# 4. Paramagnetism

We continue studying the magnetism of materials in the absence of interactions between magnetic moments. Here, we discuss the response of permanent magnetic moments to the external field; this effect is called paramagnetism, and the induced magnetization is parallel to the external field. The permanent moments can originate from partially filled electron shells, for example $3d$ (transition metals), $4f$ (rare earths) or $5f$ (actinides). The moments can also be due to the spin of the itinerant conduction electrons in metals.

4.1 Paramagnetism of the electron gas
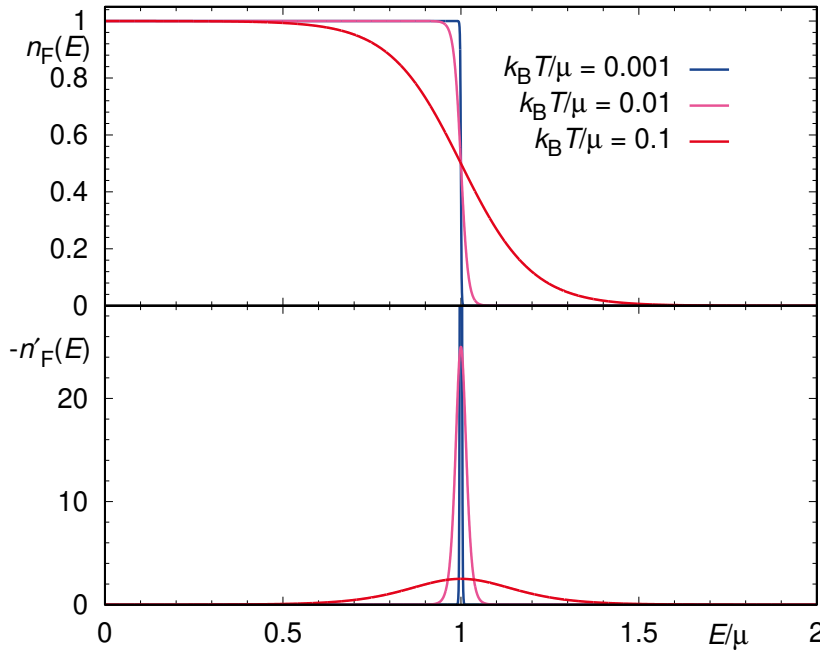
Figure 4.1: Fermi-Dirac distribution function at three different temperatures. Unit of energy is the chemical potential μ.

We already know that electrons possess spin $S = 1/2$ and a spin magnetic moment $m_s = \frac{1}{2}g\mu_B \approx 1\mu_B$ oriented oppositely to the spin. In a uniform magnetic field, the energy of a free electron is

$$\varepsilon_{\vec{k}\sigma} = \frac{\hbar^2 k^2}{2m} + \sigma\frac{1}{2}g\mu_B B_0 \quad \text{with } \sigma = \uparrow, \downarrow \equiv \pm 1 \tag{4.1}$$

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With chemical potential μ, the total energy of the Fermi gas is then

$$E = \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}\sigma} n_F\left(\varepsilon_{\vec{k}\sigma}\right) \tag{4.2}$$

with Fermi-Dirac distribution function (in short, Fermi function)

$$n_F(\varepsilon) = \frac{1}{1 + e^{\frac{\varepsilon - \mu}{k_B T}}} \,.$$

This is shown in Figure 4.1. The magnetization is given by

$$M = -\frac{g\mu_B}{2V} \sum_{\vec{k}\sigma} \sigma n_F\left(\varepsilon_{\vec{k}\sigma}\right) \tag{4.3}$$

and the susceptibility is

$$\begin{aligned}
\chi &= \frac{\partial M}{\partial B_0}\bigg|_{B_0=0} = -\frac{g\mu_B}{2V} \sum_{\vec{k}\sigma} \sigma n'_F\left(\frac{\hbar^2 k^2}{2m}\right) \sigma \frac{g\mu_B}{2} \\
&= -\frac{g^2\mu_B^2}{4V} 2 \sum_{\vec{k}} n'_F\left(\frac{\hbar^2 k^2}{2m}\right) = -\frac{g^2\mu_B^2}{2V} \sum_{\vec{k}} n'_F\left(\frac{\hbar^2 k^2}{2m}\right)
\end{aligned} \tag{4.4}$$

