Magnetic periodic table of elements (many compounds are magnetic, too):

Most materials have no permanent magnetic moment, but a moment is induced in the presence of a field. The response is called the magnetic susceptibility $\chi$:

$$\chi = \frac{\partial M}{\partial H} \approx \frac{M}{H}$$

(weak response $\approx \frac{\mu_0 M}{B}$)

$$B = \mu_0 (H + M)$$

$\mu_0 = 4\pi \times 10^{-7} \text{Vs/Am}$

$H = \text{applied field}$

$M = \text{magnetic moment/volume}$

$B = \text{macroscopic magnetic field intensity (induction)}$

$$B = \mu_0 \left( 1 + \chi \right) H$$
Diamagnetism ($\chi<0$): tendency of charges to screen applied field from interior. Small response from all systems, dominant only when permanent dipoles are absent.

\[ \chi_{dia} = -\frac{n \mu_0 Z e^2}{4m} \langle \rho^2 \rangle = -\frac{n \mu_0 Z e^2}{6m} \langle r^2 \rangle \]

A superconductor is a perfect diamagnet ($\chi = -1$): Persistent surface currents generate a field that screens the external applied field so that $B = 0$ inside.
Diamagnetism: tendency of charges to screen applied field from interior. Lenz' law. Classical treatment yields same treatment as QM.

\[ \omega = \frac{eB}{2m} \]  
Larmor frequency

\[ I = (-Ze) \frac{\omega}{2\pi} = -\frac{Ze^2B}{4\pi m} \]  
current

\[ \vec{\mu} = I\vec{A} = -\frac{Ze^2B}{4\pi m} \pi \langle \rho^2 \rangle \hat{B} \]  
magnetic moment

\[ \chi_{dia} = -\frac{n\mu_0 Ze^2}{4m} \langle \rho^2 \rangle = -\frac{n\mu_0 Ze^2}{6m} \langle r^2 \rangle \]

\[ \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \]
\[ \langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \]
\[ \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle ; \langle r^2 \rangle = \frac{3}{2} \langle \rho^2 \rangle \]
Paramagnetism ($\chi > 0$): Tendency of atomic-like dipole moments to align in presence of magnetic field. Alignment goes away if field is removed.

$$\Delta E_{\text{magnetic}} = -\mu \cdot \vec{B}$$

---

Magnetic field absent

In presence of magnetic field

Paramagnetism
Effect of a magnetic field on electron states in an atom:

The "Bohr magneton" $\mu_B$ is a magnetic moment, the scale of which is that of an electron "orbiting" an atom. $\mu_B B$ gives a scale for the energy splitting of states in a free atom. Can be orbital or spin angular momentum.

$$\mu_B = \frac{e\hbar}{2mc} = 9.27 \times 10^{-21} \text{ erg/G}$$

$$\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T} = 5.8 \times 10^{-5} \text{ eV/T}$$

Energy

\[ 
\begin{array}{ccc}
\_ \_ \_ \_ 2p & \_ \_ & \mu_B B \\
\_ \_ 2s & \mu_B B & \\
B = 0 & & B \neq 0
\end{array}
\]
Paramagnetism of a free electron with no orbital AM:

\[ E = - \vec{\mu} \cdot \vec{B} = + g \mu_B \vec{S} \cdot \vec{B} \]
\[ = + g \mu_B S_z B_z = \pm \frac{1}{2} g \mu_B B \]
\[ g_{\text{spin}} = 2 \text{ free electron} \]

\[ n_+ = Ae^{\mu_B B / k_B T}; n_- = Ae^{-\mu_B B / k_B T} \]

\[ \frac{n_+ - n_-}{n_+ + n_-} = \frac{e^{\mu_B B / k_B T} - e^{-\mu_B B / k_B T}}{e^{\mu_B B / k_B T} + e^{-\mu_B B / k_B T}} = \tanh \left( \frac{\mu_B B}{k_B T} \right) \approx \frac{\mu_B B}{k_B T} \]

\[ M = (n_+ - n_-) \mu_B = n \mu_B^2 B / k_B T \]

"Curie" paramagnetism.
\[ \chi \text{ proportional to } 1/T. \]
Diverges at \( T = 0. \)
High \( T \) - thermal energy disrupts aligning ability of field.
Rare Earths: sequentially fill f shells which are shielded by outer d, p shells. These electrons this retain much of their atomic character - paramagnetism is classic behavior in rare earth salts.

\[
\chi_{\text{para}} = \frac{C}{T}
\]

- **Dysprosium sulfate**
  \(\text{Dy}^{2+}: 4f^{10}\)

