2. Lecture: Basics of Magnetism: Paramagnetism

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1. Orbital moments
2. Spin orbit coupling
3. Zeeman splitting
4. Thermal Properties – Brillouin function
5. High Temperature – low temperature approximation
6. Van Vleck paramagnetism
7. Paramagnetism of conduction electrons
Orbital moments of the d-shell

\[ m_{z,l} = m_l g_l \mu_B = m_l \mu_B \]

\[ = (2, 1, 0, -1, -2) \mu_B \]

The upper three wave functions have maxima in the xy, xz, yz planes, the lower two have maximia along x,y and z coordinate. In a magnetic field the degenerate sublevels split.
1. Spin-Orbit-coupling

Coupling of spin and orbital moment yields the total angular momentum of electrons:

\[ \vec{J} = \vec{L} + \vec{S} \]

The spin-orbit (so) interaction or LS-coupling is described by:

\[ E_{SO} = \lambda(r) \vec{L} \cdot \vec{S}; \quad \lambda(r) = -\frac{\mu_B}{\hbar m_e e c^2} \frac{1}{r} \frac{dU}{dr} \]

\( \lambda > 0 \) for less than half filled d and f shell
\( \lambda < 0 \) for more than half filled d and f shell

Spin-orbit coupling is due to the Zeeman – splitting of the spin magnetic moment in the magnetic field that is produced by the orbital moment:

\[ E_{SO} = -\vec{m}_S \cdot \vec{B}_L \]
• In rest frame of electron, E and B – fields act on electron due to positive charge of the nucleus:

\[ \vec{B}_L = \frac{\vec{r} \times \vec{p}}{m_0 c^2} \left| \frac{E}{r} \right| \]

• The magnetic field is proportional to angular momentum of electrons: \( B_L \sim L \):

\[ \vec{B}_L = \frac{1}{m_0 e c^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} \vec{L} \]

• In magnetic field \( B_L \), S precesses with a angular velocity \( \omega_L \) and couples to \( L \):

\[ E_{SO} = -\frac{\mu_B}{\hbar m_e e c^2} \frac{1}{r} \frac{\partial U(r)}{\partial r} \vec{L} \cdot \vec{S} \]

• \( L \cdot S \) can be evaluated via:

\[ \vec{J}^2 = (\vec{L} + \vec{S})^2; \quad \vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \]

• Yielding:

\[ E_{SO} = \frac{\beta}{2} \left[ j(j+1) - l(l+1) - s(s+1) \right] \]
2. Fine structure

Terms with same n and l - quantum numbers are energetically split according to whether the electron spin is parallel or antiparallel to the orbital moment. This is called the fine structure of atomic spectra. Example hydrogen atom:

The total splitting of $3/2 \beta$ increases with the number of electrons in the atom and becomes in the order of 50 meV for 3d metals. LS-splitting lowers the energy for L and S antiparallel. Therefore level filling starts with lowest j-values.
Why is \( \lambda \) changing sign?

\[ E_{SO} = \lambda(r) \vec{L} \cdot \vec{S} < 0 \]

Less than half filled: \( L-S \)

\( \vec{L} \cdot \vec{S} < 0 \)

\[ E_{SO} = \lambda(r) \vec{L} \cdot \vec{S} < 0 \]

if \( \lambda > 0 \)

More than half filled: \( L+S \)

\( \vec{L} \cdot \vec{S} > 0 \)

\[ E_{SO} = \lambda(r) \vec{L} \cdot \vec{S} < 0 \]

if \( \lambda < 0 \)
Russel-Saunders coupling for **light atoms** (LS-coupling): This approximation assumes that the LS-coupling of individual electrons is weak compared to the coupling between electrons. Orbital moments of all electrons couple to a total angular momentum $L$ and spin moments of all electrons couple to $S$. Finally $L$ and $S$ couple to $J$:

$$
\vec{L} = \sum_{i=1}^{Z} \vec{l}_i,
\vec{S} = \sum_{i=1}^{Z} \vec{s}_i,
\vec{J} = \vec{L} + \vec{S}
$$

**jj-coupling of heavy atoms:**
In the limit of big LS coupling, the spin and orbital moment of each individual electrons couples to $j$, and all $j$ are added to total angular moment $J$.

$$
\vec{j}_i = \vec{l}_i + \vec{s}_i,
\vec{J} = \sum_{i=1}^{Z} \vec{j}_i
$$
Total angular moment and total magnetic moment

