PART I
Principles
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 CuCl₂·2H₂O, 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
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 \( \alpha \) and \( \beta \). 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 \( \alpha \) and \( \beta \) states.\(^1\) The spin vector is indicated by \( S \) 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 \( \hbar \) divided by \( 2\pi \)). Magnetic moments are usually represented in \( \hbar \) units, and in these units the magnitude or modulus of \( S \) is

\[
|S| = \sqrt{S(S + 1)}
\]

where \( S = 1/2 \) is the electron spin quantum number; therefore, \( |S| = \sqrt{3}/4 \). The usual convention is to consider the \( \alpha \) and \( \beta \) 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 (\( \alpha \) state) or \(-1/2 \) (\( \beta \) 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 \( \alpha \) and \( \beta \) states they could assume any value in the range of \(-1/2 \) to \( 1/2 \). In the absence

\(^1\)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.
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 $a$ and $b$ 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 $\mu_e$ is always associated with the electron spin angular momentum, where $\mu_e$ is proportional to $S$, meaning that $\mu_e$ and $S$ 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 $\mu_B$:

$$\mu_e = g \mu_B S$$

(1.2)

where $g$ is a number called the Landé factor or simply the $g$ factor. For a free electron $g = 2.002319$ and $\mu_B = -|e|\hbar/4\pi m_e = -9.27410^{-24}$ JT$^{-1}$, where $m_e$ is the electron mass; $e$ is the electron charge; $\hbar = 6.626 \times 10^{-34}$ Js is the Planck constant; and $\mu_B$ 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 $\mu_B$ 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 \( \alpha \) and \( \beta \) electron spin states when the electron is in the presence of a magnetic field. Suppose we apply a constant magnetic field \( B \) to an electron spin. Because the energy of a magnetic moment \( \mu_e \) is given by the scalar product between \( \mu_e \) and \( B \), the electron spin energy will depend on the orientation of \( \mu_e \) with respect to \( B \):

\[
E = -\mu_e \cdot B = g|\mu_B|S \cdot B
\]

The dot product reduces to a single term if the direction of \( B \) coincides with one of the axes with respect to which the \( B \) and \( S \) 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 \( B \). In this case the equation for the energy becomes

\[
E = g|\mu_B|B_0S_z
\]

where \( B_0 \) is the magnetic field intensity.

If one takes into account that the electron spin can be in two states, either \( \alpha \) or \( \beta \), 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,

\[
E_{\pm} = \pm (1/2)g|\mu_B|B_0
\]

where the positive sign refers to the \( \alpha \) state and the negative one to the \( \beta \) 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.

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**Fig. 1.2** The electron spin Zeeman effect. At zero field \( (B_0 = 0) \) the spin states \( \alpha \) and \( \beta \) 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 \( \beta \) spin state is shifted at low energy and the \( \alpha \) 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 $\beta$ state, which is the low energy state, can absorb a quantum of electromagnetic radiation energy, provided that the energy quantum $hv$ coincides with the energy difference between the $\alpha$ and $\beta$ states:

$$hv = E_\alpha - E_\beta = g|\mu_B|B_0$$  \hspace{1cm} (1.6)

where $v$ 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 $v = 9.5$ 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 $B_1$ associated with the electromagnetic radiation should be in the plane $xy$, which is perpendicular to the static Zeeman field $B_0$. In other words, the radiation should be polarized perpendicular to $B_0$.

An electron spin in the $\alpha$ 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 $\alpha$ state to the $\beta$ state with loss of energy and emission of a radiation quantum $hv$. 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 $B_0$ and in the presence of a microwave oscillating magnetic field $B_1$ perpendicular to $B_0$ undergoes transitions from the low energy level state $\beta$ to the upper one $\alpha$, 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 $\alpha$ and $\beta$ states. Because these states are equivalent in the absence of a magnetic field, for $B_0 = 0$ half of the spins are $\alpha$ spins and half are $\beta$ 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 $\alpha$ and $\beta$ states do not have the same energy. In thermal equilibrium with the lattice the spins distribute between $\alpha$ and $\beta$ states in such a way as to be in a small excess in the lower energy level ($\beta$ state). The ratio between the number ($N$) of $\alpha$ spins and the number of $\beta$ spins depends on the temperature. It is given by the Boltzmann distribution law:

$$N_\alpha/N_\beta = \exp \left( -g\mu_B B_0/k_B T \right)$$

(1.7)

where $k_B$ is the Boltzmann constant, which is equal to $1.3806 \times 10^{-23}$ 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), $g\mu_B B_0 \ll k_B T$ and the exponential can be expanded in series, retaining only the linear term. The approximate population ratio becomes

$$N_\alpha/N_\beta = 1 - g\mu_B B_0/k_B T$$

(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 $\beta$ spins over the $\alpha$ 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 $\beta$ to $\alpha$, and the reverse one from $\alpha$ to $\beta$, 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 $\delta$ to reduce the deviation by a factor $1/e$. 

1.6 MACROSCOPIC COLLECTION OF ELECTRON SPINS
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 $\nu_0$ 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 $\nu_0$.

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.
Let us consider the simple case of an atom with a closed shell and an extra electron. In such an atom the electron spins are all coupled in pairs, except one. The electron angular momentum has two contributions: one arises from the electron spin, and another one arises from the orbital motion of the electron around the nucleus. The magnetic moment is the sum of two terms, referring to the two contributions,

\[ \mu_e = \mu_B l + g \mu_B S \]

where \( l \) is the orbital angular momentum. The modulus of \( l \) is quantized and may assume only the values given by an equation analogous to Equation 1.1, which refer to the spin momentum:

\[ |l| = \sqrt{l(l + 1)} \]

where \( l \) is an integer, which depends on the electron spatial wavefunction. It can assume integer values or be zero, depending on the orbital occupied by the electron. Moreover, the component of \( l \) along \( z \) may assume only the \( 2l + 1 \) quantized values:

\[ l_z = -l, -l + 1, \ldots, l \]

Equation 1.9 would be correct only if the spin motion and the orbital motion were independent of each other. In reality, they are not, because spin and orbit angular momenta are coupled by the spin–orbit coupling.

Fig. 1.4  Two alternative ways to record an EPR spectrum. (a) In the first one the spin system is placed in a constant magnetic field \( B_0 \) and irradiated with microwave radiation whose frequency is linearly changed. The double arrows represent the radiation quantum energies \( h\nu \). Only when the frequency corresponds to the resonance condition given by Equation 1.6 the radiation is absorbed (solid double arrow). (b) In the second procedure, electron spins are irradiated with a microwave radiation of fixed frequency \( \nu_0 \), and the magnetic field is swept. When the latter reaches the resonance condition, microwave radiation is absorbed by the sample.
Contrary to the previous example of the electron in an atom with spherical symmetry, molecules are systems of low symmetry. For them the orbital angular momentum is quenched (its average is zero), and the electron angular momentum in the absence of spin–orbit coupling is only due to spin. The effect of spin–orbit coupling is to restore a small amount of orbit contribution, which results in a deviation $\Delta g = g - g_e$ of the $g$ factor from the free electron value entering in Equation 1.2. The consequence is the shift of the resonance field intensity from the value corresponding to the free electron spin, as given by Equation 1.6.

Because $\Delta g$ depends on the spin–orbit coupling, its value is large for metal complexes, where the electrons move in proximity to a heavy atom nucleus. For organic free radicals containing only light atoms, the spin–orbit interaction is small, and the deviation of $g$ from the free electron value is also small (≤1%). However, even such small deviations could give important structural information, as well as information about the radical environment. In any case, $g$ is a parameter that characterizes a molecular system, and its measurement is also important as an analytical tool.

Note that the spin–orbit interaction is anisotropic, because it is related to the orbital motion, which means that the amount of orbital character in the angular momentum is different for the different directions in a molecule fixed frame. Therefore, the value of $g$ to insert in Equation 1.6 will depend on the direction of the magnetic field with respect to the molecular axes. For example, for the popular nitroxy radical 2,2,6,6 tetramethyl pyrrolidine-$N$-oxyl, $g$ is 2.0090 if measured with the magnetic field directed along the N—O bond, 2.0027 if measured perpendicular to the plane formed by the N—O and N—C bonds, and 2.0060 in the direction perpendicular to the latter two (see Scheme 1.1).