- **Erbium sulfate**
  \(\text{Er}^{2+}: 4f^{12}\)

**Figure 2.**

After L.C. Jackson (1936)
Paramagnetism for general orbital angular momentum: Previous was special case for $S = 1/2$. For general angular momentum $J$ (see PH451/551 text for Landé g-factor):

$$M = n g J \mu_B B_J(x) \quad x = g J \mu_B B / k_B T$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{free atom}$$

$$B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{[2J+1]x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right)$$

(Brillouin function)

$$\chi_{\text{para}} = \frac{n J(J+1) g^2 \mu_0 \mu_B^2}{3k_B T} = \frac{np^2 \mu_0 \mu_B^2}{3k_B T} = \frac{C}{T}$$

(extra detail)
**Paramagnetism ($\chi>0$)**: Permanent, dilute, atomic-like dipole moments align in presence of field.

\[ \chi_{\text{para}} = \frac{nJ(J+1)g^2\mu_0\mu_B^2}{3k_BT} = \frac{np^2\mu_0\mu_B^2}{3k_BT} = \frac{C}{T} \]

**Pauli Paramagnetism ($\chi>0$)**: Small, temperature independent paramagnetic response of conduction electrons. Conduction electrons can’t just “flip spin” – those states may be occupied already (Pauli Exclusion). Free spin result times $T/T_F$ - only states near $E_F$ are important

\[ \chi_{\text{cond}} = \frac{n\mu_0\mu_B^2}{k_BT_F} \]
Pauli Paramagnetism (free electrons in metals):
Pictorial approach is to think of free electron parabola
displaced up (down) for aligned (anti-aligned) spins. Note
that only unmatched spins are in vicinity of Fermi level.

\[ M_{\text{cond}} = \frac{\# \text{spins}}{\text{vol}} \mu_B \approx ??(\text{hwk}) \]

\[ \chi_{\text{cond}} \approx \frac{M_{\text{cond}}}{B} \]

use free-electron model

\[ \chi_{\text{cond}} \approx \frac{3}{2} N \mu_0 \mu_B^2 / E_F \]
Pauli Paramagnetism (free electrons in metals):

Pictorial approach is to think of free electron parabola displaced up (down) for aligned (anti-aligned) spins. Note that only unmatched spins are in vicinity of Fermi level.

\[
M_{\text{cond}} = \frac{\# \text{ spins}}{\text{vol}} \mu_B \approx \frac{1}{2} D_{\uparrow\downarrow}(E_F) 2 \mu_B B \mu_B \\
\chi_{\text{cond}} \approx \frac{1}{2} \frac{V}{2 \pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E_F \mu_0 \mu_B^2} \\
E_F^{-3/2} = \left( \frac{2m}{\hbar^3} \right)^{3/2} \frac{V}{3 \pi^2 N} \\
\chi_{\text{cond}} \approx \frac{3}{2} N \mu_0 \mu_B^2 / E_F
\]
Pauli Paramagnetism (free electrons in metals):
Quantitative approach with real DoS. e.g. from Wien

\[
\begin{align*}
n^+ &= \frac{1}{2} \int_{-\mu_B B}^{\varepsilon_F} D_{\uparrow}(\varepsilon + \mu_B B) d\varepsilon \\
&\approx \frac{1}{2} \int_0^{\varepsilon_F} D_{\uparrow}(E) dE + \frac{1}{2} \mu_B B D_{\uparrow}(E_F) \\
n^- &= ? \\
M &= \mu_B (n^+ - n^-) = ?
\end{align*}
\]
Elemental Cu exhibits Pauli paramagnetism, but is not ferromagnetic
Paramagnetism ($\chi_{para}$): Tendency of atomic-like dipole moments to align in presence of magnetic field. Alignment goes away if field is removed.

$$\chi_{para} = \frac{nJ(J+1)g^2\mu_0^2}{3k_B T} = \frac{np^2\mu_0^2}{3k_B T} = \frac{C}{T}$$

Pauli Paramagnetism ($\chi_{pauli}$): Small imbalance of spin-up conduction electrons near Fermi surface in presence of magnetic field. Temperature independent, small.

$$\chi_{pauli} \approx D_{\uparrow\downarrow}(E_F)\mu_0^2$$

Ferromagnetism: e.g. Fe $\approx$ 100,000
Below the Curie temperature, dipole moments align spontaneously, even in the absence of an applied field. Cannot be explained without the concept of spin.

$$\chi_{FM,T>T_c} = \frac{C}{T - T_C}; \quad \chi_{FM,T<T_c} = "\infty"$$
Magnetic domains

