# Crystal Field Theory

1. What is the crystal field model?

    It is a model that views complex ions as being held together ionically (this is not actually the case, but it allows for a simplification of the model). The metal (M) is the cation and the ligands are negative point charges.

2. Show the interaction between the d-orbital and the negative point charge ligands

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

d_{xz} d_{yz}
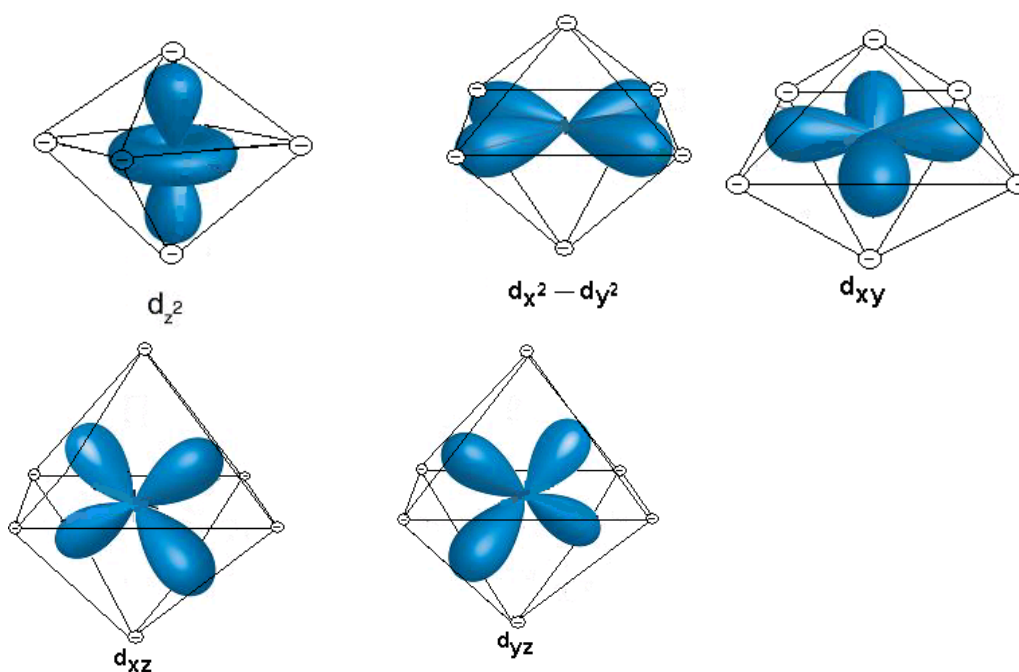
3. Based on the diagrams above, would all of the d orbitals have the same energy? If not which would be higher energy?

    d_z2 and $d_x2 _{-y}2$

    They are high energy because the orbitals (which hold electrons) are directly touching the negative point charges. Negative and negative in contact is highly repulsive.

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

They are lower energybecause the orbitals sit between the negative point charges (there is no direct contact).
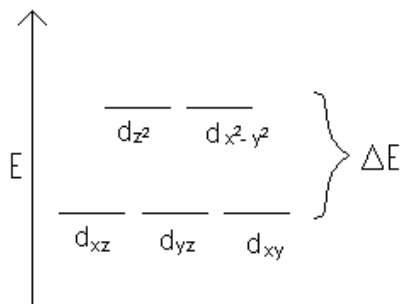
4.   The phenomena of d orbital splitting can happen two ways

   a. Large ΔE – this is called the strong field case. In this case you fill the d_{xz}, d_{xy}, d_{yz} orbitals first and then proceed onto the next level. This leads to something called the "low spin" case in which you have the smallest number of unpaired electrons

   b. Small. ΔE – this is called the weak field case. In this case you spread the electrons out over all of the orbitals, putting one electron each before you proceed to pairing the electrons up. This leads to something called the "high spin" case in which you have the largest number of unpaired electrons

5.   What affects the type of splitting that will happen?

   ●   Charge on Metal
   ●   Electronegativity of the Ligand (↑electronegativity, ↓ΔE)

   a. General Ligand Ordering

   $CN^- > NO_2^- > (en) > NH_3 > H_2O > {^-}OH > F^- > Cl^- > Br^- > I^-$

6.   The greater the charge on the metal the stronger the splitting.

       The ligands move closer to the more attractive m, increasing the

repulsion between the orbitals and negative point charge ligand.

