5.111 Principles of Chemical Science
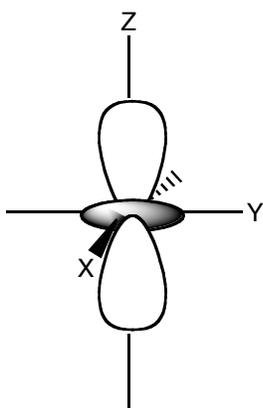Fall 2008

5.111 Lecture Summary #28
Transition Metals: Crystal Field Theory
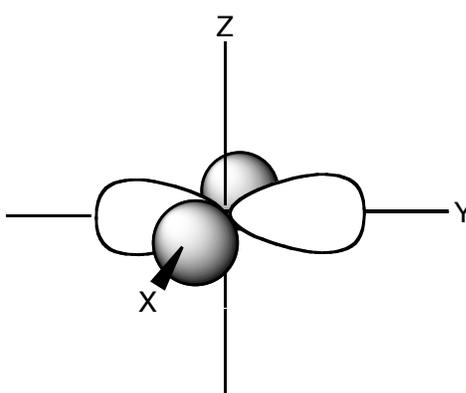Chapter 16 p 681-683   (p 631-633 in 3rd ed)

From Friday's handout

d Orbitals
There are five d orbitals: d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}.
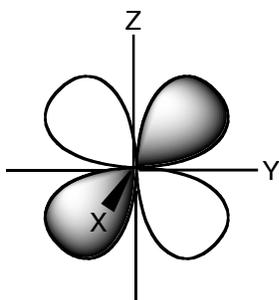
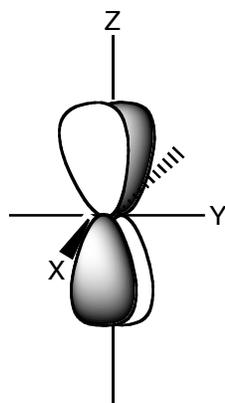You need to be able to draw their shapes.

d_{z^2} has maximum
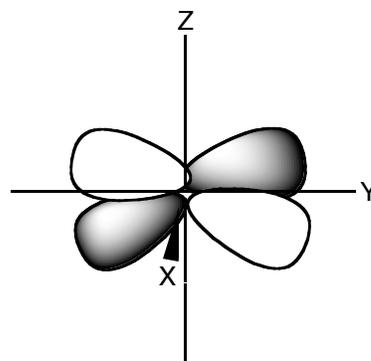amplitude along z
and doughnut in xy plane

$d_{x^2-y^2}$ has maximum
amplitude along x and y axes.