Paramagnetism

Magnetic domains

Ferromagnetism
Hysteresis in ferromagnets:

- Virgin state (no alignment)
- Domains aligning
- Saturation
Hysteresis in ferromagnets: Alignment in absence of applied field
Work done to reverse alignment (irreversible)

Domains reversing

Saturation in opposite direction

Coercive field (required to reverse M)

Remanent field (internal field with no external applied field)
Ferromagnetism & antiferromagnetism:

Some materials are strongly paramagnetic above a certain temperature. Below this temperature, the magnetic moments spontaneously order, and the material is either ferromagnetic (moments aligned) or antiferromagnetic (moments anti-aligned) even in the absence of an applied field.

\[ \frac{1}{\chi} \]

\[ T_{\text{Curie}} \]

\[ T_{\text{Neel}} \]
Ferromagnets have a paramagnetic response above the "Curie temperature", and below this, the susceptibility is infinite. There is a phase transition. The magnetization is shown below. The way in which the transition is approached from above and below can be calculated, and these "critical exponents" give information about the model.

\[ \chi \propto \frac{C}{T - T_c} \]

<table>
<thead>
<tr>
<th></th>
<th>Tc (°C)</th>
<th>Rel. µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>770</td>
<td>4,000</td>
</tr>
<tr>
<td>Co</td>
<td>354</td>
<td>600</td>
</tr>
<tr>
<td>Ni</td>
<td>1115</td>
<td>250</td>
</tr>
</tbody>
</table>
Elemental ferromagnets at room temperature:

Fe, Co, Ni (also Gd, Dy)

• Band model of ferromagnetism works well for these.

**Large DOS at $E_F$.**

Also imbalance between spin-up and spin-down bands .... What is the origin? And why so large?
Stoner criterion: Recall Pauli paramagnetism. Depends on DOS at $E_F$. If large enough, **spontaneously** causes bands to shift. If $E\_\text{exch} \times D(E_F) >> 1$, then spontaneous band splitting.
Weiss model: Large "effective field" in the ferromagnetic state stabilizes the spontaneous magnetization, producing a marked difference in energy between the "up states" and "down states" in the absence of an externally applied field.

This model explains the spontaneous magnetization, and even the form of the magnetization as a function of field, but Weiss had only magnetic dipole coupling as a mechanism, and this is too weak to produce Curie temperatures of 1000 K.

\[
\mu_0 M \equiv \chi B_{appl} \text{ (def'n)}
\]

\[
B_{Eff} \equiv \lambda \mu_0 M \text{ (postulate)}
\]

\[
\mu_0 M = \chi_p \left( B_{appl} + B_{Eff} \right) = \frac{C}{T} \left( B_{appl} + B_{Eff} \right)
\]

\[
\Rightarrow \chi = \frac{C}{T - \lambda C} = \frac{C}{T - T_c} \text{ (Curie-Weiss law)}
\]
Exchange interaction…. Enter Heisenberg: Why is there a spontaneous magnetization even in the absence of a field? Answer lies in the exchange interaction between electrons. It looks like a spin interaction, but it is really of electrostatic origin.

The Pauli exclusion principle (PEP) forbids fermions from occupying the same quantum state. So for example, two electrons with opposite spin quantum numbers could be at the same spatial location and not violate PEP, but their Coulomb energy would be large. Two electrons with the same spin quantum numbers violate the PEP if they are at the same location, so they are far apart and have lower Coulomb energy.

It is the difference between the electrostatic energies associated with these symmetric and antisymmetric states that we call the exchange energy. We did not consider this in our original band structure calculations!
A bit more detail:
Quantum mechanics says a 2-fermion wavefunction must be antisymmetric under interchange of particles. A wavefunction that it a product of a symmetric and an antisymmetric part is itself antisymmetric.

\[ \varphi_T (x_1; x_2) = \psi_{space} (x_1, x_2) \xi_{spin} (\alpha_1, \alpha_2) \]

If the spin part is symmetric (triplet spin state, \( S=1 \)), then the space part must be antisymmetric. Depicted at the right is the symmetric spin state; for this state \( S_1 \cdot S_2 = 1/4 > 0 \): "parallel spins"

\[ \varphi_T = \psi_{space,A} \xi_{spin,S} \]

If the spin part is antisymmetric (singlet spin state, \( S=0 \)), then the space part must be symmetric. Depicted at the right is the antisymmetric spin state; for this state \( S_1 \cdot S_2 = -3/4 < 0 \): "antiparallel spins"

\[ \varphi_T = \psi_{space,S} \xi_{spin,A} \]
There is a (large) difference in the energy eigenvalues of the symmetric antisymmetric spatial wave functions, and that determines the ground state of the system. (Even if the Hamiltonian does NOT explicitly contain a spin term!)

