Chapter 3
Magnetism of the Electron

1. Orbital and Spin Moments
2. Magnetic Field Effects
3. Theory of Electronic Magnetism
4. Magnetism of Electrons in Solids

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1. Orbital and Spin Moment

The electron is not really a spinning ball of charge; if it were the surface would be moving faster than the speed of light!

It is a point particle with an *intrinsic* magnetic moment of one Bohr magneton.
1.1 Orbital moment

The circulating current is \( I \); \( I = -ev/2\pi r \)

The moment is \( m = IA \) \( m = -evr/2 \)

In Bohr’s quantum theory, orbital angular momentum \( I \) is quantized in units of \( \hbar \); \( \hbar \) is Planck’s constant, \( 6.6226 \times 10^{-34} \) J s; \( \hbar = h/2\pi = 1.055 \times 10^{-34} \) J s.

The orbital angular momentum is \( I = m_e r \wedge v \); Units are J s

It is the z-component of \( I_z \) that is quantized in units of \( \hbar \), taking a value \( m_1 \hbar \)

\( m_1 \) is a quantum number, an integer with no units. Eliminating \( r \) in the expression for \( m \),

\[
m = -(e/2m_e)I = (e\hbar/2m_e)m_1 = m_1\mu_B
\]

\( m = \gamma I \)

The quantity \( \mu_B = (e\hbar/2m_e) \) is the Bohr magneton, the basic unit of atomic magnetism;

\[
\mu_B = 9.274 \times 10^{-24} \text{ A m}^2
\]

Electrons circulate indefinitely in stationary states; unquantized orbital motion radiates energy
Orbital moment

Derivation can be generalized to noncircular orbits. \( M = IA \) for any planar orbit.
Angular momentum of an electron is \( m_e r \times v \). Average around the loop \( (vm_e/s) \int \mathbf{r} \times ds \) The integral is 2A and \( l = -ev/s \), hence \( m = -(e/2m_e)l \).

The Bohr model provides us with a natural unit of length, the Bohr radius

\[
a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}
\]

\[a_0 = 52.92 \text{ pm}\]

And a natural unit of energy, the Rydberg \( R_0 \)

\[
R_0 = \frac{(m/2\hbar^2)(e^2/4\pi\varepsilon_0)^2}{(m/2\hbar^2)(e^2/4\pi\varepsilon_0)^2}
\]

\[R_0 = 13.606 \text{ eV}\]
1.2 Spin moment

The electron has a mysterious built-in spin angular momentum. Spin is a consequence of relativistic quantum mechanics. The spin quantum number is 1/2. The spin angular momentum is \( s \). The z-component is quantized in units of \( \hbar \), taking values \( \pm 1/2 \hbar \). Nonetheless, the magnetic moment associated with electron spin is also \( 1\mu_B \).

\[
m = \gamma s = -(e/m_e)s = (e\hbar/m_e)m_s.
\]

The two states \( \uparrow \) and \( \downarrow \) with \( m_s = \pm 1/2 \) have moments \( \pm 1\mu_B \).

For orbital angular momentum \( m = \gamma \ell \), hence

\[
\gamma = -(e/2m)
\]

The g-factor is defined as the ratio of \( m \) (in units of \( \mu_B \)) to \( \ell \) (in units of \( \hbar \))

\[
g = 1 \text{ for orbital motion}
\]

For spin angular momentum \( \gamma = -(e/m) \)

\[
g = 2 \text{ for spin (after higher order corrections, 2.0023)}
\]

Spin angular momentum is twice as effective as orbital angular momentum in creating a magnetic moment.

Generally there is both spin and orbital angular momentum for an atomic electron. They produce a total angular momentum \( j \), \( j = \ell + s \); \( m = -g_j(e/2m)j \)
Einstein - de Haas effect demonstrates the relation between magnetism and angular momentum. The inverse effect is the Barnett effect.

A ferromagnetic rod is suspended on a torsion fibre. The field in the solenoid is reversed, changing the direction of magnetization of the nickel. It rotates, to conserve angular momentum as the angular momenta of the electrons are reversed.

For iron, $M_s = 1710 \text{ kA m}^{-1}$, $g$ is found to be 2.09. Magnetism is essentially due to electron spin. Moment is $2.2 \mu_B$ per iron atom, yet iron has 26 electrons. Just over two of them contribute to the magnetization.
1.3 Spin-orbit coupling

From the electron’s point of view, the nucleus revolves round it. It is a current loop

\[ I = \frac{Ze}{2\pi r} \]

Which produces a magnetic field \( \mu_0 I/2r \) at the centre

\[ B_{so} = \frac{\mu_0 Ze}{2\pi r^2} \]

\[ U_{so} = -\mu B_{so} \]

Since \( r \approx a_0/Z \), and \( m_e vr \approx \hbar \)

The \( Z^4 \) variation for inner electrons shows that spin-orbit coupling increases strongly in heavy elements.