The anisotropy of $g$ can be measured by recording the EPR spectra of a single crystal, where the molecules are in fixed orientations, by rotating the crystal in the spectrometer’s magnetic field. In liquids, because of rapid molecular tumbling, the $g$ factor anisotropy is averaged out and a mean $g$ value $g_{\text{iso}}$ is measured.

Scheme 1.1  The chemical structure of nitroxide radical 2,2,6,6 tetramethyl pyrrolidine-$N$-oxyl (TEMPO). Hydrogen atoms are not shown. The figures are the values of the $g$ factor one would measure if the magnetic field were placed along the directions shown in the figure. If the same free radical is rapidly tumbling in solution, the average value $g_{\text{iso}} = (2.0090 + 2.0060 + 2.0027)/3$ is obtained.
Conversely, the EPR spectrum of a powder sample (a collection of many microcrystals randomly oriented in space) is the superposition of the EPR lines of all of the microcrystals, each one corresponding to an individual orientation. The same is true for paramagnetic systems diluted in glassy matrices. However, the anisotropy of $g$ can be measured even for such samples (see Chapter 6). Examples of powder EPR spectra of a simple ideal sample characterized by $g$ anisotropy are shown in Fig. 1.5.

If the anisotropy is small, as in the case of organic free radicals, the effect on the EPR spectrum can be hidden in the resonance linewidth. In this case it is necessary to use high frequency/high field spectrometers to resolve the anisotropy, which is the spectrum spread proportional to the operating field frequency $\nu$. High field EPR also presents other advantages, as illustrated in Chapter 2. The situation is similar to that encountered in NMR spectroscopy, where high frequency spectrometers were developed to increase the resolution of chemical shifts.

Fig. 1.5 EPR spectra of a sample of randomly oriented paramagnetic molecules with $S = 1/2$ and characterized by axial $g$ anisotropy. In this example the values along three orthogonal axes fixed in the molecule are assumed to be $g_x = g_y = 2.0023, g_z = 2.0060$. (a, c) EPR absorption; (b, d) first derivative of the absorption with respect to the magnetic field. (a, b) spectra refer to a microwave frequency $\nu = 9.5 \text{ GHz}$ (X-band); (c, d) spectra obtained with the same $g$ parameters refer to a 10 times higher microwave frequency $\nu = 95 \text{ GHz}$ (W-band). Note the different magnetic field scale and the higher resolution of the W-band spectra.
1.9 MACROSCOPIC MAGNETIZATION

In a real macroscopic system consisting of many electron spins that interact with the lattice and with each other, the spin properties are described by defining the total magnetization $M$ as a vector resulting from the sum of the magnetic moments of the individual electron spins:

$$M = \sum \mu_i$$

(1.12)

If such a system is in a magnetic field $B_0$ and it is in thermal equilibrium with the lattice, the resulting magnetization $M$ is directed along the $z$ axis, because of the excess of $\beta$ spins with respect to $\alpha$ spins, as given by Equation 1.8. The components perpendicular to $z$ are zero because the individual spins, while keeping a definite $z$ component $S_{zi}$ at either $1/2$ or $-1/2$, have random components along axes perpendicular to $z$ (see Fig. 1.1)

$$M_z = \sum \mu_{zi} = M_0$$
$$M_x = \sum \mu_{xi} = 0$$
$$M_y = \sum \mu_{yi} = 0$$

(1.13)

$M_0$ is the thermal equilibrium magnetization and $\mu_{xi}$, $\mu_{yi}$, and $\mu_{zi}$ are the respective components of the magnetic moments of the individual spins. The sum is over all of the spins in the sample.

Suppose that the system is forced out of equilibrium. The time evolution of magnetization $M$ is obtained by solving the equation of the motion of $M$. Before examining the proper equation, three points should be considered.

1. There are two ways to modify the equilibrium conditions. The first one consists of changing the $z$ component and leaving the other two components equal to zero. This happens if the relative populations of the $\alpha$ and $\beta$ spins are changed. The second one consists of tilting the magnetization with respect to $z$ and generating a nonvanishing magnetization component in the plane perpendicular to $z$.

2. Even if the individual spins behave according to quantum mechanics, the motion of the macroscopic magnetization is accounted for by classical mechanics.

3. Magnetization $M$ is associated with an angular momentum. In fact, $M$ arises from the angular momenta associated with the spins of the individual electrons. The macroscopic angular momentum is $J = \sum S_i$. The relation between $M$ and $J$ is analogous to Equation 1.2: $M = g\mu_B J$. 

14 INTRODUCTION TO ELECTRON PARAMAGNETIC RESONANCE
The time evolution of $\mathbf{M}$ in a magnetic field $\mathbf{B}$ is given by the vector product

$$\frac{d\mathbf{M}}{dt} = \mathbf{M} \times g\mu_\text{B} \mathbf{B}$$

(1.14)

This equation holds for any $\mathbf{B}$ field, static or time dependent.

Equation 1.14 indicates that the variation of the magnetization vector $\mathbf{M}$ is perpendicular to both $\mathbf{M}$ and $\mathbf{B}$. For a constant magnetic field $\mathbf{B}$, assumed to be along the $z$ axis of a reference frame $x, y, z$, the $z$ component of $\mathbf{M}$ is constant, because $d\mathbf{M}/dt$ is in the $x, y$ plane. The motion, consisting of a rotation of $\mathbf{M}$ around the $z$ axis (Fig. 1.6a) is called Larmor precession. The angular frequency is $\omega_L = g\mu_\text{B}B/\hbar$. It is called the Larmor frequency. When the magnetic field is not constant but changes with time, the motion of magnetization $\mathbf{M}$ is more complicated.

In magnetic resonance experiments (see Fig. 1.6b and c) the spin system is in the presence of both a large static magnetic field $\mathbf{B}_0$ along $z$ and a variable field oscillating at a microwave frequency in the plane perpendicular to $z$, for example, along the direction $x$: $B_{1x}(t) = B_1 \cos(\omega t)$. Note that an oscillating magnetic field can be decomposed in two mutually perpendicular components rotating at the same frequency, one clockwise and the other counterclockwise. Typical values used in EPR experiments are $B_0 = 0.3 \text{ T}$ and $B_1 = 1 \mu\text{T}$. For these conditions, a useful method to simplify the description of the motion of the magnetization is to use a rotating reference frame of axes, with $x', y'$ rotating around $z$ at angular frequency $\omega_L$, $z' = z$, and $x'$ is taken along $B_1$.

To understand the utility of this model of a rotating reference frame, let us discuss some cases. If $B_1$ is zero, in a reference system rotating around $z$ at the

![Fig. 1.6](image_url)
Larmor frequency and in the same direction as vector $\mathbf{M}$, the latter one is stationary. If $B_1 \neq 0$ and it is also rotating around $z$ at the Larmor frequency, in the rotating frame $B_1$ is seen as constant by $\mathbf{M}$ and the motion of $\mathbf{M}$ becomes a rotation (precession) around $B_1$, with an angular frequency $\omega_1 = g \mu_B B_1 / \hbar$. Note that three frequencies are considered here: the Larmor frequency $\omega_L$, the rotation frequency of the microwave field $B_1$, $\omega$ (in this simple case assumed to coincide with the Larmor frequency $\omega = \omega_L$), and the precession frequency $\omega_1$ of $\mathbf{M}$ around $B_1$ in the rotating frame. Moreover, note that $\omega_1 \ll \omega_L$.

In the general case, when $\omega \neq \omega_L$, magnetization vector $\mathbf{M}$ moves in a complex way by rotating around $z$ and around the direction of $B_1$. The equation describing the motion of the magnetization vector in the frame rotating around $z$ at angular frequency $\omega$ is the following:

$$ (d\mathbf{M}/dt)_R = \mathbf{M} \times g \mu_B \mathbf{B}_{\text{eff}} $$

where

$$ \mathbf{B}_{\text{eff}} = (B_0 - \hbar \omega / g \mu_B)k + B_1 i $$

and $k$ and $i$ are unit vectors directed along the $z$ and $x'$ axes, respectively.

