Week 6

Magnetochemistry

6.1 Magnetochemistry I

- Extension from last time: Deriving the relationship between two simple harmonic oscillators' fundamental frequencies and 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.

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

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

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

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

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

- 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.
    - 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.

- We begin with some terminology and relations.

- **Magnetic field**. *Denoted by* $\boldsymbol{H}$, $\vec{\boldsymbol{H}}$.

    - H denotes the magnitude of $\vec{H}$.

- **Magnetization**: The response of the electrons in a material to a magnetic field. *Denoted by* $\boldsymbol{M}$.

  - Alternatively: The magnetic moment per unit volume.
  - Everything with electrons has *some* degree of a response to a magnetic field.
  - Depends on the strength of the field in which the material is placed.

- **Magnetic induction**: The density of magnetic field lines within a substance. *Denoted by* $\boldsymbol{B}$. *Units* Teslas or Gauss. *Given by*

  - $1\,\mathrm{T} = 10\,000\,\mathrm{G}$.
  - The scale of these units.
    - ■ The Earth's magnetic field is about $3.1 \times 10^{-5}\,\mathrm{T}$.
    - ■ A 900 MHz NMR spectrometer is about 21 T.
    - ■ An MRI is about 1.3-3 T.

- We now give a few relations between the above quantities.

- First, we have that
$$B = \frac{F}{Qv}$$

  where F is in Newtons, Q is in Coulombs, and v is in meters per second.

- Additionally, placing a sample with magnetization M in a magnetic field $\vec{H}$ alters the magnetic induction via
$$B = \vec{H} + 4\pi\vec{M}$$

- Magnetically isotropic substances in a uniform magnetic field experience no force.

- In a region of nonhomogeneous field strength, a force is exerted along the axis of the field gradient as described by
$$\vec{f} = \vec{M} \cdot \frac{\mathrm{d}H}{\mathrm{d}z}$$

- **Magnetic susceptibility**. *Denoted by* $\boldsymbol{\chi}$. *Given by*

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

  - A tensor of rank 2.
  - It follows that $\vec{M} = \vec{\chi}\vec{H}$.

- There are different types of χ.

- **Volume susceptibility**: *Denoted by* $\boldsymbol{\chi_V}$. *Units* $\mathrm{emu\,cm^{-3}}$.

  - This is a dimensionless quantity, but we still use the units listed above.
  - Note that an emu is an "electromagnetic unit."

- **Gram susceptibility**: *Denoted by* $\boldsymbol{\chi_g}$. *Units* $\mathrm{cm^3\,g^{-1}}$. *Given by*

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

- **Molar susceptibility**: *Denoted by* $\boldsymbol{\chi_M}$. *Units* $\mathrm{cm^3\,mol^{-1}}$. *Given by*

$$\chi_m = \chi_g \cdot \mathrm{MW}$$

- The sign of χ $(+/-)$ depends on the presence of absence of unpaired electrons. In particular...

  - $\chi > 0$ indicates unpaired electrons.
  - $\chi < 0$ indicates paired electrons.

- We now move on to diamagnetism.

- Most matter is diamagnetic.

- **Diamagnetic** (compound): A compound that has no unpaired electrons. *Also known as* **diamagnet**.

  - $S = 0$ for a diamagnet.
  - These materials are weakly repelled by magnetic fields.
  - The old-school way to measure this weak repulsion is with a **Gouy balance**.

- **Gouy balance**: An instrument that measures the change in mass of a sample as it is attracted ore repelled by a powerful magnetic field.
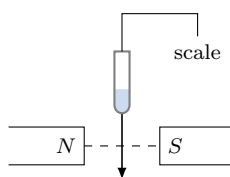

Figure 6.1: Gouy balance.

  - 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 (as opposed to varying the magnetic domain over a constant frequency).
  - Under a constant magnetic field, the sample (contained in an NMR tube) is linked to a scale. As the sample moves through that field, it experiences a changing magnetic field.
  - The change in mass of the sample at different points in the field gives information on its 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 induce 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* $\chi_{\mathbf{dia}}$.

- Since all electrons are *paired* in a diamagnetic compound, we have by the above that $\chi_{\mathrm{dia}} < 0$.

