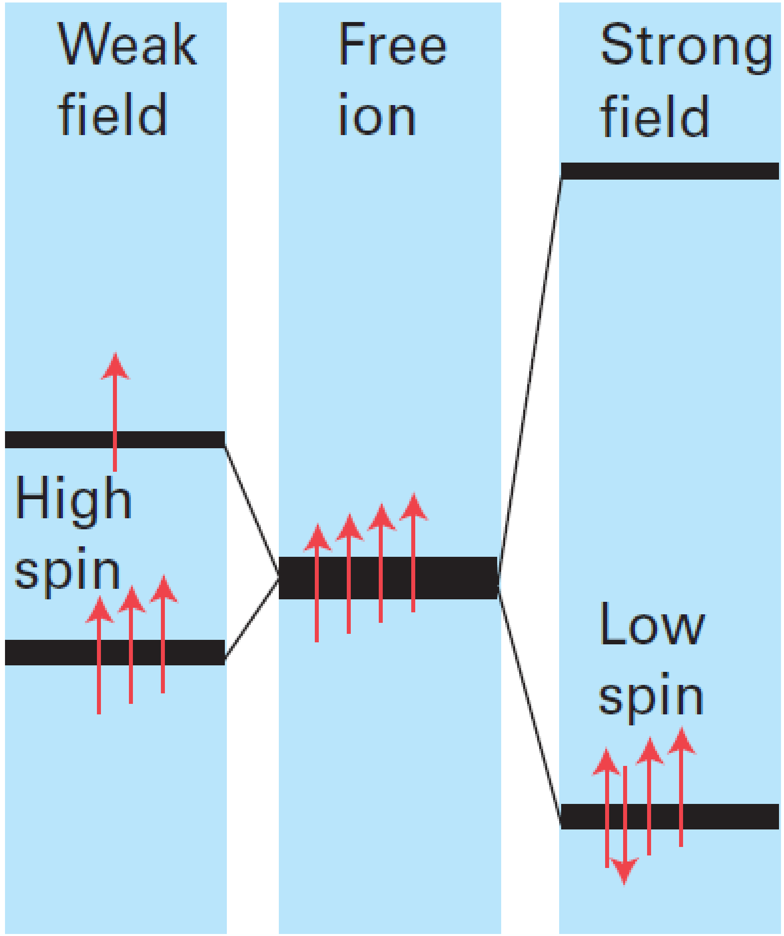


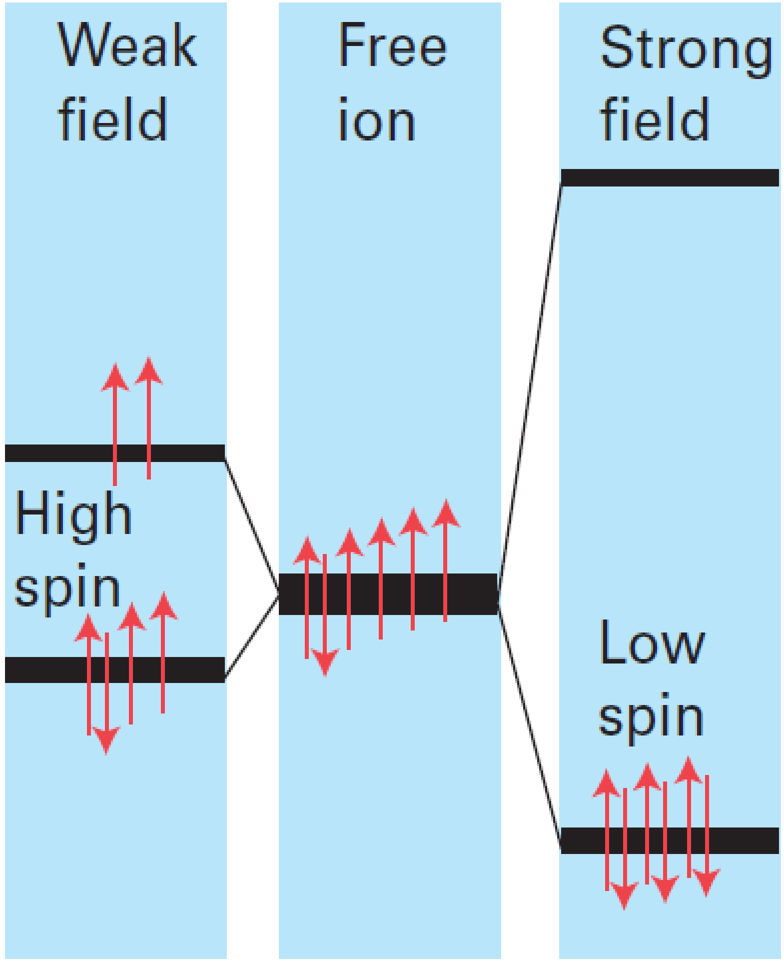
Centre of gravity or Bary centre

Crystal field stabilization energy (CFSE)



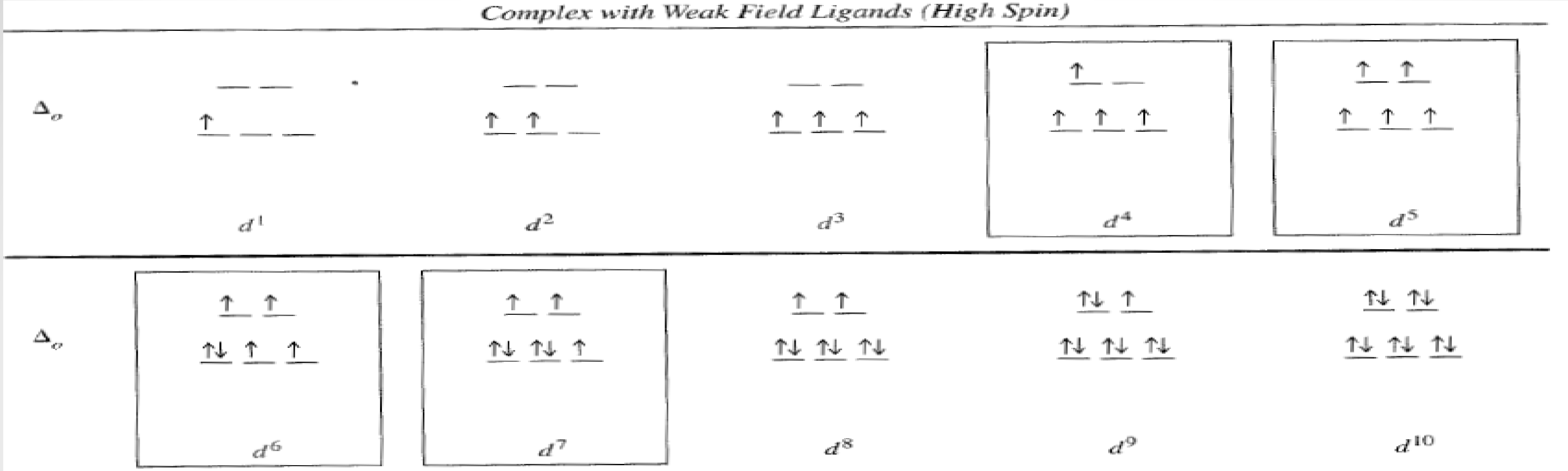
Consider a d1 case


Weak field
Free ion
Strong field
High spin
Low spin

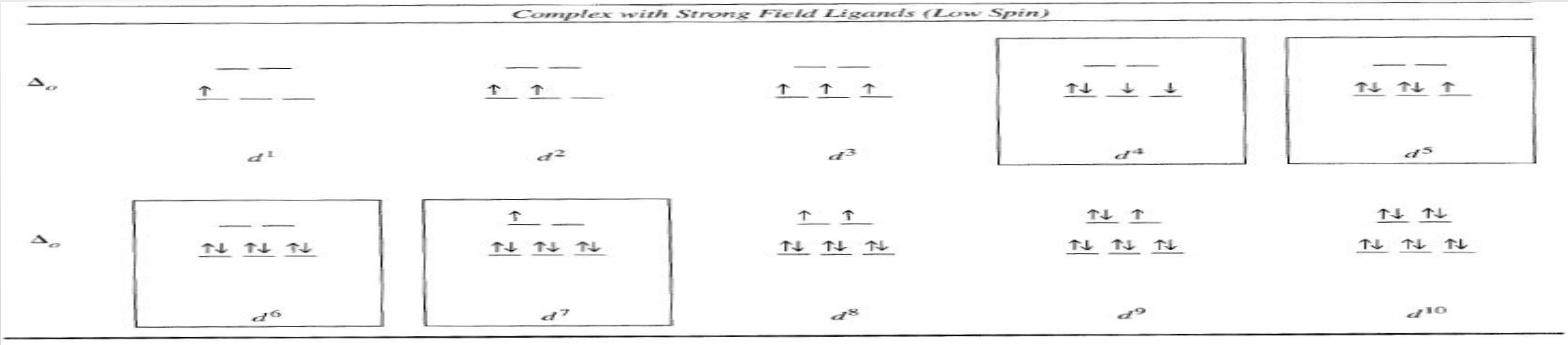

Weak field
Free ion
Strong field
High spin
Low spin

Strong ligand field = large Δ= low spin

Weak ligand field = small Δ = high spin



Complex with Weak Field Ligands (High Spin)



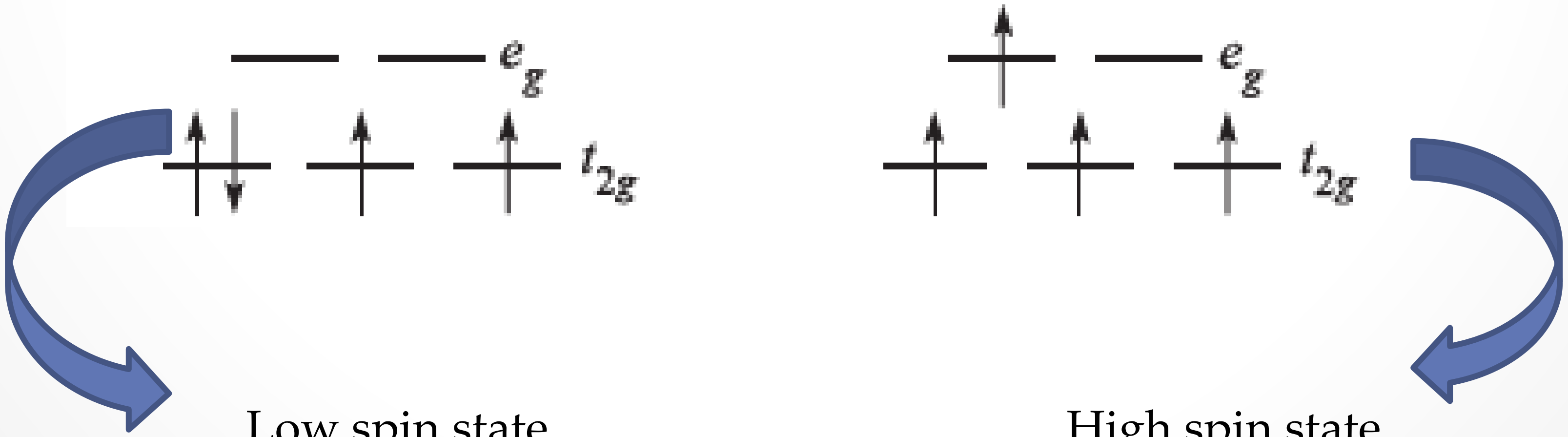
Complex with Strong Field Ligands (Low Spin)

For high-spin: $\Delta_{oct} < P$

For low-spin: $\Delta_{oct} > P$

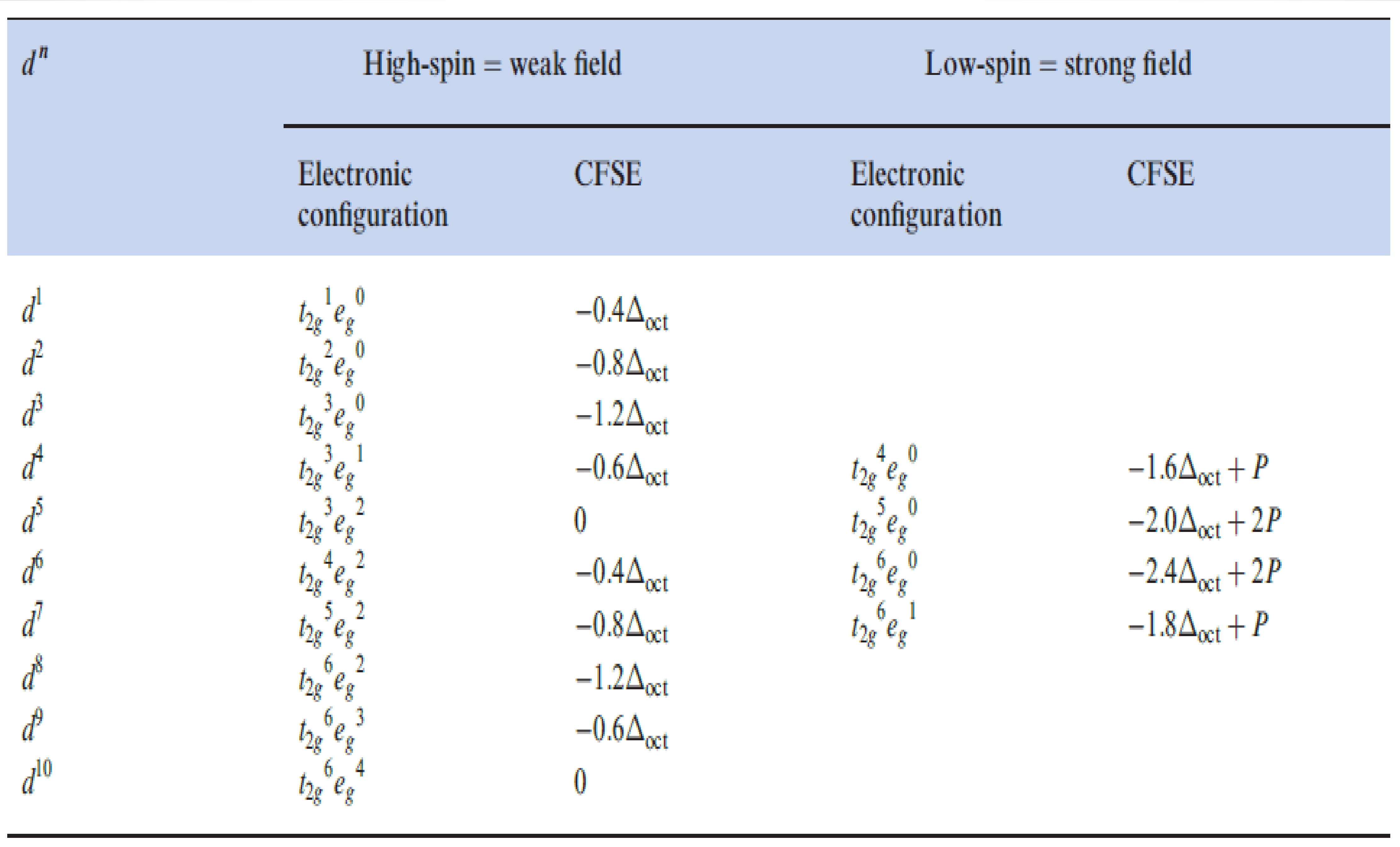
Two terms contribute to the electron-pairing energy, P, which is the energy required to transform two electrons with parallel spin in different degenerate orbitals into spin-paired electrons in the same orbital:

- the loss in the exchange energy which occurs upon pairing the electrons;
- the coulombic repulsion between the spin-paired electrons.



