WHEN WE UNDERTHE LAST LECTURE,
WE WERE DISCUSSING THE "EXCHANGE ENERGY"
OF A TWO-ELECTRON WAVEFUNCTION, WHICH IS
DEFINED AS THE DIFFERENCE BETWEEN STATES
WITH SPIN PARALLEL AND ANTI-PARALLEL. THE
ORIGIN OF THE NAME WILL BECOME APPARENT IN
A MOMENT.

RECALL THE BASIC ARGUMENT. THE OVERALL
MANY-BODY WAVEFUNCTION MUST BE ANTI-SYMMETRIC
FOR FERMIONS

\[ \Psi(\vec{r}_1, \vec{r}_2; s_1, s_2) = \frac{1}{\sqrt{2}} \chi(s_1, s_2) - \frac{1}{\sqrt{2}} \chi(s_2, s_1) \]

THUS IF YOU HAVE TWO ELECTRONS WITH ORBITAL
WAVEFUNCTIONS \( |A(\vec{r}_1)\rangle \) AND \( |B(\vec{r}_2)\rangle \), YOU CAN
EITHER HAVE SPINS PARALLEL

\[ \chi(s_1, s_2) = |\uparrow\uparrow\rangle \], WHICH IS SYMMETRIC

\[ \Rightarrow \quad \Psi_{s_1 s_2} = \frac{1}{\sqrt{2}} (|A\rangle |B\rangle - |B\rangle |A\rangle) \]

OR YOU CAN HAVE THEM ANTI-PARALLEL (AND
ANTI-SYMMETRIC)

\[ \chi(s_1, s_2) = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \]

\[ \Rightarrow \quad \Psi_{s_1 s_2} = \frac{1}{\sqrt{2}} (|A\rangle |B\rangle + |B\rangle |A\rangle) \]

NOTE THAT THIS IS JUST ANOTHER FORM OF PAULI
EXCLUSION: IF \( |A\rangle = |B\rangle \), THEN \( \Psi = 0 \) IF \( s_1 = s_2 \).
Since \( ^{1}P_{2} \) has more electron overlap, it will be the higher energy state due to Coulomb repulsion. We can calculate the difference. Let \( |AB\rangle = |A\rangle |B\rangle \) and add a Coulomb potential \( \sqrt{(r_1, r_2)} \)

\[
\text{"triplet" } \rightarrow \ E_{\uparrow \downarrow} = \frac{1}{2} \left( <AB| - <BA| \right) \sqrt{(1AB - 1BA)} \\
\text{"singlet" } \rightarrow \ E_{\uparrow \uparrow} = \frac{1}{2} \left( <AB| + <BA| \right) \sqrt{(1AB + 1BA)} \\
\]

\[
\Delta E = E_{\uparrow \downarrow} - E_{\uparrow \uparrow} = \frac{1}{2} \left( -<BA|V|AB\rangle - <AB|V|BA\rangle \right) \\
-<BA|V|AB\rangle - <AB|V|BA\rangle \\
= -2Re(<AB|V|BA\rangle) \\
\]

Since \( <BA|V|AB\rangle = ( <AB|V|BA\rangle )^* \)

Thus parallel spins have lower Coulomb energy and the size of the gain is associated with the energy to swap or "exchange" electrons \( A \uparrow \uparrow B \rightarrow "exchange\ energy" \)

You might recall that a similar calculation was done when we were considering the covalent bond and in that case spins wanted to be anti-parallel. In general, either case is possible but \( \uparrow \uparrow \) is always preferred for electrons on the same atom.
This calculation is the main justification for the first Hund's Rule.

Hund's Rule 1: Electrons on an atom will always maximize total S (by aligning their spins).

The other two are:

Hund's Rule 2: While satisfying (1), electrons will then maximize L.

Hund's Rule 3: While satisfying (1)(2), total angular momentum $J = L + S$ for shells less than half full and $J = L + S$ for shells more than half full.

The result of Rule 2 is a similar argument about electron avoidance and is coulombic in nature. Rule 3 is associated with spin-orbit (Russell-Saunders) couplings $H_{SO} = \lambda \tilde{L} \cdot \tilde{S}$, which says that each electron will want its spin and orbital axes to anti-align.

