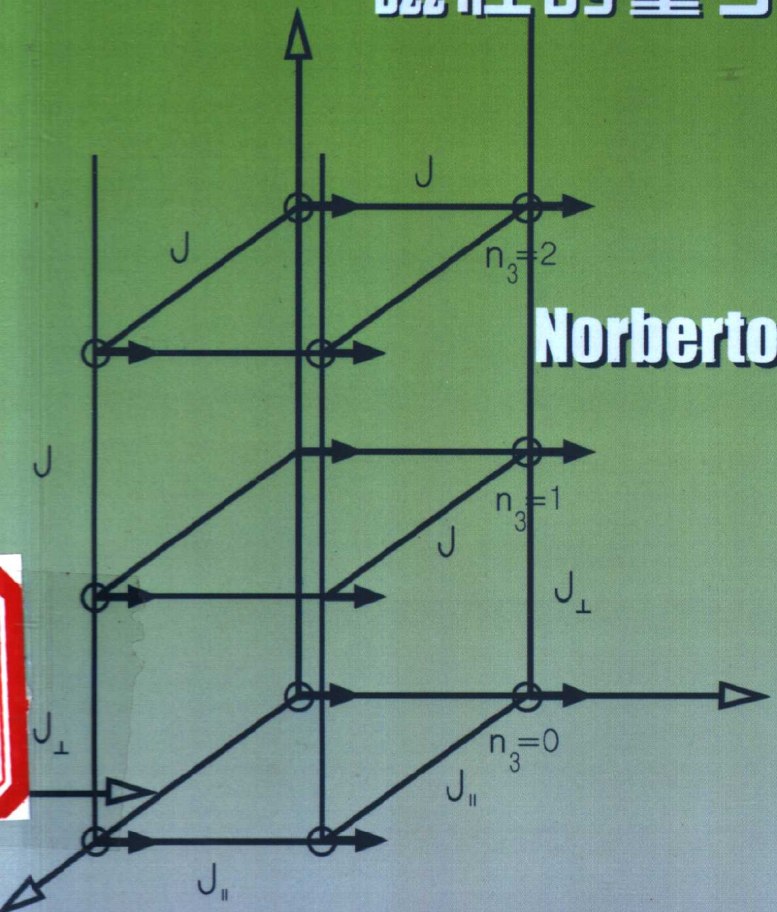
The Quantum Theory of Magnetism

磁性的量子理论



Norberto Majlis

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Norberto Majlis
McGill University, Canada

World Scientific
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作　　者：N. Majlis
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Preface

This is an advanced level textbook which grew out of lecture notes for several graduate courses I taught in different places over several years. It assumes that the reader has a background of Quantum Mechanics, Statistical Mechanics and Condensed Matter Physics. The methods of Green's functions, which are standard by now, are used fairly extensively in the book, and a mathematical introduction is included for those not very familiar with them.

The selection of subjects aims to present a description of the behaviour of systems which show ordered magnetic phases. This, plus the necessary limitation of the extension within reasonable limits, imposed the exclusion of many important subjects, among which diamagnetism, the Kondo effect, magnetic resonance, disordered systems, etc.
In turn, the reader will find a detailed presentation of the mean-field approximation, which is the central paradigm for the phenomenological description of phase transitions, a discussion of the properties of low-dimensional magnetic systems, a somewhat detailed presentation of the RKKY and related models of indirect exchange and a chapter on surface magnetism, among other characteristics which make it different from other texts on the subject.

This book can be used as a text for a graduate course in physics, chemistry, chemical engineering, materials science and electrical engineering and as a reference text for researchers in condensed matter physics.
Many exercises are included in the text, and the reader is encouraged

to take an active part by trying to solve them.

I hope readers who find errors in the book, or want to suggest improvements, get in touch with me.

It is a great pleasure to acknowledge the moral support I enjoyed from my wife and my children, the generous and extremely competent help with the software during the preparation of the manuscript from Luis Alberto Giribaldo and my daughter Flavia, and the careful reading of several chapters by June Gonçalves. I want also to express deep recognition to the Centre for the Physics of Materials of McGill University for their support, particularly to Martin J. Zuckermann, Martin Grant and Juan Gallego.

Norberto Majlis

Montréal, march 7th., 2000.

majlisn@physics.mcgill.ca

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Chapter 1

Paramagnetism

1.1 Introduction

Some examples of atomic systems with a permanent magnetic moment in the ground state are:

- atoms, molecules, ions or free radicals with an odd number of electrons, like $H, NO, C(C_6H_5)_3, Na^+$, etc.;
- a few molecules with an even number of electrons, like O_2 and some organic compounds;
- atoms or ions with an unfilled electronic shell. This case includes:
  - transition elements ($3d$ shell incomplete);
  - the rare earths (series of the lanthanides) ($4f$ shell incomplete);
  - the series of the actinides ($5f$ shell incomplete).