Note that if frequency $\omega$ equals the Larmor frequency, $\mathbf{B}_{\text{eff}}$ coincides with $\mathbf{B}_1$ and, as shown, $\mathbf{M}$ undergoes a rotation around $x'$. The same is true if $\omega$ deviates only slightly from the Larmor frequency. Conversely, if the deviation is large, $\mathbf{B}_{\text{eff}}$ is practically directed along axis $z$ because $B_1 \ll B_0$.

### 1.10 SPIN RELAXATION AND BLOCH EQUATIONS

In real macroscopic systems the spin ensemble interacts with the lattice; and whenever the $z$ component of the magnetization $M_z$ deviates from the equilibrium value $M_0$, the spin–lattice interaction tends to restore it. Moreover, the spins interact with each other, and the $\mathbf{M}$ components perpendicular to $z$ tend to become zero. To consider these processes, further terms should be included in the equations for the time evolution. These phenomenological terms transform Equation 1.15 into the following equations, called the *Bloch equations*:

$$
\begin{align*}
\frac{dM_z}{dt} &= -M_y \omega_1 - (M_z - M_0) / T_1 \\
\frac{dM_x}{dt} &= M_y (\omega - \omega_0) - M_x / T_2 \\
\frac{dM_y}{dt} &= M_z \omega_1 - M_x (\omega - \omega_0)
\end{align*}
$$

Two time constants have been introduced. The spin–lattice or “longitudinal” relaxation time $T_1$ relates to the time for recovering the equilibrium value of the magnetization $z$ component, which is also indicated as the longitudinal component. The
second characteristic time is the transverse relaxation time $T_2$, which depends on how fast the $M_x$ and $M_y$ component tend to vanish. Note that these two times are generally different, because $T_1$ characterizes a process of energy transfer from the spin system to the lattice and vice versa, depending on how tight the connection is between them, whereas $T_2$ is related to processes of energy exchange within the spin system, which do not involve the lattice.

The EPR absorption signal is proportional to the component of the magnetization measured perpendicular to $B_1$, which is $M_y$, obtained by solving Equation 1.17. If the perturbation attributable to the microwave field is a continuous one and it is small, the Bloch equations are solved in the stationary regime by placing the time derivatives of the magnetization components equal to zero. In this CW regime the solution for $M_y$ is

$$M_y = \frac{M_0}{B_0} B_1 T_2 \left[ 1 + \left( \frac{\omega - \omega_0}{C_0} \right)^2 T_2^2 \right]$$

Equation 1.18 is a function of $\omega$ called the Lorentzian function, which represents the shape of the EPR resonance line. Figure 1.7 shows a Lorentzian line and its first derivative. The width of the line is inversely proportional to relaxation time $T_2$.

In solid or glassy samples each paramagnetic species is oriented in a specific way with respect to the magnetic field, and it is immobile. Therefore, the EPR lines are due to the superposition of many lines, each corresponding to a differently oriented species or to species having different interactions with their surroundings. The width of an EPR line in this case could be much broader than that expected from relaxation time $T_2$. In this case the linewidth is called inhomogeneous to distinguish it from the homogeneous width of the lines, which occur when the species are all magnetically equivalent. The shape of the EPR line in this instance is generally a Gaussian (see Chapter 2 and Fig. 2.10).

---

![Fig. 1.7](image)

**Fig. 1.7** The EPR Lorentzian (a) absorption line and (b) its first derivative. The abscissa shows the deviation of the microwave angular frequency from the resonance frequency $\omega_0$. 
1.11 NUCLEAR SPINS

Like the electrons, the nuclei are characterized by a spin angular momentum, usually indicated by \( I \), and by the corresponding associated magnetic moment given by a relation analogous to Equation 1.2:

\[
\mu_N = g_N \mu_N I
\]  

(1.19)

Note that the \( g_N \) factor depends on the isotope, and it can be positive (as for protons) or negative (e.g., in the case of \(^{15}\text{N}\)).

Even for nuclei the magnitude (modulus) of the angular momentum and its component along a direction \( z \) are quantized. Depending on the type of nucleus, the nuclear spin quantum number \( I \) may have values other than \( 1/2 \), including 0. A few examples are reported in Table 1.1. A comprehensive table of nuclear spin properties is found in the EPR-electron nuclear double resonance (ENDOR) Frequency Table.

The magnitude and \( z \) component of the nuclear spin moment in units of \( \hbar \) are

\[
|I| = \sqrt{I(I+1)}
\]  

(1.20)

and

\[
I_z = -I, -I+1, \ldots, I
\]  

(1.21)

As it occurs for an electron spin, the energy of nuclear spins is influenced by a magnetic field according to the nuclear spin angular momentum component along the direction of magnetic field \( I_z \). This effect is called the nuclear Zeeman effect.

\[
E = -g_N \mu_N B_0 I_z
\]  

(1.22)

In the presence of a nuclear spin the electron spin experiences an additional magnetic field provided by the nuclear magnetic moment, which affects the resonance conditions. The electron–nucleus spin interaction is called hyperfine interaction. It gives rise to a splitting of the resonance EPR lines into several components: two

<table>
<thead>
<tr>
<th>Isotope</th>
<th>( I ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H}, \ ^{13}\text{C}, \ ^{31}\text{P}, \ ^{15}\text{N})</td>
<td>1/2</td>
</tr>
<tr>
<td>(^2\text{H}, \ ^{14}\text{N})</td>
<td>1</td>
</tr>
<tr>
<td>(^{12}\text{C}, \ ^{16}\text{O})</td>
<td>0</td>
</tr>
<tr>
<td>(^{55}\text{Mn})</td>
<td>5/2</td>
</tr>
<tr>
<td>(^{23}\text{Na})</td>
<td>3/2</td>
</tr>
</tbody>
</table>
components for interaction with a nuclear spin $I = 1/2$, three components for an $I = 1$ nucleus, and in general $2I + 1$ components for the interaction with a spin $I$ nucleus.

In the case of an electron spin interacting with a nuclear spin, Equation 1.4 for the energy in a magnetic field should be modified by adding two terms: the nuclear Zeeman interaction of the nuclear spin with the external magnetic field and a contribution that derives from the hyperfine field experienced by the electron spin. For the hyperfine field, two regions in the space should be distinguished: one inside the nuclear volume that is small but finite and another one outside the nuclear volume. Quantum mechanics does not exclude that the electron enters into the nucleus. In the region external to the nucleus, the hyperfine magnetic field is the classical field of a magnetic dipole. It decreases with the third power of the electron nucleus distance $r$, and it depends on the orientation of the vector connecting the electron and nucleus with respect to the directions of the dipoles. This dipole–dipole interaction is averaged out if the paramagnetic molecule is rapidly tumbling in an isotropic environment, as occurs in a normal liquid solution. In this case all orientations are covered with equal probability. Dipole–dipole interaction that is important for solid samples will be considered later.

Inside the nucleus the hyperfine field is constant, and it does not depend on the direction. The hyperfine energy contribution $E_{hf}$ is called the contact (or Fermi) contribution, which is

$$E_{hf} = a S \cdot I$$

(1.23)

where $a$ is a constant (hyperfine coupling constant) that depends on $|\Psi(0)|^2$, the square of the wavefunction that describes the electron motion calculated in the point where the nucleus is. $|\Psi(0)|^2$ gives a measure of how much electron spin enters the nucleus; $a$ is given by the equation

$$a = (8\pi/3)g\mu_Bg_N\mu_N|\Psi(0)|^2$$

(1.24)

A detailed illustration of the hyperfine interaction, its characteristics in different molecular systems, and several examples of spectra dominated by hyperfine interactions will be given in Chapter 4.