d_{yz} has maximum
amplitude 45° to
y and z axes

d_{xz} has maximum
amplitude 45° to
x and z axes

d_{xy} has maximum
amplitude 45° to
x and y axes

Today's material

Crystal field and ligand field theories were developed to explain the special properties of coordination complexes of transition metals.
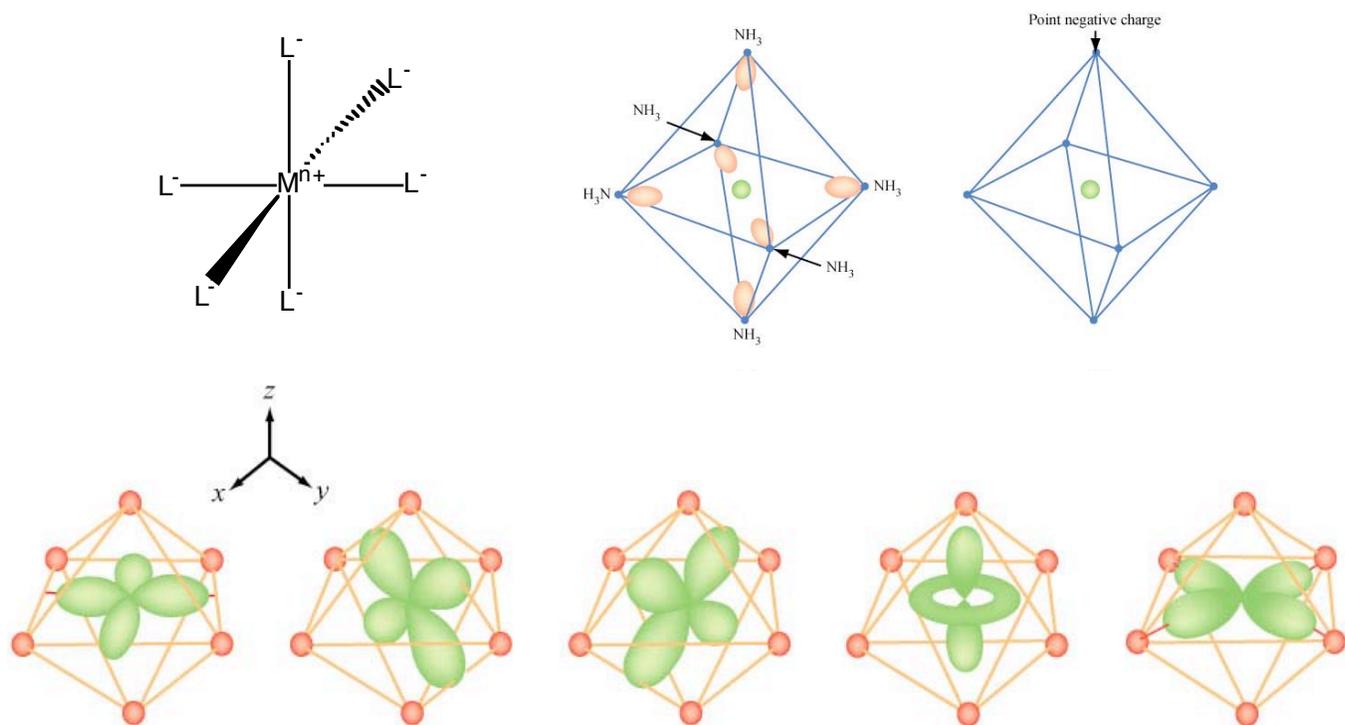
Basic idea behind theories:

> When a metal ion with a given formal oxidation number is placed at the center of a coordination sphere defined by a set of ligands, the energy levels of the d orbitals housing the metal electrons are altered from those in the free metal ions.

Crystal field theory is based on an ionic description of the metal-ligand bond.

Ligand field theory includes covalent as well as ionic aspects of coordination. It is a more powerful description of transition metal complexes. It is, however, beyond the scope of this course. (Take 5.03 if you are interested in this topic).

Crystal Field Theory considers ligands as negative point charges and considers the repulsion between the negative point charges and the d-orbitals.

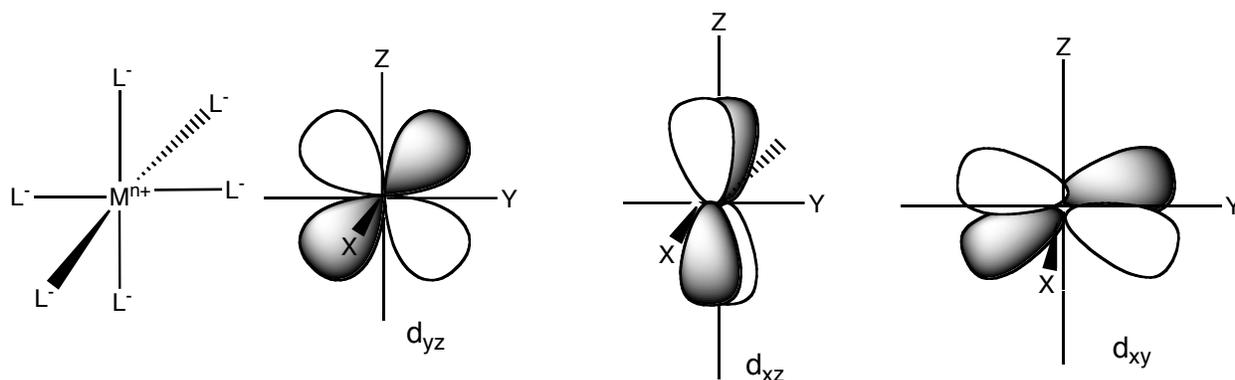Ligand (L) point charges are directed toward the d_{z^2} and $d_{x^2-y^2}$ orbitals of metal (M^{n+}), resulting in a large repulsion. The d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized, and they are destabilized by the same amount. d_{z^2} and $d_{x^2-y^2}$ are degenerate. The d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized more than d_{xy}, d_{yz}, and d_{xz}.

