Topic VI

Bonding and Physical Properties of Metal Complexes

VI.1 Module 34: Magnetic Properties of Transition Metal Complexes

2/22:

- 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:
  - 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

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

    where N is Avogadro's number, $k = 1.381 \times 10^{23}\,\text{J/K}$ 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 $e = 1.602 \times 10^{-19}\,\text{C}$ is the charge of an electron, $h = 6.626 \times 10^{-34}\,\text{J s}$ is Planck's constant, $m_e = 9.11 \times 10^{-31}\,\text{kg}$ is the mass of an electron, and $c = 2.998 \times 10^8\,\text{m/s}$ 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

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