Let us consider first the simple case of rapidly tumbling molecular systems in liquid solution. In such a system the energy terms dependent on the nuclear spin $E_n$ are nuclear Zeeman interaction 1.22 and isotropic contact hyperfine interaction 1.23:

$$E_n = -g_N\mu_N B_0 I_z + a S \cdot I$$

(1.25)

The first term in Equation 1.25 is much smaller than the electron Zeeman interaction, by virtue of the much smaller nuclear magnetic moment compared with the electron magnetic moment ($\mu_N \ll \mu_B$). The hyperfine term is also much smaller than the electron Zeeman term, provided that magnetic field $B_0$ is large enough,
as occurs for organic radicals and for most other systems studied in X-band spectrometers:

\[ |a| \ll g |\mu_B| B_0 \]  

(1.26)

Under these conditions (high field approximation) the energy term \( E_n \), due to the nuclear spin, represents a small perturbation on the electron spin energy, which becomes

\[ E_{\text{tot}} = g |\mu_B| B_0 S_z - g_N \mu_N B_0 I_z + a S_z I_z \]  

(1.27)

For a free radical \((S = 1/2)\) containing a single magnetic nucleus with \( I = 1/2 \), there are four possible values of the total energy, corresponding to the electron and nuclear spin components \( S_z = \pm 1/2 \) and \( I_z = \pm 1/2 \), as illustrated in Fig. 1.8.

The corresponding energies are the following:

\[
\begin{align*}
E_1 &= 1/2 g |\mu_B| B_0 - 1/2 g_N \mu_N B_0 + 1/4a \\
E_2 &= 1/2 g |\mu_B| B_0 + 1/2 g_N \mu_N B_0 - 1/4a \\
E_3 &= -1/2 g |\mu_B| B_0 + 1/2 g_N \mu_N B_0 + 1/4a \\
E_4 &= -1/2 g |\mu_B| B_0 - 1/2 g_N \mu_N B_0 - 1/4a
\end{align*}
\]  

(1.28)

Fig. 1.8  The energy level scheme for an electron spin \( S = 1/2 \) coupled to a nuclear spin \( I = 1/2 \) (e.g., a proton) in the presence of a magnetic field \( B_0 \). The heavy arrows represent the \( S_z = \pm 1/2 \) electron spin components along the magnetic field direction. The light arrows represent the nuclear spin components. Each electron Zeeman spin level is split into two levels (dotted lines) by the hyperfine interaction with the nuclear spin. The hyperfine levels are then shifted by the nuclear Zeeman interaction term (solid lines). The shift is \( \pm 1/2 g_N \mu_N \), and it has no effect on the energy difference between the levels connected by the allowed EPR transitions (vertical double arrows). Note that electron and nuclear Zeeman interactions have opposite sign. In the example there is a a positive sign for the hyperfine splitting constant \( a \) and \( a > g_N \mu_N B_0 \). The drawing is not to scale, because the hyperfine splitting and nuclear Zeeman interaction are exaggerated with respect to the electron Zeeman term for clarity.
EPR consists of transitions between pairs of energy levels characterized by different values of $S_z$ but the same $I_z$ value. In fact, when the electron and nuclear spin are weakly coupled, as we have assumed, the electromagnetic radiation acts by changing the component of a single spin: either the electron spin component $S_z$ (in EPR) or the nuclear spin component $I_z$ (in NMR) but not both at the same time. One says that the following selection rules apply, depending on the type of spectroscopic transition one is observing:

$$\Delta S_z = \pm 1, \quad \Delta I_z = 0$$  \hspace{1cm} (1.29) \\
for EPR transitions and

$$\Delta S_z = 0, \quad \Delta I_z = \pm 1$$  \hspace{1cm} (1.30) \\
for NMR transitions.

The NMR transitions would occur at much lower frequency than the EPR transitions (in the megahertz frequency range in the X-band spectrometer magnetic field).

It should be noted that EPR selection rule 1.29 holds for systems with hyperfine coupling such that the hyperfine field acting on the nucleus is much smaller than the external magnetic field, as pointed out. These transitions are the so-called EPR allowed transitions. When the high field approximation is no longer a good one, transitions with $\Delta S_z = \pm 1; \Delta I_z = \pm 1$ can also be observed. These are called forbidden transitions, and their intensity is lower than the allowed ones.

From Equation 1.28 it is derived that for a fixed field $B_0$ the EPR transitions allowed according to selection rules 1.29 take place at frequencies

$$v_1 = (E_2 - E_3)/\hbar = (g\mu_B B_0 - a/2)/\hbar$$  \hspace{1cm} (1.31) \\
and

$$v_{II} = (E_1 - E_4)/\hbar = (g\mu_B B_0 + a/2)/\hbar$$  \hspace{1cm} (1.32) \\

Alternatively, using a fixed frequency $v_0$ and a variable magnetic field $B$, EPR transition lines occur at magnetic field values

$$B_1 = h v_0 / g\mu_B + a/2 g\mu_B$$  \hspace{1cm} (1.33) \\
and

$$B_{II} = h v_0 / g\mu_B - a/2 g\mu_B$$  \hspace{1cm} (1.34) \\

Because for EPR transitions we consider differences in energy between levels corresponding to the same nuclear spin state, the effect of the nuclear Zeeman interaction is canceled and the EPR spectrum of a system with an unpaired electron with hyperfine interaction with a single $I = 1/2$ nucleus consists of two lines separated by the hyperfine splitting constant $a$. This treatment is easily extended to the case of a
nucleus with a generic nuclear spin \( I \) by taking into account that the allowed spin components are \( 2I + 1 \). Therefore, each electron spin Zeeman level will be separated by the hyperfine interaction into \( 2I + 1 \) levels. Because of the EPR selection rules (Equation 1.29), the spectrum will consist of \( 2I + 1 \) lines.

In most cases, as in organic free radicals, the unpaired electron interacts with many magnetic nuclei and the total spin energy contains several hyperfine terms. For \( n \) nuclei,

\[
E_{\text{tot}} = g | \mu_B | B_0 S_z + a_1 S_z I_{z1} + a_2 S_z I_{z2} + \cdots + a_n S_z I_{zn}
\]

\[
= g | \mu_B | B_0 S_z + \sum a_k S_z I_{zk}
\]  

Equation 1.35

In Equation 1.35 the nuclear Zeeman terms are omitted because, even if present, they do not contribute to the EPR spectrum. Each electron Zeeman level is separated into a manifold of several sublevels. Their number is

\[
N = (2I_1 + 1)(2I_2 + 1) \cdots (2I_n + 1) = \prod (2I_k + 1)
\]  

Equation 1.36

If all \( n \) nuclei have \( I = 1/2 \), the number of EPR lines is \( 2^n \), which means that the number of EPR lines increases very rapidly with \( n \).

In general, not all nuclei have distinct hyperfine splitting constants and several energy levels may coincide. They are said to be degenerate. For example, if two protons \( (I = 1/2) \) have the same splitting constant \( a \), the hyperfine energy will cancel if one has component \( I_z = 1/2 \) and the other one has \( I_z = -1/2 \), independently of which one is which, and the energy level corresponding to this nuclear spin configuration is twofold degenerate. The population of degenerate levels corresponds to the equilibrium Boltzmann population multiplied by the degeneration factor. Consequently, the EPR transitions involving these levels have an intensity multiplied by the same factor. The relative intensity of the hyperfine components of a set of \( N \) nuclear spins having \( I = 1/2 \) follows the binomial distribution ratio (see Chapter 4).

1.12 ANISOTROPY OF THE HYPERFINE INTERACTION

The second contribution to the hyperfine interaction arises from the classical dipole–dipole interaction between the electron spin magnetic dipole and the nuclear magnetic dipole moment (see Fig. 1.9). The nuclear moment generates a magnetic field, which adds to the Zeeman field and is experienced by the electron spin. The dipolar hyperfine interaction is important for paramagnetic systems in single crystals, powder, glasses, and any other cases of molecules not tumbling in isotropic liquids.

The energy of the dipolar interaction between two magnetic dipoles depends on the inverse cube of their distance \((1/r^3)\) and their orientation with respect to the
vector connecting them. It is given by

\[
E_{\text{dip}} = \left( \frac{\mu_0}{4\pi} \right) \left[ \frac{\mu_1 \cdot \mu_2}{r^3} - 3(\mu_1 \cdot r)(\mu_2 \cdot r)/r^5 \right]
\]  

(1.37)

where \( \mu_0 = 4\pi \times 10^{-7} \, \text{N} \, \text{A}^{-2} \) is the magnetic permeability of the vacuum.

