Pauli paramagnetism of electron gas

\[ s = \frac{1}{2} \hbar \sigma \]

Each electron has intrinsic spin \( s \) with intrinsic magnetic moment \( \vec{\mu} = -\mu_B \sigma \), \( \mu_B = \frac{e\hbar}{2mc} \) is Bohr magneton.

In an external magnetic field \( \vec{B} \), there is an interaction energy \( -\vec{\mu} \cdot \vec{B} = \mu_B \sigma \vec{B} \) where \( \sigma = \pm 1 \) for spins parallel or antiparallel to \( \vec{B} \). The energy spectra for up or down electron spins becomes

\[ E_{\pm}(k) = E(k) \pm \mu_B B \quad \text{where } E(k) \text{ is spectrum at } \vec{B} = 0 \]

Since \( T = 0 \) electrons now have different energy spectra, we should treat them as two different populations of particles \( \uparrow \) and \( \downarrow \) they will be in equilibrium when their chemical potentials are equal, \( \mu_+ = \mu_- \). This will induce a net magnetization in the system.

To see this, consider free electrons at \( T = 0 \).
when \( B = 0 \), \( E_+(\vec{k}) = E_-(\vec{k}) \)

ground state occupations look
as shown on the left. Equal
number of \( \uparrow \) and \( \downarrow \) electrons
\( n_+ = n_- \)

When \( B \) is turned on, if there were no redistribution of
electron spins, the situation would look like

clearly the system can lower its
energy by transferring \( \uparrow \) electrons
to \( \downarrow \) electrons.

At equilibrium the system will look like

again the two populations have
the same max energy \( E_F \).
But there are now more \( \downarrow \)
electrons than \( \uparrow \) electrons.

magnetization \[ \frac{M}{V} = -\mu_B (n_+ - n_-) > 0 \]

\[ \frac{\vec{M}}{V} \] is parallel to \( \vec{B} \) \( \Rightarrow \) paramagnetic effect
Let \( g(e) \) be the density of states when \( B = 0 \).

When \( B \neq 0 \), the density of states for \( \uparrow \) and \( \downarrow \) electrons are

\[
\begin{align*}
g_+ (e + \mu_B B) &= \frac{1}{2} g(e) \\
g_- (e - \mu_B B) &= \frac{1}{2} g(e)
\end{align*}
\]

where \( g_\pm (e) \) depend on \( B \).

The density of \( \uparrow \) and \( \downarrow \) electrons is then

\[ m_\pm = \int_{-\infty}^{\infty} de \ g_\pm (e) f(e, \mu(B)) \]

where

\[ f(e, \mu(B)) = \frac{1}{e^{(e-\mu(B))/k_B T} + 1} \]

\( \mu(B) \) is the chemical potential — it might depend on \( B \)

- it is same for \( \uparrow \) and \( \downarrow \)

We will consider only the case that

\[ \mu_B B \ll \mu(B) \approx E_F \]

in spin interaction is small compared to \( E_F \).
First we will show that

$$\mu(B) = \mu(B=0) \left[ 1 + o \left( \frac{\mu_B}{\epsilon_p} \right)^2 \right]$$

since we will work in the $\mu_B < \epsilon_p$ limit, we will then be able to ignore changes in $\mu$ due to the finite $B$, and just use $\mu(B=0)$.

**Proof:**

Consider the total density of electrons

$$m = m_+ + m_- = \int_{-\infty}^{\infty} dE \, f(E, \mu(B)) \left[ g_+(E) + g_-(E) \right]$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} dE \, f(E, \mu(B)) \left[ g_+(E - \mu_B) + g_+(E + \mu_B) \right]$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} dE \, g(E) \left[ f(E + \mu_B, \mu(B) ) + f(E - \mu_B, \mu(B)) \right]$$

use fact that $f(E, \mu)$ depends only on $(E-\mu)$

$$m = \frac{1}{2} \int_{-\infty}^{\infty} dE \, g(E) \left[ f(E, \mu(B) - \mu_B) + f(E, \mu(B) + \mu_B) \right]$$

expand $f$ about $\mu(B)$ for small $\mu_B$
\[ m = \frac{1}{2} \int d\epsilon \, g(\epsilon) \left[ f(\epsilon, \mu_B) - \frac{df}{d\mu} \mu_B + \frac{1}{2} \frac{d^2f}{d\mu^2} (\mu_B)^2 + \cdots \right. \]
\[ + f(\epsilon, \mu_B) + \frac{df}{d\mu} \mu_B + \frac{1}{2} \frac{d^2f}{d\mu^2} (\mu_B)^2 + \cdots \]

where derivatives above are evaluated at \( \mu = \mu_B \),

the terms linear in B cancel!

