1. Lecture: Basics of Magnetism: Magnetic response

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Lecture overview

1. Lecture: Basic magnetostatic properties
2. Lecture: Paramagnetism
3. Lecture: Local magnetic moments
Content

1. Definitions
2. Electron in an external field
3. Diamagnetism
4. Paramagnetism: classical treatment of
1. Classical magnetic moments

Loop current has an angular momentum

\[ I = \frac{q}{T} = \frac{q \omega}{2 \pi} \]

Loop current generates a magnetic field

Magnetic dipole moment = current \times enclosed area

\[ |\vec{m}| = IA = \frac{q \omega}{2 \pi} A = \frac{1}{2 \pi} \frac{q}{m_e} m_e \pi r^2 \omega = \frac{1}{2} \frac{q}{m_e} \vec{L} = \gamma \vec{\mathcal{L}} \]

\( \gamma = \text{gyromagnetic ratio}, \ m_e = \text{electron mass} \)
Torque and precession

Zeeman energy of magnetic moment in an external magnetic field:

\[ E = -\mathbf{m} \cdot \mathbf{B} \]

Energy is minimized for \( m \parallel B \). \( B \) is the magnetic induction or the magnetic field density. Applying \( B \), a torque is exerted on \( m \):

\[ \mathbf{T} = \mathbf{m} \times \mathbf{B} \]

If \( m \) were just a dipole, such as the electric dipole, it would be turned into the field direction to minimize the energy. However, \( m \) is connected with an angular momentum, thus torque causes the dipole to precess:

\[ \mathbf{T} = \frac{d\mathbf{L}}{dt} = \gamma \mathbf{L} \times \mathbf{B} \]

Assuming \( B = B_z \), the precessional frequency is:

\[ \omega_L = \gamma B_z \]

\( \omega_L \) is called the Lamor frequency. See also EPR, FMR, MRI, etc.
Bohr magneton

An electron in the first Bohr orbit with a Bohr radius $r_{Bohr}$ has the angular momentum:

$$L = m_e r_{Bohr}^2 \omega = \hbar$$

Then magnetic moment is:

$$m_{Bohr} = \frac{1}{2} \frac{q}{m_e} L = -\frac{1}{2} \frac{e}{m_e} \hbar = -\mu_B$$

Because of negative charge, $\mathbf{L}$ and $\mathbf{m}$ are opposite.

$$\mu_B = \frac{1}{2} \frac{e}{m_e} \hbar = \gamma \hbar$$

$\mu_B$ is the Bohr magneton. $[\mu_B] = 9.274 \times 10^{-24}$ Am$^2$.

Magnetic moment: $[m] = \text{A m}^2$
Spin $S$ of the electron contributes to the magnetic moment:

$$\vec{m}_{\text{spin}} = \frac{q}{m_e} \vec{S}$$

The missing factor $\frac{1}{2}$ is of quantum mechanical origin and will be discussed later.

Including orbital and spin contributions, the magnetic moment of an electron is:

$$\vec{m} = \frac{1}{2} \frac{q}{m_e} (\vec{L} + 2 \vec{S}) = -\gamma (\vec{L} + 2 \vec{S})$$
Magnetic field and magnetic induction

Oersted field $H$ due to $dc$ current:

$$H = \frac{I}{2\pi r}$$

Any time variation of the magnetic flux $\Phi = BA$ through the loop causes an induced voltage:

$$U_{\text{ind}} = -\frac{d}{dt}(\vec{B} \cdot \vec{A})$$

Therefore $B$ is called the magnetic induction or the magnetic flux density $B = \Phi/A$.

In vacuum both quantities are connected via the permeability of the vacuum:

$$B = \mu_0 H$$

$$\mu_0 = 4\pi \times 10^{-7} \frac{V \cdot s}{A \cdot m}$$

$$[B] = [0] \cdot \left[ \frac{I}{2\pi r} \right] = \frac{V \cdot s}{A \cdot m} \times \frac{A}{m} = \frac{V \cdot s}{m^2} = T$$

$$1 \frac{V \cdot s}{m^2} = 1 \text{T} = 10^4 \text{G}$$
1. Magnetization is the sum over all magnetic moments in a volume element normalized by the volume element:

\[ \vec{M} = \frac{1}{V} \sum_i \vec{m}_i \]

2. Thermal average of the magnetization:

\[ \langle \vec{M} \rangle = \frac{N}{V} \langle \vec{m} \rangle \]

3. Magnetic susceptibility:

\[ \vec{M} = \chi_{\text{mag}} \vec{H}, \quad \chi_{\text{mag}} = \frac{\partial |M|}{\partial H} \]

4. Magnetic Induction:

\[ \vec{B} = \mu_0 \left( \vec{H} + \vec{M} \right) = \mu_0 \vec{H} (1 + \chi_{\text{mag}}) = \mu_0 \mu_r \vec{H} = \mu \vec{H} \]

H = magnetic field, usually externally applied by a magnet.
\( \mu_0 = \) magnetic permeability of the vacuum.
\( \mu_r = \) relative magnetic permeability \( \mu_r = (1 + \chi) \) (tensor, or a number for collinearity)
Potential energy (Zeeman – term):

\[ E_{\text{Zeeman}} = -\vec{m} \cdot \vec{B} \]

1. Derivative → magnetic moment:

\[ |m| = -\frac{\partial E_{\text{Zeeman}}}{\partial B} \]

2. Derivative → Susceptibility:

\[ \chi_{\text{mag}} = \frac{\partial |M|}{\partial H} = -\mu_0 \frac{N}{V} \frac{\partial^2 E_{\text{Zeeman}}}{\partial B^2} \]

The susceptibility is the response f
What is more fundamental, H or B?

