Lecture 2
Lonely atoms

Luigi Paolasini
paolasini@esrf.fr
LECTURE 2: “LONELY ATOMS”

- Systems of electrons
- Spin-orbit interaction and LS coupling
- Fine structure
- Hund’s rules
- Magnetic susceptibilities

Reference books:

Dirac: "Nature is not satisfied by a point charge but require a charge with a spin!"

**Theorem:**
The magnitude of total spin \( s = s_1 + s_2 \) is \( s \), the corresponding wave function \( \psi_s(s_{1z}, s_{2z}) \) is

Dirac: "Nature is not satisfied by a point charge but require a charge with a spin!"
Pauli exclusion principle defines the quantum state of a single electron

$n = \text{Principal number}$: Defines the energy difference between shells

$l = \text{Orbital angular momentum quantum number}$:
- range: $(0, n-1)$
- magnitude: $\sqrt{l(l+1)} \hbar$

$m_l = \text{component of orbital angular momentum along a fixed axis}$:
- range: $(-l, l)$ $\Rightarrow (2l+1)$
- magnitude: $m_l\hbar$

$s = \text{Spin quantum number}$: defines the spin angular momentum of an electron.
- magnitude: $\sqrt{s(s+1)} \hbar = \sqrt{3}/2 \hbar$

$m_s = \text{component of the spin angular momentum along a fixed axis}$:
- range: $(-1/2, 1/2)$
- magnitude: $m_s\hbar=1/2\hbar$

$j = l \pm s = l \pm 1/2 = \text{Total angular momentum}$

$m_j = \text{Total angular momentum component about a fixed axis}$:
- range: $(-j, j)$
Isolated atoms

We consider “lonely atoms” or equivalently isolated atomic magnetic moments, because we ignore the interactions between them, magnetic or not magnetic in origin.

We analyse the coupling of spin and orbital moment in an atom, what we call intra-atomic single ion magnetic properties.

We investigate the behaviour of a large number of atoms when an external magnetic field is applied.

The magnetic susceptibility is then proportional to the number of atoms per unit volume N/V.
- Electrons in the **unfilled shells** can combine to give non-zero spin $S$ and orbital $L$ momentum:

\[
\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}
\]

- $\hat{\mathbf{L}}$: orbital angular momentum
- $\hat{\mathbf{S}}$: total spin angular momentum
- $\hat{\mathbf{J}}$: Total angular momentum

The new quantum numbers are: $L$, $m_L$, $S$, $m_S$, $J$, $m_J$

- $L$ and $S$ can combine in different $(2L+1)(2S+1)$ ways, which corresponds to the total number of choices of $z$-components of $m_L$ and $m_S$, i.e. the total orbital and total spin multiplicities.

- These combinations affect the spatial part of electron wavefunctions

- The difference in energy between all possible configurations affects the electrostatic repulsion between electrons
Spin-orbit interaction

Is a relativistic effect due to the relativistic interaction between the spin $S$ and the orbital part $L$ of the electron’s wave functions in an atom.

The mutual interaction between spin magnetic moment $\mu$ and magnetic field $B^p$ is generated by the positive charge of the nucleus rotating around the electron rest frame:

$$H_{so} = -\frac{1}{2} \mu \cdot B^p = \frac{e\hbar^2}{2m_e c^2 r} \frac{dV(r)}{dr} \mathbf{L} \cdot \mathbf{S} = \lambda \mathbf{L} \cdot \mathbf{S}$$

where $\frac{1}{2}$ is the relativistic Thomas factor.

**Spin-orbit Hamiltonian**

$$H_{so} = \frac{Z^4 e^4 \hbar^2}{4\pi\varepsilon_0 a_0^3 n^3 l(l+1/2)(l+1)} \langle S \cdot L \rangle$$

**Landé interval rules**

$$E(J) - E(J - 1) = \lambda J$$

**Hydrogen**

Proton frame  Electron frame
Light atoms: Russel-Saunders coupling
The spin-orbit interaction is a weak perturbation with respect to the main electrostatic interaction between spins and orbital moments ($H_{so} \sim Z^4$)

*First the total $S$ and $L$ are combined separately, then the weak spin orbit interaction split each term in a fine structure labeled by $J$.*

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

Heavy atoms: $j$-$j$ coupling
For heavy elements in which the spin-orbit coupling is strong, for each electron $j$ the $s_i$ and $l_i$ are coupled separately, and then the weaker electrostatic interaction couple the individual total magnetic moments $j_i$:

\[
\vec{j}_i = \vec{l}_i + \vec{s}_i, \quad \vec{J} = \sum_{i=1}^{Z} \vec{j}_i
\]
In general, \( L \) and \( S \) are not separately conserved, but \( J = S + L \) is conserved. (good quantum number).