$\sum_\sigma$ contributes the factor 2. We can now replace the k summation by an energy integration,

$$\sum_{\vec{k}} \to \int d\varepsilon\, D(\varepsilon)\,,$$

using the density of states for one spin direction

$$D(\varepsilon) = \frac{1}{V} \sum_{\vec{k}} \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right)$$

and find

$$\chi = -\frac{g^2\mu_B^2}{2} \int d\varepsilon\, D(\varepsilon) n'_F(\varepsilon)\,. \tag{4.5}$$

For $k_B T \ll \mu$, which is typically the case for metals, $n_F(\varepsilon)$ can be approximated by a Heaviside step function $\Theta(\varepsilon)$, and therefore $-n'_F(\varepsilon)$ as a δ function: $n'_F(\varepsilon) \approx -\delta(\varepsilon)$ (see also Figure 4.1). This means

$$\chi = \frac{g^2\mu_B^2 D(\mu)}{2} =: \chi_{\text{Pauli}}\,. \tag{4.6}$$

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This is the so-called Pauli susceptibility which describes the Pauli paramagnetism. The result is valid not only for free electrons but for any kind of dispersion if the appropriate density of states $D(\varepsilon)$ is inserted. As long as $k_B T \ll \mu$, the result is temperature independent. The Pauli susceptibility is related to the Landau susceptibility via

$$\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}} . \tag{4.7}$$

Thus, the total susceptibility of the free electron gas in three dimensions is

$$\chi = \chi_{\text{Pauli}} + \chi_{\text{Landau}} = \frac{2}{3}\chi_{\text{Pauli}} . \tag{4.8}$$

Excursion: Sommerfeld expansion

Integrals of the type

$$\int dE \, H(E) n_F(E) \tag{4.9}$$

involving the Fermi function $n_F(E) = \left(e^{\frac{E-\mu}{k_B T}} + 1\right)^{-1}$ often occur in solid state physics, for example in the internal energy of the electron system

$$U = \sum_{\vec{l k \sigma}} \langle n_{\vec{l k \sigma}} \rangle \varepsilon_l(\vec{k}) = N \int dE \, n_F(E) D(E) E \tag{4.10}$$

where $\langle n_{\vec{l k \sigma}} \rangle$ is the average occupation of the single particle states l as function of temperature, given by the Fermi function; $D(E)$ is the density of states per unit cell. The total particle number can be expressed as

$$N_e = \sum_{\vec{l k \sigma}} \langle n_{\vec{l k \sigma}} \rangle = N \int dE \, D(E) n_F(E) \tag{4.11}$$

The Sommerfeld expansion can be applied if the function $H(E)$ is multiply continuously differentiable and integrable and disappears for $E \to -\infty$; then we have (by partial integration)

$$\int_{-\infty}^{\infty} dE \, H(E) n_F(E) = \int_{-\infty}^{\infty} dE \, K(E) \left(-\frac{dn_F}{dE}\right) + \underbrace{\left[K(E) n_F(E)\right]_{-\infty}^{\infty}}_{=0} \tag{4.12}$$

where

$$K(E) = \int_{-\infty}^{E} dE' \, H(E') \tag{4.13}$$

is the antiderivative of $H(E)$. Explicitly, the negative derivative of the Fermi function is

$$-\frac{dn_F}{dE} = \frac{1}{k_b T} \frac{1}{\left(e^{\frac{E-\mu}{k_B T}} + 1\right)\left(e^{-\frac{E-\mu}{k_B T}} + 1\right)}.$$ (4.14)

Examples of this function are shown in Figure 4.1. It is symmetric with respect to the chemical potential μ and falls exponentially on both sides. For $T \to 0$ the derivative becomes a δ function. At finite temperatures, it is only nonzero in a region which grows approximately linearly with temperature. Therefore, the energy integral needs only to be done in a small interval around μ, and the function $K(E)$ is expanded in a Taylor series around μ:

$$K(E) = K(\mu) + \sum_{n=1}^{\infty} \frac{1}{n!}(E-\mu)^n \frac{d^n K(E)}{dE^n}\bigg|_{E=\mu}$$ (4.15)

