CHAPTER 1

BASIC PRINCIPLES OF PARAMAGNETIC RESONANCE

1.1 INTRODUCTION

The science of electron paramagnetic resonance (EPR) spectroscopy is very similar in concept to the more familiar nuclear magnetic resonance (NMR) technique. Both deal with the interaction between electromagnetic radiation and magnetic moments; in the case of EPR, the magnetic moments arise from electrons rather than nuclei. Whether or not the reader has an immediate interest in the multitude of systems to which EPR is applicable, the insights that it provides cannot be ignored. Furthermore, there is hardly another technique from which one can gain a clearer insight into many of the fundamental concepts of quantum mechanics.

Much of our knowledge of the structure of molecules has been obtained from the analysis of molecular absorption spectra. Such spectra are obtained by measuring the attenuation versus frequency (or wavelength) of a beam of electromagnetic radiation as it passes through a sample of matter. Lines or bands in a spectrum represent transitions between energy levels of the absorbing species. The frequency of each line or band measures the energy separation of two levels. Given enough data and some guidance from theory, one may construct an energy-level diagram from a spectrum. Comparison of an energy-level diagram and an observed spectrum shows clearly that, of the many transitions that may occur between the various levels, only a relatively few 'allowed' transitions are observed. Hence the prediction of transition intensities requires a knowledge of selection rules.

Electromagnetic radiation may be regarded classically as coupled electric ($\mathbf{E}_1$) and magnetic ($\mathbf{B}_1$) fields perpendicular to the direction of propagation (Fig. 1.1).

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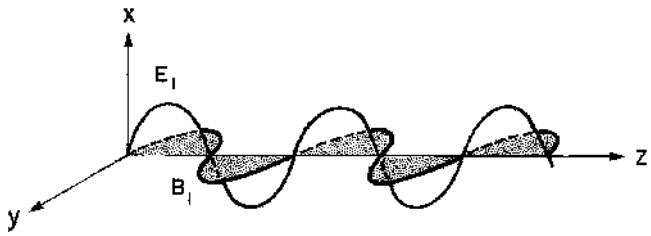

FIGURE 1.1 Instantaneous amplitudes of electric field ($\mathbf{E}_1$) and magnetic-field ($\mathbf{B}_1$) components in a propagating plane-polarized and monochromatic electromagnetic beam. We note that $\mathbf{E}_1$ is confined to plane *xz*, $\mathbf{B}_1$ is confined to plane *yz*, with wave propagation along **z**.

Both oscillate at some frequency ν, within the theoretical range 0 (DC) to infinity. For our purposes, in EPR, the commonly used frequency range is $10^9 - 10^{12}\,\mathrm{s}^{-1}$ (1–1000 GHz).

We must also consider the particulate nature of electromagnetic radiation in that it can be represented as a stream of particles called *photons*. These have no mass or net electrical charge but are to be thought of as wave packets having electromagnetic fields and a type of spin angular momentum. Furthermore, photons travel in observable directions, always at the speed of light; that is, they constitute light. The electric ($\mathbf{E}_1$) and magnetic ($\mathbf{B}_1$) components of the fields associated with them (see Appendix D) are generally perpendicular to each other and to the direction of propagation and oscillate in a narrow range centered at frequency ν.

The energy of any given photon is given by the quantity $h\nu$, where h is the famous Planck constant. When a photon is absorbed or emitted by an electron, atom or molecule, the energy and angular momentum of the combined (total) system must be conserved. For this reason, the direction of photon travel relative to the alignment of the photoactive chemical system is of crucial importance.

In most spectroscopic studies, other than magnetic resonance, it is the electric-field component of the radiation that interacts with molecules. For absorption to occur, two conditions must be fulfilled: (1) the energy ($h\nu$) of a quantum of radiation must correspond to the separation between certain energy levels in the molecule, and (2) the oscillating electric-field component $\mathbf{E}_1$ must be able to interact with an oscillating electric-dipole (or higher) moment. An example is gaseous HCl; molecular rotation of HCl creates the required fluctuation in the direction of the electric dipole along the bond. Likewise, infrared radiation interacts with the molecules in vibrational modes, dependent on the change in the electric-dipole moment magnitude with bond-length fluctuations. Similarly, a molecule containing a magnetic dipole might be expected to interact with the oscillating magnetic component $\mathbf{B}_1$ of electromagnetic radiation. This indeed is so and forms the basis for magnetic-resonance spectroscopy. Herein we are concerned with permanent dipole moments, that is, those that exist in the absence of external fields. However, in most magnetic-resonance experiments, a static magnetic field **B** is applied (in addition to $\mathbf{B}_1$) to align the moments and shift the energy levels to achieve conveniently measured splittings.

Each electron possesses an intrinsic magnetic-dipole moment that arises from its spin.[1] In most systems electrons occur in pairs such that the net moment is zero. Hence only species that contain one or more unpaired electrons possess the net spin moment necessary for suitable interaction with an electromagnetic field.

A magnetic-dipole moment in an atom or molecule (neutral or charged) may arise from unpaired electrons, as well as from magnetic nuclei. The magnetic-dipole moments of these particles in turn arise, respectively, from electronic or nuclear angular momenta. Hence one of the fundamental phenomena to be understood in EPR spectroscopy is the nature and quantization of angular momenta (see Section 1.6 and Appendix B).

1.2 HISTORICAL PERSPECTIVE

The technique of electron paramagnetic resonance spectroscopy may be regarded as a fascinating extension of the famed Stern-Gerlach experiment. In one of the most fundamental experiments on the structure of matter, Stern and Gerlach [3] in the 1920s showed that an electron magnetic moment in an atom can take on only discrete orientations in a magnetic field, despite the sphericity of the atom. Subsequently, Uhlenbeck and Goudsmit [4] (see also Ref. 5) linked the electron magnetic moment with the concept of electron spin angular momentum. In the hydrogen atom, one has additional angular momentum arising from the proton nucleus. Breit and Rabi [6] described the resultant energy levels of a hydrogen atom in a magnetic field. Rabi et al. [7] studied transitions between levels induced by an oscillating magnetic field. This experiment was the first observation of magnetic resonance.

The first observation of an electron paramagnetic resonance peak was made in 1945 when Zavoisky [8] detected a radiofrequency absorption line from a $CuCl_2 \cdot 2H_2O$ sample. He found a resonance at a magnetic field of 4.76 mT for a frequency of 133 MHz; in this case the electron Zeeman factor g is approximately 2 (Sections 1.7 and 1.8). Zavoisky's results were interpreted by Frenkel [9] as showing paramagnetic resonance absorption. Later experiments at higher (microwave) frequencies in magnetic fields of 100–300 mT showed the advantage of the use of high frequencies and fields.

