

Part 2. Theories / Concepts

Bonding in transition metal compounds

Werner Coordination Theory
Valence Bond Theory
Crystal field theory

High spin and low spin complexes
Spectrochemical series
Crystal Field Stabilization Energy (CFSE)
Jahn-Teller distortions
Spinel

Werner Coordination Theory

Werner : Nobel prize in 1913. In complexes, metal ions show two types of valencies:

Primary Valence: Non-directional, is the number of charges on the complex ion.

Secondary Valency: Directional, equals to the number of ligands coordinated to the metal.

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

		Charges	Primary valency ionizable chlorines	Secondary valency
$[\text{Co}(\text{NH}_3)_6]^{3+}$	3Cl^-	6	3	$6\text{NH}_3 = 6$
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	2Cl^-	4	2	$5\text{NH}_3 + 1\text{Cl}^- = 6$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	Cl^-	2	1	$4\text{NH}_3 + 2\text{Cl}^- = 6$

{Colligative + Ion Conductivity} → Structure

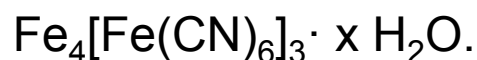
Table 7.5 Establishing the structure of complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4 particles	6 charges	$[\text{Co}(\text{NH}_3)_6]^{3+} \quad 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3 particles	4 charges	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \quad 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2 particles	2 charges	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \quad \text{Cl}^-$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1 particle	0 charge	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
$\text{Co}(\text{NO}_2)_3 \cdot \text{KNO}_2 \cdot 2\text{NH}_3$	2 particles	2 charges	$\text{K}^+ \quad [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$
$\text{Co}(\text{NO}_2)_3 \cdot 2\text{KNO}_2 \cdot \text{NH}_3$	3 particles	4 charges	$2\text{K}^+ \quad [\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{2-}$
$\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$	4 particles	6 charges	$3\text{K}^+ \quad [\text{Co}(\text{NO}_2)_6]^{3-}$

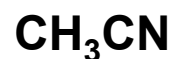
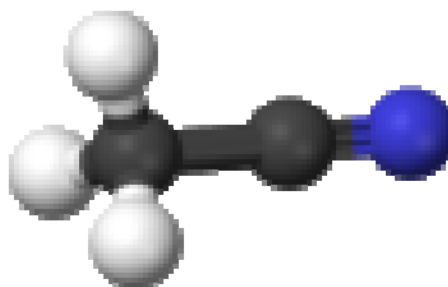
How strong are the Co-ordinate bond?



Prussian blue



Prussian blue is used for certain heavy metal poisons.



**Modest toxicity.
Can be metabolised to produce HCN, which is very toxic**



KCN is a poison by itself....

Valence Bond Theory

The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902.

In 1927, Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the VBT.

The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the *sp*, *sp*², *sp*³, *dsp*², *dsp*³, and *d*²*sp*³ orbitals.

VBT – Assumptions / Features

- Coordination compounds contain metal ions, in which ligands form covalent-coordinate bonds to the metal.
- Ligands must have lone pair of electrons.
- Metal should have an empty orbital of suitable energy available for bonding.
- Atomic (hybrid) orbitals are used for bonding (rather than molecular orbitals)
- This theory is useful to predict the shape and stability of the metal complexes.
- Limitations: (1) Does not explain why some complexes are colored and others are not; (2) Does not explain the temp. dependence of the magnetic properties, etc.

VALENCE BOND THEORY

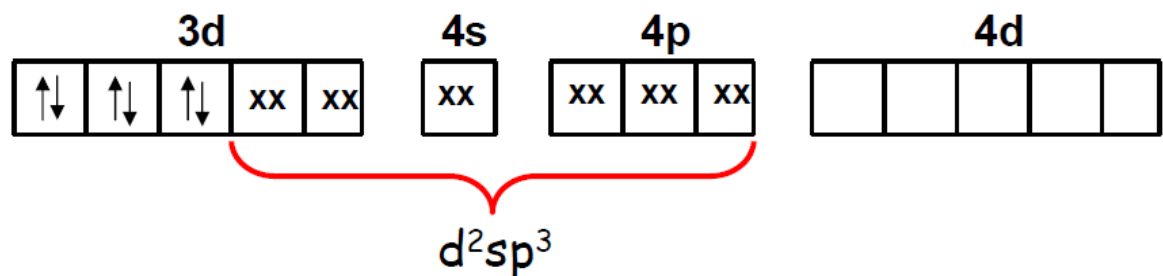
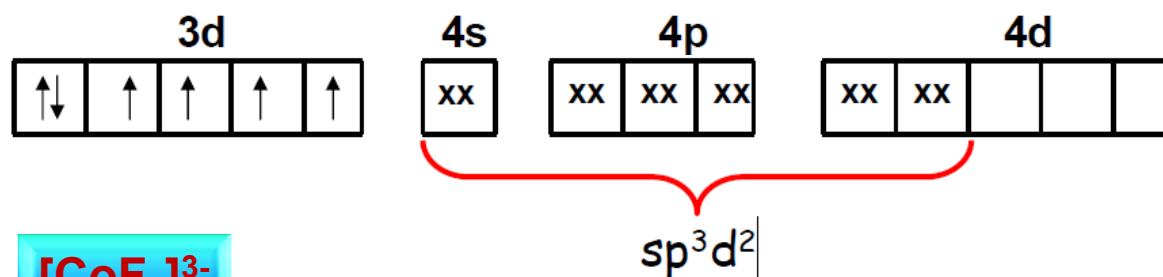
According to this theory, the metal atom/ion under the influence of ligands can use its $(n-1)d$, ns , np or ns , np , nd orbitals for hybridisation to yield a set of definite geometry such as octahedral, tetrahedral, square planar. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination Number	Type of Hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

VBT - Example

➤ Co: $3d^7 4s^2$

➤ Co^{3+} : $3d^6 4s^0$

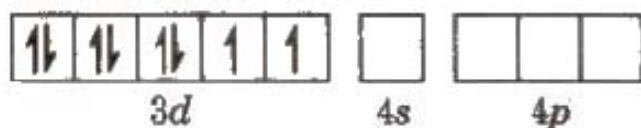


Outer sphere
complex
Reactive/Labile
High spin
Paramagnetic

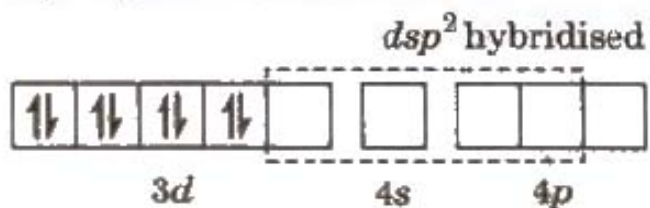
Inner sphere
complex
Less reactive
Low Spin
Diamagnetic

VBT – Few examples

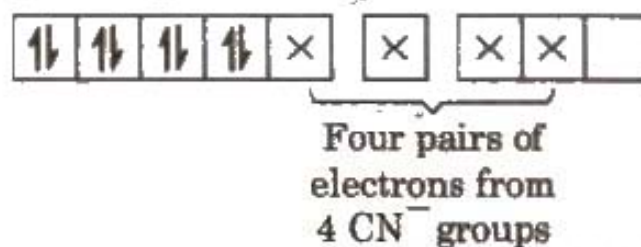
Orbitals of Ni^{2+} ion



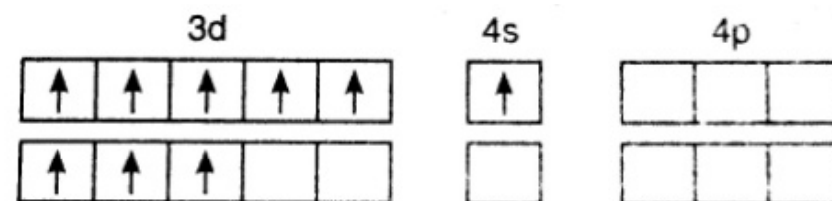
dsp^2 hybridised orbitals of Ni^{2+}



$[\text{Ni}(\text{CN})_4]^{2-}$



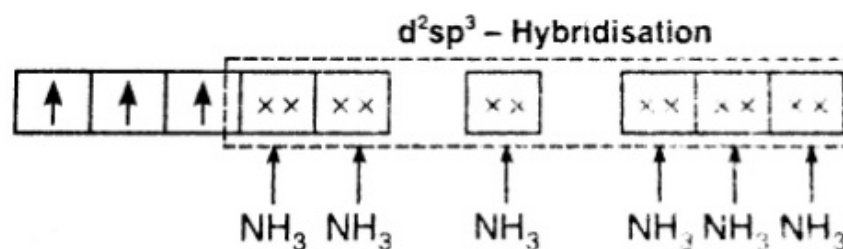
Cr-atom



Cr (III)



$[\text{Cr}(\text{NH}_3)_6]^{3+}$



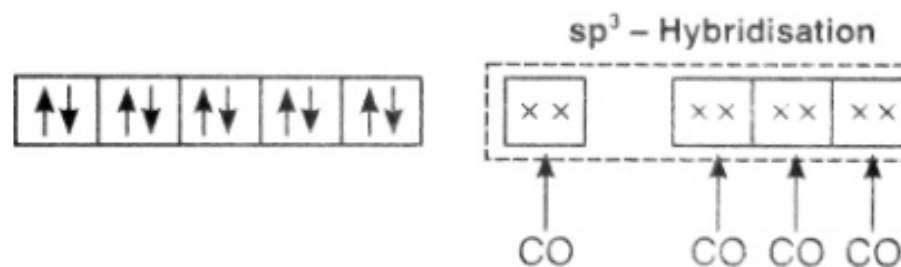
Ni-atom



Ni (0)



$[\text{Ni}(\text{CO})_4]$



Crystal Field Theory

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

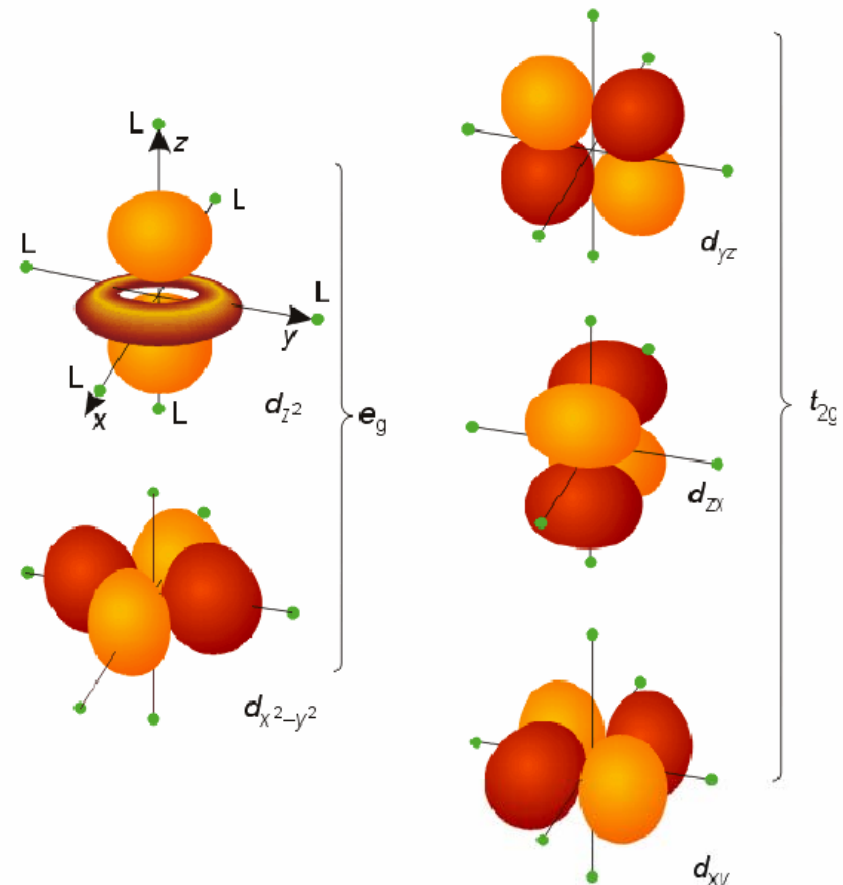
- This theory (**CFT**) largely replaces **VB Theory** for interpreting the chemistry of coordination compounds.
- It was proposed by the physicist Hans Bethe in 1929.
- Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications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

For a review on the evolution of bonding models see:

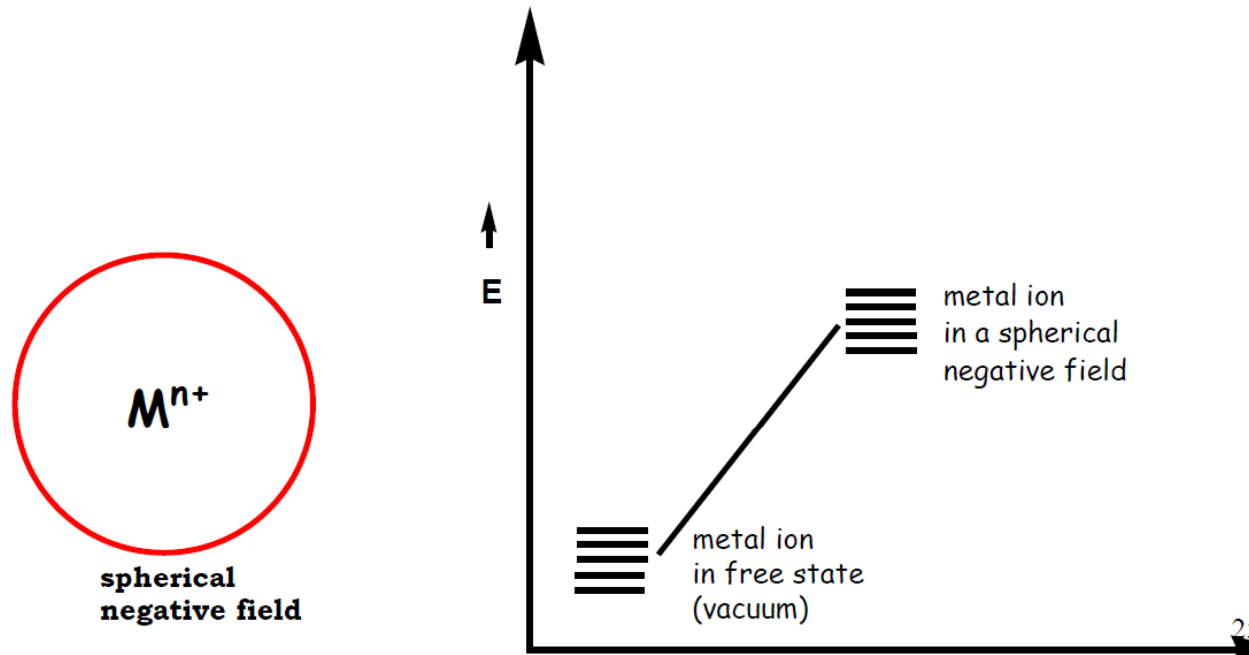
C. J. Ballhausen, *J. Chem. Ed.* 1979, 56, 294-297, 215-218, 357-361.