Inserting the integral that we want to calculate, we find

$$\int_{-\infty}^{\infty} dE\, H(E)n_F(E) = \int_{-\infty}^{\mu} dE\, H(E) + \sum_{n=1}^{\infty} \frac{d^{n-1}H(E)}{dE^{n-1}}\bigg|_{E=\mu} \int_{-\infty}^{\infty} dE\, \frac{(E-\mu)^n}{n!}\left(-\frac{dn_F}{dE}\right)$$

$$\text{because } \int_{-\infty}^{\infty} dE\left(-\frac{dn_F}{dE}\right)K(\mu) = \left[-n_F(E)K(\mu)\right]_{-\infty}^{\infty} = K(\mu)$$

(4.16)

Thus, the series contains only derivatives of the function we want to integrate, taken at the chemical potential μ as well as integrals that are independent of $H(E)$. As $-\frac{dn_F}{dE}$ is symmetric around μ, integrals over odd powers of $(E-\mu)$ drop out. With the substitution $x = \frac{E-\mu}{k_B T}$ we have

$$\int_{-\infty}^{\infty} dE\, H(E)n_F(E) = \int_{-\infty}^{\mu} dE\, H(E) + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \frac{d^{2n-1}H(E)}{dE^{2n-1}}\bigg|_{E=\mu}$$

$$\text{with } a_n = \int_{-\infty}^{\infty} dx \frac{x^{2n}}{(2n)!} \frac{1}{(e^x + 1)(e^{-x} + 1)}$$

(4.17)

The a_n can be calculated analytically:

$$a_n = \left(2 - \frac{1}{2^{2(n-1)}}\right)\zeta(2n)$$ (4.18)

with the **Riemann zeta function**

$$\zeta(x) = \sum_{m=1}^{\infty} \frac{1}{m^x} = 1 + \frac{1}{2^x} + \frac{1}{3^x} + \dots$$

In particular,

$$a_1 = \zeta(2) = \frac{\pi^2}{6}, \qquad a_2 = \frac{7}{4}\zeta(4) = \frac{7}{4}\frac{\pi^4}{90} = \frac{7\pi^4}{360}$$

Thus, the expansion up to fourth order in $k_B T$ is

$$\int_{-\infty}^{\infty} dE\, H(E) n_F(E) = \int_{-\infty}^{\mu} dE\, H(E)$$
$$+ \frac{\pi^2}{6}(k_B T)^2 \frac{dH(E)}{dE}\bigg|_{E=\mu} + \frac{7\pi^4}{360}(k_B T)^4 \frac{d^2 H(E)}{dE^2}\bigg|_{E=\mu}$$

$$(4.19)$$

Using the Sommerfeld expansion, we find

$$Z_e = \frac{N_e}{N} = \int dE\, D(E) n_F(E) = \int_{-\infty}^{\mu} dE\, D(E) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu) + \mathcal{O}(T^4)$$

$$\frac{U}{N} = \int dE\, n_F(E) D(E) E = \int_{-\infty}^{\mu} dE\, D(E) E + \frac{\pi^2}{6}(k_B T)^2 \big(\mu D'(\mu) + D(\mu)\big) + \mathcal{O}(T^4)$$

$$(4.20)$$

## 4.2 Paramagnetism of localized electrons

Now we discuss the paramagnetism of insulators. Here, the electrons that are responsible for the paramagnetism are strictly localized at fixed lattice points and produce a permanent magnetic moment there. This picture is almost ideally realized in rare earths and their compounds; they are often called 4f systems because of the electron shell that is successively filled. The neutral rare earth atom has the configuration

$$[\text{Xe}]4f^p 6s^2 \,,$$

i.e. a noble gas configuration of xenon plus 4f and 6s electrons. In the periodic table, the rare earths start with La (lanthanum) and then add 4f electrons until Lu (lutetium). Usually, the rare earths are trivalent, *i.e.* $(\text{RE})^{3+}$, and they give away the 6s electrons and one 4f electron. The

partially filled 4f shell is situated inside the xenon core and is strongly screened by the fully filled $5s^2 5p^6$ shells which lie outside the xenon core. This strongly localizes the magnetic moments of the 4f electrons to their respective lattice points.