Rapid exploitation of paramagnetic resonance after 1946 was catalyzed by the widespread availability of complete microwave systems following World War II. For example, equipment for the 9-GHz region had been extensively used for radar, and components were easily available at low cost. Almost simultaneously, EPR studies were undertaken in the United States (Cummerow and Halliday [10]) and in England (Bagguley and Griffiths [11]). Major contributions toward the interpretation of EPR spectra were made by many theorists. Important figures in this endeavor include Abragam, Bleaney, Pryce and Van Vleck. The early history of magnetic resonance has been summarized by Ramsey [12] and others.[2]

The state of the art has advanced on many fronts. In general, pulsed spin-excitation schemes and ultra-rapid-reaction techniques have now become not only feasible but almost commonplace. One remarkable accomplishment in recent years has been the

observation of an EPR signal from a single electron held in space by a configuration of applied electric and magnetic fields (in a so-called Penning trap) [15].

1.3 A SIMPLE EPR SPECTROMETER

The use of a magnetic field is the unique aspect of magnetic-dipole spectroscopy. We shall illustrate the effect of the field and the components of a basic EPR spectrometer, but first we must consider the energy states of the chemical species being examined.

The simplest energy-level diagram for a particle of spin $\frac{1}{2}$ in a magnetic field is shown in Fig. 1.2. The levels are labeled with the symbols α and β, or with the numbers $M = \pm\frac{1}{2}$, to be defined. By varying the static field **B**, one may change the energy-level separation, as indicated. Resonant absorption occurs if the frequency is adjusted so that $\Delta U = h\nu$. Here ν is the center frequency of the source of incident radiant energy. The magnitude of the transition shown is the energy that must be absorbed from the oscillating $\mathbf{B}_1$ field to move from the lower state to the upper state. No numerical values appear on the qualitative diagram. We merely note that, for many simple unpaired-electron systems, resonance occurs at a field of about 0.3 T if ν is approximately 9 GHz. The variation of energy with magnetic field need not be linear, and more complex systems have additional pairs of energy levels.

The energies of the magnetic dipoles in a typical static magnetic field **B** are such that frequencies in the microwave region are required. A possible experimental arrangement for the detection of magnetic-dipole transitions is the microwave EPR spectrometer shown in Fig. 1.3*a*. An optical spectrometer is shown in Fig. 1.3*b* to suggest by analogy the function of components in the two spectrometers.

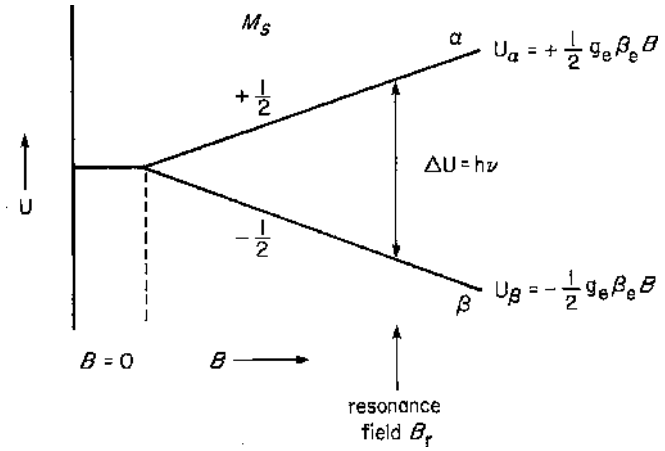

FIGURE 1.2 Energy-level scheme for the simplest system (e.g., free electron) as a function of applied magnetic field **B**, showing EPR absorption. U_α and U_β represent the energies of the $M = \pm\frac{1}{2}$ states. For electron spins, M is written as M_S. The constants g_e and β_e are defined in Section 1.7.

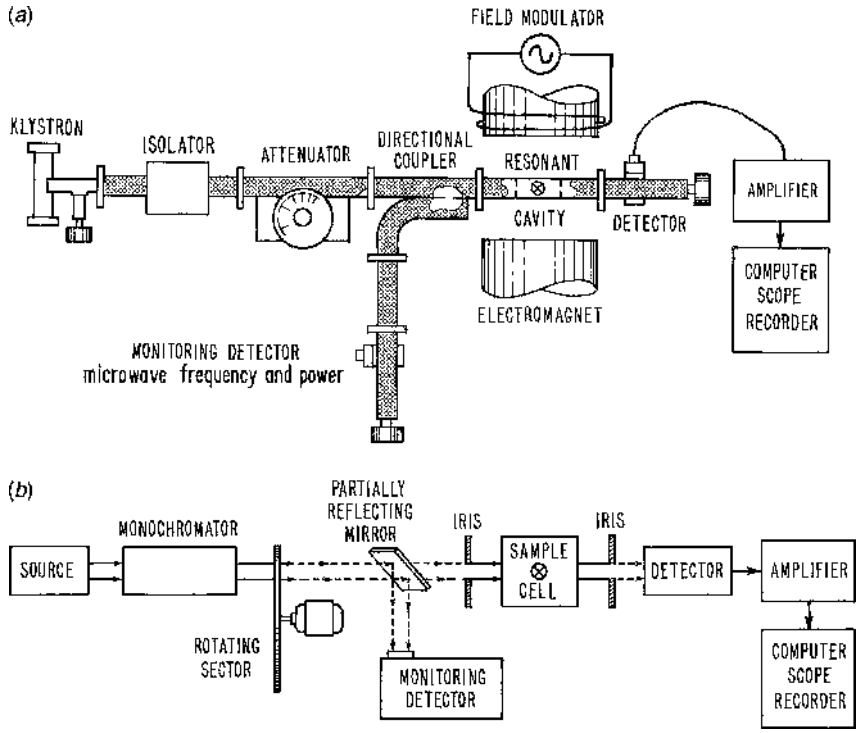

FIGURE 1.3 (*a*) Block diagram of a continuous-wave (cw) electron paramagnetic resonance (EPR) spectrometer; (*b*) block diagram of an optical spectrometer, where ⊗ denotes the sample. Note that there is a pair of irises in the end faces of the transmission cavity.

In either case, approximately monochromatic radiation falls on a sample in an appropriate cell, and one looks for changes in the intensity of the transmitted (or reflected) radiation by means of a suitable detector. Two primary classes of fixed-frequency spectrometers exist: either continuous or pulsed in the amplitude of $\mathbf{B}_1$. We shall now describe briefly the principal components of a simple EPR spectrometer. More details can be found in Appendix E.

