Ligand Field Theory

By

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- Ligand field theory considers the effect of different ligand environments (ligand fields) on the energies of the *d*-orbitals

- The energies of the *d* orbitals in different environments determines the magnetic and electronic spectral properties of transition metal complexes

- **Ligand field theory** combines an electrostatic model of metal-ligand interactions (crystal field theory) and a covalent model (molecular orbital theory)

Relative energies of metal-ion 3d electrons

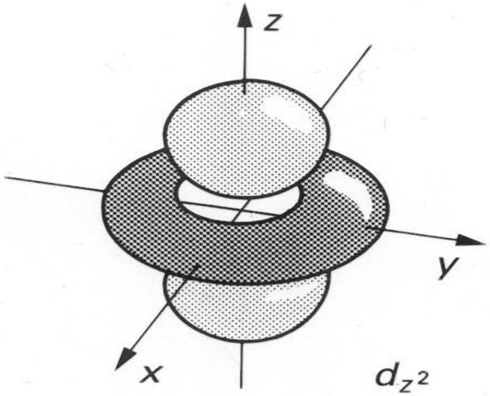
- Because the $4s^2$ electrons are lost before the 3*d*, the highest occupied molecular orbitals (HOMOs) in transition metal complexes will contain the 3*d* electrons

M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

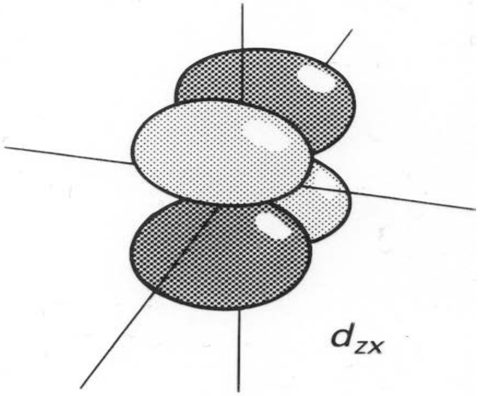
- The distribution of the 3*d* electrons between the *d*-orbitals in any given complex will determine the magnetic properties of the complex (the number of unpaired electrons, the total spin (S) and the magnetic moment of the complex)

- Electronic transitions between the highest occupied *d*-orbitals will be responsible for the energies (λ_{max}) and intensities (e) of the *d*-*d* bands in the electronic spectra of metal complexes

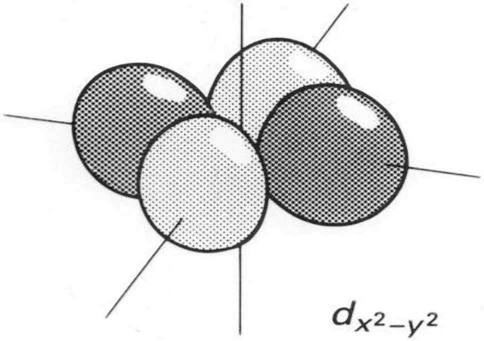
- Electronic transitions to and from the highest occupied *d*-orbitals will be responsible for the energies and intensities of the ligand-to-metal (LMCT) and metal-to-ligand (MLCT) charge transfer bands appearing in the electronic spectra of metal complexes