- Diamagnetic contributions can be calculated as follows.

$$\chi_{\mathrm{dia}} = \sum \lambda + \sum n_i \chi_i$$

  - λ is a **constitutive correction** related to ring currents for bonds/ring delocalization.
  - $n_i \chi_i$ is contributions from individual atoms.

- The values in the above equation can be looked up for a compound.

  - In particular, see 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 *do* need to do these corrections when you're doing a lot of these calculations.
    - ◼ The result will be on the order of 10^{-6} emu, but that can be significant enough to effect your work.
  - 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.

- **Paramagnetic** (compound): A compound that has unpaired electrons. *Also known as* **paramagnet**.

  - Positive χ values; thus, they get pulled into applied magnetic fields.

- Temperature dependence of χ.

  - There is an inversely proportional relationship between χ and T; in other words, a plot of $1/\chi$ vs. T is linear.
  - This notion is formalized by **Curie's law**.

- **Curie constant**: The following constant. *Denoted by* $\boldsymbol{C}$. *Given by*

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

  - g is the **gyromagnetic ratio**.
  - μ_B is the Bohr magneton.
  - N_A is Avogadro's number.
  - S is the spin quantum number.

- **Gyromagnetic ratio**: The quotient of the magnetic moment of an electron by its angular momentum. *Also known as* **magnetogyric ratio**. *Denoted by* $\boldsymbol{g}$.

  - There are even more names that the gyromagnetic ratio is sometimes called, just for added complexity :)
  - 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.
  - More on this later.

- **Curie's law**: The relationship between χ and T. *Given by*

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

- From the written notes: We have that

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m_e} = 9.3 \times 10^{-24}\,\mathrm{J\,K^{-1}}$$

- We want to take the picture provided by Curie's law and simplify it down now.

- For the spin-only case (this restriction is very important), we can define the effective magnetic moment

$$\mu_{\mathrm{eff}} = \sqrt{\frac{k_{\mathrm{B}}}{N_{\mathrm{A}}\mu_{\mathrm{B}}{}^2}}\sqrt{\chi T} = 2.828\sqrt{\chi T} = \sqrt{g^2(S(S+1))}$$

  – What is the origin of the first equality??

- We also frequently write

$$\chi T = \frac{N_{\mathrm{A}}g^2\mu_{\mathrm{B}}}{3k_{\mathrm{B}}}(S(S+1)) = \frac{g^2}{8}(S(S+1))$$

- Magnetochemists almost exclusively use χT, but μ_{eff} is oft reported for room temp characterizations.

- Know the end results below: Very important for how stuff is computed and talked about in the lit.

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

  – Approximating $g \approx 2$, we can rewrite the above as

$$\mu_{\mathrm{eff}} = \sqrt{4(S(S+1))} \qquad\qquad \chi T = \frac{1}{2}S(S+1)$$

  – $g \not\approx 2$ always, though — take a look at the following examples.

- Elements and some paramagnetic parameters.

	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.

  – Notation: SO for spin only. HS for high spin. exp for experimental.
  – To calculate the data in Table 6.1, find the number of unpaired electrons and go from there.
  – Example: Cu^{2+}. From the periodic table, Cu^{2+} is d^9. Hence it has 1 unpaired electron. Thus...
    ▪ $S = 1 \cdot 1/2 = 1/2$.
    ▪ $\mu_{\mathrm{eff}} = \sqrt{4(S(S+1))} = \sqrt{4(1/2(1/2+1))} = \sqrt{3} = 1.73$.
    ▪ $\chi T_{\mathrm{SO}} = 1/2 \cdot S(S+1) = 1/2 \cdot 1/2(1/2+1) = 3/8 = 0.375$.
    ▪ The calculated effective μ often (not always) agrees with the experimental range.

- We now move on to spin-orbit coupling.

- 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 $S = 0$, coupled feromagnetically so $S = 1$, or uncoupled so both behave as their own spin center but are chemically/mechanically linked within the molecule.

- Now for a specific example of metal centers with different spins: Consider Cu−L−Mn, which has $S = 1/2$ and $S = 5/2$. Then

$$\langle \mu \rangle = \sqrt{\mu_{\text{Cu}}^2 + \mu_{\text{Mn}}^2} = \sqrt{3 + 35} = 6.16 \mu_{\text{B}}$$

  - How does this work?? What is $\langle \mu \rangle$?
  - Alternatively, χT can be calculated (this is easier??).