Source. The frequency of radiant energy used in the majority of EPR spectrometers is approximately 9.5 GHz, in the medium-frequency microwave region. This frequency corresponds to a wavelength of about 32 mm. The microwave source is usually a klystron, which is a vacuum tube well known for its low-noise characteristics (see Appendix E). The field $\mathbf{B}_1$ is generated by oscillations within its own tunable cavity. In the range of about 1–100 GHz the mode of energy transmission is either by special coaxial cables or by waveguides. The latter are usually rectangular brass pipes, flanged to facilitate assembly of discrete components. In standard instruments, the microwave power is incident on the sample continuously (i.e., continuous wave, commonly abbreviated cw). Alternatively, in certain modern spectrometers, the power is pulsed.

In Fig. 1.3*a* and in Appendix E, in addition to the waveguide-connected klystron, there are other components; the most important are a resonator, a magnet and a detector. These components perform the following functions:

Resonator. This is most commonly a resonant cavity, which admits microwaves through an iris. The frequency of the source is tuned to the appropriate resonant frequency of the cavity. The corresponding resonant wavelengths are related to the dimensions of the cavity. One wishes to operate in a resonant mode that maximizes $\mathbf{B}_1$ at the location of the sample. At resonance, the energy density in the resonator may be thousands of times that in the waveguide, which maximizes the opportunity to detect resonant absorption in a sample. A recently developed loop-gap resonator has been advocated as an alternative to the usual resonant cavities for energy-dissipative samples (Appendix E).

Figure 1.3*a* features a transmission cavity, with separate input and output irises. In practice, a reflection cavity, in which a single iris fulfills both functions, is usually used.

Magnetic Field. In magnetic resonance experiments, the static magnetic field $\mathbf{B}$ usually must be very well controlled and stable. Variations of this field are translated into corresponding variations in energy separation ΔU. The magnitude of B may be measured and controlled by a Hall-effect detector. Since every absorption line has a non-zero width, one finds it convenient to use a scanning unit to traverse the region of field B encompassing the line. Unless B is uniform over the sample volume, the observed spectral line is broadened.

Detector. Numerous types of solid-state diodes are sensitive to microwave energy. Absorption lines can be observed in the EPR spectrum when the separation of two energy levels is equal to (or very close to) the quantum energy $h\nu$ of an incident microwave photon. The absorption of such photons by the sample in Fig. 1.3*a* is indicated by a change in the detector current.

The direct detection of the absorption signal, as in Fig. 1.3*a*, is possible only for samples containing an unusually high concentration of unpaired electrons; noise components over a wide range of frequencies appear with the signal, making its detection difficult. In the optical spectrometer (Fig. 1.3*b*), the signal-to-noise ratio may be improved greatly by chopping the light beam at a preselected frequency. This permits narrow-band amplification of the detected signal; hence noise components are limited to those in a narrow band centered at the chopping frequency.

In a typical fixed-frequency magnetic-resonance spectrometer, the role of the light chopper is taken by a field modulator to impose an alternating component on the static magnetic field $\mathbf{B}$ (Appendix E). This results in an alternating signal at the microwave detector that can be amplified in a narrow-band amplifier. Typically, the resulting signal is rectified and takes on a B dependence that resembles the first derivative of an absorption line. The shape of the absorption line often is fitted to a functional formula (e.g., gaussian, lorentzian or elaboration thereof; Appendix F) approximating its field or frequency dependence.

An alternative to detection of magnetic resonance via energy absorption is measurement of the direct change in the angular momentum of the spin system occurring as a

result of photon absorption [16]. Other means of detecting EPR lines continue to be developed but also remain unconventional. These include use of magnetic force microscopy [17], optical detection (e.g., of EPR absorption from a single molecule) [18] and use of a superconducting quantum interference device (SQUID) [19,20].

1.4 SCOPE OF THE EPR TECHNIQUE

In almost all cases encountered in EPR spectroscopy, the electron magnetic dipole arises from spin angular momentum with only a small contribution from orbital motion. Resonant absorption of electromagnetic radiation by such systems is variously called 'paramagnetic resonance', 'electron spin resonance' or 'electron paramagnetic resonance'. The term *resonance* is appropriate, since the well-defined separation of energy levels is matched to the energy of a quantum of incident monochromatic radiation. Resonant transitions between energy levels of nuclear dipoles are the subject of study in *nuclear magnetic resonance* (NMR) spectroscopy. The term *electron paramagnetic resonance* (EPR)[3] was introduced as a designation taking into account contributions from electron orbital as well as spin angular momentum. The term *electron spin resonance*[4] (ESR) has also been widely used because in most cases the absorption is linked primarily to the electron-spin angular momentum. Electron magnetic resonance (EMR) is an alternative. We note also that the term *paramagnetic resonance* was employed at the Clarendon Laboratory in Oxford, England, where much of the early inorganic EPR work was carried out. After considering the various options, we have decided to use the designation electron paramagnetic resonance since this encompasses all the phenomena observable by the technique.

In any given molecule or atom there exists literally an infinite set of electronic states that are of importance in optical spectroscopy. However, in EPR spectroscopy the energy of the photons is very low; hence one can ignore the multitude of electronic states except the ground state (plus perhaps a few very nearby states) of the species. The unique feature of EPR spectroscopy is that it is a technique applicable to systems in a paramagnetic state (or that can be placed in such a state), that is, a state having net electron angular momentum (usually spin angular momentum). The species exists either in a paramagnetic ground state or may be temporarily excited into a paramagnetic state, for instance, by irradiation. Thus, in principle, *all* atoms and molecules are amenable to study by EPR (see Section F.1). Typical systems that have been studied include

1. *Free Radicals in the Solid, Liquid or Gaseous Phases*. A free radical is herein defined as an atom, molecule or ion containing one unpaired electron. (Transition ions and 'point' defects in solids fitting this description are not normally called 'free radicals'.)
2. *Transition Ions Including Actinide Ions*. These routinely may have up to five or seven unpaired electrons (Chapter 8).
3. *Various 'Point' Defects (Localized Imperfections, with Electron Spin Distributed over Relatively Few Atoms) in Solids*. Best known in this class

is the *F* center (Fig. 4.2*a*), an electron trapped at a negative-ion vacancy in crystals and glasses. Deficiency of an electron (a 'positive hole') may also give rise to a paramagnetic entity.