If \( \mu_1 \) and \( \mu_2 \) are substituted by the electron spin and nuclear spin magnetic dipoles \( \mu_e \) and \( \mu_N \) given by Equations 1.2 and 1.19, respectively, Equation 1.37 becomes

\[
E_{\text{dip}} = \left( \frac{\mu_0}{4\pi} \right) g_B g_N \mu_N \left[ S \cdot I / r^3 - 3(S \cdot r)(I \cdot r)/r^5 \right]
\]  

(1.38)

where \( r \) is a vector with components \( x, y, \) and \( z \), which represents the position of the electron in a proper coordinate frame centered on the nucleus; and \( r = \sqrt{x^2 + y^2 + z^2} \) is the electron nucleus distance.

When using Equation 1.38, one should take into account that the electron is not localized on a point but is distributed in space. Therefore, the terms contributing to the hyperfine dipolar interaction energy \( E_{\text{dip}} \) have to be averaged over the electron distribution. Because of the dot products, Equation 1.38 comprises nine terms that have the following form:

\[
T_{ij}S_iI_j = \left( \frac{\mu_0}{4\pi} \right) g_B g_N \mu_N \langle \delta_{ij}/r^3 - 3ij/r^5 \rangle S_iI_j
\]  

(1.39)

where \( i, j = x, y, z \) and the angle brackets \( \langle \rangle \) are used to indicate the average over the electron spatial coordinates. Moreover, \( \delta_{ij} = 0 \) and \( \delta_{ii} = 1 \). The nine quantities \( T_{ij} \) can be arranged as the elements of a \( 3 \times 3 \) symmetrical matrix \( (T_{ij} = T_{ji}) \) called the \textit{hyperfine dipolar interaction tensor} or \textit{hyperfine anisotropic tensor}, which is
indicated by $T$:

$$
T = \begin{pmatrix}
T_{xx} & T_{xy} & T_{xz} \\
T_{yx} & T_{yy} & T_{yz} \\
T_{zx} & T_{zy} & T_{zz}
\end{pmatrix}
$$  \hspace{1cm} (1.40)

The elements of $T$ depend on the choice of the reference frame $x$, $y$, and $z$. However, whatever is the reference frame, because of the particular form of Equation 1.39 the sum of the diagonal elements (the tensor trace) is zero, because $x^2 + y^2 + z^2 = r^2$:

$$
T_{xx} + T_{yy} + T_{zz} = 3/r^3 - 3(x^2 + y^2 + z^2)/r^5 = Tr(T) = 0
$$  \hspace{1cm} (1.41)

This property of tensor $T$ has an important consequence. Let us suppose that the electron spin distribution is spherical symmetric around the nucleus. In this case the three diagonal tensor elements are equal, and they are zero according to Equation 1.41. Moreover, all other tensor elements are also zero because for a spherical distribution the average over all directions of the products $xy$, $xz$, and $yz$ vanishes. To have anisotropic hyperfine interaction, the electron spin should not be spherically distributed around the nucleus.

Because $T$ is symmetric about the diagonal ($T_{ij} = T_{ji}$), it is always possible to find a particular reference frame $X$, $Y$, $Z$ such that all tensor elements $T_{ij}$ are zero if $i \neq j$. The $X$, $Y$, $Z$ axes are called principal axes and the corresponding tensor elements $T_{XX}$, $T_{YY}$, and $T_{ZZ}$ are called principal values of tensor $T$. Using the principal axes system, the dipolar energy ($E_{\text{dip}}$) assumes the simple form

$$
E_{\text{dip}} = T_{XX}S_XI_X + T_{YY}S_YI_Y + T_{ZZ}S_ZI_Z
$$  \hspace{1cm} (1.42)

The dipolar energy adds to the isotropic hyperfine term and to the Zeeman interaction to determine the total energy of the electron–nuclear spin system in the magnetic field. The dipolar term is anisotropic, because the electron and nuclear spin components depend on the direction of the Zeeman magnetic field $B$ with respect to the $X$, $Y$, $Z$ axes. Consequently, the hyperfine separation of the EPR transitions depends on the orientation of the paramagnetic molecule with respect to $B$.

If the paramagnetic molecule is rapidly tumbling in a normal liquid solution, all molecular orientations are explored and the dipolar contribution is averaged. Because the dipolar tensor has zero trace, the average is zero and the only contribution to the hyperfine interaction is the isotropic one.

This is not true if the liquid is partially oriented as occurs, for example, in liquid crystal solvents partially oriented in the magnetic field. In this case not all orientations occur with the same probability, and a residual dipolar interaction contribution remains.
1.13 ENDOR

With reference to Fig. 1.8, we note that the hyperfine coupling constant $a$ is obtained from the difference $\Delta_{EPR} = \Delta_{14} - \Delta_{23} = (E_1 - E_4) - (E_2 - E_3) = a$ between the energy of the two allowed EPR transitions. Note that, because of the selection rule $\Delta I_z = 0$ (Equation 1.29), no information can be obtained in this way about $\mu_N$, and therefore about the type of nucleus to which coupling $a$ is referring. In general this is not too important because the type of nucleus is obtained from other information.

Hyperfine coupling $a$ could also be obtained by taking the sum of the NMR transition energies:

$$\Delta_{34} + \Delta_{12} = (E_3 - E_4) + (E_1 - E_2) = a$$

In fact, the NMR transitions allowed according to the selection rules of Equation 1.29 have energies

$$\Delta_{34} = E_3 - E_4 = a/2 + g_N\mu_NB_0$$

and

$$\Delta_{12} = E_1 - E_2 = a/2 - g_N\mu_NB_0$$

These values are obtained by considering $a > 0$. The hyperfine coupling constants can be positive or negative, depending on the system (see Chapter 4). If $a < 0$, the two values of $\Delta_{34}$ and $\Delta_{12}$ reported in Equations 1.44 and 1.45 would be exchanged.

The two NMR transitions are centered at the frequency $a/2\hbar$, separated by 2 times the nuclear Larmor frequency $\nu_N = g_N\mu_NB_0/\hbar$. These transitions occur in the RF range. However, the normal observation of the NMR absorption using a traditional NMR instrument would be prevented in this case by the low sensitivity and by the large width of the lines due to the fast electron spin relaxation. To overcome these difficulties, a different technique for observing the NMR transitions in paramagnetic species was introduced. It consists of the observation of the effect on the saturation properties of an EPR line, which is produced by an RF field that induces NMR transitions. ENDOR can be considered as NMR detected via EPR. Compared to normal NMR, it has the advantage of the much higher intensity of EPR transitions.

The principles of ENDOR are described in the following example referring to a simple system of an electron spin and a nuclear spin $I = 1/2$ with $g_N > 0$ and a positive hyperfine coupling $a$, as illustrated in Fig. 1.10. The energy levels are the same as in Fig. 1.8, with the two sets of levels corresponding to the two nuclear spin states, shifted one relative to the other for clarity.

In the absence of a microwave radiation field and at thermal equilibrium with the lattice, the populations of levels $E_1$, $E_2$, $E_3$, and $E_4$ are determined by the Boltzmann statistics. In particular, the populations of energy levels $E_4$ and $E_3$ are larger than those of levels $E_2$ and $E_1$. Low power microwave radiation at frequencies $(E_1 - E_4)/\hbar$ or $(E_2 - E_3)/\hbar$ would induce EPR transitions without perturbing the population distribution.
Let us suppose that microwave radiation is applied at a frequency corresponding to the EPR transition $E_1 \leftrightarrow E_4$ with a power high enough to partially saturate the EPR transition, as indicated by the solid arrow in the left part of Fig. 1.10. This means that the spin relaxation is not fast enough to compete with the rate of transitions induced by the microwaves, and the population difference between levels 1 and 4 is therefore reduced.