Low spin state

High spin state



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

- The Crystal field stabilization energy of low spin d7 oh complex is

a) -4/5 Δo +2P

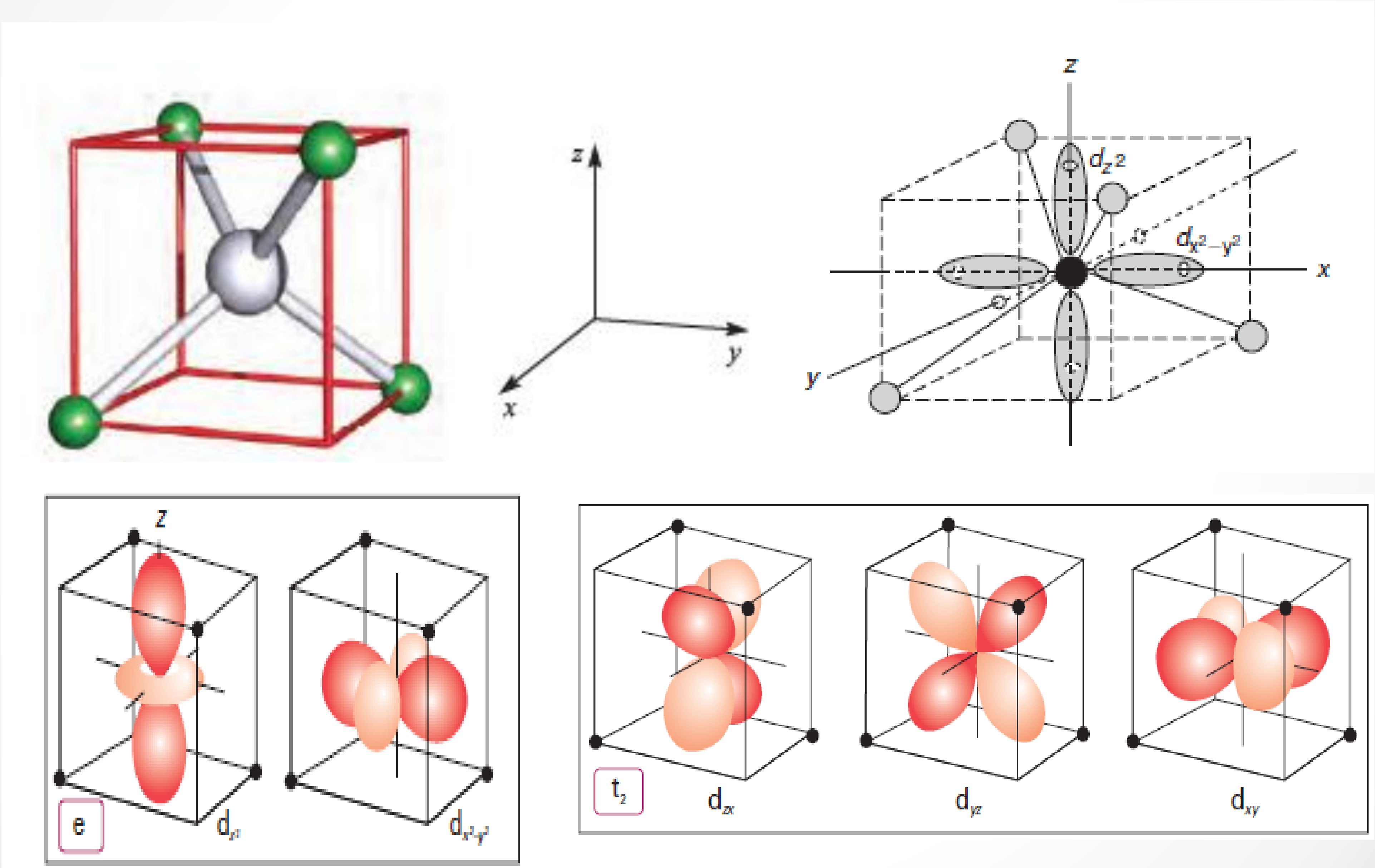
b) -4/5 Δo + P

c) -9/5 Δo + P

d) -9/5 Δo + 2P

The number of unpaired electrons in Co2+ low spin Oh complex is

Tetrahedral field



A regular tetrahedron is related *to a cube. One atom is at the centre of the* cube, and four of the eight corners of the cube are occupied by ligands

The directions *x, y and z point to the centres of the faces of the cube* . The *eg orbitals point along x, y and z (that is to .the centres of the faces)* . The t_2g orbitals point between *x, y and z (that is towards the centres of the* edges of the cube) The direction of approach of the ligands does not coincide exactly with either the eg or the t_2g orbitals.

The angle between an *eg orbital, the central* metal and the ligand is half the tetrahedral angle = **109°28' /2 = *54°44'.***

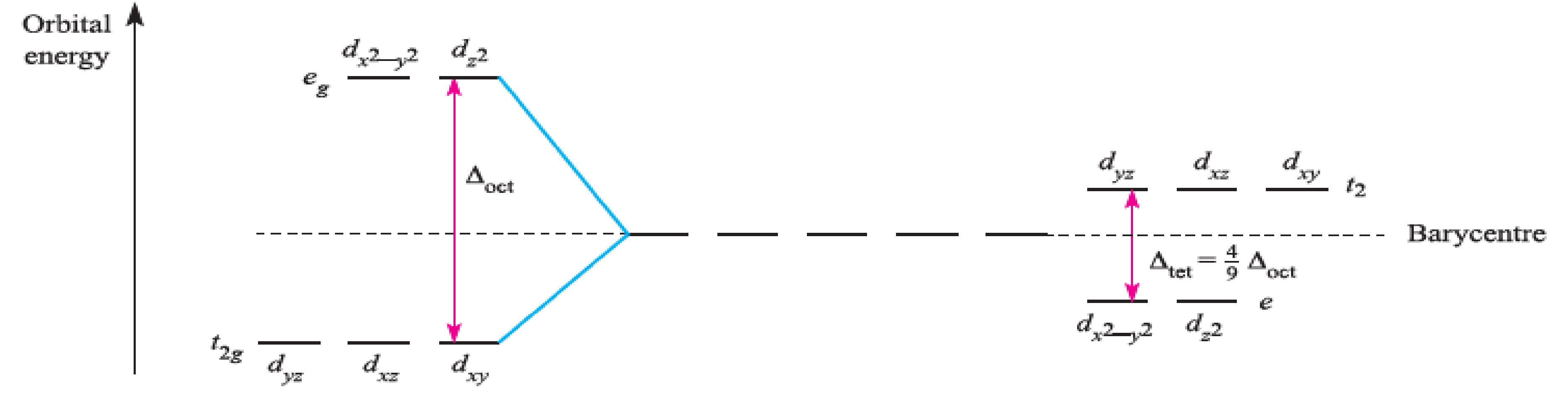
The angle between a t_2g orbital, the central metal and the ligand is **35°16’.**

Thus the t2g orbitals are nearer to the direction of the ligands than the *eg orbitals*.

The approach of the ligands raises the energy of both sets of orbitals.

The energy of the t_2g orbitals is raised most because they are closest to the ligands. This crystal field splitting is the opposite way round to that in octahedral complexes

Tetrahedral complexes are almost invariably high-spin.

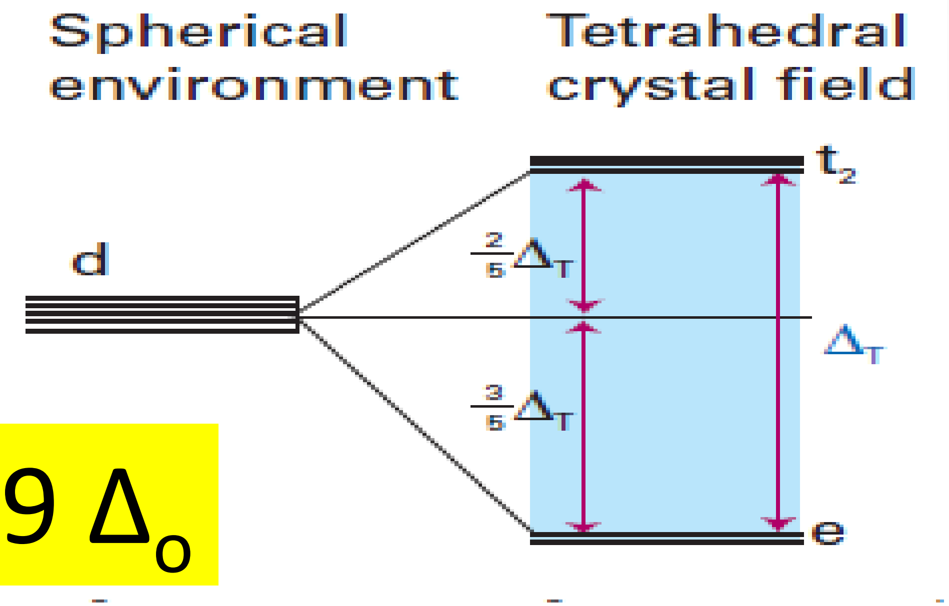


The magnitude of the crystal field splitting Δt in tetrahedral complexes is considerably less than in octahedral ·fields. There are two reasons for this:

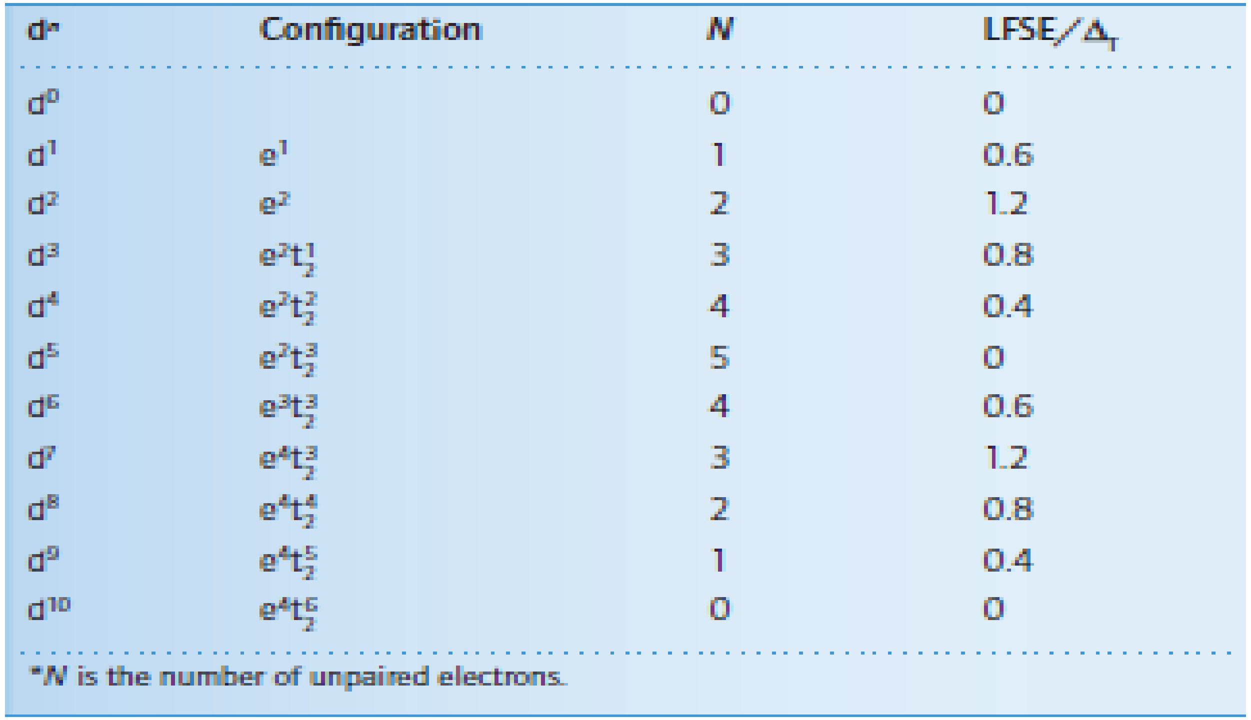
1. There are only four ligands instead of six, so the ligand field is only two thirds the size: hence the ligand field splitting is also two thirds the size.