4. *Systems with More than One Unpaired Electron*. Excluding ions in category 2, these include: (a) *Triplet-state systems*. Here the interaction between the two unpaired electrons is strong. Some of these systems are stable in a triplet ground state but most are unstable, requiring excitation, either thermal or usually optical, for their creation (Sections 6.3.4–6.3.6). (b) *Biradicals*. These systems contain two unpaired electrons that are sufficiently remote from one another so that interactions between them are very weak. Such a system behaves as two weakly interacting free radicals (Section 6.4). (c) *Multiradicals*. Such species (having more than two unpaired electrons) also exist.
5. *Systems with Conducting Electrons*. These (e.g., semiconductors and metals) are not treated extensively in this book.

EPR spectra may convey a remarkable wealth of significant chemical information. A brief summary of structural or kinetic information derivable from Figs. 1.4–1.6 foreshadows the diversity of the applications of the method. Each of these spectra is considered at a later point.

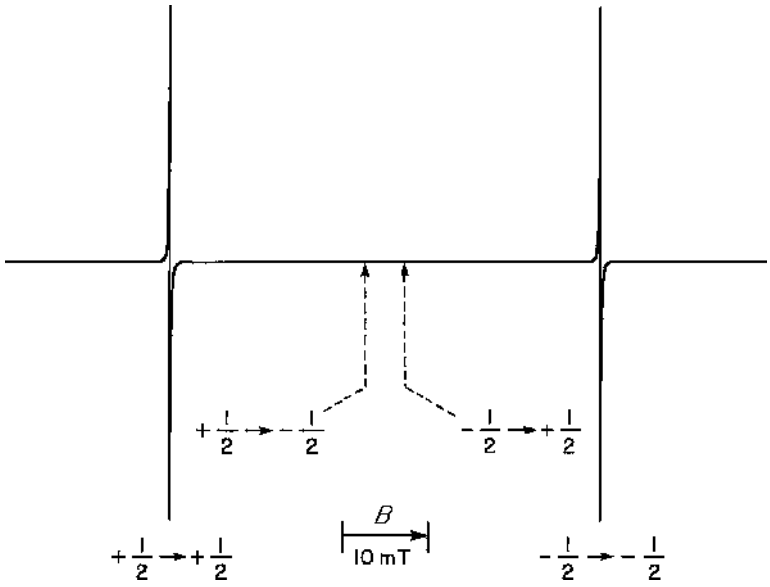

FIGURE 1.4 Simulated first-derivative EPR spectrum of a hydrogen atom (^{1}H) in the gas phase ($\mathbf{B} \perp \mathbf{B}_1$, $\nu = 10$ GHz). The quantum number M_I, denoting the EPR transitions, is defined in Chapter 2 and is consistent with $g_n > 0$. Note that two EPR transitions are allowed, occurring at $B = 329.554545$ and 380.495624 mT, and two transitions (dashed lines) are forbidden.

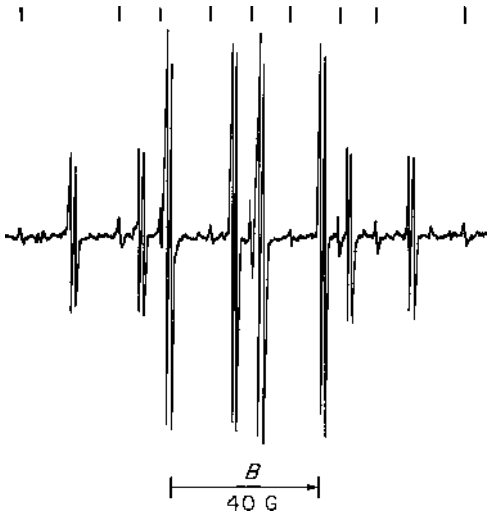

FIGURE 1.5 First-derivative EPR spectrum of the CH_3CHOH radical produced by continuous ultraviolet photolysis of a mixture of H_2O_2 and CH_3CH_2OH. The photolysis produces the OH radical, which then abstracts a hydrogen atom from the ethanol molecule. The weak lines, which are marked above the spectrum, arise from the radical CH_2CH_2OH. [After R. Livingston, H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966).]

Figure 1.4 presents a gas-phase EPR spectrum of hydrogen atoms (^1H). This simplest atom, since it has only one electron, of necessity has electronic spin $S = \frac{1}{2}$. Here the atom can exist in any one of four spin energy levels. One can think of the system as being composed effectively of two chemical 'species' (the proton has a spin $I = \frac{1}{2}$

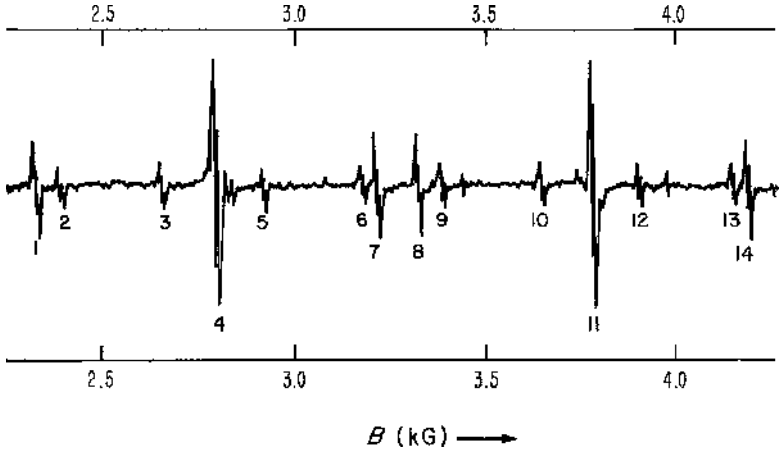

FIGURE 1.6 First-derivative EPR spectrum (9070 MHz) of XeF trapped in a single crystal of XeF_4 at 77 K. The numbered lines are examined in Problem 3.12. [After J. R. Morton, W. E. Falconer, *J. Chem. Phys.*, **39**, 427 (1963).]

and hence all atoms having the nuclear spin component $M_I = +\frac{1}{2}$ constitute one species and those with $M_I = -\frac{1}{2}$ constitute the other) giving rise to the two lines observed. As is usual, the lines are presented as first derivatives (dY/dB: see Sections E.1.6 and F.2.1) of the power absorbed by the spins. This system is treated extensively in Appendix C.

Figure 1.5 shows the liquid-phase EPR spectrum of the CH_3CHOH radical produced as a transient species via H-atom removal in the ultraviolet photolysis of a solution of H_2O_2 in ethanol. The photolysis produces the ·OH radical, which then abstracts a hydrogen atom from the ethanol molecule. This is an excellent example of the use of EPR spectra in the identification of radical intermediates in chemical reactions.