\[ m = \int d\epsilon \, g(\epsilon) \left[ f(\epsilon, \mu_B) + \frac{1}{2} \frac{d^2f}{d\mu^2} (\mu_B)^2 + \cdots \right] \]

If we ignored the \( (\mu_B)^2 \) term the above would be

\[ m = \int d\epsilon \, g(\epsilon) \, f(\epsilon, \mu_B) \]

But this is just the same result we use to compute \( m \) at \( B = 0 \)!

The magnetic field \( B \) appears nowhere in the above, except via \( \mu_B \).

Since the density is physically fixed by the sample and cannot change as one varies \( B \), we would conclude that

\[ \mu(B) = \mu(0) \text{ is independent of } B \]

This depends on our having ignored the \( (\mu_B)^2 \) term.
So we can expect

\[ \mu(B) = \mu(0) + \frac{(\mu_B)^2}{\epsilon_F} \]

where \( \frac{1}{\epsilon_F} \) appears on dimensional grounds.
To see this in so more explicit, let's include the $(\mu B)^2$ term and continue to calculate.

\[ m = \int d\epsilon \, g(\epsilon) \left[ f(\epsilon, \mu B) + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu B)^2 \right] \]

Write $\mu B = \mu(B=0) + \delta \mu$ and expand in first term:

\[ m = \int d\epsilon \, g(\epsilon) \left[ f(\epsilon, \mu(B=0) + \delta \mu) + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu B)^2 \right] \]

\[ = \int d\epsilon \, g(\epsilon) \, f(\epsilon, \mu(B=0)) \]

\[ + \int d\epsilon \, g(\epsilon) \frac{df}{d\mu} \bigg|_{\mu = \mu(B=0)} \delta \mu \]

\[ + \frac{1}{2} \int d\epsilon \, g(\epsilon) \frac{d^2 f}{d\mu^2} \bigg|_{\mu = \mu(B)} (\mu B)^2 \]

The first term is just the density when $B = 0$, i.e., $m$. Hence we get:

\[ 0 = \int d\epsilon \, g(\epsilon) \frac{df}{d\mu} \bigg|_{\mu = \mu(B=0)} \delta \mu + \frac{1}{2} \int d\epsilon \, g(\epsilon) \frac{d^2 f}{d\mu^2} \bigg|_{\mu = \mu(B=0)} (\mu B)^2 \]

So the correction to $\mu$ due to finite $B$ is:

\[ \delta \mu = \frac{1}{2} \frac{1}{\int d\epsilon \, g(\epsilon) \frac{df}{d\mu} \bigg|_{\mu = \mu(B=0)}} \int d\epsilon \, g(\epsilon) \frac{d^2 f}{d\mu^2} \bigg|_{\mu = \mu(B)} (\mu B)^2 \]
To see how big the \( \delta \) is, consider the limit \( T \to 0 \) where \( \mu(B=0) = E_F \), and \( f \) is a step function.

\[
\frac{df}{d\mu} = -\frac{df}{de} = \delta(e - \mu)
\]

\[
\frac{d^2f}{d\mu^2} = \frac{d^2f}{de^2} = -\frac{d\delta(e - \mu)}{de}
\]

So

\[
\int de g(e) \frac{df}{d\mu} \bigg|_{\mu = \mu(B=0)} = g(\mu(B=0)) = g(E_F)
\]

\[
\int de g(e) \frac{d^2f}{d\mu^2} \bigg|_{\mu = \mu(B)} = -g'(\mu(B)) (\mu B)^2
\]

\[
8\mu = \frac{1}{2} \frac{g'(\mu(B)) (\mu B)^2}{g(E_F)}
\]

To lowest order, evaluate \( g'(\mu(B)) \) as \( g'(E_F) \).

