

Week 6

Magnetochemistry

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.

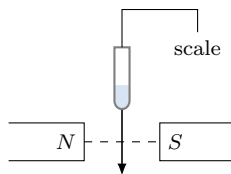


Figure 6.1: Gouy balance.

- 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

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

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

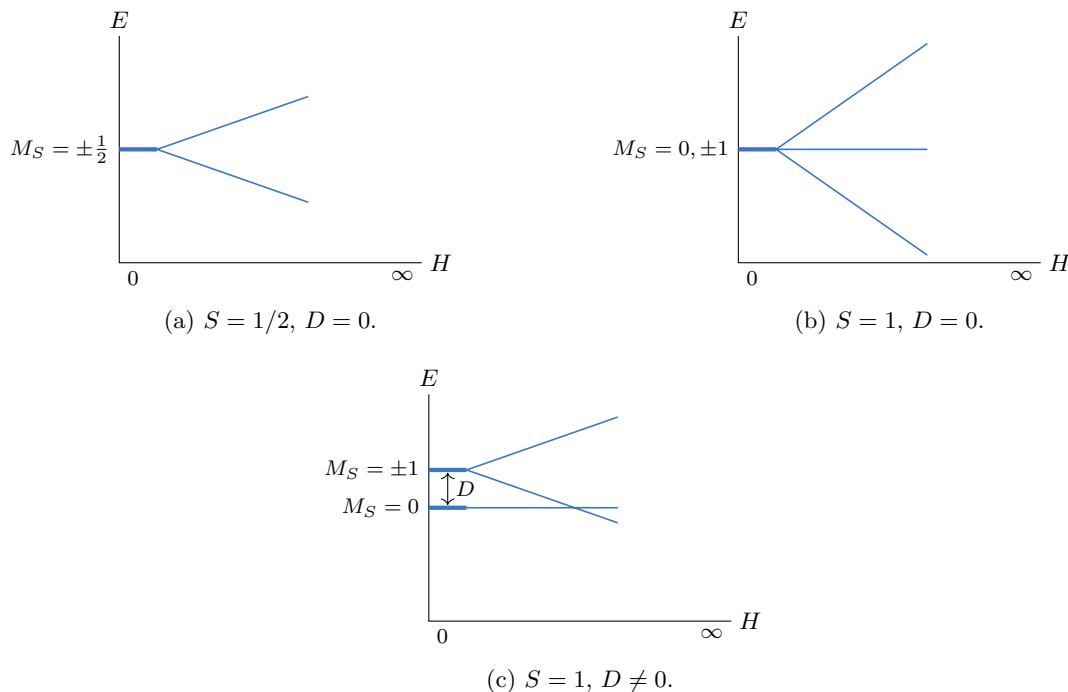


Figure 6.2: Zero field splitting.

- 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.

6.2 Magnetochemistry II

2/9:

- We just about wrapped up molecular magnetism last time.
- There are notes posted online for all of the lectures.
- Today: Materials magnetism.
- We start with some review from last time and lead into new content from there.
- Classical example of zero-field splitting for an $S = 1$ compound.

- We have $M_s = -1, 0, 1$.
- 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).
 - 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.
 - AM 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*

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

- J is the coupling constant in cm^{-1} .
- **Bleaney-Bowers equation**: The equation describing the shape of the χ vs. T plot for two spin centers of $S = 1/2$. *Given by*

$$\chi = \frac{N\beta^2 g^2}{3k_B T} \cdot \frac{3}{3 + e^{2J/k_B T}}$$
 - Fitting data to this functional form allows you to pull out a value of J .
 - Works best for two spin centers of $S = 1/2$.
 - There are softwares to do this fitting such as 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.

- First system: Picture two spin centers A,B coupled with some diamagnetic bridging ligand X such that we have A–X–B.
- 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. We reexpress them as LCAOs.

$$\phi_0 = \phi_X + \varepsilon(\phi_A + \phi_B) \qquad \phi_1 = \phi_A - \phi_B \qquad \phi_2 = (\phi_A + \phi_B) - \varepsilon\phi_X$$

- ε is an overlap parameter dictated by both spatial and energetic overlap.
- In general TM chemistry, X will be more electronegative than A,B. So the more electropositive X gets, the greater our coupling??

- 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?
- There's a lot of data on compounds like di-copper compounds with bridging ligands.

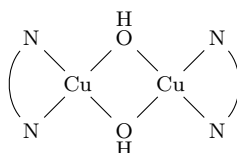


Figure 6.3: A di-copper compound with bridging ligands.

- See Olivier Kahn's book: *Molecular Magnetism*.
- Anderson presents data showing that J varies quite a bit as a function of the Cu–O–Cu angle.
- 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 that 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.
- Two copper orbitals combining.
 - Recall that each copper center will have the orbital structure depicted in Figure 6.4a due to the extreme Jahn-Teller distortions commonly associated with the element.
 - 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} gets less strong and b_{1u} gets more strong (correct??).
 - Linearizing increases AF character.
 - Three open-shell states corresponding to M_s values all get rolled into one closed shell state??

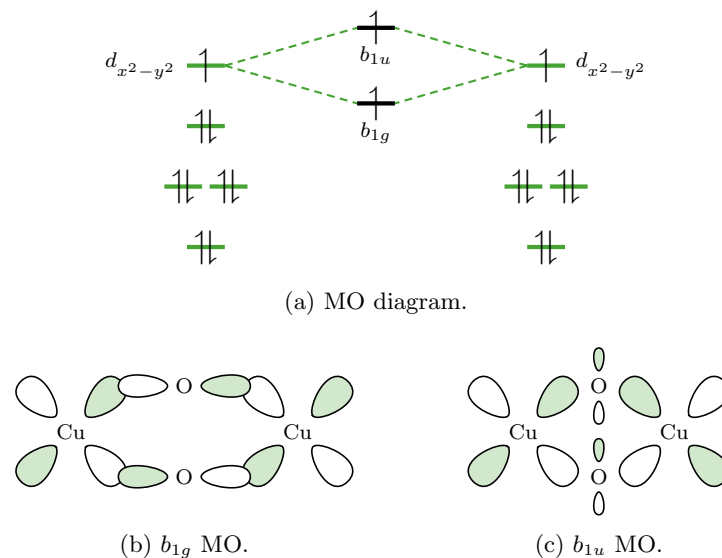


Figure 6.4: Molecular orbitals in a di-copper compound.