7. The Crystal Field Method can be used to explain the

    a. Magnetism

    a. Color (ΔE)

8. How does this model explain color?

    Color that is seen is related to the ΔE between the separated d orbitals. That difference in energy is equivalent to the energy found in the visible light spectrum. Electrons can be promoted if they are provided enough energy to promote from a lower orbital level to a higher level (assuming that the higher level orbitals are not full).

9. How can we determine the color we will see?

    Using the color wheel – we will see the color opposite to the one absorbed.

    Remember that violet is high energy (i.e. wavelength associated with stronger field cases) and red is low energy (i.e. wavelength associated with weaker field cases).
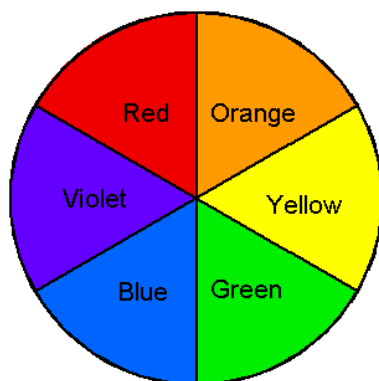

For example, is you were told that a complex ion absorbed light in the green area, you would see the color red. If you saw the color blue that would mean that the energy absorbed is associated with the orange portion of the spectrum.
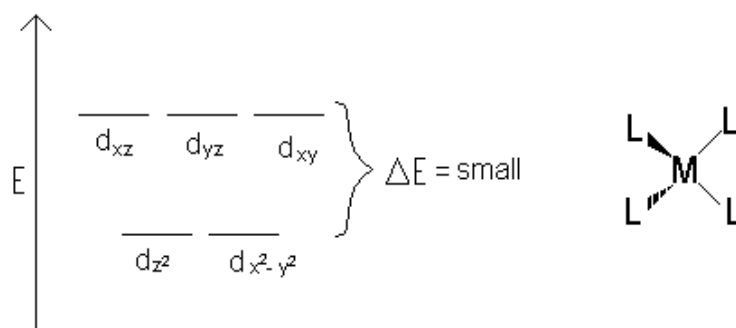
10.   What is the d-orbital splitting for

    a. Tetrahedral

Weak field case *always* applies. There is no direct contact with any of the orbitals and the negative point charges. d_{xz}, d_{yz}, d_{xz} just come closer to the charges, so they are slightly higher energy.
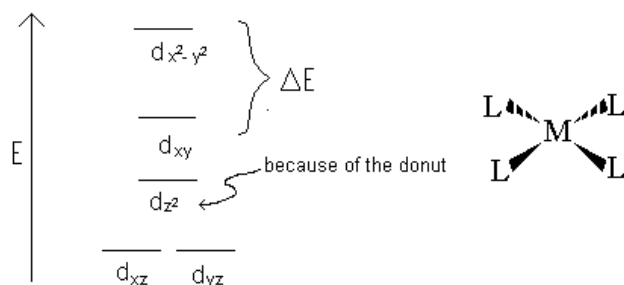
d_{z^2} $d_{x^2-y^2}$