Figure 1.6 shows an EPR spectrum of species formed by γ irradiation of a single crystal of XeF_4; again the number, spacing and intensity of the lines provide identification of one xenon atom and one fluorine atom, that is, the unstable XeF molecule. Here the positive identification of xenon comes from the observation of lines arising from several of its isotopes occurring in natural abundance.

The proper interpretation of EPR spectra requires some understanding of basic quantum mechanics, especially that associated with angular momentum. A full understanding is best obtained by reconstruction of the spectrum from the parameters of the quantum-mechanical treatment. To understand an EPR spectrum, it is desirable to have a working acquaintance with the following topics:

1. Mathematical techniques such as operator[5] methods, matrix algebra and matrix diagonalization (summarized in Appendix A). These are required for the solution of the Schrödinger equation, for the representation of angular momentum by quantum numbers, and for relating vectors (e.g., angular momentum and the magnetic moment) (Appendix B).
2. Familiarity with the operation of microwave magnetic-resonance spectrometers, including interfacing with computers (Appendixes E and F).

The elementary aspects of these topics are treated where needed in the text or in appendixes. *Even the reader who has had no previous training in quantum mechanics should be able to acquire considerable understanding of the fundamentals of electron paramagnetic resonance.* Indeed, we believe that this is a fine way to learn quantum mechanics! We shall undertake the development of the necessary background in a step-by-step fashion. Beyond this fundamental background, there are certain special areas of EPR that require particular background material:

1. Understanding of EPR requires an analysis of the energy levels of the system and of the influence of the surrounding environment on these levels. For example:
   a. The interpretation of EPR spectra of organic free radicals, π-electron free radicals, is aided by use of the elementary molecular-orbital approach due to Hückel (HMO approach; Chapter 9). In most cases more refined

theoretical treatments are necessary to obtain a completely satisfactory interpretation of the data.

b. Understanding of transition-ion spectra requires knowledge of the splitting of orbital and spin energy levels by local electric fields of various symmetries (Chapter 8).

2. The properties of some systems are independent of orientation in a magnetic field; that is, they are *isotropic*. Most systems are *anisotropic*, and thus their energy-level separations and the magnitude of the observable properties depend strongly on orientation in the applied magnetic field. The description of systems showing anisotropic behavior usually requires that each spectroscopic property be described by six independent parameters. It is convenient to order these parameters in a symmetric 3×3 array known as a *matrix*. Each such matrix can be considered in terms of the intrinsic information provided by its numerical components that define a set of spatial coordinate axes (its principal-axis system) and a set of three basic numerical parameters (its principal values). Simple examples of matrices are given in Appendix A, and numerous other examples are encountered in the text.
3. Time-dependent phenomena, such as the formation or decay of paramagnetic species, molecular motions (e.g., internal rotation or reorientation by discrete jumps), changes in the population polarization of spin states and chemical or electron exchange, can affect EPR spectra in many ways. An analysis of these effects leads to information about specific kinetic processes (both internal and external). These various phenomena are described in Chapter 10.

The last two points (2 and 3 above) are related in that most free radicals in fluid solution of low viscosity exhibit simplified EPR spectra with narrow lines. These are characterized by parameters arising from an effective averaging of the anisotropic interactions by the (sufficiently) rapid molecular tumbling. Thus such solutions effectively act as isotropic media. The key requirement is that the characteristic time, inverse of the tumbling rate, must be much less than the *time scale* appropriate for the EPR experiment (Chapter 10). Fortunately, this condition is easily met in most fluids at moderate temperatures.

The simple spectra we examine in the next two chapters are of systems that are either inherently isotropic (e.g., the hydrogen atom) or are effectively isotropic by virtue of rapid molecular tumbling.

1.5 ENERGY FLOW IN PARAMAGNETIC SYSTEMS

It is important at an early stage to note how the appearance of EPR spectral lines, or even the ability to detect them, is dependent on energy flows in the chemical sample. This is depicted in Fig. 1.7, which shows the net flow beginning at the excitation source (photons, B_1) and ending in the thermal motions of the atoms including the surroundings of the paramagnetic sample.

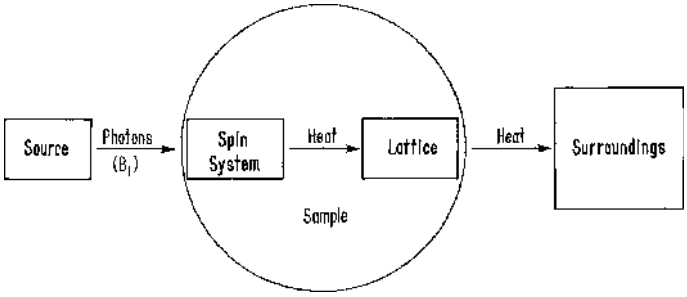

FIGURE 1.7 Energy flow in a magnetic-resonance experiment. The spin system is irradiated by a photon source (usually a microwave oscillator) at the frequency ν of $\mathbf{B}_1$. The absorbed radiation is lost by energy diffusion to the lattice at an exponential rate, which allows continuing absorption of photons to occur. Energy ultimately passes from the sample to the surroundings.

The reader seeking to understand some aspects of EPR spectra is likely to have encountered closely analogous phenomena in nuclear magnetic resonance. In optical spectroscopy one may use intense sources to irradiate in absorption bands without causing a significant temperature rise of the sample. But in many NMR samples, even at low power levels, the NMR signal amplitude diminishes as the radiofrequency power level (i.e., B_1) is increased. The same is true in many EPR samples as the microwave power is increased. For these samples one speaks of power saturation or alternatively of heating the spin system.

This behavior results from a limited ability of the sample to dissipate energy from its spin system to its internal thermal motions. The surroundings of the spin are commonly referred to as the 'lattice', regardless of the sample's physical state. Samples differ widely in their ability to relax to the ground spin state after absorbing a quantum of energy.

The coupling between the spins and the lattice is measured by a characteristic spin-lattice relaxation time τ_1 (Chapter 10).[6] The same symbol is used extensively in NMR systems, for which it was first defined. Efficient relaxation implies a sufficiently small value of τ_1.

The magnitude of the observed EPR signal is proportional to the net resultant (polarization) of the spin orientations of the set of paramagnetic species. The system is said to be saturated when the rate of upward and of downward transitions is equalized; then no net energy is transferred between $\mathbf{B}_1$ and the spin system.

If the electron spin-lattice relaxation time τ_1 is very long, one may have to make observations at very low microwave power to avoid saturation. In the opposite case of very short τ_1, lifetime broadening (Chapter 10) may be so great that the line is broadened beyond detection. This is a difficulty frequently observed with transition ions (Chapter 8). It is usually dealt with by taking spectra at very low temperatures, since the value of τ_1 tends to increase dramatically with decreasing temperature.

