Topic VI

Bonding and Physical Properties of Metal Complexes

VI.1 Module 31: Crystal Field Theory

- The first attempt to understand and rationalize the electronic structure of transition metal complexes.

    - Originally introduced to analyze crystals' electronic structure.
    - Since the coordination of a central atom in a crystalline lattice closely mimics that of it in a coordination complex, the concepts of crystal field theory can easily be transferred to chemistry.

- Suggested reading: Miessler et al. (2014) Section 10.2.

- Refresher on d-orbitals.

    - There are four d-orbitals with four lobes and one strange d_{z^2} orbital.
    - Higher energy level ones have lobes corresponding to the change in sign of the radial component.
    - The d_{z^2} orbital is a linear combination of two four-lobed orbitals; it is created to reconcile mathematical theory with physical reality (the Pauli exclusion principle).

- Crystal field theory describes an electrostatic (ionic) approach to bonding — it is so named because it was first applied to crystalline substances.

    - Interactions between filled d-orbitals and ligands with excessive electrons are repulsive.

- Assumptions:

    1. Metal ion at the center.
    2. Ligands are treated as point charges.
    3. Bonding occurs through M^+ and L^- electrostatic attraction.
    4. Bonding is purely ionic.
    5. M and L electrons repel each other.
    6. d-orbital degeneracy is broken as ligands approach.

- Consider d-orbitals bonding to six ligands.

    - Keep Coulomb's Law ($E \propto \frac{q_1 q_2}{r}$) in mind: d-orbitals that overlap more with the ligands (smaller r) will be more destabilized (higher E).
    - d_{z^2} overlaps with the two axial ligands, and $d_{x^2-y^2}$ overlaps with the four equatorial ligands.
    - None of d_{xy}, d_{xz}, and d_{yz} overlap significantly with any ligands.

     – Therefore, the five degenerate d-orbitals split into the $\boldsymbol{t_{2g}}$ **set** and the $\boldsymbol{e_g}$ **set**.

     – When the orbitals split, they maintain an energetic "center of mass," i.e., their combined energy as molecular orbitals must still be equal to their combined energy as degenerate, atomic orbitals. Thus, the stabilization energy of the three orbitals in the t_{2g} set is $-\frac{2}{5}\Delta$ while the destabilization energy of the two orbitals in the e_g set is $\frac{3}{5}\Delta$, where Δ is the **crystal field splitting parameter**.

- $\boldsymbol{t_{2g}}$ **set**: The three orbitals that lie between the ligand donor atoms.

- $\boldsymbol{e_g}$ **set**: The two orbitals that lie along the Cartesian coordinates, and so are adjacent to the donor atoms of the ligands, raising the set in energy.

- **Crystal field splitting parameter**: Different ligands produce different extents of splitting between the e_g and the t_{2g} levels. This energy difference is the crystal field splitting parameter. *Units* cm^{-1}. *Also known as* $\boldsymbol{\Delta}$, $\boldsymbol{10Dq}$.

- Experimental verification of orbital splitting.

     – Consider a coordination complex with just one d-electron, i.e., electron configuration d^1.

        ■ An example is $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

     – In such a complex, the electron will occupy the lowest energy orbital available, i.e., one of the three degenerate t_{2g} orbitals.

     – Shining light on the complex can promote the t_{2g} electron into the e_g energy level.

     – The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at $20\,300\,\text{cm}^{-1}$, or $\Delta = 243\,\text{kJ/mol} \neq 0$.

- Note that $1000\,\text{cm}^{-1} = 11.96\,\text{kJ/mol} = 2.86\,\text{kcal/mol} = 0.124\,\text{eV}$.

- **Crystal field stabilization energy**: The overall change in energy when the d-subshell splits, which is given by $(0.4n(t_{2g}) - 0.6n(e_g))\Delta$ where $n(t_{2g})$ and $n(e_g)$ are the numbers of electrons in the t_{2g} and e_g levels respectively. *Also known as* **CFSE**.

     – When splitting of the d-subshell occurs, the occupation of the lower energy t_{2g} level by electrons causes a stabilization of the complex, whereas occupation of the e_g level causes a rise in energy. The t_{2g} level drops by 0.4Δ, whereas the e_g level is raised by 0.6Δ.

- High and low-spin complexes:

     – Whether a complex is **high-spin** or **low-spin** depends on Δ.

     – If $\Delta > P$ where P is the **spin-pairing energy**, then the complex is low-spin, and vice versa if $\Delta < P$.

- **High-spin** (complex): A complex with d^4 to d^8 electron configuration, where the electrons spread out and occupy the whole d-subshell.

     – High-spin complexes are often paramagnetic.

     – Electrons fill the whole d-subshell according to Hund's rule.

- **Low-spin** (complex): A complex with d^4 to d^8 electron configurations, where the t_{2g} energy level is filled first.

     – Low-spin complexes are often diamagnetic.

- **Spin-pairing energy**: The energy required to take pairs of electrons with the same spin orientation, and pair them up with the opposite spin. *Also known as* $\boldsymbol{P}$.

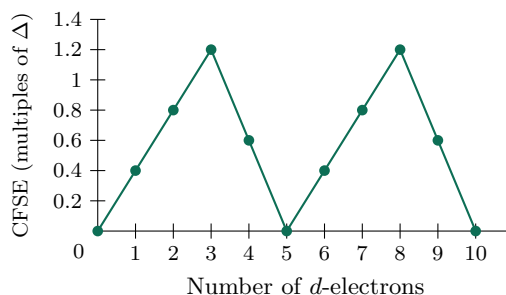- Calculating CFSE of d^0 to d^{10} high-spin M (II) ions.

Figure VI.1: CFSE as a function of the number of d-electrons.

  – Most first row and many second and third row transition elements will be prone to forming high-spin complexes.
  – The variation shown in Figure VI.1 reveals that complexes of metal ions with high CFSE (such as Ni (II)) will undergo greater stabilization, and vice versa for metal ions with low CFSE (such as Ca (II)).
  – The predicted variation matches relatively well with formation constant values ($\log K_1$) obtained experimentally for these compounds.

- We can also look at orbital splitting in coordination compounds of other geometries.

  – In T_d compounds, for example, the splitting is flipped with the $d_{xy,xz,yz}$ orbitals destabilized and the $d_{x^2-y^2,z^2}$ orbitals stabilized.
  – We can also look analyze linear and square planar geometries.

- Merits of crystal field theory:

  – Can be used to predict the most favorable geometry for the complex.
  – Can account for why some complexes are tetrahedral and others are square planar.
  – Useful in interpreting magnetic properties.
  – The colors of many transition metal complexes can be rationalized.

- Limitations of crystal field theory:

  – Becomes less accurate as delocalization (covalent character) increases.
  – Point charge does not accurately represent complexes.
  – Does not account for π bonding interactions.
  – Does not account for the relative strengths of the ligands.

VI.2 Module 32: Ligand Field Theory for the O_h σ-Only Case

2/17:
- Suggested reading: Miessler et al. (2014) Section 10.3.

- Ligand field theory:

  – Application of molecular orbital theory to transition metal complexes.
  – Ligands are not point charges.
  – Takes into account π bonding.

■ I.e., accounts for the fact that ligands can be σ-donors, π-donors, π-acceptors, or sometimes multiple simultaneously.

– Can be used to explain the spectrochemical series.

– Better than valence-bond model or crystal field theory at explaining experimental data.

- Octahedral σ-only MO diagram workflow:

  1. Assign a point group.
  2. Choose basis function.
  3. Apply operations.
  4. Generate a reducible representation.
  5. Reduce to irreducible representations.
  6. Combine orbitals by their symmetry.
  7. Fill MOs with e^-.
  8. Generate SALCs of peripheral atoms.
  9. Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs.

- MH_6 example.

  – Point group: O_h.

  – Basis funtions: $1s$-orbitals on the ligands (you can also choose the σ-bond vectors if you wish [if it's easier for you]), and s, p, d-orbitals on the metal center.
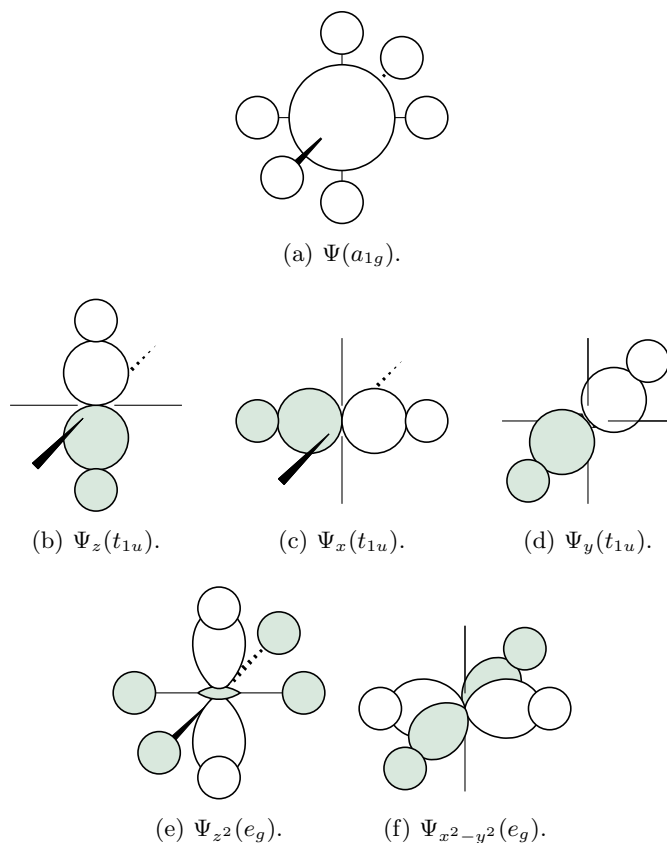
  – Apply operations & generate a reducible representation.

$$\Gamma_H = (6, 0, 0, 2, 2, 0, 0, 0, 4, 2) = A_{1g} + T_{1u} + E_g$$
$$\Gamma_{M_s} = A_{1g}$$
$$\Gamma_{M_p} = T_{1u}$$
$$\Gamma_{M_{d_{x^2-y^2, z^2}}} = E_g$$
$$\Gamma_{M_{d_{xy, xz, yz}}} = T_{2g}$$

  – Combine orbitals by their symmetry.

    ■ In a transition metal compound/coordination complex, the t_{2g} MOs would be the HOMOs and the antibonding e_g MOs would be the LUMOs.

    ■ Since the t_{2g} orbitals are nonbonding, they are reflective of the energy of the metal d-orbitals. Thus, the energy difference between them and the e_g orbitals is equal to the amount by which the e_g orbitals' energy changes during bonding, i.e., the splitting parameter. This energy change is also indicative of the antibonding character of the e_g orbitals, and consequently the strength of the bonding (bigger Δ implies higher energy e_g orbitals implies stronger bonding).

    ■ In LFT, we call this quantity the **ligand field splitting parameter**, as opposed to the crystal field splitting parameter.

    ■ Pauses to consider **weak field ligands** and **strong field ligands**.