Note that various relaxation paths can be active in reestablishing the population difference between states 1 and 4, as the direct electron spin lattice relaxation between these latter states, as well as, for example, the path $1 \leftrightarrow 2 \leftrightarrow 3 \leftrightarrow 4$, with a sequence of steps consisting of a nuclear spin flip ($1 \leftrightarrow 2$), an electron spin flip ($2 \leftrightarrow 3$), and another nuclear spin flip ($3 \leftrightarrow 4$). In some systems, “cross relaxations” steps $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$ (not indicated in Fig. 1.10) involving both electron and nuclear spin flips can also be very fast and important in determining the ENDOR effect. The curved arrow in Fig. 1.10 symbolically represents the combined efficiency of all of the paths.

In an ENDOR experiment the magnetic field is kept constant on an EPR line, and the RF frequency is swept. When the RF equals $(E_1 - E_2)/h$ (corresponding to $v_1 = a/2 - g_N\mu_N B_0$) or $(E_3 - E_4)/h$ ($v_2 = a/2 + g_N\mu_N B_0$), inducing one of the corresponding NMR transitions, the rate of the population recovery for state 4 increases, together with the EPR intensity. In fact, the $1 \leftrightarrow 2$ or the $3 \leftrightarrow 4$ nuclear spin flip steps become more efficient.
The ENDOR signal is the difference between the intensity of the EPR line with and without, respectively, the RF driving one of the two NMR transitions (ENDOR enhancement). If the intensity of the partially saturated EPR line is plotted as a function of the RF, the ENDOR spectrum schematically shown in Fig. 1.11 is obtained. In this example ($g_N > 0$, $a > 0$) the low frequency ENDOR line corresponds to the $E_1 - E_2$ NMR transition and the high frequency ENDOR line to the $E_3 - E_4$ NMR transition. Note that with a negative hyperfine coupling constant a different energy level scheme would be obtained, with the result of having the $E_3 - E_4$ transition at low frequency and the $E_1 - E_2$ transition at high frequency. However, the ENDOR spectrum looks the same, independently of the sign of the hyperfine constant $a$, and therefore it is not possible to get this sign from it. It is possible to get the relative signs of two hyperfine coupling constants by performing the so-called electron–nuclear–nuclear triple resonance or TRIPLE experiment, where two RF frequencies are used at the same time. This experiment is described in Chapter 2.

The CW-ENDOR effect heavily depends on the ratio of the various relaxation times. Sometimes it can be too small to be detected, in particular for radicals in solution, where often the ENDOR enhancement is detectable only with a convenient choice of solvent and temperature. Pulsed ENDOR, which is described in Chapter 5, is based on different principle. It can often be detected in cases where CW-ENDOR would be undetectable.

Two possible situations are encountered when the hyperfine coupling constant $a$ is larger or smaller than the nuclear Zeeman interaction. In the first case the two ENDOR lines are centered at the frequency $a/2\hbar$ and are separated by $2g_N\mu_N B_0/\hbar$. In the second case the ENDOR lines are centered at $g_N\mu_N B_0/\hbar$ and are separated by $a/\hbar$ (see Fig. 1.11). The same spectrum is obtained by saturating the second EPR line occurring between energy levels $E_2$ and $E_3$ of Fig. 1.10.

---

**Fig. 1.11** The schematic ENDOR spectrum of an electron spin system coupled to a nuclear spin $I = 1/2$. The ENDOR lines represent the intensity variation of a partially saturated EPR line as the sample irradiated with RF radiation. An ENDOR line occurs when the RF radiation frequency matches the energy difference between energy levels 1 and 2 and between levels 3 and 4 (see Fig. 1.10). (a) If the hyperfine coupling $a$ is larger then the nuclear Zeeman interaction ($|a| > g_N\mu_N B_0$), the ENDOR lines are centered at $a/2\hbar$ and are separated by 2 times the nuclear Larmor frequency $g_N\mu_N B_0/\hbar$. (b) If $|a| < g_N\mu_N B_0$, the ENDOR lines are centered at the nuclear Larmor frequency and are separated by $a/\hbar$. In both cases information about hyperfine coupling and nuclear Larmor frequency is obtained.
If the unpaired electron system contains several hyperfine coupled nuclei, a pair of ENDOR lines is obtained for each set of nuclei having the same hyperfine coupling constant, independently of their number. This makes an ENDOR spectrum much simpler than the EPR spectrum, and it enhances the spectral resolution. For example, for an electron spin coupled to \( N \) spin \( 1/2 \) nuclei one has \( 2^N \) ENDOR lines instead of \( 2^N \) EPR lines. In contrast, the information about the number of nuclei responsible for the coupling is lost.

Note that in the case of small hyperfine couplings the ENDOR frequency could be very low, if the couplings refer to nuclei also having a small nuclear magnetic moment. Because at low frequencies the sensitivity is quite low, the use of high field/high frequency spectrometers is a big advantage. In fact, an increase of the nuclear Zeeman term permits the shifting of the frequency at higher values, but also its allows the discrimination of ENDOR lines corresponding to different nuclei with similar magnetic moments. This increase in sensitivity and resolution is parallel to the resolution increase obtained by high frequency NMR spectrometers. Examples of applications of high frequency ENDOR are provided in Chapter 12.

### 1.14 TWO INTERACTING ELECTRON SPINS

Some molecular systems have two unpaired electron spins. This could happen, for example, in some transition metal ion complexes or in high symmetrical molecules where electronic orbitals with the same energy (degenerate levels) are present. In fact, two electrons with unpaired spins may coexist if they are placed in different orbitals. Other systems in which two unpaired spins may coexist are some excited states of organic molecules. In this case the two unpaired electron spins are placed on levels of different energies. A short list of systems with two unpaired electrons can be found in Chapter 3.

A system with two unpaired electron spins could be in a state characterized by the total spin quantum number \( S \), either with value \( S = 0 \) or \( 1 \), corresponding to situations where the spins are antiparallel or respectively parallel to each other. The two electron spin configurations, called *singlet* and *triplet* states, respectively, correspond to different electron spatial distributions and have different energies, the separation of which is characterized by the exchange interaction parameter \( J \). The names triplet and singlet derive from the fact that for a spin \( S = 1 \) three states are available with \( z \) components \( S_z = 1, 0, -1 \), whereas for \( S = 0 \) only \( S_z = 0 \) is possible. In the absence of a magnetic field the energy is independent of the \( z \) component, but in the presence of a magnetic field \((B_0 \neq 0)\) the degeneration is removed and three separate energy levels are obtained for a triplet state.

If the electron distribution had spherical symmetry, the levels would be equally spaced. Consequently, transitions \(-1 \leftrightarrow 0\) and \(0 \leftrightarrow 1\), obeying the selection rule \( \Delta S_z = \pm 1 \), would coincide. This is not true if the symmetry is lower. In fact, for a
two electron spin system one should take into account the dipolar interaction between the electron magnetic moments. This classical interaction is analogous to that of an electron spin magnetic moment with a nuclear magnetic moment discussed in Section 1.12.

Here, both magnetic moments are attributable to electron spins and the dipolar energy is

\[ E_{\text{dip}} = (\mu_0/4\pi)g^2\mu_B^2 [S_1 \cdot S_2/r^3 - 3(S_1 \cdot r)(S_2 \cdot r)/r^5] \] (1.46)

which comprises nine terms of the type

\[ (\mu_0/4\pi)g^2\mu_B^2(\delta_{ij}/r^2 - 3ij/r^5)S_iS_j \] (1.47)

where \( i, j = x, y, z \) are three orthogonal axes and \( S_i \) and \( S_j \) are the respective magnetic moment components along these axes of the individual electrons. Both electron spins are distributed in space orbitals, with a probability depending on the spatial coordinates \( x, y, \) and \( z \). Therefore, the dipolar interaction should be averaged over the distribution of both electrons. This can be done because spatial and spin coordinates are separated. Upon integration the equation for the dipolar energy may be written as

\[ E_{\text{dip}} = \sum_{i,j} D_{ij}S_iS_j \] (1.48)

\[ D_{ij} = (\mu_0/4\pi)g^2\mu_B^2((\delta_{ij}/r^2 - 3ij/r^5)) \] (1.49)

The nine parameters \( D_{ij} \) constitute the elements of the electron–electron dipolar interaction tensor.

