

Week 6

???

6.1 Magnetochemistry I

2/7:

- Extension of last time's material: The derivation of the relationship for the between spring harmonic oscillator frequencies and the oscillators' reduced masses.
 - Suppose you have two homonuclear diatomic molecules A–A and B–B, and you wish to relate their vibrational frequencies.
 - Reduced masses of the molecules.

$$\mu_{AA} = \frac{m_A m_A}{m_A + m_B} \qquad \mu_{BB} = \frac{m_B m_B}{m_B + m_B}$$

- Vibrational frequencies of the molecules in terms of the reduced masses.

$$\nu_{AA} = k \sqrt{\frac{F}{\mu_{AA}}} \qquad \nu_{BB} = k \sqrt{\frac{F}{\mu_{BB}}}$$

- Take the ratio of the above two quantities to relate them.

$$\frac{\nu_{AA}}{\nu_{BB}} = \frac{k \sqrt{\frac{F}{\mu_{AA}}}}{k \sqrt{\frac{F}{\mu_{BB}}}} = \frac{\sqrt{\mu_{BB}}}{\sqrt{\mu_{AA}}}$$

- Anything else I missed??
- Today: Magnetochemistry.
 - 1-2 lectures on this.
 - Labalme [1] has a good write-up of the derivation at the beginning of today's lecture (see Module 34: Magnetic Properties of Transition Metal Complexes), and Labalme [2] has more on the content at the end of the lecture (see Lecture 3: TM Magnetism).
- Magnetism really is the province of inorganic chemistry since it's here that we find the compounds with unpaired electrons.
 - Organic compounds don't have these outside of free radicals.
- The nuclei interact with...??
- **Magnetic field.** Denoted by \mathbf{H} , \vec{H} .
 - H denotes the magnitude of \vec{H} .

- **Magnetization:** The response of a material to a magnetic field. *Denoted by M .*
 - Alternatively: The magnetic moment per unit volume.
 - Everything with electrons has *some* degree of a response to a magnetic field.
- **Magnetic induction:** The density of magnetic field lines within a substance. *Denoted by B . Units Teslas or Gauss.*
 - 1 T = 10 000 G.
 - The scale of these units.
 - The Earth's magnetic field is about 3×10^{-5} T.
 - A 900 MHz NMR spectrometer is about 21 T.
 - An MRI is about 1.3-3 T.
 - Additionally, $B = F/Qv$ where F is in Newtons, Q is in Coulombs, and v is in meters per second.

- Placing a sample with magnetization M in a magnetic field \vec{H} alters the magnetic induction via

$$B = \vec{H} + 4\pi\vec{M}$$

- The force that an object in a magnetic fields feels is

$$\vec{f} = \vec{M} \cdot \frac{dH}{dz}$$

- **Magnetic susceptibility.** *Denoted by χ . Given by*

$$\chi = \frac{\vec{M}}{\vec{H}}$$

- A tensor of rank 2.
 - It follows that $\vec{M} = \vec{\chi}\vec{H}$.
- **Volume susceptibility:** *Denoted by χ_V . Units emu cm^{-3} .*
- **Gram susceptibility:** *Denoted by χ_g . Units $\text{cm}^3 \text{g}^{-1}$. Given by*

$$\chi_g = \frac{\chi_V}{d}$$

- **Molar susceptibility:** *Denoted by χ_M . Units $\text{cm}^3 \text{mol}^{-1}$. Given by*

$$\chi_m = \chi_g \cdot MW$$

- $\chi > 0$ indicates unpaired electrons. $\chi < 0$ indicates paired electrons.
- Diamagnetism
- Most matter is diamagnetic.
- **Gouy balance:** An instrument that measures the change in mass of a sample as it is attracted or repelled by a powerful magnetic field.
 - Historically, varying a magnetic field precisely has been very difficult (we didn't always have electromagnets into which we could just dial any field).
 - In fact, even today, varying a magnetic field super precisely is difficult. This is why NMR machines vary the frequency domain over a constant magnetic field.

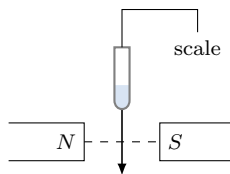


Figure 6.1: Gouy balance.