Total angular moment is: \( \vec{J} = \vec{L} + \vec{S} \)

Total magnetic moment is:

\[
\vec{m}_{(J+S)} = -\mu_B \left( g_L \vec{L} + g_S \vec{S} \right) = -\mu_B \left( \vec{L} + 2\vec{S} \right) = -\mu_B \left( \vec{J} + \vec{S} \right)
\]

Total angular moment \( J \) and the total magnetic moment are not collinear. However, in an external magnetic field, \( m_{J+S} \) precesses fast about \( J \), and \( J \) precesses much slower about \( H_z \). Thus the time average component of the magnetic moment \( \langle \vec{m} \rangle = m_{||} \) is parallel to \( J \).

\[\vec{S} : \text{Total spin} \]
\[\vec{L} : \text{Total orbital moment} \]
\[\vec{J} : \text{Total angular moment} \]
Different total angular moments $J$

\[ E = E_{\text{Coulomb}} + E_{\text{SO}} \]

\[ |L + S| \geq J \geq |L - S| \]

Which one is the ground state?

- Next lecture: Hund‘s rule

\[ \lambda < 0 \]
3. Zeeman-splitting

- In an external field the quantization axis is defined by the field axis $H_z$.
- A state with total angular momentum $J$ has a degeneracy of $2J+1$ without field. These states are labeled according to the magnetic quantum number $m_J$: $-J \leq m_J \leq J$.
- In an external field $H_z$ the states with different $m_J$ have different energy eigenstates, their degeneracy is lifted:

$$E_{m_J}(H_z) = E_0 + E_{\text{SO}} + \mu_0 g_J \mu_B m_J H_z$$

$$= E_0 + E_{\text{SO}} + \mu_0 m_{z,J} H_z$$

- The energy eigenstate are equidistant and linearly proportional to the external field $H_z$.

$$m_J = -J, J+1, J+2, \ldots, J$$
LS and Zeemann Splitting
for $L=3, S=3/2, \lambda < 0$

$\lambda < 0$

Conversation:
$1000 \text{ cm}^{-1} = 0.124 \text{ eV}$
Landé factor

Z-component of the total magnetic moment:

\[ m_{z,j} = m_J g_J \mu_B \]

Landé factor:

\[ g_J = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \]

\[ = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)} \]

Notice: \( g_j = 1 \) for \( J=L \) and \( 2 \) for \( J=S \)
Evaluating the Landé-factor

From 1. Lecture we have for the paramagnetic response in an external \( B \)-field:

\[
E = \mu_B \left( \vec{L} + 2\vec{S} \right) \cdot \vec{B}
\]

Considering \( L+2S \) projected onto \( J \) and \( J \) project onto the \( B \)-axis:

\[
E = \mu_B \frac{(\vec{L} + 2\vec{S}) \cdot \vec{J}}{J} \frac{\vec{J} \cdot \vec{B}}{J} = \mu_B \frac{J^2}{J^2} \left( \vec{L} + 2\vec{S} \right) \cdot \left( \vec{L} + \vec{S} \right) \vec{z} B_z
\]

This yields:

\[
E = \frac{\mu_B}{J^2} \left( \vec{L}^2 + 3\vec{L} \cdot \vec{S} + 2\vec{S}^2 \right) \vec{z} B_z
\]

Using:

\[
\vec{J}^2 = (\vec{L} + \vec{S})^2; \quad 3\vec{L} \cdot \vec{S} = \frac{3}{2} \left( \vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right)
\]

We find:

\[
E = \mu_B \frac{3J^2 - \vec{L}^2 + \vec{S}^2}{2J^2} J z B_z
\]

Which must equal:

\[
E = g_J \mu_B m_J B_z
\]

With:

\[
g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}
\]
4. Thermal properties

Thermal population of the Zeeman-split levels in the ground state (gs).