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



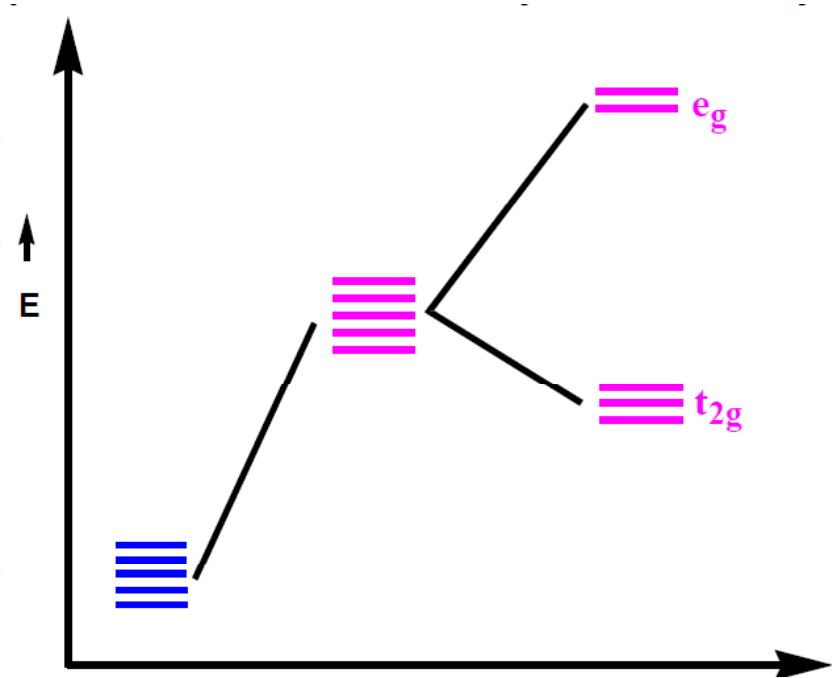
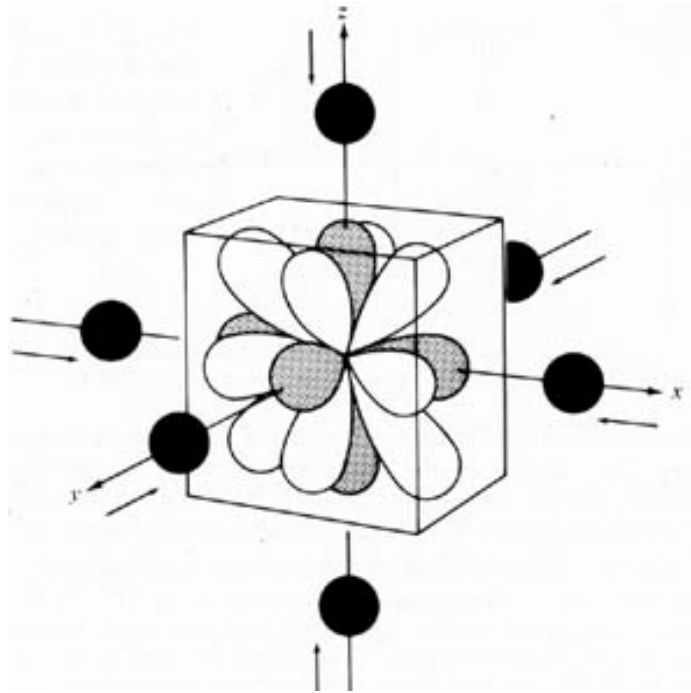
Symmetric field



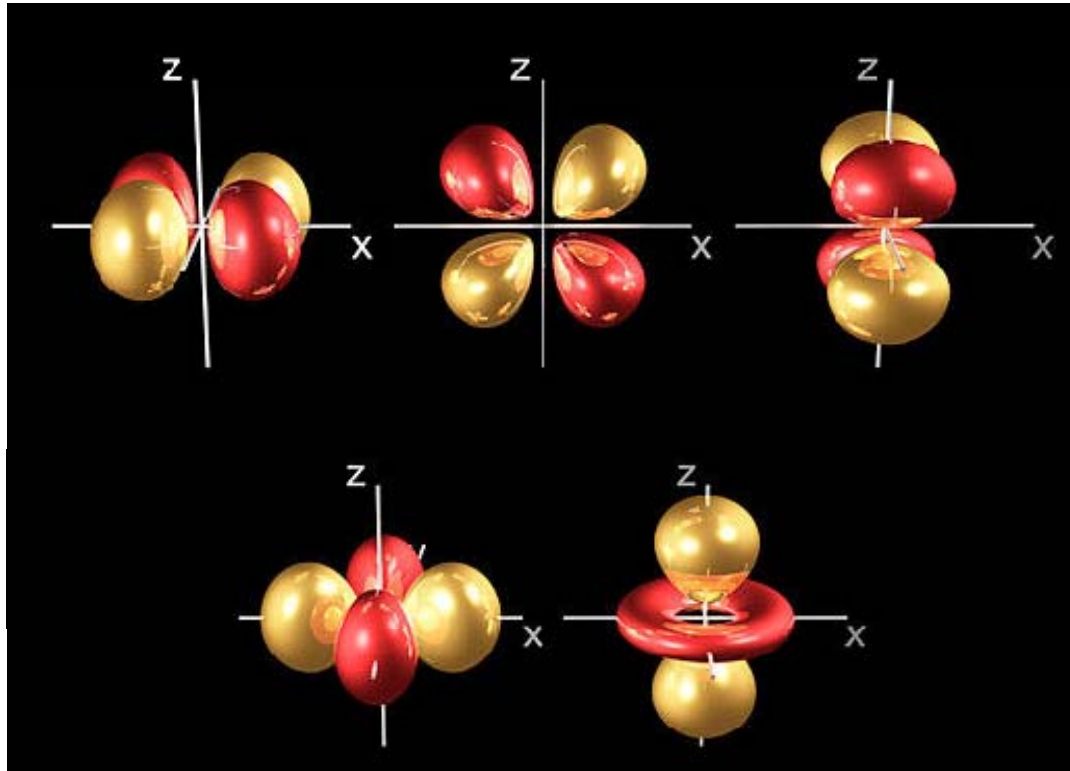
The 5 x d orbitals in an isolated gaseous metal are degenerate

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 electrons present in the d orbitals.

Octahedral Field



- 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 than the orbitals which lie in-between the axes (i.e. xy , xz , yz).



