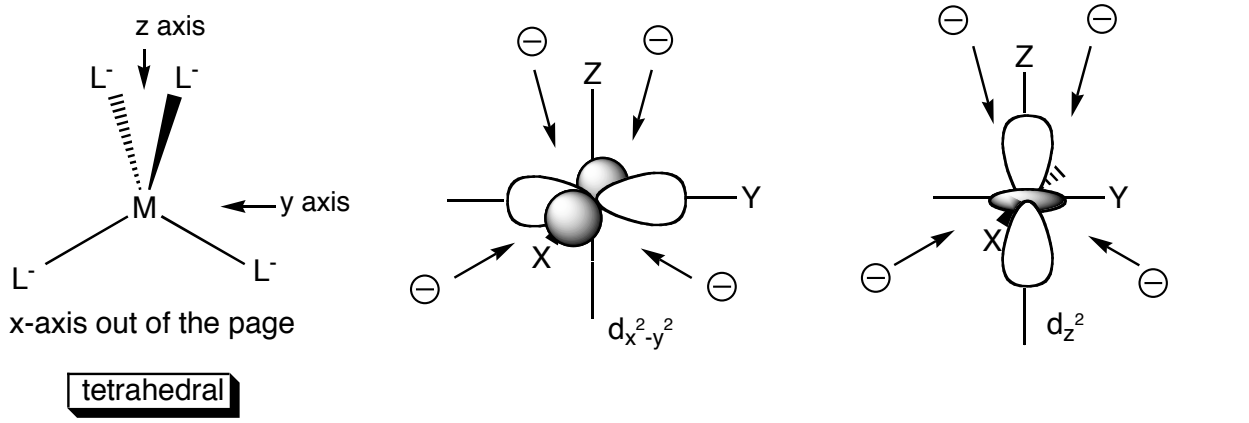
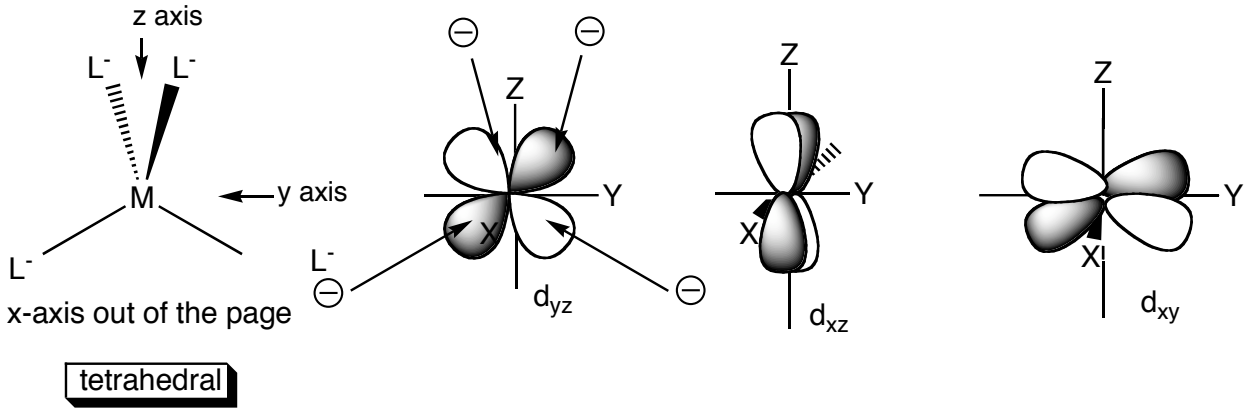
5.111 Lecture Summary #29
Transition Metals
Topic: Crystal Field Theory Continued, and Magnetism Chapter 16 p 631-637