2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting Δ, is roughly 2/3 x 2/3 = *4/9 of* the octahedral crystal field splitting Δo , Strong field ligands cause a bigger energy difference between t2g and *eg than weak field ligands. However, the* tetrahedral splitting Δt is always much smaller than the octahedral splitting Δo . Thus it is never energetically favourable to pair electrons, and **all tetrahedral complexes are high-spin.**



$\Delta_t = 4/9\ \Delta_o$



d^n	Configuration	N	LFSE/Δ_T
d^0		0	0
d^1	e^1	1	0.6
d^2	e^2	2	1.2
d^3	$e^2t_2^1$	3	0.8
d^4	$e^2t_2^2$	4	0.4
d^5	$e^2t_2^3$	5	0
d^6	$e^3t_2^3$	4	0.6
d^7	$e^4t_2^3$	3	1.2
d^8	$e^4t_2^4$	2	0.8
d^9	$e^4t_2^5$	1	0.4
d^{10}	$e^4t_2^6$	0	0

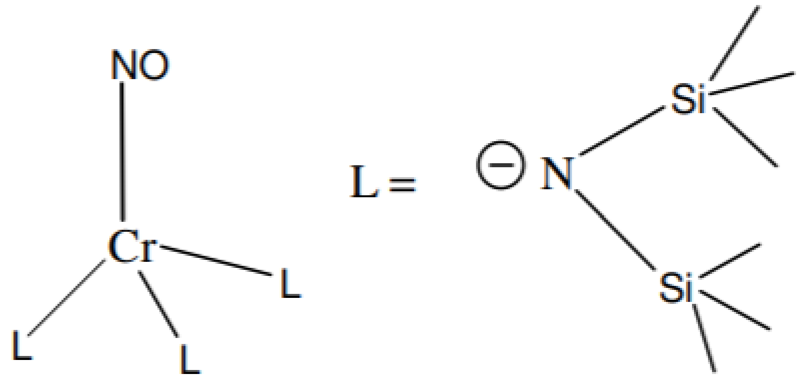
*N is the number of unpaired electrons.

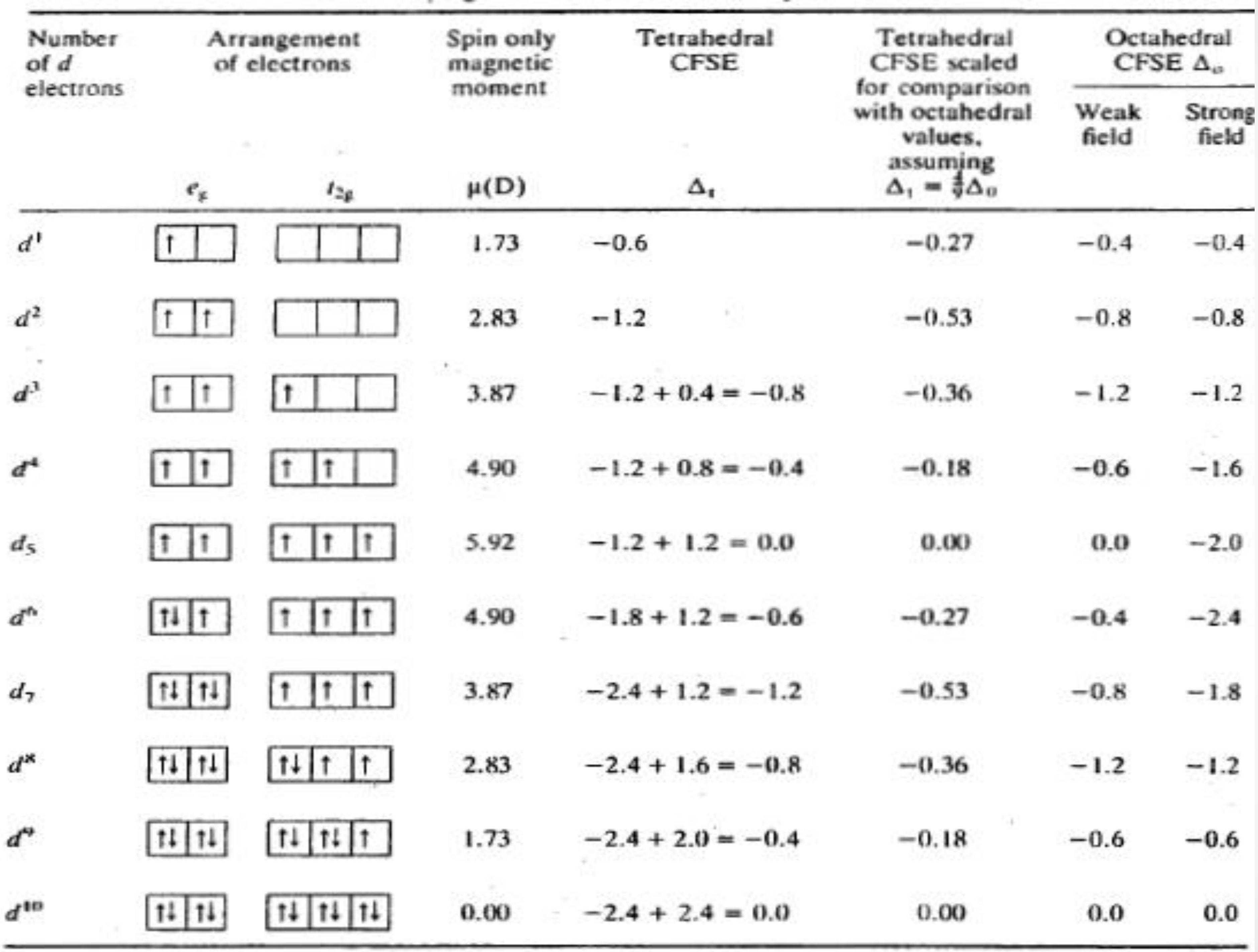
When to expect Tetrahedral geometry?

Ligands are large, less ligand-ligand repulsion metal ions with zero CFSE (d0 , d5 , d10) or small CFSE (d2 and d7).

Examples: MnO4 - (d0), FeCl4 - (d5 , h.s.), CoCl4 2- (d7 , h.s.), ZnCl4 2- (d10)

Having fewer number of ligands (four) and they are not aligned along the orbital axis, the CFSE in most cases are too small to overcome the spin pairing energy, therefore, tetrahedral low-spin complexes are rare.
A rare example is Cr[N(SiMe3)2]3[NO].





Number of d electrons	Arrangement of electrons e_g	Arrangement of electrons t_{2g}	Spin only magnetic moment μ(D)	Tetrahedral CFSE Δ_t	Tetrahedral CFSE scaled for comparison with octahedral values, assuming $\Delta_t = \frac{4}{9}\Delta_o$	Octahedral CFSE Δ_o Weak field	Octahedral CFSE Δ_o Strong field
d^1	↑ □	□ □ □	1.73	−0.6	−0.27	−0.4	−0.4
d^2	↑ ↑	□ □ □	2.83	−1.2	−0.53	−0.8	−0.8
d^3	↑ ↑	↑ □ □	3.87	$-1.2 + 0.4 = -0.8$	−0.36	−1.2	−1.2
d^4	↑ ↑	↑ ↑ □	4.90	$-1.2 + 0.8 = -0.4$	−0.18	−0.6	−1.6
d_5	↑ ↑	↑ ↑ ↑	5.92	$-1.2 + 1.2 = 0.0$	0.00	0.0	−2.0
d^6	↑↓ ↑	↑ ↑ ↑	4.90	$-1.8 + 1.2 = -0.6$	−0.27	−0.4	−2.4
d_7	↑↓ ↑↓	↑ ↑ ↑	3.87	$-2.4 + 1.2 = -1.2$	−0.53	−0.8	−1.8
d^8	↑↓ ↑↓	↑↓ ↑ ↑	2.83	$-2.4 + 1.6 = -0.8$	−0.36	−1.2	−1.2
d^9	↑↓ ↑↓	↑↓ ↑↓ ↑	1.73	$-2.4 + 2.0 = -0.4$	−0.18	−0.6	−0.6
d^{10}	↑↓ ↑↓	↑↓ ↑↓ ↑↓	0.00	$-2.4 + 2.4 = 0.0$	0.00	0.0	0.0

A reminder about symmetry labels

The two sets of d orbitals in an octahedral field are labelled eg and t_2g. In a tetrahedral field the labels become e and t_2. The symbols t and e refer to the degeneracy of the level:

- **a triply degenerate level is labelled t;**
- **a doubly degenerate level is labelled e.**

The subscript **g means gerade** and the subscript **u means ungerade.**

- Gerade and ungerade designate the behaviour of the wavefunction under the operation of inversion, and denote the parity (even or odd) of an orbital. The u and g labels are applicable only if the system possesses a centre of symmetry (centre of inversion) and thus are used for the octahedral field, but not for the tetrahedral one.

Q7 $[CoF_6]^{4-}$ is a

A. diamagnetic weak field complex B. Diamagnetic strong field complex

C. paramagnetic weak field complex D. paramagnetic strong field complex

Q8 For which one of the following would it not possible to distinguish high spin from low spin complexes in Oh geometry

A Co(III) B.Fe(II) C. Co(II) D. Ni(II)

Q9 The CFSE of Co(III) Oh complex in strong field is (P-paring energy)

A) -24Dq+2P B) -24Dq + 3P C) -4Dq +P D) -24Dq

Q10 Considering the two complexes (A) $[Ni(H_2O)_6]^{2+}$ and (B) $[Ni(NH_3)_6]^{2+}$, the right statement is

A. Complex (A) is diamagnetic and complex (B) is paramagnetic

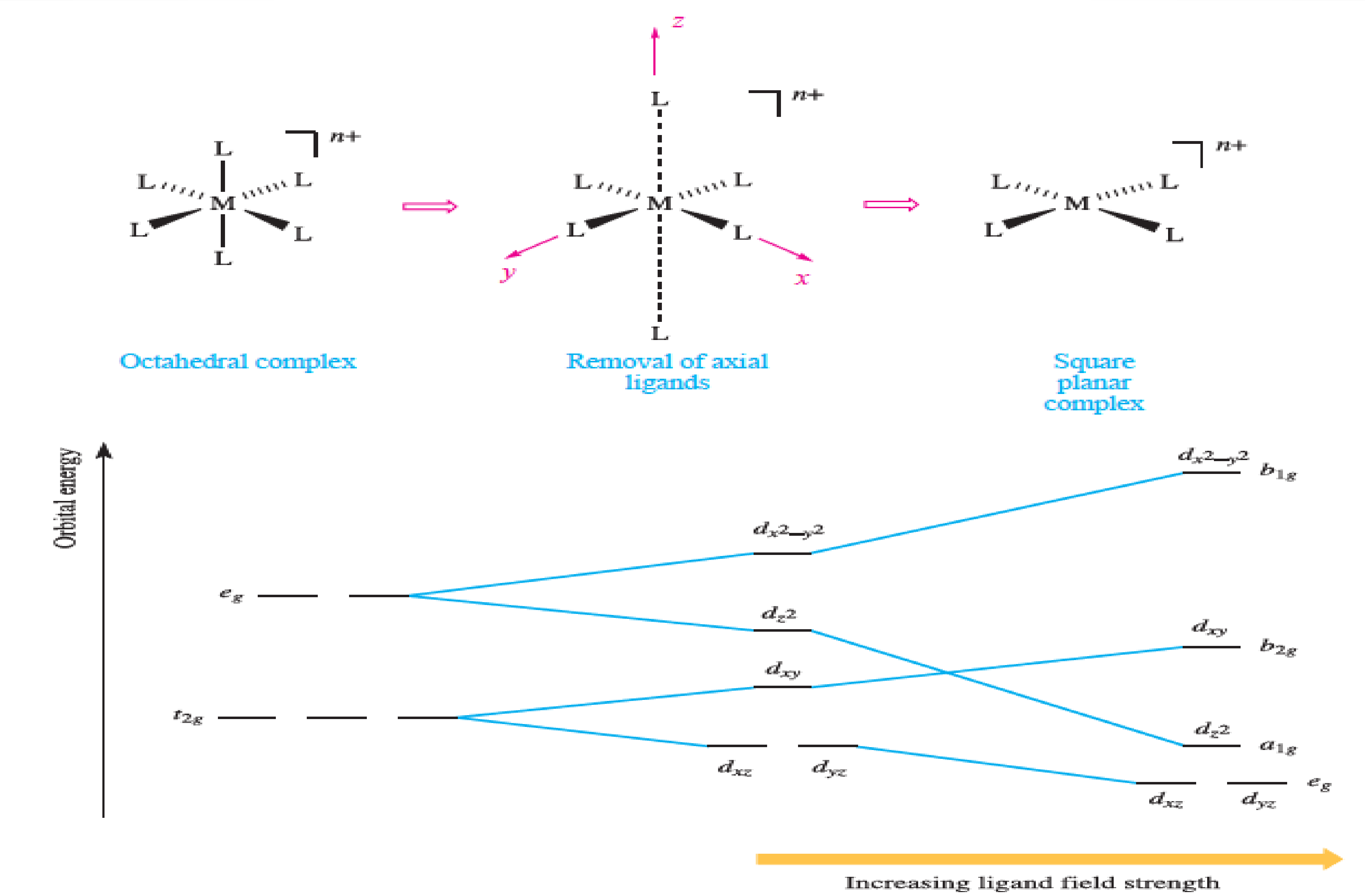
B. Complex (A) is paramagnetic and complex (B) is diamagnetic

C. Both are paramagnetic D. Both are diamagnetic

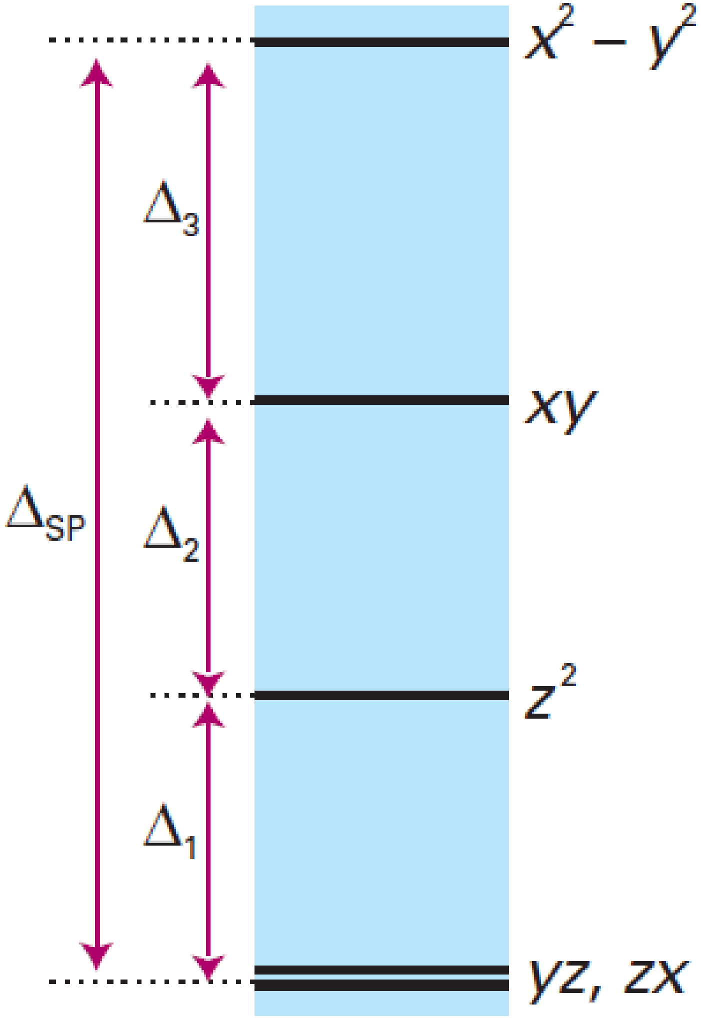
Square-planar complexes

- A d^8 configuration, coupled with a strong ligand field, favours the formation of square planar complexes. This tendency is enhanced with the 4d and 5d metals due to their larger size and the greater ease of electron pairing.
- A square planar arrangement of ligands can be formally derived from an octahedral array by removal of two trans ligands.
- Here the approach direction is along the XY plane
- $\Delta \text{SP} = 1.3\ \Delta_o$