  – Generate SALCs of peripheral atoms.

$$\Psi(a_{1g}) = c_1(4s) + c_2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$
$$\Psi_z(t_{1u}) = c_3(4p_z) + c_4(\sigma_1 - \sigma_6)$$
$$\Psi_x(t_{1u}) = c_3(4p_x) + c_4(\sigma_4 - \sigma_2)$$
$$\Psi_y(t_{1u}) = c_3(4p_y) + c_4(\sigma_3 - \sigma_5)$$
$$\Psi_{z^2}(e_g) = c_5(3d_{z^2}) + c_6(\sigma_1 + \sigma_6) + c_7(-\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5)$$
$$\Psi_{x^2-y^2}(e_g) = c_8(3d_{x^2-y^2}) + c_9(\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5)$$
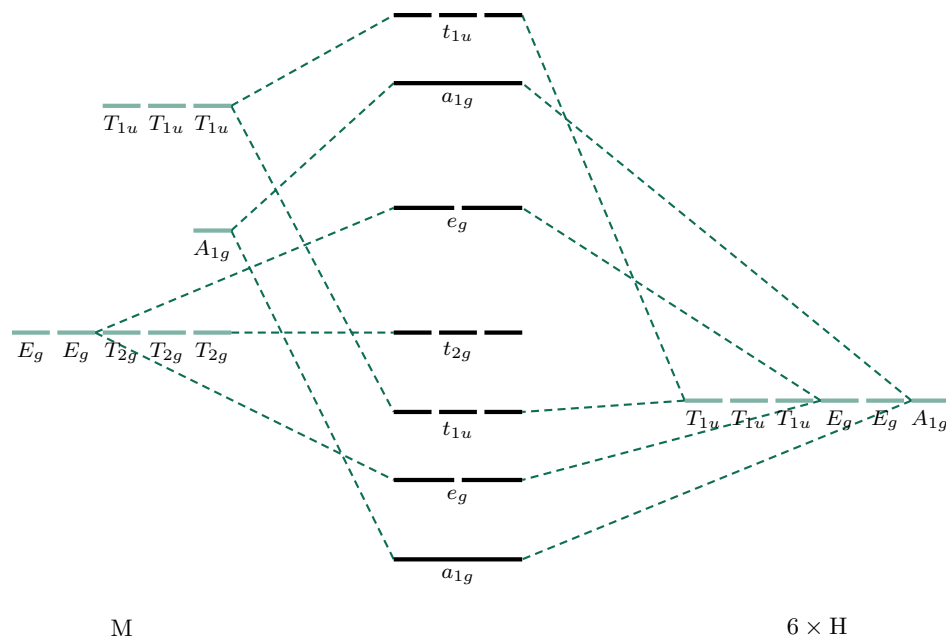
Figure VI.2: MH_6 orbital diagram.

- ■ Recall that the coefficients reflect the degree of overlap.
- ■ Note that for the $\Psi(t_{1u})$ wavefunctions, the in-plane σ-orbitals have zero overlap with the perpendicular $4p$ orbital, hence their coefficient of 0.
  - – Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs.

- • **Weak field ligand**: A ligand with high electronegativity, and thus low energy frontier orbitals.

  - – Weak σ donor.
  - – Weak Lewis base.
  - – Weaker bonding interaction.
  - – Smaller Δ_o.

- • **Strong field ligand**: A ligand with comparable energy frontier orbitals to the d-orbitals of the metal cation.

  - – Strong σ donor.
  - – Strong Lewis base.
  - – Stronger bonding interaction.
  - – Larger Δ_o.

- • Size matters more than Lewis basicity:

  - – Stronger Lewis base $\Rightarrow$ larger Δ_o.
  - – Smaller ligand $\Rightarrow$ larger Δ_o.
  - – However, size overall is more important.
    - ■ This is related to hardness and softness — with a hard Lewis acid metal center, harder ligands will bond with greater strengths.

- • For the halides' Δ_o: $I^- < Br^- < Cl^- < F^-$.

(a) $\Psi(a_{1g})$.

(b) $\Psi_z(t_{1u})$.   (c) $\Psi_x(t_{1u})$.   (d) $\Psi_y(t_{1u})$.

(e) $\Psi_{z^2}(e_g)$.   (f) $\Psi_{x^2-y^2}(e_g)$.

Figure VI.3: MH$_6$ bonding and antibonding MOs.

- If we use p-orbitals pointing toward the center as bases for our peripheral atoms instead of s-orbitals, we get the exact same result.

- Factors that influence $\Delta_{\text{oct}} = \Delta_o = 10Dq$.

  - Metal oxidation state: Increasing the charge increases Δ.

  - Principal quantum number: Increasing n (going down a period on the periodic table) increases Δ, too.

  - Nature of the ligand:

L	Ligand Type	z	Δ_o (cm^{-1})
Cl$^-$	σ, π-donor	$3-$	13 700
H$_2$O	σ-donor	$3+$	17 400
NH$_3$	σ-donor	$3+$	21 500
CN$^-$	σ-donor/π-acceptor	$3-$	26 600

Table VI.1: How the nature of the ligand influences Δ.

VI.3   Module 33: Ligand Field Theory for the O_h $\sigma + \pi$ Case
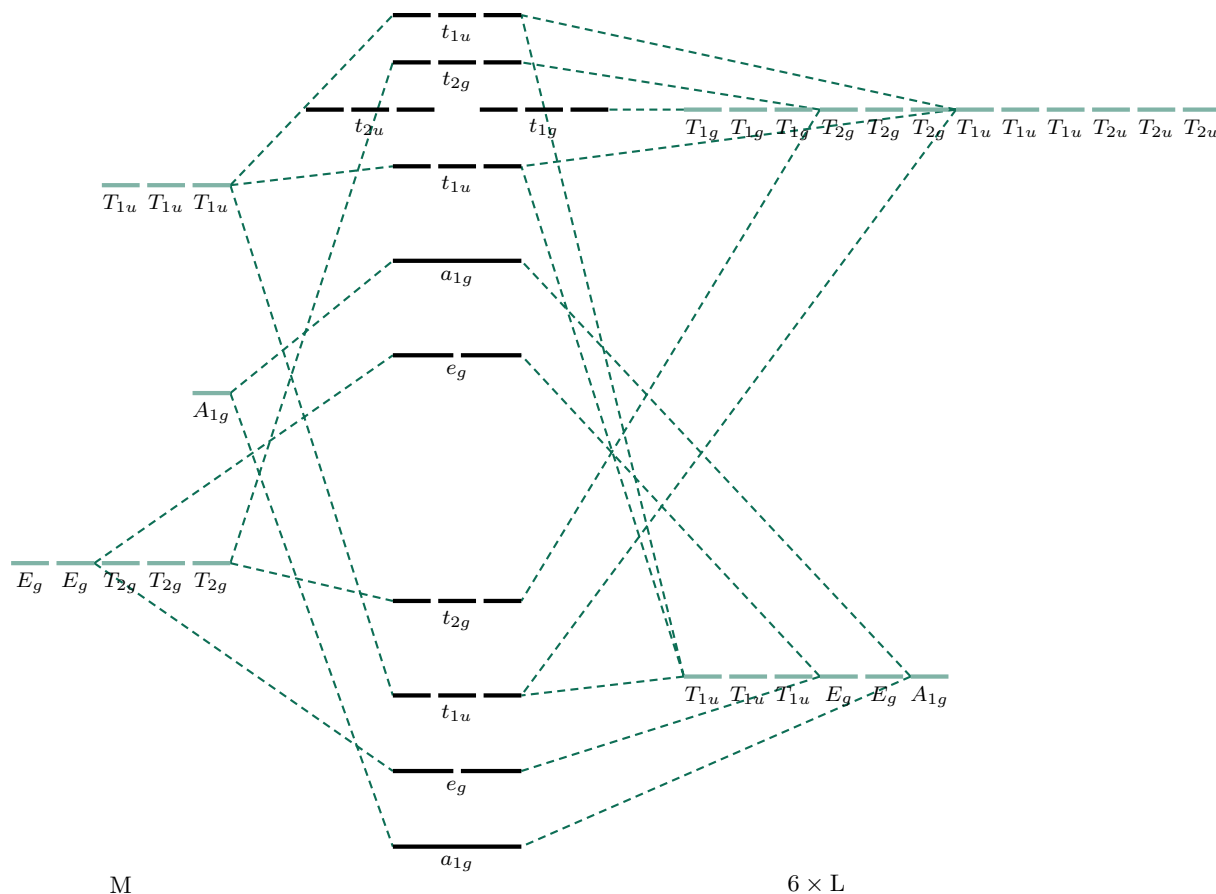
- Consider cyano-ligands (isoelectronic to CO and NO$^+$).

– HOMO is perfect for σ bonding via donation.

– LUMO is perfect for π acceptance from metal d-orbitals.
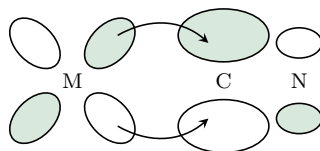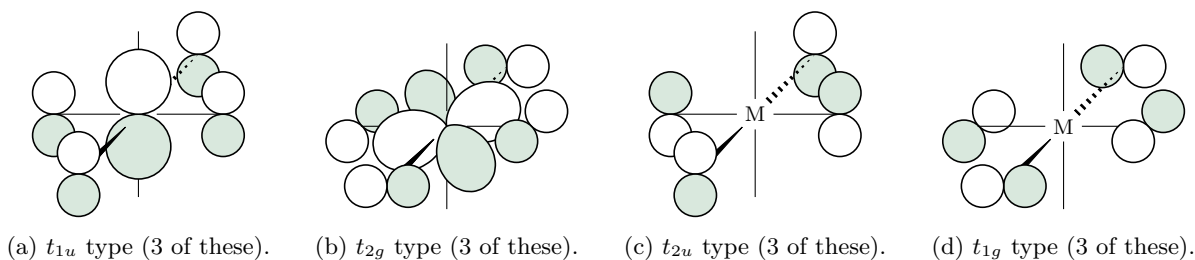

Figure VI.4: LUMO π-acceptance.

■ d_{xz} and π^* orbitals combine with stabilization energy e_π.

– This is how we determine what kinds of donors the ligands in Table VI.1 are. For H_2O, for example, it is not a π-acceptor because its LUMO is a σ^* orbital, not a π^* one (see Figure **??**).

• Octahedral $\sigma + \pi$ bonding:
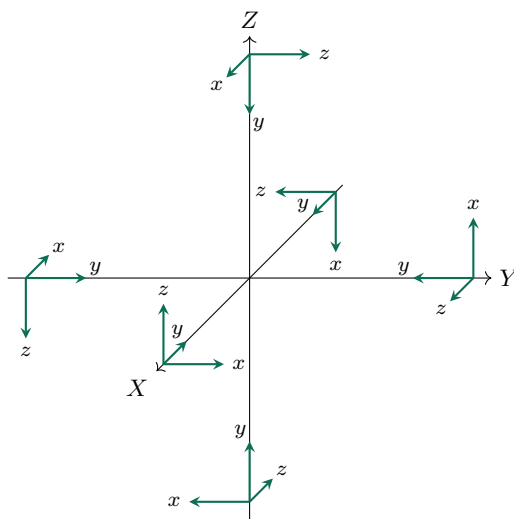
Figure VI.5: Octahedral π-ligand coordinate systems.