The formula is wrong by a factor 2

\[ U_{so} \approx -\mu_0 \mu_B^2 Z^4/4\pi a_0^3 \]
1.4 Quantum mechanics of angular momentum

In quantum mechanics, physical observables are represented by operators - differential or matrix.

e.g. momentum $\mathbf{p} = -i\hbar \nabla$; energy $\mathbf{p}^2/2m_e = \hbar^2 \nabla^2$; angular momentum $\mathbf{l} = \mathbf{r} \times \mathbf{p}$
Quantum mechanics of angular momentum

A useful way of representing angular momentum (indispensable for half-integer quantum numbers) is by matrices. Magnetic systems with \( \nu \) states are represented by \( \nu \times \nu \) square hermitian matrices.

Hermitian matrices have real eigenvalues.

The electron, with spin \( s = 1/2 \), has 2 basis states, denoted by \( m_s = \pm 1/2 \); these \( \uparrow \) and \( \downarrow \) states are represented by column vectors

\[
\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

Then \( s_z \) takes the form

\[
\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

By rotation \( s_x \) is

\[
\begin{pmatrix} 0 & \hbar/2 \\ 1 & 0 \end{pmatrix}
\]

and \( s_y \) is

\[
\begin{pmatrix} 0 & -i \hbar/2 \\ i & 0 \end{pmatrix}
\]

Hence

\[
s_z^2 = s_x^2 + s_y^2 + s_z^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \hbar^2/4
\]

Pauli spin matrices

\[
\hat{\sigma} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]
Quantum mechanics of angular momentum

The fundamental property of angular momentum in quantum mechanics is that the operators satisfy the commutation relations

\[ [s_x, s_y] = i\hbar s_z \quad \text{and cyclic permutations} \quad s_x s_x = i\hbar s \]

Commute

\[ s_x s_y - s_y s_x \]

In quantum mechanics only variables whose operators commute can be measured simultaneously. Hence if \( s_z \) is measured precisely, \( s_x \) and \( s_y \) are indeterminate etc. All three have eigenvalues \( \pm \hbar/2 \)

To determine the eigenvalues of a matrix \( O \), solve the eigenvalue equation

\[ |O - \lambda I| = 0 \quad \text{where } I \text{ is the unit matrix} \]

This procedure diagonalizes the matrix. The eigenvalues appear on the diagonal; other elements are 0

e.g. For \( s_y, |s_y - \lambda| = 0 \)

\[ \begin{vmatrix} -\lambda & -i\frac{\hbar}{2} \\ -i\frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \]

\[ \lambda^2 - (\hbar/2)^2 = 0; \quad \lambda = \pm \hbar/2. \]

Diagonal matrices commute. \( [s^2, s_z] = 0 \)

\( s^2 \) and \( s_z \) can be measured simultaneously

\[ \text{Zeeman splitting } H_Z = -m.B \]

\[ = (e/m_e) s.B = \pm \mu_B B \]
Quantum mechanics of angular momentum

Other useful operators are the ladder operators

\[ s_+ = s_x + s_y \quad \text{and} \quad s_- = s_x - s_y \]

They raise or lower \( m_s \) by unity. They are represented by matrices

\[
\begin{pmatrix}
0 & 1 & \hbar/2 \\
0 & 0 & 1 \\
0 & 0 & 1
\end{pmatrix}
\]

Commutation relations

\[ [s^2, s_\pm] = 0 \quad \quad [s_z, s_\pm] = \pm i\hbar s_\pm \]

**Magnetic moment** of the electron \( m \) (in units of Bohr magnetons) associated with the angular momentum (in units of \( \hbar \)) can be represented by similar matrices, with \( g \) factors of 1 or 2 for orbital or spin moments. The matrix elements of the operators for \( m \) and \( l \) or \( s \) are proportional.

Generally

\[ m = (\mu_B/\hbar) (l + 2s) \]
Polarization

An electron in a general state has wave function $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$

Normalization $\langle\psi|\psi\rangle = 1$ requires $\alpha^2 + \beta^2 = 1$.

For example, the state $\alpha = \beta = (1/\sqrt{2})$ $|\psi\rangle = (1/\sqrt{2})\uparrow$ corresponds to a spin along Ox.

It is an equal superposition of $|\uparrow\rangle$ and $|\downarrow\rangle$ states. A measurement of $s_z$ for such an electron gives $\hbar/2$ and $-\hbar/2$ with equal probability.