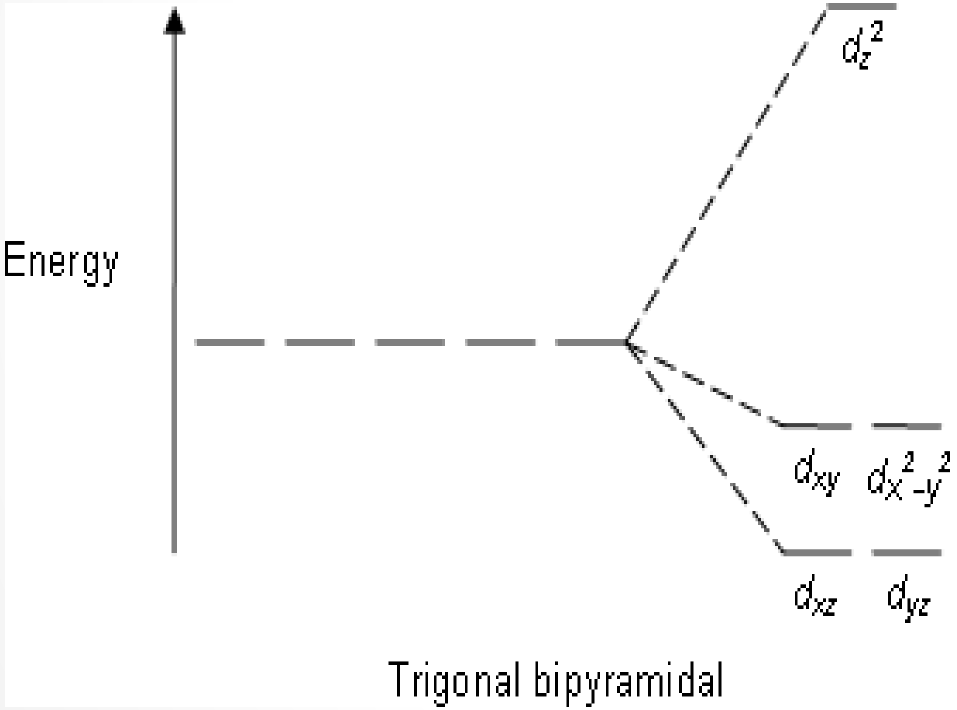
If we remove the ligands lying along the z axis, then the dz^2 orbital is greatly stabilized; the energies of the dyz and dxz orbitals are also lowered. ie. Orbits with Z components are stabilized.



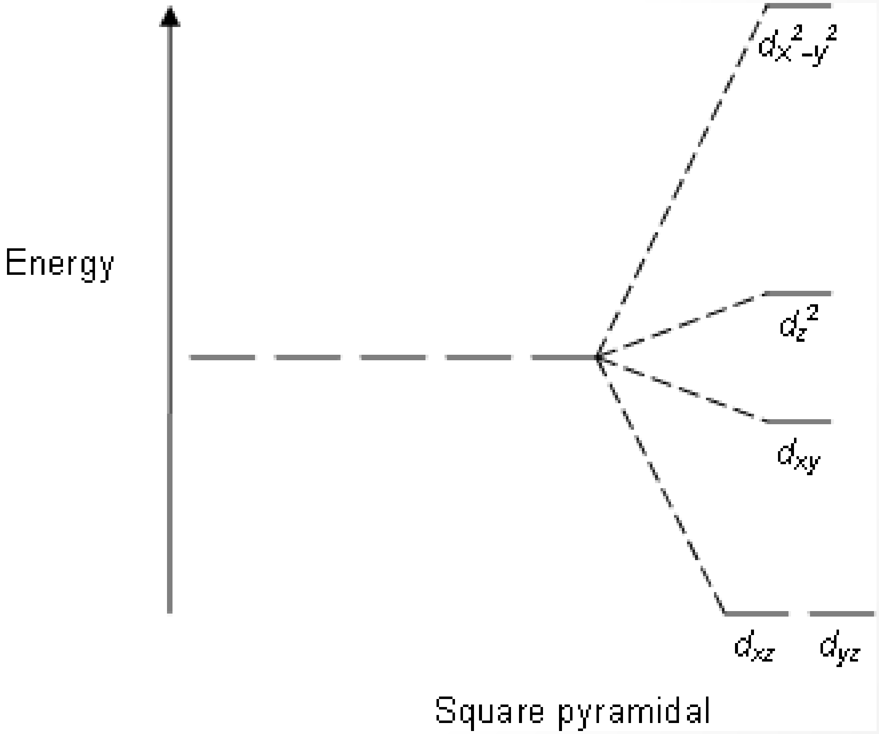
Splitting in square planar complex



Splitting in Trigonal bipyramidal and square pyramidal

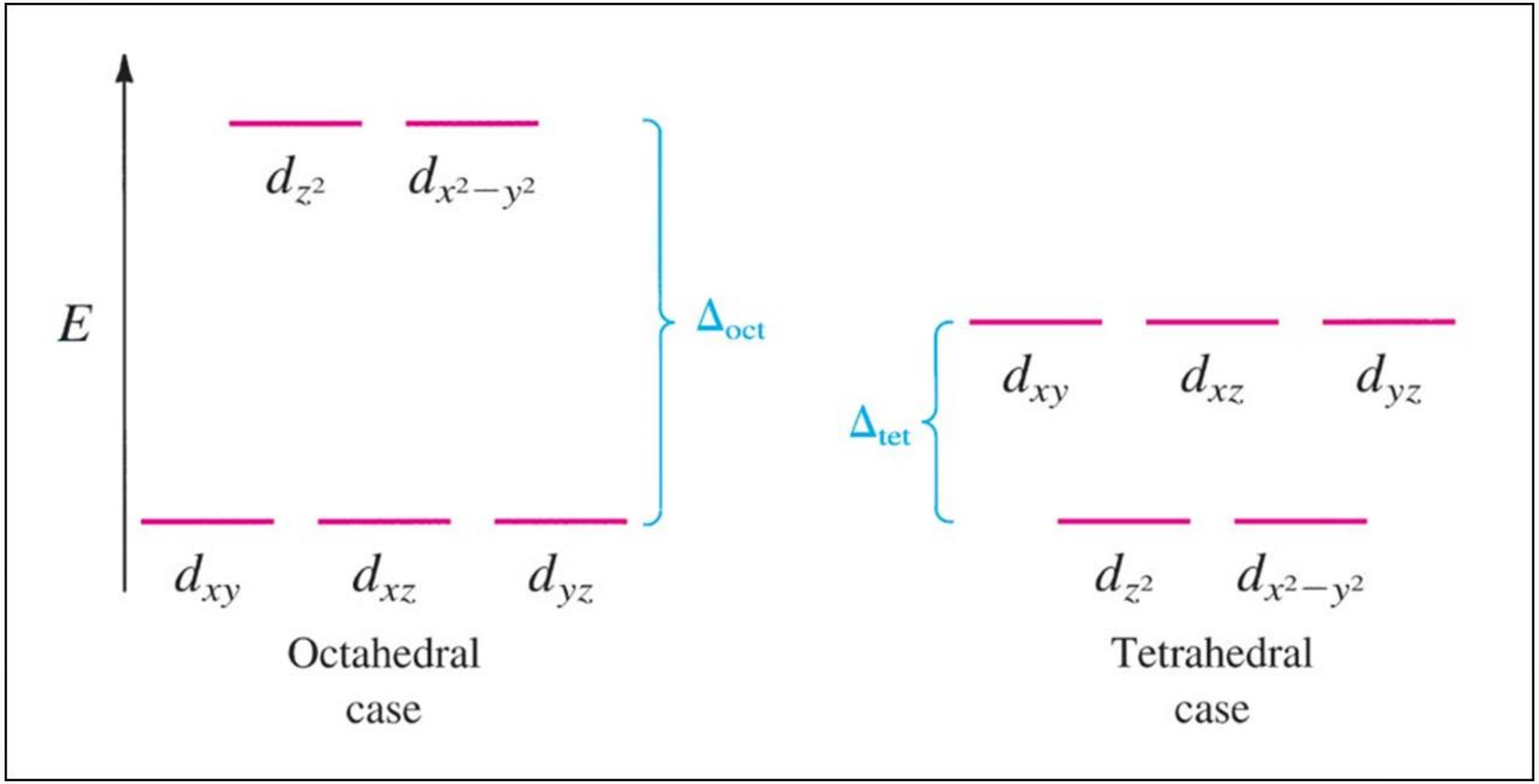


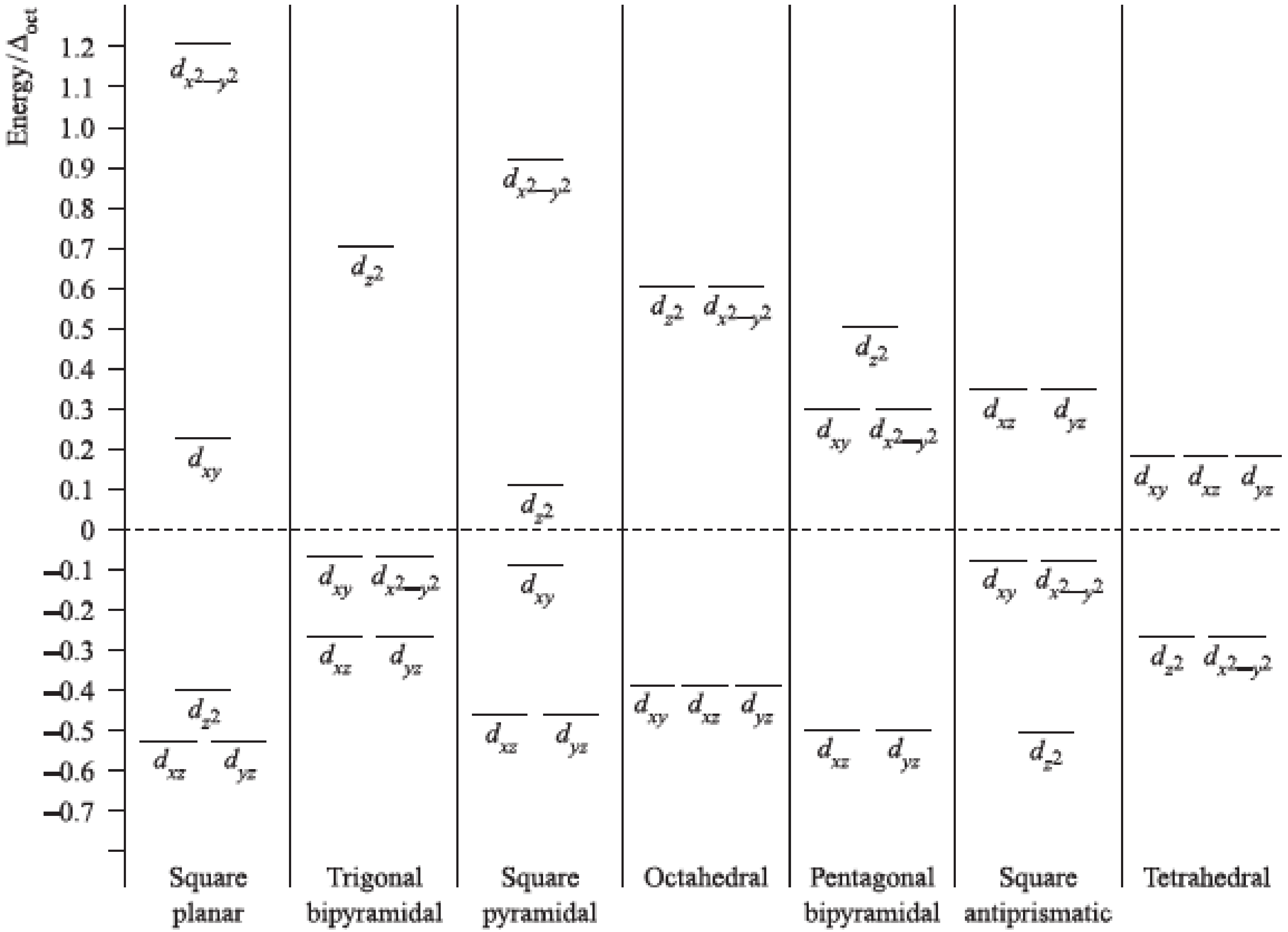
Trigonal bipyramidal



Square pyramidal

The Crystal Field Diagrams for Octahedral and Tetrahedral Complexes

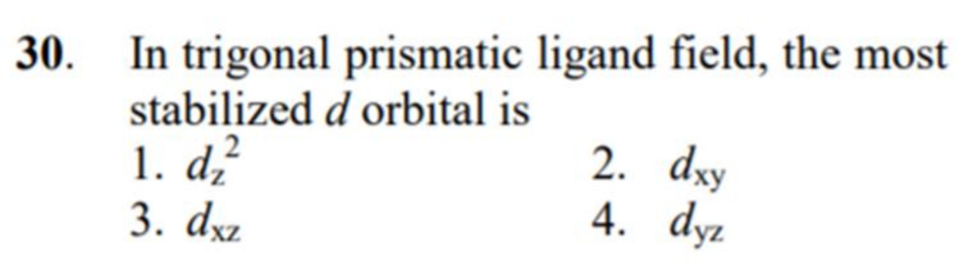



Energy/Δ_{oct}
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
$d_{x^2-y^2}$
d_{xy}
d_{z^2}
d_{xz} d_{yz}
Square planar
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Trigonal bipyramidal
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz} d_{yz}
Square pyramidal
d_{z^2} $d_{x^2-y^2}$
d_{xy} d_{xz} d_{yz}
Octahedral
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Pentagonal bipyramidal
d_{xz} d_{yz}
d_{xy} $d_{x^2-y^2}$
d_{z^2}
Square antiprismatic
d_{xy} d_{xz} d_{yz}
d_{z^2} $d_{x^2-y^2}$
Tetrahedral