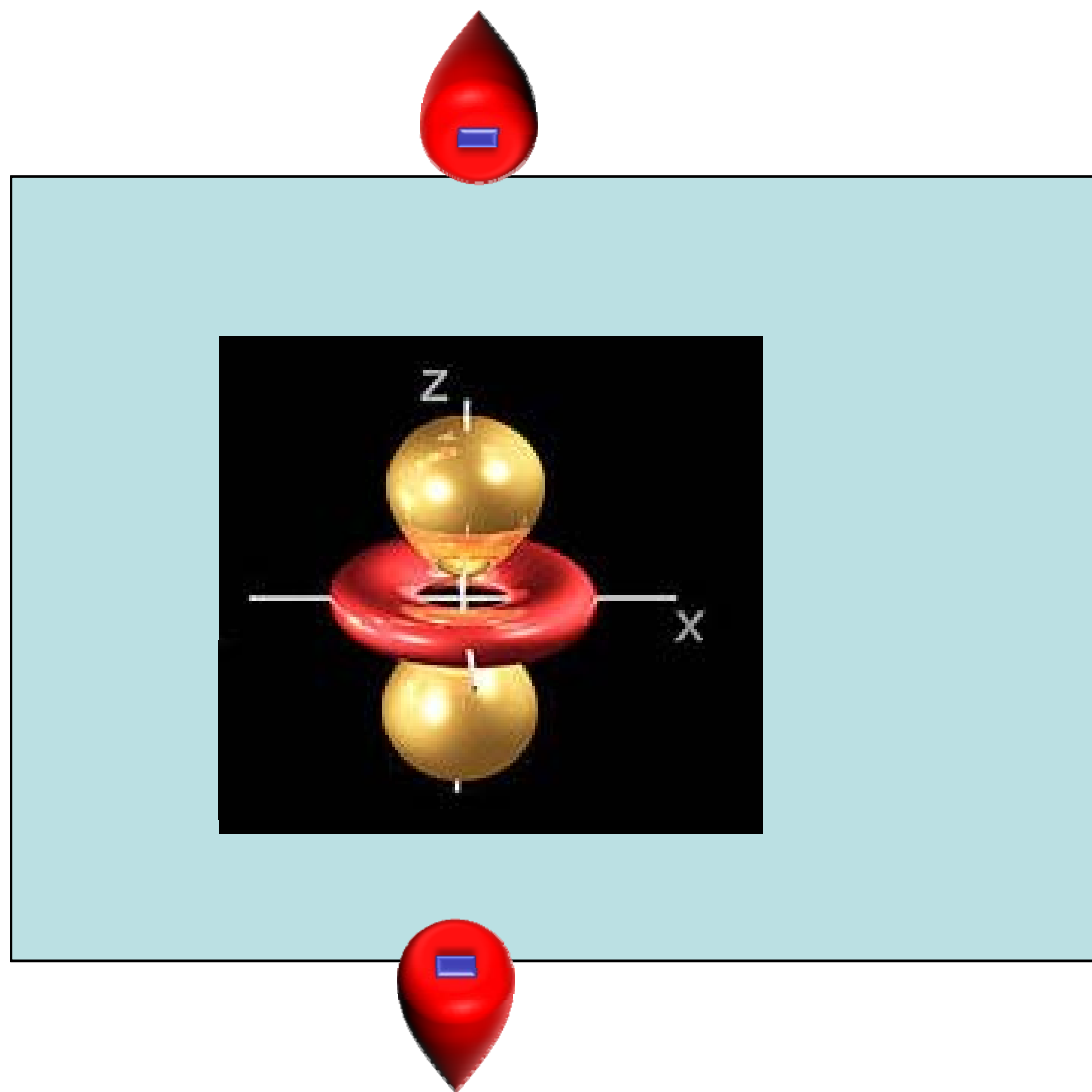
d_z^2

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

d_{xy}

d_{xz}

d_{yz}



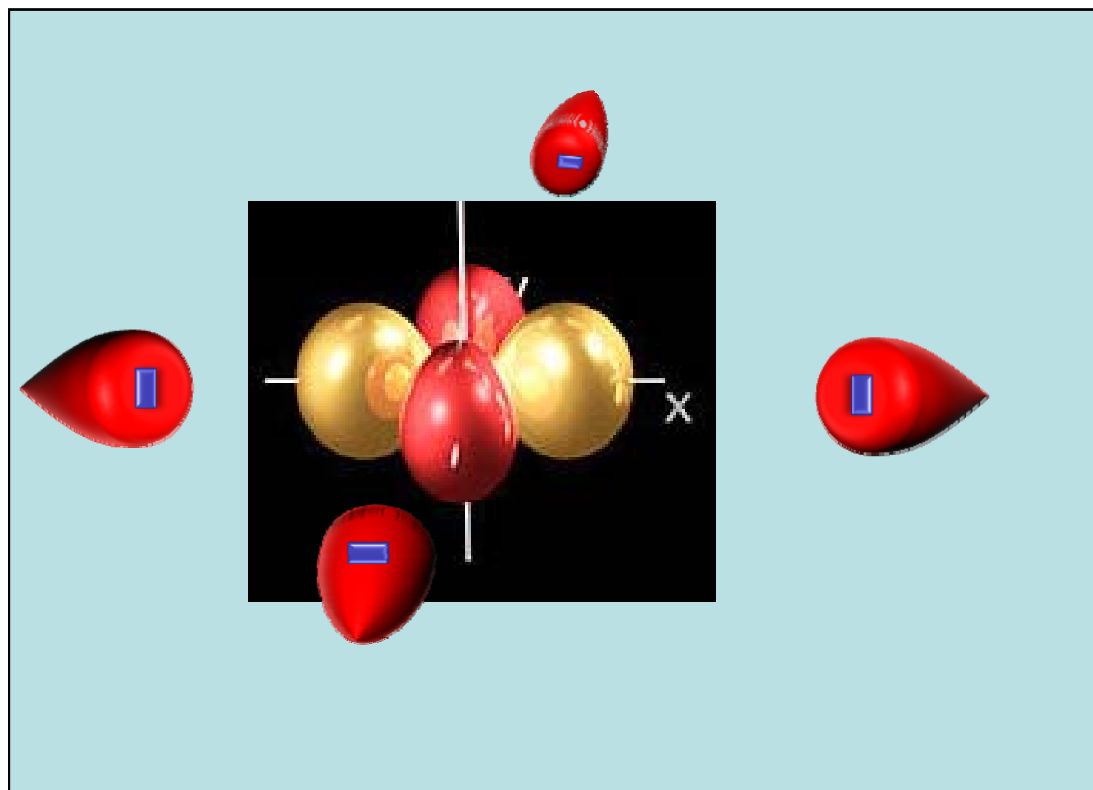
d_{z^2}

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

d_{xy}

d_{xz}

d_{yz}



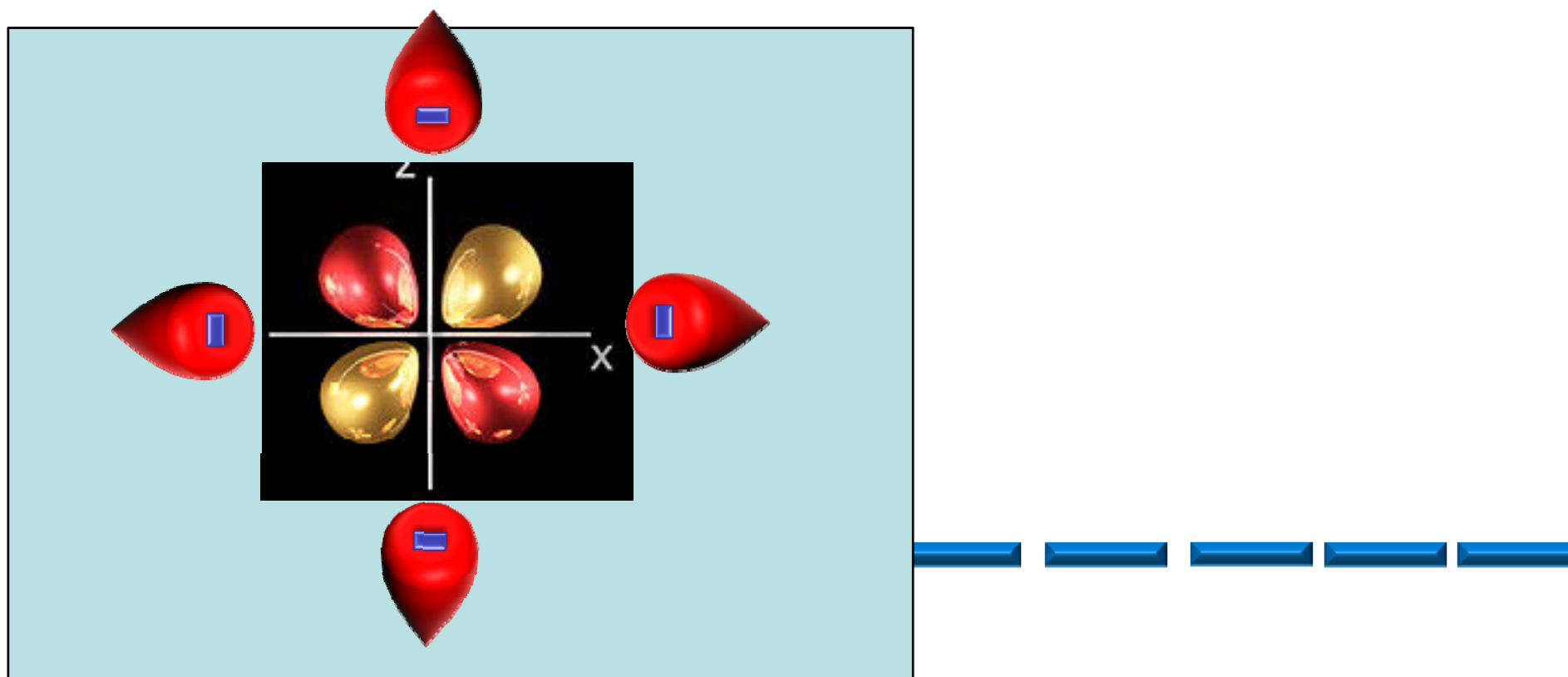
d_z^2

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

d_{xy}

d_{xz}

d_{yz}



d_{z^2}

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

d_{xy}

d_{xz}

d_{yz}



d_z^2

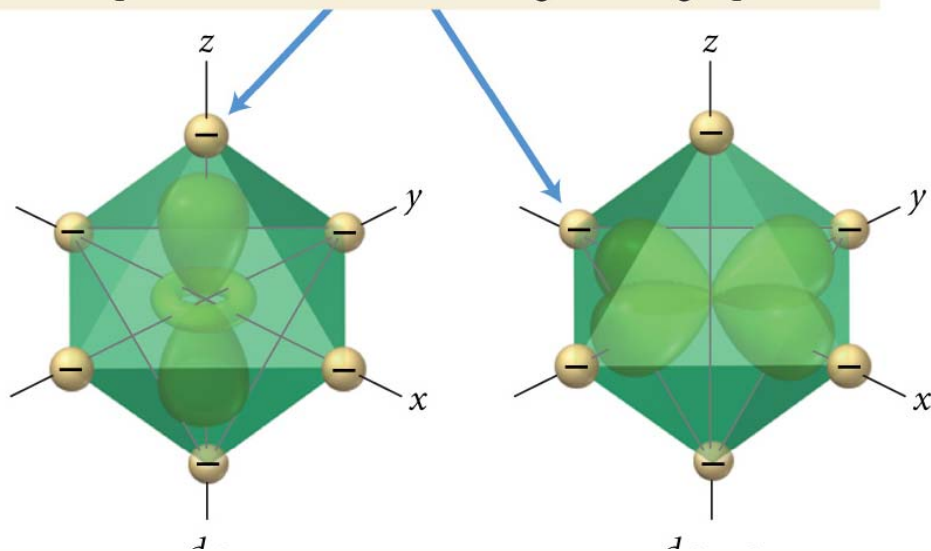
$d_{x^2-y^2}$

d_{xy}

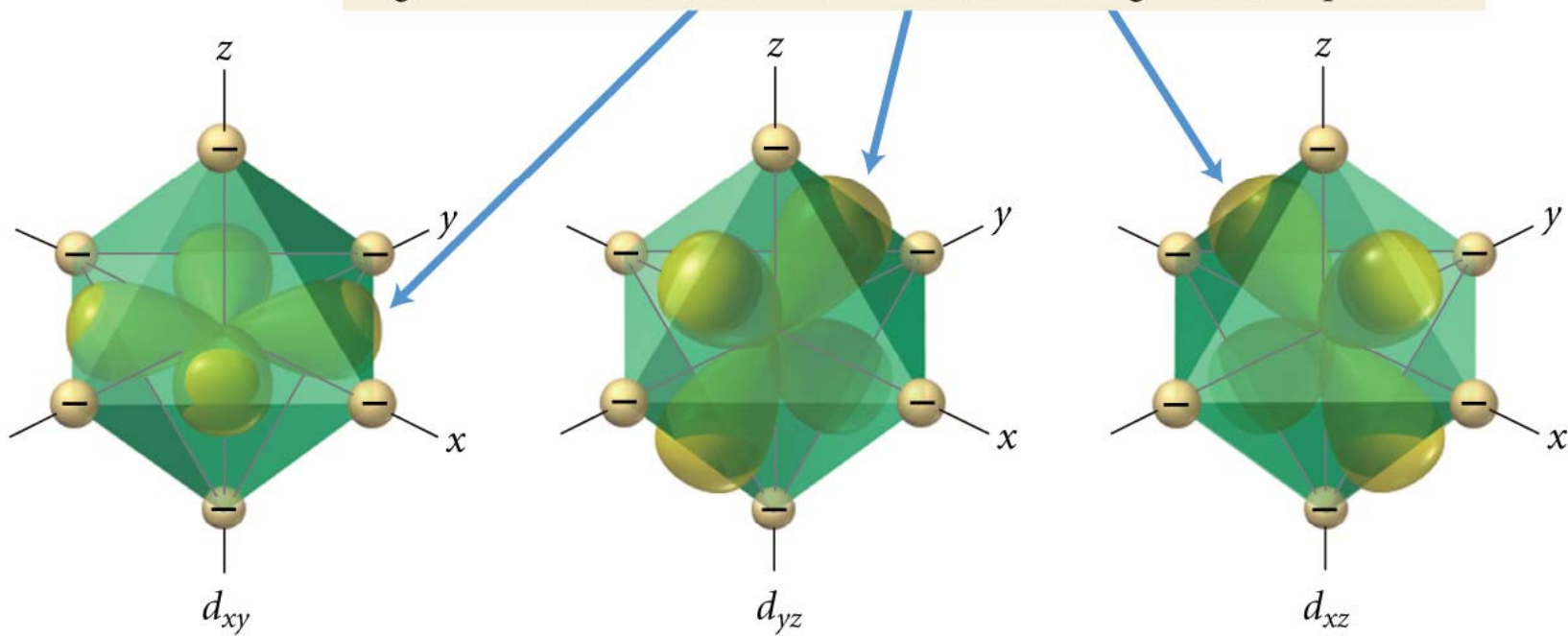
d_{xz}

d_{yz}

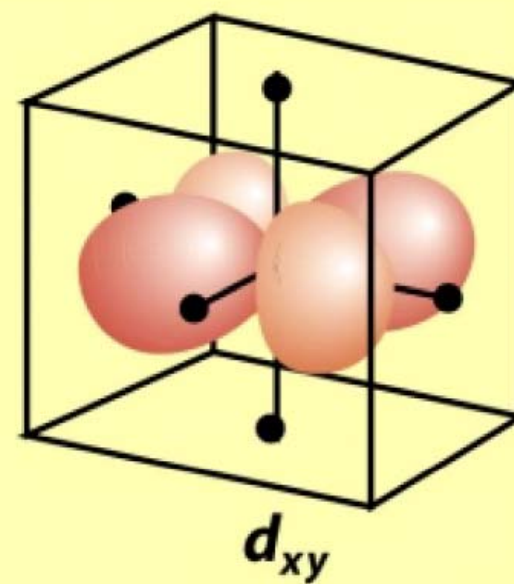
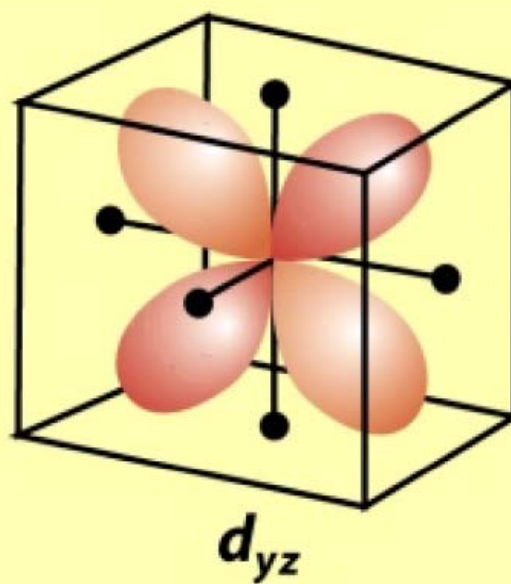
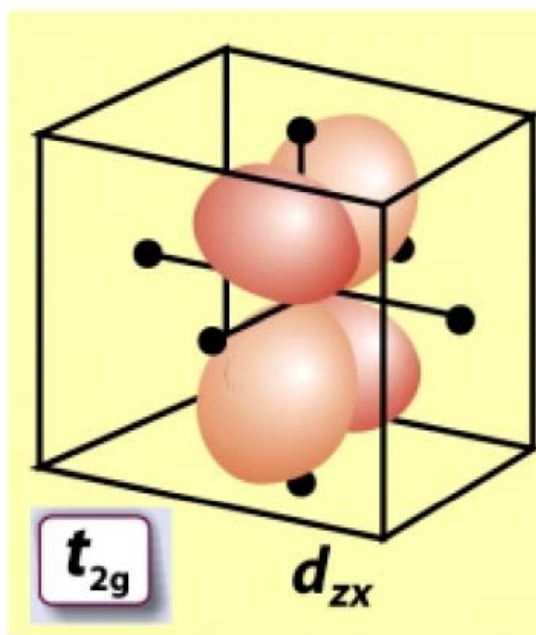
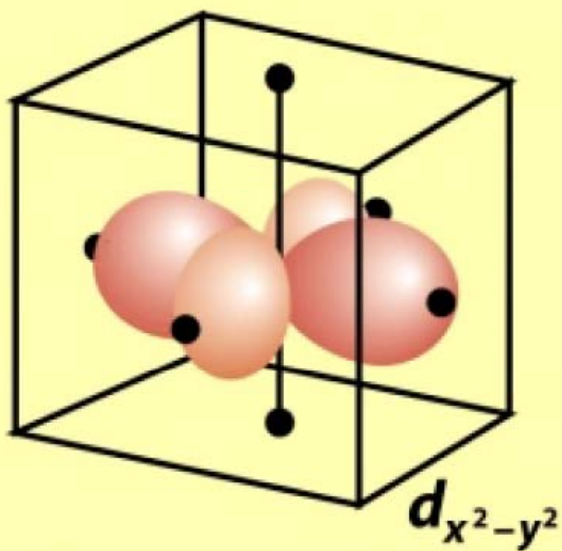
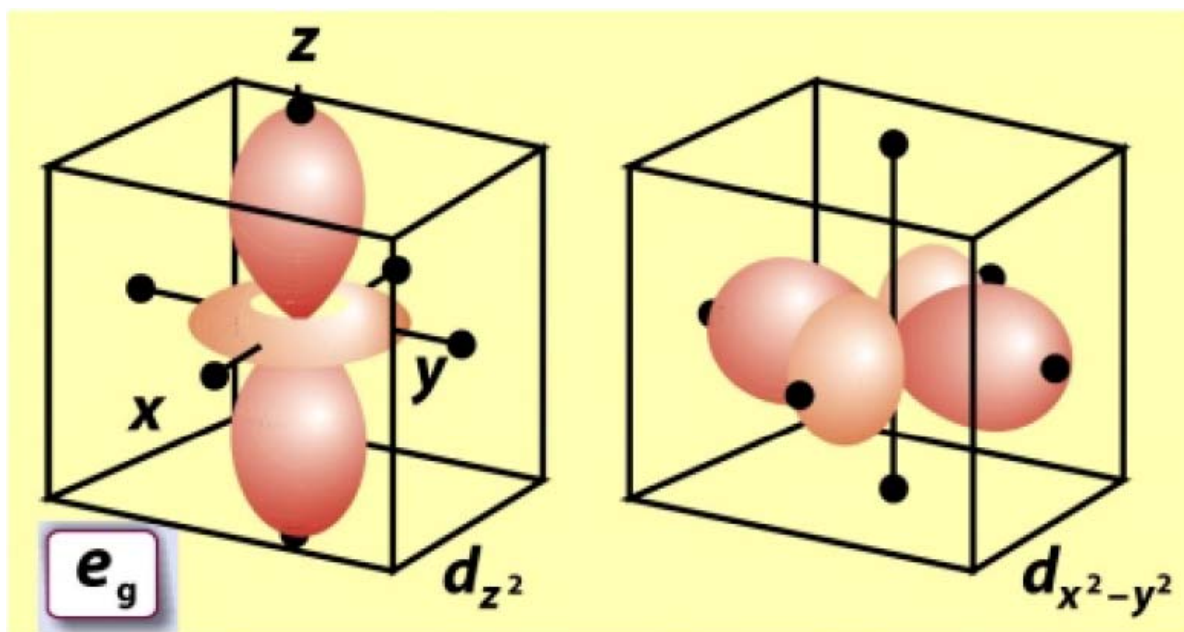
Ligands overlap with orbital lobes, resulting in strong repulsions.