Polarization of an ensemble of electrons is defined as $P = (n\uparrow - n\downarrow)/(n\uparrow + n\downarrow)$

$P = (\alpha^2 - \beta^2)/(\alpha^2 + \beta^2)$

Stern Gerlach experiment

An atomic beam of Ag ....5s
splits in two.
Rotation of quantization axis

Rotate quantization axis by $\theta$ about Oy

$$s \cdot e_z' = s_z \cos \theta + s_x \sin \theta$$

$$= \begin{vmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{vmatrix} \frac{\hbar}{2}$$

Eigenvalue equation is

$$|M - \lambda| = 0$$

$$\left( \frac{\hbar}{2} \cos \theta - \lambda \right) \left( - \frac{\hbar}{2} \cos \theta - \lambda \right) - \frac{\hbar^2}{4} \sin^2 \theta = 0$$

$$\lambda^2 = \pm \frac{\hbar^2}{4}$$

If $c_1$ is an eigenvector

$$c_1 \cos \theta + c_2 \sin \theta \frac{\hbar}{2} = \lambda \ c_1$$

$$c_1 \sin \theta - c_2 \cos \theta \ c_2$$

Equations for $c_1, c_2$

$$c_1(\cos \theta - \lambda) + c_2 \sin \theta = 0 \ldots$$

$$c_1/c_2 = -\sin \theta / (\cos \theta - \lambda)$$

Eigenvectors in the rotated frame are

$$\begin{vmatrix} \cos \theta/2 \\ \sin \theta/2 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} -\sin \theta/2 \\ \cos \theta/2 \end{vmatrix}$$

$$R_y(\theta) = \begin{vmatrix} \cos \theta/2 & -\sin \theta/2 \\ \sin \theta/2 & \cos \theta/2 \end{vmatrix}$$
A transformation of an operator in a rotated frame is achieved by the procedure

\[
R^{-1}MR
\]

\[
R = \begin{bmatrix}
\cos\theta/2 & -\sin\theta/2 \\
\sin\theta/2 & \cos\theta/2 \\
\end{bmatrix}
\]

\[
R^{-1} = \begin{bmatrix}
\cos\theta/2 & \sin\theta/2 \\
-\sin\theta/2 & \cos\theta/2 \\
\end{bmatrix}
\]

Hence

\[
\begin{bmatrix}
\cos\theta/2 & -\sin\theta/2 \\
\sin\theta/2 & \cos\theta/2 \\
\end{bmatrix} \begin{bmatrix}
1 & 0 \\
0 & -1 \\
\end{bmatrix} \begin{bmatrix}
\cos\theta/2 & \sin\theta/2 \\
-\sin\theta/2 & \cos\theta/2 \\
\end{bmatrix}
\]

\[
= \begin{bmatrix}
\cos\theta/2 & -\sin\theta/2 \\
\sin\theta/2 & \cos\theta/2 \\
\end{bmatrix} \begin{bmatrix}
\cos\theta/2 & \sin\theta/2 \\
\sin\theta/2 & -\cos\theta/2 \\
\end{bmatrix}
\]

\[
= \begin{bmatrix}
\cos\theta & \sin\theta \\
\sin\theta & -\cos\theta \\
\end{bmatrix}
\]

as expected.
Rotation by an angle \( \phi \) around Oz

\[
R_z(\phi) = \begin{pmatrix}
\exp\phi/2 & -\exp\phi/2 \\
\exp\phi/2 & \exp\phi/2
\end{pmatrix}
\]

The phase change created by rotating a spinor is the Berry phase.

Note you have to rotate by \( 4\pi \) to get back to where you began.
These ideas about angular momentum can be extended beyond the $s = \frac{1}{2}$ case, corresponding to the electron spin. For example, if an electron is an orbital p-state with $\ell = 1$, there are three possible eigenstates for $\hat{L}$, corresponding to $m_l = 1, 0, -1$. The three states are represented by column vectors

\[
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix}, \quad \begin{bmatrix}
0 \\
1 \\
0
\end{bmatrix}, \quad \begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix}
\]

and the three components of the angular momentum $\hat{L}_x, \hat{L}_y, \hat{L}_z$ are represented by the matrices

\[
\begin{bmatrix}
0 & 1/\sqrt{2} & 0 \\
1/\sqrt{2} & 0 & 1/\sqrt{2} \\
0 & 1/\sqrt{2} & 0
\end{bmatrix}_l, \quad \begin{bmatrix}
0 & -i/\sqrt{2} & 0 \\
i/\sqrt{2} & 0 & -i/\sqrt{2} \\
0 & i/\sqrt{2} & 0
\end{bmatrix}_l, \quad \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{bmatrix}_l
\]

Each has eigenvalues $\hbar, 0,$ and $-\hbar$. The square of the total angular momentum $\hat{L}$ has eigenvalues $\ell(\ell + 1)\hbar^2$. It is represented by the matrix

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

while the raising and lowering operators $\hat{L}$ and $\hat{L}$ are

\[
\begin{bmatrix}
0 & \sqrt{2} & 0 \\
0 & 0 & \sqrt{2} \\
0 & 0 & 0
\end{bmatrix}_l \quad \text{and} \quad \begin{bmatrix}
0 & 0 & 0 \\
\sqrt{2} & 0 & 0 \\
0 & \sqrt{2} & 0
\end{bmatrix}_l, \quad \text{respectively.}
\]
2. Magnetic Field Effects

3.1 Cyclotron frequency

Lorentz force: \( F = -e\mathbf{v} \times \mathbf{B} \)

\( F = m_e v^2/r = evB \)

Cyclotron frequency \( f_c = v/2\pi r = eB/2\pi m_e \)

