ELECTRON PARAMAGNETIC RESONANCE

A Practitioner's Toolkit

Edited by

Marina Brustolon
University of Padova

Elio Giamello
University of Torino

WILEY

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On Exactitude in Science

. . . In that Empire, the Art of Cartography attained such Perfection that the map of a single Province occupied the entirety of a City, and the map of the Empire, the entirety of a Province. In time, those Unconscionable Maps no longer satisfied, and the Cartographers Guilds struck a Map of the Empire whose size was that of the Empire, and which coincided point for point with it. The following Generations, who were not so fond of the Study of Cartography as their Forebears had been, saw that vast Map was Useless, and not without some Pitilessness was it, that they delivered it up to the Inclemencies of Sun and Winters. In the Deserts of the West, still today, there are Tattered Ruins of that Map, inhabited by Animals and Beggars; in all the Land there is no other Relic of the Disciplines of Geography.

Suarez Miranda, Viajes de varones prudentes, Libro IV, Cap. XLV, Lerida, 1658
From Jorge Luis Borges, *Collected Fictions*, Translated by Andrew Hurley

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Einar Sagstuen and Eli Olaug Hole

FOREWORD

It is more than 50 years since I ran my first electron paramagnetic resonance (EPR) spectrum. At that time the newly emergent field was developing rapidly, but it was still small so that in many ways life was simpler than it is today. For example, it was quite easy to keep up with the literature, and seminal papers on the understanding of hyperfine coupling constants in free radicals were not totally impenetrable even for a naive graduate student. Again, there was no sophisticated choice to be made about the type of experimental technique to use: it was continuous wave EPR or nothing. Of course, there were things that some today might regard as the downside: for example, if you wanted to make EPR measurements, you had to use a homemade spectrometer that contained thermionic valves (tubes). Its functioning tended to be idiosyncratic, and its operation was an art in itself. Further, all of the calculations that I performed, diagonalization of matrices, for instance, were done manually on electromechanical machines. Life in EPR could be tedious and frustrating, but it was exciting and it was fun and I reckon it still is.

Nowadays the field is amazingly more complex, not to say labyrinthine. There are numerous different types of experiments one can do in seeking answers to questions about fields ranging from solid-state physics to medicine. The Editors of this book perceived the need for a volume that would cover the whole of modern EPR and that would be useful both to newcomers to the field and to established practitioners who wished to broaden their perspectives. However, they recognized that it would not be feasible for them to write a comprehensive treatment themselves and were thus led to a multiple-author book. This was a brave decision: it is all very well for two people to share a concept, but to persuade authors to grasp that concept and shape their contributions to it so that the assembled volume would have coherence must have been like trying to herd cats. Thus, in my view, this book is a triumph of indefatigability.

When you are going to visit somewhere to which you have never been previously, or at best with which you are unfamiliar, it is always a good idea to study a map of the area you plan to visit and to carry a guidebook. I hope very much that this book will come to be seen both as a definitive map and as an indispensable *vade mecum* for the EPR community.

NEIL ATHERTON

PREFACE

The family of electron paramagnetic resonance (EPR) methods has expanded in the last 20 years, with new methods ushered in by instrumental and conceptual achievements. The basic qualities of the progenitor X-band continuous wave EPR, namely, its selectivity, sensitivity, and resolution, have been enhanced with the new generations of spectroscopies, which take advantage of multifrequency approaches, time resolution, pulsed techniques, and multiple irradiations. These developments have extended the range of applications and amplified the heuristic power of EPR spectroscopies, which are now increasingly employed in research in different fields, such as biology, medicine, material science, chemistry, physics, and earth sciences.

As soon as we began working on the book, we realized that our plan was somehow too ambitious. We were thinking of a book as a tool for the newcomers in the field; at the same time, we wished to address the developments of the experimental and theoretical EPR methods in recent years while also describing their most important applications in distinct fields. Assembling a book like this may be too great a task for anybody. However, we were also aware that the complexity was unavoidable for a book seeking to give an idea of what EPR means for science today.