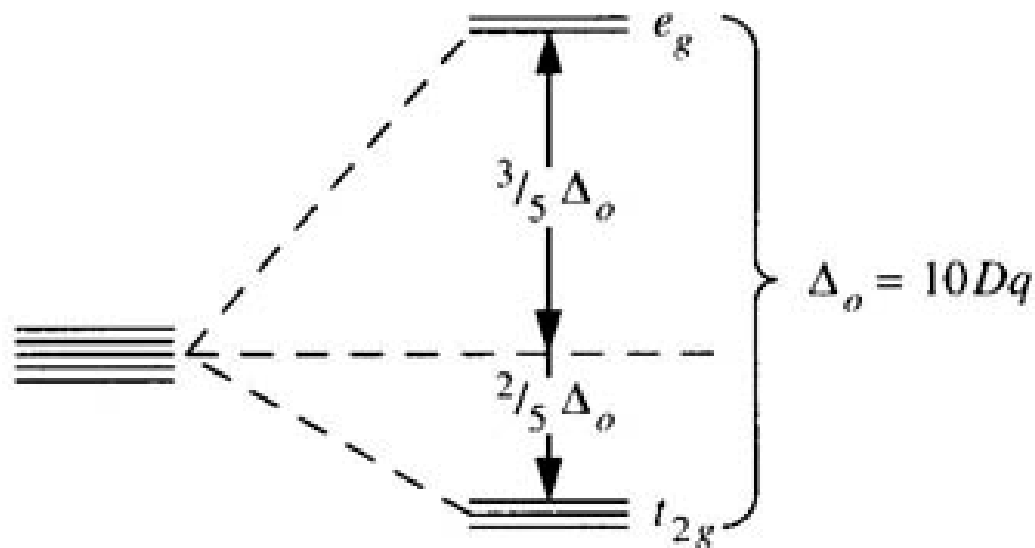
Ligands come in between orbital lobes, resulting in weak repulsions.



Octahedral Complexes



CFT-Octahedral Complexes



For the O_h 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_o 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

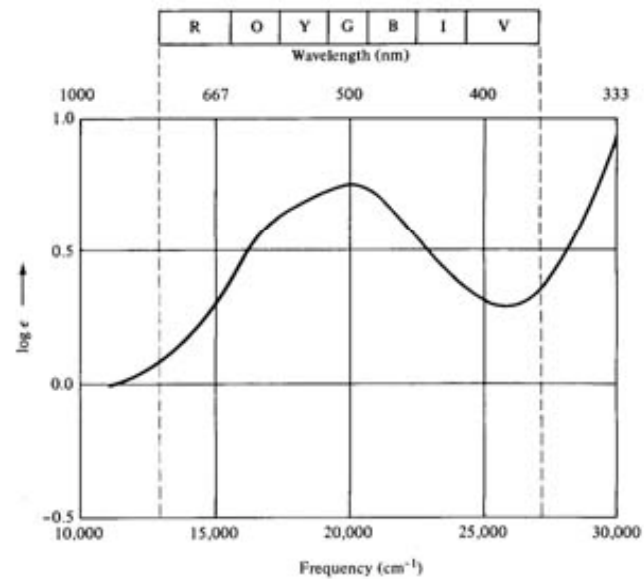
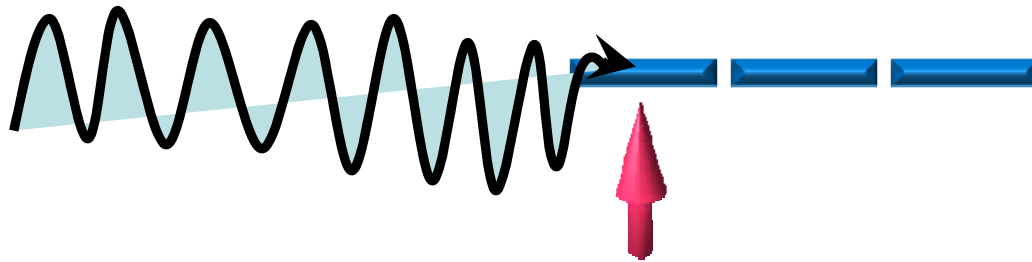
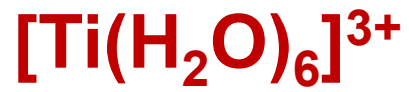
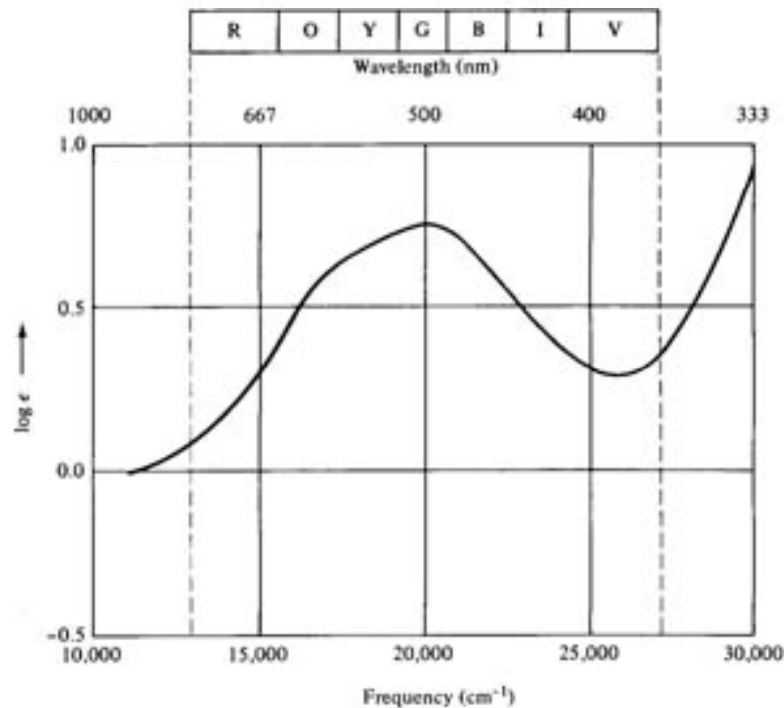


ILLUSTRATION OF CFSE



$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: 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. $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$

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

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

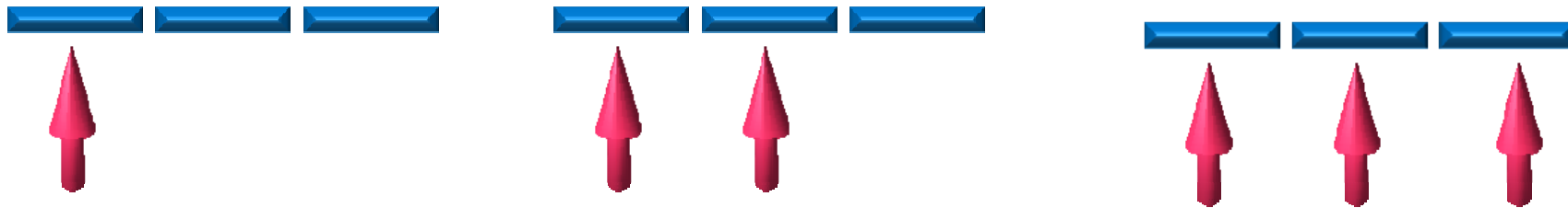
•What happens for more than 1 electron in d orbitals?

•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}

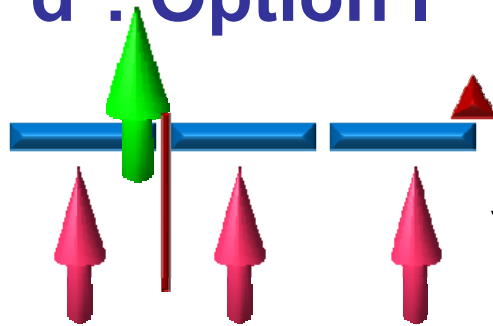
•For d^4 - d^7 systems (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (low spin case or strong field situation**). Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case or weak field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

For d^1 - d^3 systems



For d^4 - d^7 systems

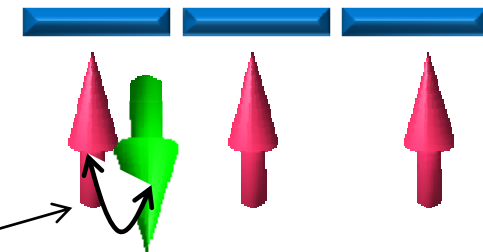
d^4 : Option I



High spin
complexes



d^4 : Option II



Low spin
complexes

So which one?

Decided by

(i) Δ_0

(ii) Pairing E.

- Therefore, there are two important parameters to consider:

The Pairing energy (P) [is a repulsive energy], and the e_g to t_{2g} Splitting (referred to as Δ_0 , $10Dq$)

- For both the high spin (H.S.) and low spin (L.S.) situations, it is possible to compute the CFSE.

Δ_o vs. Pairing Energy (repulsive 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 L & M

$[\text{CrCl}_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	259
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800 cm^{-1}	297 kJ/mol
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	407
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	490