Large repulsion- destabilized relative to d_{xy}, d_{yz}, d_{xz}.

Ligand point charges are directed in between d_{xy}, d_{xz}, and d_{yz} orbitals (not directly toward them). The d_{xy}, d_{xz}, and d_{yz} orbitals are stabilized relative to d_{z^2} and $d_{x^2-y^2}$ orbitals, and they are stabilized by the same amount (i.e. d_{xy}, d_{xz}, and d_{yz} orbitals are degenerate).

Small repulsion - stabilized relative to d_{z^2} and $d_{x^2-y^2}$

label for degenerate $d_{x^2-y^2}$ and d_{z^2} orbitals

(e_g)

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

Δ_O

$+\dfrac{3}{5}\,\Delta_O$

$-\dfrac{2}{5}\,\Delta_O$

average energy of d orbitals with ligands

(Spherical crystal field)

d_{xy} d_{xz} d_{yz}

(t_{2g})

(Octahedral crystal field)

label for degenerate d_{xy}, d_{xz}, d_{yz} orbitals

Δ_o is the overall splitting between e_g and t_{2g} orbitals = octahedral field splitting energy ("o" in Δ_o is for octahedral)
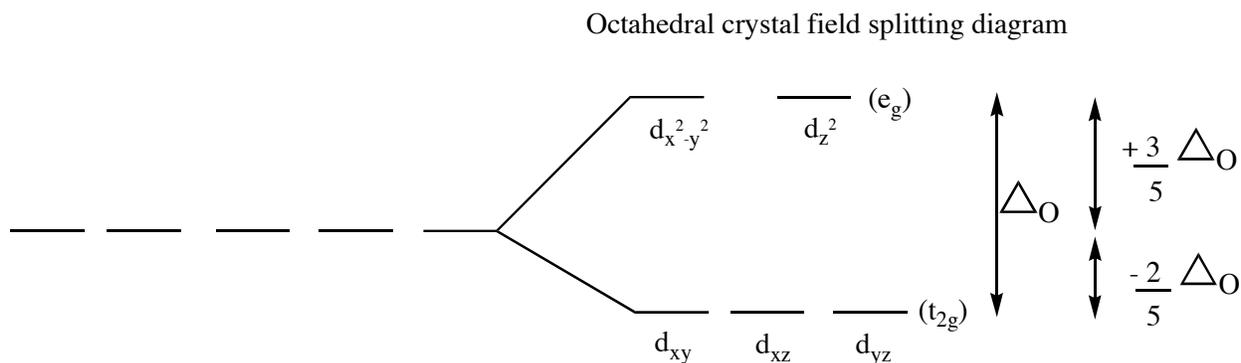
Because the overall energy is maintained, the energy of the three t_{2g} orbitals are lowered by (2/5) Δ_o and the energy of the two e_g orbitals are raised by (3/5) Δ_o relative to the spherical crystal field.

Example 1. $[Cr(NH_3)_3Br_3]$

(a) figure out the oxidation number of Cr?

(b) figure out d count

(c) draw octahedral crystal field splitting diagram

Octahedral crystal field splitting diagram

(e_g)

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

Δ_O

$+\dfrac{3}{5}\,\Delta_O$

$-\dfrac{2}{5}\,\Delta_O$

(t_{2g})

d_{xy} d_{xz} d_{yz}

(d) Write d^n electron configuration:

(e) Predict <u>Crystal Field Stabilization Energy (CFSE)</u> - energy change relative to that of the hypothetical spherical crystal.