We shall consider in the rest of this chapter that the atomic entities carrying angular momenta occupy sites on a perfect crystalline insulator, that they are very well localized on their respective sites, and that their mutual interactions are negligible. This implies that we can neglect the unavoidable dipole-dipole interactions, which we assume are so weak that they could only affect the behaviour of the

system at extremely low temperatures. If such a system is placed in an external uniform magnetic field **B** the Zeeman energy term is:

$$V = -\mathbf{B} \cdot \sum_{i=1}^{N} \mu_i \tag{1.1}$$

where μ_i is the magnetic moment at site i. If the magnetic moments are replaced by classical vectors, as in the semi-classic, large J limit, the corresponding partition function for this system in the canonical ensemble is:

$$\mathcal{Z} = \int \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 \cdots \mathrm{d}\Omega_N \, \exp\left(\beta\mu_0 B \sum_{i=1}^{N} cos\theta_i\right) = (z(a))^N \tag{1.2}$$

where we have defined

$$z(a) = \int \exp\left(a \, cos\theta\right) \mathrm{d}\Omega = \frac{\pi}{a} \sinh(a) \tag{1.3}$$

with $a = \beta\mu_0 B$, μ_0 = magnetic moment of each atom, $\beta = 1/k_B T$, $\mathrm{d}\Omega_i$ is the differential element of solid angle for the i-th dipole and θ is the angle between that dipole and the applied magnetic field.
The Gibbs free energy per particle is:

$$f = -k_B T \log z \tag{1.4}$$

and the average magnetic moment $\overline{\mu}$ per atom along the applied field direction is, in units of μ_0:

$$\frac{\overline{\mu}}{\mu_0} = -\frac{1}{\mu_0} \frac{\partial f}{\partial B} = \coth(a) - 1/a \equiv L(a) \tag{1.5}$$

here $L(a)$ is the Langevin function [1].

Exercise 1.1
Prove that for $a \ll 1$, that is for $B \to 0$ or $T \to \infty$ or both, the magnetization approaches

$$m_z \approx (N/V)\mu_0^2 B/3k_B T \tag{1.6}$$

(Curie's law) [2].

Equation 1.5 describes *Langevin paramagnetism.* The typical value of μ_0 is a few Bohr magnetons $\mu_B \approx 10^{-20}$ erg gauss $^{-1}$, so that only at very low temperatures or very high fields, like those produced with superconducting and/or pulsed refrigerated magnets, can saturation effects be observed in the $m_z(T)$ curve. We show in Fig. 1.1 a comparison of Langevin theory with experimental measurements of the magnetization of Cr potassium alum. These measurements were performed in fields of up to 50,000 gauss and at temperatures down to 1.29 K, which allowed for a large saturation degree. It is evident from Fig. 1.1 that Langevin's theory, which assumes continuity of the observable values of the magnetic dipolar moment of an ion or atom, does not fit the experiments, except at high temperatures and/or low fields. In order to reach agreement with experiment one must incorporate those changes which are due to the quantum nature of the ions. The main effects of angular momentum quantization are twofold:

- the discrete character of the eigenvalue spectrum of the vector components of angular momentum operators, or *space quantization*, leads to a statistical distibution for the magnetization different from that obtained by Langevin. The consequence is the substitution of Langevin's function $L(a)$ by Brillouin's function $B_J(a)$ (section 1.3).

- the paramagnetic substances we are considering in this chapter are ionic crystals which contain some ions with non-zero permanent magnetic moment in the ground-state. In the solid, they have of course an electronic spectrum different from that of the free ion. The main effect of the crystalline environment that will concern us here is known as *quenching* of the orbital angular momentum under certain circumstances. This effect is observed for instance in magnetization measurements. We define the effective magneton number p as the modulus of the ionic magnetic moment in units of Bohr magnetons:

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

where J = total angular momentum of ion in units of $\hbar$ and g = gyromagnetic ratio (see section 1.3). One verifies that

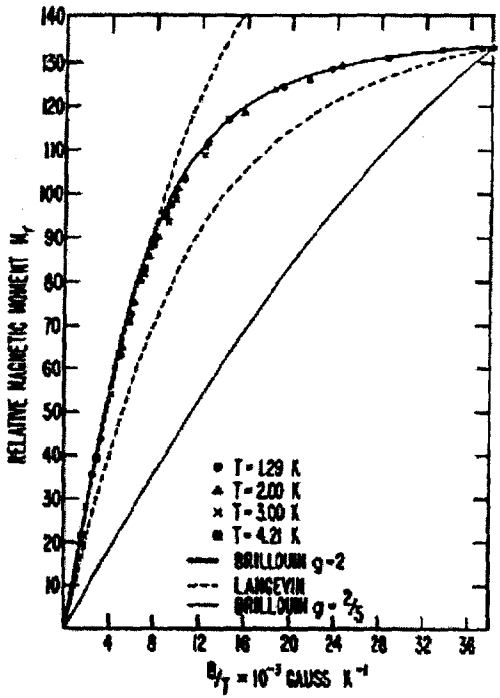

Figure 1.1: *Plot of $\overline{\mu}/\mu_0$, in arbitrary units, vs. B/T for potassium chromium alum. The heavy solid line is a Brillouin curve for $g = 2$ (complete quenching of L) and $J = S = 3/2$, fitted to experimental data at the highest value of B/T. The thin solid line is a Brillouin curve for $g = 2/5$, $J = 3/2$ and $L = 3$ (no quenching). The broken lines are Langevin curves fitted at the highest value of B/T (lower curve) and at the origin (slope fitting) (upper curve). From ref.* [5].