$3d < 4d < 5d$

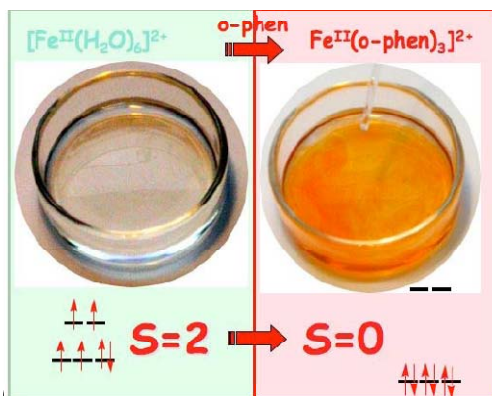
$M^{2+} < M^{3+} < M^{4+}$

Table 19.1 Ligand-field splitting parameters Δ_o of ML_6 complexes*

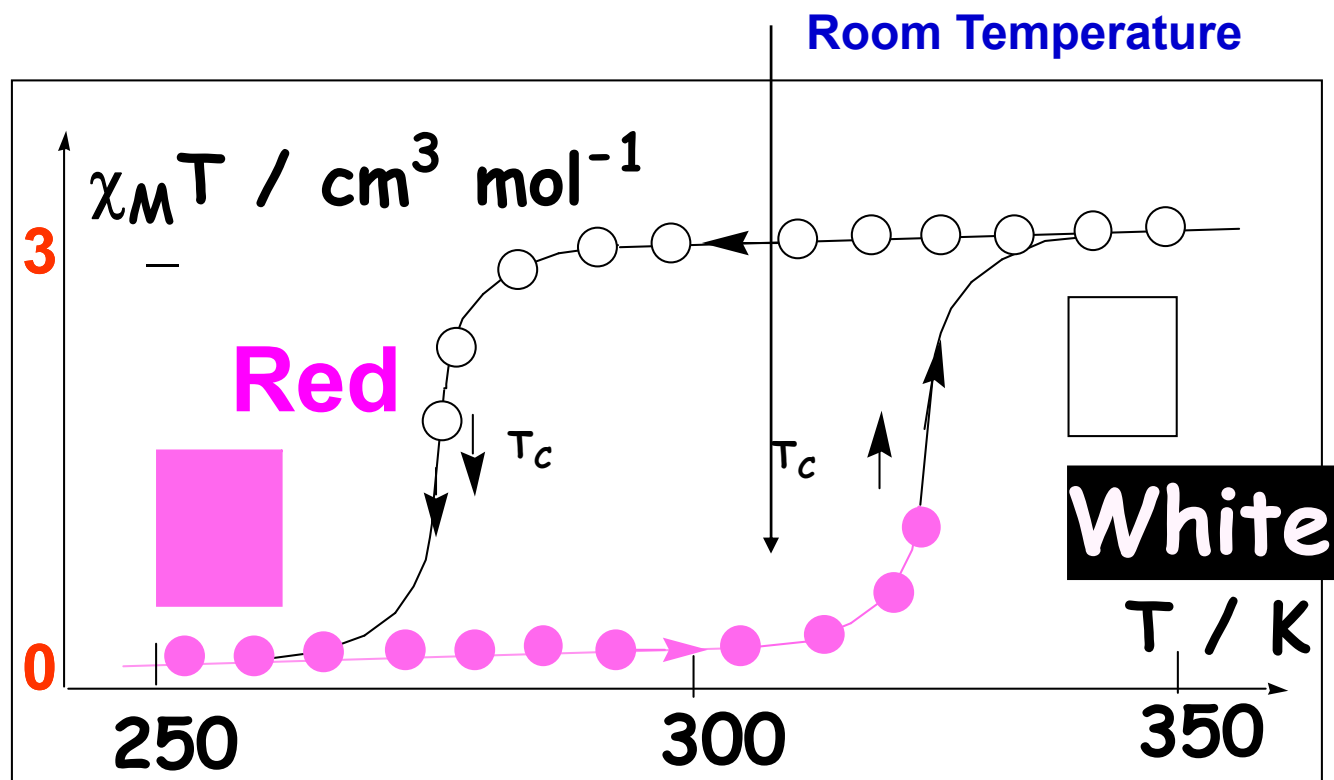
Ions		Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13 700	17 400	21 500	21 900	26 600
d^5	Mn^{2+}	7500	8500		10 100	30 000
	Fe^{3+}	11 000	14 300			(35 000)
d^6	Fe^{2+}		10 400			(32 800)
	Co^{3+}		(20 700)	(22 900)	(23 200)	(34 800)
	Rh^{3+}	(20 400)	(27 000)	(34 000)	(34 600)	(45 500)
d^8	Ni^{2+}	7500	8500	10 800	11 500	

* Values are in cm^{-1} ; entries in parentheses are for low-spin complexes.

From Basic Science to Real time applications: Story on HS-LS complexes (Not for exam)

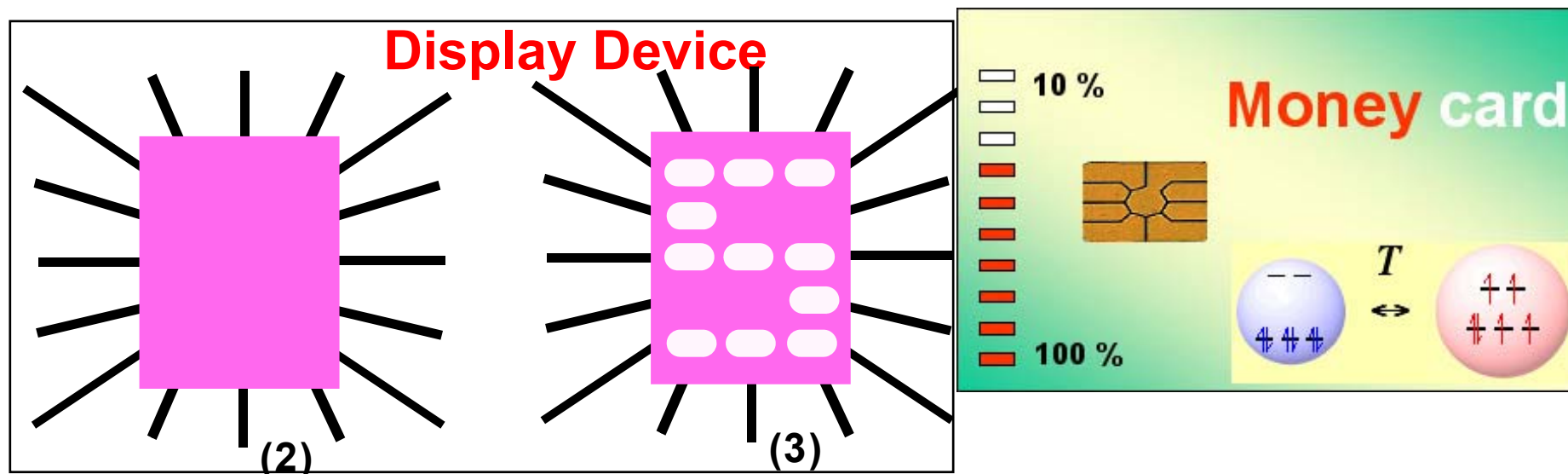


A Fe(II) HS-LS compound: Colour change



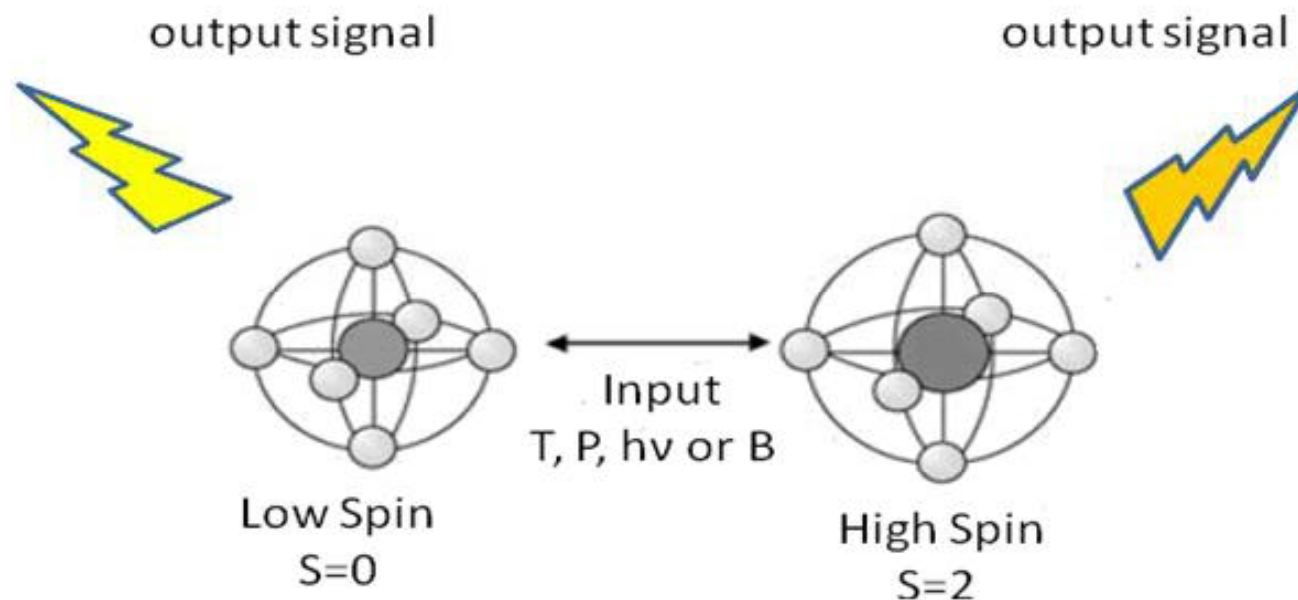
O. Kahn, C. Jay
and ICMC
Bordeaux

LS-HS transition tuneable with light: Applications



Compound in
Low spin state
(Thin Layer)

Display



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

Spectrochemical Series

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-$, $\text{F}^- < \text{urea}$, $\text{OH}^- < \text{ox}$, $\text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}$, $\text{NH}_3 < \text{en} < \text{bpy}$, $\text{phen} < \text{NO}_2^- < \text{CH}_3^-$, $\text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$.

Pi-bases < weak pi-bases < no pi-effect < pi-acids

For an octahedral complex, CFSE

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

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

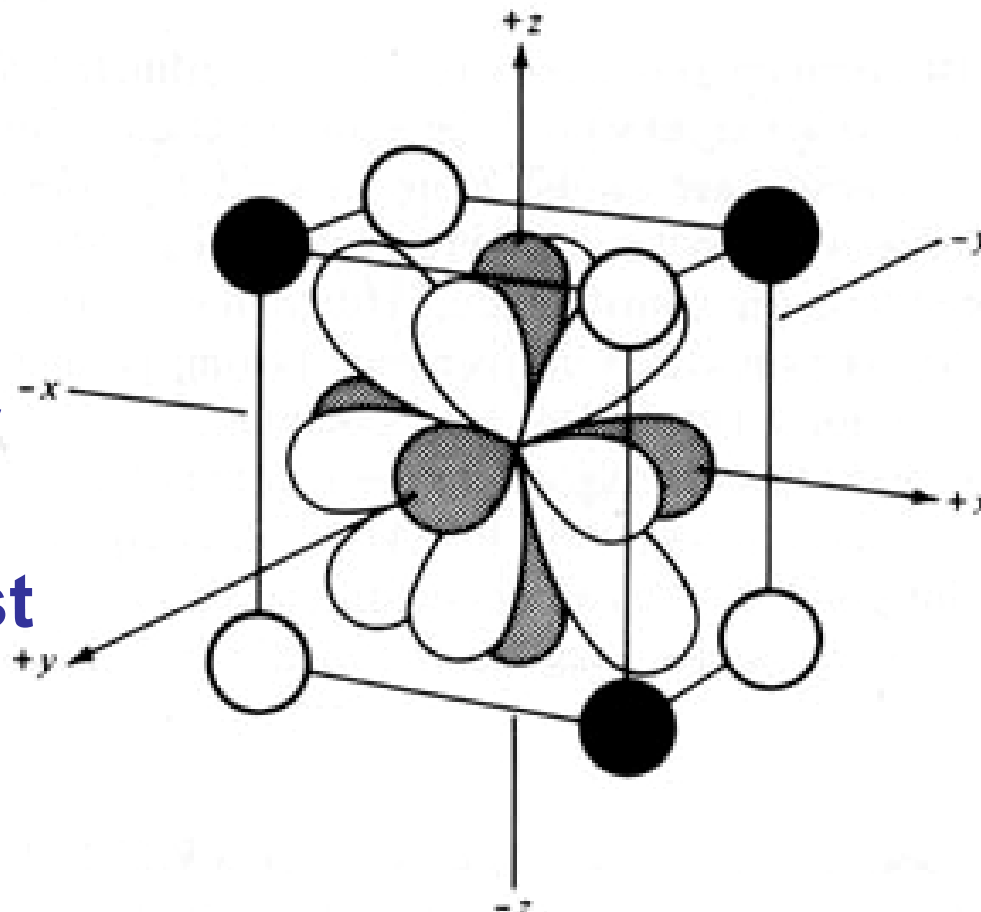


Case I results in LS complex

Case II results in HS complex

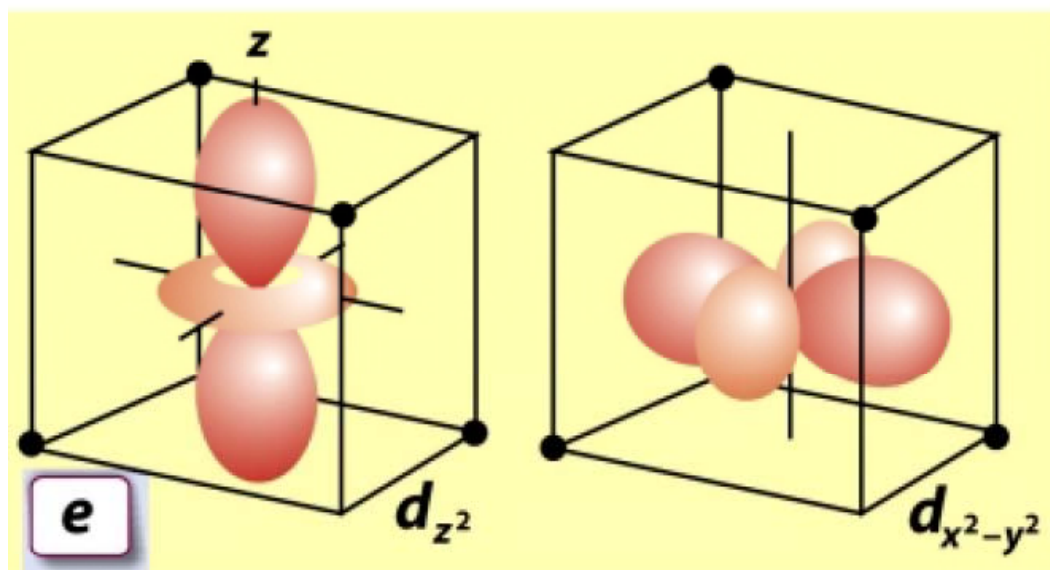
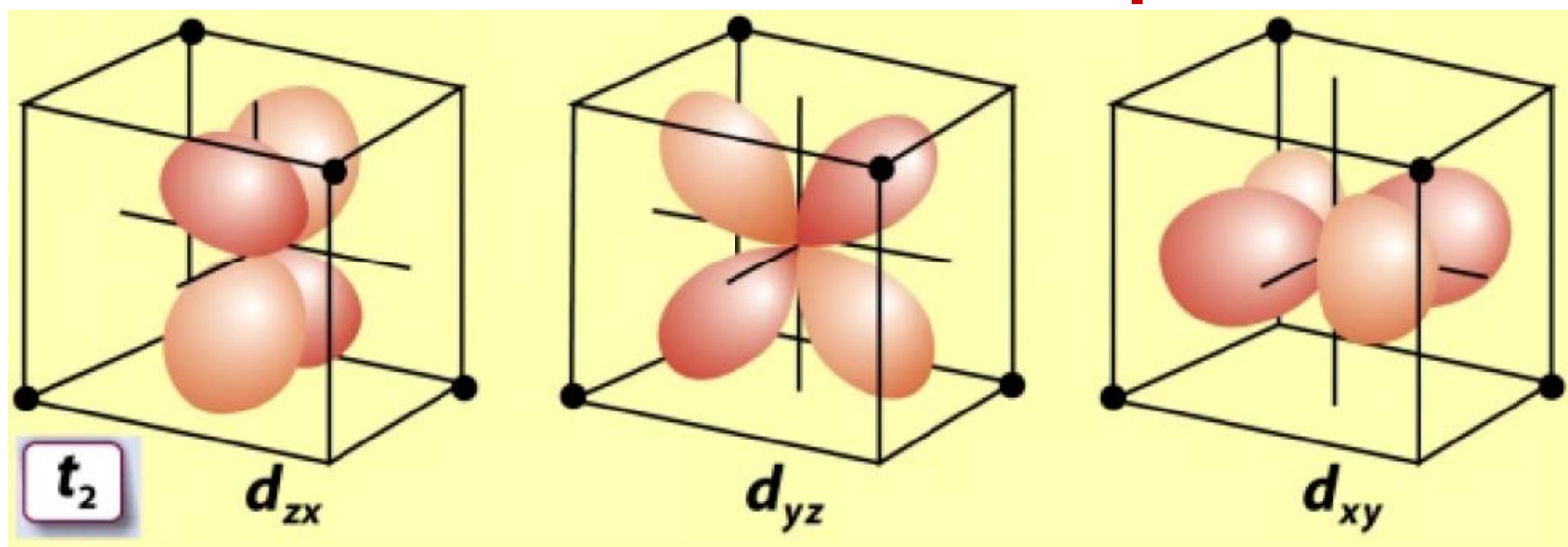
Tetrahedral Field- Considerations

