
FIP10604 – Text 02 – ATOMIC MAGNETIC MOMENTS

In Text 01 we presented the physical quantities that are relevant to describe magnetic properties of materials, including a brief comment about observed types of magnetic behavior. Here we begin to analyze the microscopic origins of magnetic properties.

From a classical point of view, the effect of a magnetic field on a particle is associated to the electric charge. We know that the equation $\nabla \cdot \mathbf{B} = 0$ allows to define a *vector potential* \mathbf{A} , such that

$$\mathbf{B} = \nabla \times \mathbf{A} . \quad (1)$$

The classical equations of motion for a particle with electric charge q in the presence of a magnetic field are consistent with a Hamiltonian in which the kinetic-energy term (in the SI) takes the form $(\mathbf{p} - q\mathbf{A})^2/2m$. In the case of microscopic models, effects of the *medium* are explicitly taken into account through the interactions between particles, so that the magnetization does not appear at this level. Then it is interesting to work with the Gaussian system, replacing the magnetic induction \mathbf{B} by the magnetic field \mathbf{H} (which is the **external** applied field), and writing directly $\mathbf{H} = \nabla \times \mathbf{A}$. In this unit system, the particle's kinetic energy is written as $(\mathbf{p} - q\mathbf{A}/c)^2/2m$, where c is the speed of light in vacuum. Unless otherwise stated, this formulation will be adopted throughout the course.

From a thermodynamic point of view, the magnetization induced by the presence of an applied magnetic field is obtained by deriving the free energy with respect to the field. Classical statistics for a system in thermodynamic equilibrium involves the Maxwell-Boltzmann distribution and integrals over the phase space. But a simple change of variables on the momentum integration allows to totally eliminate the vector potential! Therefore, **in a classical treatment, the magnetization of a system of particles, at any finite temperature and for any applied magnetic field, is null.** This statement is known as *Bohr-van Leeuwen Theorem*, because it initially appeared in Niels Bohr's PhD thesis, in 1911, and was rediscovered (!) eight years later in the thesis of Miss H. J. van Leeuwen.

It is, therefore, evident that magnetism can only be described by a **quantum** theory. It should be noted that we are referring to a **microscopic** theory. It is possible to construct phenomenological or effective classical models of magnetic systems, as we will see later.

Based on the above observations, we will first address a very simple problem, the occurrence of magnetic moment in isolated atoms or ions, starting with a one-electron atom.

One-electron atom in the presence of magnetic field

For an electron, the presence of a magnetic field involves replacing $\mathbf{p} \rightarrow (\mathbf{p} + e\mathbf{A}/c)$, since the charge is $q = -e$. Then, initially neglecting the electron spin, the Hamiltonian for a single-electron atom in the presence of a magnetic field associated to a vector potential \mathbf{A} takes the form

$$\mathcal{H} = \frac{1}{2m_e} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 + V(r) , \quad (2)$$

where $V(r)$ is the Coulomb potential due to the nucleus and m_e is the electron mass. Developing the quadratic term, we have

$$\mathcal{H} = \mathcal{H}_0 + \frac{e}{2m_e c} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2m_e c^2} A^2 \quad (3)$$

where A is the magnitude of \mathbf{A} , and \mathcal{H}_0 denotes the Hamiltonian of the atom in the absence of applied field. Using $\mathbf{p} = -i\hbar\nabla$, choosing a *gauge* such that $\nabla \cdot \mathbf{A} = 0$ (which means that \mathbf{p} commutes with \mathbf{A}), and in particular

$$\mathbf{A} = -\frac{1}{2} \mathbf{r} \times \mathbf{H} , \quad (4)$$

it follows that

$$\mathcal{H} = \mathcal{H}_0 + \frac{e}{2m_e c} \mathbf{L} \cdot \mathbf{H} + \frac{e^2}{8m_e c^2} r_{\perp}^2 H^2 . \quad (5)$$

$\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is the orbital angular momentum, and \mathbf{r}_{\perp} is the projection of the position vector \mathbf{r} on a plane perpendicular to \mathbf{H} .

Orbital magnetic moment

Remembering that the potential energy of a classical (permanent) magnetic dipole $\boldsymbol{\mu}$ subjected to a magnetic induction \mathbf{B} is $E = -\boldsymbol{\mu} \cdot \mathbf{B}$, we have (replacing \mathbf{B} by \mathbf{H})

$$E = -\boldsymbol{\mu} \cdot \mathbf{H} . \quad (6)$$

More generally, we can identify the magnetic dipole moment with minus the derivative of the magnetic energy with respect to magnetic field. Thus, in a quantum formulation we can identify the components of the magnetic-dipole-moment **operator** as minus the derivative of the Hamiltonian with respect to the corresponding components of \mathbf{H} .