– Generate a reducible representation: $\Gamma_{L\pi_{x,z}} = (12, 0, 0, -4, 0, 0, 0, 0, 0, 0) = T_{1g} + T_{2g} + T_{1u} + T_{2u}$.

– Combine orbitals by their symmetry.

Figure VI.6: ML_6 orbital diagram.

2/22:

(a) t_{1u} type (3 of these).   (b) t_{2g} type (3 of these).   (c) t_{2u} type (3 of these).   (d) t_{1g} type (3 of these).

Figure VI.7: ML_6 bonding and antibonding MOs.

- There are three of each type of triply degenerate orbital, formed as in Figure VI.7.

- If the ligand is an empty π-acceptor, π-acid that accepts electrons from M and thus has high energy T_{2g} orbitals, there is a stabilization energy.

  - If the ligand is a filled π-donor, π-base that donates electrons to M and thus has low energy T_{2g} orbitals, there is increased antibonding character.

- The following is a more formal treatment of the effects of π-bonding on Δ in an octahedral complex.

  - If the ligand possesses π-orbitals as well as σ-symmetry (as in Figure VI.4), we need to take into account the overlap of these orbitals with the t_{2g} orbitals of the metal.

- – Two situations may arise: Either the ligand π-orbitals are empty and of higher energy than the metal t_{2g} orbitals, or the ligand π-orbitals are filled and of lower energy than the metal t_{2g} orbitals.
  - – The former case may increase Δ and is the most important case, including ligands such as CO, NO^+, and CN^-. This type of covalency, called π-bonding or back bonding, provides a plausible explanation of the position of these ligands in the spectrochemical series.

- Ligand field strength:

  - – Characteristics of σ-bonding that make for a stronger field:
    - ■ Stronger σ-donor.
    - ■ Strong Lewis base.
    - ■ Stronger bonding interaction.
  - – Characteristics of π-bonding that make for a stronger field:
    - ■ Empty π-acceptor.
    - ■ π-acid.
    - ■ Accepts from M.
  - – And vice versa for what makes a weaker field.

- **Spectrochemical series**: An arrangement from greatest to least of ligands by ligand field strength.

  $$CO, CN^- > phen > NO_2{}^- > en > NH_3 > NCS^- > H_2O > F^- > RCO_2{}^- > OH^- > Cl^- > Br^- > I^-$$

  - – Note that en is ethylenediamine and phen is phenanthroline.
  - – As in Table VI.1, we see that π-acceptors are stronger than pure σ-donors are stronger than π-donors.
  - – With different metal ions, the order of increasing Δ with different ligands is often the same. All metal ions produce high values of Δ in their hexacyano complex, while the hexafluoro complex always produces a low value of Δ. The increase in Δ with the changing of ligands can be placed in an order known as the spectrochemical series.

- Increasing Δ correlates with a color change (because of electron transitions because t_{2g} and e_g orbitals).

VI.4 TA Review Session 2

2/19:
- σ bonds are stronger than π bonds.

- Steric number is also one-half the sum of the number of electrons around the central atom plus the number of bonding electrons each ligand contributes.

  - – For example, in SF_4, SN $= \frac{6+4}{2} = 5$.
  - – A_1 orbitals mix more than B_1, mix more than B_2.

- Determining symmetry of SALCs:

  - – Multiply unmoved atoms by each row in the character table; nonzero rows indicate symmetry under that SALC.
  - – In the SF_4 example, let $F_{a,d}$ be the axial hydrogens and let $F_{b,c}$ be the equatorial ones. Then the projections of F_a are F_a, F_d, F_a, F_d. Multiplying by A_1 gives us $2F_a + 2F_d$...

- When numbering MOs, you're good to start with 1 at the bottom of the diagram (not taking into account the lower energy states).

- We're good to use arcs for bidentate ligand instead of drawing out the full structure.

- We can denote enantiomers with the dashed line (like a mirror plane) between them.

- For neutral coordination centers, put a 0 in parentheses after the compound (in place of a Roman numeral oxidation number).

    - Rubitium tetrafluoroaurate(III).
    - Learn Greek/Latin names!

- BH_2^+ is linear since it is isoelectronic to BeH_2, i.e., the central atom only has two bonding electrons.

    - Reduce $D_{\infty h}$ to D_{2h}.
    - Empty orbitals can still mix occupied orbitals; empty p orbitals are still present in the orbital diagram.
    - BH_2^- would have a different structure (bent).
        - C_{2v}.
    - Know how to create a Walsh diagram!
        - An extra p orbital mixes, lowering energy, in the bent form.

- Compressing a 1D crystal:

    - α decreases, overlap increases, β (interaction integral) increases, band width ($|4\beta|$) increases.
    - Effective mass: $\frac{1}{m^*} = \frac{1}{\hbar^2}(\partial^2 E/\partial k^2)_{k=0}$.

- Review reference materials; skim chapter 9; read over notes.

VI.5   Office Hours (Talapin)

- What is "d.I." and "r.I." with respect to band theory (on the slide with the Wigner-Seitz cell)?

    - Direct lattice (the lattice in physical space) and reciprocal lattice (the lattice in the k-space, the momentum space).
    - FCC is very common lattice in metals and semiconductors.
    - It's reciprocal lattice is the Brillouin zone, the Wigner-Seitz cell (the boronomic cell/boronomic tesselation in mathematics?).
    - In CHEM 39000, he covers this more (after a more direct treatment of what a direct and reciprocal lattice is).

- Aquo or aqua?

- When Wooje went through the SF_4 example on the practice exam today, he applied the projection operator to two different atoms to generate 4 SALCs. Why?

    - SALCs generated from the same atom the same way are similar. However, linear combinations of two SALCs are distinct from their components.
    - We *do* have three SALCs for NH_3, but we only have two states, so we have to eliminate one SALC by combining it with another to arrive at two solutions (one original and one linear combination) with physical meaning (we will actually see in NH_3 both of the final SALCs we arrive at).

- Does the d_{z^2} orbital actually exist (like can we get one of those electron density plots for an atom that shows its outline), or is it just a mathematical tool?

    - Yes — see explanation of previous question.

- It won't harm you to put the numbers on the MOs.

    - If we number, we can number from the bottom and put a note that we are not counting for more core electrons.

VI.6 Module 34: Magnetic Properties of Transition Metal Complexes

- Electrons occupy the lowest energy triply degenerate orbitals in d^1, d^2, and d^3 configurations.

- However, in the d^4 configuration:
  - Low spin: The fourth electron will pair up in the lower t_{2g} energy level.
  - High spin: The fourth electron will occupy a higher energy e_g orbital.

- The pairing energy Π is made up of two parts (refer to Figure 0.9 and the associated discussion):
  1. Coulombic repulsion energy caused by having two eletrons in the same orbital. Destabilization energy contribution of Π_c for each doubly occupied orbital. Has a positive sign because it increases the energy of the system.
  2. Exchange stabilization energy for each pair of electrons having the same spin and same energy. Stabilizing contribution of Π_e for each pair having same spin and same energy. Has a negative sign because it reduces the energy of the system.

- Deciding whether the fourth electron will go into the higher energy e_g orbital at an energy cost of Δ, or be paired at an energy cost of Π.
  - Strong field ligand has big Δ so $\Pi < \Delta$; this implies a low spin configuration.
  - Weak field ligand has small Δ so $\Pi > \Delta$; this implies a high spin configuration.

- We can experimentally discriminate between high- and low-spin compounds by measuring magnetic properties.
  - The Gouy balance can determine the magnetic susceptibility of materials.
  - A more modern way to measure magnetic properties uses a Superconducting Quantum Interference Device, or SQUID.
    - This device is just about the most sensitive machine humanity can build (can detect the magnetic field of the heart/brain).

- Main types of magnetic behavior:

Type	Sign of χ_M	Magnetude of χ_M (cgs units)	Dependence of χ_M on H	Origin
Diamagnetism	−	$1\text{-}500 \times 10^{-6}$	Independent	Electron charge
Paramagnetism	+	$0\text{-}10^{-2}$	Independent	Spin and orbital motion of electrons on individual atoms
Ferromagnetism	+	$10^{-2}\text{-}10^6$	Dependent	Cooperative interaction between magnetic moments of individual atoms
Antiferromagnetism	+	$0\text{-}10^{-2}$	May be dependent	

Table VI.2: Main types of magnetic behavior.

  - Diamagnetism (from electron charge).
  - Paramagnetism (spin and orbital motion of electrons on individual atoms).
  - Ferromagnetism and antiferromagnetism (cooperative interaction between magnetic moments of individual atoms).

- Paramagnetism is much stronger than diamagnetism and overpowers it.

- Ferromagnetism overpowers both.

• Theoretical background for determining magnetic spins experimentally:

  - When we place a sample in a magnetic field of magnitude H, the sample will interact with the magnetic field and magnetize. This magnetization causes the magnetic flux B in the material to differ from the magnetic flux through the space the sample occupies (were the sample not there) by an amount determined by the magnetization parameter M, which is specific to each material. These three quantities are related via the equation

  $$B = H + 4\pi M$$

  - If we divide the flux by the magnetic field, we obtain the magnetic susceptibility per unit volume κ of the material:
  $$\frac{B}{H} = 1 + 4\pi \cdot \frac{M}{H} = 1 + 4\pi\kappa$$

  - This quantity can be normalized by the molecular weight and density of the substance to give the magnetic susceptibility per mole

  $$\chi_M = \kappa \cdot \frac{\text{molecular weight}}{\text{density}}$$

  - Dividing χ_M by Avogadro's number gives the magnetic susceptibility per molecule χ_M^{corr}.
  - **Curie's law** relates χ_M^{corr} to the magnetic moment μ by the formula

  $$\chi_M^{\text{corr}} = \frac{N\mu^2}{3kT}$$

  where N is Avogadro's number, $k = 1.381 \times 10^{23}$ J/K is the Boltzmann constant, and T is the absolute temperature of the substance.

    ■ Note that μ is measured in units of Bohr magnetons where $1\,\text{B\,M} = \frac{eh}{4\pi m_e c}$. As per usual, we have $e = 1.602 \times 10^{-19}$ C is the charge of an electron, $h = 6.626 \times 10^{-34}$ J s is Planck's constant, $m_e = 9.11 \times 10^{-31}$ kg is the mass of an electron, and $c = 2.998 \times 10^8$ m/s is the speed of light.
    ■ We can rearrange Curie's law to express the magnetic moment in terms of χ_M^{corr} as follows.

  $$\mu = \sqrt{3k/N} \cdot \sqrt{\chi_M^{\text{corr}} T}$$

  - Magnetic moment μ and the spin-only formula: Materials that are diamagnetic are repelled by a magnetic field, whereas paramagnetic substances are attracted into a magnetic field, i.e., show magnetic susceptibility. The unpaired electrons in paramagnetic complexes of $3d$-block metal ions create a magnetic field. The magnetic moment μ is then given by the spin-only formula

  $$\mu_{\text{spin-only}} = \sqrt{n(n+2)}$$

  where n is the number of unpaired electrons.