Imagine a tetrahedral molecule inside a cube with metal ions at 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 't₂' orbitals point to the center of the edges of the cube.

Tetrahedral complexes



The three ' t_2 ' orbitals point to the center of the edges of the cube
 $109^\circ28' / 3 = 35^\circ16'$.

The two ' e ' orbitals point to the center of the face of the cube
 $109^\circ28' / 2 = 54^\circ44'$.

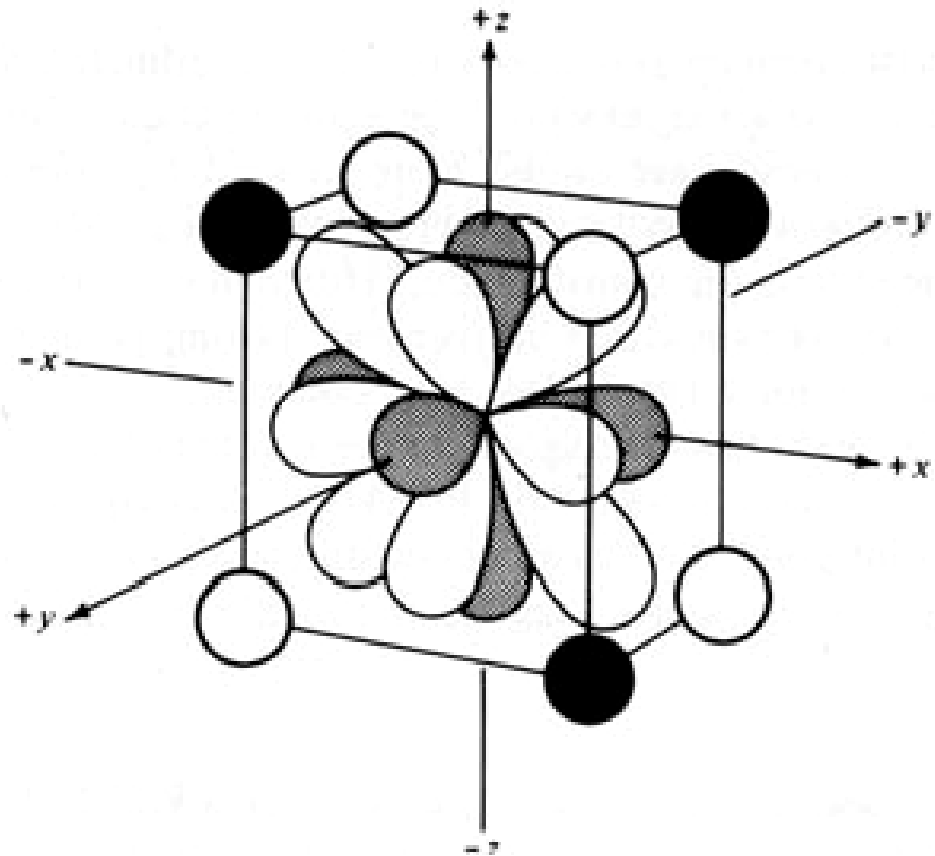
Figure 19-8

Shriver & Atkins Inorganic Chemistry, Fourth Edition

© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

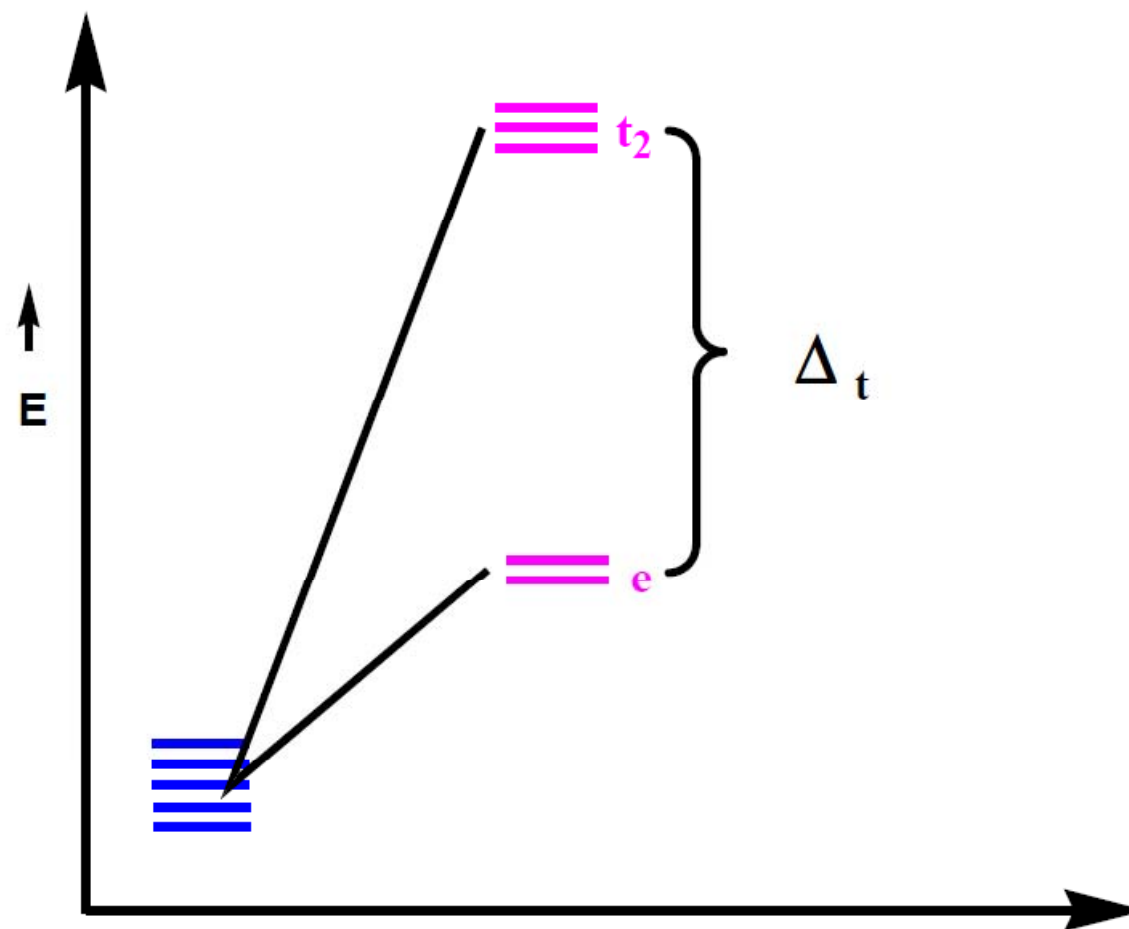
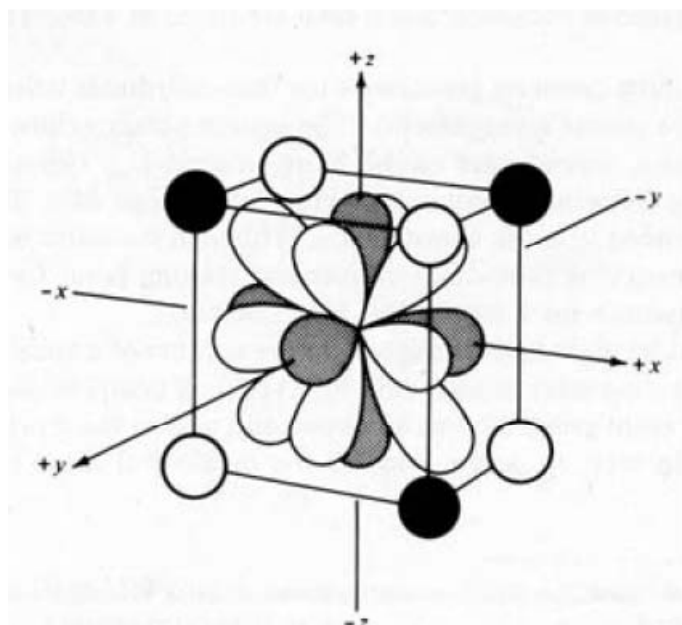
Tetrahedral Field- Considerations

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



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 $2/3 \times 2/3 = 4/9$ of Δ_o .

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

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

Table 19.4 Values of Δ_T for representative tetrahedral complexes

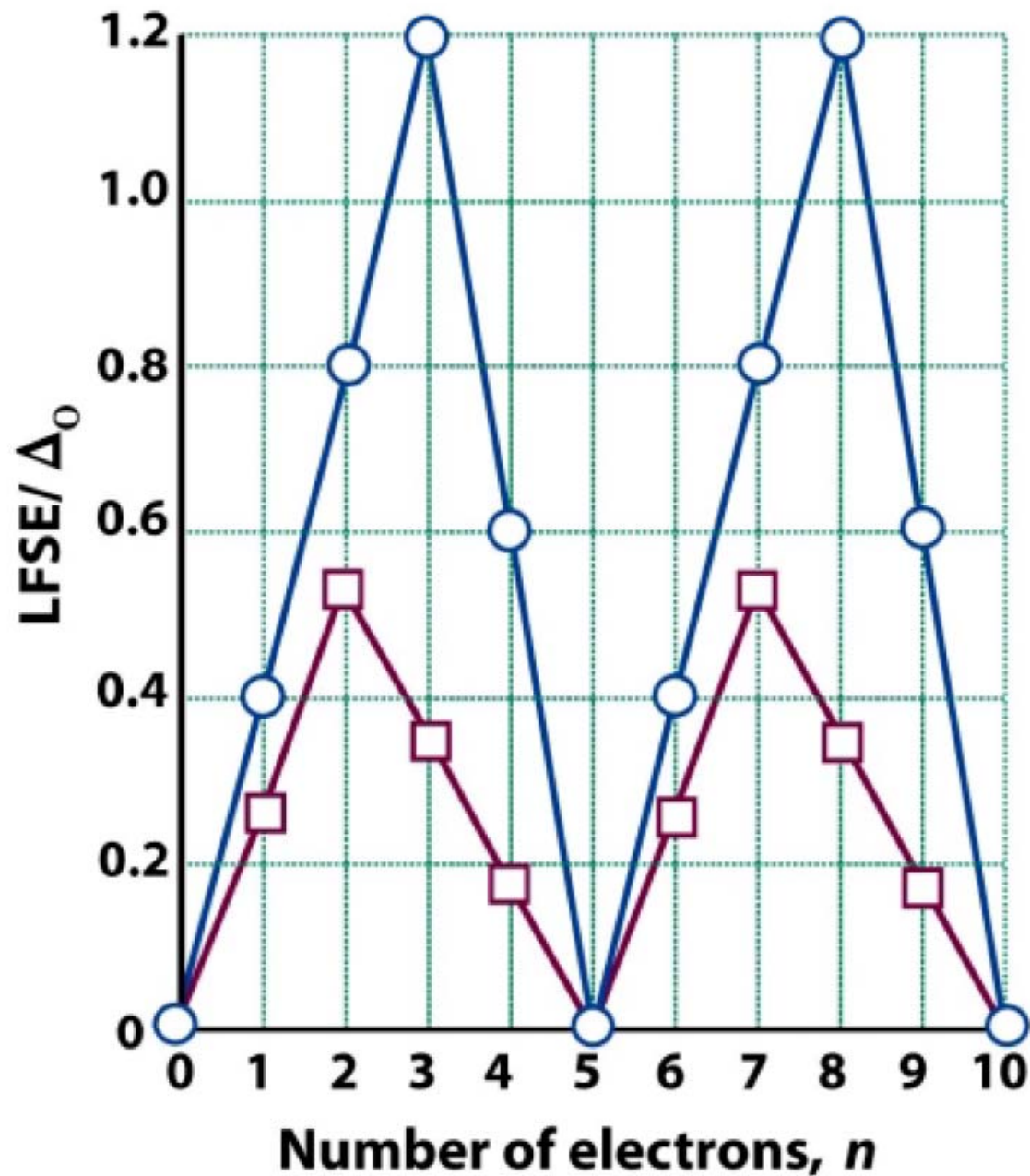
Complex	Δ_T/cm^{-1}
VCl_4	9010
$[\text{CoCl}_4]^{2-}$	3300
$[\text{CoBr}_4]^{2-}$	2900
$[\text{CoI}_4]^{2-}$	2700
$[\text{Co}(\text{NCS})_4]^{2-}$	4700

Table 19.2 Ligand-field stabilization energies*

d^n	Example	Octahedral				Tetrahedral	
				N	LFSE	N	LFSE
d^0				0	0	0	0
d^1	Ti ³⁺			1	0.4	1	0.6
d^2	V ³⁺			2	0.8	2	1.2
d^3	Cr ³⁺ , V ²⁺			3	1.2	3	0.8
		Strong-field				Weak-field	
d^4	Cr ²⁺ , Mn ³⁺	2	1.6			4	0.4
d^5	Mn ²⁺ , Fe ³⁺	1	2.0			5	0
d^6	Fe ²⁺ , Co ³⁺	0	2.4			4	0.6
d^7	Co ²⁺	1	1.8			3	1.2
d^8	Ni ²⁺			2	1.2	2	0.8
d^9	Cu ²⁺			1	0.6	1	0.4
d^{10}	Cu ⁺ , Zn ²⁺			0	0	0	0

* N is the number of unpaired electrons; LFSE is in units of Δ_0 for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx 0.45\Delta_0$.