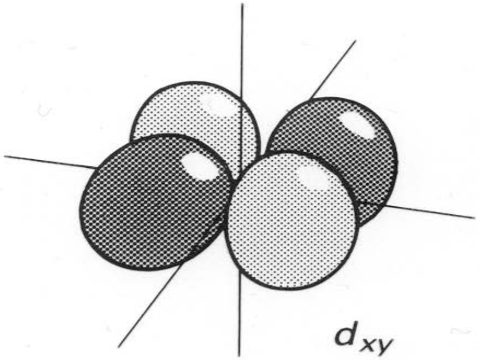
d_{z^2}



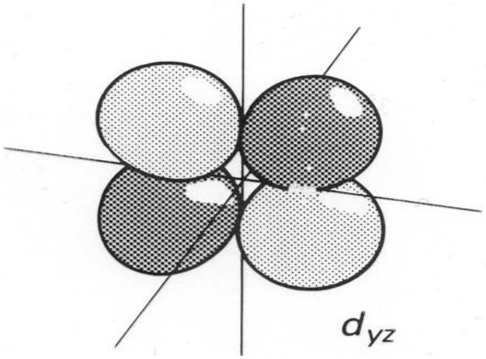
d_{zx}



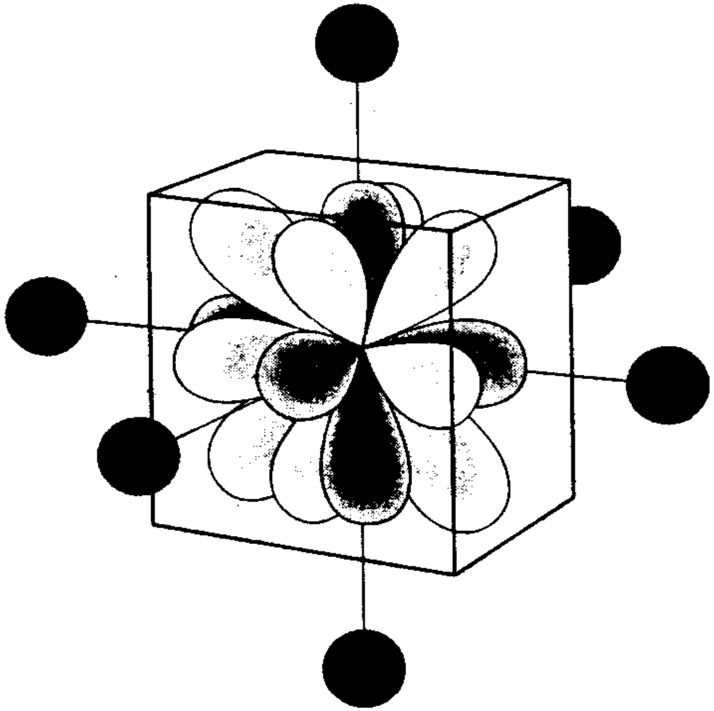
$d_{x^2-y^2}$



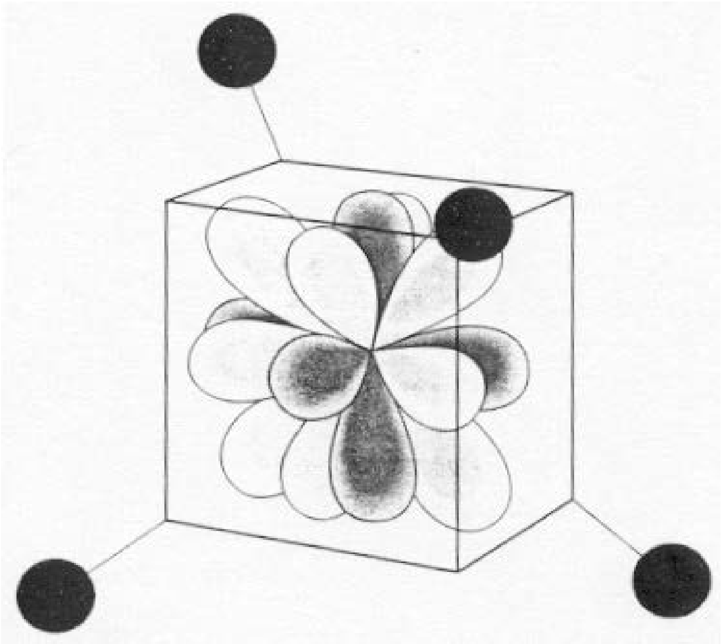
d_{xy}



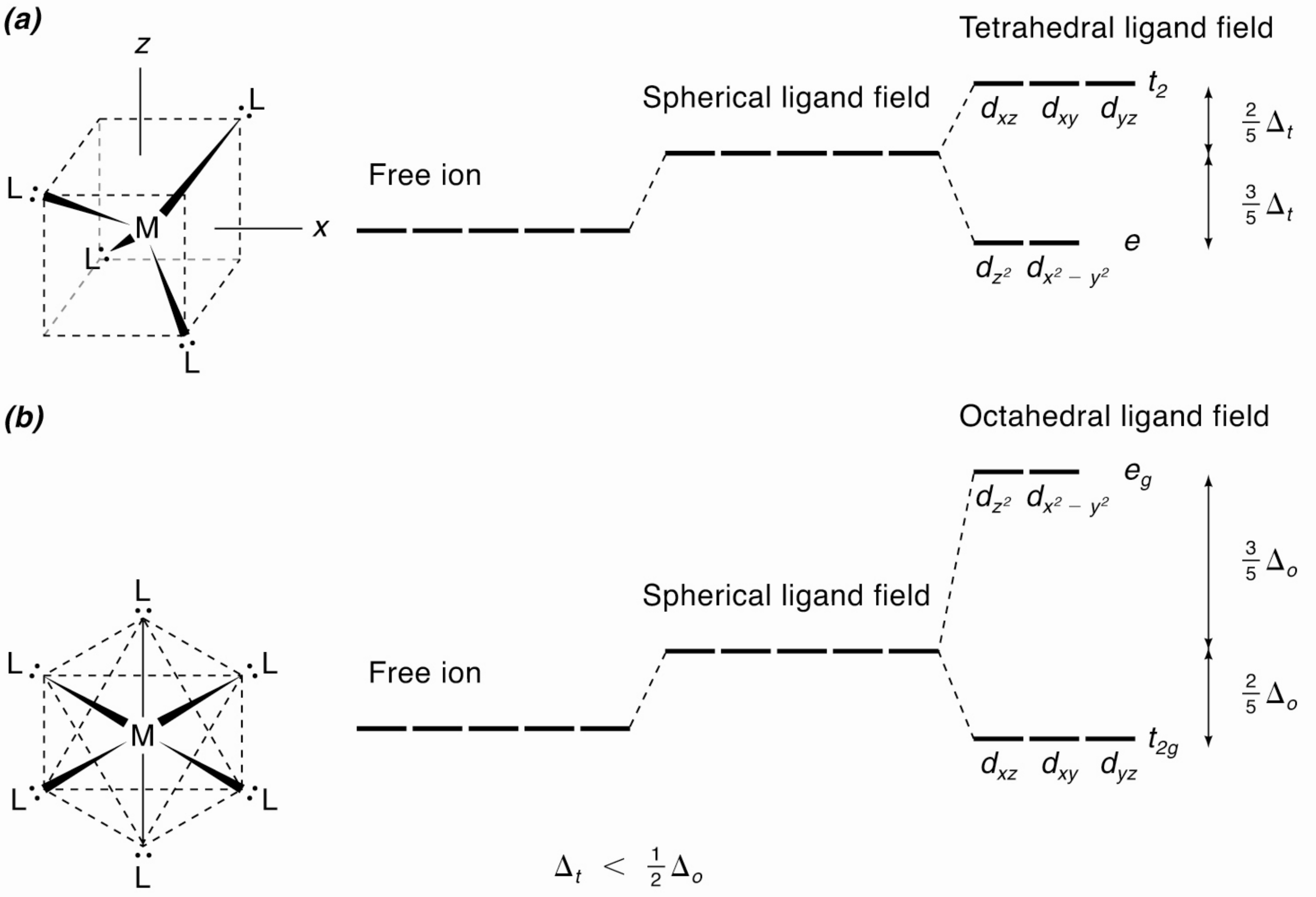
d_{yz}



O_h



T_d



(a)

Free ion

Spherical ligand field

Tetrahedral ligand field

t_2: d_{xz} d_{xy} d_{yz}

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

$\frac{2}{5}\Delta_t$

$\frac{3}{5}\Delta_t$

(b)

