Crystal Field Theory
- the colors and magnetic properties of metal complexes are related to the d-orbitals they possess
- crystal field theory attempts to explain these phenomena thru electrostatic interactions
- octahedral complexes

-- recall what an octahedral looks like and the shapes of the d-orbitals
-- we know the bond between the metal center and a ligand occurs thru the donation of a lone pair (lp) of the ligand donor atom to the central metal
-- if we think of this lp approaching the d-orbitals along the corner points of the octahedral there will be more repulsion btwn the lp and the d-orbital that is pointing toward one of these corners
-- the 5 d-orbitals no longer have the same energy - the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are higher in energy than the $d_{xy}$, $d_{xz}$, and $d_{yz}$ due to the increased repulsive energy

-- the difference in energy btwn the two sets of orbitals is the crystal field splitting energy, $\Delta_0 = \frac{hc}{\lambda}$ where $h = 6.63 \times 10^{-34}$ Js and $c = 3.00 \times 10^8$ m/s
- back to color - e.g. $[\text{Ti(H}_2\text{O)}_5]^{3+}$ (500 nm)
  -- $\Delta E = \Delta_0$ therefore the absorption energy is the amount of energy needed to overcome the crystal field so to speak

-- this is the relationship btwn CFT and the complex color
- high spin vs. low spin
  -- recall that when we ionize a transition metal the first e-'s to go are the 4s not the 3d
  -- we call the metallic ion a $d^n$ - e.g. Fe$^{3+}$ is a $d^5$ because it has 5 e-'s in the
d-orbitals
-- depending on the magnitude of $\Delta_0$ and the number of d e-'s, the metal center is refer to as low spin or high spin
-- when $\Delta_0$ is large, the $d_{x^2-y^2}$ & $d_{z^2}$ are much higher in E than the other three then the system is low spin
--- e-'s pair in the lower orbitals before jumping to higher ones
--- another consideration is pairing energy, PE (amount of energy needed to pair two electrons spin-up/spin down in a single atomic orbital)
  -> if PE < $\Delta_0$ the system is low spin
-- when $\Delta_0$ is small, $d_{x^2-y^2}$ & $d_{z^2}$ are comparable in E and so the e-'s will go to these slightly higher orbitals before pairing up - this is high spin
--- in this case PE > $\Delta_0$ - it take more energy to pair than to promote
-- Some metals may be both high-spin/low-spin, here are the 1st row TMs:
  Sc$^{+2}$ ($d^{1}$), Ti$^{+2}$ ($d^{2}$), V$^{+2}$ ($d^{3}$) don't have enough e-'s to make a difference
  btwn high-spin/low-spin
  Cr$^{+2}$ ($d^{4}$), Mn$^{+2}$ ($d^{5}$), Fe$^{+2}$ ($d^{6}$), Co$^{+2}$ ($d^{7}$) may be either high-spin/low-spin
  Ni$^{+2}$ ($d^{8}$), Cu$^{+2}$ ($d^{9}$), Zn$^{+2}$ ($d^{10}$) have too many e-'s to make a difference
  btwn high-spin/low-spin
- high field vs weak field
  -- depending on the identity of the ligand attached to the metal center $\Delta_0$ will be large or small
  -- weak-field ligands: produce small electrostatic repulsion btwn the lp and the d-orbitals
    --- this leads to $\Delta_0$ which is small
    --- when $\Delta_0$ is small the PE is higher and therefore the system will more likely be high spin in nature
    --- examples of weak-field ligands: halides (I, Br, Cl)
  -- strong-field ligands: produce large electrostatic repulsion btwn the lp and the d-orbitals
    --- this lead to a large $\Delta_0$
    --- therefore the PE < $\Delta_0$ and the system will be low spin
    --- examples: ethylenediamine (en) and cyanide (CN)
  -- spectrochemical series ranks the ligands in order of the $\Delta_0$
    (weak field) $I^{−} < Br^{−} < S^{−} < SCN^{−} < Cl^{−} < NO_{3}^{−} < F^{−} < OH^{−} < C_2O_4^{2−} < H_2O < NCS^{−} < CH_3CN < NH_3 < en < bipy < phen < NO_2^{−} < PPh_3 < CN^{−} < CO (strong-field)

-- Ex: Which of the following has the shortest wavelength?
  [Ti(H_2O)_6]^{3+}, [Ti(en)_6]^{3+}, [TiCl_6]^{3+}
  We start by looking at the spectrochemical series and ranking them by increasing field: [TiCl_6]^{3+} < [Ti(H_2O)_6]^{3+} < [Ti(en)_6]^{3+}
  the stronger the field the larger the $\Delta_0$ and therefore the shorter the $\lambda$
Therefore, [Ti(en)_6]^{3+} must have the shortest λ
- tetrahedral and square planar complexes

* Back to Electronic Spectra
- the color a solution containing one of these complex ions has is the complementary color of the absorbing photon
- the transition which occurs upon this absorption is between MOs which are primarily d in character which is why we refer to them as d-d
- the symmetry of wavefunctions for S, P, D, F, etc have the same symmetry as their atomic orbital counterparts s, p, d, f, etc
  -- the splitting of these terms in the presence of an octahedral field is similar to the splitting that occurs for their AO counterparts
  -- overall degeneracy is also conserved – the number of microstates will remain constant
- Splitting of the d^n terms in an octahedral field
  -- you may recognize these terms from the Character table of \( \text{O}_h \)

\[
\begin{array}{ccc}
S & \rightarrow & A_{1g} \\
P & \rightarrow & T_{1g} \\
D & \rightarrow & E_{g} + T_{2g} \\
F & \rightarrow & A_{2g} + T_{1g} + T_{2g} \\
G & \rightarrow & A_{1g} + E_{g} + T_{1g} + T_{2g} \\
H & \rightarrow & E_{g} + T_{1g} + T_{2g} \\
I & \rightarrow & A_{1g} + A_{2g} + E_{g} + T_{1g} + T_{2g} + T_{2g}
\end{array}
\]

- spin selection rule: \( \Delta S = 0 \) allowed \( \Delta S \neq 0 \) forbidden

- Tanabe-Sugano Diagrams
  -- represent the energies of the different microstates and their dependence on the field strength generated by the ligands
  -- using these diagrams we can predict how many peaks we would expect to see in our UV-vis spectrum as well as where they are located
  -- the abscissa is always the ground state
  -- Example d^6 T-S Diagram Co^{3+}
    --- x-axis crystal field splitting term (CFSE), y-axis transition energy
-- for the high spin case, $\text{CFSE} \leq 20$, i.e. $\text{[CoF}_6^3^{-}\text{]}
\text{the only allowable transition is } ^5T_{2g} \rightarrow ^5E_g \text{ so we would expect to see}
\text{one absorption peak in the spectrum}

-- for the low spin case, $\text{CFSE} \geq 20$, i.e. $\text{[Co(en)}_3^{3+}\text{]}
\text{we have two allowable transitions so we should see two peaks}
\quad ^1A_g \rightarrow ^1T_{1g} \quad ^1A_g \rightarrow ^1T_{2g}

-- it turns out this does in fact work pretty well at predicting spectra