d_{xy} d_{xz} d_{yz}
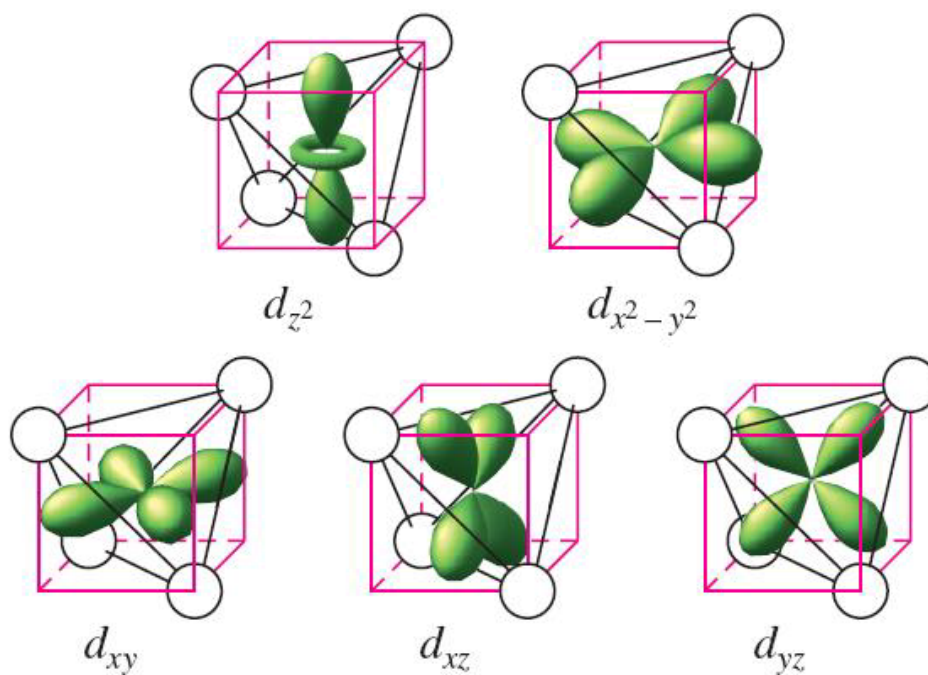
Leading to the following ordering:

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

ΔE = small

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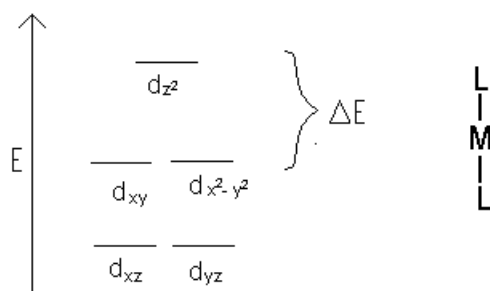
E

b. Square Planar

Using similar process of lining d orbitals up with the point charge locations for a square planar molecule we arrive with the following ordering:

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

ΔE

E

d_{xy}

—— because of the donut

d_{z^2}

d_{xz} d_{yz}

c. Linear

d_{z^2}

ΔE

E

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

d_{xz} d_{yz}

11.   How does the electronegativity of a ligand affect the d orbital splitting?

The more electronegativity, the lower the energy of the electrons, the more tightly bound the electrons are to the ligand. Due to this, the ligand/metal atomic orbitals don't mix as much, meaning a smaller energy split between d orbitals.

12.   Compounds of copper(II) are generally colored, but compounds of copper(I) are not. Explain. Would you expect $Cd(NH_3)_4Cl_2$ to be colored?

Looking at the electron configuration can help to explain this observation.

Cu^+: $3d^{10}$ for this compound the d orbitals are full – meaning there si no

room for the electrons to be promoted up. If electrons cannot be promoted up, there can be no release of energy when they fall back down – no release of energy means we see no color. Remember that the color that we see is related to the ΔE of the d orbitals split.
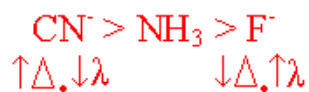
Cu^{2+}: $3d^9$: here is there is room for electrons to promote up.

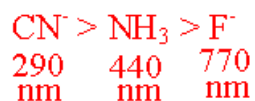Cd^{+2}: $4d^{10}$: full orbital, no rrom for promotion → no color.