Free ion

Spherical ligand field

Octahedral ligand field

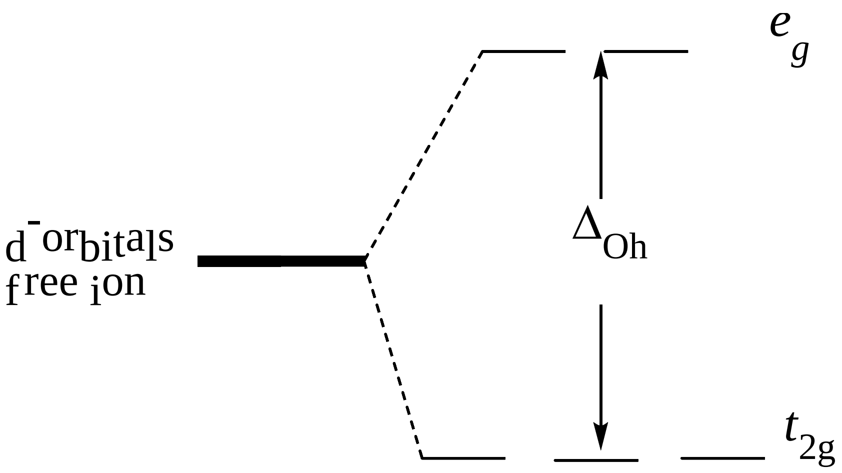
e_g: d_{z^2} $d_{x^2-y^2}$

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

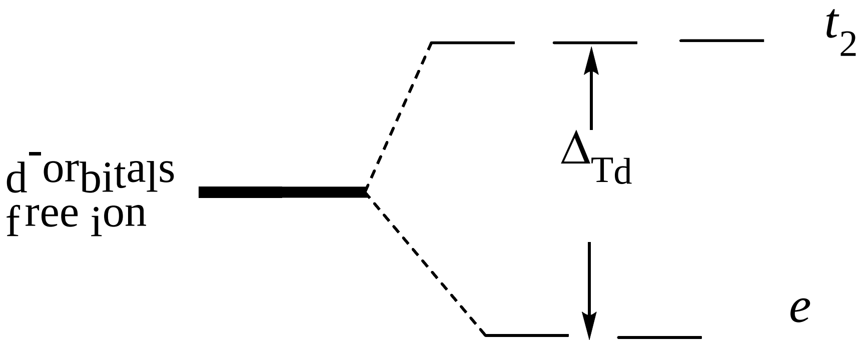
$\frac{3}{5}\Delta_o$

$\frac{2}{5}\Delta_o$

$$\Delta_t < \tfrac{1}{2}\Delta_o$$



O_h ligand field



T_d ligand field

High-Spin and Low-Spin Complexes for $3d^4 – 3d^7$ ions

- Octahedral 3*d* Complexes

$\Delta_o \approx$ P(pairing energy)

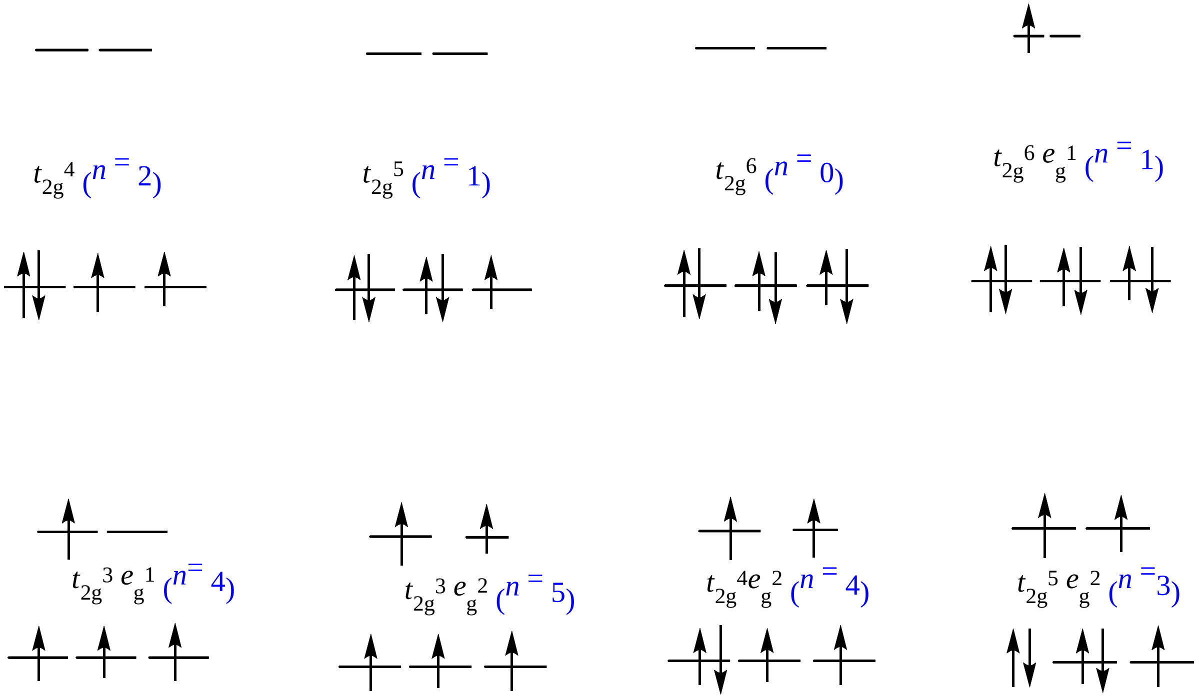
Both low-spin ($\Delta_o \leq P$) and high-spin ($P \geq \Delta_o$) complexes are found

- Tetrahedral Complexes

$\Delta_{Td} = 4/9\ \Delta_o$ hence $P >> \Delta_{Td}$ and tetrahedral complexes are always high spin

Electronic structure of *high-spin* and *low-spin* O_h complexes

Low Spin, $\Delta > P$



t_{2g}^4 ($n = 2$)

t_{2g}^5 ($n = 1$)

t_{2g}^6 ($n = 0$)

$t_{2g}^6 e_g^1$ ($n = 1$)

$t_{2g}^3 e_g^1$ ($n = 4$)

