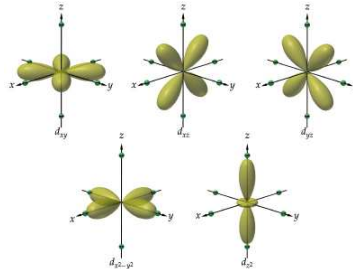
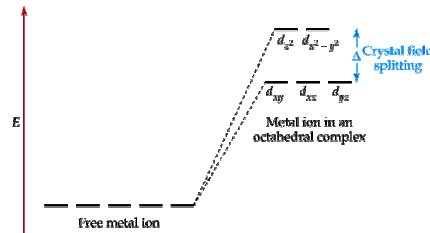


*** Crystal Field Theory**

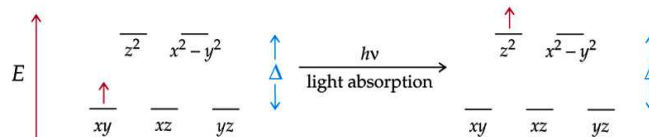
- the colors and magnetic properties of metal complexes are related to the d-orbitals they possess
- crystal field theory attempts to explain these phenomena thru electrostatic interactions
- octahedral complexes



- 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



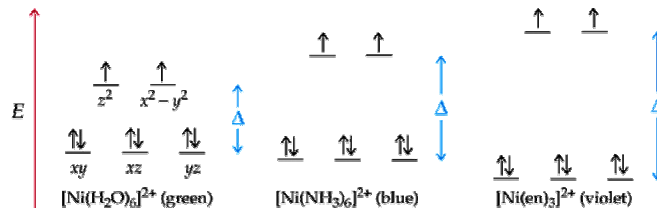
- the difference in energy btwn the two sets of orbitals is the crystal field splitting energy, $\Delta_0 = hc/\lambda$ where $h = 6.63 \times 10^{-34}$ Js and $c = 3.00 \times 10^8$ m/s
- back to color - e.g. $[\text{Ti}(\text{H}_2\text{O})_5]^{3+}$ (500 nm)
- $\Delta E = \Delta_0$ therefore the absorption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

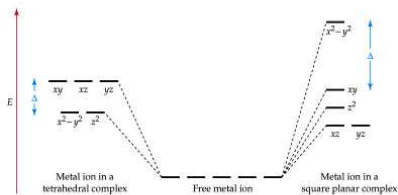
d-orbitals

- depending on the magnitude of Δ_0 and the number of d e-'s, the metal center is refer to as low spin or high spin
 - when Δ_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 Δ_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 Δ_0 will be large or small
 - weak-field ligands: produce small electrostatic repulsion btwn the lp and the d-orbitals
 - this leads to Δ_0 which is small
 - when Δ_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 Δ_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 Δ_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 Δ_0 and therefore the shorter the λ

Therefore, $[\text{Ti}(\text{en})_6]^{3+}$ 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

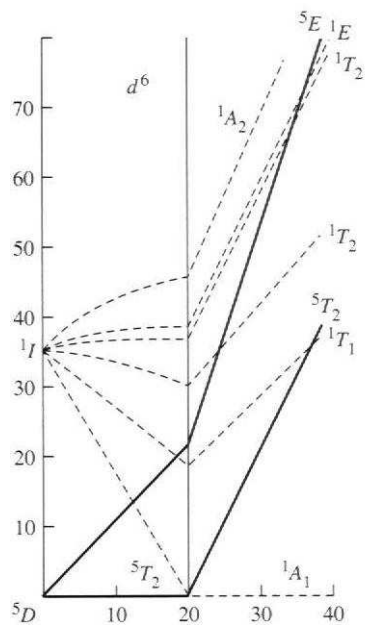
-- you may recognize these terms from the Character table of O_h

	Microstates
$S \rightarrow A_{1g}$	1
$P \rightarrow T_{1g}$	3
$D \rightarrow E_g + T_{2g}$	2 + 3
$F \rightarrow A_{2g} + T_{1g} + T_{2g}$	1 + 3 + 3
$G \rightarrow A_{1g} + E_g + T_{1g} + T_{2g}$	1 + 2 + 3 + 3
$H \rightarrow E_g + T_{1g} + T_{1g} + T_{2g}$	2 + 3 + 3 + 3
$I \rightarrow A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$	1 + 1 + 2 + 3 + 3 + 3

- 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, $CFSE \leq 20$, i.e. $[CoF_6]^{3-}$
the only allowable transition is ${}^5T_{2g} \rightarrow {}^5E_g$ so we would expect to see
one absorption peak in the spectrum
- for the low spin case, $CFSE \geq 20$, i.e. $[Co(en)_3]^{3+}$
we have two allowable transitions so we should see two peaks
 ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ${}^1A_{1g} \rightarrow {}^1T_{2g}$
- it turns out this does in fact work pretty well at predicting spectra