Octahedral vs. Tetrahedral Fields



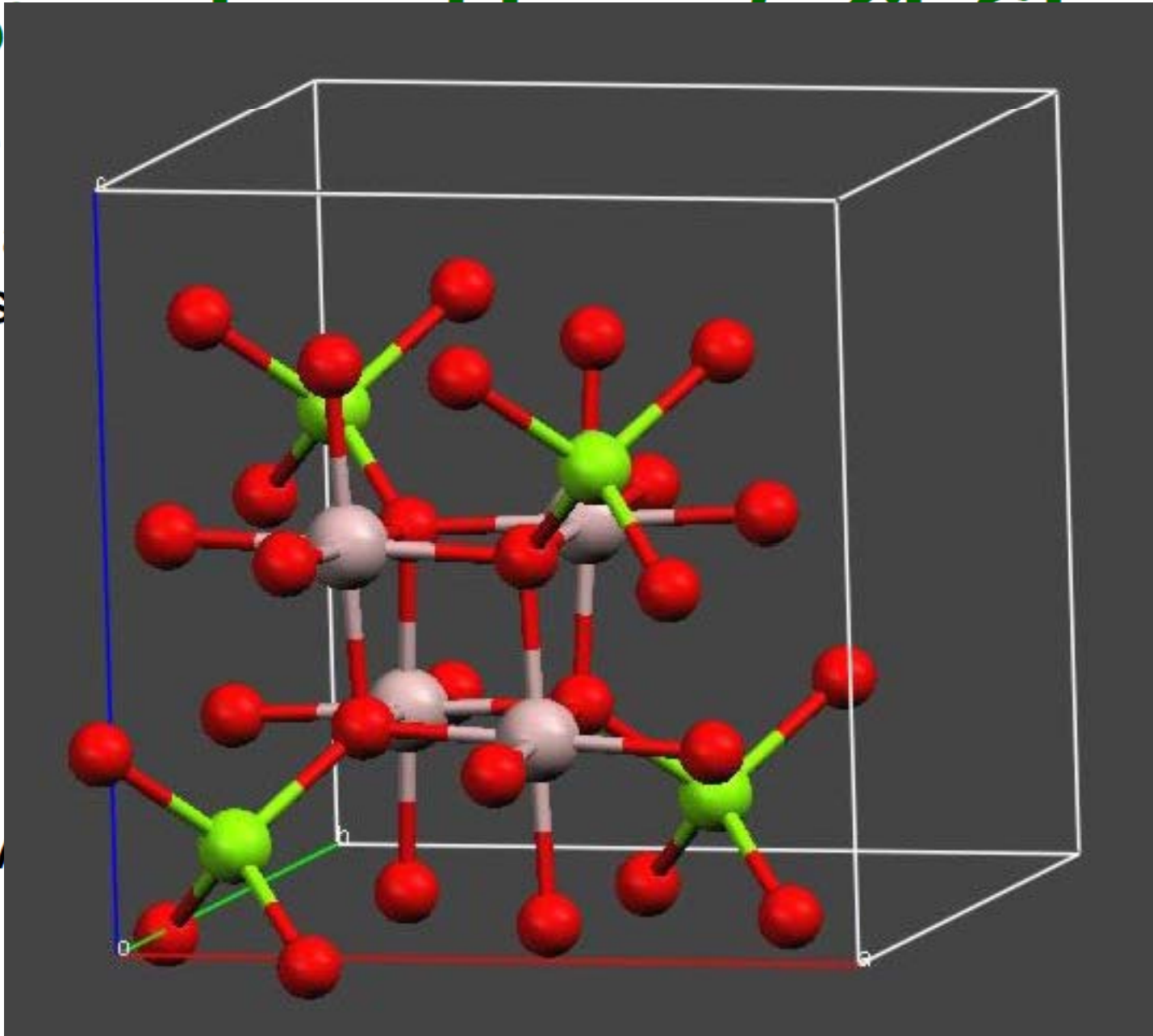
Spinels

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Spinel - 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.



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

How about Fe_3O_4 ?

Spinel - Use of CFSE

Fe_3O_4 (oxygen weak field ligand)

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

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

Structure: Inverse Spinel

Spinels - Use of CFSE

How about MnCr_2O_4 and FeCr_2O_4 ? Work out.

Tip:

If $\text{A}^{2+} = \text{d}^6, \text{d}^7, \text{d}^8$, or d^9 ion, and $\text{B}^{3+} = \text{Fe}^{3+}$,

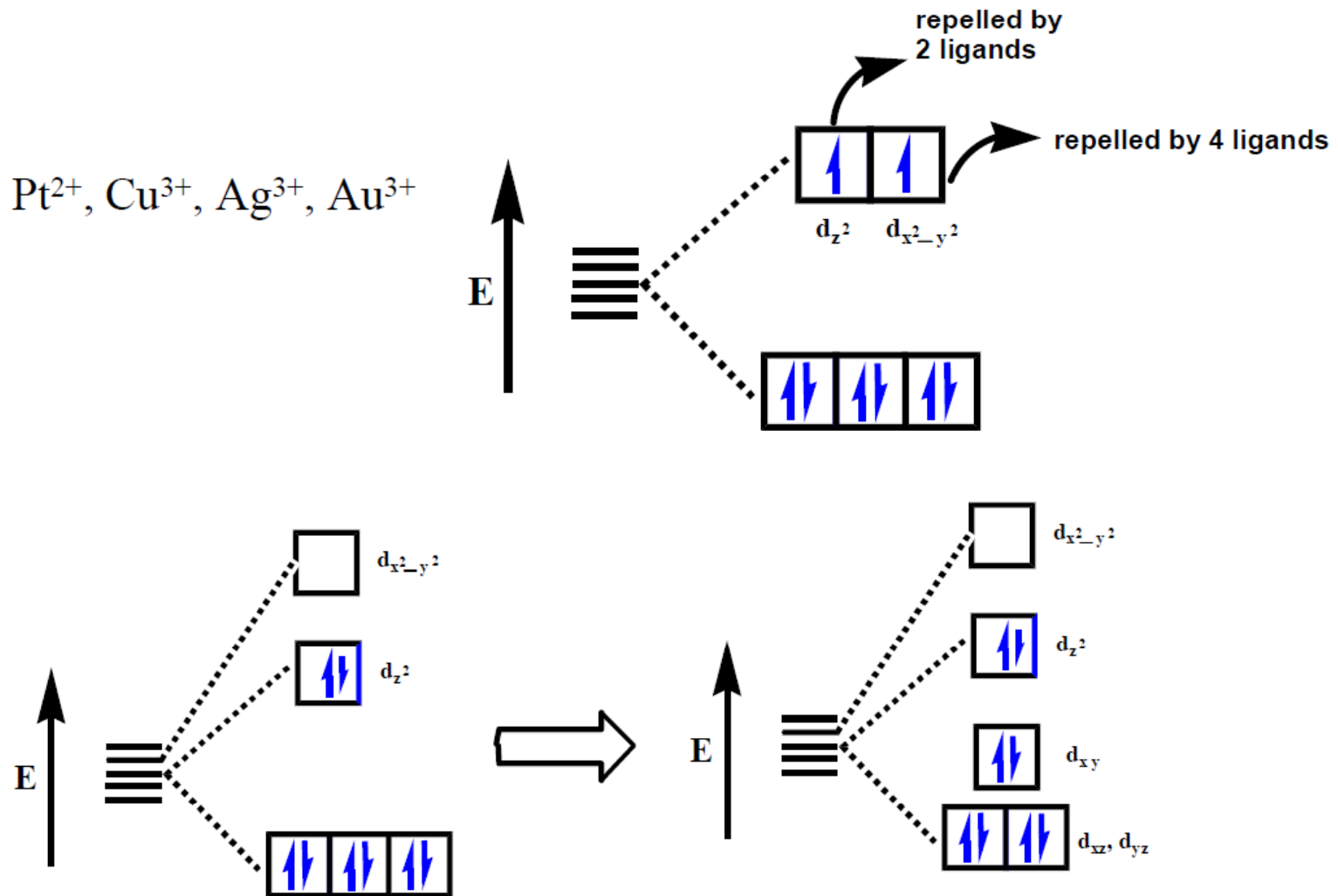
AB_2O_4 is always INVERSE.

Why ?

Special case of d^8 Octahedral

Examples:

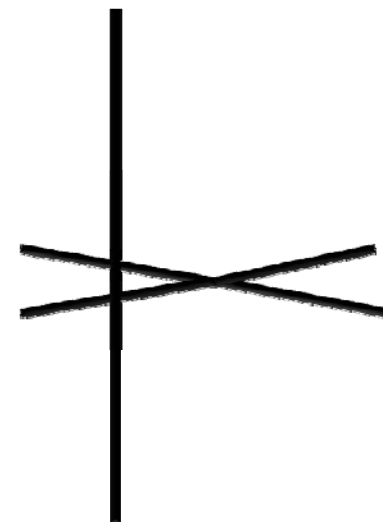
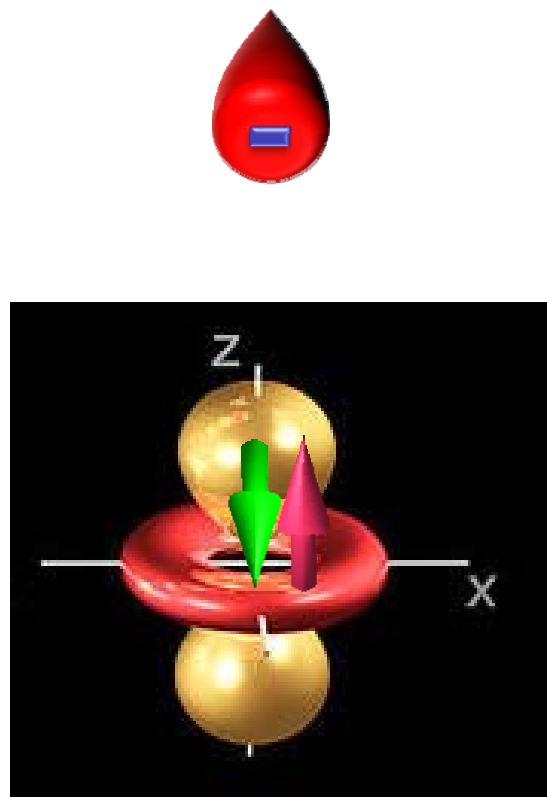
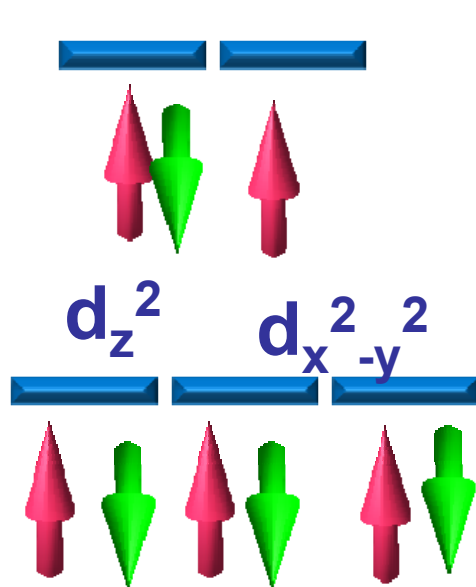
Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^{3+} , Ag^{3+} , Au^{3+}



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

Case of degeneracy: Jahn-Teller distortion

Assume: d^9 electronic configurations (Cu(II))