Lorentz force: \[ \vec{F} = q(\vec{v} \times \vec{B}) \] \[ [F] = N \]

Zeeman energy: \[ E = -\vec{m} \cdot \vec{B} \] \[ [E] = J = VAs = Vs \]

Vector potential: \[ \vec{B} = \vec{\nabla} \times \vec{A} \] \[ [B] = T = Vs / m^2 \]

Oersted field: \[ H = \frac{I}{2\pi r} \] \[ [H] = A/m \]

Magnetization: \[ M = \chi H \] \[ [M] = A/m \]
Classification

Application of an external field:

a. Paramagnetism: \( \chi > 0 \) und \( \mu_r > 1 \)

Magnetic moments align parallel to external field, field lines are more dense in the material than in vacuum.

b. Diamagnetism: \( \chi < 0 \) und \( \mu_r < 1 \)

External field is weakened by inducing screening currents according to Lenz rule. Field lines are less dense than in vacuum.

Ideal diamagnetism, realized in superconductors with \( M \) and \( B \) antiparallel, for \( \chi = -1 \) and \( \mu_r = 0 \).

c. Ferromagnetism:

Spontaneous Magnetization without external field due to the interaction of magnetic moments

\( \mu_r \) attains very high values for ferromagnets, \( > 10^4 - 10^5 \)
Consider a non-relativistic Hamilton operator for electrons in an external magnetic field:

\[ H = \frac{1}{2m_e} \left( \vec{p} + q\vec{A} \right)^2 \]

The vector potential: \( \vec{A} \) is defined by the Coulomb gauge: \( \vec{B} = \vec{\nabla} \times \vec{A} \) and using

\[ \vec{B} = (0, 0, B_z) \]

\[ H = \frac{p^2}{2m_e} + \frac{\mu_B B_z L_z^*}{e^2} B_z^2 \langle a^2 \rangle + \frac{e^2}{12m_e} B_z^2 \langle a^2 \rangle \]

*L_z is here a dimensionless quantum number

Where we assumed an average over the electron orbit perpendicular to the magnetic field:

\[ \langle x^2 \rangle + \langle y^2 \rangle = \frac{2}{3} \langle a^2 \rangle \]
Hamiltonian for electron with spin

Considering the electron spin in the external field with a Zeeman energy:

\[ E_{\text{Zeeman}} = -\vec{m}_s \cdot \vec{B} = -g_s \mu_B \vec{S} \cdot \vec{B} = \frac{e\hbar}{m} \vec{S} \cdot \vec{B} \]

Landé factor

\[ g_s = 2 \]

Bohr magneton

\[ \mu_B = -\frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ Am}^2 \]

Hamilton operator for spin and orbital contributions of a single bond electron then is:

\[ H = \frac{p^2}{2m_e} + \mu_B B_z \left( L_z + 2S_z \right) + \frac{e^2}{12m_e} B_z^2 \left\langle a^2 \right\rangle \]

The \( g_S = 2 \) for the electron is put into the Schrödinger equation by „hand“ but would occur naturally using the Dirac equation. The exact value of 2.0023 is determined by QED.
Response functions

1. derivative

\[ |\vec{m}| = -\frac{\partial H}{\partial B_z} \]

2. derivative

\[ \chi_{mag} = -\mu_0 \frac{N}{V} \frac{\partial^2 H}{\partial B_z^2} \]

Diamagnetic response for Z electrons

\[ \frac{Ze^2}{6m_e} \langle a^2 \rangle B_z \]

Paramagnetic response

\[ \mu_B (L_z + 2S_z) > 0 \]

*For single atom we can not define a paramagnetic susceptibility. This is only possible for an ensemble of atoms.
3. Properties of the Langevin diamagnetism

With $Z$ electrons in an atom and an effective radius of $<a>$

\[
\chi_{\text{Langevin}} = -\mu_0 \frac{N}{V} \frac{e^2}{6m_e} \sum_i \langle r_i^2 \rangle = -\mu_0 \frac{N}{V} \frac{Ze^2}{6m_e} \langle a^2 \rangle
\]

- $\chi_{\text{Langevin}}$ is constant, independent of field strength;
- $\chi_{\text{Langevin}}$ is induced by external field;
- $\chi_{\text{Langevin}} < 0$, according to Lenz‘ rule;
- $\chi_{\text{Langevin}}$ is always present, but mostly covered by bigger and positive paramagnetic contribution;
- $\chi_{\text{Langevin}}$ is the only contribution to magnetism for empty or filled electron orbits;
- $\chi_{\text{Langevin}}$ yields $\langle a \rangle$ and the symmetry of the electron distribution;
- $\chi_{\text{Langevin}}$ is proportional to the area of an atom perpendicular to the field direction, important for chemistry;
- $\chi_{\text{Langevin}}$ is temperature independent.
Examples for Diamagnetism