The derivative will only give higher order corrections of \( 0(\mu B)^4 \)

\[
8\mu = \frac{g'(E_F)(\mu B)^2}{2g(E_F)}
\]

for free electrons with \( g(e) = \sqrt{2} \) so

\[
g'(e) = \frac{1}{2} \frac{e}{\sqrt{2}} \quad \text{we get}
\]

\[
8\mu = \frac{(\mu B)^2}{4E_F}
\]

so

\[
\mu(B) = E_F \left( 1 + \frac{(\mu B)^2}{2E_F^2} \right)
\]
Now we compute

\[ M = -\mu_B (m_+ - m_-) = \mu_B (m_+ - m_-) \]

\[ \frac{M}{V} = \mu_B \int_{-\infty}^{\infty} d\epsilon \cdot f(\epsilon, \mu) \left[ g(\epsilon - \mu + \mu_B) - \frac{1}{2} g(\epsilon - \mu - \mu_B) \right] \]

\[ = \frac{1}{2} \mu_B \int_{-\infty}^{\infty} d\epsilon \cdot g(\epsilon) \left[ f(\epsilon, \mu + \mu_B) - f(\epsilon, \mu - \mu_B) \right] \]

\[ \text{as before, expand } f(\epsilon, \mu \pm \mu_B) = f(\epsilon, \mu) \pm \frac{df}{d\mu} \mu_B \]

\[ \frac{M}{V} = \frac{1}{2} \mu_B \int_{-\infty}^{\infty} d\epsilon \cdot g(\epsilon) \left[ \frac{df}{d\mu} \mu_B \right] \]

\[ = \mu_B^2 B \int_{-\infty}^{\infty} d\epsilon \cdot g(\epsilon) \left( -\frac{df}{d\epsilon} \right) \quad \text{since } \frac{df}{d\mu} = -\frac{df}{d\epsilon} \]

To lowest order in temperature, \(-\frac{df}{d\epsilon} \approx \delta(\epsilon - \mu)\) with \(\mu = \varepsilon_F\)

\[ \frac{M}{V} = \mu_B^2 B \delta(\varepsilon_F) \]

\[ \text{could use Sommerfeld expansion to get corrections of order } \left( \frac{k_B T}{\varepsilon_F} \right)^2 \]

\[ \chi = \frac{\partial (M/V)}{\partial B} \]

\[ \chi_p = \mu_B^2 g(\varepsilon_F) \]

\[ \chi_p \approx \text{density of states at } \varepsilon_F \]

\[ \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \]

For free electron gas, we earlier had \(g(\varepsilon_F) = \frac{3}{2} \frac{m}{\varepsilon_F} \)

\[ \Rightarrow \chi_p = \mu_B^2 \frac{3}{2} \frac{m}{\varepsilon_F} \]

\(\chi_p > 0 \Rightarrow \) paramagnetic
Compare this to classical result. Average magnetization of a single spin is:

\[
\langle m \rangle = \mu_B \tanh (\beta \mu_B B)
\]

\[
\frac{M}{V} = \frac{\langle m \rangle N}{V} = \mu_B m \tanh (\beta \mu_B B)
\]

\[
\chi = \frac{d \left( \frac{M}{V} \right)}{dB}
\]

At low T \(T \rightarrow 0\), \(\tanh (\beta \mu_B) \rightarrow 1\), \(\frac{M}{V} \rightarrow \mu_B m\), all spins aligned.

Compare to quantum case:

\[
\frac{M}{V} = \frac{3}{2} \frac{M}{V} \mu_B^2 B
\]

Smaller than classical result by factor \(\frac{3}{2} \frac{M}{V} \mu_B^2 B \ll 1\)

At high T (\(\beta \rightarrow 0\)) \(\tanh (\beta \mu_B) \rightarrow \beta \mu_B B\)

\[
\frac{M}{V} = \frac{\mu_B^2 B m}{k_B T}, \quad \chi = \frac{\mu_B^2 m}{k_B T} \sim \frac{1}{T}
\]

Compare to quantum case - at room temp, finite T corrections remain negligible ad stil

\(\chi_0 = \mu_B^2 \frac{3}{2} \frac{m}{V} \), order of T

Smaller than classical by factor \(\frac{3}{2} \left( \frac{k_B T}{\mu_B^2} \right) \ll 1\)