- A brief note about temperature-independent paramagnetism.

  - If we measure Cu^{II} and Co^{II}, we get 60×10^{-6} emu and 400×10^{-6} emu.

    ■ These come from excited state mixing: These excited states are not thermally populated, but they are a quantum mechanically admixed state (what does this mean??).
    ■ What are these values??

- Note: Curie's law doesn't always hold. In cases where it doesn't, we can correct it to the **Curie-Weiss law**.

- **Weiss constant**: A constant describing certain magnetic interactions. *Denoted by $\boldsymbol{\theta}$.*

  - $\theta = 0$ for a pure paramagnet.
  - $\theta \neq 0$ for a long range magnetic interaction in a solid sample.

- **Curie-Weiss law**: The following relation, where C is the Curie constant, T is temperature, and θ is the Weiss constant. *Given by*

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

  - Don't rush to use the Curie-Weiss law if your data isn't fitting to Curie's law, though: Magnetic measurements are very sensitive and 90% of the time you're data isn't fitting, it's because your sample isn't clean.

- We now return to the question of when g deviates from 2: Indeed, this only happens when there is a substantial magnetic contribution from the orbital angular momentum.

- S is our spin angular momentum quantum number, and L is our orbital angular momentum quantum number.

  - If spin and orbital angular momenta couple, then S, L are no longer good quantum numbers.
  - To fix this problem, we define a new one: J.

- We define $J = L + S$ to characterize coupling.

  - J is very important with the lanthanides where our coupling is extremely large.

    ■ In fact, in the lanthanides, coupling is 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

$$L = \sum_i \ell_i \qquad\qquad S = \sum_i s_i$$

- Thus, our Hamiltonian is

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

  - SO denotes spin-orbit
  - We have that

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

  where λ is the SOC constant.
  - 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**.

- An intuitive mental picture of SOC.

  - 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.

- Aside on free atom configurations.

  - These 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**: The removal of spin degeneracy in the absence of an applied magnetic field. *Denoted by* $\boldsymbol{D}$.

  - 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.
  - In the $S = 3/2$ case, we have multibranched splitting??

(a) $S = 1/2$, $D = 0$.

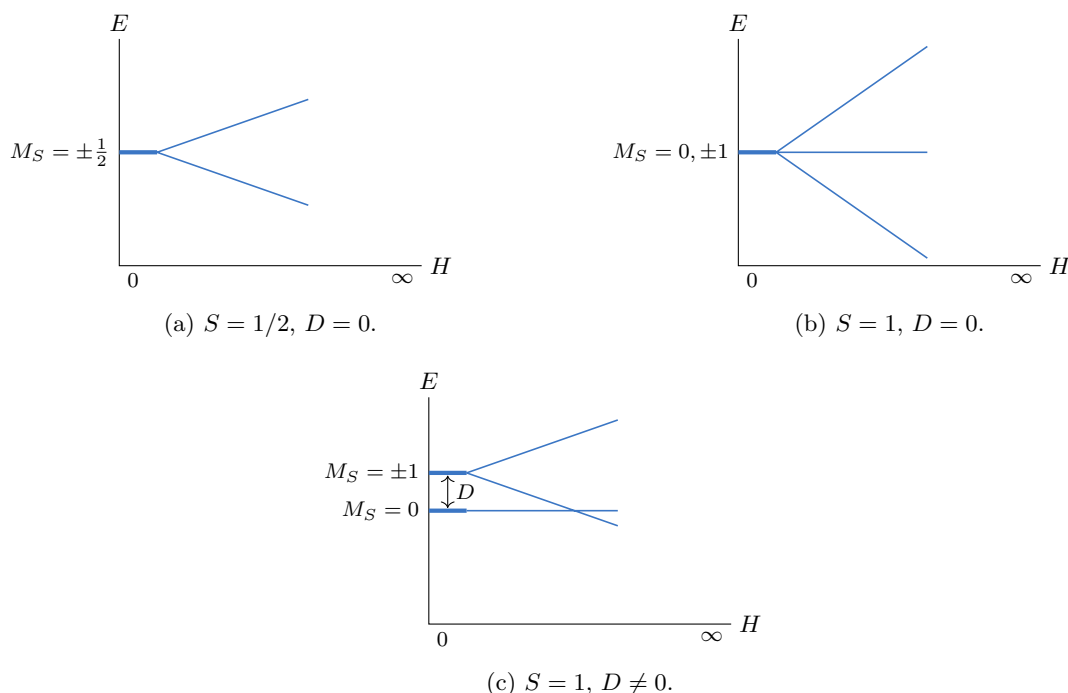(b) $S = 1$, $D = 0$.