  - In heavier transition metals, we need to account for not just the S quantum number but also L (which accounts for some ground state relativistic effects) by using the formula

  $$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

VI.7 Module 35: Reflections on the Ligand Field Effects in O_h and T_d Complexes

2/24:
- Note that 2nd and 3rd row metals are almost always low-spin, and 4th row transition metals often high-spin.
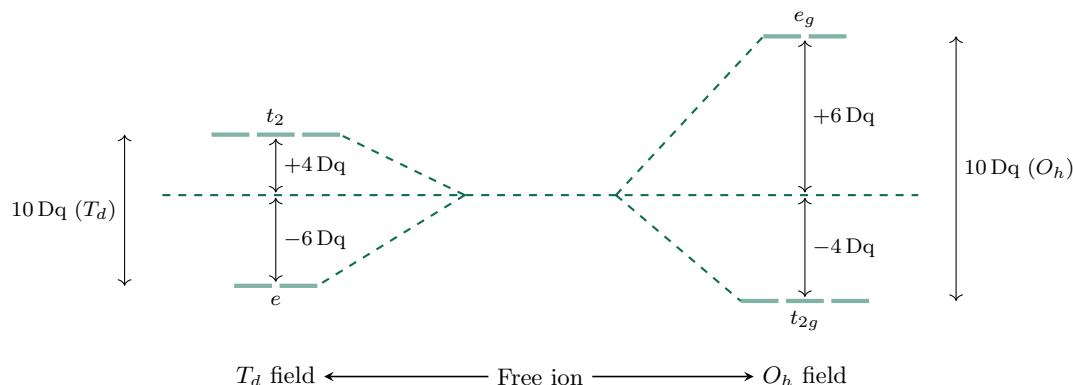
- T_d vs. O_h splitting.

Figure VI.8: T_d vs. O_h splitting.

  - For T_d, 2 e-type orbitals are lower in energy and 3 t_2 orbitals are higher.
    - Note that we do not mark with gerade because T_d molecules lack an inversion center.
  - For O_h, it's reversed.
  - Note that the splitting energy of tetrahedral complexes is less than that of octahedral complexes. This is because there are fewer ligands acting on the d-orbitals of the metal center (4 vs. 6), and the angular overlap of the d-orbitals and the ligand group orbitals is less favorable when tetrahedral (there is a directional factor of $\frac{2}{3}$). Indeed, the tetrahedral splitting energy is generally $\frac{4}{6} \cdot \frac{2}{3} = \frac{4}{9}$ that of a relative octahedral splitting energy.
  - Conclusion: T_d complexes are always weak-field and thus high spin.

- Rationalization of coordination geometries (factors that influence the geometry adopted):
  - Electronic factor (the number of bonds): Electrostatic and covalent model favor O_h (6 vs. 4).
  - Steric factor: Ligand-ligand repulsions favor T_d.
    - High charge on cation increases Δ — favors O_h coordination and O_h low spin. Indeed, O_h (l.s.) $> O_h$ (h.s.) $> T_d$.
    - CFSE(O_h) $\geq$ CFSE(T_d), always.

- In d^5 complexes (e.g., with Mn^{2+} and Fe^{3+}), there is no stabilization energy. Thus, L-L repulsions dominate and T_d complexes are formed.
  - Note however that the higher charge on Fe^{3+} favors low spin O_h complexes in more cases than Mn^{2+}.

- In d^6 complexes (e.g., with Fe^{2+} and Co^{3+}), the stabilization is much higher for O_h low spin than high spin than T_d. Thus, we form low spin complexes.
  - Note that there are exceptions — extremely weak field ligands such as F^- can still form high spin complexes as with CoF_6^{3-}.

VI.8   Module 36: Angular Overlap Model

- In many catalytic cycles, the coordination environment (molecular geometry) changes frequently through-out the cycle.

- To account for changes in the coordination environment, we use the **angular overlap model**.

  - We can also use this model to help account for complexes with different ligands in the coordination sphere.

- Recall that σ-bonding is stabilizing, but π-bonding is stabilizing only in the case of π-acceptance by a ligand, not π-donation.

- Angular overlap parameters:

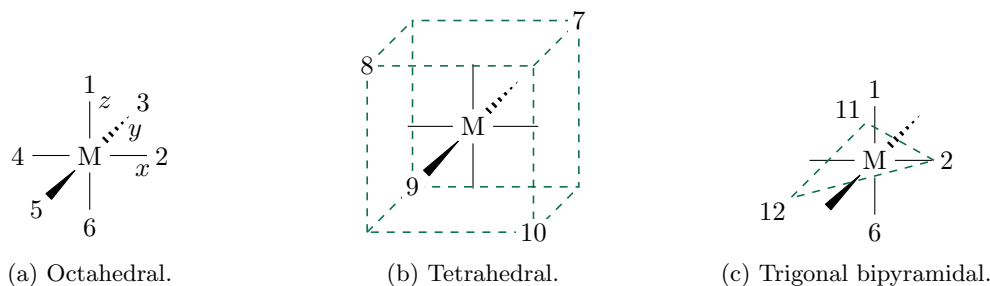(a) Octahedral.   (b) Tetrahedral.   (c) Trigonal bipyramidal.

Figure VI.9: Angular overlap model: Labeling of positions.

  - With multiple ligands and multiple orbitals, we add the angular overlap interaction coefficients.
  - These are tabulated for each orbital of each ligand at each position in the coordination sphere with each metal-center d-orbital.
  - Suggested reading (on coefficients' derivation): *TBD*.

- Trigonal planar coordination example:

  - From Figure VI.9c, the ligand positions are 2, 11, and 12.
  - Thus, we add the coefficients in these rows to get $e_\sigma = (\frac{3}{4}, \frac{9}{8}, \frac{9}{8}, 0, 0)$ and $e_\pi = (0, \frac{3}{2}, \frac{3}{2}, \frac{3}{2}, \frac{3}{2})$, where the respective d-orbitals are $z^2, x^2 - y^2, xy, xz, yz$.
  - With these energies, we can now sum $e_\sigma + e_\pi$ to determine that the energies of the orbitals are $(\frac{3}{4}, \frac{21}{8}, \frac{21}{8}, \frac{3}{2}, \frac{3}{2})$.
  - This gives us three sets of degenerate orbitals: Lowest energy $(d_{xz,yz})$, medium energy (d_{z^2}), and high energy (d_{xy,x^2-y^2}).
  - Assigning Mulliken symbols with the D_{3h} character table, we have from lowest to highest energy: $e'' < a_1' < e'$.

- Note that e_σ is always positive (because ligands are σ-donors), but e_π can be negative (because ligands can be π-acceptors).

- Changing the metal and/or ligand affects the magnitudes of e_σ and e_π, thereby changing the value of Δ.

- $e_\sigma > e_\pi$ always.

- Values decrease with increasing size and decreasing electronegativity.

- Both positive and negative values for e_π.

VI.9   Module 37: Jahn-Teller Effect

- The **Jahn-Teller theorem** helps explain why the d^9 configuration is far more stable (far higher peak) than predicted by Figure VI.1.

- **Jahn-Teller theorem**: For nonlinear molecules/ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy. *Also known as* **J-T theorem**.

  - When orbitals in the same level are occupied by different numbers of electrons, this will lead to distortion of the molecule.
  - If the two orbitals of the e_g level have different numbers of electrons, this will lead to J-T distortion so as to stabilize the doubly occupied e_g orbital and destabilize the singly occupied e_g orbital.
  - Cu(II) with its d^9 configuration is degenerate and has J-T distortion.

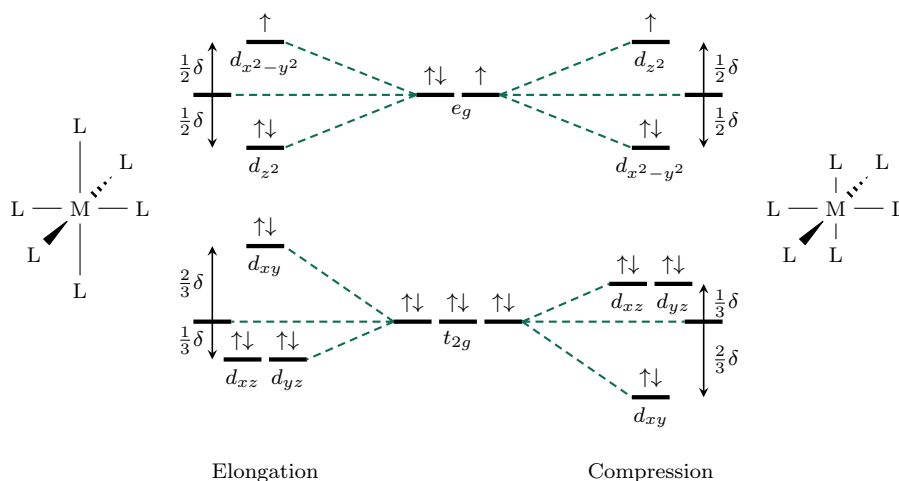- Consider the two degenrate e_g orbitals ($d_{x^2-y^2,z^2}$).

Figure VI.10: Jahn-Teller elongation and compression.

  - Elongating the z-axis in an O_h complex stabilizes the d_{z^2} orbital and destabilizes the $d_{x^2-y^2}$ orbital.
  - Vice versa for compressing the z-axis.

- Thus, we can see significant elongation of the z-axis bonds in $[\text{Cu(H}_2\text{O)}_6]^{2+}$.

- History: Before the rigorous formulation and verification of the J-T theorem by Jahn and Teller, Landau proposed the **Landau statement** from his observations.

- **Landau statement**: A molecule in an orbitally degenerate electronic state is unstable with respect to spontaneous distortion of the nuclear configuration that removes the degeneracy.

- Strength of the J-T effect in various configurations:

Number of electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn-Teller	w	w		s		w	w		s	
Low-spin Jahn-Teller	w	w		w	w		s		s	

Table VI.3: Jahn-Teller effects in various configurations.

- Unequal occupation of t_{2g} orbitals leads to the J-T effect in principle, but only weakly in practice because t_{2g} orbitals are nonbonding in σ-bonded complexes, i.e., localized on the metal center, i.e., not strongly perturbed by ligand bonding.

- Unequal occupation of e_g orbitals leads to a strong J-T effect since they are antibonding.

- Structural effects of J-T distortion:

  - In $[Cu(en)_2(H_2O)_2]^{2+}$, we will have axial aqua groups and equatorial en groups for two reasons.
    - The aqua groups are weaker field ligands that interact less efficiently with the metal center, so it is easier for them to be farther from it.
    - Having the en groups in plane means they don't have to be structurally distorted.
  - In $[Cu(en)_3]^{2+}$, we observe strong structural distortion from perfect octahedral forced by the J-T distortion; this angle strain is not energetically favorable.