Q13 In TBP, the d orbital with higher energy is

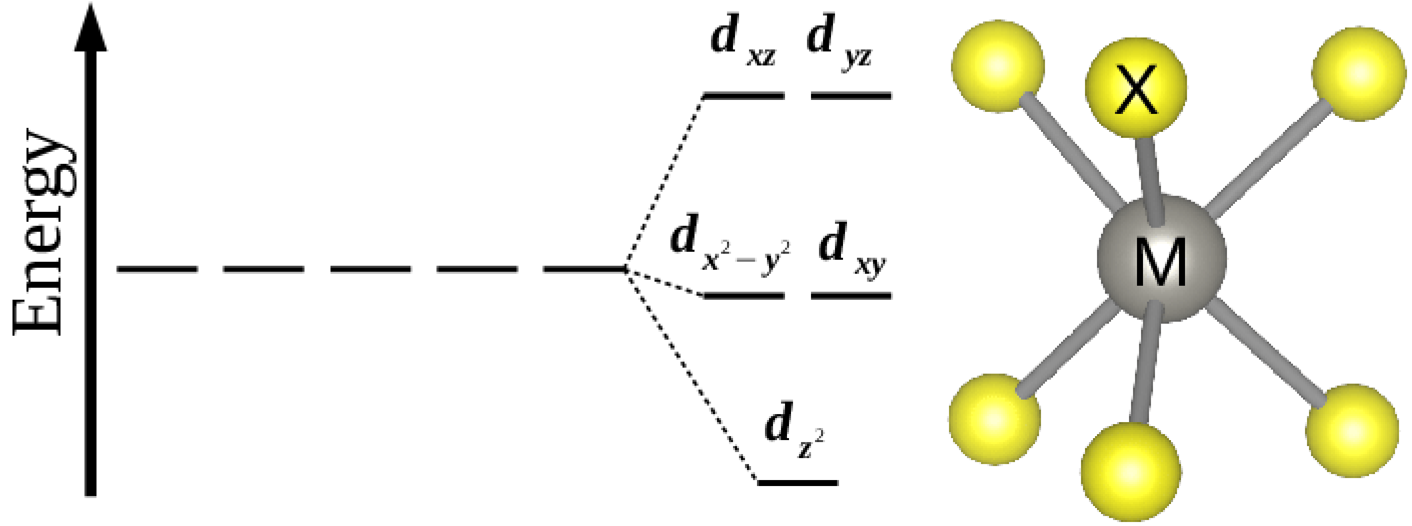
A) dxy B)d x^2-y^2 C) dyz D) dz^2

Q14



30. In trigonal prismatic ligand field, the most stabilized *d* orbital is

1. d_{z^2}
2. d_{xy}
3. d_{xz}
4. d_{yz}



In the solid state, the $[CuCl_5]^{3-}$ 3-ion having a D3h point group has two types of bonds. These are

(a) **Three long and two short**

(b) **Two long and three short**

(c) **One long and four short**

(d) **Four long and one short**

Sp / TBP

sp^3d

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

C_{4v} D_{3h}

Factors affecting the magnitude of Δ

1. Nature of the metal ion --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}

2. Oxidation state of the metal ion

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

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

3.Number and geometry of the ligands

Δt 4 /9 Δo

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

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

4.Nature of the ligands

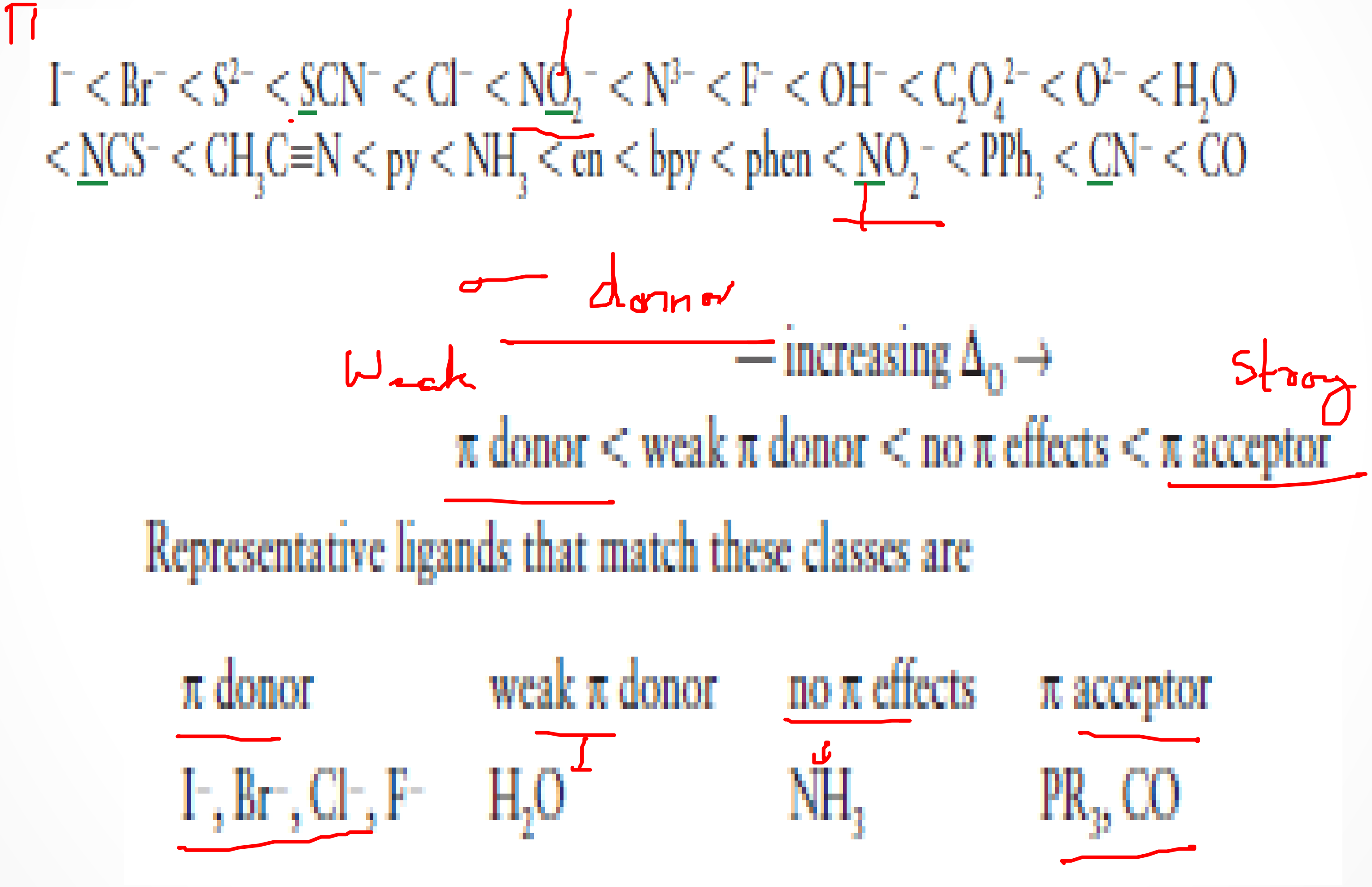
Spectro chemical series

- It is the list of ligands in order of increasing field strength

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN <$ py (pyridine) $< NH_3 <$ en (ethylenediamine) $<$ bipy (2,2'-bipyridine) $<$ phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- < CO$

$M \leftarrow :L$

π



$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O$
$< NCS^- < CH_3C{\equiv}N < py < NH_3 < en < bpy < phen < NO_2^- < PPh_3 < CN^- < CO$

σ donor

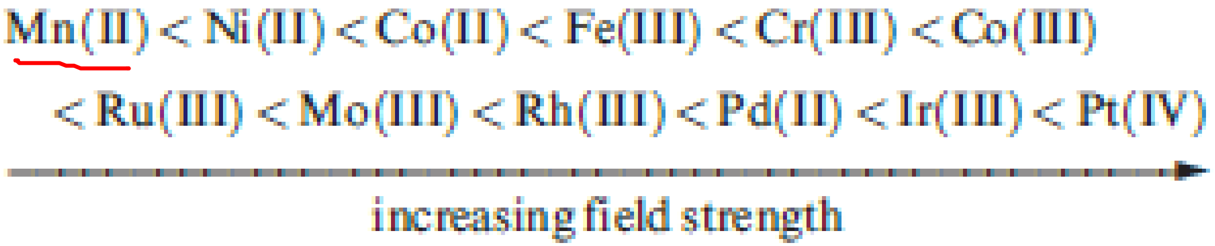
Weak — increasing Δ_O → Strong

π donor < weak π donor < no π effects < π acceptor

Representative ligands that match these classes are

π donor	weak π donor	no π effects	π acceptor
I^-, Br^-, Cl^-, F^-	H_2O	NH_3	PR_3, CO

Trends in values of oct lead to the conclusion that metal ions can be placed in a spectrochemical series which is independent of the ligands:

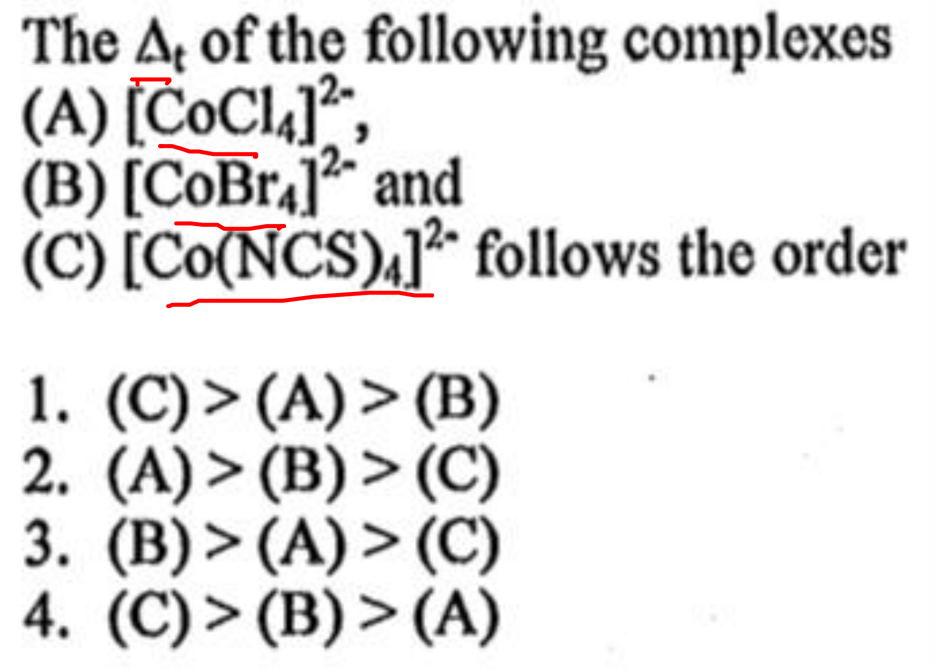


Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III)

< Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)

increasing field strength

Q11



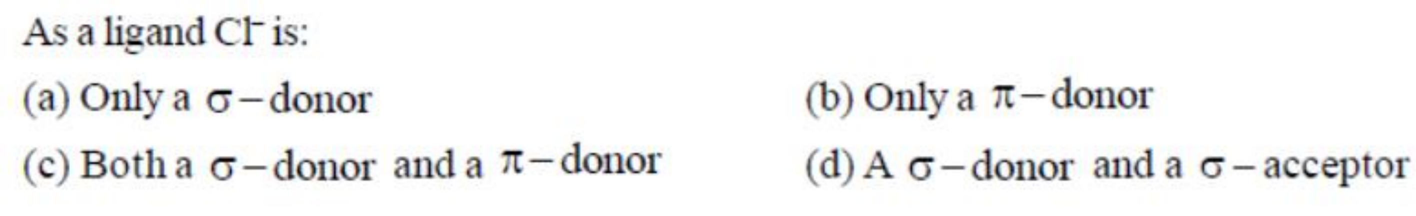
The Δ_t of the following complexes
(A) $[CoCl_4]^{2-}$,
(B) $[CoBr_4]^{2-}$ and
(C) $[Co(NCS)_4]^{2-}$ follows the order

1. (C) > (A) > (B)
2. (A) > (B) > (C)
3. (B) > (A) > (C)
4. (C) > (B) > (A)

$I^- < Br^- < SCN^- < Cl^- < F^-$

$< NCS^-$

Q12



As a ligand Cl^- is:

(a) Only a $\sigma-$donor

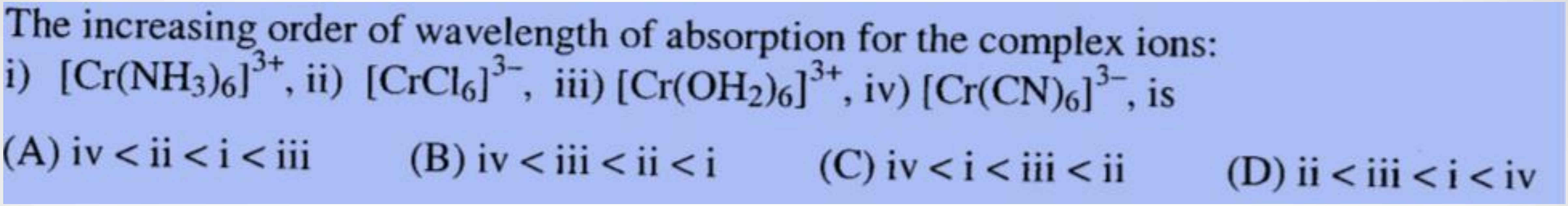
(b) Only a $\pi-$donor

(c) Both a $\sigma-$donor and a $\pi-$donor

(d) A $\sigma-$donor and a $\sigma-$acceptor

Applications of Crystal field theory

- It account for the magnetic and spectral properties of complexes
- Electronic spectra can be explained
- The theory predicts the most favorable geometry of a complex
- CFT account for the stability of particular oxidation state
- CFT accounts whether a crystalline material has spinels or inverse spinel structure.