If the relativistic effects are taken as small perturbations, \( L^2 = L(L+1) \) and \( S^2 = S(S+1) \) are conserved (Russel-Saunders coupling scheme).

Expected value of spin-orbit energy

\[
\langle \lambda \cdot L \rangle = \frac{\lambda}{2} [J(J+1) - L(L+1) - S(S+1)]
\]

The states defined by \( L \) and \( S \) are split in levels with different \( J \):
Zeeman splitting
In an external magnetic field $H_z$ the different $j$-states have different energy eigenstates $E_{mj}(H_z)$ because and their degeneracy is lifted:

$$E_{mj}(H_z) = E_{\text{Coulomb}} + E_{\text{so}} + \mu_0 g_J \mu_B m_J H_z$$

Each J-level could be split by a magnetic field in $(2J+1)$ $m_l$ values, with $-J \leq m_J \leq +J$ and the energy levels are equidistant, and proportional to the applied magnetic field $H_z$. 

![Diagram showing Zeeman splitting](image)
Fine structure III

Ex. $L=3, S=3/2$

$2L+1=7$

$2S+1=4$

$|L-S| \leq J \leq L+S$

Degeneracy of each $J$ level

$2J+1=7/2 \times 2 + 1 = 8$

$28 = \text{Total number of multiplets}$

$\sum_{J=|L-S|}^{L+S} 2J + 1 = (2L + 1)(2S + 1)$

$-J \leq m_J \leq J$
Landé factor $g$

The total magnetic moment in one atom is given by

$$\mu = g\mu_B \sqrt{J(J+1)}$$

where the Landé factor $g_J$ is given by:

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

Notice that g-factors are $g_L=1$ for $J=L$ and $g_S=2$ when $J=S$.

The z-component of the total magnetic moment $m_{z,j}$ is:

$$m_{z,j} = m_J g_J \mu_B$$

Where $m_J$ is the magnetic quantum number.
The total angular moment: $J = L + S$ and the total magnetic moment $\mu$ are not collinear.

In fact, the total magnetic moment $\mu$ of one atom is defined as:

$$\mu = -\mu_B (g_L L + g_S S) = -\mu_B (L + 2S) = -\mu_B (J + S)$$

where the Landé’ g-factors are $g_L = 1$ for $L$ and $g_S = 2$.

Notice that $\mu$ precess **fast** about $J$ and $J$ precess slowly about $H_z$.

Thus the time average of the magnetic moment $<\mu> = m_{\parallel}$ is parallel to $J$.
Hund rules - 1

Describe the minimal energy configuration of ground state of electrons in the unfilled shells:

1\textsuperscript{st} rule: \textbf{Maximization of total spin }$S$
consistent with Pauli’s exclusion principle because prevent the electron with the same spin to be in the same place reduces the Coulomb repulsion between electrons

2\textsuperscript{nd} rule: \textbf{Maximization of total orbital angular momentum }$L$
filling the electrons in the orbit rotating in the same direction electrons avoid each other the Coulomb repulsion is reduced

3\textsuperscript{rd} rule: $J=|L-S|$ (minimum) in shells less than half filled $J=|L+S|$ (maximum) in shells more than half filled minimization of spin-orbit energy valid for the rare earths but not for transition metals
**Hund rules - II**

Mn$^{3+}$ \((3d^4)\)

\[m_i = +2, +1, 0, -1, -2 (l)\]

\[\begin{array}{c|c|c|c|c}
  n=4 & 4s & 3p & 3d \\
  n=3 & 3s & 2p \\
  n=2 & 2s \\
  n=1 & 1s \\
\end{array}\]

\[S = 1/2 + 1/2 + 1/2 + 1/2 = 2\]
\[L = 1 + 2 + 1 + 0 - 1l = 2\]
\[J = L - S = 0\]
\[5D_0\]