- Jahn-Teller distortion of the excited state:

  - In high spin d^6 complexes such as $[Fe(H_2O)_6]^{2+}$, there will only be weak J-T distortion of the ground state. Thus, we expect to see only one peak in the absorption spectrum, corresponding to the promotion of a t_{2g} electron to the e_g orbitals and its fall back down.
  - However, we observe two bands.
  - This is because promotion of an electron from the t_{2g} orbitals to the e_g orbitals leads to a much stronger J-T distortion (unequally occupied e_g orbitals).
  - The resultant d-orbital splitting causes the two absorption peaks.

- Square planar complexes:

  - Jahn-Teller distortion leads to tetragonal distortion of the octahedron, with the extreme of tetragonal distortion being the complete loss of axial ligands, and formation of a square-planar complex. Tetragonal distortion is the stretching of the axial $M-L$ bonds, and shortening of the in-plane bonds. Cu(II) is usually tetragonally distorted, while low-spin Ni(II) is usually square planar.
  - Since the axial bonds get weaker as they lengthen, eventually we can have enough thermal energy to break them entirely, resulting in a square planar complex.
  - This occurs in the case of Ni(II) bonded to strong field ligands, such as cyano ligands. Essentially, what happens is the splitting of the e_g orbitals exceeds the spin-pairing energy, causing the $d_{x^2-y^2}$ electron to pair with the d_{z^2} electron.
    - The filled d_{z^2} orbital now occupies two coordination sites, and the four donor atoms occupy the plane.
    - The structure is comparable to that of $[IF_4]^-$, where two lone pairs occupy the axial sites.
    - This is a particularly important special example because such compounds are very reactive, owing to their frontier d_{z^2} orbitals, and can be involved in nucleophilic attacks.
  - All high-spin d^8 metal ions are octahedral (or tetrahedral). Low-spin d^8 metal ions are usually square planar.
  - Both Wilkinson's catalyst and Crabtree's catalyst are square planar!

VI.10   Module 38: Applying MO Theory Beyond "Simple" ML_6 Complexes

2/26:
- Reviews Figure VI.6 and the difference between π-acceptor and π-donor ligands.

- Mixing different ligands within the same coordination sphere:

– The MO diagram for O_h complexes proves to be a convenient starting point for deducing the electronic structure of many lower symmetry metal complexes.

– To analyze lower symmetry compounds, we use the descent in symmetry technique.

- $[Co(CN)_5Br]^{3-}$ example:

  – Five strong-field cyano ligands and one weak-field bromo ligand.

  – Choose to orient the Br^- ligand along the positive z-axis.

  – To build the MO, we could use DFT (first principles), but it's an unintuitive black box.

  – Alternatively, we can start with hexacyanocobaltate(III), remove one cyano ligand and see how the MOs are perturbed, and add one bromo ligand and see how the MOs are perturbed. This process correlates the electronic structure of this C_{4v} complex with its O_h parent complex.

  – To begin, consider perturbations to σ and π interactions upon substituting π-accepting CN^- with π-donating Br^-.

  – First, let's simply remove the CN^- ligand.
    ■ The $d_{x^2-y^2}$ orbital is not greatly perturbed by substitution along the z-axis.
    ■ The d_{z^2} orbital was $M-L\sigma^*$; thus, removal of 1 σ ligand from the z-axis will stabilize it.
    ■ The $d_{xz,yz}$ orbitals are destabilized owing to the removal of 1 $M-L\pi$ bonding interaction.
    ■ The d_{xy} orbital is in-plane and nodal with respect to σ- and π-bonding along the z-axis; thus, it is not greatly perturbed by such substitution.
    ■ The d_{z^2} orbital is more greatly stabilized than the $d_{xz,yz}$ orbitals are destabilized because the former is involved in stronger σ-interactions, as opposed to weaker π-interactions.

  – Now let's add the Br^- ligand. Addition of Br^- to the C_{4v} fragment will give rise to new interactions.
    ■ σ: $Br(p_z)$ will interact with the d_{z^2}, s, and p_z orbitals of cobalt. All of these will be $M-L\sigma^*$ with respect to M orbitals, and $M-L\sigma$ with respect to the ligand.
    ■ π: $Br(p_x, p_y)$ will interact with $d_{xz,yz}$ in $M-L\pi^*$ interactions.
    ■ The formation of a bonding pair causes $Br(p_z)$ orbital stabilization, at the cost of the destabilization of the d_{z^2} orbital.
    ■ The metal p_z and d_{z^2} orbitals will be destabilized, but will remain below $Co-CN\sigma^*$ orbitals because the $Co-Br$ interaction is not as great as the $Co-CN$ interaction.

VI.11 Module 39: Metal-Metal Bonding

- First, a historical puzzle:

  – Copper (II) acetate crystalizes with four $O-CR-O$ bridges joining two square pyramidal copper atoms that are also bonded to one aqua group, each.

  – Copper is d^9, so $\mu = 1.73$ in theory. However, we observe $\mu = 1.4$.

  – We resolve this conflict by noting that the copper atoms are not square pyramidal — they bond to each other, giving both an octahedral geometry.
    ■ This is important because it gives us a new pair of bonding and antibonding orbitals. We thus have low-spin and high-spin states, and the existence of a nonzero but not super high magnetic moment hints at a high-spin state with some preference for low-lyingness.

- Metal-metal bonding is common for metals in low oxidation state, and generally increases in strength along the series $3d << 4d < 5d$.

- Single metal-metal bonded complexes:

  – We will consider the paradiamagnetic single $M-M$ complex $M_2(CO)_{10}$.

- ■ Possible metals are Fe^{2+}, manganese, and uranium.
  - – Strategy for group fragment approach: Correlate to $M(CO)_6$ (O_h), remove a ligand to give $M(CO)_5$, and dimerize.
    - ■ Note that $Mn(CO)_5$ is the inorganic analog to CH_3, i.e., the $Mn(CO)_5$ fragment is said to be isolobal with CH_3.
  - – The HOMO of $Mn(CO)_5$ is a singly occupied d_{z^2} orbital.
  - – The energetic stabilization of the electrons in d_{z^2} into a σ-bond by dimerization is the driving force for metal-metal bond formation.
  - – Note that a diamagnetic complex is formed from the dimerization of two metallic radicals.
  - – Also note that the d_{z^2} orbital is cylindrically symmetric, i.e., indicates no preference for the staggered vs. eclipsed conformation. Thus, the molecule will adopt the more torsionally favorable staggered D_{4d} configuration.

- • Cluster formation:
  - – As mentioned above, odd electron occupancy of the e_g orbitals (O_h) prompts ligand loss in order to stabilize d_{z^2}. Further stabilization occurs by metal-metal single bond formation. We can take limiting argument to explain cluster formation across the periodic table:
  - – In each case, the clusters assume an octahedral coordination as a result of burying 7 d-electrons in what are formally t_{2g} orbitals. The system loses a number of COs equivalent to the number of electrons in $M-L\sigma^*$; this permits maximum $M-M$ bond formation and thus maximum stabilization.
  - – Clusters can trimerize or form higher polymers.
  - – Clusters can act as super atoms, combinations of atoms that you can add and remove electrons from with similar effects to changing the oxidation state in one atom.

- • Multiple metal-metal bonded complexes:
  - – Inorganic chemists synthesized a compound with a quadruple bond in 1964.
  - – The MO strategy will be to correlate $Re_2Cl_8{}^{2-}$ with $ReCl_6{}^{3-}$ (O_h), remove two axial Cl^- ligands to give a square planar $ReCl_4{}^-$ fragment, and then dimerize.
    - ■ Here, we see stabilization of the $d_{xz,yz}$ (the Cl^- ligand had been giving antibonding character) orbitals and massive stabilization of the d_{z^2} orbital (same reason).
  - – The d_{z^2} orbital reacts the most to form an a_{1g} σ-bond.
  - – The $d_{xz,yz}$ orbitals react the second most to form two e_u π-bonds.
  - – The d_{xy} orbitals react the third most to form one b_{2g} δ-bond.
  - – The eclipsed D_{4h} structure is a result of the δ bond.
  - – Adding up our 8 bonding and 0 antibonding electrons and dividing by two gives us our first quadruple bond.

- • Metal-metal bonding vs. configuration: Increases single to quadruple bond as $d^1 \rightarrow d^4$; decreases triple to no bond as $d^5 \rightarrow d^8$.

- • f orbitals are deep within the core of the atom and not generally available for bonding, so we will not see higher bonding *because* of f orbitals in lanthanides and actinides.

- • The d^8 case:
  - – No bonding predicted, but. . .
  - – We actually see one-dimensional crystals, as in band theory.
  - – The orbitals responsible are the d_{z^2} orbitals, which mix with the higher energy p_z orbitals to stabilize the d_{z^2} σ-bonding MO (and destabilize the p_z bonding MO, but this orbital is unfilled).
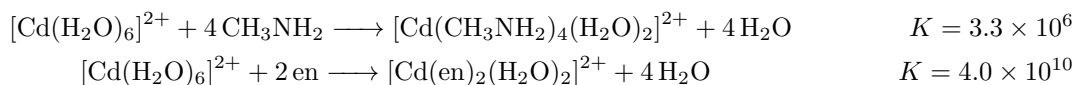
- The $d_{x^2-y^2}$ orbitals cannot participate in ML_4 coupling since they are used for ligand bonding.

  - Thus, the only orbitals available for coupling are $d_{z^2, xz, yz, xy}$.

- Inorganic chemists (including Phil Power, who is probably the greatest currently living main-group inorganic chemist) synthesized a compound with a quintuple bond in 2005.

  - They had to change the coordination environment around the metal center to free up the $d_{x^2-y^2}$ orbital. They did so with sterically bulky ligands that hindered more bonding.
  - The quintuple bonding was verified by observing a very short bond length (not super short on the scheme of things, but shorter than ever reported before, indicating the presence of a weak fifth bond).
  - C_{2h} symmetry.
  - Suggested reading: The full paper.

VI.12 Chapter 10: Coordination Chemistry II (Bonding)

From Miessler et al. (2014).

3/3:
- We seek to review experimental observations of coordination complexes and show how these observations have been reconciled with electronic structure and bonding theories.

- **Stability constant**: An equilibrium constant in a reaction that forms a coordination complex, typically by replacing one or more aqua ligands with another type. *Also known as* **formation constant**.

  - A measure of bond strength frequently used by inorganic chemists.

- Stronger field ligands preferably bond to the metal center.

- Polydentate ligands bond more readily than one split into chunks each with fewer attachment sites because bonding once makes bonding a second time easier (proximity), and ligand dissociation is more difficult.

  - Thus, for example, $[\text{Ni(en)}_3]^{2+}$ is more stable than $[\text{Ni(CH}_3\text{NH}_2)_6]^{2+}$.

- The chelate effect has the largest impact on formation constants when the ring is 5-6 atoms long (shorter causes strain; longer means less proximity, hence tougher bond formation).

- "Thermodynamic parameters such as ΔH°, ΔS°, and the dependence of K with T are useful for comparing reactions of different metal ions reacting with the same ligand or a series of different ligands reacting with the same metal ion" (Miessler et al., 2014, p. 358).