(c) $S = 1$, $D \neq 0$.

Figure 6.2: Zero field splitting.

6.2 Magnetochemistry II

2/9:
- Today: Materials magnetism.

  - We finish up last time's material first, and then head into new content.

- Classical example of zero-field splitting for an $S = 1$ compound (see Figure 6.2c).

  - The magnitude of spin-orbit coupling determines zero-field splitting.
  - D can be both positive and negative, so it can vary whether the higher state goes up or the lower state goes down. The short answer is just that splitting occurs.
  - Recent example from the literature (unpublished): An aryl-bismuth compound with $S = 1$ and massive $D \approx 500\,\text{cm}^{-1}$. Another one is $\text{Bi}-\text{Bi}^{2-}$.

- Coupling.

  - Electrons can couple parallel (FM — ferromagnetic) or antiparallel (AF — antiferromagnetic).
    - AF is more common.
    - Relevant Hamiltonian: The **Heisenberg-Dirac-Van Vleck Hamiltonian**.
  - We measure coupling by measuring χ vs. T.
    - FM systems: As temperature decreases, χ slightly increases until the **Curie/critical temperature** T_C. At this point, the curve turns upwards sharply. For a bulk compound, the curve peaks at T_C and then goes down.
    - AF systems: As temperature decreases, there is a similar rise to a peak (this time at the **Neel temperature** T_N) and drop.
    - As J gets larger, the FM curve increases (i.e., χ increases). On the other hand, the AF curve decreases and flattens.
    - See Figure 1.13 of Labalme [2] and the picture from class.

- **Heisenberg-Dirac-Van Vleck** (Hamiltonian): The Hamiltonian defined as follows. *Given by*

$$\hat{H}_{\mathrm{HDVV}} = -2J \cdot \vec{S}_1 \cdot \vec{S}_2$$

  - J is the coupling constant in cm^{-1}.
  - $J < 0$ for AF; $J > 0$ for FM.

- **Bleaney-Bowers equation**: The equation describing the shape of the χ vs. T plot for two spin centers of $S = 1/2$. *Given by*

$$\chi = \frac{N\beta^2 g^2}{3k_{\mathrm{B}}T} \cdot \frac{3}{3 + \mathrm{e}^{2J/k_{\mathrm{B}}T}} + P \cdot \frac{C}{T}$$

  - Fitting data to this functional form allows you to pull out a value of J.
  - Works best for two spin centers of $S = 1/2$.
  - P is the percentage of paramagnetic impurities.
  - If $S > 1/2$, the functional form becomes much more complicated and we need softwares to do the fitting.
    - One example is Dave (contact Anderson if you need it).
  - Which of the previously discussed plots (FM/AM and bulk/molecular) can we fit with this equation?? Also check the functional form — 2 in the numerator and negative sign in the exponent?

- Orbital interactions for coupling.

  - The goal here is to use our understanding of bonding and MO theory to predict magnetic coupling interactions.
  - It is a challenging question, but also quite fundamental.
  - Example question in this field: If two electrons couple antiferromagnetically, at what point does a strong antiferromagnetic interaction become a bond?
    - Depends on orientation and orbital overlap.
  - There are many approaches, but we shoot for a general qualitative picture, only good enough to help us predict the sign and magnitude of coupling in a given system.

- First system to analyze: Picture two spin centers A, B coupled with some diamagnetic bridging ligand X such that we have A$-$X$-$B.