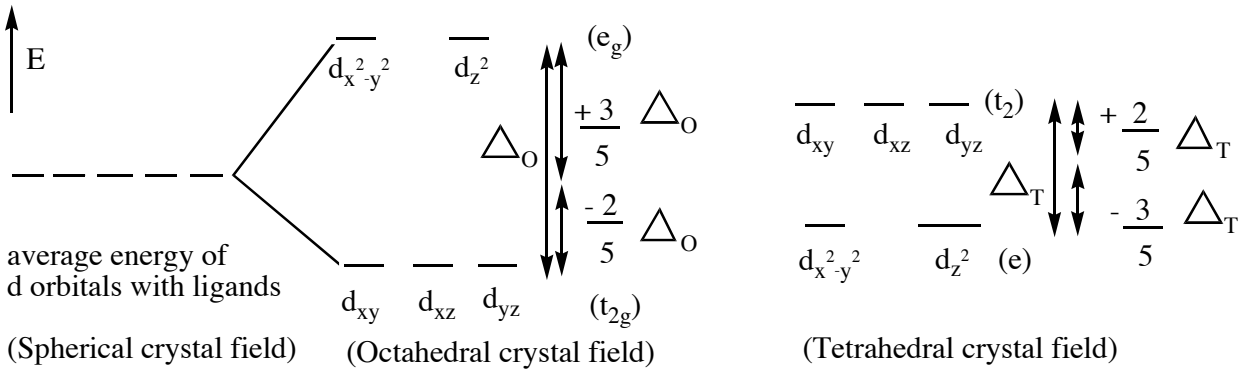
Magnetism
Compounds possessing unpaired electrons are paramagnetic (attracted by magnetic field); those in which the electrons are paired are diamagnetic (repelled by magnetic field).

Crystal Field Theory: Octahedral Case (See Lecture #28)
Crystal Field Theory: Tetrahedral Case
The tetrahedral crystal field splitting energy (Δ_T) is smaller than for octahedral complexes because the point charges are not directed at any orbital set.





Geometry of tetrahedral complexes result in greater orbital destabilization for d_{yz}, d_{xz}, d_{xy} than for $d_{x^2-y^2}$ and d_{z^2} (opposite of octahedral). There is more repulsion between the ligand negative point charges and the d-orbitals that are 45° off axis (d_{yz}, d_{xz}, d_{xy}) than there is between the ligand negative point charges and the d-orbitals that are on axis (d_{z^2} and $d_{x^2-y^2}$). d_{yz}, d_{xz}, d_{xy} have the same energy with respect to each other (degenerate). d_{z^2} and $d_{x^2-y^2}$ have the same energy with respect to each other (degenerate).



Δ_T is the tetrahedral crystal field splitting energy

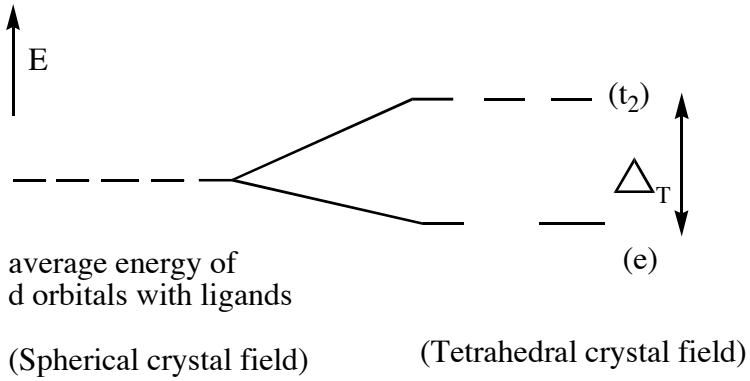
Again, Δ_T is smaller than Δ_o because the point charges are not directed at any orbital set in a tetrahedral crystal field. Because Δ_T is small, many tetrahedral complexes are high spin. You can assume that they are all high spin.

Because the overall energy in the tetrahedral crystal field is maintained, t_2 orbitals (d_{xy}, d_{xz}, and d_{yz}) go up in energy by 2/5, and the e orbitals ($d_{x^2-y^2}$ and d_{z^2}) go down in energy by 3/5.