Note that parameters \( D_{ij} \) depend on the choice of the coordinate frame used for describing the electron distribution. As for the hyperfine dipolar tensor, there is a particular axes frame \( X, Y, Z \) (principal axes) such that all dipolar tensor elements are zero except the diagonal ones \( D_{XX}, D_{YY}, \) and \( D_{ZZ} \), which are called the principal values of the dipolar tensor. Using the dipolar tensor principal axes frame, the electron dipolar interaction energy assumes the following simple form:

\[ E_{\text{dip}} = [D_{XX}S_X^2 + D_{YY}S_Y^2 + D_{ZZ}S_Z^2] \] (1.50)

Note that in Equation 1.50 the components of the total electron spin \( S = S_1 + S_2 \) are used instead of those of the individual spins. Moreover, because of the particular form of Equation 1.49, \( D_{XX}, D_{YY}, \) and \( D_{ZZ} \) are not independent:

\[ D_{XX} + D_{YY} + D_{ZZ} = 0 \] (1.51)
Taking into account Equation 1.51, the dipolar interaction energy can be written in terms of two independent parameters:

\[ D = -\frac{3}{2}D_{ZZ} \quad (1.52) \]

and

\[ E = \frac{1}{2}(D_{YY} - D_{XX}) \quad (1.53) \]

\[ E_{\text{dip}} = DS_Z^2 + E(S_Y^2 - S_X^2) \quad (1.54) \]

Usually the label \( Z \) is used for the largest principal value while \( X \) and \( Y \) are taken in such a way that \( E \) has an opposite sign to that of \( D \). The latter parameter offers information on the electron spin distribution and depends inversely on \( r^3 \), the cube of the average distance between the electron spins, whereas \( E \) is a measure of the deviation of the electron distribution from axial symmetry.

The effect of the electron dipolar interaction is to modify the energy spacing between the triplet sublevels in such a way that two distinct EPR lines occur. The line separation depends on the orientation of the magnetic field with respect to molecule fixed axes \( X, Y, Z \).

In a frozen solution of molecules in a triplet state, all possible orientations are covered with equal probabilities and the EPR absorptions occur over a broad range of magnetic field values. However, the number of molecules responsible for the absorption at a particular field is not the same throughout the range. In fact, there are particular orientations where small changes of orientation have little effect on the resonant field value. At these field positions there is a piling up of EPR intensity. Consequently, the EPR spectrum assumes a particular shape, the analysis of which allows the determination of the characteristic parameters entering into Equations 1.53 and 1.54. Examples of EPR spectra of random orientation distributions of triplet state molecules are provided in Figs. 1.12 and 1.13.

Fig. 1.12 The EPR spectrum expected for a random distribution of triplet state molecules \((S = 1)\) characterized by an axial symmetry of the electron distribution \((E = 0)\). The dotted line represents EPR absorption, and the solid line indicates the EPR first derivative spectrum. The linewidth is assumed as 0.3 mT, and \( D' = D/g|\mu_b| \) is in magnetic field units.
This section deals with a more formal treatment of the general concepts of EPR outlined earlier. It is based on the quantum mechanical description of the interaction of electron and nuclear spins with a magnetic field and the quantum description of their hyperfine interaction. A basic outline of the quantum mechanics rules is now provided.

A quantum system, such as an electron or a nuclear spin, can be found in states described by a function that is usually represented by a Greek letter or by a symbol within a pair of brackets: a vertical line and an angular bracket as, for example, \( |m \rangle \).

In quantum mechanics, to each mechanical quantity is associated an operator, which is indicated by placing a circumflex (caret) over the quantity symbol. An operator acts on a state function by transforming it into another one. There are particular cases where an operator corresponding to a mechanical property acting upon a state function has the effect of multiplying the function by a constant. In such a case the state is said to be an eigenstate of that particular operator (property) and the constant is called its eigenvalue. In that state the property considered has a definite value equal to the eigenvalue.

In EPR one deals with angular momenta, which are described by vector operators \( \vec{S} \) (or \( \vec{I} \) for a nuclear spin) with three components \( S_x, S_y, S_z \) associated with the momentum components along the axes of an orthogonal frame.

Quantum mechanics does not allow us to know simultaneously the three components of an angular momentum \( J \), which means that there are no quantum states that are simultaneously eigenstates of the three operators \( \hat{J}_x, \hat{J}_y, \hat{J}_z \). The maximum allowed information consists of knowing one component, usually set as the \( z \) component \( J_z \) and the square of the angular momentum \( J^2 \).

Fig. 1.13 The EPR spectrum of a random distribution of triplet state molecules (\( S = 1 \)) with low symmetry (\( E \neq 0 \)). The dotted line represents EPR absorption, and the solid line indicates the EPR first derivative spectrum. The linewidth is assumed as 0.3 mT, and \( D' = D/g|\mu_B| \) and \( E' = E/g|\mu_B| \) are in magnetic field units.
The eigenvalues of the square of the angular moment operator \( J^2 \) are limited to those given in \( \hbar^2 \) units by the products \( j(j+1) \), where \( j \) is a characteristic quantum number that may be either an integer or a half-integer number. The eigenvalues of the \( J_z \) operator are the \( 2j+1 \) values:

\[
j_z = -j, -j + 1, \ldots, j
\]  

(1.55)

The state functions that are simultaneously eigenfunctions of both operators \( J^2 \) and \( J_z \) can be indicated with the symbols that refer to the quantum number \( j \), and the value of \( j_z \) placed within a vertical bar and angle bracket, as \( |j, j_z\rangle \).

An electron spin angular momentum is characterized by the quantum number \( \frac{1}{2} \) and the eigenvalue of the squared angular momentum operator \( S^2 \) in \( \hbar^2 \) units is \( (1/2)(1/2 + 1) = 3/4 \). The eigenvalues of operator \( \hat{S}_z \) corresponding to the spin component along \( z \) are 1/2 and -1/2. The electron spin eigenfunctions of \( \hat{S}^2 \) and \( \hat{S}_z \) can be written as \( |1/2, 1/2\rangle \) and \( |1/2, -1/2\rangle \). They correspond to those indicated in the previous paragraphs with letters \( \alpha \) and \( \beta \), respectively. The notation with Greek letters is used only for spin 1/2 systems.

In quantum mechanics the total energy of a system is associated to an operator called the Hamiltonian operator \( (H) \), which contains all energy terms, and the eigenvalues of which are the quantum allowed energies of the system. Some examples of spin Hamiltonians, their eigenstates, and their eigenvalues are described in the following section.

### 1.16 ELECTRON SPIN IN A STATIC MAGNETIC FIELD

The simplest example of a spin Hamiltonian for EPR is that representing the energy of an electron spin placed in a static magnetic field \( B_0 \) directed along the \( z \) direction. It consists of the electron Zeeman term

\[
H = g\mu_B|B_0 S_z
\]  

(1.56)

Because \( g \), \( \mu_B \), and \( B_0 \) are constants, the eigenfunctions of \( H \) are the same as \( \hat{S}_z \); that is, \( |1/2, 1/2\rangle \) and \( |1/2, -1/2\rangle \) (or \( \alpha \) and \( \beta \)). The eigenvalues of \( H \) are those of \( \hat{S}_z \) multiplied by the factor \( g\mu_B|B_0\):

\[
E_\pm = \pm 1/2 g\mu_B|B_0
\]  

(1.57)

Here, \( E_\pm \) is the allowed energies of the spin in the magnetic field.