\[ E_{\text{exc}} = -2JS_1 \cdot S_2 \quad \text{Exchange energy} \]
Define the quantity $J$:
\[
\langle \psi_S | H | \psi_S \rangle - \langle \psi_A | H | \psi_A \rangle = J
\]

antiparallel spins (singlet) \hspace{1cm} parallel spins (triplet)

\[
E_{exch} = -2J \vec{S}_1 \cdot \vec{S}_2 \quad \text{Exchange energy}
\]

Parallel spins ($S_1 \cdot S_2 > 0$) have lower energy if $J > 0$;
Antiparallel spins ($S_1 \cdot S_2 < 0$) have lower energy if $J < 0$.

Molecules: $J < 0$ usually, but important exception is $O_2$ - it is paramagnetic.
Solids with isolated spins: Need to account for pairwise interaction of all spins (coupled problem). Depends on the details …
The two-body wave function (electrons 1 and 2) in a simple molecule (nuclei \( a \) \( ad \) \( b \)) is already complicated! This is for the antisymmetric spin state, which requires a symmetric space state...

\[
\psi_T(r_1, r_2) = \left[ \psi_a(1) + \psi_b(1) \right] \times \left[ \psi_a(2) + \psi_b(2) \right] \xi_{\text{spin}, A}
\]

\[
\psi_T(1, 2) = \left[ \psi_a(1) \psi_b(2) + \psi_b(1) \psi_a(2) \right] + \left[ \psi_a(1) \psi_a(2) + \psi_b(1) \psi_b(2) \right] \xi_{\text{spin}, A}
\]

\[
\psi_T(1, 2) = \left[ \psi_a(1) \psi_b(2) + \psi_b(1) \psi_a(2) \right] \xi_{\text{spin}, A}
\]

Imagine this for \( 10^{23} \) atoms!
When we calculate the Coulomb energy from this wave function for the singlet spin state, there are terms that simply don’t appear in a 1-body picture

\[
E = \frac{\langle \phi_T (r_1, r_2) | H (1) + H (2) + H_{\text{int}} | \phi_T (r_1, r_2) \rangle}{\langle \phi_T (r_1, r_2) | \phi_T (r_1, r_2) \rangle} = 2E_I + \frac{C - A}{1 - S}
\]

\[
C = \frac{e^2}{4\pi\varepsilon_0} \int \left( \frac{1}{R_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) |\phi_a (1)|^2 |\phi_b (2)|^2 \, dr_1 dr_2
\]

\[
A = \frac{e^2}{4\pi\varepsilon_0} \int \left( \frac{1}{R_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} \right) \phi_a^*(1) \phi_a (2) \phi_b (1) \phi_b^* (2) \, dr_1 dr_2
\]

\[
S = \int \phi_a^*(1) \phi_a (2) \phi_b (1) \phi_b^* (2) \, dr_1 dr_2
\]

\[
C = \text{Coulomb Integral} \\
A = \text{Exchange integral} \\
S = \text{overlap integral}
\]
When we calculate the Coulomb energy from this wave function for the symmetric triplet spin state (antisymmetric space state),

\[ \Phi_T(1,2) = [\Phi_a(1)\Phi_b(2) - \Phi_b(1)\Phi_a(2)]r \xi_{spin,S} \]

\[ E = \frac{\langle \Phi_T(r_1,r_2)|H(1) + H(2) + H_{int}|\Phi_T(r_1,r_2) \rangle}{\langle \Phi_T(r_1,r_2)|\Phi_T(r_1,r_2) \rangle} = 2E_I + \frac{C + A}{1 + S} \]

\[ C = \frac{e^2}{4\pi\varepsilon_0} \int \left( \frac{1}{R_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) |\Phi_a(1)|^2 |\Phi_b(2)|^2 \, dr_1 dr_2 \]

\[ A = \frac{e^2}{4\pi\varepsilon_0} \int \left( \frac{1}{R_{ab}} + \frac{1}{r_{12}} + \frac{1}{r_{a1}} + \frac{1}{r_{b2}} \right) \Phi_a^*(1)\Phi_a(2)\Phi_b(1)\Phi_b^*(2) \, dr_1 dr_2 \]

\[ S = \int \Phi_a^*(1)\Phi_a(2)\Phi_b(1)\Phi_b^*(2) \, dr_1 \, dr_2 \]

\[ C = \text{Coulomb Integral} \]

\[ A = \text{Exchange integral} \]

\[ S = \text{overlap integral} \]
The difference between the triplet and singlet states is

\[ E_t - E_s = -J = 2 \frac{CS - A}{1 - S^2} \]

Whichever is lower determines whether the material is magnetic in its ground state.