In addition to τ_1, there are a number of other 'relaxation' times defined to describe the linewidth. These are dealt with at appropriate places (e.g., Chapters 10 and 11) in this book.

1.6 QUANTIZATION OF ANGULAR MOMENTA

In quantum mechanics the allowed values of the magnitude of any angular momentum arising from its operator $\hat{\mathbf{J}}$ (Appendix B) are given by $[J(J+1)]$ where J is the primary angular-momentum quantum number ($J = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$). We adopt the usual convention that all angular momenta and their components are given in units of $\hbar$. The allowed values of the component of vector $\hat{\mathbf{J}}$ along any selected direction are restricted to the quantum numbers M_J, which range in unit increments from $-J$ to $+J$, giving $2J+1$ possible components along an arbitrary direction.

An example of the conditions described above is the spin angular momentum operator $\hat{\mathbf{S}}$ for a single electron that has a quantum number S with the value $\frac{1}{2}$. For systems of two or more unpaired electrons, S is $1, \frac{3}{2}, 2, \ldots$. The spin angular-momentum vectors and their projected components for $S = \frac{1}{2}$, 1 and $\frac{3}{2}$ are represented in Fig. 1.8. States with $S = \frac{1}{2}$ are referred to as *doublet states* since the multiplicity $2S+1$ is equal to 2. This situation is certainly of most interest, since it includes free radicals. States with $S = 1$ are called *triplet states* (Chapter 6). For paramagnetic ions, especially those of the transition ions, states with $S > \frac{1}{2}$ are common. EPR transitions do not alter the value of S.

The nuclear-spin angular-momentum operator $\hat{\mathbf{I}}$ is quantized in an exactly analogous fashion. The nuclear-spin quantum number is I (a non-negative number, which may be integral or half-integral).[7]

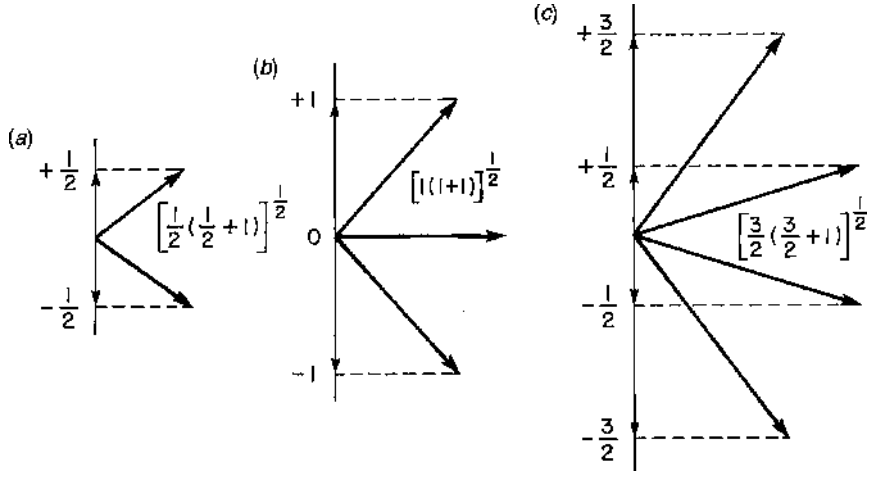

FIGURE 1.8 Allowed values (in units of) of the total spin angular momentum $[S(S+1)]^{1/2}$ and of its component M_S along a fixed direction (vertical line, e.g., B) for (*a*) $S = \frac{1}{2}$, (*b*) $S = 1$, and (*c*) $S = \frac{3}{2}$.

Very often we must consider a whole set of spin-bearing nuclei. Parameters such as the nuclear Zeeman factor, hyperfine coupling, or quadrupole factors, that determine line positions are required for each. In addition, there are other parameters (e.g., relaxation times) to define the lineshapes and intensities. Finally, one often is interested in the quantitative analytical aspects of EPR spectroscopy [21].

For the sake of simplicity, we shall often discuss and give examples of single-nucleus systems. When dealing with more than one unpaired electron, because of their mobility and delocalization, it is often useful and correct to work with a single total electron spin operator $\hat{\mathbf{S}}$ and a single Zeeman parameter matrix $\mathbf{g}$ associated with it.

In certain cases there may exist non-zero electronic (orbital angular momentum, designated by the quantum number L, which is a non-negative integer). Usually electron-spin and orbital angular momenta initially can be considered separately, later introducing a small correction to account for the 'spin-orbit' interaction. For systems containing light atoms (such as free radicals) that have essentially zero orbital angular momentum, the spin-orbit interaction is usually very small; hence for most purposes, attention may be focused wholly on the spin angular momentum. However, spin-orbit interaction must necessarily be included in discussion of the EPR behavior of transition ions (Chapters 4 and 8). Further details about angular momentum are to be found in Appendix B.

The notation we shall use in dealing with angular momenta (i.e., $J =$ any of S, I, L, ...) is that when there are several particles of one type (electron, nuclei, etc.), we shall append a subindex indicating the individual particle being considered. When no subindex is present, then it is the *total* angular momentum that is at hand. Thus for the operators one has

$$\hat{\mathbf{J}} = \sum_{i=1}^{N} \hat{\mathbf{J}}_i \tag{1.1a}$$

and for the component values one has

$$M_J = \sum_{i=1}^{N} M_{J_i} \tag{1.1b}$$

When $N = 1$, the index is omitted. At times a pre-superscript t will be attached to $\hat{\mathbf{J}}$ and M_J to emphasize 'total'.

1.7 RELATION BETWEEN MAGNETIC MOMENTS AND ANGULAR MOMENTA

The magnetic moment and angular momentum are proportional to each other, in both classical and quantum mechanics. An analog of an orbital magnetic dipole is a classical particle of mass m and charge q, rotating with velocity $\mathbf{v}$ (speed v) in a

circle of radius r, taken to lie in the xy plane. Associated with the circulating electric current i is a magnetic field equivalent to that produced by a point magnetic dipole. Such a dipole has a moment $i\mathcal{A}$ and is normal to the plane, where $\mathcal{A} = \pi r^2$ is the area of the circle. The effective electrical current i (charge flow per unit time) is $qv/2\pi r$. The magnetic moment points along the direction **z** perpendicular to the plane of the circle and is given by

$$\mu_z = i\mathcal{A} = \pm\frac{qv\pi r^2}{2\pi r} = \pm\frac{q}{2m}mvr = \frac{q}{2m}l_z \tag{1.2}$$

The sign choice depends on the direction of rotation of the particle. Here l_z is the orbital angular momentum of the particle about the axis z. The proportionality constant γ ($=q/2m$) is called the *magnetogyric ratio* (or sometimes the *gyromagnetic ratio*) and has units C $kg^{-1} = s^{-1}\,T^{-1}$ (Section 1.8). Factor γ converts angular momentum to magnetic moment. More generally $\gamma = gq/2m$, where g is the Zeeman (correction) factor. Thus, quantum mechanically, each integral multiple $\hbar$ of orbital angular momentum has an associated orbital magnetic moment of magnitude $\beta = |q|\hbar/2m = |\gamma\hbar/g|$. The latter equality is valid for particles when they are free, but must be generalized further when electric fields are acting on them [22].