agreement with experiments in the estimate of p for the Cr^{3+} ion is only achieved if the ground state expectation value of $\mathbf{L}$ is assumed to vanish in the crystal, although for the free ion $L = 3$. This *quenching* of $\mathbf{L}$ is the result of the local symmetry of the electrostatic potential at the Cr^{3+} ion site in the

solid. This potential generates the so called *crystal-field*, which, having a symmetry lower than spherical, in general mixes degenerate atomic orbitals with different M_L values, and lifts the degeneracy of the orbital manifold of states. The new orbital ground state will be the lowest energy one among those arising from the original ground state multiplet under the effect of the crystal-field potential. When the symmetry of the crystal-field admits a singlet orbital ground state one can prove that time reversal invariance leads to $< \vec{L} >= 0$. This theorem is proven in Section 1.5 and appendix B. We shall see that a non-degenerate ground state requires an even number of electrons in the outer shell of the ion.

In the experiments we refer to in this chapter the Zeeman term in the Hamiltonian lifts the $2J + 1$ degeneracy of the ground state of the ions. For low fields the level separation is proportional to $g\mu_B B$ which is typically of the order of $1K$, much smaller than the level separation with the excited states, so that to a good approximation we can neglect all excited states and consider, as in Sect. 1.3, a problem very similar to Langevin paramagnetism.

Before we discuss the quantum theory of paramagnetism, we shall make a brief review of the quantum mechanics of atoms.

1.2 Quantum mechanics of atoms

1.2.1 L-S (Russel-Saunders) coupling

Let us write the Hamiltonian for an atom with Z valence electrons (that is, Z electrons in shells exterior to a filled atomic core of total charge $+Z$) as:

$$H = H_0 + V_1 + V_2 \tag{1.7}$$

where

$$H_0 = \sum_{i=1}^{Z} p_i^2/2m + V_c(r_i) \tag{1.8}$$

and $V_c(r)$ is a central effective potential, which is usually calculated in the *Hartree-Fock* approximation. The next two terms in Eq. 1.7

the corrections to this approximate one-electron potential [3]. The second one contains all the Coulomb interaction corrections to the effective self-consistent potential $V_c(r_i)$:

$$V_1 = \sum_{i<j}^{Z} \frac{e^2}{|\mathbf{r_i} - \mathbf{r_j}|} - \sum_{i=1}^{Z} \frac{Ze^2}{r_i} - V_c(r_i) \tag{1.9}$$

Finally, V_2 contains the magnetic interactions resulting from relativistic effects, of which the dominant ones are the spin-orbit coupling terms.

The relative quantitative importance of V_1 and V_2 varies along the periodic table. V_1 reflects the fluctuations of the exact electrostatic potential relative to the *Hartree-Fock* potential. The average fluctuations should be negligible if the effective one-electron potential had been well chosen. Their root mean square value is roughly proportional to $\sqrt{Z}$ for large Z [3].

The contribution of the spin-orbit coupling can be estimated through a simple calculation based on the *Thomas-Fermi* approximation for the many-electron atom. This yields [3] $V_2 \propto Z^2$.

As an immediate consequence, one expects that the spin-orbit contributions to the energy become comparable to -or even greater than- the Coulomb corrections given by Eq. 1.9, only for the heavier atoms. In the case $V_1 \gg V_2$, which applies in the transition elements,

$$H \approx H_0 + V_1 \tag{1.10}$$

which, being spin independent, commutes with $\mathbf{S}$ and with S_z. Besides, rigid coordinate rotations around the nucleus leave the Hamiltonian (1.10) invariant, so it commutes with the total angular momentum $\mathbf{L}$ and with L_z. One can take advantage of the fact that $\mathbf{L}$ and $\mathbf{S}$ are independently conserved by separately adding $\mathbf{L} = \sum_i^Z \mathbf{l_i}$ and $\mathbf{S} = \sum_i^Z \mathbf{s}_i$, and afterwards combining both to obtain the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, which commutes with the total Hamiltonian. This is the *L-S* or *Russel-Saunders* coupling. The Hamiltonian

$$H^{LS} = H_0 + V_1 \tag{1.11}$$

can then be diagonalized in the many-electron basis of states

$$\{\, |\, L\, S\, M_L\, M_S > \,\}$$