Weiss Theory

Remember, for paramagnets:—

\[ \chi = \frac{C}{T - \Theta} \]

At \( T_c \) the Weiss molecular field is so strong that it magnetizes the substance even if there's no external field.

Next, we'll apply Weiss theory BELOW \( T_c \).
Why does spontaneous magnetization occur?

Langevin theory of PM \( \rightarrow M = NmL(\alpha) \)

Weiss \( \rightarrow M = \frac{H_0}{8} = \frac{kT}{3\alpha} \) (because \( \alpha = \frac{MH}{kT} \))

Two expressions for \( M \) - the only physical solutions are where they intersect

@ \( M = 0 \) (unstable)

AND \( M = M_s \) - the spontaneous magnetization

\( M_s \) depends on temperature \( T \uparrow \), slope \( \uparrow \) : \( M_s \downarrow \)
Spontaneous magnetization \( \rightarrow 0 \) smoothly as \( T \) increases towards \( T_c \)

**Calculation of \( T_c \)**

Equate slope of

\[
\begin{align*}
M &= Nm \xi(x) \\
\text{and} &
M = \frac{kT x}{m\gamma}
\end{align*}
\]

at origin

\[
\frac{kT_c}{m\gamma} = \frac{1}{3} Nm \quad \Rightarrow \quad T_c = \frac{\gamma N m^2}{3k}
\]

Large molecular field constant

\( \downarrow \)

High \( T_c \)

(Using AM Brillouin fn. \( \Rightarrow \)

\[
T_c = \frac{\gamma N \text{Meff}^2}{3k}
\]

Where \( \text{Meff} = g\sqrt{J(J+1)/\mu_B} \)
The spin of a system of interacting electrons affects the spatial distribution and affects the Coulomb repulsion.

\[ U = \frac{e^2}{4\pi \varepsilon_0 r} = \frac{(1.6 \times 10^{-19})^2}{(9 \times 10^{-9})(1 \times 10^{-10})} \approx 2.1 \times 10^{-18} \text{ J} \]
\[ \approx 1.4 \times 10^5 \text{ K} \]

\[ \Rightarrow E = -U \cdot H \]  
(from HW1)

\[ \therefore \text{ small change in spatial distribution } \rightarrow \text{ large } \Delta E ! \]
He atom excited state \((1s)^1 (2s)^1\)

\[ \Psi = \phi_1 + \phi_2 + \phi_{12} \]

\[-\frac{\hbar^2}{2m} \nabla_1^2 \frac{-Ze^2}{4\pi \varepsilon_0 r_1} \quad \frac{-\hbar^2}{2m} \nabla_2^2 \frac{-Ze^2}{4\pi \varepsilon_0 r_2} \quad \frac{e^2}{4\pi \varepsilon_0 r_{12}} \]

Pauli Principle (more rigorous)

Total electronic wavefunction must be antisymmetric w.r.t. interchange of two electrons.

Two Options

1. symmetric spin \(\uparrow \uparrow\)
   \[ \downarrow \text{antisymmetric spatial} \]

2. antisymmetric spin \(\uparrow \downarrow\)
   \[ \downarrow \text{symmetric spatial} \]
The total wavefunction is the product of spin and spatial parts, and that product always ends up with the opposite sign.

Any state which is antisymmetric for the interchange of spin coordinates is always symmetric for the interchange of spatial coordinates. A molecular wavefunction which satisfies the spatial symmetry criterion has the form

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_{1s}(r_1)\phi_{2s}(r_2) + \phi_{2s}(r_1)\phi_{1s}(r_2)]$$

where $\phi_{1s}$ and $\phi_{2s}$ are the $1s$ and $2s$ atomic orbitals and $r_1$ and $r_2$ are the positions of electrons 1 and 2. (The $\frac{1}{\sqrt{2}}$ is for normalization). Similarly, a state which is symmetric for the interchange of spin coordinates must be antisymmetric for the interchange of spatial coordinates. A molecular wavefunction which satisfies this criterion has the form

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_{1s}(r_1)\phi_{2s}(r_2) - \phi_{2s}(r_1)\phi_{1s}(r_2)].$$