Such a system can be described by a very simple model: We assume that in volume V, there are N identical independent ions; we only care about the magnetic moments produced by these ions. We can assume that intra-atomic correlations are so strong that the localized magnetic moment is determined by the atomic Hund's rules. The temperature and field dependence of the magnetization M is essentially an atomic problem.

Figure 4.2: Paramagnetic local moments in an external magnetic field.
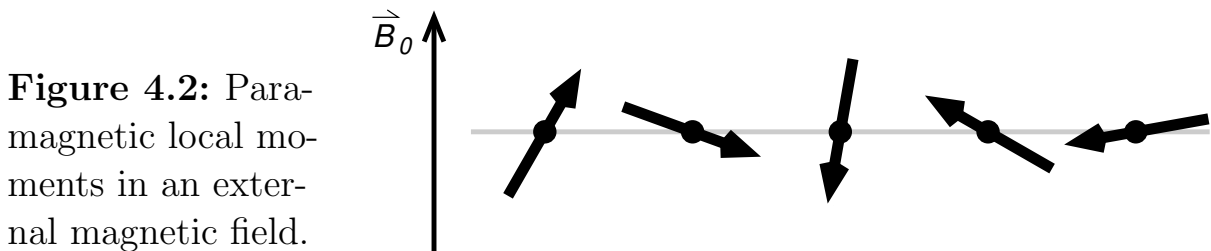
We now assume LS-coupling which is valid for not too strong spin-orbit coupling. The distances between different LS multiplets are so large that transitions among them are improbable and we can assume that quantum numbers L and S belonging to the squares L^2 and S^2 of the total angular momentum and total spin quantum numbers are good quantum numbers. The magnetic moment $\vec{m}_j$ of the ion at lattice site j is given by

$$\vec{m}_j = -\frac{\mu_B}{\hbar}\left(\vec{L}_j + 2\vec{S}_j\right) = -\frac{\mu_B}{\hbar}\left(\vec{J}_j + \vec{S}_j\right). \tag{4.21}$$

In the following, we disregard the minus sign in the definition of the magnetic moment. The model Hamiltonian is

$$H = \sum_{j=1}^{N}\left(H_0^{(j)} + H_{SO}^{(j)} - \vec{m}_j \cdot \vec{B}_0\right) = \sum_{j=1}^{N} H_1^{(j)} \tag{4.22}$$

As we are restricting the discussion to a single LS multiplet, $H_0^{(j)}$ which determines the coarse structure of the terms is not important. The spin orbit coupling of each ion $H_{SO}^{(j)}$ determines the fine structure of the terms. The last expression in the bracket represents the Zeeman energy, and its relative strength in comparison to $H_{SO}^{(j)}$ is decisive for the calculation of the magnetization

$$\vec{M} = n\langle m \rangle \quad \text{with } n = \frac{N}{V}.$$

Here, the bracket $\langle\ldots\rangle$ means quantum mechanical expectation value and thermal averaging; in general

$$\langle A \rangle = \frac{1}{Z}\mathrm{Tr}\left(A e^{-\beta H}\right)$$

with canonical partition function $Z = \mathrm{Tr}\left(e^{-\beta H}\right) = Z_1^N$ which factorizes for the model (4.22) into a product of single-particle partition functions

$$Z_1 = \mathrm{Tr}\left(e^{-\beta H_1}\right)$$

because the moments do not interact. β is the inverse temperature $\beta = \frac{1}{k_B T}$. If we now apply a homogeneous magnetic field $\vec{B}_0$ in z direction, the x and y components of the magnetization vanish, and we find for $M_z = M$

$$M = n\frac{1}{Z_1}\mathrm{Tr}\left(m e^{-\beta H_1}\right) = k_B T n \frac{\partial}{\partial B_0}\ln Z_1 \tag{4.23}$$

Determining the single-particle partition function Z_1 already solves the problem; however, we can calculate the trace only for particular situations. M is influenced by the thermal energy $k_B T$, by the spin-orbit interaction $H_{SO} = \Lambda(\gamma, LS)\vec{L}\cdot\vec{S}$ (γ stands for other quantum numbers) and the magnetic field $H_z = -\frac{\mu_B}{\hbar}(J_z + S_z)B_0$. Only if there are orders of magnitude between these three terms can the partition function Z_1 be determined easily.