### 1.17 ELECTRON SPIN COUPLED TO A NUCLEAR SPIN

Let us consider a single electron spin coupled to a nuclear spin with an isotropic hyperfine coupling \( a \). We consider an \( I = 1/2 \) nucleus to make the example
as simple as possible. In this case Hamiltonian operator $H$ comprises three terms: the electron Zeeman interaction, the nuclear Zeeman interaction, and the hyperfine interaction.

$$H = g|\mu_B|B_0\hat{S}_z - g_N\mu_N B_0\hat{I}_z + a\hat{S} \cdot \hat{I}$$

(1.58)

The spin functions of a system of noninteracting electron and nuclear spins ($a = 0$) can be written as the product of electron and nuclear spin functions represented by the symbols

$$\begin{align*}
\Psi_1 &= |1/2, 1/2\rangle \\
\Psi_2 &= |1/2, -1/2\rangle \\
\Psi_3 &= |-1/2, -1/2\rangle \\
\Psi_4 &= |-1/2, 1/2\rangle
\end{align*}$$

(1.59)

where the first number refers to the electron spin $z$ component and the second one refers to the $z$ component of the nuclear spin. The symbols referring to the square of the angular momenta $S^2$ and $I^2$ are omitted in this case to simplify the notation. They would be 1/2 for both electron and nuclear spins. The above functions are eigenfunctions of the first two terms of the Hamiltonian with the corresponding eigenvalues:

$$\begin{align*}
E_1 &= 1/2 g|\mu_B|B_0 - 1/2 g_N\mu_N B_0 \\
E_2 &= 1/2 g|\mu_B|B_0 + 1/2 g_N\mu_N B_0 \\
E_3 &= -1/2 g|\mu_B|B_0 + 1/2 g_N\mu_N B_0 \\
E_4 &= -1/2 g|\mu_B|B_0 - 1/2 g_N\mu_N B_0
\end{align*}$$

(1.60)

For interacting electron and nuclear spins ($a \neq 0$) the same functions are not eigenfunctions of the total Hamiltonian because the hyperfine terms comprise the products $a\hat{S}_x\hat{I}_x$ and $a\hat{S}_y\hat{I}_y$. In fact, these operators transform the functions into different ones. For example, $\hat{S}_x$ and $\hat{S}_y$, acting only on the electron spin (the first number in the bracket) and leaving the nuclear spin unchanged, give the following:

$$\begin{align*}
\hat{S}_x|1/2, 1/2\rangle &= 1/2|1/2, 1/2\rangle \\
\hat{S}_x|1/2, -1/2\rangle &= 1/2|1/2, -1/2\rangle \\
\hat{S}_x|-1/2, 1/2\rangle &= 1/2|-1/2, 1/2\rangle \\
\hat{S}_x|-1/2, -1/2\rangle &= 1/2|-1/2, -1/2\rangle \\
\hat{S}_y|1/2, 1/2\rangle &= i/2|-1/2, 1/2\rangle \\
\hat{S}_y|1/2, -1/2\rangle &= i/2|-1/2, -1/2\rangle
\end{align*}$$

(1.61-1.63)

For interacting electron and nuclear spins ($a \neq 0$) the same functions are not eigenfunctions of the total Hamiltonian because the hyperfine terms comprise the products $a\hat{S}_x\hat{I}_x$ and $a\hat{S}_y\hat{I}_y$. In fact, these operators transform the functions into different ones. For example, $\hat{S}_x$ and $\hat{S}_y$, acting only on the electron spin (the first number in the bracket) and leaving the nuclear spin unchanged, give the following:
\[ \hat{S}_z \left| -\frac{1}{2}, \frac{1}{2} \right\rangle = -i/2 \left| 1/2, \frac{1}{2} \right\rangle \]

\[ \hat{S}_z \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle = -i/2 \left| 1/2, -\frac{1}{2} \right\rangle \]  

(1.64)

where \( i = \sqrt{-1} \). Analogous equations hold for \( \hat{I}_x \) and \( \hat{I}_y \), which act on the nuclear spin (the second number in the bracket).

According to quantum mechanics, if the energy associated with the hyperfine Hamiltonian \( a\hat{S} \cdot \hat{I} \) is small compared to that corresponding to the Zeeman Hamiltonian, the terms \( a\hat{S}_x\hat{I}_x \) and \( a\hat{S}_y\hat{I}_y \) can be neglected in the computation of the energies and the operator \( a\hat{S} \cdot \hat{I} \) can be replaced by \( a\hat{S}_z\hat{I}_z \). This latter operator has functions in Equation 1.59 as eigenfunctions. The eigenvalues of the approximate hyperfine Hamiltonian are \( \pm a/4 \), which add to the Zeeman Hamiltonian energies given by Equation 1.60. The positive sign applies to the functions \( \Psi_1 \) and \( \Psi_4 \), corresponding to states with the same electron and nuclear spin \( z \) components (both \( 1/2 \) or both \(-1/2 \)), and the negative sign applies to the functions \( \Psi_2 \) and \( \Psi_3 \) relative to states having opposite electron and nuclear spin \( z \) components. These values correspond to the energy values reported in Equation 1.28.

1.18 ELECTRON SPIN IN A ZEEMAN MAGNETIC FIELD IN THE PRESENCE OF A MICROWAVE FIELD

This section considers the effect of the magnetic field associated to microwave radiation acting on the electron spin, considering first an isolated electron spin.

If an electron spin is placed in a magnetic field \( B_0 \) directed along the \( z \) axis and it is in the presence of a weak time dependent field \( B_1 \cos(\omega t) \), perpendicular to \( B_0 \), say, directed along the \( x \) axis, the Hamiltonian becomes

\[ H = g|\mu_B|B_0\hat{S}_z + g|\mu_B|B_1 \cos(\omega t)\hat{S}_x \]  

(1.65)

The state functions \( |\pm 1/2 \rangle \) are not eigenfunctions of the complete Hamiltonian because the operator \( \hat{S}_x \) acting on these spin functions gives as a result

\[ \hat{S}_x |1/2 \rangle = 1/2 |1/2 \rangle \]

\[ \hat{S}_x |-1/2 \rangle = 1/2 |-1/2 \rangle \]  

(1.66)

that is, it changes one function into the other one. The symbol referring to the spin squared moment is omitted here.

Because \( B_1 \ll B_0 \) and it changes with time, the effect of its presence can be considered in the frame of the time dependent perturbation theory. This theory states that a system initially in a state \( |a \rangle \) will be found successively in the state \( |b \rangle \), provided that the perturbation oscillates in time at an angular frequency \( \omega = \hbar^{-1}(E_b - E_a) \), where \( |a \rangle \),
\[ |b\rangle \text{ and } E_b, E_a \text{ are the respective eigenfunctions and eigenvalues of the unperturbed system time independent Hamiltonian.} \]

Moreover, to produce a transition from \[|a\rangle\] to \[|b\rangle\], it is necessary for the perturbing Hamiltonian \(H'\) to connect the two states in the sense that \(H'|a\rangle = c|b\rangle\) with \(c \neq 0\). This condition selects the allowed transitions between pairs of quantum states of a system. Furthermore, a perturbation that induces transitions from \[|a\rangle\] to \[|b\rangle\] also induces the opposite transition from \[|b\rangle\] to \[|a\rangle\].

When applied to the electron spin system, these rules describe the effect of the time variable field \(B_1\) on the electron spin. If the latter is initially in the state \[|\frac{-1}{2}\rangle\], it will be found in the state \[|\frac{1}{2}\rangle\], provided that the perturbation varies in time at an angular frequency \(\omega = \frac{h}{\gamma B_0}\). Note that this is the Larmor frequency introduced earlier. For this case there are only two states, and the transition between them is allowed in virtue of the Equation 1.66, which ensures that the two states are connected by the \(S_z\) operator.

If a nucleus is also present, the time dependent Hamiltonian to be added to the Zeeman Hamiltonian contains two terms:

\[
H(t) = g\mu_B|B_1\cos(\omega t)\hat{S}_z - g_N\mu_N B_1 \cos(\omega t)\hat{I}_z
\] (1.67)

The first one acts only on the electron spin, inducing a change in its \(z\) component and leaving unchanged the nuclear \(z\) spin component. Conversely, the second term acts only on the nuclear spin, changing the nuclear spin \(z\) component. The Hamiltonian does not connect states differing by both components. This is the basis of the selection rules \(\Delta S_z = \pm 1; \Delta I_z = 0 \text{ and } \Delta S_z = 0; \Delta I_z = \pm 1\) (Equations 1.29 and 1.30).

To produce the electron spin flip transition, the oscillating field frequency should match the energy difference corresponding to states differing in \(S_z\) (those shown as allowed transitions in Fig. 1.8). Conversely, for producing nuclear spin transitions the oscillating field frequency should match the energy difference corresponding to states with the same \(S_z\) component and differing in \(I_z\). These are NMR transitions observed by ENDOR.