With more electrons, and whether they are localized or itinerant, the problem becomes more complicated. We really do need computational aids, but even those need to be very carefully tuned to represent the real world properly. We call this procedure “including exchange terms”, and we don’t try to write down all \(10^{23}\) terms, but we use yet more approximations …

And you thought Wien was complicated!
DIRECT EXCHANGE

SUPER EXCHANGE

INDIRECT EXCHANGE

Overlapping e- wf

Closed shell ion

Magnetic ion

Conduction electrons
Antiferromagnetism: order, but no net magnetization. Example: MnO
Antiferromagnetism

\[ \chi^{-1} \propto \frac{C}{T + \theta} \]

\[ \chi \propto \frac{C}{T + \theta} \]

\[ \theta \]

\[ T_{\text{Neel}} \]

\[ \text{BaVS}_3 \]

\[ \chi^{-1} (10^3 \text{ mole/emu}) \]

\[ \text{Temperature (K)} \]
Ferrimagnetism: antiferromagnetic-type order, but a net magnetization. Example magnetite FeO·Fe$_2$O$_3$

\[
\frac{1}{\chi} \propto \frac{T + \theta}{C} - \frac{W}{T - \theta'}
\]
Half metals are ferromagnets with only one type of conduction electron, either spin up, or spin down. Half metals have great potential for spin electronics as they can be used as sources and analysts of fully spin polarized electrons in device structure. Half metals are uncommon. All are compounds of more than one element and most are either oxides or Heusler alloys.

The density of states of a half metal shows only one occupied spin polarized sub-band at the Fermi Energy $E_F$, Unlike normal ferromagnets such as Fe or Co, which have not only spin polarized 3d electrons but also unpolarized 4s electrons at $E_F$.

Chromium dioxide has the distinction of being the only simple oxide that is a ferromagnetic metal. The resistivity of CrO$_2$ increases rapidly as the temperature approaches the Curie point (TC=398K), and the mean free path of the electrons is reduced to the scale of the interatomic spacing by strong spin-flip scattering. (Magnetic Properties of a New Series of Rare Earth Iron Nitrides - R$_2$Fe$_{17}$N$_2$Y$_2$ (30): 6465 (1990))
Oxides of the type $(\text{La}_{1-x}A_x)\text{MnO}_3 ; A=\text{Ca, Ba, Sr} ; x\sim 0.3$ with the perovskite structure show a metal-insulator transition at the Curie temperature $T_C$. This is accompanied by **colossal magnetoresistance**, an intrinsic effect associated with a field-induced increase of spontaneous magnetisation near $T_C$.


The oldest magnetic material known to man, $\text{Fe}_3\text{O}_4$ is also the half-metal with the highest Curie temperature $870K$. The electrons form small polarons and hop among the $B$ sites. The formula can be written $[\text{Fe}^{3+}](\text{Fe}^{2+}, \text{Fe}^{3+})\text{O}_4$. $A$ sites gold, $B$ sites yellow.

Double perovskites such as $\text{Sr}_2\text{FeMo}_6$ and $\text{Sr}_2\text{FeReO}_6$ are claimed to be half metals with $T_C$ higher than 400K. As the $T_C$ of mixed-valence manganites cannot be increased above 400K, and the $T_C$ of $\text{CrO}_2$ is also 400K, these materials, along with $\text{Fe}_3\text{O}_4$, currently offer the best prospects for high temperature applications.

The spin valve is the simplest magnetoresistive device. It consists of two ferromagnetic layers separated by a metallic spacer. One FM layer is pinned; the other is free to switch between parallel and antiparallel alignments corresponding to the low and high resistivity states, respectively.

If the magnetization in the two layers is parallel => easy passage of spin polarized electrons ; if not then very difficult passage.

“GMR” = giant magnetoresistance

Already (1997) in your computers - market was worth billions. Now (2000’s) replaced by magnetic tunnel junctions.
(1) Perovskite-type lead zirconate titanate (PZT) unit cell in the symmetric cubic state above the Curie temperature.
(2) Tetragonally distorted unit cell below the Curie temperature.
(1) Electric dipoles are randomly oriented in absence of electric field
(2) Application of an electric field ("poling") aligns dipoles and causes a distortion of the lattice that causes the dipoles to remain aligned (3) after removal of the field

http://www.physikinstrumente.de/primages/pi_dipoles_d2c_o_eps.jpg