Weak spin-orbit interaction.- This is the case $\hbar^2\Lambda(\gamma, LS)\vec{L} \ll k_B T$. Furthermore, we have to distinguish small and large field compared to the temperature of interest.

a) $\hbar^2\Lambda(\gamma, LS)\vec{L} \ll k_B T, \mu_B B_0$

We can assume that we have the so-called normal Zeeman effect

$$E_{\gamma LSJM_J} = E_{\gamma LS}^{(0)} - (M_L + 2M_S)\mu_B B_0\,,$$

and all terms of the LS multiplet are occupied with almost equal probability. M_L and M_S are "still good" quantum numbers, but J is not a good quantum number. $E_{\gamma LS}^{(0)}$ are eigenenergies of H_0 without field and without spin-orbit coupling. We calculate the partition function in energy representation

$$Z_1 = e^{-\beta E_{\gamma LS}^{(0)}} \sum_{M_L=-L}^{+L} \sum_{M_S=-S}^{+S} e^{\beta\mu_B B_0(M_L+2M_S)} \tag{4.24}$$

We focus on the lowest LS multiplet as the prefactor will be very small for the higher ones. With the notation $b = \beta \mu_B B_0 > 0$ we calculate

$$
\sum_{M_L=-L}^{+L} e^{bM_L} = e^{bL} \sum_{n=0}^{2L} (e^{-b})^n = e^{bL} \frac{1 - e^{-b(2L+1)}}{1 - e^{-b}}
$$

$$
= e^{bL} \frac{e^{b/2} - e^{-b/2-2Lb}}{e^{b/2} - e^{-b/2}} = \frac{e^{b(L+1/2)} - e^{-b(L+1/2)}}{e^{b/2} - e^{-b/2}}
$$

$$
= \frac{\sinh\left(b(L + 1/2)\right)}{\sinh\left(\frac{b}{2}\right)} \tag{4.25}
$$

The same calculation also gives

$$
\sum_{M_S=-S}^{+S} e^{bM_S} = \frac{\sinh\left(b(2S + 1)\right)}{\sinh b} . \tag{4.26}
$$

Therefore, the partition function is

$$
Z_1 = e^{-\beta E_{\gamma LS}^{(0)}} \frac{\sinh\left(\beta \mu_B B_0 (L + 1/2)\right)}{\sinh\left(\frac{1}{2}\beta \mu_B B_0\right)} \frac{\sinh\left(\beta \mu_B B_0 (2S + 1)\right)}{\sinh(\beta \mu_B B_0)} . \tag{4.27}
$$

With the magnetization of a paramagnet (4.23), we now need to differentiate the partition function with respect to the field:

$$
\frac{\partial}{\partial B_0} \ln Z_1 = \frac{1}{Z_1^{(L)}} \frac{\partial Z_1^{(L)}}{\partial B_0} + \frac{1}{Z_1^{(S)}} \frac{\partial Z_1^{(S)}}{\partial B_0} . \tag{4.28}
$$

We do the first term explicitly:

$$
\frac{1}{Z_1^{(L)}} \frac{\partial Z_1^{(L)}}{\partial B_0} = \frac{\sinh\left(\frac{b}{2}\right)}{\sinh\left(b(L + 1/2)\right)} \left\{ \frac{\sinh\left(\frac{b}{2}\right)\beta \mu_B (L + 1/2) \cosh\left(b(L + 1/2)\right)}{\sinh^2\left(\frac{b}{2}\right)} - \right.
$$

$$
\left. - \frac{\sinh\left(b(L + 1/2)\right)\frac{1}{2}\beta \mu_B \cosh\left(\frac{b}{2}\right)}{\sinh^2\left(\frac{b}{2}\right)} \right\}
$$

$$
= \beta \mu_B (L + 1/2) \coth\left(b(L + 1/2)\right) - \frac{1}{2}\beta \mu_B \coth\left(\frac{b}{2}\right) \tag{4.29}
$$