Ni$^{2+}$ \((3d^8)\)

\[m_i = +2, +1, 0, -1, -2 (l)\]

\[\begin{array}{c|c|c|c|c}
  n=4 & 4s & 3p & 3d \\
  n=3 & 3s & 2p \\
  n=2 & 2s \\
  n=1 & 1s \\
\end{array}\]

\[S = 1/2 + 1/2 = 1\]
\[L = 1 - 1l = 3\]
\[J = L + S = 4\]
\[3F_4\]

**Classification of shells:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>S</th>
<th>P</th>
<th>D</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

**Term symbols:**

\[2S + 1 \quad L \cdot J\]
Hund rules III

Dy\(^{3+}\) \((4f^9)\)

\[
\begin{align*}
m_i &= +3 \quad +2 \quad +1 \quad 0 \quad -1 \quad -2 \quad -3 \quad (l_z) \\
&\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\quad 4f
\end{align*}
\]

\[
\begin{align*}
n=6 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 6s \quad 5p \\
n=5 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 5s \quad 4p \quad 4d \\
n=4 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 4s \quad 3d \\
n=3 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 3s \quad 3p \\
n=2 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 2s \quad 2p \\
n=1 &\quad \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\quad 1s \quad 1s \\
S &= 7\times1/2 - 2\times1/2 = 5/2 \\
L &= 1 + 1 + 0 - 1 - 2 - 3l = 5 \\
J &= L + S = 15/2
\end{align*}
\]

\[6H_{15/2}\]
### Lantanides

<table>
<thead>
<tr>
<th>Ion</th>
<th>Shell</th>
<th>$m_l$</th>
<th>$S$</th>
<th>$L$</th>
<th>$J$</th>
<th>Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>$4f^0$</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$^1S_0$</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>$4f^1$</td>
<td>2</td>
<td>1/2</td>
<td>3</td>
<td>5/2</td>
<td>$^2F_{5/2}$</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>$4f^2$</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>$^3H_4$</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>$4f^3$</td>
<td>0</td>
<td>3/2</td>
<td>6</td>
<td>1/2</td>
<td>$^4I_{9/2}$</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>$4f^4$</td>
<td>-1</td>
<td>5/2</td>
<td>6</td>
<td>5</td>
<td>$^5I_{4}$</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>$4f^5$</td>
<td>-2</td>
<td>2/2</td>
<td>6</td>
<td>0</td>
<td>$^6I_{15/2}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$4f^6$</td>
<td>-3</td>
<td>3/2</td>
<td>0</td>
<td>7/2</td>
<td>$^7F_6$</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>$4f^7$</td>
<td>-4</td>
<td>3</td>
<td>0</td>
<td>7/2</td>
<td>$^8S_{7/2}$</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>$4f^8$</td>
<td>-5</td>
<td>3</td>
<td>6</td>
<td>2</td>
<td>$^9H_{15/2}$</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>$4f^9$</td>
<td>-6</td>
<td>5</td>
<td>15/2</td>
<td>8</td>
<td>$^{10}I_8$</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>$4f^{10}$</td>
<td>-7</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>$^{11}I_{15/2}$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>$4f^{11}$</td>
<td>-8</td>
<td>6</td>
<td>8/2</td>
<td>15/2</td>
<td>$^{12}H_{15/2}$</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$4f^{12}$</td>
<td>-9</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>$^{13}I_{15/2}$</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>$4f^{13}$</td>
<td>-10</td>
<td>3/2</td>
<td>6</td>
<td>3/2</td>
<td>$^{14}H_6$</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>$4f^{14}$</td>
<td>-11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$^{15}S_0$</td>
</tr>
</tbody>
</table>
Magnetic attraction
The magnetization is defined from the free energy (Helmholtz function)

\[ M = -\frac{\partial F}{\partial B} \]

In the free space the magnetization vanish:

\[ B = \mu_0 H \]

Magnetic induction (Magnetic flux density)  
Permittivity in vacuum  
Magnetic field strength

In a solid material the magnetic field is given by

\[ B = \mu_0 (H + M) \]

Tesla (T)  
\[ \mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1} \]  
Am\(^{-1}\)
Magnetic susceptibility: change in magnetization produced by the change of applied field

\[ \chi = -\frac{\partial M}{\partial B} = \frac{\partial^2 F}{\partial^2 B} \]