The cyclotron frequency \( f_c \) is 28 MHz T\(^{-1}\)

Electrons in cyclotron orbits radiate at the cyclotron frequency

Examples: The microwave oven

The research synchrotron source
3.2 Larmor frequency

\[ m = \gamma l \]
\[ \Gamma = m \times B \]
\[ \Gamma = \frac{dl}{dt} \]

\[ \frac{dm_x}{dt} = \gamma m_y \]
\[ \frac{dm_y}{dt} = -\gamma m_x \]
\[ \frac{dm_z}{dt} = 0 \]

\[ \Gamma = m \times B \]

Solution is \[ m(t) = m \left( \sin \omega_L t, \sin \omega_L t, \cos \theta \right) \] where \[ \omega_L = \gamma B \]

Magnetic moment precesses at the Larmor precession frequency \[ f_L = \frac{\gamma B}{2\pi} \]

The Larmor precession is half the cyclotron frequency for orbital moment, but \[ \gamma = -\frac{e}{2m_e} \] equal to it for spin moment. \[ \gamma = -\frac{e}{m_e} \]
3.3 Orbital diamagnetism

Semi-classical expression for diamagnetic susceptibility is deduced from Larmor precession.

Induced angular momentum (magnetic moment) is induced by the applied field.

*Angular momentum:* \( m_e \omega_L \langle \rho^2 \rangle \) where \( \langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \)

Since \( \omega_L = \gamma B \), the induced moment is \( -\gamma^2 m_e \langle \rho^2 \rangle B \)

*Susceptibility* \( \chi = \mu_0 M/B \)

\[
\chi = -\mu_0 n e^2 \langle r^2 \rangle / 6 m_e
\]

The order of magnitude deduced from \( n \approx 6 \times 10^{28} \text{ m}^3 \) and \( \langle r^2 \rangle^{1/2} \approx 0.2 \text{ nm} \) is \( 10^{-5} \)

Orbital diamagnetism is the dominant contribution for atoms and molecules with filled orbits

Larger values are seen in samples with separated benzene rings

**BUT Bohr - van Leuven** theorem, At any finite temperature and in all finite electric or magnetic fields the net magnetization of any collection of electrons in thermal equilibrium vanishes identically!

The magnetic force \( \mathbf{F} = -e \mathbf{v} \times \mathbf{B} \) is perpendicular to the electron velocity. No work is done, and so no change of magnetization.
3.4 Curie law paramagnetism

Zeeman splitting is observed even for atoms with $s$ state outer electrons with $l = 0, m_l = 0$.

The electron possesses intrinsic spin angular momentum, which arises naturally from the Dirac equation - relativistically-invariant quantum mechanics.

The spin angular momentum is $s = 1/2$, i.e. eigenvalues of $s_z$ are $\pm \hbar/2$

The spin hamiltonian is
\[
\mathcal{H}_{\text{spin}} = - \mathbf{m} \cdot \mathbf{B} = (\mu_B/\hbar)2s_zB_z
\]

Here $g$ is the electronic g-factor $2.0023$ ($g \approx 2$)

The eigenvalues are $E_i = g\mu_B m_s B$; $m_s = \pm 1/2$

Generally, the magnetic moment of the electron is represented by the operator
\[
\mathbf{m} = (\mu_B/\hbar)[l + 2s]
\]

The Zeeman Hamiltonian
\[
\mathcal{H}_{\text{zeeman}} = -\mathbf{m} \cdot \mathbf{B} = (\mu_B/\hbar)[l_z + 2s_z]B
\]
The electrons have only two eigenstates, ‘spin up’ (\(\uparrow, m_s = 1/2\)) and ‘spin down’ (\(\downarrow, m_s = -1/2\)), which correspond to two possible orientations of the spin moment relative to the applied field. The population of an energy level is given by Boltzmann statistics; it is proportional to \(\exp\{-E_i/k_BT\}\). The thermodynamic average \(\langle m \rangle\) is evaluated from these Boltzmann populations.

\[
\langle m \rangle = [(1/2)g\mu_B\exp(x) - (1/2)g\mu_B\exp(-x)]/[\exp(x) + \exp(-x)]
\]

\[
\langle m \rangle = m \tanh(x)
\]

where \(x = \mu_B B/k_BT\).

In small fields, \(\tanh(x) \approx x\), hence the susceptibility \(\chi = N\langle m \rangle/H\) is

\[
\chi_{\text{Curie}} = \mu_0 n\mu_B^2/k_B T
\]

This is the famous Curie law for the susceptibility, which varies as \(T^{-1}\).

In other terms \(\chi = C/T\), where \(C = \mu_0 n\mu_B^2/k_B\) is a constant with dimensions of temperature; Assuming an electron density \(n\) of \(6 \times 10^{28} \text{ m}^{-3}\) gives \(C \approx 0.5 \text{ K}\). The Curie law susceptibility at room temperature is of order \(10^{-3}\).