Example: $J=1$, $m_J=-1,0,+1$

$H_z = 0, \ T=0$

gs degenerate, all atoms in the same state

$H_z > 0, \ T= 0$

Lifting of degeneracy, all atoms in the gs

$H_z > 0, \ T>0$

At high temperature population of higher energy states

Discrete energy levels with $m_J=-J,\ldots, J$

Average thermal energy:

$$E(m_J) = -\mu_0 g_J \mu_B H_z m_J$$

$$\langle E(m_J) \rangle = -\mu_0 g_J \mu_B H_z \langle m_J \rangle$$

$$M = -\frac{N}{V} \frac{1}{\mu_0} \frac{\partial \langle E \rangle}{\partial H_z} = \frac{N}{V} g_J \mu_B \langle m_J \rangle$$
Thermal average of the magnetization

\[ \langle M \rangle = \frac{N}{V} g_j \mu_B \langle m_j \rangle \]

Thermal average of the magnetic moment follows from the partition function:

\[ \langle m_j \rangle = \frac{\sum_{m_j} m_j \exp(-\alpha m_j)}{\sum_{m_j} \exp(-\alpha m_j)} \]

with:

\[ \alpha = \frac{g_j \mu_B H_z}{k_B T} \]

\[ \langle M(T, H_z) \rangle = \frac{N}{V} g_j \mu_B jB_j(\tilde{\alpha}) \]

Bi is the Brillouin function. The Brillouin function replaces the Langevin function in case of discrete energy levels.
Brillouin Function

\[ B_j(\tilde{\alpha}) = \frac{2j+1}{2j} \coth\left( \frac{2j+1}{2j} \tilde{\alpha} \right) - \frac{1}{2j} \coth\left( \frac{\tilde{\alpha}}{2} \right) \]

mit \[ \tilde{\alpha} = \alpha_j = \frac{g_j \mu_B j H_z}{k_B T} \]

\[ \frac{M}{M_{sat}} \left( \frac{E}{k_B T} \right) \]

Langevin
Examples for the Brillouin-Function $B_J$:
4. Low and high temperature approximations

Low temperature approximation (LTA) for:

\[ \tilde{\alpha} = \frac{g_j \mu_B H_z j}{k_B T} \gg 1 \]

the Brillouin function approaches 1 \( B(\tilde{\alpha}) \rightarrow 1 \)

The thermally averaged magnetization then becomes:

\[ \langle M \rangle = \frac{N}{V} g_j \mu_B j = M_S = M(T = 0) \]

This corresponds to the saturation magnetization \( M_S \). The saturation magnetization can not become bigger than given by \( j \). It corresponds to a state in which all atoms occupy the ground state.
High temperature approximation

In HTA for $\tilde{\alpha} << 1$ the Brillouin function $B_j(\tilde{\alpha})$ can be approximated by

$$\coth(x) \approx \frac{1}{x} + \frac{x}{3}$$

Then follows for the magnetization

$$\langle M(T) \rangle = \frac{N}{V} \frac{p_{\text{eff}}^2 \mu_B^2 H_z}{3 k_B T} = \frac{C}{T} H_z$$

With the effective moment:

$$p_{\text{eff}} = g_j \sqrt{J(J + 1)}$$

And the Curie constant:

$$C = \frac{N}{V} \frac{p_{\text{eff}}^2 \mu_B^2}{3 k_B}$$
Curie law of the magnetic susceptibility

\[ \chi = \frac{\partial \langle M \rangle}{\partial H_z} = \frac{C}{T} \]

With C we can calculate \( p_{\text{eff}} \) and \( j \). From \( j \) the valence of a chemical bond can be determined. Thus \( p_{\text{eff}} \) is important for chemistry.
5. Van Vleck paramagnetism

- For $J = 0$ the paramagnetic susceptibility becomes zero.
- $J = 0$ occurs for shells, which are less than half filled by one electron.
- In this case higher order terms contribute to the susceptibility, in particular a diamagnetic term of second order, which is positive.
- The higher order terms are due to excited states which may have a $J \neq 0$, even if for the ground state $J = 0$.
- Calculating in second order perturbation theory contributions to only the ground state, one obtains:

$$\Delta E_0^{Van Vleck} = - \sum_{m=1,2,...} \frac{\mu_0 \langle m | \mu_B (L_z + g_S S_z) H_z | 0 \rangle^2}{E_m - E_0}$$

- Van Vleck contribution to the susceptibility is weak, positive and temperature independent. But it plays a decisive role for the paramagnetism of Sm and Eu ⇒ 3. Lecture.
6. Paramagnetism of conduction electrons

For Fermi particles with spin \( S = 1/2 \) we expect:

\[
\chi = \frac{N}{V} \frac{\mu_B^2 p_{\text{eff}}^2}{3k_B T} = \frac{N}{V} g_s^2 S(S+1) \frac{\mu_B^2}{3k_B T} = \frac{N}{V} \frac{2^2 \cdot 1\cdot 3}{2 \cdot 2 \cdot 3k_B T} \mu_B^2 = \frac{N}{V} \frac{\mu_B^2}{k_B T}
\]

Expected magnetization:

\[
\langle M_z \rangle = \chi H_z = \frac{N}{V} \frac{\mu_B^2 H_z}{k_B T}
\]

which has \( 1/T \) dependence.