- Under this constant magnetic field, we linked a sample to a scale. As we move our sample through that field, we have a changing magnetic field.
- How the mass of the sample changes at different points in the field gives information on the magnetic susceptibility.
- Modern update to the Gouy balance: The superconducting quantum interference device, or SQUID.
 - We still measure the magnetic susceptibility essentially the same way, just with fancier toys.
 - Today, we move our sample through an electromagnet-generated magnetic field and then see what kind of current gets induced in a superconducting coil (recall that moving magnets induces currents).
 - The underlying physics is well beyond the scope of this course, but also fascinating. It involves **Josephson junctions**, etc.
- **Diamagnetic magnetic susceptibility.** Denoted by χ_{dia} .
- Per the above, since all electrons are paired in a diamagnetic compound, $\chi_{\text{dia}} < 0$.
- We have

$$\chi_{\text{dia}} = \sum \lambda + \sum n_i \chi_i$$
 - λ is a **constitutive correction** related to ring currents for bonds.
 - $n_i \chi_i$ is contributions from individual atoms.
- Info on the quantities in the above equations can be found in Bain and Berry [3].
 - The paper has a nice introduction and does the derivation that Anderson just did, too.
 - Then it contains a bunch of tables of different corrections for various bond types.
 - These values are all pretty small, so it doesn't really matter if you just miss one or two things in ambiguous cases, but Anderson tries to sum over all of them.
 - You need to do these corrections when you're doing a lot of these calculations.
 - These tables give both λ and χ_i values; you need to sum over the individual atom χ_i values and then constitutive corrections for groups. For example, for a Cp group, you have 5 carbons, 5 hydrogens, and a constitutive correction for the whole group (which should be equal to that of 5 carbons, 5 hydrogens, and 5 C=C double bonds??).
 - These values are field-independent and pretty constant.
- That's the contribution from paired electrons. What we really care about in general are the unpaired electrons, though.
- Paramagnetism.
- Paramagnets.
 - Positive χ values. The substance will be pulled into the magnetic field.
 - Inversely proportional relationship between χ and T so that $1/\chi$ vs. T is linear.

- Implies **Curie's law**, where $\chi = C/T$ and C is the Curie constant.

$$C = \frac{N_A g^2 \mu_B (S(S+1))}{3k_B (\text{inhertz??})}$$

- g is the **gyromagnetic ratio** and, occasionally, some other names for added complexity :)
- μ_B is the Bohr magneton.
- N_A is Avogadro's number.
- S is our spin quantum number.
- **Gyromagnetic ratio**: The quotient of the magnetic moment by the angular momentum. *Also known as magnetogyric ratio. Denoted by g .*
 - Any fundamental particle can have one of these.
 - Nuclei have them, but we're only worried about electrons here.
 - Magnetic moment divided by angular momentum.
 - 2.011 for electrons.

- We want to take this picture and simplify it down now.

- We have

$$\mu_{\text{eff}} = \sqrt{\frac{k_B}{N_A \mu_B^2} \chi T} = 2.828 \sqrt{\chi T} = \sqrt{g^2 (S(S+1))}$$

- $\mu_{\text{eff}} = \sqrt{g^2 (S(S+1))}$, $\chi T = g^2/8$ are our big results.

- We also frequently write

$$\chi T = \frac{N_A g^2 \mu_B}{3k_B} (S(S+1)) = \frac{g^2}{8} (S(S+1))$$

- Magnetochemists will almost exclusively use χT , but you see μ_{eff} reported a lot, especially for room temperature characterizations.
- Know the two end results below because they're very important for how stuff is computed and talked about in the literature.

$$\mu_{\text{eff}} = \sqrt{g^2 (S(S+1))} \qquad \chi T = \frac{g^2}{8} S(S+1)$$

- Elements vs. their spin quantum numbers. Find the number of unpaired electrons and go from there.

	S	μ_{eff}	χT_{SO}	μ_{exp}
Cu^{2+}	1/2	1.73	0.375	1.7-2.2
Ni^{2+}	1	2.83	1	2.8-3.5
Cr^{3+}	3/2	3.87	1.875	3.7-3.9
Fe^{2+} HS	2	4.90	3	5.1-5.7
Fe^{3+} HS	5/2	5.92	4.375	5.7-6

Table 6.1: Magnetic parameters for example elements.

- SO for spin only. HS for high spin. exp for experimental.
- Spin-orbit coupling: $g > 0$ for a more than half-filled shell; $g < 0$ for a less than half-filled shell.

- Consider a generic metal M with $S = 1/2$ and another with $S = 1/2$ and a bridging ligand L between them.
- Three possibilities to determine magnetism: The spins can be coupled antiferromagnetically (opposite directions) so $S = 0$, ferromagnetically coupled ($S = 1$), and uncoupled (both behave as their own spin center but are chemically/mechanically linked within the molecule).
- Now switch to having Cu-L-Mn to have $S = 1/2$ and $S = 5/2$. Then

$$\langle \mu \rangle = \sqrt{\mu_{M_1}^2 + \mu_{M_2}^2} = \sqrt{3 + 35} = 6.16\mu_B$$

- How does this work?? What is $\langle \mu \rangle$?
- Alternatively, χT can be calculated.
- Temperature-independent paramagnetism.
 - If we measure Cu^{II} and Co^{II} , we get $60 \times 10^{-6} \text{ emu}$ and $400 \times 10^{-6} \text{ emu}$.
 - Correcting Curie's law with the **Curie-Weiss law**

$$\chi = \frac{C}{T - \theta}$$

where $\theta = 0$ for a pure paramagnet and $\theta \neq 0$ for a long range magnetic interaction.