CFSE =

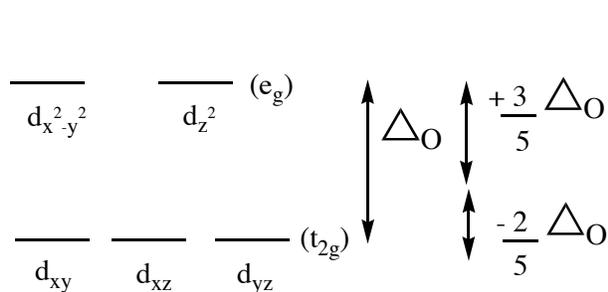**Example 2.** $[Mn(H_2O)_6]Cl_3$

(a) figure out the oxidation number of Mn?

(b) figure out d count
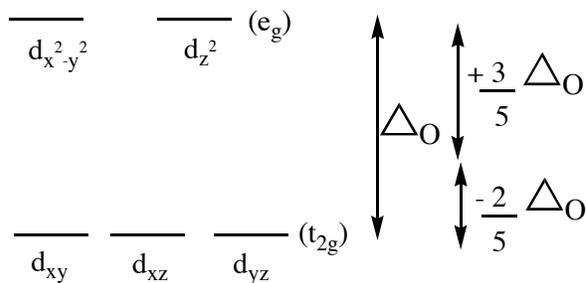
(c) draw octahedral crystal field splitting diagram

There are two possible octahedral crystal field splitting diagrams for Mn^{3+}: one for the case where the magnitude of Δ_o is greater than the pairing energy (PE), and one for the case where it is less. <u>Pairing energy</u> is the energy of the electron-electron repulsion.

Mn^{3+} d^4

weak field (Δ_o <PE)   Strong field (Δ_o >PE)

(d) d^n electron configuration = d^n electron configuration =

Δ_o is small (weak octahedral field), (Δ_o<PE). Electrons are placed singly with parallel spins to the fullest possible extent in both t_{2g} and e_g orbitals.

This arrangement of electrons gives the maximum number of unpaired electrons (high spin).

Δ_o is large (strong octahedral field) (Δ_o>PE). Electrons are paired in lower energy t_{2g} orbitals. e_g orbitals are not occupied until t_{2g} orbitals are filled.

This arrangement of electrons gives the minimum number of unpaired electrons (low spin).

NOTE: Mn^{3+} in $[Mn(H_2O)_6]Cl_3$ is high spin, why? We will come back to this.

(e) Predict Crystal Field Stabilization Energy (CFSE)

For High spin Mn^{3+} d^4
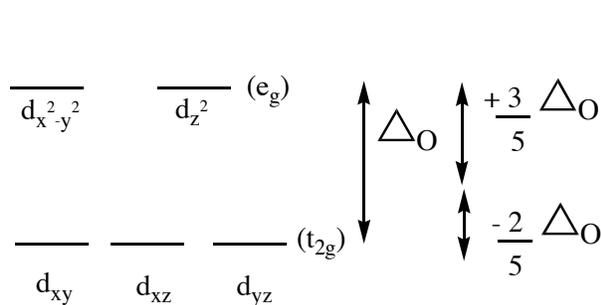
CFSE =

Low spin Mn^{3+} d^4

CFSE =

Example 3. Co^{2+} in an octahedral coordination complex
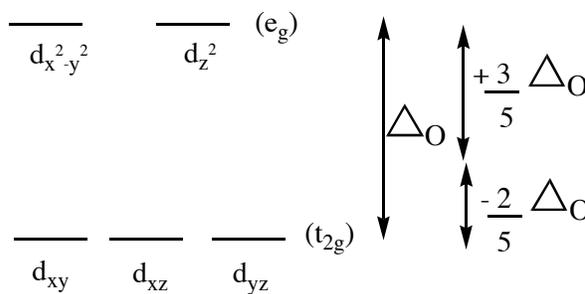**(a)** figure out oxidation number (given)

(b) figure out d count

(c) draw octahedral crystal field splitting diagram

Weak Field

_____Spin
(d) d^n electron configuration =

Strong Field

_____Spin
d^n electron configuration =

(e) CSFE=

CFSE=