  - There are two possible ground states: $S = 0$ (singlet) and $S = 1$ (triplet).
    - Relevant quantitative parameter: the **singlet-triplet gap**.
  - The only structure we assert is an orbital ϕ_{A} on A and likewise on X and B.
  - These three orbitals mix to create a bonding, nonbonding, and antibonding set with zero nodes, one node, and two nodes, respectively. We call these ϕ_0, ϕ_1, ϕ_2, respectively. As LCAOs:

$$\phi_0 = \phi_{\mathrm{X}} + \varepsilon(\phi_{\mathrm{A}} + \phi_{\mathrm{B}}) \qquad \phi_1 = \phi_{\mathrm{A}} - \phi_{\mathrm{B}} \qquad \phi_2 = (\phi_{\mathrm{A}} + \phi_{\mathrm{B}}) - \varepsilon\phi_{\mathrm{X}}$$

  - ε is an overlap parameter dictated by both spatial and energetic overlap.
    - Specifically, ϵ quantifies overlap with X by A and B.
    - In general TM chemistry, X will be more electronegative than A,B. Since it is lower in energy, this will lead to lesser splitting.
    - Thus, more electropositive X have greater coupling, splitting, and singlet ground states.

- **Singlet-triplet gap**: The splitting between the ground states $S = 0$ and $S = 1$ in a 2$\times$ $S = 1/2$ setup. *Denoted by* J.

  - This J is identical to the exchange coupling constant between A and B.

- Quantifying FM and AF contributions: The total coupling constant is given by

$$J_{\text{tot}} = 2K + 4\beta S - 2S^2(2\alpha + J)$$

  - S is the overlap integral and hence kind of replaces ε.
  - The second order term is usually negligible.
  - $2K$ is J_{FM}.
    - ■ Notice that J_{FM} is only related to distance.
    - ■ What does K denote?? What are its units?
  - $4\beta S$ is J_{AF}.
  - To maximize FM, we want a short distance and no overlap; to maximize AF, we want a long distance and big overlap.
    - ■ How does this make sense?? Don't short distances and big overlaps already correlate?
    - ■ Takeaway: This allows us to use our chemical intuition of orbital interactions to predict AF vs. FM interactions, and their rough magnitude.
- Examples.
- Example: There's a lot of data on compounds like di-copper compounds with bridging ligands.
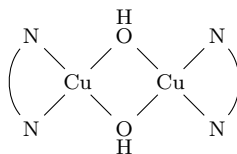

Figure 6.3: A di-copper compound with bridging ligands.

  - See Kahn [4].
  - Anderson presents data showing that J varies quite a bit as a function of the $Cu-O-Cu$ angle.
    - ■ The exact data can be found in the notes.
  - As the bond becomes more linear, J gets more negative.
  - Performing a linear fit on Anderson's data yields

$$J = -74 \cdot \text{angle} + 7270 \, \text{cm}^{-1}$$

    - ■ It follows by comparison to the J_{tot} equation that $2K = 7270$ and $4\beta S = -74 \cdot \text{angle}$.
  - The above comparison suggests that J_{FM} is constant. Is this a good or a bad approximation?
    - ■ Changing the angles changes the distance, so assuming J_{FM} is constant is a *bad* approximation.
    - ■ Indeed, the linear fit is not at all fundamentally correct. However, it's not bad as a first approximation, which is remarkable in its own right.
- Example (continued): Two copper orbitals combining.

(a) MO diagram.

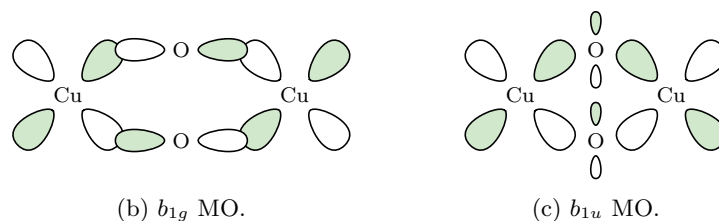(b) b_{1g} MO.   (c) b_{1u} MO.
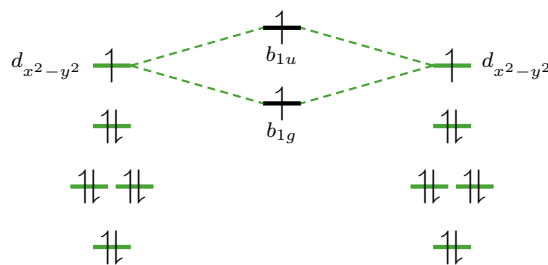
Figure 6.4: Molecular orbitals in a di-copper compound.