A few EPR textbooks, some of which have been re-edited, have been used by generations of students. We have leaned heavily on those by Atherton and by Wertz and Bolton (and Weil), and one of our objectives here has been to update these. In thinking about how to give a comprehensive account of EPR today, we realized that it is like the Empire in the celebrated novel by Jorge Luis Borges, and that we ought not to act like the unwise Cartographers, set to draw “a Map of the Empire whose size was that of the Empire, and which coincided point for point with it.” A real map was indeed necessary, with the right scale for each region, like an aerial photo taken by a plane flying at different altitudes. Moreover, to map such a wide territory we needed to enlist many more cartographers than the authors of the previous books. We looked therefore for 18 fine explorers of the various regions, including ourselves, and we have done our best to collect and assemble the diverse contributions. We have endeavored to connect the contents of the different chapters as much as possible to provide a compass to the reader.

We hope that this book will help to gauge the extent of the magnificent territory of EPR while also providing some indications as to where the path is easy and where it is difficult and how to find the way to one’s destination.

Then, the readers will be just at the beginning of their tasks: exploring the real territory.

We want to thank our sixteen colleagues and friends, co-authors of this book, for participating to a living debate during its preparation, and to some intense discussions during the main EPR conferences of the past few years (Madrid 2006, Oxford 2007).

Without their knowledge, efforts and patience this book would have never be published.

We are also grateful to the support and precious advice of those colleagues of the international EPR community who have followed the progress of this book with keen interest.

Many thanks are also due to Dr. Marco Ruzzi (Università di Padova) for his kind assistance in various steps of the book editing.

MARINA BRUSTOLON, ELIO GIAMELLO

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PART I

Principles

1 Introduction to Electron Paramagnetic Resonance

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Electron paramagnetic resonance (EPR), which is also called electron spin resonance (ESR), is a technique based on the absorption of electromagnetic radiation, which is usually in the microwave frequency region, by a paramagnetic sample placed in a magnetic field. EPR and ESR are synonymous, but the acronym EPR is used in this book. The absorption takes place only for definite frequencies and magnetic field combinations, depending on the sample characteristics, which means that the absorption is resonant.

The first EPR experiment was performed more than 60 years ago in Kazan (Tatarstan), which is now in the Russian Federation, by E. K. Zavoisky, a physicist who used samples of $CuCl_2 \cdot 2H_2O$, a radiofrequency (RF) source operating at 133 MHz, and a variable magnetic field operating in the range of a few millitesla and provided by a solenoid. More than five decades from the first experiment the technique has progressed tremendously and EPR has a broad range of applications in the fields of physics, chemistry, biology, earth sciences, material sciences, and other branches of science. Modern EPR spectrometers are much more complex than those used for demonstrating the phenomenon; they have much higher sensitivity and resolution and can be used with a large number of samples (crystalline solids, liquid solutions, powders, etc.) in a broad range of temperatures.

1.1 CHAPTER SUMMARY

The aim of this chapter is to provide the reader with the basic information about the phenomenon of electron magnetic resonance and the ways to observe it and to record an EPR spectrum. EPR spectra of very simple molecular systems will be

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Electron Paramagnetic Resonance. Edited by Brustolon and Giamello

described together with the properties that influence the shape of the spectra and the intensity of the spectral lines. Moreover, it will be anticipated how the parameters characterizing the spectrum are related to molecular structure and dynamics. The approach will be as simple and *intuitive* as possible within the constraints of a rigorous treatment. Details on instrumentation, types of paramagnetic species studied, specific characteristics of EPR in solids and in solution, and theory are the subjects of the ensuing chapters. The second part of the book will consider applications to the investigation of complex chemical and biological systems and the improvements of the technique suitable for them.

An illustration of the spin properties of a single electron and its behavior in a magnetic field will be presented first, followed by a short discussion about the behavior of an electron spin when it is confined in a molecule, as well as when it interacts with one or several nuclear spins.

The macroscopic observation of EPR requires a collection of many electron spins the properties for which will be treated in a semiclassical way, leaving to more advanced EPR descriptions the quantum mechanical *density matrix* method. (You can find, e.g., a short account of the density matrix method applied to ensembles of spins in appendix A9 in the Atherton book in the Further Reading Section.) However, a quantum mechanical description is necessary to a deeper understanding of complex experiments, in particular pulse EPR experiments. A short introduction to quantum mechanics formalism will be presented at the end of this chapter. The concepts of spin–lattice (longitudinal) and spin–spin (transverse) relaxation processes will be introduced, and how the rate of these processes influences the spectra will be anticipated. Chapter 5 describes how the relaxation rates can be measured by pulsed EPR methods.