For a “linear material” the magnetization is proportional to the applied magnetic field

\[ M = \chi H \]

\[ \chi = \frac{\Delta M}{B} \]

\[ B = \mu_0(1 + \chi)H = \mu_0\mu_r H \]

Relative permeability

\[ \mu_r = (1 + \chi) \]

Molar susceptibility

\[ \chi_m = \chi V_m \]

\( V_m \) is the molar volume

1 mole = 6.022 × 10^{23}

Mass susceptibility

\[ \chi_g = \frac{\chi}{\rho} \]

m^3 kg^{-1} units

\( \rho \) is the density (in kg m^{-3})
Mass susceptibility of the first 60 elements

**Paramagnetic**

**Diamagnetic**
Langevin’s diamagnetism

- The orbital motion of electrons generate an electromotive force that opposes to the applied magnetic field (Lenz’s law).

- All materials are weakly diamagnetics, because all paired electrons, including the core electrons of an atom will always make a weak diamagnetic contribution, but only for those with closed shells (non magnetic elements and alkali halides) the diamagnetism is appreciable.

- The diamagnetic susceptibility is negative and for a system of N ions, each with Z electrons of mass m, is given by:

\[
\chi = \frac{N\mu}{B} = -\frac{NZe^2\langle r^2 \rangle}{6m}
\]

The diamagnetic susceptibilities are usually largely temperature independent.
One of the strange effect of diamagnetism is the “levitation”,

- Superconductors may be considered to be perfect diamagnets ($\chi_V = -1$) (Meissner effect)
- All conductors exhibit an effective diamagnetism when they move through a magnetic field. The Lorenz force on electrons causes them to circulate around forming Eddy currents. The eddy currents then produce an induced magnetic field which opposes the applied field, resisting the conductors motion.
Curie paramagnetism - I

The paramagnetism corresponds to a positive susceptibility and the applied magnetic field induces a magnetization which aligns parallel to it.

The magnetic field lines up the magnetic moments \( \mu \) which are the tendency to be randomly distributed at finite temperatures.

The average magnetic moment along the direction of the magnetic field could be evaluated in a semi-classical treatment, considering the Boltzmann distribution.

Curie’s law:

\[
\frac{M}{M_s} = \frac{\langle \mu_z \rangle}{\mu} \approx \frac{y}{3} = \frac{\mu B}{3k_B T}
\]

\[
\chi = \frac{n\mu_0 \mu^2}{3k_B T}.
\]
Thermal population of energy levels

Let we consider now a quantum mechanical traitement for a simple case of system $J=\frac{1}{2}$, two level system => $m_J=\pm \frac{1}{2}$

The equilibrium populations of these two levels, are:

$$\frac{N^+}{N} = \frac{\frac{\mu_B B}{e^{\frac{B}{k_BT}}} + e^{-\frac{\mu_B B}{k_BT}}}{e^{\frac{B}{k_BT}}}$$

$$\frac{N^{-}}{N} = \frac{e^{-\frac{\mu_B B}{k_BT}}}{e^{\frac{B}{k_BT}} + e^{-\frac{\mu_B B}{k_BT}}}$$

- $H_z=0$, $T=0$
  - Ground state degenerate all atoms in the same state

- $H_z>0$, $T=0$
  - Lifted degeneracy all atoms in the ground state

- $H_z>0$, $T>0$
  - Higher energy states populated
The magnetization is defined as the difference between the equilibrium populations of the two occupied levels: $N^+$ (for $m_J=+1/2$) and $N^-$ (for $m_J=-1/2$)

\[
\frac{N^+}{N} = \frac{e^{\mu \frac{B}{k_BT}}}{e^{\mu \frac{B}{k_BT}} + e^{-\mu \frac{B}{k_BT}}} \quad \frac{N^-}{N} = \frac{e^{-\mu \frac{B}{k_BT}}}{e^{\mu \frac{B}{k_BT}} + e^{-\mu \frac{B}{k_BT}}}
\]

\[
M = (N^+ - N^-) \mu = N\mu \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh(x)
\]

\[
x = \mu B / k_B T.
\]

For small fields the magnetization is linear

\[
\tanh(x) \approx x
\]

In this case the can deduce the Curie susceptibility:

\[
\chi = \frac{n\mu_0 \mu_B^2}{k_B T}.
\]
The thermal average of the magnetization is proportional to the thermal average of the magnetic moments:

\[
\langle M \rangle = \frac{N}{V} g_J \mu_B \langle m_J \rangle
\]

where \( n = N/V \) is the number of atoms per volume unit.