- Recall that each copper center will have the orbital structure depicted in Figure 6.4a due to the extreme Jahn-Teller distortions associated with the square planar geometry.
- The $d_{x^2+y^2}$ orbitals are singly occupied. Thus, they couple and split.
  - The magnitude of the splitting is that of your AF coupling.
  - Are you sure you don't mean the d_{xy} orbitals?? That's what it looks like you've drawn.
- The b_{1g} orbital (Figure 6.4b) is antibonding.
- The b_{1u} orbital (Figure 6.4c) is nonbonding.
- As we linearize, b_{1g} will be stabilized (better overlap) and b_{1u} will be destabilized (less overlap).
  - This increases splitting and favors a lower spin state.
  - Thus, as we linearize, eventually the electrons (which have been coupled ferromagnetically in different orbitals) will pair (antiferromagnetically) in the same orbital. This is also the point at which the data anderson presents flips signs from positive J_{tot} (FM dominates) to negative J_{tot} (AF dominates).
- Three open-shell states corresponding to M_s values all get rolled into one closed shell state??

- Another example: Goodenough-Kanamori rules.

  - Started out very empirically (experimental work by John Goodenough) and then grew into a more robust theory (theoretical work by Junjiro Kanamori) as our understanding of orbitals grew.
  - John Goodenough won the Nobel prize for lithium ion batteries, made foundational contributions to metal oxides, and was a UChicago physics PhD.
    - "These people that are super important somewhere tend to crop up everywhere" - Anderson.
  - Consider a generic metal with an unpaired electron in the d_{z^2} orbital. Connect two of these with the p-orbital of a bridging oxygen.
    - The singly occupied states (d_{z^2} orbitals) will mix and split.
    - The splitting determines $S = 0$ and $S = 1$.
    - **Superexchange**, **direct exchange**, and **double exchange** can take place.
  - Rule 1: Linearity maximizes AF exchange.
    - To obtain molecules of this type, we build in symmetry, linearity, etc. via ligands, etc.
  - Rule 2: 90° maximizes FM exchange.
    - To obtain molecules of this type, we build in orbital orthogonality by design.
  - In between 90 and 180 isn't readily experimentally accessible.
  - What is all of this??

- **Superexchange**: Coupling/virtual electron transfers between atoms with a net spin through a diamagnetic linker.

- **Direct exchange**: The electrons of magnetic atoms interact with their nearest neighbors.

- **Double exchange**: A magnetic exchange that arises between ions in different oxidation states.

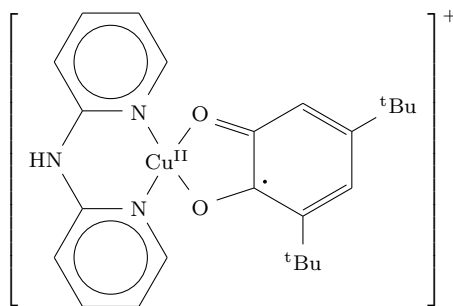- Getting a large FM interaction: An example of orthogonality by design.

Figure 6.5: Designing a compound with orthogonal electrons.

- – A dipyridyl and semiquinoid ligand on copper. This is overall a monocation.
- – We search for compounds like this (high FM) when we want to make magnetic materials.
- – Key: The unpaired electron on the semiquinoid is rigorously orthogonal to the copper one since they are in $d_{x^2-y^2}$ vs. p_z orbitals.
  - ■ Moreover, the Cu electron has σ symmetry, while the C electron has π symmetry. This is further evidence of rigorous orthogonality.
  - ■ Recall that we are (simplistically) looking to bring spins as close together as possible while having no orbital overlap: In addition to the rigorous orthogonality here, spacing is 2-3 Å.
- – $J > 200\,\text{cm}^{-1}$ here.
- – χT vs. temperature.
  - ■ Our emphasis on FM coupling means that spins certainly couple parallel here, making $S = 1/2 + 1/2 = 1$. This means that we have a triplet ($2S + 1 = 3$) ground state.
  - ■ We see a triplet ground state at super low temperatures.
  - ■ The slope fits the Boltzmann population of the spin manifold.
  - ■ Thermal energy can break the triplet and populate some singlet states, as observed in the variable temperature susceptibility??

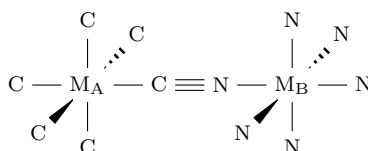- General structure of Prussian blue analogs.