Many ‘two-level systems’ in physics are treated by assigning them a ‘pseudospin’ \(s = 1/2\).
3.5 Free electron model

\[ \mathcal{H} = \frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r}) \]

Schrodinger’s equation

\[-(\hbar^2/2m_e)\nabla^2 \psi = E \psi\]

Solutions are free-electron waves

\[ \psi = L^{-3/2} \exp (i \mathbf{k} \cdot \mathbf{r}) \]

Allowed values

\[ k_i = \pm 2\pi n_i / L, \quad n_i \text{ is an integer} \]

2 electrons/state

lattice of points in \( k \)-space

Momentum:

\[ \mathbf{p} = -i\hbar \nabla \]

\[ \mathbf{p} = \hbar \mathbf{k} \]

Energy:

\[ \mathcal{H} = \frac{\mathbf{p}^2}{2m_e} \quad E = \hbar^2 k^2 / 2m \]

Occupied states fill a sphere; Since

\[ (4/3) \pi k_F^3 = 2N (2\pi/L)^3 \]

\[ k_F = (3\pi^2 n)^{1/3} \]

\[ \mathcal{E}_F = (\hbar^2 / 2m_e)(3\pi^2 n)^{2/3} \]

\[ \mathcal{D}_{\uparrow, \downarrow}(\mathcal{E}) = (1/4\pi^2)(2m_e/\hbar^2)^{3/2} \mathcal{E}^{1/2} \]

\[ \mathcal{D}_{\uparrow, \downarrow}(\mathcal{E}_F) = 3n/4\mathcal{E}_F \]

\[ E_F = E(T=0) \]

Density of States \( N(E) \)

Energy \( E \)

\( N_{\text{total}} \)
Fermi function

\[
f(E) = \frac{1}{\{\exp[(E - \mu)/k_B T] + 1\}}
\]

Table 3.1. Properties of the free-electron gas

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Expression</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermi wavevector</td>
<td>(k_F)</td>
<td>((3\pi^2 n)^{1/3})</td>
<td>1.2 (10^{10})</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>Fermi velocity</td>
<td>(v_F)</td>
<td>(\hbar k_F/m_e)</td>
<td>1.4 (10^6)</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>Fermi energy</td>
<td>(E_F)</td>
<td>((\hbar k_F)^2/2m_e)</td>
<td>9 (10^{-19})</td>
<td>J</td>
</tr>
<tr>
<td>Fermi temperature</td>
<td>(T_F)</td>
<td>(E_F/k_B)</td>
<td>65,000</td>
<td>K</td>
</tr>
<tr>
<td>Density of states for one spin</td>
<td>(D(E_F))</td>
<td>(3n/4E_F)</td>
<td></td>
<td>m(^{-3}) J(^{-1})</td>
</tr>
<tr>
<td>Pauli susceptibility</td>
<td>(\chi_p)</td>
<td>(2\mu_0\mu_B^2 D(E_F))</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Numerical values are for \(n = 6 \times 10^{28} \text{ m}^{-3}\). Density of states is for one spin.
**Pauli paramagnetism**

The calculation for metals proceeds on a quite different basis. The electrons are indistinguishable particles which obey Fermi-Dirac statistics. They are not localized, so Boltzmann statistics cannot be applied. The electrons have \( s = 1/2, \ m = \mu_B \). They partly-fill some energy band up to the Fermi level \( E_F \).

A rough calculation gives the susceptibility as follows:

\[
\chi = (N^\uparrow - N^\downarrow)\mu_B/H
\]

\[
\approx 2[D(E_F)\mu_0\gamma \mu_B H]\mu_B/H \text{ where } D(E_F) \text{ is the density of states at the Fermi level for one spin direction.}
\]

\[
\chi_{Pauli} \approx 2\mu_0 D(E_F)\mu_B^2
\]

\[
\chi_{Pauli} = 3\mu_0\gamma \mu_B^2/2k_B T_F
\]

This is known as the **Pauli** susceptibility. Unlike the Curie susceptibility, it is very small, and temperature independent.

The density of states \( D(E_F) \) in a band is approximately \( N/2W \), where \( W \) is the bandwidth (which is typically a few eV). Comparing the expression for the Pauli susceptibility with that for the Curie susceptibility \( \chi_{curie} = \mu_0\gamma \mu_B^2/k_B T \), we see that the Pauli susceptibility is a factor \( k_B T/W \) smaller than the Curie susceptibility. The factor is of order 100 at room temperature. \( \chi_{Pauli} \) is of order \( 10^{-5} \).
Some metals have narrow bands and a large density of states at the Fermi level; in this case it is possible for the band to split *spontaneously*, and for ferromagnetism or antiferromagnetism to appear.

<table>
<thead>
<tr>
<th>metal</th>
<th>order</th>
<th>( m(\mu_B) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>af</td>
<td>0.6</td>
</tr>
<tr>
<td>Mn</td>
<td>af</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>ferro</td>
<td>2.2</td>
</tr>
<tr>
<td>Co</td>
<td>ferro</td>
<td>1.7</td>
</tr>
<tr>
<td>Ni</td>
<td>ferri</td>
<td>0.6</td>
</tr>
</tbody>
</table>

*Strong ferromagnets* like Co or Ni have all the states in the \( \uparrow \) d-band filled (5 per atom).