Now let's calculate the energy of each of these states using the Hamiltonian of Eqn. 6.10. The total energy, $E$, is

$$E = \langle \Psi(r_1, r_2) | H | \Psi(r_1, r_2) \rangle = \int d\tau_1 d\tau_2 \Psi^*(\tau_1, \tau_2) \mu \Psi(\tau_1, \tau_2)$$

$$= \frac{1}{2} \left[ \langle \phi_{1s}(r_1) | H_1 | \phi_{1s}(r_1) \rangle + \langle \phi_{2s}(r_1) | H_1 | \phi_{2s}(r_1) \rangle \right]$$

$$+ \langle \phi_{1s}(r_2) | H_2 | \phi_{1s}(r_2) \rangle + \langle \phi_{2s}(r_2) | H_2 | \phi_{2s}(r_2) \rangle$$

$$+ \langle \phi_{1s}(r_1) \phi_{2s}(r_2) | H_{12} | \phi_{1s}(r_1) \phi_{2s}(r_2) \rangle$$

$$+ \langle \phi_{2s}(r_1) \phi_{1s}(r_2) | H_{12} | \phi_{2s}(r_1) \phi_{1s}(r_2) \rangle$$

$$\pm \langle \phi_{1s}(r_1) \phi_{2s}(r_2) | H_{12} | \phi_{2s}(r_1) \phi_{1s}(r_2) \rangle$$

$$\pm \langle \phi_{2s}(r_1) \phi_{1s}(r_2) | H_{12} | \phi_{1s}(r_1) \phi_{2s}(r_2) \rangle$$

$$E = E_1 + E_2 + K \pm J,$$ say.

Remember that the $+$ sign corresponds to anti-parallel spins, and the $-$ sign to parallel spins. We see that the energy for parallel orientation of the spins is less than the energy for anti-parallel orientation by an amount $2J$ when $J$ is positive. So a positive $J$ favors parallel spins, which corresponds to ferromagnetic ordering. Here

$$E_1 = \langle \phi_{1s}(r_1) | H_1 | \phi_{1s}(r_1) \rangle = \langle \phi_{1s}(r_2) | H_2 | \phi_{1s}(r_2) \rangle$$

$$E_2 = \langle \phi_{2s}(r_1) | H_1 | \phi_{2s}(r_1) \rangle = \langle \phi_{2s}(r_2) | H_2 | \phi_{2s}(r_2) \rangle$$

$$K = \langle \phi_{1s}(r_1) \phi_{2s}(r_2) | H_{12} | \phi_{1s}(r_1) \phi_{2s}(r_2) \rangle$$

$$= \langle \phi_{2s}(r_1) \phi_{1s}(r_2) | H_{12} | \phi_{2s}(r_1) \phi_{1s}(r_2) \rangle$$

$$J = \langle \phi_{1s}(r_1) \phi_{2s}(r_2) | H_{12} | \phi_{2s}(r_1) \phi_{1s}(r_2) \rangle$$

$$= \langle \phi_{2s}(r_1) \phi_{1s}(r_2) | H_{12} | \phi_{1s}(r_1) \phi_{2s}(r_2) \rangle$$

$E_1$ and $E_2$ represent the energies of the $1s$ and $2s$ orbitals respectively in the field of the helium nucleus. $K$ is the Coulomb interaction between the electron densities $\phi_{1s}^2$ and $\phi_{2s}^2$. $J$ is the exchange interaction, which clearly has no classical analog.
**Band Structure of Transition Metals (without exchange interactions)**

[Diagram showing energy levels for different atoms, such as Zn, Cu, Ni, Co, Fe, Mn, with 3d and 4s labels.]

**Rigid Band Model →** Band structure is the same across the series. But changing the # of valence electrons changes the position of the Fermi level.

**4s band** - broad, low DOS at Fermi level: the band energy required to promote an e- is large.

**3d band** - narrow: higher DOS at Ef: band energy required to promote an e- can be less than the exchange energy!
An alternative way of drawing the DOS for Fe, Ni + Co is:

This shows that there will be more e's of one spin than the other (giving a net magnetization because of the exchange interaction!)

(c/ Pauli paramagnets in the presence of an applied field!)
FIG. 4. Calculated band structure of bcc iron at lattice constant a = 5.25 a.u. Closed circles are for majority-spin states and open circles are for minority-spin states. The Fermi level is indicated by a horizontal line.

FIG. 6. Calculated density of states of bcc iron at lattice constant a = 5.25 a.u. The Fermi level is indicated by a broken line. The upper (lower) panel is for the majority (minority) spin states.
Slater Pauling Curve:

Figure 16 Average atomic moments of binary alloys of the elements in the iron group. (Bozorth.)

straight line for Magnetization

⇒ alloying shifts position of \( E_r \) saturation magnetization is \( \sim \) linearly dependent on the \# of valence electrons.