Two contributions to the magnetic dipole moment appear in Eq. (5): an orbital magnetic moment

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e c} \mathbf{L} , \quad (7)$$

which is independent of the field and hence paramagnetic, and an **induced** diamagnetic moment (opposite to the applied field)

$$\boldsymbol{\mu}_d = -\frac{e^2}{4m_e c^2} r_{\perp}^2 \mathbf{H} . \quad (8)$$

In the ground state, we have $l = 0$, l being the quantum number associated with the magnitude of the orbital angular momentum [the eigenvalues of L^2 are $l(l+1)\hbar^2$, with $l = 0, 1, 2, \dots$]. Thus, the expected value of the orbital magnetic moment is $\langle \boldsymbol{\mu}_L \rangle = 0$, and there is no paramagnetic behavior. On the other hand, we can write

$$\langle \mu_d \rangle = -\frac{e^2}{6m_e c^2} \langle r^2 \rangle H , \quad (9)$$

where we use $\langle r_{\perp}^2 \rangle = \frac{2}{3} \langle r^2 \rangle$ due to rotation symmetry (the average is evaluated at zero field, considering the linear-response limit for sufficiently weak fields). Notice that the magnetic susceptibility of a system consisting of this kind of atoms, which is proportional to $\partial \langle \mu_d \rangle / \partial H$, is non-zero and negative.

As the eigenvalues of angular-momentum components are integer multiples of \hbar , it is usual to rewrite Eq. (7) as

$$\boldsymbol{\mu}_L = -\mu_B \mathbf{L} / \hbar , \quad (10)$$

where

$$\mu_B = \frac{e\hbar}{2m_e c} = 9.27 \times 10^{-21} \text{ emu} \quad (11)$$

(equivalent to $9.27 \times 10^{-24} \text{ Am}^2$ in the SI) is the *Bohr magneton*, which defines the order of magnitude of microscopic magnetic moments.

Inclusion of spin

We know that the most important correction to the one-electron-atom Hamiltonian consists in taking into account the electron *spin* (operator \mathbf{S} , with quantum numbers s and m_s), adding two terms to Eq. (5), which now reads

$$\mathcal{H} = \mathcal{H}_0 + \frac{e}{2m_e c} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} + \xi \mathbf{L} \cdot \mathbf{S} + \frac{e^2}{8m_e c^2} r_{\perp}^2 H^2 . \quad (12)$$

We see the presence of a *spin magnetic moment*

$$\boldsymbol{\mu}_S = -2\mu_B \mathbf{S} / \hbar , \quad (13)$$

and a *spin-orbit interaction* term involving the scalar product of \mathbf{L} and \mathbf{S} . If the spin-orbit interaction is weak in comparison to the magnetic-field effect, it can be neglected, and we have two independent contributions (orbital and spin) to the total magnetic moment, which may be written as

$$\boldsymbol{\mu} = -\mu_B (\mathbf{L} + 2\mathbf{S}) / \hbar . \quad (14)$$

However, if the spin-orbit interaction is important, the *total angular momentum* \mathbf{J} ($= \mathbf{L} + \mathbf{S}$) must be taken into account, with quantum numbers j and m_j . Now, m_l and m_s are no longer good quantum numbers, and the states are specified by the set $\{n l j m_j\}$. In this case, by projecting $\boldsymbol{\mu}$ into a subspace of fixed j , one can show (a demonstration is found in most textbooks on Quantum Mechanics) that the atomic magnetic moment is parallel to \mathbf{J} and can be written as

$$\boldsymbol{\mu} = -g_J \mu_B \mathbf{J} / \hbar , \quad (15)$$

where

$$g_J = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (16)$$

is the *Landé g-factor*. Note that $g_J = 1$ if $s = 0$ and $g_J = 2$ if $l = 0$.

This is not very relevant for a one-electron atom because the ground state has $l = 0$. But the single-atom response is no longer diamagnetic because there is a nonzero $\langle \mu_s \rangle$ aligned with an applied magnetic field. In practice, the only electrically neutral one-electron atom is the hydrogen atom (and its isotopes), but hydrogen naturally appears in the molecular form H_2 , with a zero-spin ground state. The above discussion becomes more relevant when generalized to many-electron atoms.