*Weak ferromagnets* like Fe have both \( \uparrow \) and \( \downarrow \) d-electrons at the \( E_F \).
3.6 Landau diamagnetism

Free electron model was used by Landau to calculate the orbital diamagnetism of conduction electrons. The result is:

\[ \chi_L = -n\mu_0\mu_B^2/2k_BT_F \]

exactly one third of the Pauli susceptibility, and opposite in sign.

The real band structure is taken into account in an approximate way by renormalizing the electron mass. Replace \( m_e \) by an effective mass \( m^* \).

Then \( \chi_L = -(1/3)(m_e/m^*)\chi_P \)

In some semimetals such as graphite or bismuth, \( m^* \) can be \( \approx 0.01 m_e \), hence the diamagnetism of the conduction electrons may sometimes be the dominant contribution to the susceptibility. (\( \chi_L = -4 \times 10^{-4} \) for graphite)
Susceptibility of the elements
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi$ $10^{-9}$ m$^3$ kg$^{-1}$</th>
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<th>Compound</th>
<th>$\chi$ $10^{-9}$ m$^3$ kg$^{-1}$</th>
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<tbody>
<tr>
<td>MgO</td>
<td>-3.1</td>
<td>C(diamond)</td>
<td>-6.2</td>
<td>Cu</td>
<td>1.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-4.5</td>
<td>C(graphite)</td>
<td>$\chi_{\parallel}$ -6.3</td>
<td>Ag</td>
<td>2.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
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<td>$\chi_{\perp}$ -138.0</td>
<td>Au</td>
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<tr>
<td>SrTiO$_3$</td>
<td></td>
<td>Si</td>
<td>-1.8</td>
<td>Al</td>
<td>7.9</td>
</tr>
<tr>
<td>ZnO</td>
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<td>Ge</td>
<td>-1.5</td>
<td>Ta</td>
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</tr>
<tr>
<td>ZrO$_2$</td>
<td>-1.1</td>
<td>NaCl</td>
<td>-6.4</td>
<td>Zn</td>
<td>-2.2</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>-1.4</td>
<td>GaAs</td>
<td></td>
<td>Pd</td>
<td>67.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>-7.1</td>
<td>GaN</td>
<td></td>
<td>Pt</td>
<td>12.2</td>
</tr>
<tr>
<td>MgAl$_2$O$_4$</td>
<td></td>
<td>InSb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-9.0</td>
<td>Perspex</td>
<td>-5.0</td>
<td>Bi</td>
<td>-17.0</td>
</tr>
</tbody>
</table>
3. Theory of electronic magnetism

Maxwell’s equations and the Lorentz force are the basic equations of electrodynamics.

\[ F = q(E + \mathbf{v} \times \mathbf{B}) \]

The separation of magnetic and electric fields depends on the reference frame.

When charged particles move in a magnetic field, the momentum and energy are sum of kinetic and potential terms

\[ P = p_{\text{kin}} + qA \]
\[ \mathcal{H} = (1/2m_e) p_{\text{kin}}^2 + q\phi_e \]

The total, canonical momentum is represented by 
\[ -i\hbar \nabla \mathbf{B} = \nabla \times \mathbf{A} \text{ and } \mathbf{E} = -\nabla\phi_e \]

Hence
\[ \mathcal{H} = (1/2m_e)(p + eA)^2 + \nabla(\mathbf{r}) \]

where \( \nabla(\mathbf{r}) = -e\phi_e \)
3.1 Orbital moment and susceptibility of the electron

Consider an electron in a central potential $V(r)$ subject to a uniform $B$ field along $e_z$.

The vector potential $A = (1/2)B \times r = (1/2)B e_z \times r = (1/2)B \begin{bmatrix} e_x & e_y & e_z \\ \partial / \partial x & \partial / \partial y & \partial / \partial z \\ -y & x & 0 \end{bmatrix} = (1/2)B [-y, x, 0]$

Hence $B = \nabla \times A = (1/2)B \begin{bmatrix} e_x & e_y & e_z \\ \partial / \partial x & \partial / \partial y & \partial / \partial z \\ -y & x & 0 \end{bmatrix} = Be_z$

The Hamiltonian for the electron in a central potential is

$$\mathcal{H} = \frac{p^2}{2m_e} + V(r)$$

In the presence of a magnetic field this becomes

$$\mathcal{H} = (p + eA)^2/2m_e + V(r)$$
\[ \mathcal{H} = \frac{p^2}{2m_e} + e\mathbf{p} \cdot \mathbf{A}/m_e + \frac{e^2 A^2}{2m_e} + V(r) \]

Note that \([\mathbf{p}, \mathbf{A}] = \mathbf{p} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{p} = 0\) if \(\nabla \cdot \mathbf{A} = 0\).

\[ \mathcal{H} = [\frac{p^2}{2m_e} + V(r)] + e\mathbf{p} \cdot \mathbf{B} \mathbf{e}_z \times \mathbf{r}/2m_e + \frac{e^2 B^2 (x^2 + y^2)}{8m_e} \]

\[ \mathcal{H}_0 \quad \mathcal{H}_{\text{para}} \quad \mathcal{H}_{\text{dia}} \]

The first term is the Hamiltonian for an electron in a potential with no field.