The thermal average of the magnetic moments is expressed in term of the partition function \( Z \):

\[
\langle m_J \rangle = \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x}}{\sum_{m_J=-J}^{J} e^{m_J x}} = \frac{1}{Z} \frac{\partial Z}{\partial x}
\]

\[
x = g_J \mu_B B / k_B T
\]

partition function \( Z \)
In general, for larger $J$, we have $(2J+1)$ levels $(-m_J, \ldots, 0, \ldots, +m_J)$ and the magnetization is:

$$\langle M(T, H_z) \rangle = \frac{N}{V} g_j \mu_B J B_J(y)$$

where $B_J(y)$ is the Brillouin function defined as:

$$B_J(y) = \frac{2J+1}{2J} \coth \left( \frac{2J+1}{2J} y \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} y \right)$$

For small $y$, i.e. when $|\mu| \ll k_B T$

$$B_J(y) = \frac{(J+1)y}{3J} + O(y^3)$$

For $J \gg \infty$, Langevin function

$$B_\infty = L(y) = \coth y - \frac{1}{y}$$
Low/high temperature approximations

Low temperatures
The magnetization approach the saturation magnetization $M_s$:

$$\frac{g_j \mu_B H_z j}{k_B T} \gg 1 \quad B(y) \to 1 \quad \langle M \rangle = \frac{N}{V} g_j \mu_B j = M_s = M(T = 0)$$

High temperatures
The magnetization follows the Curie’s law

$$\frac{g_j \mu_B H_z j}{k_B T} \ll 1 \quad B(y) \to \coth(x) \approx \frac{1}{x} + \frac{x}{3} \quad \langle M(T) \rangle = \frac{N}{V} \frac{P_{eff}^2 \mu_B^2 H_z}{3k_B T} = \frac{C}{T} H_z$$

Effective moment

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

Curie constant

$$C = \frac{N}{V} \frac{P_{eff}^2 \mu_B^2}{3k_B}$$
Curie's Law

For small applied magnetic fields (compared to the high temperatures), the paramagnetic susceptibility is:

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

\[ C = \frac{N \mu_{\text{eff}}^2 \mu_B^2}{V 3k_B} \]

Notice that with the Curie constant we can calculate the effective magnetic moment \( \mu_{\text{eff}} \) and then \( j \), which is associated to the valence of chemical bond, an important parameter in chemistry!
If the ground state of one atom is $J=0$, the paramagnetic susceptibility is 0.

$J=0$ occurs for shells which are less than half filled by one electron. Ex.: Sm and Eu

Second order perturbation theory takes into account excited states with $J\neq 0$.

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

The resulting susceptibility is

$$
\chi = \frac{N}{V} 2\mu_B^2 \sum_n \frac{|\langle 0 | (L_z + g S_z) | n \rangle|^2}{E_n - E_0}
$$

Notice that Van Vleck contribution to the susceptibility is weak, positive and temperature independent.
Conduction electrons have spin $J=S=\frac{1}{2}$

If we try to calculate the magnetic susceptibility, we have:

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

The resulting magnetization is then:

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

But this is in contradiction with measurements, because in metals:
- $\chi$ is independent of $T$.
- The calculated value at 300K is 100 times weaker than that measured

Pauli spin susceptibility: Valid for a free electron gas model

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

\[ \chi_{\text{tot}} = \chi_{\text{Langevin}} + \chi_{\text{Curie}} + \chi_{\text{Pauli}} + (\chi_{\text{Van Vleck}}) \]

- \( \chi_{\text{Langevin}} \) Induced
- \( \chi_{\text{Curie}} \) Single ion
- \( \chi_{\text{Pauli}} \) Induced
- \( \chi_{\text{Van Vleck}} \) Single ion J=0

\( \chi_{\text{Curie}} = \frac{C}{T} \)

\( \chi_{\text{free electron}} = \frac{N}{V} \frac{\mu_B^2}{k_B T_F} \)

\( \chi_{\text{Langevin}} = -\mu_0 \frac{Ze^2}{6m_e} \left\langle a^2 \right\rangle \)