Experiment shows:

\( \alpha. \) \( \chi \) is independent of \( T \)

\( \beta. \) has a value 1/100 of the calculated value at 300 K.

\( \mathfrak{F} \) Contradiction!
Magnetization of a free electron gas

Spin split DOS for free electrons in an external field

\[ M = \mu_B \frac{N_\uparrow - N_\downarrow}{V} = \mu_B \frac{\Delta N}{V} = \mu_B \frac{\frac{1}{2} D(E_F) \times 2 \mu_B H_z}{V} = \mu_B^2 \frac{H_z D(E_F)}{V} \]

With:

\[ D(E_F) = \frac{3}{2} \frac{N}{E_F} \]

Follows:

\[ M = \mu_B^2 \frac{H_z D(E_F)}{V} = \frac{3}{2} \mu_B^2 \frac{N}{V} \frac{H_z}{k_B T_F} = \frac{3}{2} \mu_B^2 \frac{N}{V} \frac{H_z}{k_B T} \left( \frac{T}{T_F} \right) \]
Pauli Spin Susceptibility of a free electron gas

$$\chi_{Pauli} = \frac{\partial M}{\partial H} = \frac{N}{V} \frac{\partial}{\partial H} \left( \frac{3}{2} \frac{\mu_B^2}{k_B T_F} \frac{H}{k_B T_F} \right) = \frac{3}{2} \frac{N}{V} \mu_B^2 \frac{1}{k_B T_F}$$

• Pauli spin susceptibility has the correct form.
• It is independent of temperature
• It is reduced by the factor $T/T_F \sim 100$.
• Closed shells have no density of states at the Fermi level, thus closed shells do not contribute to $\chi_{Pauli}$. Only $s,p$ and $d$-electrons of unfilled shells contribute.
• Free electrons also contribute to the diamagnetic response in an external field, forming Landau cylinders.

• According to Ginzburg und Landau the diamagnetic contribution to the susceptibility of the conduction electrons is:

\[ \chi_{\text{Landau}} = -\frac{1}{3} \chi_P \]

• Exemption superconductors, in which case \( \chi = -1 \).

• Considering the paramagnetic and diamagnetic response, the total susceptibility of a free electron gas is:

\[ \chi_{\text{free electron}} = \chi_{\text{Pauli}} + \chi_{\text{Landau}} = \frac{N}{V} \frac{\mu_B^2}{k_B T_F} \]
Experimental Pauli susceptibilities

Experimental results for susceptibilities of monovalent and divalent metals:

<table>
<thead>
<tr>
<th>Element</th>
<th>$\chi_{\text{total}}$ (expt)</th>
</tr>
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<tbody>
<tr>
<td>K</td>
<td>0.47</td>
</tr>
<tr>
<td>Rb</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu</td>
<td>$-$ 0.76</td>
</tr>
<tr>
<td>Ag</td>
<td>$-$ 2.1</td>
</tr>
<tr>
<td>Au</td>
<td>$-$ 2.9</td>
</tr>
<tr>
<td>Mg</td>
<td>0.95</td>
</tr>
<tr>
<td>Ca</td>
<td>1.7</td>
</tr>
</tbody>
</table>

From E.Y. Tysmbal
Summary of susceptibilities

\[ \chi_{\text{tot}} = \chi_{\text{Langevin}} + \chi_{\text{Curie}} + \chi_{\text{Pauli}} \]

- \( \chi_{\text{Langevin}} \): induced, always negative
- \( \chi_{\text{Curie}} \): single ion, no interaction
- \( \chi_{\text{Pauli}} \): induced, positive

Curie paramagnetism
\[ \chi_{\text{Curie}} = \frac{C}{T} \]

Pauli paramagnetism
\[ \chi_{\text{free electron}} = \frac{N}{V} \frac{\mu_B^2}{k_B T_F} \]

Langevin diamagnetism
\[ \chi_{\text{Langevin}} = -\mu_0 \frac{Ze^2}{6m_e} \langle a^2 \rangle \]