13.   Consider the complex ions $Co(NH_3)_6^{3+}$, $Co(CN)_6^{3-}$, and CoF_6^{3-}/ The wavelengths of absorbed electromagnetic radiation for these compounds are (in no specific order) 770 nm, 440 nm, and 290 nm. Match the complex ion to the wavelength of absorbed electromagnetic radiation.

All of the ligands are attached to the same metal. So we just have to consider the ordering of the ligands and which lead to the strongest field. Remember that energy and wavelength are inversely proportional, so as energy goes up, wavelength goes down.

Based on our previous ordering listing (#38) we see:

$$CN^- > NH_3 > F^-$$
$$\uparrow\Delta,\downarrow\lambda \qquad \downarrow\Delta,\uparrow\lambda$$

This means that

$$CN^- > NH_3 > F^-$$
$$290 \quad 440 \quad 770$$
$$nm \quad\; nm \quad\; nm$$
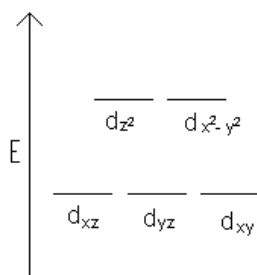
14.   How many unpaired electrons are in the following complex ions?
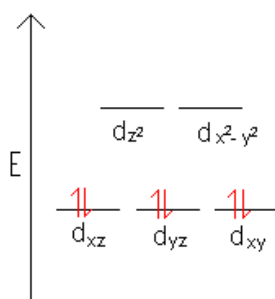
a. $Ru(NH_3)_6^{2+}$ (low spin case)

The charge on the Ru = +2
It would have a d orbital electron configuration of $4d^6$

As NH_3 is a monodentate ligand, the coordination number for Ru = 6
This tells us that it has octahedral geometry. So we will be looking at
the d orbital split for the octahedral case.

We have six electrons to put into the diagram, because it is a low spin
case, that means it is strong field and we fill the lower d orbitals
before moving onto the higher energy d orbitals.
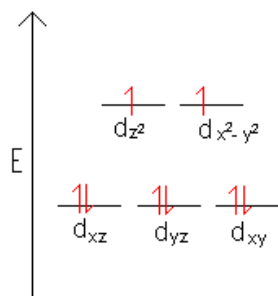

There are no unpaired electrons.

b. $Ni(H_2O)_6^{2+}$

The charge on the Ni = +2
It would have a d orbital electron configuration of $3d^8$

As H_2O is a monodentate ligand, the coordination number of Ni = 6
This tells us that it has octahedral geometry. So we will be looking at
the d orbital splitting for the octahedral case:

We have 8 electrons to put in. In this case they did not indicate
whether it was high spin or low spinp; that, is because it would be
irrelevant as we will have to start filling the higher d orbitals
regardless of the energy split based on number of electrons present.

E

$\underset{d_{z^2}}{\uparrow} \quad \underset{d_{x^2-y^2}}{\uparrow}$

$\underset{d_{xz}}{\uparrow\downarrow} \quad \underset{d_{yz}}{\uparrow\downarrow} \quad \underset{d_{xy}}{\uparrow\downarrow}$

There are 2 unpaired electrons.
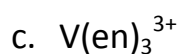
c. $V(en)_3{}^{3+}$

The charge on the V = +3
It would have a d orbital electron configuration of $3d^2$

As (en) is a bidentate ligand, the coordination number of V = 6
This tells us that it has octahedral geometry. So we will be looking at the d orbital splitting for the octahedral case:

We have 2 electrons to put in. In this case they did not indicate whether it was high spin or low spin, that is because it would be irrelevant as we will would not have to use the higher energy orbitals (there are not enough electrons).