$t_{2g}^3 e_g^2$ ($n = 5$)

$t_{2g}^4 e_g^2$ ($n = 4$)

$t_{2g}^5 e_g^2$ ($n = 3$)

High Spin $P > \Delta$

Other factors influencing the magnitude of Δ-splitting

- Oxidation State

  $\Delta_o\ (M^{3+}) > \Delta_o(M^{2+})$

  e.g. Δ_o for Fe(III) > Fe(II)

  The higher oxidation state - low-spin

- 5*d* > 4*d* >3*d*

e.g. Os(II) > Ru(II) > Fe(II)

All 5*d* and 4*d* complexes - low-spin

The nature of the ligand

Spectrochemical Ligand Series

The ordering of the ligands in their ability to cause *d*-orbital splitting

$I^- < Br^- < Cl^- < SCN^- < NO_3^- < OH^- < C_2O_4^{2-} < H_2O \sim RS^- < NCS^- < NH_3 \sim$ imidazole $<$ en $<$ bipy $<$ phen $< NO_2^- < PPh_3 < CN^- < CO$

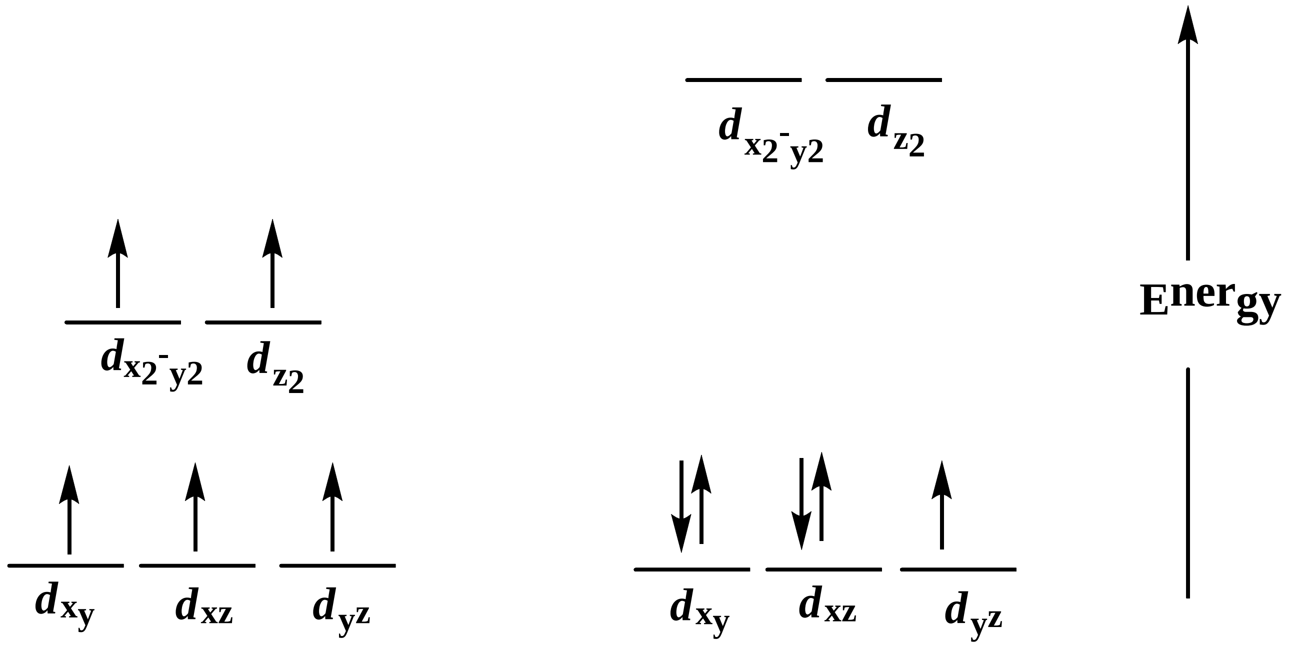
Variations are due to σ-donating and Π-accepting properties of the ligand.

Small Δ-splitting ligands - ***weak field*** ligands
Large Δ-splitting ligands - ***strong field*** ligands

Halide ions < O-donors < N-donors < Π-unsaturated

Weak field ligands ________________ *Strong field ligands*

Small Δ-splitting Large Δ-splitting



High spin $3d^5$

n = 5, S = 5/2

$[Fe(H_2O)_6]^{3+}$
Weak field ligand

Low spin $3d^5$

n = 1, S = 1/2

$[Fe(CN)_6]^{3-}$
Strong field ligand