Many-electron atoms

The Hamiltonian of an atom with two or more electrons contains the interaction between electrons, which makes the problem much harder. Actually, there is no exact solution. The simplest treatment is the Hartree approximation. It considers the electrons as independent (not explicitly interacting), so that one still has a single-particle problem, but the potential $V(r)$ in Eq. (2) is replaced by an effective potential that takes (partly) into account the effect of the other electrons. It is basically the sum of two Coulomb potentials, one due to the nucleus and one due to a static and spherically symmetric charge distribution obtained from the radial probability distribution of the other electrons. This implies a self-consistent solution, since this probability distribution is obtained from the wavefunctions. At this level, the spin-orbit interaction is neglected.

We will not develop here a detailed study of the Hartree approximation for many-electron atoms. We will just highlight some relevant aspects for determining atomic magnetic moments, which is our immediate goal.

The energy eigenfunctions of the system involve products of single-electron wavefunctions. The latter are similar in form to those of one-electron atoms, i.e.,

$$\psi_{nlm_l m_s}(r, \theta, \phi) = R_{nl}(r)Y_{lm_l}(\theta, \phi)\chi_{m_s}, \quad (17)$$

differing only by the radial function $R_{nl}(r)$, which depends on details of the effective potential. The quantum number m_s specifies the spin state.

Energy eigenvalues of the atom are obtained by filling up the available one-electron states obeying Pauli's Exclusion Principle, but the eigenfunctions are simple products, not enforcing antisymmetry under particle exchange. It should be noted that, unlike the hydrogen atom, individual energies depend on the quantum number l in addition to the principal quantum number n . The origin of this effect is that electrons in states with higher l are, on average, farther away from the nucleus, thus feeling its attraction weakened due to screening by the "inner" electrons. Individual states continue to be degenerate in m_l and m_s .

We thus have one-electron energies arranged in *shells* which are basically defined by the quantum number n , with *subshells* essentially differing by the value of l . However, the above-mentioned dependence of one-electron energies on l may take states from one shell

to another. With some exceptions, the sequence of subshell occupation for atomic ground states is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 \dots, \quad (18)$$

where the subscripts denote the maximum number of electrons in the subshell, and we employ the usual notation of letters s, p, d, f, ... respectively associated to $l = 0, 1, 2, 3, \dots$

For the one-electron atom, we saw that the atomic magnetic moment is directly related to the total angular momentum \mathbf{J} of the electron. We can infer that the magnetic moment of a many-electron atom involves a total angular momentum resulting from the coupling of all the individual ones. So, in principle, we have to take into account the *spin-orbit interaction*. But there is another correction to the Hartree Hamiltonian that plays a role here. It is called *residual Coulomb interaction*, which is just the difference between the actual sum of interactions between electrons and its approximate description via an effective potential. The relative importance of these two corrections determines two different scenarios for many electron atoms:

J-J coupling: If the spin-orbit correction dominates, each individual electron develops its total angular momentum $\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i$. Then the \mathbf{J}_i 's of all the electrons combine to form the total angular momentum **of the atom**, $\mathbf{J} = \sum_i \mathbf{J}_i$.

L-S coupling: If the residual Coulomb interaction is the most important correction, electrons cannot independently occupy individual (Hartree) states, as will be discussed below. In this case, the individual spins couple to make an atomic spin $\mathbf{S} = \sum_i \mathbf{S}_i$, individual orbital angular momenta couple to form an atomic orbital angular momentum $\mathbf{L} = \sum_i \mathbf{L}_i$, and coupling of these give the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ of the atom. The last step involves a spin-orbit interaction for the atomic quantities that derives from the individual ones.

We will only consider *L-S coupling*, which applies in the majority of cases. It is important to note that completely filled subshells do not contribute to the atomic \mathbf{L} and \mathbf{S} , implying that in the ground state these vectors are determined only by the **highest** subshell.

For a single electron, we used lower-case letters l , s , and j to represent quantum numbers determining the eigenvalues of \mathbf{L}^2 , \mathbf{S}^2 , and \mathbf{J}^2 , respectively, while m_l , m_s , and m_j were associated to the corresponding z components. For the sake of clarity, we will use **upper-case** letters (L, M_L, S, M_s, J, M_J) in connection to quantum numbers of **atomic** angular momenta. Consequently, the sequence s,p,d,f... becomes S,P,D,F...