The presence of a second electron spin in the investigated paramagnetic system will be considered briefly. A second electron spin introduces the electron dipolar interaction, which constitutes a new important term in the energy. Chapters 3 and 6 contain more information on paramagnetic species with two or more unpaired electrons.

Analogies and differences with respect to the related phenomena of nuclear magnetic resonance (NMR), involving nuclear spins, will be provided when appropriate.

1.2 EPR SPECTRUM: WHAT IS IT?

The EPR spectrum is a diagram in which the absorption of microwave frequency radiation is plotted against the magnetic field intensity. The reason why the magnetic field is the variable, instead of the radiation frequency as it occurs in other spectroscopic techniques (e.g., in recording optical spectra), will be explained in Chapter 2. There are two methods to record EPR spectra: in the first traditional method, which is called the continuous wave (CW) method, low intensity microwave radiation continuously irradiates the sample. In the second method, short pulses of high power microwave radiation are sent to the sample and the response is recorded in the absence of radiation (pulsed EPR). This chapter is mainly focused on the CW method, and pulsed EPR is treated in Chapter 5. In CW spectra, for technical reasons explained in Chapter 2 (§2.1.4), the derivative of the absorption curve is plotted instead of the absorption itself. Therefore, an EPR spectrum is the derivative of the absorption curve with respect to the magnetic field intensity.

Microwave absorption occurs by varying the magnetic field in a limited range around a central value B_0, and the EPR spectrum in most cases consists of many absorption lines. The following main parameters and features characterize the spectrum: the positions of the absorptions, which are the magnetic field values at which the absorptions take place; the number, separation, and relative intensity of the lines; and their widths and shapes. All of these parameters and features are related to the structure of the species responsible for the spectrum, to their interactions with the environment, and to the dynamic processes in which the species are involved. This chapter will address these issues.

1.3 THE ELECTRON SPIN

Elementary particles such as an electron are characterized by an intrinsic mechanical angular momentum called spin; that is, they behave like spinning tops. Angular momentum is a vector property that is defined by the magnitude or modulus (the length of the vector used to represent the angular momentum) and by the direction in space. However, because an electron is a quantum particle, the behavior of its spin is controlled by the rules of quantum mechanics. For a first approach to the magnetic resonance phenomenon, it is sufficient to know that the electron spin can be in two states, usually indicated by the first letters of the Greek alphabet α and β. These states differ in the orientation of the angular momentum in space but not in the magnitude of the angular momentum, which is the same in the α and β states.[1] The spin vector is indicated by $\boldsymbol{S}$ and the components along the x, y, z axes of a Cartesian frame by S_x, S_y, S_z, respectively. The angular momenta of quantum particles are of the order of $\hbar$ (Planck constant h divided by 2π). Magnetic moments are usually represented in $\hbar$ units, and in these units the magnitude or modulus of $\boldsymbol{S}$ is

$$|\boldsymbol{S}| = \sqrt{S(S+1)} \tag{1.1}$$

where $S = 1/2$ is the electron spin quantum number; therefore, $|\boldsymbol{S}| = \sqrt{3/4}$. The usual convention is to consider the α and β electron spin states as those having definite components S_z along the z axis of the Cartesian frame. For an electron spin, quantum mechanics requires that S_z be in $\hbar$ units of either $1/2$ (α state) or $-1/2$ (β state). The components along the axes perpendicular to z are not defined in the sense that they cannot be determined (another requirement of quantum mechanics), and in the α and β states they could assume any value in the range of $-1/2$ to $1/2$. In the absence

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[1] We are dealing here with a free electron, which is an electron whose motion is not constrained by Coulomb interactions with nuclei or with other electrons. In real systems studied by EPR the electrons belong to atoms, molecules, polymers, defects in crystalline solids or metal ion complexes, and so forth. However, in most cases their properties are not strongly influenced by the environment and their magnetic properties can be viewed as if they were free spins, at least in a first approximation.