Now we introduce a function which is central to the theory of magnetism, the Brillouin function:

$$
B_D(x) = \frac{2D + 1}{2D} \coth\left(\frac{2D + 1}{2D}x\right) - \frac{1}{2D} \coth\left(\frac{x}{2D}\right) \tag{4.30}
$$
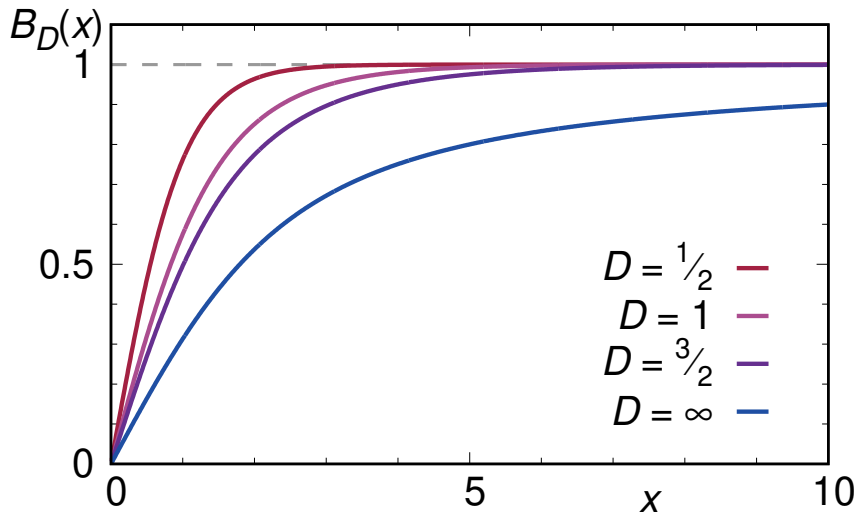
Figure 4.3: Brillouin function $B_D(x)$ as function of x for several parameters D.

Using this function, we can write the magnetization of Eq. (4.23) in the form

$$M(T, B_0) = n\mu_B\left[LB_L(\beta\mu_B B_0 L) + 2SB_S(2\beta\mu_B B_0 S)\right] \tag{4.31}$$

A few general properties of the Brillouin function are:

1. $D = 1/2$: In this special case,

$$B_{1/2}(x) = \tanh x.$$

2. $D \to \infty$: In this limit, the Brillouin function reduces to the Langevin function $L(x)$:

$$B_{D\to\infty}(x) = L(x) = \coth x - \frac{1}{x}.$$

This function appears in the classical treatment of paramagnetism if the quantization of the orbital angular momentum is neglected (moments can assume any angle in space).

3. Small x: By expanding $\coth x$, one finds

$$B_D(x) = \frac{D+1}{3D}x - \frac{D+1}{3D}\frac{2D^2 + 2D + 1}{30D^2}x^3 + \dots, \tag{4.32}$$

and, in particular

$$B_D(0) = 0.$$

Due to this property, according to (4.31), the magnetization of a paramagnet is zero if either $B_0 = 0$ or $T = \infty$. Physically, this means that a paramagnet does not possess spontaneous magnetization.

4. $B_D(-x) = -B_D(x)$: This means that if the direction of the magnetic field is reversed, the direction of the magnetization is also reversed.

5. $\lim\limits_{x\to\infty} B_D(x) = 1$: The magnetization shows saturation for $B_0 \to \infty$ or for $T \to 0$. This means that all the moments are oriented parallel to the field: $M \to M_0 = n\mu_B(L+2S)$. The high temperature behavior of the magnetization is interesting. With the precondition we are discussing here $\hbar^2\Lambda(\gamma, LS) \ll \mu_B B_0 \ll k_B T$ or $\beta\mu_B B_0 \ll 1$, the argument of the Brillouin function is small, and the expansion (4.32) can be terminated after the linear term:

$$M \approx \frac{n\mu_0\mu_B^2}{3k_BT}B_0\left[L(L+1) + 4S(S+1)\right] \tag{4.33}$$