The increasing order of wavelength of absorption for the complex ions:
i) $[Cr(NH_3)_6]^{3+}$, ii) $[CrCl_6]^{3-}$, iii) $[Cr(OH_2)_6]^{3+}$, iv) $[Cr(CN)_6]^{3-}$, is

(A) iv < ii < i < iii

(B) iv < iii < ii < i

(C) iv < i < iii < ii

(D) ii < iii < i < iv

Using CFSE it is able to predict

- Enthalpy of Hydration
- Lattice Enthalpy

Directly proportional to CFSE

- Ionic radii
- Rate of ligand exchange

Inversely proportional to CFSE

Q13 Among the following Oh complexes, the one that has the highest enthalpy of hydration

a) [Sc(H2O)6]2+ **b) Mn(H2O)6]2+**

c) [V(H2O)6]2+ **d) [Cr(H2O)6]2+**

Normal Spinel & Inverse Spinel

- Spinel's are of the formula **AB_2O_4**
- **A** can be a Group II A (2) metal or a transition metal in the **+ 2** oxidation state
- **B** is a group IIIA(3) metal or a transition metal in the **+3** oxidation state
- The oxide ions form a close packed cubic lattice with eight tetrahedral holes and four octahedral holes per AB_2O_4 unit
- Normal Spinel – **$(A)_t\,(B_2)_oO_4$** – ***Mn_3O_4, Co_3O_4***
- Inverse Spinel – **$(B)_t\,(A,B)_oO_4$**- ***Fe_3O_4 , $NiAl_2O_4$***

- In the Inverse spinels A(II) ions occupy octahedral holes along with one-half of the B(III) ions while the other one-half of the B(III) ions are in the tetrahedral holes

Mn_3O_4 is a normal spinel since the Mn2+ ion is a high spin d5 system with zero LFSE. Whereas, Mn3+ ion is a high spin d4 system with considerable LFSE.

In oh site CFSE B^{3+} > CFSE A^{2+} --- Normal Spinel

Fe_3O_4 is an inverse spinel since the Fe(III) ion is a high spin d^5 system with zero CFSE. Whereas the divalent Fe(II) is a high spin d^6 system with more CFSE.

In oh site CFSE B^{3+} < CFSE A^{2+} --- Inverse Spinel

$NiFe_2O_4$ is again an inverse spinel since the divalent Ni^{2+} (a d^8 ion) has more CFSE than the trivalent Fe^{3+} (a d^5 ion).

- **$FeCr_2O_4$ is a normal spinel** since the divalent Fe^{2+} is a high spin d^6 ion with CFSE = 4 Dq and the trivalent Cr^{3+} is a high spin d^3 ion with CFSE = 12 Dq.
- **Co_3O_4 is a normal spinel**. Even in the presence of weak field oxo ligands, the Co^{3+} is a low spin d^6 ion with very high CFSE. It is due to high charge on Co^{3+}. Hence all the Co^{3+} ions occupy the octahedral sites.

(Co^{3+} is always low spin expect in fluoro complexes)

- **$MgAl_2O_4$ is a normal spinel** since both the divalent and trivalent ions are non transition metal ions.

- **If both di and tri valent ions are non-transition metals – Normal spinel**

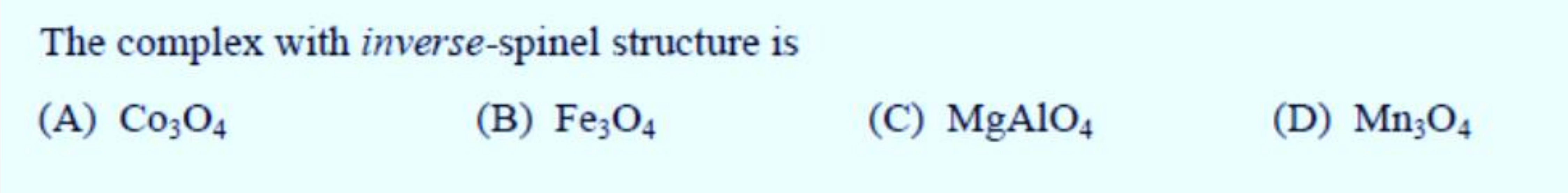
A^{II}	B^{III}	Structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	Non transition metal	Spinel structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Spinel structure
A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Non transition metal or transition meta with d^0 or d^5 or d^{10} configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

Q 14 The spinals $CoFe_2O_4$ and $FeFe_2O_4$ respectively are

a) Inverse and inverse b) Inverse and normal
C) Normal and normal d) normal and inverse

Q 15 Fe_3O_4 and Co_3O_4 are metal oxides having spinel structure. Considering their CFSEs the correct statement regarding their structure is

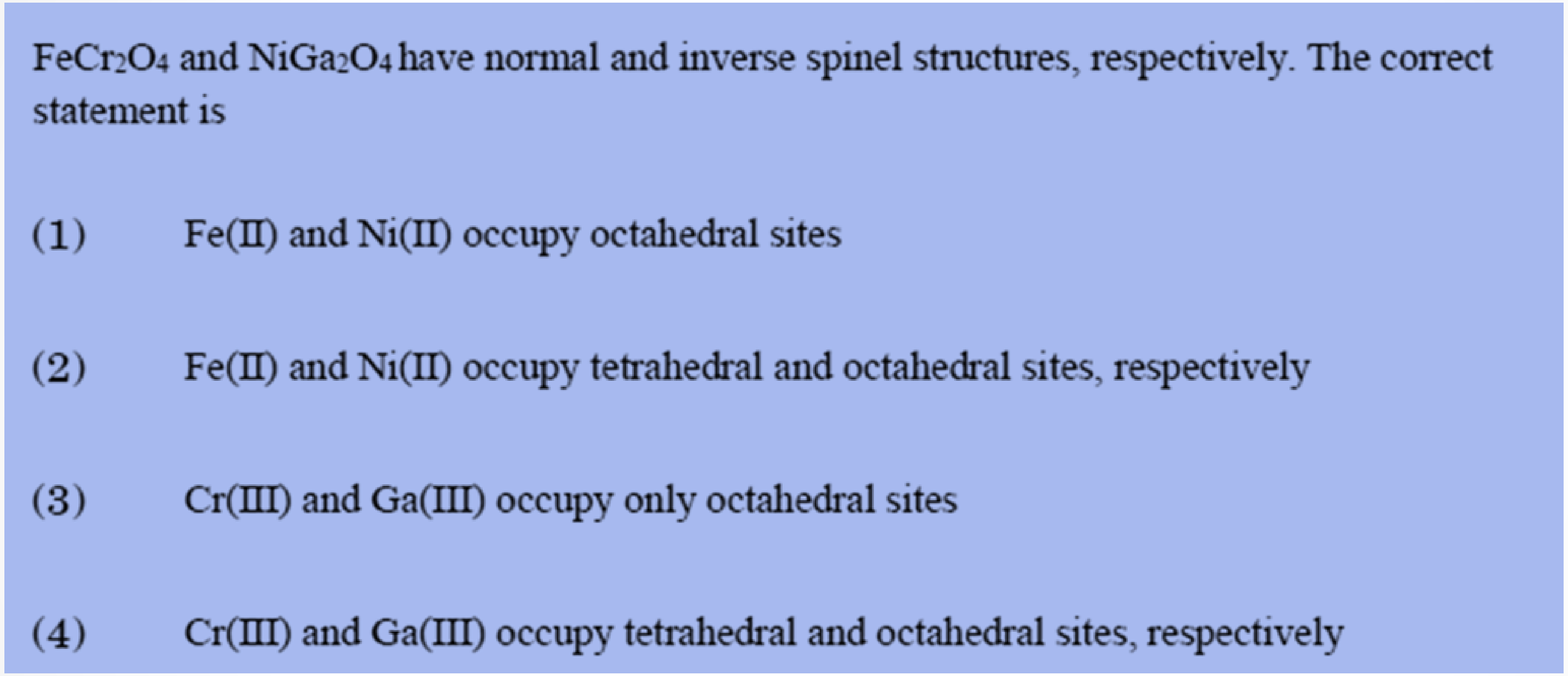
a) Both have normal spinel structure
b) both have inverse spinel structure
c) Fe_3O_4 has normal and Co_3O_4 has inverse spinel structure
d) Fe_3O_4 has inverse and Co_3O_4 has normal spinel structure



The complex with *inverse*-spinel structure is

(A) Co_3O_4 (B) Fe_3O_4 (C) $MgAlO_4$ (D) Mn_3O_4

Q16



$FeCr_2O_4$ and $NiGa_2O_4$ have normal and inverse spinel structures, respectively. The correct statement is

(1) Fe(II) and Ni(II) occupy octahedral sites

(2) Fe(II) and Ni(II) occupy tetrahedral and octahedral sites, respectively

(3) Cr(III) and Ga(III) occupy only octahedral sites

(4) Cr(III) and Ga(III) occupy tetrahedral and octahedral sites, respectively

Dec 2019

Q17 The correct spinel structure of Co_3O_4 is

a) $(Co^{2+})_t\,(2Co^{3+})_o\,O_4$

b) $(Co^{3+})_t\,(Co^{2+}Co^{3+})_o\,O_4$

c) $(Co^{3+}Co^{2+})_t\,(Co^{3+})_o\,O_4$

d) $(2Co^{3+})_t\,(Co^{2+})_o\,O_4$

Limitations of CFT

1. It cannot explain the covalency in M-L interactions
2. In CFT only d- electrons of the metal ion are considered the other orbitals such as s, p_x, p_y, p_z are not taken into consideration.
3. It cannot explain the charge transfer transitions . Ex CFT could not explain the color of compounds like KMnO4 (Mn7+ has no d-electrons)
4. The theory fails to explain the behaviour of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H_2O is a stronger ligand as compared to OH^-.
5. It is 'silent about the possibility of TT-bond formation.

Distortions in Octahedral Geometry Jahn-Teller Theorem

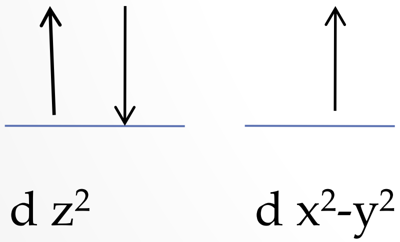
- For any non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy
- The Jahn–Teller theorem states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy.

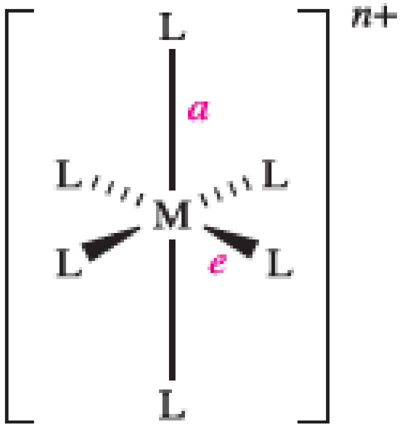
- Z-in and Z-out
- Static and dynamic distortion

- Consider a d9 system in which

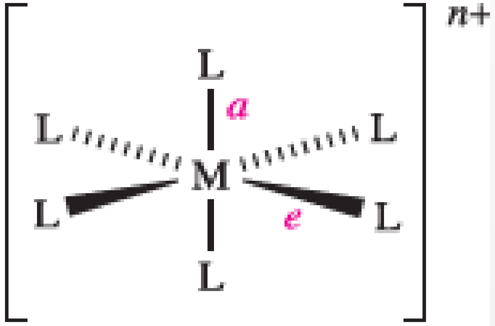
1) Two electrons in dZ^2 and one electron in $d\ x^2\text{-}y^2$
2) Two electron in $dx^2\text{-}y^2$ and one electron in dz^2 orbital

In case (1) the ligand in Z-axis is more repelled than other 4 ligands . The repulsion and distortion result in elongation of the octahedron along the z-axis. This is called tetragonal distortion (elongation) . Here because the z-axis bond length increase it is also called Z- out distortion or 4 short bond- 2long bond distortion

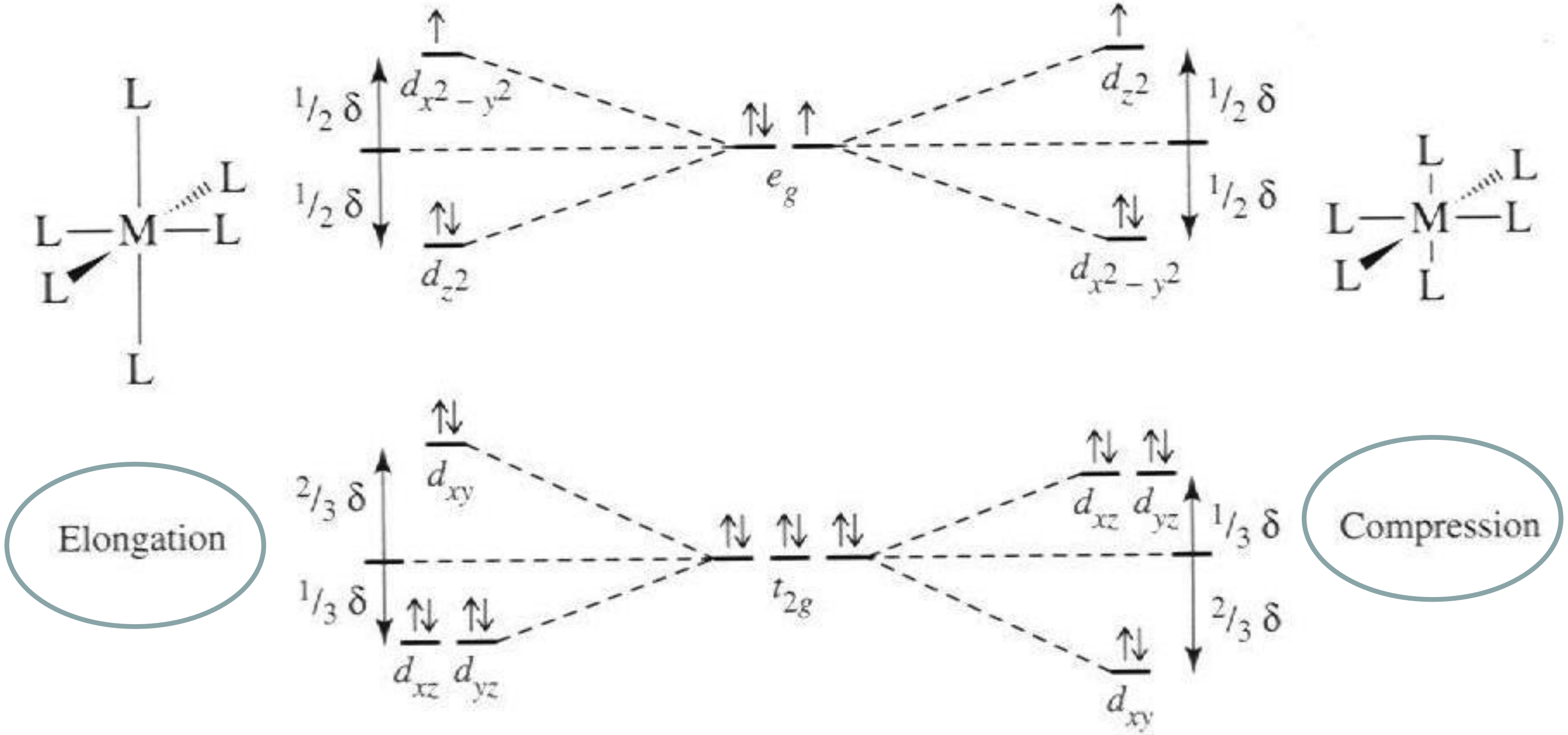




Bond length $a > e$



Bond length $a < e$



Number of electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn-Teller	w	w		s		w	w		s	
Low-spin Jahn-Teller	w	w		w	w		s		s	

w = weak Jahn-Teller effect expected (t_{2g} orbitals unevenly occupied); s = strong Jahn-Teller effect expected (e_g orbitals unevenly occupied); No entry = no Jahn-Teller effect expected.