E.g. Dy$^{3+} [Xe] 4f^9$

Could have drawn it:

- $L = 3$
- $S = \frac{5}{2}$
- $J = \frac{15}{2}$

Li anti-parallel.
Magnetization of Long Atoms

Hund's Rules allow one to work out the total angular momentum
\[ J = L + S \]

which is great, but recall the Hamiltonian for the lone atom was

\[ H = H_0 + \mu_B B_0 (L + gS) + e^2 \sum B_0 \frac{1}{r_i^3} \]

The paramagnetic term doesn't involve \( J \), but \( L + gS \), which has an extra \( g \)-factor in front of the \( S \).

I'm not going to show it here (but you may on your homework), but it turns out that it reduces to

\[ H_{\text{param}} = g \mu_B \vec{B} \cdot \vec{J} \]

If we define the Landé \( g \)-factor

\[ g = \frac{1}{2} \left( g_1 + \frac{1}{2} (g_2 - 1) \right) \left( \frac{S(S+1) - L(L+1)}{J(J+1)} \right) \]

Note that this would imply that the total moment is best thought of as

\[ \vec{M}_5 = g \mu_B \vec{J} \]

often informally (and incorrectly) referred to as "spin."
With this information, we are now in a position to calculate magnetization. Let's consider the two terms separately. Simple case first.

**Larmor Diamagnetism**

Consider the special case $J = 0$. This occurs when:
1. All shells are full
2. Shell is one less than half full

Then the paramagnetic term is zero, and magnetization is entirely determined by the diamagnetic term. For a single orbital:

\[
\mathbf{H}_{\text{diam}} = \frac{e^2}{8m_e} |\mathbf{B} \times \mathbf{r}|^2 = \frac{e^2 B_0^2}{8m_e} (\mathbf{r}^2) \]

If $\mathbf{\hat{D}} = B_0 \mathbf{\hat{z}}$

Since there is nothing special about the $\mathbf{\hat{z}}$ direction:

\[
\langle \mathbf{r}^2 \rangle = \frac{1}{3} \langle \mathbf{r}^2 \rangle = \frac{1}{2} \langle \mathbf{r}^2 \rangle
\]

\[\Rightarrow \quad \mathbf{E}_{\text{diam}} = \frac{e^2 B_0^2}{12mc} \langle \mathbf{r}^2 \rangle
\]

\[\mathbf{M} = -\frac{d\mathbf{E}}{dB} = -\frac{e^2}{6m_e} \langle \mathbf{r}^2 \rangle B_0 \]
\[ X = -\frac{\mu_0 M}{\beta} = -\frac{e^2 \mu_0 \langle r^2 \rangle}{6mc} \]

Assuming there is a density \( \rho \), or such atoms you get what is known as "Larmor diamagnetism".

\[ \chi_{\text{Larmor}} = -\frac{\rho e^2 \mu_0 \langle r^2 \rangle}{6me} = -\frac{N e^2 \mu_0}{V} \sum_{i=1}^{Z} \langle r_i^2 \rangle \]

For \( N \) atoms containing \( Z \) electrons.

This is comparable to Pauli paramagnetism but order of magnitude weaker than response when \( J \neq 0 \), considered next.

Curie (or Langevin) paramagnetism.

Recall \( H_{\text{para}} = \vec{g} \mu_B \vec{B} \cdot \vec{J} \)

\[ = \vec{g} \mu_B \vec{B} J_z \]

If \( \vec{B} = B \hat{z} \). For total angular momentum \( J \), we know allowed values for \( J_z = -J, -J+1, \ldots, J \).

To find magnetization, we need to know the relative populations of each of these states, which is a classic problem in statistical mechanics.
For those unfamiliar with such calculations, it is informative to consider the simplest case: \( l=0, s=1/2 \). The partition function for this case is

\[
Z = e^{-\frac{\mu_B B}{k_B T}} + e^{\frac{\mu_B B}{k_B T}} \quad \text{using} \quad g = 2
\]

The average value for \( S_2 \) is then

\[
\langle S_2 \rangle = \frac{1}{2} \sum_{i} s_i e^{-\frac{\mu_B B s_i}{k_B T}}
\]

\[
= -\frac{1}{2} e^{\frac{\mu_B B}{k_B T}} + \frac{1}{2} e^{-\frac{\mu_B B}{k_B T}}
\]

\[
= -\frac{1}{2} \tanh \left( \frac{\mu_B B}{k_B T} \right)
\]

\[
= M = -g \mu_B \langle S_2 \rangle = \mu_B \tanh \left( \frac{\mu_B B}{k_B T} \right)
\]