The second term gives the \textit{paramagnetic} response of the orbital moment (Zeeman splitting)

\[ \mathcal{H}_{\text{para}} = e l_z B / 2m_e \] where \( \mathbf{l} = \mathbf{r} \times \mathbf{p} \) is the angular momentum.

The third term gives the \textit{diamagnetic} response of the electrons (Lenz’s law)

\[ \mathcal{H}_{\text{dia}} = \frac{e^2 B^2 (x^2 + y^2)}{8m_e} \]
Diamagnetic term

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{para}} + \mathcal{H}_{\text{dia}} \]

Take \( \mathcal{H}_0 + \mathcal{H}_{\text{para}} = \mathcal{H}' \) as the unperturbed Hamiltonian and \( \mathcal{H}_{\text{dia}} \) as the perturbation.

\[ E'_{n,l,ml} = E_{n,l} - \mu_B m_l B \]

Perturbation theory:

\[ E_{n,l,ml} = E'_{n,l,ml} + \langle \psi_{n,l,ml} | \mathcal{H}_{\text{dia}} | \psi_{n,l,ml} \rangle \]

\[ \langle \psi_{n,l,ml} | \mathcal{H}_{\text{dia}} | \psi_{n,l,ml} \rangle = (e^2 B^2/8m_e) \int |\psi_{n,l,ml}|^2 (x^2 + y^2) \, d^3r \]

\[ = (e^2 B^2/8m_e) \left[ \langle x^2 \rangle + \langle y^2 \rangle \right] \]

For a central potential, \( \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle r^2 \rangle/3 \)

Hence the energy shift is \( e^2 \langle r^2 \rangle B^2/12m_e \)

\[ m_{\text{dia}} = -\partial(\delta E)/\partial B = -e^2 \langle r^2 \rangle B/6m_e \]

\[ M_{\text{dia}} = N m_{\text{dia}} = \chi_{\text{dia}} H \]

\[ \chi_{\text{dia}} = -\mu_0 Ne^2 \langle r^2 \rangle /6m_e \]

Note: All electron shells contribute to \( \chi_{\text{dia}} = -\mu_0 e^2 /6m_e \sum_i \langle r_i^2 \rangle \). \( \chi_{\text{dia}} = 10^{-6} \)
3.2 Quantum oscillations

Let $B = B_z$, $A = (0, xB, 0)$. $V(r) = 0$ and $m = m^*$

Schrodinger’s equation

$$\frac{1}{2m^*} \left[ p_x^2 + (p_y + xB)^2 + p_z^2 \right] \psi = E' \psi$$

$$\psi(x) e^{ik_y y} e^{ik_z z}$$

$$\left[ -\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + \frac{1}{2} m^* \omega_c (x - x_0)^2 \right] \psi(x) = E' \psi(x)$$

$$\omega_c = \frac{eB}{m^*}, \quad x_0 = -\frac{\hbar}{eB} y \quad E' = E - (\frac{\hbar^2}{2m}) k_z^2$$

$$E_n = (n + \frac{1}{2}) \hbar \omega_c$$

$$E = \frac{\hbar^2 k_z^2}{2m^*} + (n + \frac{1}{2}) \hbar \omega_c$$

The motion is a plane wave along $Oz$, plus a simple harmonic oscillation at $f_c$ in the plane.
3.2 Quantum oscillations

When a magnetic field is applied, the states in the Fermi sphere collapse onto a series of tubes. Each tube corresponds to one Landau level (n - value). As the field increases, the tubes expand and the outer one empties periodically as field increases. An oscillatory variation in $1/B^2$ of magnetization (de Haas - van Alphen effect) or of conductivity (Shubnikov - de Haas effect) appears.

From the period, it is possible to deduce the cross section area of the Fermi surface normal to the tubes.
3.3 Spin moment

The time-dependent Schrödinger equation

\[-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = i \hbar \frac{\partial \psi}{\partial t}\]

is not relativistically invariant because the operators \( \partial / \partial t \) and \( \partial / \partial x \) do not appear to the same power.

We need to use a 4-vector \( X = (ct, x, y, z) \) with derivatives \( \partial / \partial X \).