  - Sometimes, properties of coordination complexes can be predicted directly off of this information, but it's rare.

- An example of the thermodynamics of the chelate effect:

$$[\text{Cd(H}_2\text{O})_6]^{2+} + 4\,\text{CH}_3\text{NH}_2 \longrightarrow [\text{Cd(CH}_3\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+} + 4\,\text{H}_2\text{O} \qquad K = 3.3 \times 10^6$$
$$[\text{Cd(H}_2\text{O})_6]^{2+} + 2\,\text{en} \longrightarrow [\text{Cd(en)}_2(\text{H}_2\text{O})_2]^{2+} + 4\,\text{H}_2\text{O} \qquad K = 4.0 \times 10^{10}$$

  - Differences in ΔS° play the dominant role in the chelate effect. ΔH° is similar for the above two reactions, but for the en substitution, we dramatically increase entropy by binding two en particles and liberating four H_2O particles, as opposed to conserving the number of particles as in the methylamine reaction.

- **Magnetic susceptibility**: A molecule's attraction to or repulsion from a magnetic field. *Also known as χ.*

- $\mu = 2.828\sqrt{\chi T}$, where $2.828 \approx \sqrt{3k/N}$.

- "The total spin magnetic moment for a configuration of electrons is characterized by the spin quantum number S, which is equal to the maximum total spin, the sum of the m_s values" (Miessler et al., 2014, p. 360).

- "The orbital angular momentum [is] characterized by the quantum number L, where L is equal to the maximum possible sum of the m_l values for an electronic configuration" (Miessler et al., 2014, p. 360).

  - For a p^4 ground state electron configuration, L is maximized when two electrons occupy the orbital with $m_l = +1$, and the other two occupy the $m_l = 0, -1$ orbitals, respectively. Thus, $L_{p^4} = 1 + 1 + 0 - 1 = 1$.

- Technically, $\mu_S = 2.00023\sqrt{S(S+1)}$ where 2.00023 is the gyromagnetic ratio.

  - However, if we round the gyromagnetic ratio to 2 and note that $S = \frac{n}{2}$ where n is the number of unpaired electrons, we obtain $\mu_S = \sqrt{n(n+2)}$.

- Recall from Chapter 2 that in transition metals, ns electrons are lost before $(n-1)d$ electrons.

- Number of unpaired electrons examples:

  - Fe is $4s^2 3d^6$, so 4 unpaired d-electrons.
  - Fe^{2+} is $3d^6$, so 4 unpaired d-electrons.
  - Cr is $4s^1 3d^5$, so 6 unpaired electrons (1 unpaired s-electron and 5 unpaired d-electrons).
  - Cu is $4s^1 3d^{10}$, so 1 unpaired s-electron.
  - Cu is $4s^2 3d^9$, so 1 unpaired d-electron.

- The unit symbol for Bohr magnetons is μ_B, so we say, for instance, that the magnetic moment of copper is $1.73\,\mu_B$.

- Miessler et al. (2014) gives a full explanation of the Gouy method.

  - Modern magnetic susceptibility measurements are taken with a magnetic susceptibility balance (for solids), via the Evans NMR method (for solutes), or with a SQUID.

- **Mass susceptibility**: The magnetic susceptibility of a substance per gram.

- "A complex with one unpaired electron exhibits ideal **Curie paramagnetism** if the inverse of the molar susceptibility (for a given applied external field) increases linearly with temperature and has a y-intercept of 0" (Miessler et al., 2014, p. 362).

- "In a paramagnetic complex, the magnetic moments of individual species do not effectively couple, but act more or less independently of each other" (Miessler et al., 2014, p. 362).

  - This contrasts with ferromagnetism.

- **Antiferromagnetism**: An alternate long-range arrangement of magnetic moments where adjacent moments line up in opposite directions.

- Electronic spectra and molecular shapes provide further evidence for electronic structures.

- There are three main bonding models for coordination complexes.

- **Crystal field theory**: This is an electrostatic approach, used to describe the split in metal d-orbital energies within an octahedral environment. It provides an approximate description of the electronic energy levels often responsible for the ultraviolet and visible spectra of coordination complexes, but it does not describe metal-ligand bonding.

- **Ligand field theory**: This is a description of bonding in terms of the interactions between metal and ligand frontier orbitals to form molecular orbitals. It uses some crystal field theory terminology but focuses on orbital interactions rather than attractions between ions.

- **Angular overlap method**: This is a method of estimating the relative magnitudes of molecular orbital energies within coordination complexes. It explicitly takes into account the orbitals responsible for ligand binding as well as the relative orientation of the frontier orbitals.

- **Born-Oppenheimer approximation**: Atomic nuclei are in fixed positions in comparison with rapidly moving electrons.

- **Extended Hückel theory**: The simplest approach to approximating the many-body problem of electronic movements.

- Thoughts on CFT:

  - "When the d orbitals of a metal ion are placed in an octahedral field of ligand electron pairs, any electrons in these orbitals are repelled by the field. As a result, the $d_{x^2-y^2}$ and d_{z^2} orbitals, which have e_g symmetry, are directed at the surrounding ligands and are raised in energy. The d_{xy}, d_{xz}, and d_{yz}, orbitals (t_{2g} symmetry), directed between the ligands, are relatively unaffected by the field" (Miessler et al., 2014, p. 364).

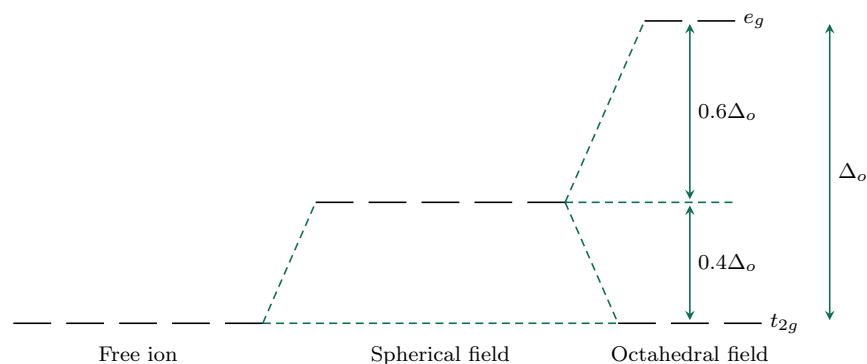 - In Δ_o, the o stands for octahedral.

Figure VI.11: Crystal field splitting from the free ion.

  - "The average energy of the five d orbitals [in a coordination complex] is above that of the free ion orbitals [i.e., those in the metal ion before it is surrounded by ligands], because the electrostatic field of the ligands raises their energy" (Miessler et al., 2014, p. 364).

  - CFT is flawed because as we can see from Figure VI.11, there is no energetically favorable bonding; at best, we could have zero energy difference between the free ion and bonded octahedral field state (this occurs if only the t_{2g} orbitals are occupied).

3/4:
- Ligand field theory was synthesized from CFT and MO theory by Griffith and Orgel.

- The ligand HOMO often serves as the basis for group orbitals.

- Based on their shapes, it makes sense that the symmetry of the $d_{xy,xz,yz}$ orbitals doesn't match that of the ligand σ orbitals.

- The colors of transition metal complexes are often due to the energy difference between the t_{2g} and $e_g{}^*$ orbitals, which is often equal to the energy of photons of visible light.

  - $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, for example, is green because Δ_o matches well with the energy of red light, so when white light passes through a solution of this compound, red light is absorbed and the complement (green light) passes through to be perceived.

- "Δ_o is also used in ligand field theory as a measure of the magnitude of metal-ligand interactions" (Miessler et al., 2014, p. 367).

- Perhaps the orbital labeling scheme in Figure VI.5 isn't actually procedural; it's just a consistent reference frame.

- The interaction of ligand $\pi(t_{1u})$ orbitals with metal $p(T_{1u})$ orbitals is relatively weak since metal p orbitals largely interact with ligand $\sigma(t_{1u})$ orbitals.

- "Strong π acceptor ligands have the ability to increase the magnitude of Δ_o by lowering the energy of the t_{2g} orbitals" (Miessler et al., 2014, p. 368).

- "Electrons in the lower bonding orbitals are largely concentrated on the ligands. It is the stabilization of these ligand electrons that is primarily responsible for why these ligands bind to the metal center" (Miessler et al., 2014, p. 368).

- Electrons in higher energy orbitals are affected by ligand field effects and determine "structural details, magnetic properties, electronic spectrum absorptions, and coordination complex reactivity" (Miessler et al., 2014, p. 368).

- **Metal-to-ligand (M $\longrightarrow$ L) π bonding**: Electron donation from metal $d_{xy,xz,yz}$ orbitals to ligand π^* orbitals. *Also known as π back-bonding*.

- Δ_o is the splitting between the *highest occupied* t_{2g} (which can be either t_{2g} or t_{2g}^*) orbital and the e_g^* orbital.
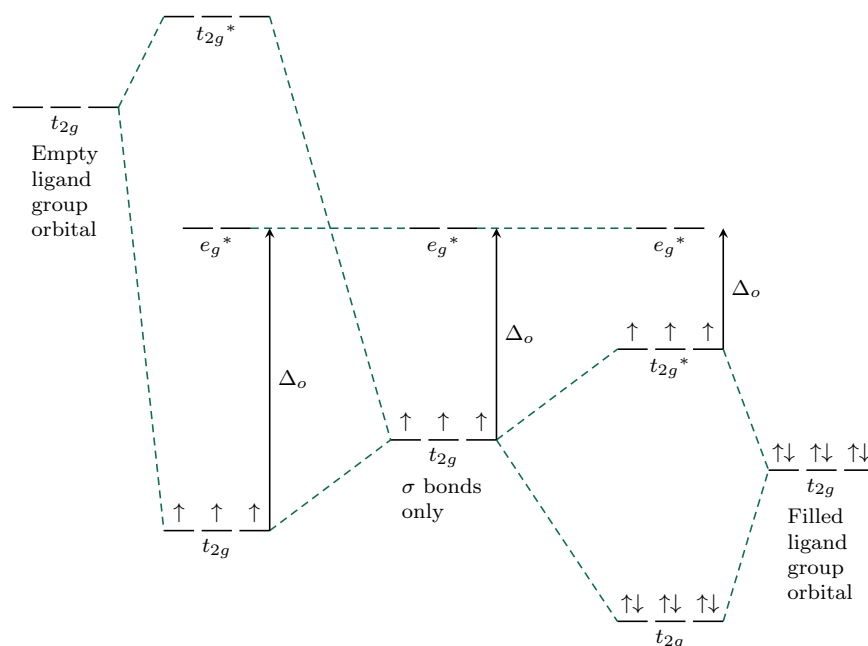
Figure VI.12: Effects of π bonding on Δ_o using a d^3 ion.

- This is why we consider Δ_o to be the energy difference between the t_{2g} and e_g^* orbitals in complexes with π-accepting ligands (where the t_{2g} orbitals are filled and lie beneath the e_g^* orbitals), but the difference between the t_{2g}^* and e_g^* orbitals in complexes with π-donating ligands (where the t_{2g} *and* t_{2g}^* are filled and *both* lie beneath the e_g^* orbitals).