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.

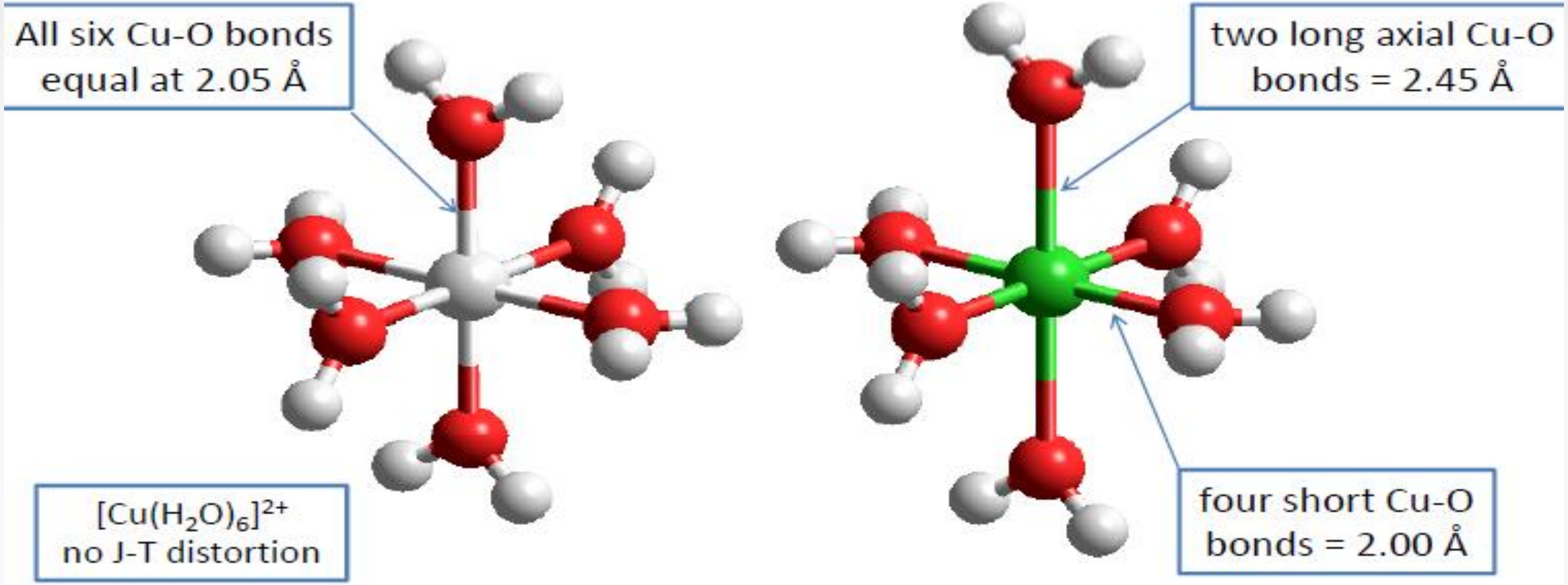
Here, M= K, Rb, Cs, Tl;

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.

2) The complex $[Fe(H_2O)_6]^{2+}$ shows dynamic Jahn-Teller distortion and appears octahedral. In this case, the distortion is small since the degeneracy occurs in t_{2g} orbitals. Remember Fe^{2+} in above complex is a high spin d^6 system with $t_{2g}^4\ e_g^2$ configuration.

Consequences of Jahn- Teller distortion

1. Six coordinated complexes are found to possess distorted Oh structure due to this effect.
2. The absorption spectra of complexes having this distortion are different from the other spectra. A shoulder appears in the presence of Jahn Teller distortion
3. Due to JTD oh point group changes to D4h point group & Oh loses its centre of symmetry
4. Even though $[Cu(en)_3]^{3+}$ contains three chelate rings, it is less stable than $[Cu(en)_2(H_2O)_2]^{2+}$ which contain only two chelate rings.

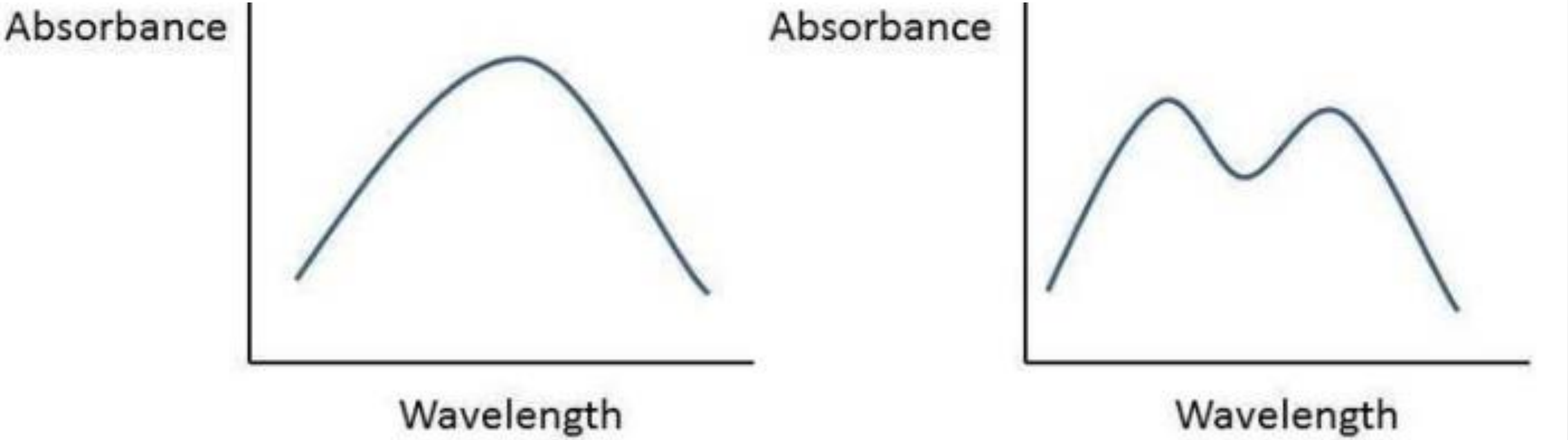


All six Cu-O bonds equal at 2.05 Å

$[Cu(H_2O)_6]^{2+}$
no J-T distortion

two long axial Cu-O bonds = 2.45 Å

four short Cu-O bonds = 2.00 Å



Q 18 Jahn Teller distortion of CuSO4.5H2O acts to

a) Raise symmetry
b) Remove an electronic degeneracy
c) Cause loss of H2O ligand
d) Promote a d-electron to an antibonding molecular orbital

Q19 The correct statement about the Cu-N bond distances in [Cu(NH3)6]2+ is

a) All the bond distances are equal
b) The axial bonds are longer than the equatorial ones
c) The equatorial bonds are longer than the axial ones
d) All the bond distances are unequal

Q 20 Compounds which exhibits Jahn-Teller distortion is

a) [Mn(H2O)6]2+ b) Mn(H2O)6]3+
c) [Cr(H2O)6]3+ d) $[Fe(CN)6]^{4-}$

Q21 The d-d absorption band of [Fe(H2O)6] $^{2+}$ is split due to

a) **Presence of Oh geometry**

b) **Static Jahn-Teller Distortion**

c) **Dynamic Jahn- Teller Distortion**

d) **Presence of TBP geometry**

Q22 The set of ions expected to show Jahn-Teller distortion in their complexes is

a) **Ti(III), Cu(II), High spin Fe(III)**

b) **Cu(I), Ni(II) High-spin Fe(III)**

c) **Cu(II),Low spin Fe(III), Ti(III)**

d) **Low-spin Fe(III), Mn(II), Cu(I)**

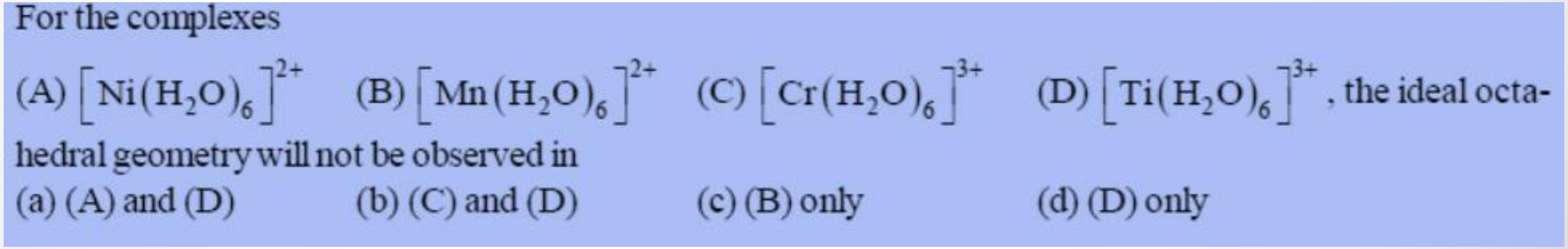
- Q 23 Low spin Oh complexes are maximum distorted in which of the following state?

a) t_2g3 eg0 **b) t_2g3 eg1**
c) t_2g6 eg2 **d) t_2g6 eg4**

- Q24 Which one of the following pairs of electronic configurations of high spin transition metal ions (3d) is an Oh field undergoes a substantial JT distortion

a) d3 ,d9 **b) d4, d9**
c) d5, d9 **d) d6, d9**

Q25

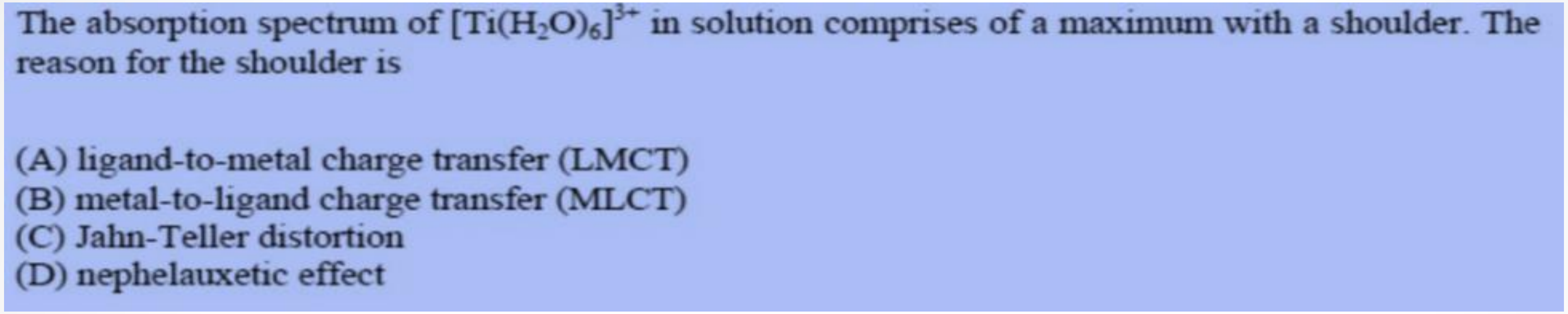


For the complexes

(A) $\left[\mathrm{Ni(H_2O)_6}\right]^{2+}$ (B) $\left[\mathrm{Mn(H_2O)_6}\right]^{2+}$ (C) $\left[\mathrm{Cr(H_2O)_6}\right]^{3+}$ (D) $\left[\mathrm{Ti(H_2O)_6}\right]^{3+}$, the ideal octahedral geometry will not be observed in

(a) (A) and (D) (b) (C) and (D) (c) (B) only (d) (D) only

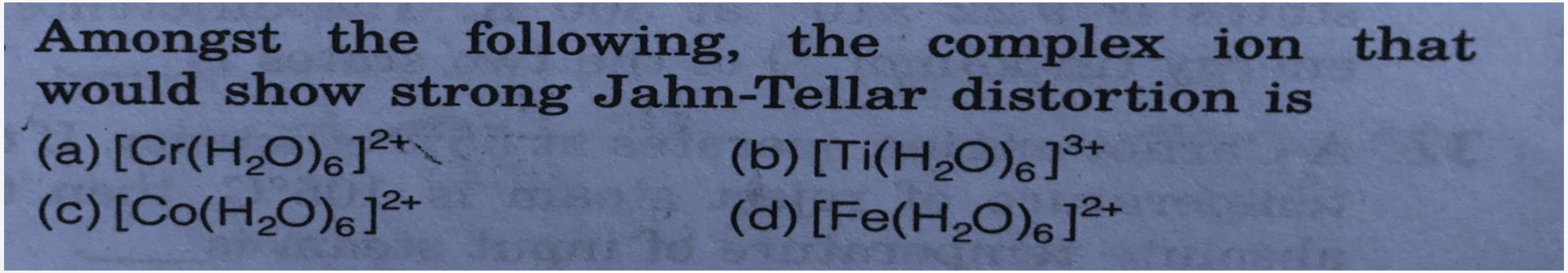
Q26



The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ in solution comprises of a maximum with a shoulder. The reason for the shoulder is