Dirac discovered the relativistic quantum mechanical theory of the electron, which involves the Pauli spin operators \( \sigma_i \), with coupled equations for electrons and positrons. The nonrelativistic limit of the theory, including the interaction with a magnetic field \( B \) represented by a vector potential \( A \), can be written as

\[
H = \left[ \frac{(1/2m)(p + eA)^2}{8m^3c^2} + V(\mathbf{r}) \right] - \frac{p^4}{8m^3c^2} + (e/m) \mathbf{B} \cdot \mathbf{s} + (1/2m^2c^2)(dV/dr) - (1/4m^2c^2)(dV/dr) \frac{\partial}{\partial r}
\]

- The second term is a higher-order correction to the kinetic energy
- The third term is the interaction of the electron spin with the magnetic field, so that the complete expression for the Zeeman interaction of the electron is

\[
H_Z = (\mu_B/\hbar) \mathbf{B} \cdot (\mathbf{l} + 2\mathbf{s})
\]

The factor 2 is not quite exact. The expression is \( 2(1 + \alpha/2\pi - \ldots) \approx 2.0023 \), where \( \alpha = e^2/4\pi\varepsilon_0\hbar c \approx 1/137 \) is the fine-structure constant.

- The fourth term is the spin-orbit interaction, which for a central potential \( V(\mathbf{r}) = -Ze^2/4\pi\varepsilon_0 r \) with \( Z \) as the nuclear charge becomes \( -Ze^2\mu_0 \mathbf{l} \cdot \mathbf{s}/8\pi m^2r^3 \) since \( \mu_0\varepsilon_0 = 1/c^2 \). In an atom <1/r^3> \( \approx (0.1 \text{ nm})^3 \) so the magnitude of the spin-orbit coupling \( \lambda \) is 2.5 K for hydrogen \((Z = 1)\), 60 K for 3d elements \((Z \approx 25)\), and 160 K for actinides \((Z \approx 65)\).

In a non-central potential, the spin-orbit interaction is \( \mathbf{s} \times \nabla V \cdot \mathbf{p} \)

- The final term just shifts the levels when \( l = 0 \).
3.3 Magnetism and relativity

The classification of interactions according to their relativistic character is based on the kinetic energy

\[ E = mc^2 \sqrt{1 + (v^2/c^2)} \]

The order of magnitude of the velocity of electrons in solids is \( \alpha c \). \( \alpha \) is the fine structure constant \( 1/137 \). Expanding the equation in powers of \( c \) gives

\[ E = mc^2 + (1/2)\alpha^2 mc^2 - (1/8)\alpha^4 mc^2 \]

Here the rest mass of the electron, \( mc^2 = 511 \text{ keV} \); the second and third terms, which represent the order of magnitude of electrostatic and magnetostatic energies are respectively 13.6 eV and 0.18 meV. Magnetic dipolar interactions are therefore of order 2 K.
4. Magnetism of electrons in solids

Magnetism of free atoms
Assembling the atoms together to form a solid is a traumatic process insofar as the atomic moments are concerned. Magnetism in solids tends to be destroyed by chemical interactions of the outermost electrons, which can occur in various ways:

- electron transfer to form filled shells in ionic compounds
- covalent bond formation in semiconductors
- band formation in metals.
It must be emphasized that the nature of the chemical bonding, and therefore the character of the magnetism depends critically on crystal structure and composition. The very existence of a moment in face-centred cubic \( \gamma \text{Fe} \) depends on the lattice parameter. Intermetallic compounds such as \( \text{YFe}_2\text{Si}_2 \) exist where there is no spontaneous spin splitting of the d-band. Insulating ionic compounds containing the \( \text{Fe}^{3+} \) ion have large unpaired spin moments of \( 5\mu_B \) per iron, but covalent compounds with low-spin \( \text{Fe}^{II} \) are nonmagnetic. A few examples to illustrate the scope of the magnetism of this most common magnetic element are given in Table 3.2

<table>
<thead>
<tr>
<th>( \gamma \text{-Fe}_2\text{O}_3 )</th>
<th>( \alpha \text{-Fe} )</th>
<th>( \text{YFe}_2 )</th>
<th>( \gamma \text{-Fe} )</th>
<th>( \text{YFe}_2\text{Si}_2 )</th>
<th>( \text{FeS}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferrimagnet</td>
<td>ferromagnet</td>
<td>ferromagnet</td>
<td>antiferromagnet</td>
<td>Pauli paramagnet</td>
<td>diamagnet</td>
</tr>
<tr>
<td>5.0</td>
<td>2.2</td>
<td>1.45</td>
<td>( \text{unstable} )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
3.4 Localized and delocalized electrons

**LOCALIZED MAGNETISM**
Integral number of 3d or 4f electrons
on the ion core; Integral number of unpaired spins;
Discreet energy levels.

with

\[
\text{Ni}^{2+} \quad 3d^8 \quad m = 2 \mu_B
\]

\[
\text{Ni} \quad 3d^9.4s^{0.6} \quad m = 0.6 \mu_B
\]

\[\psi \approx \exp(-r/a_0)\]
Boltzmann statistics

\[\psi \approx \exp(-i\mathbf{k}.\mathbf{r})\]
Fermi-Dirac statistics

**DELOCALIZED MAGNETISM**
Nonintegral number of unpaired spins per atom.
Spin-polarized energy bands
strong correlations.

Above the Curie temperature, neither localized nor delocalized moments disappear, they just become disordered in the paramagnetic state, \(T > T_C\).