We now return specifically to the free electron. The component μ_z of electron-spin magnetic moment along the direction of the magnetic field **B** applied along the direction **z** is

$$\mu_z = \gamma_e\hbar M_S = -g_e\beta_e M_S \tag{1.3}$$

where g_e is the free-electron g factor. The negative sign arises because of the negative charge on the electron and the choices of β_e and g_e as positive quantities (Eqs. 1.10 and 1.11).

1.8 MAGNETIC FIELD QUANTITIES AND UNITS

In this book, we shall use the Système International (SI) [23] for units of all parameters. This comprises use of the meter, the kilogram, the second and the coulomb, that is, the rationalized mksC scheme of units. Among other benefits, this system offers a convenient and self-consistent way of checking equations. Especially with regard to the units for electromagnetic parameters, there has been much inconsistency and carelessness in the EPR literature. We shall attempt herein to encourage appropriate usage.

The two magnetic-field vectorial quantities[8] **B** and **H** are related to each other via

$$\mathbf{H} = \mathbf{B}/\mu_m \tag{1.4}$$

where the permeability

$$\mu_m = \kappa_m\mu_0 \tag{1.5}$$

is expressed in terms of the permeability μ_0 of the vacuum and κ_m is a dimensionless parameter (unity for the vacuum) describing the (isotropic) medium considered. Subindex m labels the medium. Here

$$\mu_0 = 4\pi \times 10^{-7}\,\mathrm{J\,C^{-2}\,s^2\,m^{-1}} (= \mathrm{T^2\ J^{-1}\ m^3}) \tag{1.6}$$

is, of course, a universal constant; J denotes the unit *joule* (=kg $\mathrm{m^2 s^{-2}}$). The unit ampere A is just coulombs per second (C $\mathrm{s^{-1}}$). We see that the magnetic flux density (alias *magnetic induction*) **B** has dimensions and units *different* from those of the magnetic 'field' **H**. Nevertheless, the term 'magnetic field' (meaning **B**) is in almost universal usage in magnetic resonance; hence we shall continue to use the term *magnetic field* for the quantity **B**.[9] Specifically, the more fundamental quantity **B** has the unit of tesla (T = kg $\mathrm{s^{-1}\ C^{-1}}$), where

$$\begin{aligned} 1 \text{ tesla (T)} &= 1 \text{ kg } \mathrm{s^{-1}\ C^{-1}} \\ &= 1 \text{ J } \mathrm{C^{-1}\ m^{-2}\ s} \\ &= 1 \times 10^4 \text{ gauss (G)} \end{aligned} \tag{1.7}$$

We shall use for **B** either the unit of tesla or less frequently the unit of gauss. On the other hand, **H** has the derived unit of coulombs per meter per second (C $\mathrm{m^{-1}\ s^{-1}}$, which is identical to J $\mathrm{T^{-1}\ m^{-3}}$). One such unit is equal to $4\pi \times 10^{-3}$ oersted (Oe). The vector **H** measures the total magnetic field (externally applied from distant current-carrying conductors), plus contributions from any (almost) fixed and sufficiently close particles that may be present [24–26]. The vector **B** deals only with the former. It follows that $\mathbf{B} = \mu_0 \mathbf{H}$ when there are no neighbors (vacuum).

A very important quantity in this book is the magnetic-dipole moment μ, which has units of J $\mathrm{T^{-1}}$. The classical dipole moment can be regarded as being the 'handle' by which each magnetic species can change its energy, that is, its orientation in an external field **B**, by reacting to external magnetic excitation. The macroscopic collection of N such dipoles in a given volume V has the resultant macroscopic moment

$$\mathbf{M} = \frac{1}{V} \sum_{i=1}^{N} \boldsymbol{\mu}_i \tag{1.8}$$

per unit volume, called the *magnetization* (Section 10.3), which has units of J $\mathrm{T^{-1}\ m^{-3}}$ (the same as for **H**). **M** is thus the net magnetic moment per unit volume.[10]

Since the magnetic moments of nuclei, atoms and molecules are proportional to the angular momenta of these species, it is convenient to write each such proportionality factor as a product of a dimensionless g factor and a dimensioned factor (a conglomeration of physical constants) called the *magneton*. Thus typically

$$\boldsymbol{\mu} = \alpha g \beta \mathbf{J} \tag{1.9}$$

where β has the same units as vector $\boldsymbol{\mu}$; g is the magnitude of the electron Zeeman factor for the species considered, and $\mathbf{J}$ is the general angular-momentum vector. This is taken to be dimensionless (in units of $\hbar\, h = h/2\pi$), as its units (J s) have been incorporated into β; the factor α ($= \pm 1$) is defined below. The circumflex ($\hat{}$) is placed above symbols such as J and μ when it is desirable that these be interpreted as quantum-mechanical operators. Such operators can simultaneously be vectors.

For free electrons (i.e., single electrons *in vacuo*; see Eq. 1.3), $\alpha_e = -1$ and $\hat{\mathbf{J}}$ is the electron spin operator $\hat{\mathbf{S}}$, so that β becomes[11]

$$\beta_e \equiv \frac{|e|\hbar}{2\, m_e} = 9.27400949(80) \times 10^{-24}\ \text{J T}^{-1} \tag{1.10}$$

which is called the *Bohr magneton*; e is the electronic charge, $2\pi\hbar = h$ is Planck's constant, and m_e is the mass of the electron (Table H.1). The Zeeman splitting constant (2006 measurement [28]) for the free-electron Zeeman factor

$$g_e = 2.0023193043617(15) \tag{1.11}$$

is one of the most accurately known of the physical constants. For those readers with masochistic tendencies, we furnish some references [29–31] to the quantum electrodynamic theory of the electron magnetic moment, which has been spectacularly successful in matching the observed value of g_e (Eq. 1.11), and continues to evolve with ever-increasing sophistication; the plain symbol g is utilized when electrons interact with other particles, in which case $g \neq g_e$.