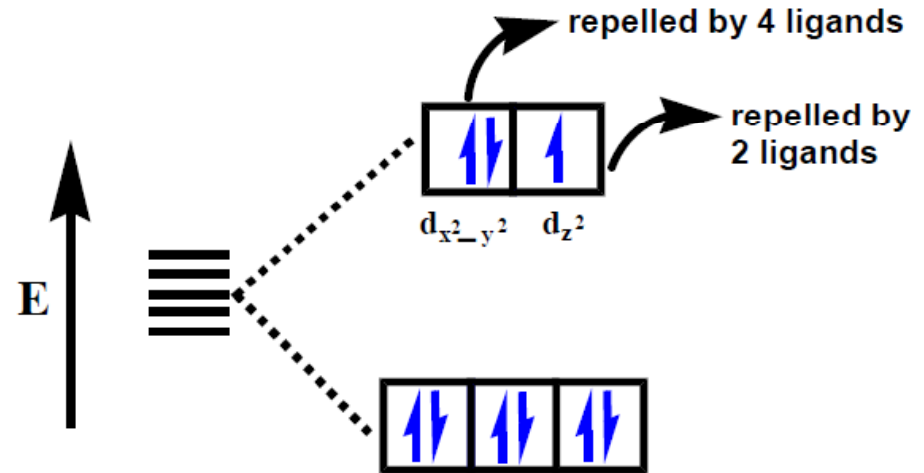
Lead to Longer
M-L distance along
Z axis



Jahn-Teller Distortion

If both 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 others. **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: $(d_{z^2})^2 d_{x^2-y^2})^1$

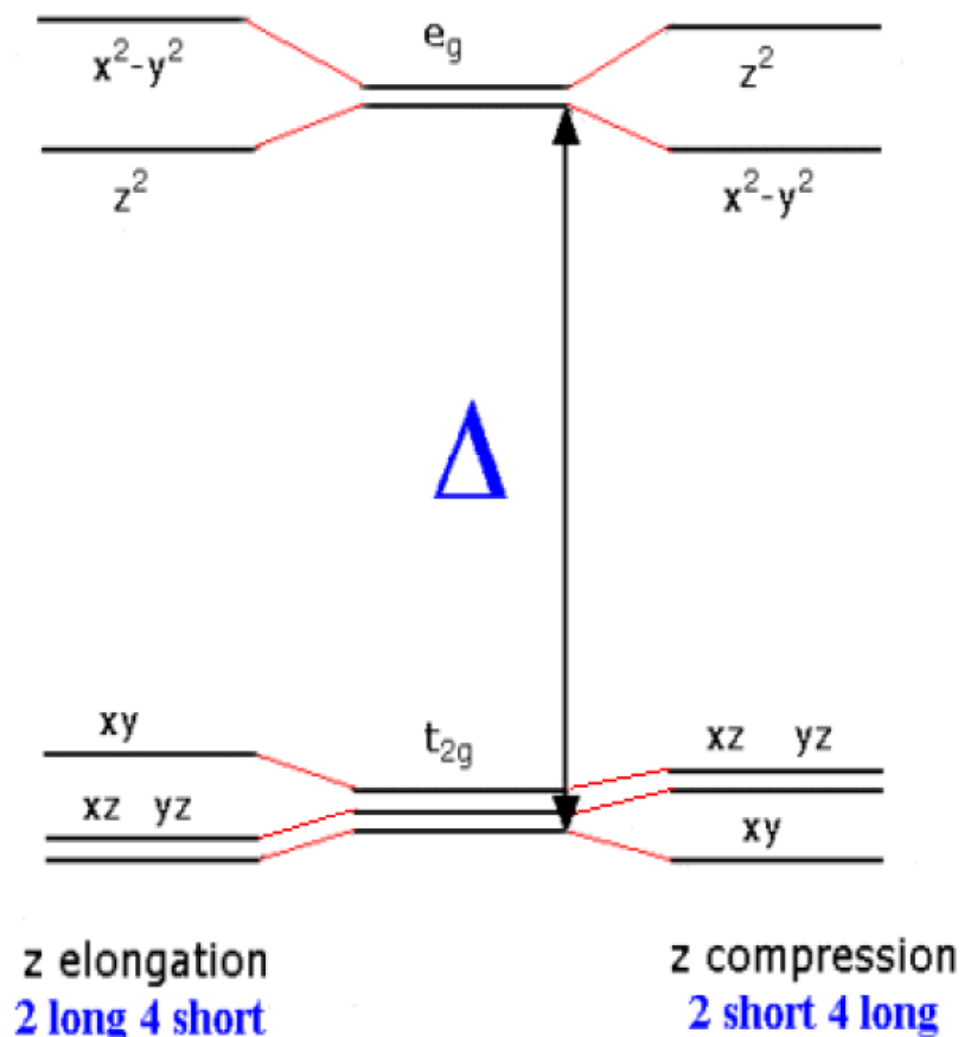
Ligands along z, -z will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.

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.

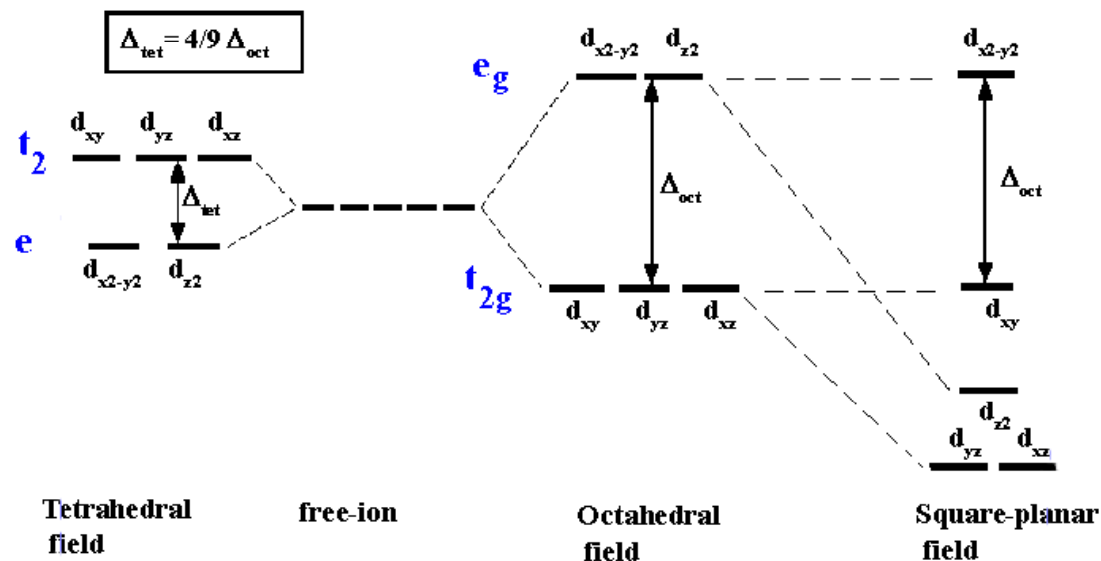
The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



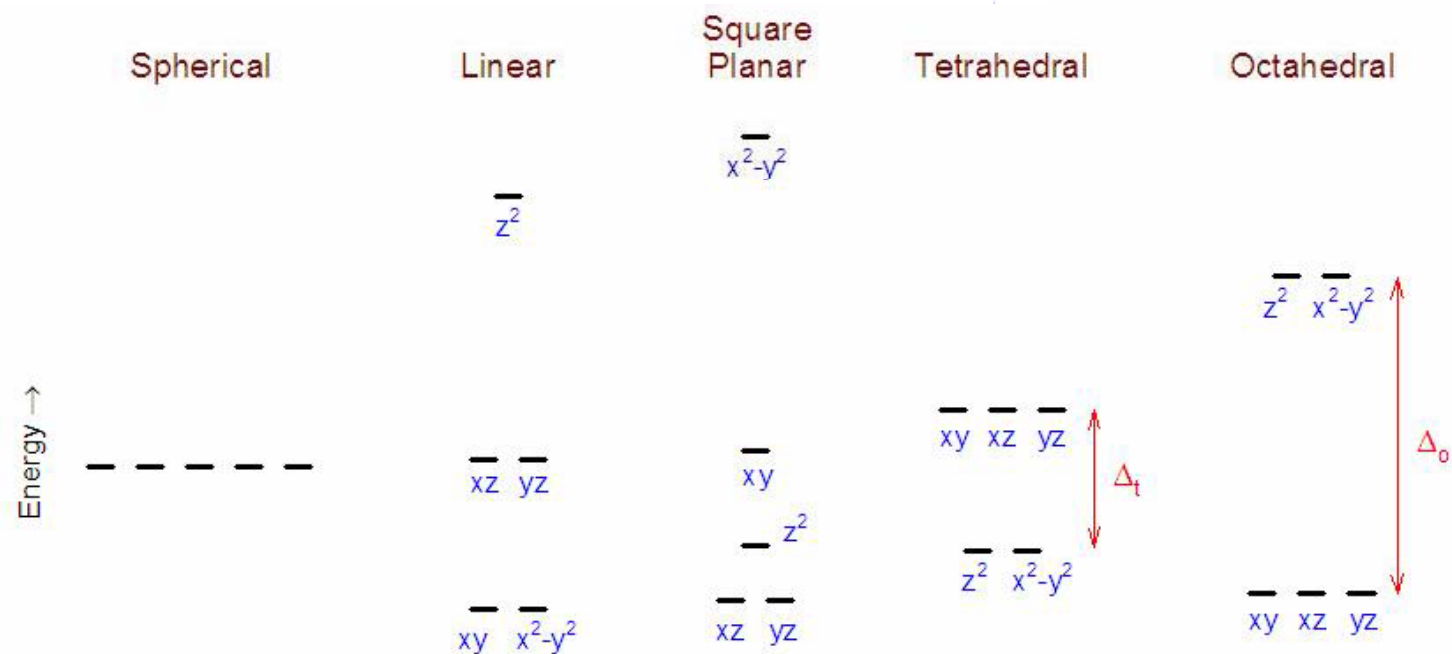
Jahn-Teller distorted complexes

CuBr_2	4 Br at 240pm 2 Br at 318pm
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	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
$\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$	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

Energy levels of the d-orbitals in common stereochemistries



Crystal Field Splitting of d-orbital



Only tetrahedral, octahedral and square planar

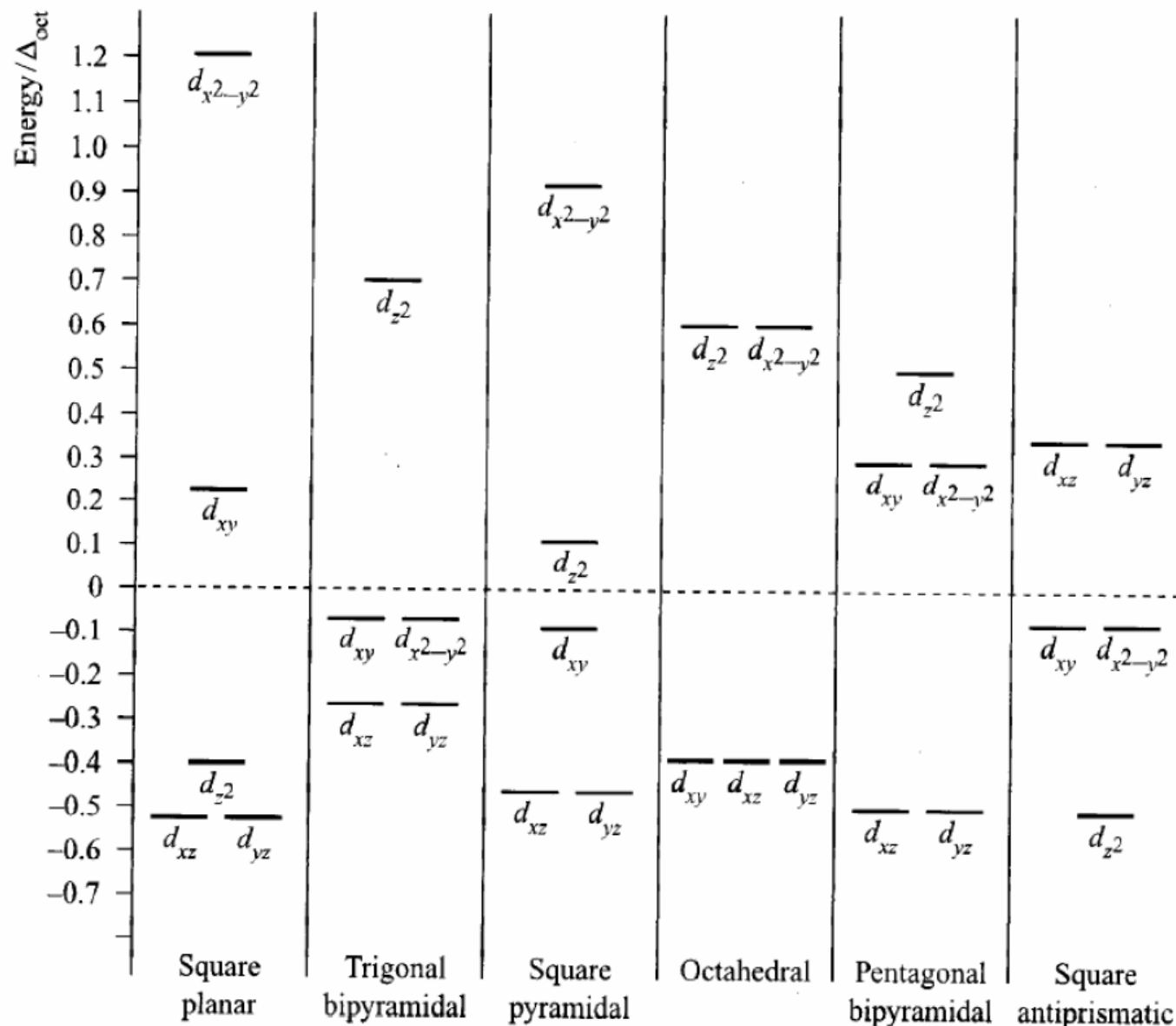


Figure 2 Crystal field splittings of d orbitals