Tetrahedral Example for Cr^{3+}

(**a**) figure out d electron count

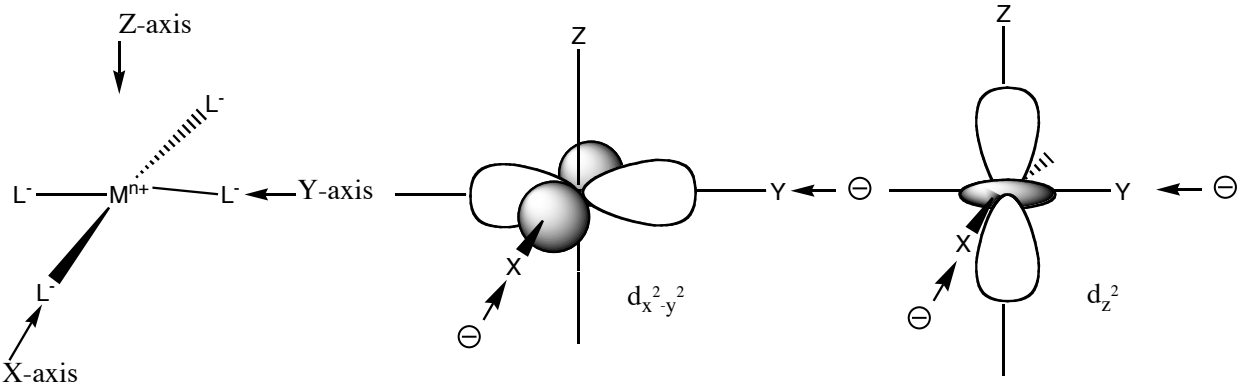
(**b**) draw tetrahedral crystal field splitting diagram, label orbitals, and fill in electrons



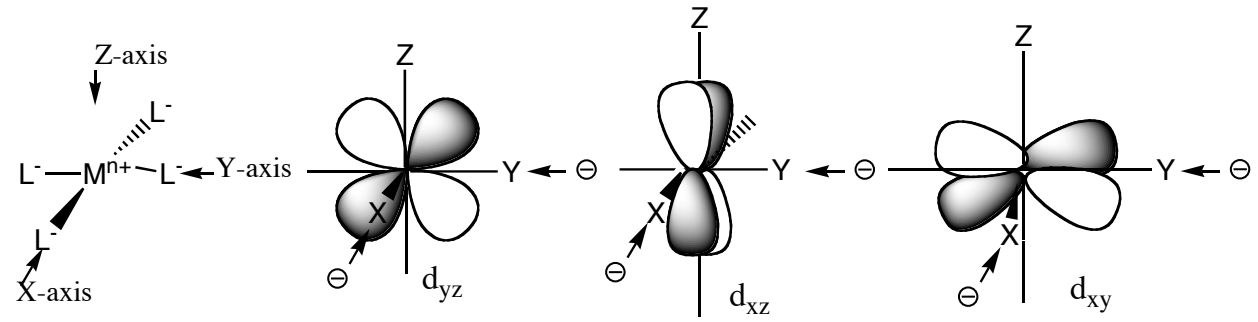
(c) Write d^n electron configuration:

(**d**) How many unpaired electrons?

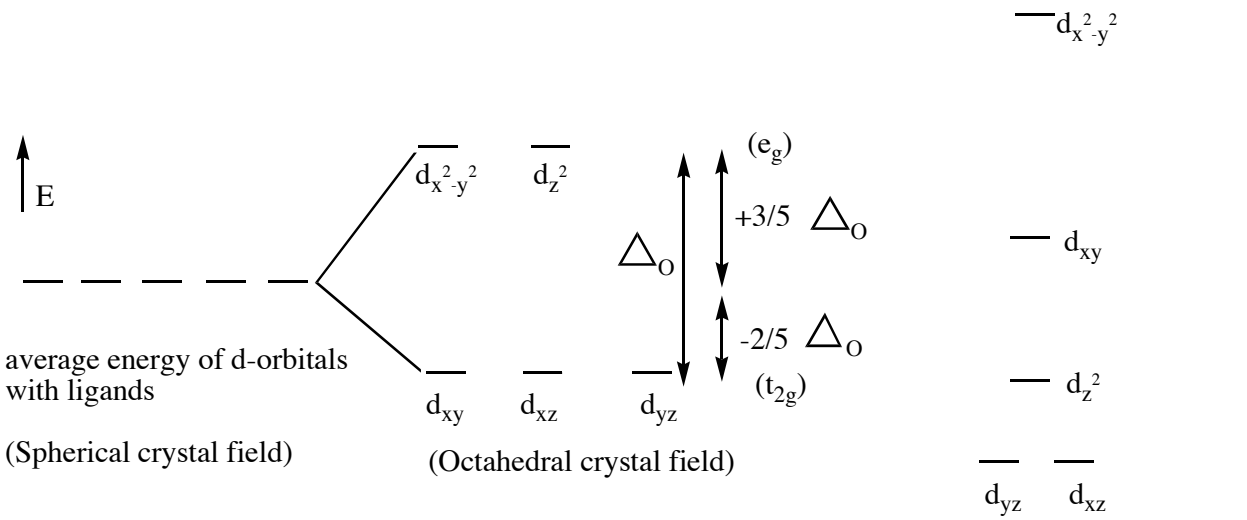
Crystal Field Theory: Square Planar Case