- Empty ligand group orbitals engage in M $\longrightarrow$ L bonding while filled ligand group orbitals engage in **L $\longrightarrow$ M bonding**.

- **Ligand-to-metal (L $\longrightarrow$ M) π bonding**: Electron donation from the ligand π orbitals to metal $d_{xy,xz,yz}$ orbitals.

- L $\longrightarrow$ M bonding favors high-spin configurations while M $\longrightarrow$ L bonding favors low-spin configurations.

- Part of the stabilization of M $\longrightarrow$ L bonding comes from donation of excess electron density on the metal cation resulting from σ acceptance back to the ligands (metals prefer to be relatively positive because of their low electronegativity).

- Note that because backbonding orbitals are composed of π^* orbitals, filling of them results in weakening of the ligand π bond.

- "In octahedral coordination complexes, electrons from the ligands fill all six bonding molecular orbitals, and the metal valence electrons occupy the t_{2g} and e_g^* orbitals" (Miessler et al., 2014, p. 372).

- Strong field ligands interact more strongly with metal orbitals, leading to greater stabilization of the t_{2g} set, leading to a larger Δ_o and low-spin configurations.

  - Weak field ligands interact more weakly with metal orbitals, leading to lesser stabilization of the t_{2g} set, leading to a smaller Δ_o and low-spin configurations.

- Recall that increases in Π_c *destabilize* the complex, whereas increases in Π_e *stabilize* the complex.

- Is there any case in which we would have a d^5 configuration with four t_{2g} electrons and one $e_g{}^*$ electron?

- Co^{3+} is the third row cation that most easily adopts a low-spin configuration.

- Magnitudes of Δ_o values:

  - Values for d^5 ions are smaller than those of d^4 and d^6 ions.

  - Increases in the principal quantum number n increase Δ_o because of two effects:

    - There is greater overlap between the larger $4d$ and $5d$ orbitals and the ligand orbitals.
    - There is a decreased pairing energy due to a larger available volume for electrons in the $4d$ and $5d$ orbitals relative to with $3d$ orbitals.

- **Ligand field stabilization energy**: The difference[1] between the energy of the t_{2g} / e_g electronic configuration resulting from the ligand field splitting and the hypothetical energy of the t_{2g} / e_g electronic configuration with all five orbitals degenerate and equally populated. *Also known as* **LFSE**.

- Note that LFSE can only be calculated using the $\frac{2}{5}$ / $\frac{3}{5}$ method for σ-bonded octahedral complexes.

- Although we might expect transition metal ions to have linearly[2] increasingly exothermic ΔHs for hydration reactions (see below) across a period (as decreasing atomic radius makes them more concentrated [hence more unstable] sources of postive charge), we observe two loops similar to Figure VI.1 but inverted.

$$M^{2+} + 6\,H_2O \longrightarrow [M(H_2O)_6]^{2+}$$

  - This is because the LFSE provides extra stabilization.

  - It is also because of spin-orbit coupling, a relaxation effect caused by contraction of the metal-ligand distance, and an interelectronic repulsion energy (see Chapter 11 for a more detailed description of the first and third phenomena).

  - Small corrections must be made in cases where the J-T distortion is present.

- **Nephelauxetic effect**: The magnitude of the reduction in the interelectron repulsion energy between the free ion and coordination complex.

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[1]This is equivalent to the CFSE defined in the lecture.
[2]Errata: Miessler et al. (2014) refers to the linear line in the graph as "blue," even though it should be green (a relic from the previous edition).

- Is this due to increases in delocalization?
- Factors that increase the nephelauxetic effect:
  ■ Softness of the ligand.
  ■ Increase in metal oxidation state magnitude.
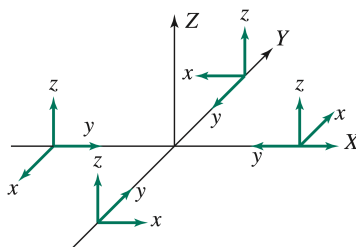
3/8:   • Square-planar complexes.

Figure VI.13: Square-planar π-ligand coordinate system.

- Point group: D_{4h}.
- "Unlike the octahedral case, there are two distinctly different sets of potential π-bonding orbitals, the parallel set ($\pi_\parallel$ or p_x, in the molecular plane) and the perpendicular set ($\pi_\perp$ or p_z, perpendicular to the plane)" (Miessler et al., 2014, p. 377).
- Apply operations, generate reducible representations, and reduce them to irreducible representations:

$$\Gamma_{\sigma(y)} = (4, 0, 0, 2, 0, 0, 0, 4, 2, 0) = A_{1g} + B_{1g} + E_u$$
$$\Gamma_{\parallel(x)} = (4, 0, 0, -2, 0, 0, 0, 4, -2, 0) = A_{2g} + B_{2g} + E_u$$
$$\Gamma_{\perp(z)} = (4, 0, 0, -2, 0, 0, 0, -4, 2, 0) = A_{2u} + B_{2u} + E_g$$

- For the σ-only case, the metal's $3d_{x^2-y^2}$, $4p_x$, and $4p_y$ orbitals primarily participate in bonding, with smaller contributions from the less directed $3d_{z^2}$ (see Figure VI.3e) and $4s$.
- Combine orbitals by their symmetry.
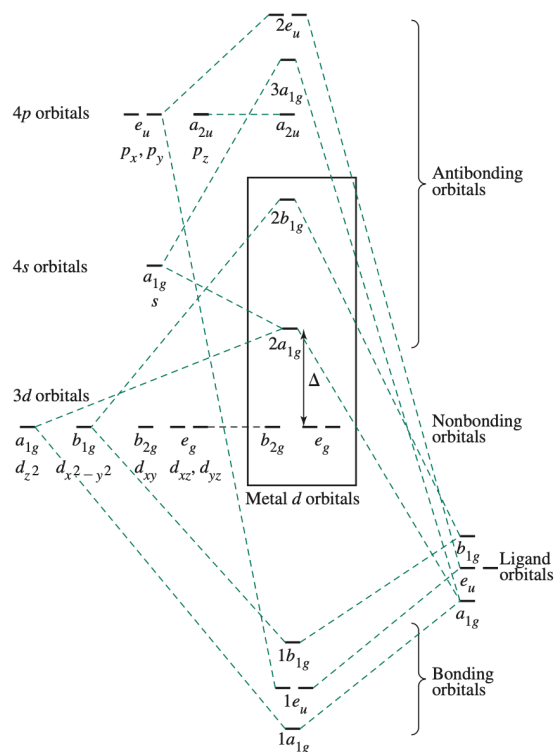
Figure VI.14: Square planar MH_4 orbital diagram.

■ Note that Figure VI.14 is more complex than Figure VI.2 since the lower symmetry reduces degeneracy.

– For the $\sigma + \pi$ case, the metal's $3d_{xy}$, $4p_x$, and $4p_y$ orbitals primarily participate in bonding with the $p_x(\pi_\parallel)$ ligand orbitals, and the metal's $3d_{xz}$, $3d_{yz}$, and $4p_z$ orbitals primarily participate in bonding with the $p_z(\pi_\perp)$ ligand orbitals.

– Combine orbitals by their symmetry:
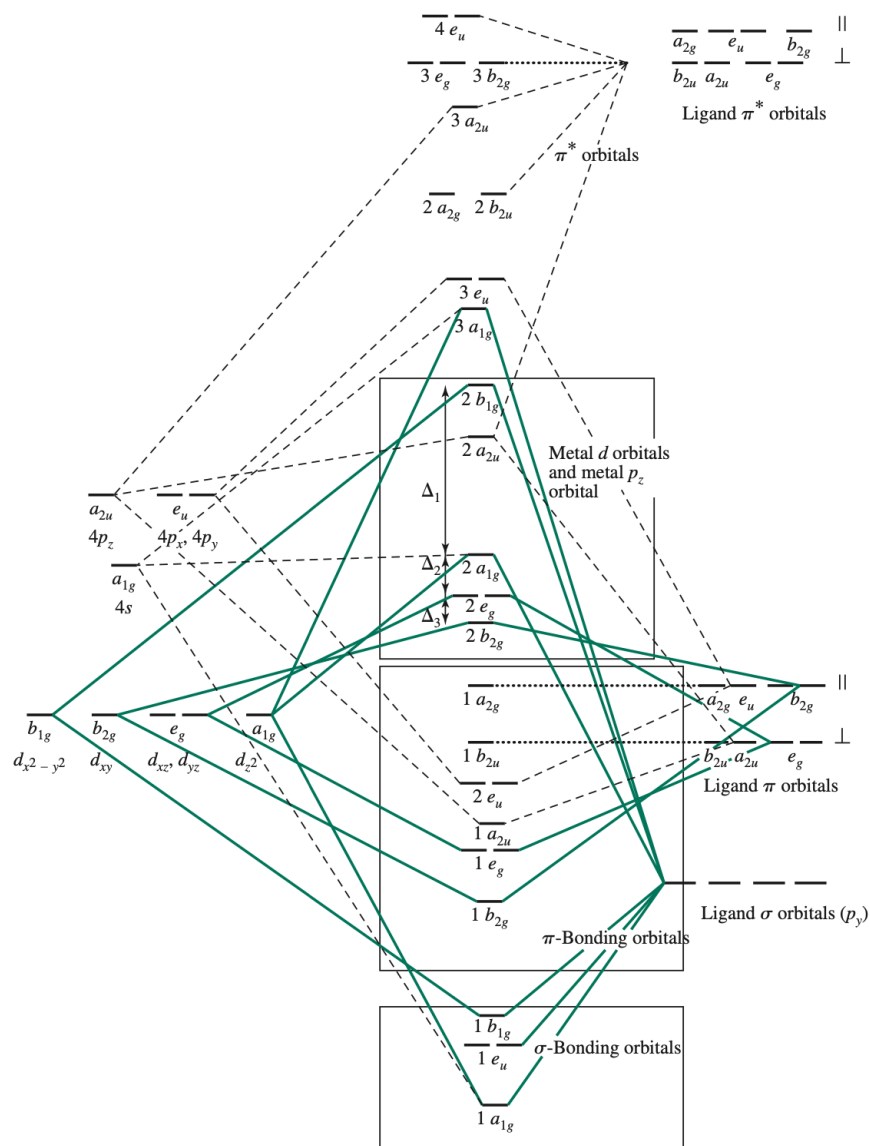
Figure VI.15: Square planar ML_4 orbital diagram.

- ■ The lowest energy boxed set of orbitals in Figure VI.15 contains the σ-bonding orbitals.
- ■ The next higher set is involved in π bonding.
- ■ The highest set's order is a subject of debate: The bottom three are the lowest and b_{1g} is much higher, for sure, but the ranking of the bottom three is uncertain. The remaining orbital in the box is not particularly relevant.
- ■ The remaining high-energy orbitals are only important in excited states.

- • **Homoleptic** (complex): A coordination complex with all the ligands identical.

- • **Heteroleptic** (complex): A coordination complex with variation within the ligand set.

- • Tetrahedral complexes.