(A) ligand-to-metal charge transfer (LMCT)
(B) metal-to-ligand charge transfer (MLCT)
(C) Jahn-Teller distortion
(D) nephelauxetic effect

Q27



Amongst the following, the complex ion that would show strong Jahn-Tellar distortion is

(a) $[Cr(H_2O)_6]^{2+}$
(b) $[Ti(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$
(d) $[Fe(H_2O)_6]^{2+}$

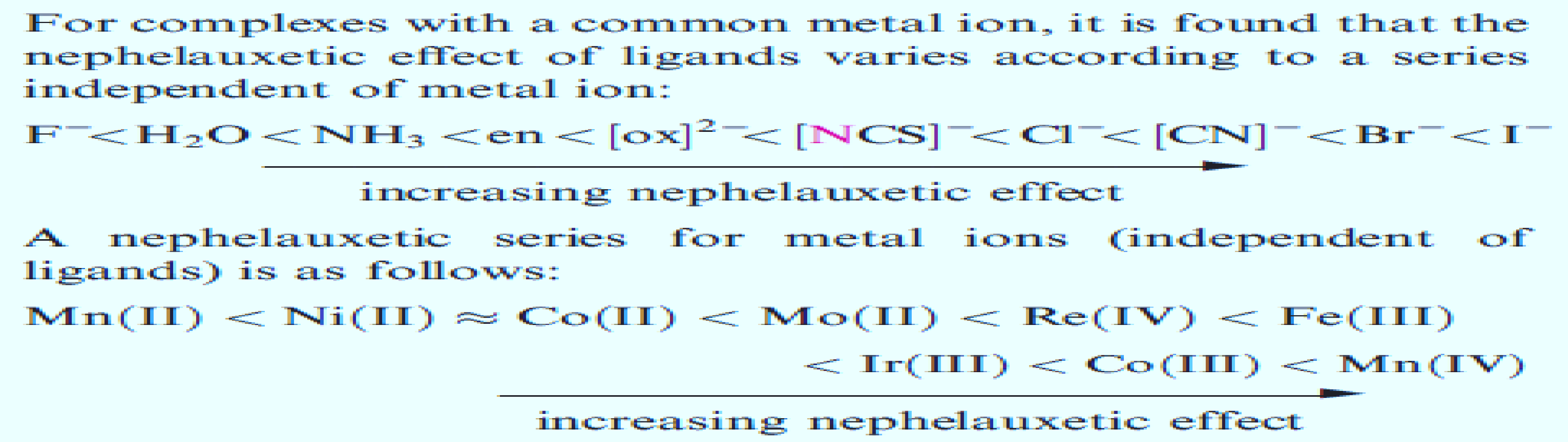
Evidence for covalency

- **Nephelauxetic effect**
- **EPR spectra**
- **NMR spectra**
- **NQR spectra**
- **Magnetic susceptibility results**

Nephelauxetic effect

In metal complexes, there is evidence for sharing of electrons between metal and ligand. Pairing energies are lower in complexes than in gaseous M^{n+} ions, indicating that interelectronic repulsion is less in complexes and that the effective size of the metal orbitals has increased; this is the nephelauxetic effect.

Nephelauxetic means (electron) 'cloud expanding'.



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:

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

increasing nephelauxetic effect

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

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

$$\xrightarrow{\hspace{6cm}}$$

increasing nephelauxetic effect

Ligand field, like crystal field, theory is confined to the role of d orbitals, but unlike the crystal field model, the ligand field approach is not a purely electrostatic model. It is a freely parameterized model, and uses oct and Racah parameters

(to which we return later) which are obtained from electronic spectroscopic (i.e. experimental) data.

- Three interaction parameters involved are Spin orbit coupling constant λ and the Racah parameters or Inter electronic repulsion parameters B and C.

$$\beta = B(\text{complex})/B(\text{free ion})$$

A small value of ***indicates a large measure of d-electron delocalization on to the ligands*** **and hence a significant covalent character in the complex.**

No. of microstates $= \dfrac{n!}{r!(n-r)!}$

No of possible electrons in the orbitals

No of electrons

Electronic configurations	Number of microstates
d1	10
d2	45
d3	120
d4	210
d5	252
d6	210

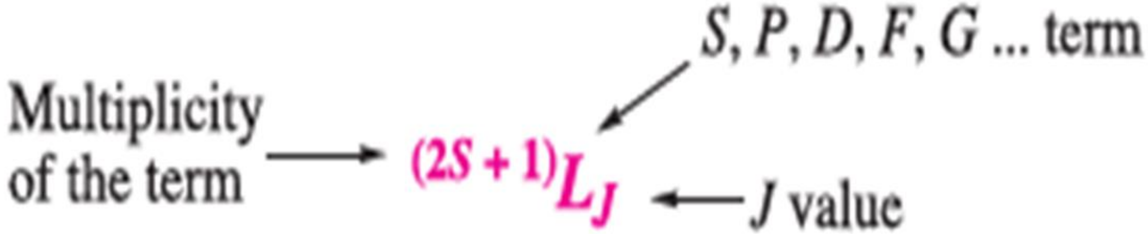
Q28 The number of microstate for d^5 configuration is

a) 9×6^2 **b) 8×6^3**

c) 7×6^2 **d) 14×6^2**

Term symbols or L-S coupling

- Spin angular momentum (s) and orbitals angular momentum (l) interact or couple together to give a resultant angular momentum for the entire multi electron system in an atom. This resultant angular momentum and the energy of the system is represented as a term symbol.
- Term symbol is used to define the electronic configuration and the resultant angular momentum of an atom.



J- Total angular momentum qn

S- resultant spin qn

L- Resultant angular momentum qn

Selection rules

(determine intensities)

Laporte rule

g → g forbidden (that is, d-d forbidden)

but g → u allowed (that is, d-p allowed)

Spin rule

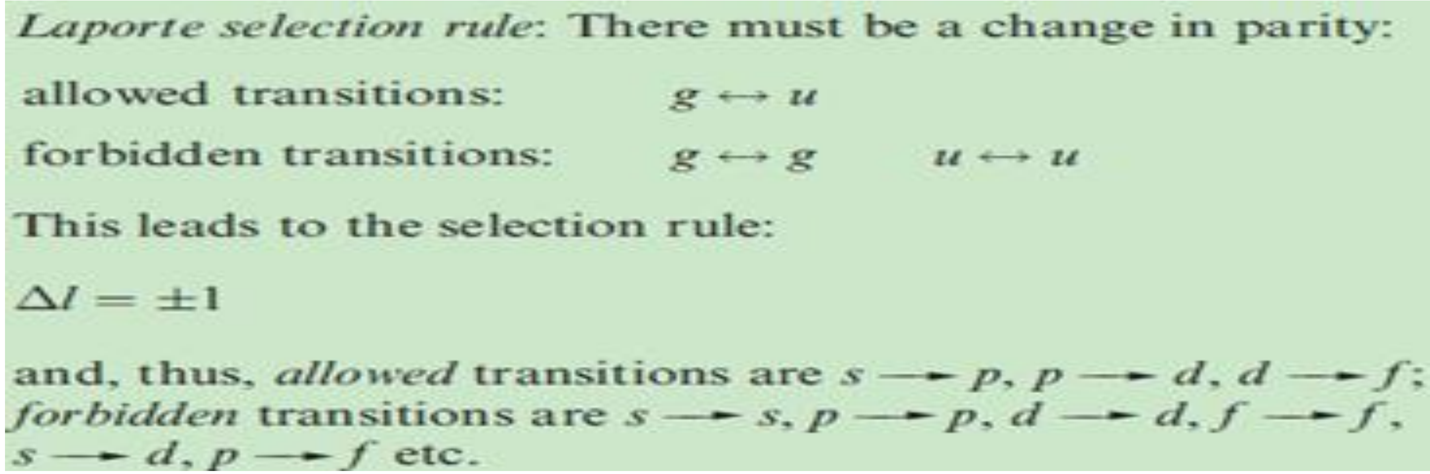
Transitions between states of different multiplicities forbidden

Transitions between states of same multiplicities allowed

These rules are relaxed by molecular vibrations, and spin-orbit coupling

The Laporte selection rule

- The only allowed transitions in a centerosymmetric molecule or ion are those accompanied by a change in parity.
- This rule implies that transitions between g(gerade) and u (ungerade) terms are permitted, but not between two g and between two u terms.
- All d-orbitals have gerade symmetry so in Oh complex d-d transition is formally forbidden. This accounts for the weak transition in oh complex.



Laporte selection rule: There must be a change in parity:

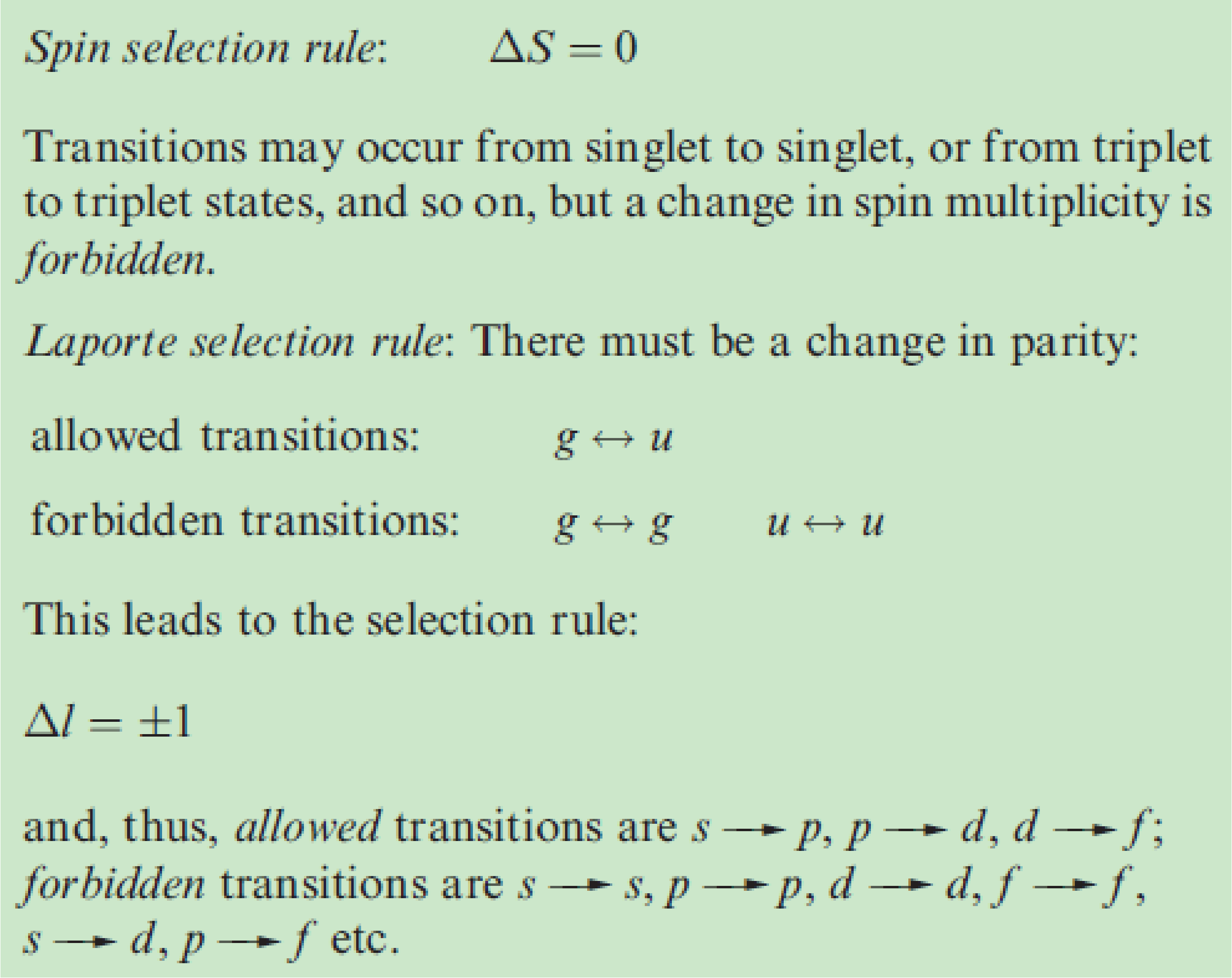
allowed transitions: $g \leftrightarrow u$

forbidden transitions: $g \leftrightarrow g$ $u \leftrightarrow u$

This leads to the selection rule:

$\Delta l = \pm 1$

and, thus, *allowed* transitions are $s \longrightarrow p$, $p \longrightarrow d$, $d \longrightarrow f$; *forbidden* transitions are $s \longrightarrow s$, $p \longrightarrow p$, $d \longrightarrow d$, $f \longrightarrow f$, $s \longrightarrow d$, $p \longrightarrow f$ etc.



Spin selection rule: $\Delta S = 0$

Transitions may occur from singlet to singlet, or from triplet to triplet states, and so on, but a change in spin multiplicity is *forbidden*.

Laporte selection rule: There must be a change in parity:

allowed transitions: $g \leftrightarrow u$

forbidden transitions: $g \leftrightarrow g$ $u \leftrightarrow u$

This leads to the selection rule:

$$\Delta l = \pm 1$$

and, thus, *allowed* transitions are $s \longrightarrow p$, $p \longrightarrow d$, $d \longrightarrow f$; *forbidden* transitions are $s \longrightarrow s$, $p \longrightarrow p$, $d \longrightarrow d$, $f \longrightarrow f$, $s \longrightarrow d$, $p \longrightarrow f$ etc.

- In the first row high-spin transition metal complexes $[M(H_2O)_6]Cl_2$ with d5 and d7 metal ions, the d-d transitions are

a) spin-forbidden for both

b) Spin-allowed for both

c) Spin-forbidden for d5 and spin-allowed for d7

d) Spin-allowed for d5 and spin-forbidden for d7