<table>
<thead>
<tr>
<th>Material</th>
<th>$\chi_{\text{Langevin at RT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$-1.9 \cdot 10^{-6}$ cm$^3$/mol</td>
</tr>
<tr>
<td>Xe</td>
<td>$-43 \cdot 10^{-6}$ cm$^3$/mol</td>
</tr>
<tr>
<td>Bi</td>
<td>$-16 \cdot 10^{-6}$ cm$^3$/g</td>
</tr>
<tr>
<td>Cu</td>
<td>$-1.06 \cdot 10^{-6}$ cm$^3$/g</td>
</tr>
<tr>
<td>Ag</td>
<td>$-2.2 \cdot 10^{-6}$ cm$^3$/g</td>
</tr>
<tr>
<td>Au</td>
<td>$-1.8 \cdot 10^{-6}$ cm$^3$/g</td>
</tr>
</tbody>
</table>

($\chi$ is normalized to the magnetization of 1 cm$^3$ containing one 1 Mol of gas at 1 Oe)

- All noble metals and noble gases are diamagnetic. In case of the noble metals Ag, Au, Cu mainly the d-electrons contribute to the diamagnetism.
- In 3d transition metals the diamagnetismus is usually exceeded by the much bigger paramagnetic response.
Anisotropy of diamagnetismus for Li$_3$N

Levitation of diamagnetic materials
4. Paramagnetism of free local moments: classical treatment

(free = without interactions)

Orientation of permanent and isolated magnetic moments in an external field $B_z = \mu_0 H_z$ parallel to the z-axis (orientational polarization)

$$L(x) = L\left(\frac{m_z B_z}{k_B T}\right)$$

$$L(x) = \coth(x) - \frac{1}{x} \quad \text{Langevin function}$$
Langevin function

\[ \langle \cos \theta \rangle = \frac{\int \cos \theta e^{\frac{E_{\text{pot}}(\theta)}{k_B T}} \, d\Omega}{\int e^{\frac{E_{\text{pot}}(\theta)}{k_B T}} \, d\Omega} = \frac{\int_0^{\pi} 2\pi \sin \theta \cos \theta e^{\frac{mB \cos \theta}{k_B T}} \, d\theta}{\int_0^{\pi} 2\pi \sin \theta \, d\theta} \]

using \[ d\Omega = \sin \theta d\theta d\phi = 2\pi \sin \theta d\theta \]

\[ s = \cos \theta \quad \text{and} \quad x = \frac{\mu B_0}{k_B T} \]

\[ \langle \cos \theta \rangle = \frac{\int_1^1 se^{sx} \, ds}{\int_{-1}^{-1} e^{sx} \, ds} = \frac{d}{dx} \ln \int_{-1}^1 e^{sx} \, ds = \coth(x) - \frac{1}{x} \equiv L(x) \]

\[ \boxed{M = N_0 \mu L\left(\frac{m_z B_0}{k_B T}\right)} \]

L(x): Langevin-Funktion
Magnetization of paramagnetic moments in an external field

\[ \mu_0 H_z / k_B T \]

Magnetization vs. \( \mu_0 H_z / k_B T \)
Curie-Suszeptibilität $\chi_{\text{Curie}}$ in HTA with the Curie-constant $C$:

$$\chi_{\text{Curie}} = \frac{\partial \langle M \rangle}{\partial H_z} = \frac{N \mu_0 m_z^2}{V 3k_B T} = \frac{C}{T}$$

$$C = \frac{N \mu_0 m_z^2}{V 3k_B}$$

Magnetic moment:

$$m_z = \mu_B \left( L_z + 2S_z \right)$$

Linear dependence fulfilled at high temperatures. At low $T$ often deviations observed due to interactions.

But: However, magnetism is not a classical problem, thus Langevin function is only a rough approximation. As quantum mechanics allows only discrete values for the $z$-component of the magnetic moments, a different approach has to be chosen ⇒ 

Brillouin function replaces the Langevin function. – The susceptibility of superparamagnetic particles containing a macrospin can be treated classically as the spin orientation of nanoparticles in the field is continuous.
Susceptibility of the Elements

From J.M.D. Coey
Summary

1. Hamilton operator for an electron in an external field:

\[ H = \frac{p^2}{2m_e} + \mu_B B_z (L_z + 2S_z) + \frac{e^2}{12m_e} B_z^2 \langle a^2 \rangle \]

   - kinetic energy
   - paramagnetism spin + orbital
   - diamagnetism

2. Diamagnetic response:

\[ \chi_{\text{diamagnetic}} = -\mu_0 \frac{N Ze^2}{V 6m_e} \langle a^2 \rangle \]

3. Paramagnetic response (HTA):

\[ \chi_{\text{Curie}} = \frac{N \mu_0 m_z^2}{V 3k_B T} \]

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

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