Square planar	lots of repulsion ligand point charges directed at orbitals Destablized compared to all other d-orbitals	much less repulsion than in octahedral crystal field. Less repulsion than for $d_{x^2-y^2}$ and for d_{xy}

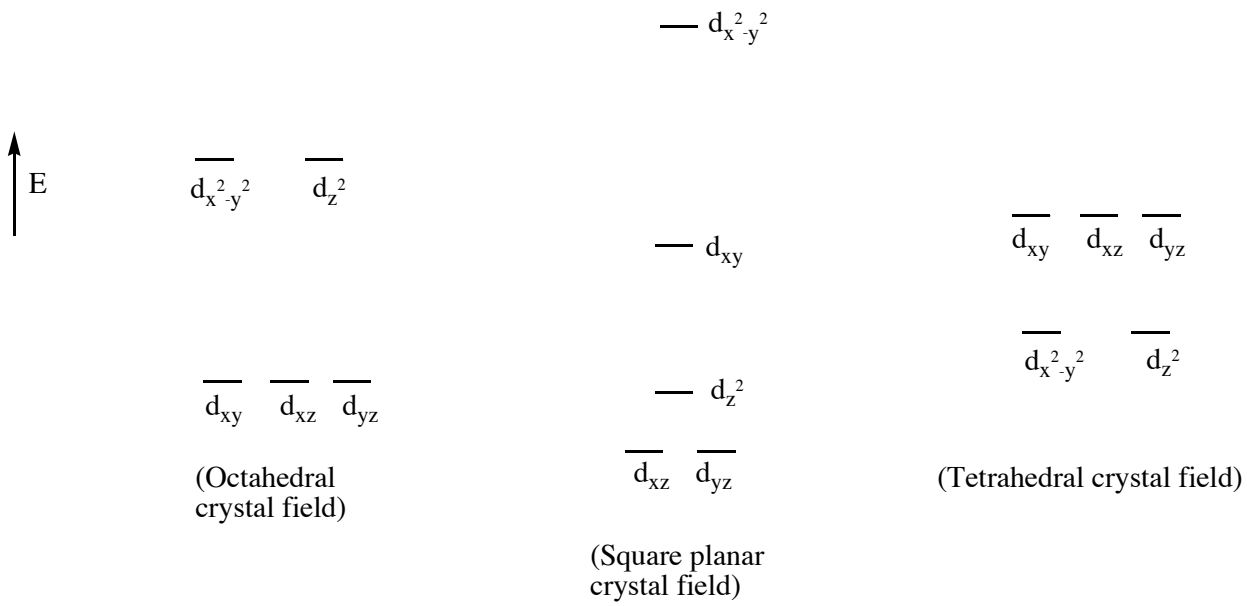


Square planar	stabilized compared to d_{xy} and $d_{x^2-y^2}$	stabilized compared to d_{xy} and $d_{x^2-y^2}$	more repulsion than for d_{yz}, d_{xz}, and d_{z^2}. Less repulsion than for $d_{x^2-y^2}$ since orbitals are 45° off axis in d_{xy}.



The overall energy of the square planar crystal field is maintained as well, but the relative energies of each of the d-orbitals are more complicated and you are not expected to know them.

<u>Putting it all together</u>: If a Ni^{2+} (d^8) center in an enzyme is found to be diamagnetic, does it have square planar, tetrahedral, or octahedral geometry?



Answer:

An example of a square planar Ni site in Nature is found in enzyme called acetyl-CoA synthase.

5.111 Principles of Chemical Science

Fall 2008