At the Hartree level of approximation, atomic ground-states are specified by configurations written as in Eq. (18). For example, the ground-state configuration of an atom with 8 electrons (oxygen) is $1s^2 2s^2 2p^4$. But the values of S and L are not uniquely defined. Its easy to check that we can distribute 4 electrons in the three p-orbitals with $S = 1$ or 0, and $L = 2, 1$ or 0. In principle, this could yield $J = 3, 2, 1$, or 0. However, constraints due to the exclusion principle forbid $J = 3$.

Possible combinations of L , S and J are specified as a *term* in the form $(^{2S+1}[L])_J$, where the brackets indicate that one uses S,P,D,F,... to represent the L values. For example, the term corresponding to $L = 1$, $S = 1$, and $J = 3$ is written as 2P_3 . Sometimes a term is written omitting the J subscript. In this case it represents a *multiplet*. The number of terms of a multiplet, i.e., the number of possible values of J , is equal to $2S + 1$ when $S \leq L$. For this reason the left superscript is usually referred to as the term's *multiplicity*.

In the Hartree approximation, all terms corresponding to the same configuration are degenerate in energy. This degeneracy is lifted by the residual Coulomb interaction and the spin-orbit interaction. With these corrections, the ground-state term can be determined from a given configuration by the so-called **Hund's rules**:

1. The lowest energy corresponds to the largest possible S , and to the largest possible L for a given S .
2. In each multiplet, the lowest energy corresponds to the smallest possible J if the subshell is less than half-filled, and to the largest possible J if it is more than half-filled.

The first rule reflects an effect of the residual Coulomb interaction associated with the *exchange symmetry* of the total wavefunction (absent in the Hartree approximation). Electrons, being spin-1/2 particles, are *fermions*, which means that the system wavefunction must be *antisymmetric* with respect to the exchange of any two electrons. This wavefunction can be written as a product of orbital (position-dependent) and spin functions, neglecting spin-orbit coupling at this stage. A large total spin implies that the spin wavefunction is symmetric against exchange. This yields an antisymmetric orbital wavefunction, implying that it is less likely to find two electrons in the same region of space, thus minimizing the Coulomb repulsion between them. For the same total spin, a large L provides a large number of orbitals (with distinct m_l 's) to distribute the electrons, which also reduces their repulsion energy by increasing the average distance between them.

The second rule reflects the effect of spin-orbit interaction, and the fact that there is a change of sign of the coefficient of $\mathbf{L} \cdot \mathbf{S}$ as a function of subshell filling, favoring antiparallel alignment between \mathbf{S} and \mathbf{L} (smallest J) in one case and parallel (largest J) in the other.

Atomic magnetic moments

Since we now know how to determine the ground-state quantum numbers S , L , and J for a many electron atom, we are finally able to determine the atomic magnetic moment. Equations (14) and (15) still hold, provided that we use the atomic Landé g -factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (19)$$

This applies to **isolated** atoms. It may change for atoms in a crystalline solid due to the effect of neighboring atoms, as we will see later.

From the above results, we conclude that isolated atoms tend to have permanent magnetic moments. Therefore, we should expect a system of non-interacting atoms to be in general **paramagnetic**. The exceptions are a ground-state configuration with all subshells completely filled, or in cases where the ground state corresponds to $J = 0$ even though the relevant subshell is not filled (carbon is an example: 6 electrons in the configuration $1s^2 2s^2 2p^2$ imply that the ground-state term is 3P_0).

In fact, to confirm that a system of non-interacting atoms with $J \neq 0$ should be paramagnetic we must compare the relative intensities of the paramagnetic and diamagnetic effects. The magnetic energy contributed by the Zeeman term is of the order of $\mu_B H$. On the other hand, considering that $\langle r_{\perp}^2 \rangle \sim a_0^2$ (a_0 is the Bohr radius), one can estimate the relative contribution of the (diamagnetic) last term of Eq. (5), multiplied by the number of electrons, as

$$\frac{\langle \mathcal{H}_d \rangle}{\mu_B H} \sim 10^{-9} Z H / \text{Oe} . \quad (20)$$

Even for $B \sim 1$ T ($H \sim 10$ kOe) this ratio is typically of order 10^{-4} . This confirms that paramagnetic behavior is dominant in systems of independent atoms that have non-zero total angular momentum. Magnetic order, as we discussed in Text 01, can only occur if there are interactions between atoms. These possibilities will be explored in the following texts.