E

$\underset{d_{z^2}}{\quad} \quad \underset{d_{x^2-y^2}}{\quad}$

$\underset{d_{xz}}{\uparrow} \quad \underset{d_{yz}}{\uparrow} \quad \underset{d_{xy}}{\quad}$
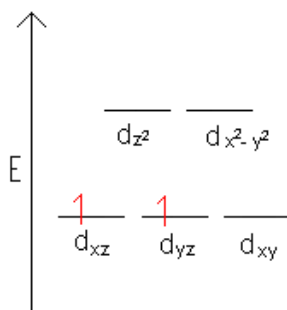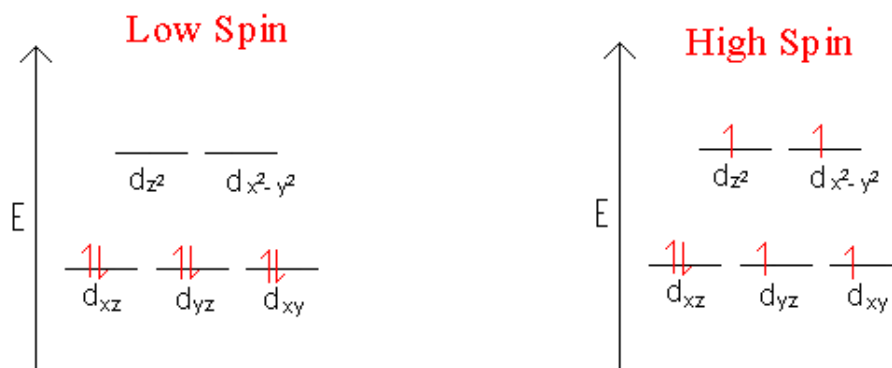
There are 2 unpaired electrons.

15. Draw the *d*-orbital splitting for the octahedral complex ions in each of the following.

a. Fe^{2+} (high and low spin)

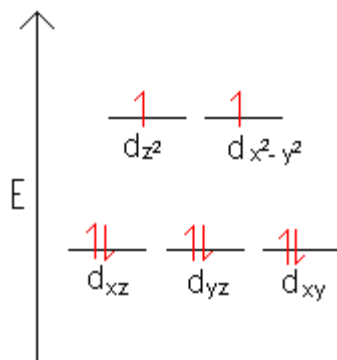First determine the number of electrons in the d orbital.
Fe^{2+}: $3d^6$

Low Spin

$$\frac{\quad}{d_{z^2}} \quad \frac{\quad}{d_{x^2-y^2}}$$

E

$$\frac{\uparrow\downarrow}{d_{xz}} \quad \frac{\uparrow\downarrow}{d_{yz}} \quad \frac{\uparrow\downarrow}{d_{xy}}$$

High Spin

$$\frac{\uparrow}{d_{z^2}} \quad \frac{\uparrow}{d_{x^2-y^2}}$$

E

$$\frac{\uparrow\downarrow}{d_{xz}} \quad \frac{\uparrow}{d_{yz}} \quad \frac{\uparrow}{d_{xy}}$$

b. Ni^{2+}

First determine the number of electrons in the d orbital.
Ni^{2+}: $3d^8$

$$\frac{\uparrow}{d_{z^2}} \quad \frac{\uparrow}{d_{x^2-y^2}}$$

E

$$\frac{\uparrow\downarrow}{d_{xz}} \quad \frac{\uparrow\downarrow}{d_{yz}} \quad \frac{\uparrow\downarrow}{d_{xy}}$$

c. Zn^{2+}

First determine the number of electrons in the d orbital.
Zn^{2+}: $3d^{10}$

E

$\underset{d_{z^2}}{\underline{\uparrow\downarrow}} \qquad \underset{d_{x^2-y^2}}{\underline{\uparrow\downarrow}}$

$\underset{d_{xz}}{\underline{\uparrow\downarrow}} \qquad \underset{d_{yz}}{\underline{\uparrow\downarrow}} \qquad \underset{d_{xy}}{\underline{\uparrow\downarrow}}$