- Goodenough-Kanamori rules.
 - Started out very empirically and then grew into a more robust theory 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.
 - Unpaired electrons in d_{z^2} orbitals.
 - **Superexchange**, **direct exchange**, and **double exchange**.
 - Splitting of singly occupied states.
 - Linearity maximizes AF exchange.
 - To obtain molecules of this type, we build in symmetry, linearity, etc. via ligands, etc.
 - 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.
- An example of orthogonality by design.
 - The compound in Figure 6.5 is composed of a dipyridyl and semiquinoid ligand on copper. It is overall a monocation.
 - 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.
 - $J > 200 \text{ cm}^{-1}$ here.

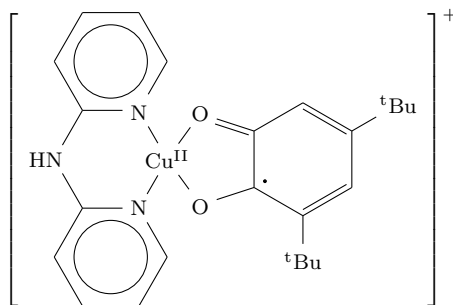


Figure 6.5: Designing a compound with orthogonal electrons.

- χT vs. temperature.
 - We see a triplet ground state at super low temperatures.
 - The slope fits the Boltzmann population of the spin manifold.
- General structure of Prussian blue analogs.

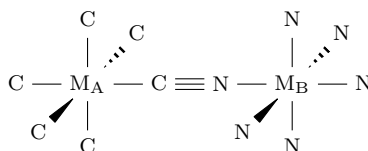


Figure 6.6: Prussian blue analogs.

- Metals with ligands linked by a tightly bound cyanide.
- Gadet et al. [4] recognized that if $\text{M}_\text{A} = \text{Ni}^{\text{II}}$ and $\text{M}_\text{B} = \text{Cr}^{\text{III}}$, 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 due to the long distance.
- Prediction of the nature of interaction between differently occupied orbitals table.
 - Don't memorize the table; in many cases, it's just better to draw our your d -orbital diagrams.
- We *now* start materials.
- Summary of bulk coupling in materials.
 - 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.
- **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.

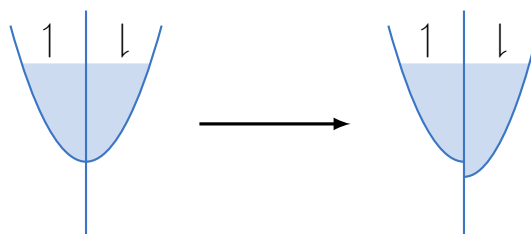
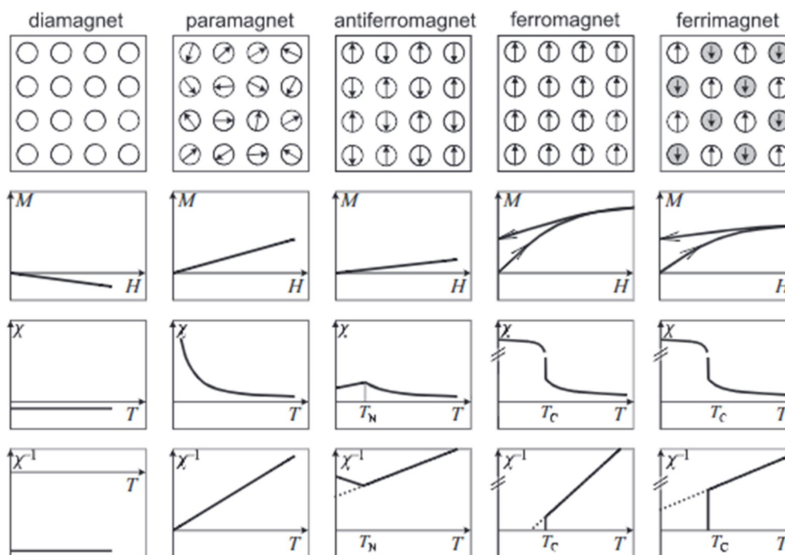


Figure 6.7: Pauli paramagnetism.

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

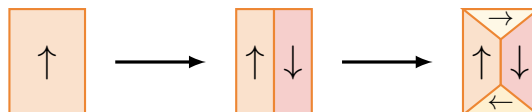


Figure 6.8: Ferromagnetic domains.

- Over time, under different magnetic fields, you'll get fracturing domains. These 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_{sat} .
- **Remnant magnetization:** The magnetization of a magnetized material after the external field is dialed back. Denoted by M_{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 .

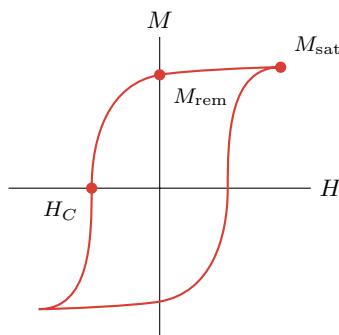


Figure 6.9: Hysteresis loop.

- $H_C \propto \text{SOC}$, 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.
 - 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.
 - 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.
- Next week: EPR.