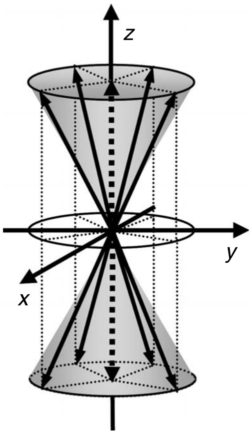

Fig. 1.1 The electron spin angular momentum is a vector represented in the figure as a solid arrow, whose length is $|\boldsymbol{S}| = \sqrt{3/4}\ \hbar$. According to quantum mechanics, when a Cartesian frame x, y, z is chosen, only a component of the spin vector (usually assumed as the z component) has a definite value S_z of either $1/2\ \hbar$ or $-1/2\ \hbar$. The z component is shown in the figure as a dotted arrow pointing in the positive (α spins) or negative z direction (β spins). The components in the plane perpendicular to z are not defined: the α and β spins could point in any direction on the surface of a cone.

of any particular preferential direction in the space, connected with possible interactions of the electron spin with its environment, any choice for the direction in space of the z axis is allowed. As long as this space isotropy condition holds, the α and β electron spin states have the same energy (Fig. 1.1) and they are said to be *degenerate*. This is not the case if the electron spin is placed in a magnetic field.

1.4 ELECTRON SPIN IN A MAGNETIC FIELD (ZEEMAN EFFECT)

In EPR a crucial point to be considered is that a magnetic moment $\boldsymbol{\mu}_e$ is always associated with the electron spin angular momentum, where $\boldsymbol{\mu}_e$ is proportional to $\boldsymbol{S}$, meaning that $\boldsymbol{\mu}_e$ and $\boldsymbol{S}$ are vectors parallel to each other. They have opposite directions because the proportionality constant is negative. The latter is written as the product of two factors g and μ_B:

$$\boldsymbol{\mu}_e = g\,\mu_B\,\boldsymbol{S} \tag{1.2}$$

where g is a number called the Landé factor or simply the g factor. For a free electron $g = 2.002319$ and $\mu_B = -|e|h/4\pi m_e = -9.27410^{-24}\,\mathrm{J\,T^{-1}}$, where m_e is the electron mass; e is the electron charge; $h = 6.626 \times 10^{-34}$ Js is the Planck constant; and μ_B is the atomic unit of the magnetic moment, which is called the *Bohr magneton*. Because $\mu_B < 0$, to avoid confusion about the sign, the absolute value of μ_B will be used in several equations. The existence of a magnetic moment associated with the electron spin is the reason for having an energy separation between the α and β electron spin states when the electron is in the presence of a magnetic field. Suppose we apply a constant magnetic field $\boldsymbol{B}$ to an electron spin. Because the energy of a magnetic moment $\boldsymbol{\mu}_e$ is given by the scalar product between $\boldsymbol{\mu}_e$ and $\boldsymbol{B}$, the electron spin energy will depend on the orientation of $\boldsymbol{\mu}_e$ with respect to $\boldsymbol{B}$:

$$E = -\boldsymbol{\mu}_e \cdot \boldsymbol{B} = g|\mu_B|\boldsymbol{S} \cdot \boldsymbol{B} \tag{1.3}$$

The dot product reduces to a single term if the direction of $\boldsymbol{B}$ coincides with one of the axes respect to which the $\boldsymbol{B}$ and $\boldsymbol{S}$ are represented. The choice of the reference frame is arbitrary, and it can be chosen in such a way that the z axis is along the direction of $\boldsymbol{B}$. In this case the equation for the energy becomes

$$E = g|\mu_B|B_0 S_z \tag{1.4}$$

where B_0 is the magnetic field intensity.

If one takes into account that the electron spin can be in two states, either α or β, in which the z component of the spin is $1/2$ and $-1/2$, respectively, in the presence of a magnetic field the electron spin energy could assume only the two values,

$$E_\pm = \pm(1/2)g|\mu_B|B_0 \tag{1.5}$$

where the positive sign refers to the α state and the negative one to the β state.

The splitting of the electron spin energy level into two levels in the presence of a magnetic field is called the *Zeeman effect*, and the interaction of an electron magnetic moment with an external applied magnetic field is called the electron *Zeeman interaction*. The Zeeman effect is represented graphically in Fig. 1.2.

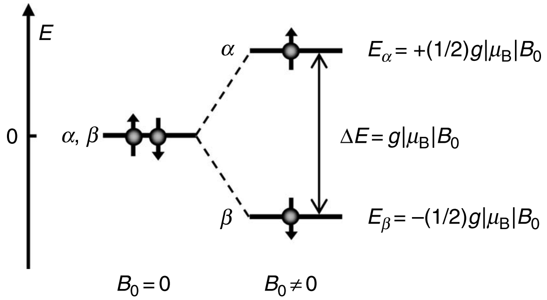

Fig. 1.2 The electron spin Zeeman effect. At zero field ($B_0 = 0$) the spin states α and β represented by up and down arrows have the same energy, which is zero in the energy scale. In the presence of a static magnetic field ($B_0 \neq 0$) the β spin state is shifted at low energy and the α one at high energy. The energy separation is proportional to the magnetic field intensity. It also linearly depends on the electron g factor.