Figure 6.6: Prussian blue analogs.

- – Metals with ligands linked by a tightly bound cyanide.
- – Gadet et al. [5] recognized that if $M_A = Ni^{II}$ and $M_B = Cr^{III}$, then M_A is d^8 and M_B is d^3. Thus, the two metals are rigorously orthogonal.
  - ■ What we mean by this is that drawing out the d-orbital MO diagrams (t_{2g} and e_g sets), we see that Ni^{II} has 2 unpaired electrons in the e_g set, and Cr^{III} has 3 unpaired electrons in the t_{2g} set. Thus, the molecule overall has *five* unpaired electrons in MOs.
- – This is one of the highest ordering magnetic materials known.
  - ■ FM coupling is still not great, though, due to the long distance.
- – This material can be extended into a 3D crystal.

- Prediction of the nature of interaction between differently occupied orbitals table.

	d^3	d^4 elongated	d^5	d^8	d^9 elongated
d^3	AF $\leftarrow$ AF	AF	AF	F	F
d^4 elongated	AF	AF $\leftarrow$ AF	F	F	F
d^5			AF (or F) $\rightarrow$ AF	F $\rightarrow$ AF	F $\rightarrow$ AF
d^8				F $\rightarrow$ AF	F $\rightarrow$ AF
d^9 elongated				F $\rightarrow$ AF	

Table 6.2: Predicting the nature of magnetic orbital interactions.

- Reading the table.
    - ■ F: Ferromagnetic.
    - ■ AF: Antiferromagnetic.
    - ■ $\rightarrow$: The interaction is expected to be more antiferromagnetic when the bridging angle *increases* from 90°.
    - ■ $\leftarrow$: The interaction is expected to be more antiferromagnetic when the bridging angle *decreases* toward 90°.
- Don't memorize the table!
    - ■ In many cases, it's just better to draw our your d-orbital diagrams.
    - ■ I am including it solely for practice checking my predictions.
- General rules:
    - ■ Certain compounds will have rigorous orthogonality.
    - ■ In general, though, we'll have a mix of FM and AF interactions.
    - ■ In these cases, we have to carefully consider the strength and orthogonality of all possible magnetic orbital interactions (that is, all possible interactions between singly occupied orbitals).
    - ■ Rough guess: AF interactions typically win out.

- We *now* start materials.
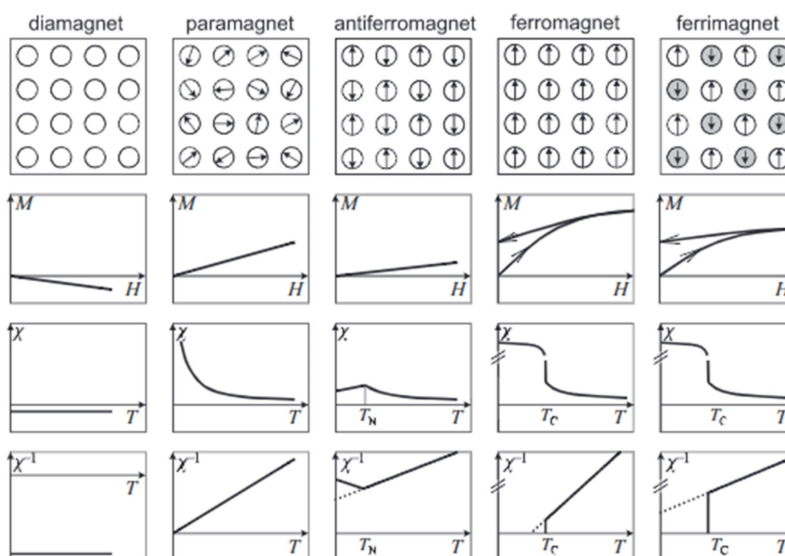
- Summary of bulk coupling in materials.

Table 6.3: Bulk magnetic coupling.

- Paramagnets have a bunch of spins with no preference for alignment. Note that $1/\chi$ is linear as discussed last lecture!

- Ferromagnet: We would need thermal energy to break the paired spins. This is an unstable equilibrium.

- Ferrimagnet: Closer to an antiferromagnet theoretically. Treats alloys where we have oppositely aligned differing spin populations. Behavior is almost exactly ferromagnetic.