  – In Figure VI.16, the local coordinate systems are ostensibly chosen so that "the y axis of the ligand orbitals is chosen along the bond axis, and the x and z axes are arranged to allow the C_2 operation to work properly" (Miessler et al., 2014, p. 381).
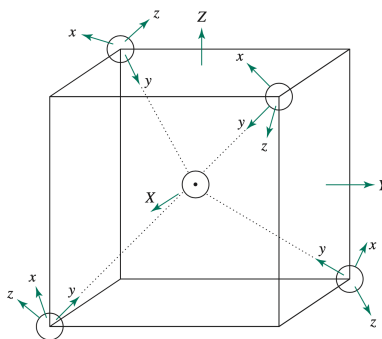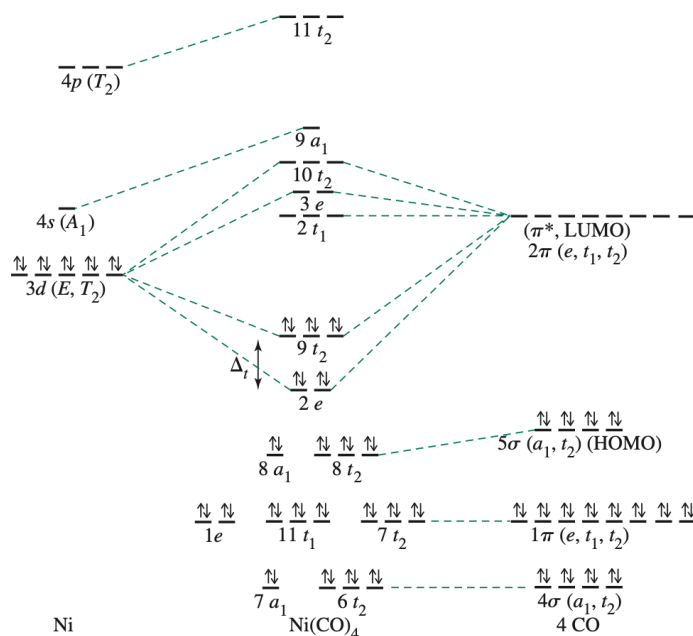
Figure VI.16: Tetrahedral π-ligand coordinate system.

- Point group: T_d.
- Apply operations, generate representations:

$$\Gamma_\sigma = (4, 1, 0, 0, 2)$$
$$\Gamma_\pi = (8, -1, 0, 0, 0)$$

- Combine orbitals by their symmetry:

Figure VI.17: Tetrahedral MH$_4$ orbital diagram.

■ Recall that $\Delta_t \approx \frac{4}{9}\Delta_o$ under the same ligands.

- For the σ case, ignore all π^*-derived orbitals in Figure VI.17. For the π case, consider them.

3/9:   • **Angular overlap model**: A method for estimating orbital energies in coordination complexes with the flexibility to deal with a variety of geometries and ligands, including heteroleptic complexes. *Also known as* **AOM**.

- Determines the energy of a molecular orbital with high metal d-orbital contribution by summing the varying effects of each ligand on the parent metal d orbital.

- Limited since it exclusively focuses on the d orbitals, neglecting the role of the s and p valence orbitals.

  ■ However, this is not a big problem since the frontier orbitals are typically MOs with high d-orbital contribution, so considering only d-based MOs can still provide useful information.

- The strength of all σ interactions in the AOM is defined relative to the strength of the strongest one, namely that between the valence d_{z^2} metal orbital and a p_z ligand orbital.

  - The strength of this reference interaction is denoted by e_σ.

  - Note that since the d_{z^2} orbital is higher in energy than the p_z orbital, the interaction of the two forms a bonding MO most like the ligand orbital, and an antibonding MO most like the metal orbital.

  - Although the antibonding MO is slightly more destabilized than the bonding MO is stabilized, we treat both energy changes as equal and equal to e_σ.

Ligand Position	z^2	x^2-y^2	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0
7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0

(a) Sigma interactions.

| Ligand Position	z^2	x^2-y^2	xy	xz	yz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1
7	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
8	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
10	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
11	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
12	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$

(b) Pi interactions.

Table VI.4: Angular overlap parameters.

- $[\text{M(NH}_3)_6]^{n+}$ example:

  - NH_3 is a σ-only ligand, and it bonds mostly through the nitrogen p_z orbital.

  - d_{z^2} orbital: Interacts most strongly with the 1 and 6 ligands, for a contribution of $1e_\sigma$ from each of them. It also interacts in a less significant fashion with the 2, 3, 4, and 5 ligands, for a contribution of $\frac{1}{4}e_\sigma$, each. Thus, in total, it is raised in energy by $3e_\sigma$.

  - $d_{x^2-y^2}$ orbital: Interacts well with the 2, 3, 4, and 5 ligands (for a contribution of $\frac{3}{4}e_\sigma$ each) and not at all with the 1 and 6 ligands. Thus, in total, it is also raised in energy by $3e_\sigma$.

  - $d_{xy,xz,yz}$ orbitals: No σ interactions with the ligand orbitals. Thus, their energy does not change.

  - Ligand orbitals: Sum across a row in Table VI.4a. Ligands in positions 1 and 6 interact with d_{z^2} significantly and no other orbital, for an energy lowering of $1e_\sigma$ each. Ligands in positions 2, 3, 4, and 5 interact with d_{z^2} for an energy lowering of $\frac{1}{4}e_\sigma$, and with $d_{x^2-y^2}$ for an energy lowering of $\frac{3}{4}e_\sigma$; thus, they are lowered by $\frac{1}{4}e_\sigma + \frac{3}{4}e_\sigma = 1e_\sigma$, each, in total. Thus, it so happens that each ligand orbital is lowered in energy by e_σ.

  - Since the ligand orbitals are all filled and lowered, the total stabilization energy is

$$\frac{6 \text{ ligands}}{1} \times \frac{2 \text{ electrons}}{1 \text{ ligand}} \times \frac{1e_\sigma}{1 \text{ electron}} = 12e_\sigma$$

- The AOM predicts $\Delta_o = 3e_\sigma - 0e_\sigma = 3e_\sigma$.

- The strength of all π-acceptor interactions in the AOM is defined relative to the strength of the strongest one, namely that between the valence d_{xz} metal orbital and a π^* ligand orbital.

    - The strength of this reference interaction is denoted by e_π.
    - "Because the overlap for these orbitals is generally smaller than the sigma overlap, $e_\pi < e_\sigma$" (Miessler et al., 2014, p. 385).

- $[M(CN)_6]^{n-}$ example:
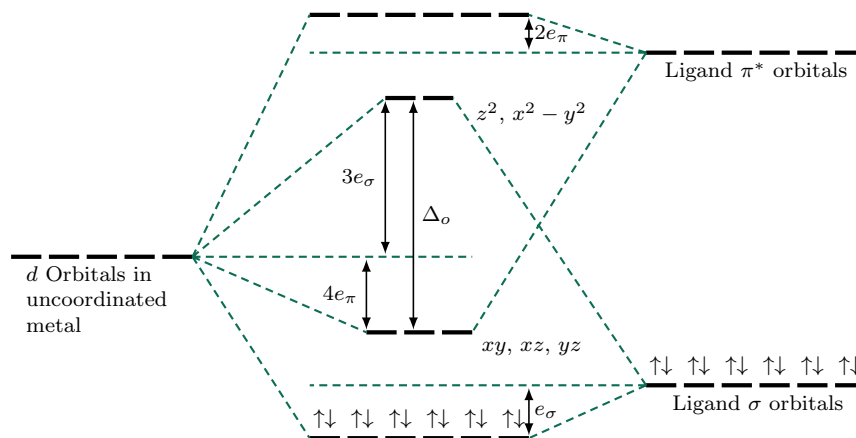
Figure VI.18: σ-donor, π-acceptor ML_6 angular overlap model orbital diagram.

- Similar to $[M(NH_3)_6]^{n+}$, except that the $d_{xy,xz,yz}$ orbitals are now lowered by $4e_\pi$ each, and the π^* orbitals are raised by $2e_\pi$ each.
- Note that this gives us $\Delta_o = 3e_\sigma + 4e_\pi$.
- Cyano ligands tend to be π acceptors.

- π-donor interactions are equivalent to π-acceptor interactions, except that the signs of the energy changes are reversed.
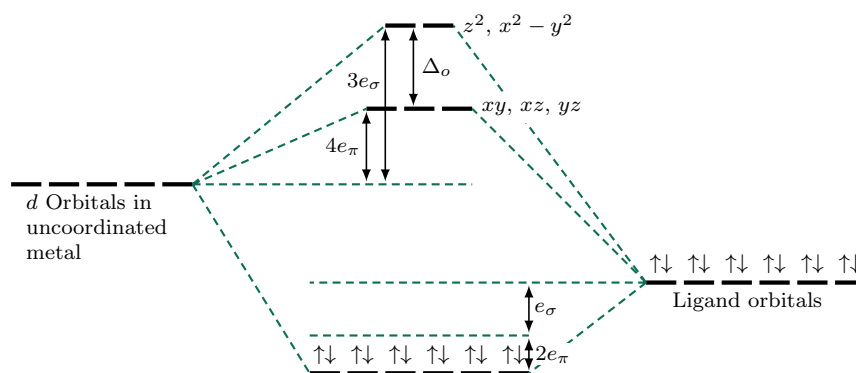
Figure VI.19: σ, π-donor ML_6 angular overlap model orbital diagram.

- Additionally, σ and π orbitals are not separate, but treated as the same orbitals. This further emphasizes that the AOM is primarily useful for predicting d-orbital splitting.
- Halide ions tend to be π donors.

- "With ligands that behave as both π acceptors and π donors (such as CO and CN^-), the π-acceptor nature predominates" (Miessler et al., 2014, p. 388).

  - This is largely because d-orbital overlap is generally more effective with π^*-acceptor orbitals than with π-donor orbitals.

- **Ligand field molecular mechanics**: A more mathematically sophisticated approach to metal-ligand interactions in which the angular overlap approach was used as a component. *Also known as* **LFMM**.

- Constructing the spectrochemical series:

  - First, consider pure σ donors.

    - Among these, en > NH_3. This is also the order of their proton basicity.

  - Next, consider π-donors.

    - Among the halides, $F^- > Cl^- > Br^- > I^-$. This is also the order of their proton basicity.
    - Others fit into the series as follows (note that OH^- is below H_2O since OH^- has more π-donating ability): $H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$.

  - Finally, consider π-acceptors.

    - CN^- and CO will be particularly strong, but here are some others: $CO, CN^- >$ phen $> NO_2^- > NCS^-$.

- Increasing ligand size and the corresponding bond length decreases angular overlap.

- Miessler et al. (2014) lists the wavenumbers of some angular overlap parameters.

- **Magnetochemical series**: A ligand ranking correlated to Δ.

- **Tetragonal distortion**: A distortion from O_h symmetry to D_{4h} symmetry.

- Considers four- and six-coordinate preferences, as well as possibilities for other shapes (such as trigonal bipyramidal).

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4{}^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Table VI.5: Character table for the O_h point group.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear	quadratic
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Table VI.6: Character table for the T_d point group.