1.5 EFFECT OF ELECTROMAGNETIC FIELDS

An electron spin in the β state, which is the low energy state, can absorb a quantum of electromagnetic radiation energy, provided that the energy quantum $h\nu$ coincides with the energy difference between the α and β states:

$$h\nu = E_\alpha - E_\beta = g|\mu_\mathrm{B}|B_0 \tag{1.6}$$

where ν is the radiation frequency. Equation 1.6 is the fundamental equation of EPR spectroscopy.

In a 3.5-T magnetic field, which is the standard magnetic field intensity used in many EPR spectrometers, for $g = 2.0023$, Equation 1.6 gives $\nu = 9.5$ GHz. This radiation frequency is in the microwave X-band region (8–12 GHz). The EPR spectrometers operating in this frequency range are called X-band spectrometers.

Other regions of higher microwave frequencies used in commercial EPR spectrometers are Q-band ($\sim$34 GHz) and W-band (95 GHz). Spectrometers operating at frequencies higher than 70 GHz are considered as high field/high frequency spectrometers. See Chapter 2 (§2.2.5) for a general introduction to multifrequency EPR. Applications of high field/high frequency EPR are described in Chapters 6 and 12.

For the spin system to absorb the radiation energy, the oscillating magnetic field $\boldsymbol{B}_1$ associated with the electromagnetic radiation should be in the plane xy, which is *perpendicular* to the static Zeeman field $\boldsymbol{B}_0$. In other words, the radiation should be polarized perpendicular to $\boldsymbol{B}_0$.

An electron spin in the α state cannot absorb energy because there are no allowed states at higher energy. However, the presence of an oscillating magnetic field of proper frequency corresponding to Equation 1.6 induces a transition from the α state to the β state with loss of energy and emission of a radiation quantum $h\nu$. This process is called *stimulated emission*, and it is just the opposite of the absorption. The spontaneous decay of an isolated spin to the lower energy state in the absence of radiation, with emission of microwave radiation (*spontaneous emission*), is a process occurring with negligible probability.

In conclusion, an *isolated* electron spin placed in a static magnetic field $\boldsymbol{B}_0$ and in the presence of a microwave oscillating magnetic field $\boldsymbol{B}_1$ perpendicular to $\boldsymbol{B}_0$ undergoes transitions from the low energy level state β to the upper one α, and vice versa. The net effect is zero because absorption and stimulated emission compensate each other. The next section will show that electron spins are never completely isolated, and the behavior of a collection of many electron spins is different.

1.6 MACROSCOPIC COLLECTION OF ELECTRON SPINS

In the usual experimental setup one considers samples of many electron spins, their number being on the order of 10^{10} or higher. Moreover, these electron spins are not independent, interacting with each other and with their environment. Furthermore, electron spins are not free; they are confined in atomic or molecular systems. The latter aspects will be considered later.

The electron spins of an ensemble are statistically distributed in the α and β states. Because these states are equivalent in the absence of a magnetic field, for $B_0 = 0$ half of the spins are α spins and half are β spins. In these conditions the z component of the total angular momentum is zero, as are also the components along any other direction. In fact, all directions in space are equivalent. The situation changes in the presence of a magnetic field B_0 *if the spin ensemble is allowed to interact with its environment* (*the* "*lattice*"). As learned in the previous section, if $B_0 \neq 0$, the α and β states do not have the same energy. In thermal equilibrium with the lattice the spins distribute between α and β states in such a way as to be in a small excess in the lower energy level (β state). The ratio between the number (N) of α spins and the number of β spins depends on the temperature. It is given by the Boltzmann distribution law:

$$N_\alpha/N_\beta = \exp\left(-g|\mu_{\mathrm{B}}|B_0/k_{\mathrm{B}}T\right) \tag{1.7}$$

where k_{B} is the Boltzmann constant, which is equal to 1.3806×10^{-23} J K^{-1}; and T is the absolute temperature of the lattice.