The susceptibility

$$\chi = \mu_0\left(\frac{\partial M}{\partial B_0}\right)_T$$

then shows a characteristic $\frac{1}{T}$ behavior, which is called the Curie law:

$$\chi(T) = \frac{C_1}{T} \,. \tag{4.34}$$

C_1 is the so-called Curie constant which is given by

$$C_1 = \frac{n\mu_0\mu_B^2}{3k_B}\left[L(L+1) + 4S(S+1)\right] \,.$$

A purely classical calculation would have given a similar high-temperature behavior:

$$\chi_{cl}(T) = \frac{C_{cl}}{T}, \quad C_{cl} = \frac{n\mu_0\mu^2}{3k_B}\,, \tag{4.35}$$

where μ is the magnetic moment. In analogy, one therefore defines

$$\mu_{eff} = \mu_B p_{eff}, \quad p_{eff} = \sqrt{L(L+1) + 4S(S+1)} \tag{4.36}$$

with the effective number of Bohr magnetons p_{eff}.

b) So far, we assumed that both thermal energy and field energy are large compared to the spin-orbit interaction. If we now allow the spin-orbit coupling energy to be of the same order of magnitude as the magnetic energy but still smaller than the thermal energy

$$\hbar^2\Lambda(\gamma, LS), \mu_B B_0 \ll k_B T$$

the calculation becomes more complicated because the spin-orbit coupling term enters the partition function. However, after considering all terms, the result for the magnetization is

$$M = \frac{n\mu_0\mu_B^2}{3k_BT}B_0\big[L(L+1) + 4S(S+1)\big] \tag{4.37}$$

which is the same as the high temperature limit of case a), Eq. (4.33).

Strong spin-orbit interaction.- $\hbar^2\Lambda(\gamma, LS) \gg k_BT, \mu_BB_0$. This case is different; it is often discussed as Langevin paramagnetism and occurs for 4f systems in moderate fields. Rather than a uniform distribution over the fine structure terms of the LS multiplets, only the lowest term is occupied to a certain degree. J is still a "good" quantum number, and non-diagonal terms of S^z only play a marginal role; this region is called the anomalous Zeeman effect, and the energies are

$$E_{\gamma LSJM_j} = E_{\gamma LSJ}^{(0)} + g_J(L, S)M_J\mu_BB_0 \tag{4.38}$$

with Landé g factor from Eq. (2.21). Then, the partition function is

$$Z_1 = e^{-\beta E_{\gamma LSJ}^{(0)}} \sum_{M_J=-J}^{+J} e^{-\beta g_J M_J \mu_B B_0} . \tag{4.39}$$

Only the energetically most favorable J value, according to Hunds' third rule, has to be taken into account. The partition function is calculated as shown above for weak spin-orbit coupling, Eq. (4.27):

$$Z_1 = e^{-\beta E_{\gamma LSJ}^{(0)}}\frac{\sinh\big(\beta g_J\mu_BB_0(J + 1/2)\big)}{\sinh\big(\frac{1}{2}\beta g_J\mu_BB_0\big)} \tag{4.40}$$

This gives us the magnetization

$$M = M_0 B_J\big(\beta g_J J\mu_BB_0\big) \tag{4.41}$$

with saturation magnetization

$$M_0 = nJg_J\mu_B . \tag{4.42}$$

As before, the susceptibility follows from differentiating with respect to the field B_0. The high temperature behavior is again the Curie law (for $\beta\mu_BB_0 \ll 1$)

$$\chi = \frac{C}{T} \quad \text{with } C = n\mu_0\frac{p_{\text{eff}}^2}{3k_B}\mu_B^2 \tag{4.43}$$

where in the Curie constant C now a different effective magneton number is found:

$$p_{\text{eff}} = g_J \sqrt{J(J+1)}. \tag{4.44}$$

The Curie law is experimentally very well confirmed, and the order of magnitude of χ_{Langevin} is normally much larger than the Pauli magnetism of the conduction electrons:

$$\frac{\chi_{\text{Pauli}}}{\chi_{\text{Langevin}}} = \frac{9}{2} \frac{1}{g_J^2 J(J+1)} \frac{k_B T}{\epsilon_F} \tag{4.45}$$