- Magnetic measurements are very sensitive; any time you're not fitting the data, 90% of the time it's that your sample isn't clean.
- Spin-orbit coupling is up next.
- S is our spin angular momentum quantum number, and L is our orbital angular momentum quantum number.
- We define $J = L + S$ to characterize coupling. J is very important with the lanthanides where our coupling is extremely large. So strong that you have to start with only a J quantum number. For first-row transition metals, we treat J just as a perturbation.
- We know that $L = \sum_i \ell_i$ and $S = \sum_i s_i$. Our Hamiltonian is

$$H = \hat{H}_0 + \hat{H}_{\text{elec}} + \hat{H}_{\text{SO}}$$

where SO denotes spin-orbit here and

$$\hat{H}_{\text{SO}} = \lambda \hat{L} \cdot \hat{S} + \beta(\hat{L} + g_e \hat{S}) - H$$

- The energy that we get out of this Hamiltonian is

$$E_n = E_n^0 + H E_n^1 + H^2 E_n^2$$

- The first-order correction is Zeeman; the second-order is 2nd order Zeeman.
- Consider a perfectly octahedral d^1 complex. The electron can migrate through a degenerate set of orbitals, inducing a ring current. This is a useful classical analogy with predictive power; however, it is not quantum mechanically accurate at all.
- In a nutshell, we expect to see SO-coupling when we have unequally occupied degenerate orbitals.
 - Consider Ni^{2+} . It can be O_h or T_d . It's tetrahedral because Ni^{2+} is d^8 and thus if you draw out the orbital diagram, we'll have one excess electron in the upper triply degenerate orbital. This unequal occupation will lead to a Jahn-Teller distortion, though.

- Free atom configurations are not a real thing; in this class, we'll always assume that transition metals are realistic, i.e., elemental, in a compound, etc., and thus any higher-level s electrons fall down to d electrons.
- Lanthanides' bonding orbitals are too deeply buried.
- **Zero-field splitting:** A difference in energy between “degenerate” electronic energy levels even in the presence of zero magnetic field. Denoted by D .

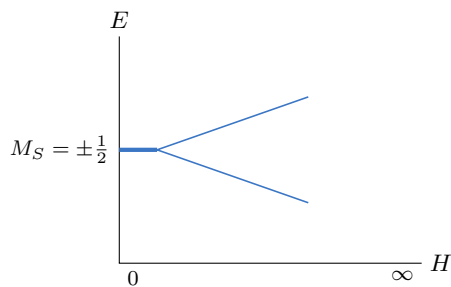
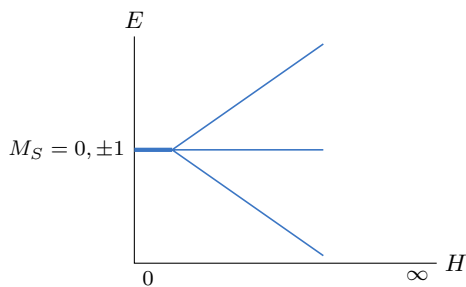
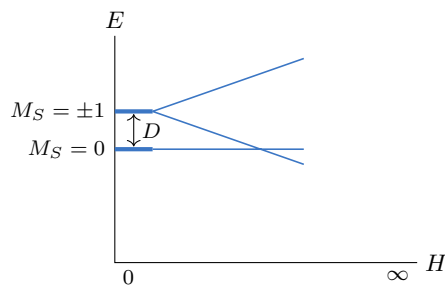
(a) $S = 1/2, D = 0$.(b) $S = 1, D = 0$.(c) $S = 1, D \neq 0$.

Figure 6.2: Zero field splitting.

- Important for Qbits or more exotic materials.
- Look at graphs of energy as a function of applied magnetic field H (see Figure 6.2).
- We get Zeeman splitting as we increase the magnetic field. In the $D = 0$ case, our splitting begins from a single point as in Figures 6.2a-6.2b.
- In Figure 6.2c, however, we can observe splitting even at $H = 0$.
- D is on the order of single wavenumbers.
- Affects what EPR values you can excite and other important things. The $M_s = 0$ state is still a triplet with parallel or antiparallel spins.