At room temperature (300K) and for magnetic fields on the order of 0.3 T (X-band spectrometer), $g|\mu_{\mathrm{B}}|B_0 \ll k_{\mathrm{B}}T$ and the exponential can be expanded in series, retaining only the linear term. The approximate population ratio becomes

$$N_\alpha/N_\beta = 1 - g|\mu_{\mathrm{B}}|B_0/k_{\mathrm{B}}T \tag{1.8}$$

This approximation is quite good, unless the spin system is at very high field or at very low temperature. According to Equation 1.8, at room temperature in the magnetic field of an X-band spectrometer there is an excess of β spins over the α spins of $1/1000$. This small excess is enough for the microwave absorption to overcome the emission and to make possible the observation of an EPR absorption signal. In fact, a microwave field induces transitions from β to α, and the reverse one from α to β, in a number proportional to the number of spins in the initial state.

A further point should be considered regarding the interaction of the spin system with the lattice. If the spin system were not coupled with the lattice or weakly coupled to it, the microwave field acting continuously on the spin system (CW-EPR) would eventually equalize the level populations and after a short time the absorption EPR signal would disappear. Conversely, spin lattice interaction restores the thermal equilibrium, which is the excess spins in the low energy level, allowing the continued observation of the EPR absorption signal. Of course, because there is competition between the spin lattice interaction and microwave field, if the latter is strong enough with respect to the spin lattice interaction, the EPR signal *saturates*. The rate of the spin lattice process is usually reported as the inverse of a characteristic time T_1, which is called the *spin lattice relaxation time*. This is the time taken by a spin system forced out of equilibrium by an amount δ to reduce the deviation by a factor $1/e$.

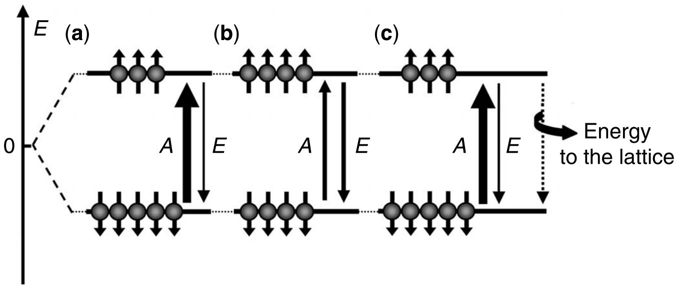

Fig. 1.3 The electron spin ensemble in a magnetic field. The populations of spin levels N_α and N_β are schematically indicated. (a) The A and E arrows indicate stimulated absorption and emission in the presence of resonant microwave radiation. The absorption is more efficient than the emission because of the difference in populations, corresponding to thermal equilibrium with the lattice. (b) The phenomenon of saturation with the two levels equally populated occurs when the energy transfer to the lattice is not efficient. No EPR signal is detectable in this case. (c) The energy transfer from the spin system to the lattice (spin lattice relaxation) indicated by the dotted arrow reestablishes a population difference.

Time T_1 is a measure of how strongly the spin system is coupled to the lattice. The experiments designed to determine T_1 are described in Chapter 5 (§5.3.2.2). The behavior of a spin ensemble in a magnetic field is shown schematically in Fig. 1.3.

1.7 OBSERVATION OF MAGNETIC RESONANCE

Equation 1.6 suggests two possible ways for performing an EPR experiment, which are illustrated in Fig. 1.4. The first one (Fig. 1.4a) consists of placing a spin ensemble in a constant magnetic field B_0 and irradiating it with microwave radiation of linearly variable frequency and constant intensity. When the frequency matches the resonance conditions for the magnetic field intensity B_0, microwaves are absorbed and the absorption is revealed by a microwave detector.

The alternative way (Fig. 1.4b) consists of irradiating the sample with microwave radiation of constant frequency ν_0 in a magnetic field of linearly variable intensity. In this second case EPR absorption is observed when the field intensity reaches the resonance conditions dictated by Equation 1.6 for the chosen frequency value ν_0.

For technical reasons discussed in Chapter 2, the preferred experimental procedure is the second one. However, in order to discuss the pattern of the EPR spectra, it will be more convenient to present energy level schemes for constant magnetic field conditions.

The resonance absorption line has a width, which means that the absorption of microwave radiation occurs in a range of magnetic field values, with a probability decreasing as the deviation from the value given by Equation 1.6 increases. The width is determined by dynamical processes and interactions described in a following section.