- Bulk behavior is dictated by nearest neighbor interactions.

  - One exception is as follows, where the delocalized electron cloud can be polarized by a magnetic field.

- **Pauli paramagnetism**: A metal that's a pool of electrons which are sloshing around in a band structure. Pool of positive and negative spins. Treat it as an electron gas. Applying a magnetic field changes the relative energies of the pool or electrons.
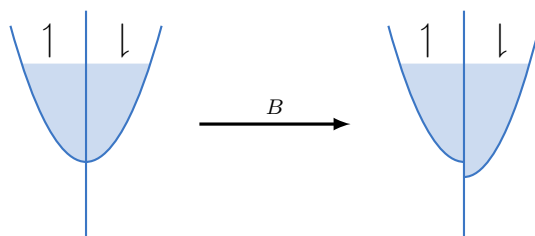

Figure 6.7: Pauli paramagnetism.

  - We now have more spin down, creating a net magnetic field that will be very small. *This* is Pauli paramagnetism.

- Ferromagnets.

  - Most applications for magnets are with ferromagnetic materials.
  - NdFeB is the strongest **hard** ferromagnet.
  - The most classic case of a ferrimagnet is magnetite (mixed Fe^{2+} and Fe^{3+}).

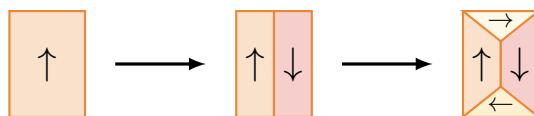- Ferromagnets ideally have only one magnetic domain.

Figure 6.8: Ferromagnetic domains.

  - Over time, different magnetic fields fracture domains. The products may align antiparallel.
  - Applying a strong external magnetic field can anneal the domain walls and get you back to a single domain.

- **Saturation magnetization**: The maximal magnetization of a material. *Denoted by $M_{\mathbf{sat}}$.*

- **Remnant magnetization**: The magnetization of a magnetized material after the external field is dialed back. *Denoted by $M_{\mathbf{rem}}$.*

- **Coercive field**: The amount of external field required to flip a magnet. *Denoted by H_C.*

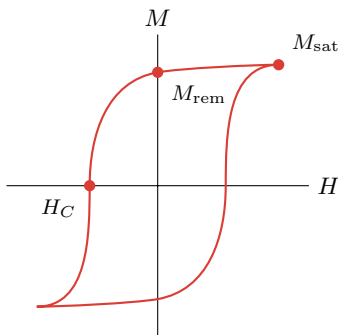- Visualizing M_{sat}, M_{rem}, and H_C.

Figure 6.9: Hysteresis loop.

- A hysteresis loop characterizes the energy penalty to homogenize away domain boundaries and then flip the spin of a bulk domain; this quantity is what gives ferromagnets their useful properties.
- $H_C \propto$ SOC, i.e., spin-orbit coupling.
- Things like Fe^{3+} HS d^5 with equally (singly) occupied d orbitals have no preferred orientation.
    - Ti^{3+} with d^1 can generate "ring currents," giving it a preferred orientation.
- The wider the curve, the **harder** the ferromagnet.
- **Soft** is much skinnier (good for things like transformers that you want to be able to switch).
- To mediate coupling between f orbitals in lanthanides, we mix in a bit of iron to use its free electrons.

- Exotic things just to be aware of.

    - Ferrometals: Iron is an example.
        - Metallic band structure even in the absence of a magnetic field.
    - Ferro half metal.
        - Charge carriers are spin-polarized.
        - Important in spin-tronic type applications, P/N junctions, etc.
        - Example: CrO_2.
    - Metals have a continuous set of bands at the Fermi level regardless.
    - Ferro insulator.
        - Filled band with no density of states. A magnet that is not conductive, essentially.
        - Example: EuO.
    - Weak coupling or frustration. AF exchange with spins that get frozen in. Frustration: Triangular lattice with up/down/what's the third.
    - Spin glass: Freeze-in spin orientations such that when you get back to a certain magnetization, you auto-drop.

- Magnetic properties of some anonymized commercial polycrystalline hard magnets.

- Do we have to learn the stuff at the end of the notes on exotic materials, ferrimagnetism, and commercial magnets??

- Next week: EPR.