To find \( \chi \), we are interested in the low field limit, \( \mu_B B \ll k_B T \). We thus note

\[
\lim_{B \to 0} M(B) = \frac{\mu_B^2 B}{k_BT}
\]

\[
\Rightarrow \chi = \frac{\mu_B M}{B} = \frac{N \mu_0 \mu_B^2}{k_BT}
\]

For a density, \( N \), of free atoms
Now let's generalize to any integer $J$

\[
Z = \sum_{J_z = -J}^{J} e^{-\frac{J_z \mu_B B}{k_0 T}} = \sum_{J_z = -J}^{J} e^{-J_z x}
\]

where $x = \frac{\mu_B B}{k_0 T}$

\[
Z = e^{-Jx} + e^{-(J+1)x} + e^{-(J+2)x} + \ldots + e^{Jx}
\]

\[
e^{-Jx} \left(1 + e^{x} + e^{2x} + \ldots + e^{(2J+1)x}\right)
\]

\[
e^{-Jx} \left(\frac{1 - e^{(2J+1)x}}{1 - e^x}\right)
\]

\[
= \frac{\sinh \left(\frac{(2J+1)x}{2}\right)}{\sinh \left(\frac{x}{2}\right)}
\]

Thus, just as before

\[
\langle J_z \rangle = \frac{1}{Z} \sum_{J_z = -J}^{J} J_z e^{-J_z x} = -\frac{1}{2} \frac{dZ}{dx}
\]

\[M = n \bar{g} \gamma_B \langle J_z \rangle = n \bar{g} \gamma_B J \bar{g} B_J(x)
\]

where you can show with some algebra

\[
B_J(x) = \frac{2J+1}{2J} \coth \left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth \left(\frac{x}{2J}\right)
\]
This function is called the "Brillouin function" and describes the entire evolution of magnetization with field from 0, to where all moments are aligned.

\[ B_\perp(x) \]

To find \( x \), we look at the low field limit where \( M = B \), and use the fact that

\[ \coth x \approx \frac{1}{x} + \frac{x}{3} \quad \text{when } x \ll 1 \]

In this limit, one can show

\[ x = \frac{\mu_0 M}{B} \approx 4 \frac{J(J+1)}{3 k_B T} \frac{\mu_B}{\mu_0} \equiv \frac{C}{T} \]

This is known as Curie paramagnetism, named after Pierre Curie, who first worked it out with his student Paul Langevin. "C" is called Curie's constant, and is sometimes written

\[ C = \frac{\mu_0}{3 k_B} \left( \frac{\mu_0}{3} \right)^2 \]

Where \( \mu_0 = \sqrt{\frac{J(J+1)}{2}} \) is called the "effective moment"
We thus have two convenient ways to extract total moment $M$ from measurement of magnetization:

1. Field dependence (and saturation) of $M$
2. Temperature dependence at low field

This is exactly what is done in real magnetic materials, where the formula for $T_c$ (Curie) is modified in some important ways. We will do that soon, but first it is worth asking: Do you ever get local moments in a real material?

This is not a stupid question. According to band theory, electron orbitals are given metallic behavior if partially full

$$\Rightarrow \chi = \chi_{Pauli}$$

and are only insulators if all shells are completely filled

$$\Rightarrow \chi = \chi_{Larmor}$$

From whence come these insulators with partially filled bands?
The answer is that magnetism involving local moments represents a breakdown of band theory and in fact is closely related to what I called a "mott insulator".

Think tight binding model. You have a series of orbitals on individual atoms. When atoms are far apart, they form moments as according to Hund's rules, as we discussed.

However, it is these same orbitals which lead to bands in the tight binding model. In particular, we found that when atoms are brought close together, electrons "hop" between atoms. Bandwidth is proportional to the overlap ("hopping") integral, but band theory neglects coulomb repulsion! Sometimes the energy cost of having two electrons on the same site (U) is so great that $U \rightarrow 0$.

No hopping -> gridlock

-> imobile electrons

-> "local moments"