There is an instructive area of EPR spectroscopy, or at least a close relative thereof, one that features electrons in a vacuum circulating normal to a large magnetic field: the electron beam in a synchrotron storage ring. Here, in applying the theory, the choice of coordinate system [fixed laboratory, or moving with the electron(s)] is important, and the macroscopic orbital motion enters appreciably together with the spin dynamics, in setting up the observed g factor. The equilibrium magnetic polarization (distribution of spins among the two M_S states) is distinctive, and explains the continuous emission of spin-flip synchrotron radiation [32,33].

For nuclei, $\hat{\mathbf{J}}$ is the nuclear-spin operator $\hat{\mathbf{I}}$ and $\alpha_n = +1$. Here the *nuclear magneton* is defined (Table H.1) as

$$\beta_n \equiv \frac{|e|\hbar}{2m_p} = 5.05078343(43) \times 10^{-27}\,\text{J T}^{-1} \tag{1.12}$$

where m_p is the mass of the proton (^{1}H). Values of nuclear g factors g_n are given in Table H.4.

We next consider the magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathbf{B}$, where $\boldsymbol{\mu}$ may describe either a nuclear or an electron magnetic dipole. Its component μ_z along

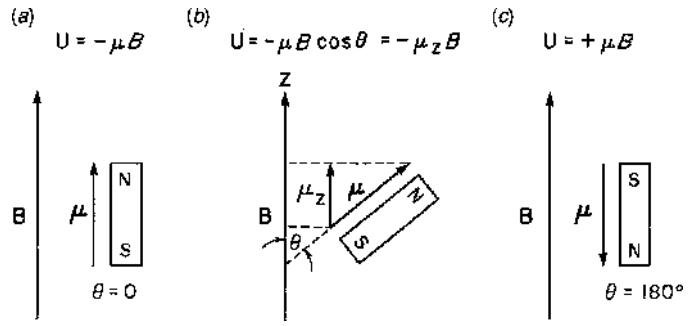

FIGURE 1.9 Energy of a classical magnetic dipole in a magnetic field as a function of the angle θ between the magnetic field and the axis of the dipole: (*a*) $\theta = 0$ (configuration of minimum energy); (*b*) arbitrary value of θ. (*c*) $\theta = 180^\circ$ (maximum energy).

B (taken along **z**) is generally defined as

$$\mu_z = -\left.\frac{\partial U}{\partial B}\right|_{B=0} \tag{1.13}$$

Here $U(B)$ is the energy of a magnetic dipole of moment $\boldsymbol{\mu}$ in a field **B**, and the use of the partial derivative symbols indicates that the only parameter to be varied is the field. In most situations, $\boldsymbol{\mu}$ may be defined in terms of its scalar product with **B**

$$U = -\boldsymbol{\mu}^{\mathrm{T}} \cdot \mathbf{B} \tag{1.14a}$$

$$= -\mathbf{B}^{\mathrm{T}} \cdot \boldsymbol{\mu} \tag{1.14b}$$

$$= -|\mu \mathrm{B}| \cos(\mu, \mathbf{B}) \tag{1.14c}$$

where $(\boldsymbol{\mu}, \mathbf{B})$ represents the angle between μ and **B**.[12] The form given in Eq. 1.14*b* proves to be advantageous in our future usage. For a given value of **B**, there is a minimum energy $-|\mu B|$, which occurs when $(\mu, \mathbf{B})$ is equal to 0, that is, the dipole is parallel to the direction of **B** (Fig. 1.9*a*); the maximum energy $+|\mu B|$ occurs when $(\boldsymbol{\mu}, \mathbf{B}) = \pi$ (Fig. 1.9*c*); at intermediate angles, U lies between these two extremes (Fig. 1.9*b*).

1.9 BULK MAGNETIC PROPERTIES

Now consider a large ensemble of non-interacting (with each other) classical magnetic moments $\boldsymbol{\mu}$ in a uniform magnetic field **B**. If the mean interaction energy $-\mathbf{B}^{\mathrm{T}} \cdot \boldsymbol{\mu}$ is large compared with the thermal energy $k_b T$ (e.g., in a field $\sim$1 T and at 1 K), then practically all dipoles are aligned along the direction of **B** (corresponding to the case of minimum energy). Here k_b is Boltzmann's constant and T the absolute temperature. The resultant macroscopic magnetization **M** would be approximately equal to $N_V \boldsymbol{\mu}$, where N_V is the number of dipoles per unit volume.

However, $|\mu B/k_bT| \ll 1$ in almost all cases because the dipoles point in various directions. Thus the magnitude M is ordinarily several orders of magnitude smaller than $N_V\mu$, even for the relatively strong electronic magnetic dipoles.

Another equivalent approach to understanding these quantities is via the vector relation

$$\mathbf{H} = {\mu_0}^{-1}\mathbf{B} - \mathbf{M} \tag{1.15}$$

with the realization that $\mathbf{M} = \mathbf{M}(\mathbf{H})$ is dependent on the laboratory medium at hand, whereas $\mathbf{B}$ is based on the atom-free vacuum as the relevant medium.[13] Both $\mathbf{B}$ and $\mathbf{H}$ may be functions of the location of the observation point and/or of time. Usually, one can utilize the approximation that $\mathbf{M}$ is proportional to $\mathbf{H}$ (but not necessarily collinear with it), as seen in Eq. 1.15.

The magnetization $\mathbf{M}$ is related to the applied field $\mathbf{H}$ by a dimensionless proportionality factor χ_m, the rationalized volume magnetic susceptibility,[14] which can be evaluated by measuring the force on a macroscopic sample in an inhomogeneous static magnetic field [35,36]. The contribution to χ_m of a set of non-interacting magnetic dipoles in the simplest (isotropic) case is

$$\mathbf{M} = -\alpha[g/|g|]\,\chi_m\mathbf{H} \tag{1.16}$$

so that for electrons ($\alpha = -1$, $g > 0$), one has

$$\chi_m = \frac{M}{H} \tag{1.17a}$$

$$= \frac{M}{B/(\kappa_m\mu_0)} \tag{1.17b}$$

With assumption of equilibrium (i.e., Boltzmann distribution) [35, Sections 7.5 and 11.2; 37] and independent behavior of the members of the electron spin ensemble, this becomes

$$\chi_m = \frac{N_V\mu^2}{3k_bT}\,\mu_0 \tag{1.17c}$$

$$\equiv \frac{C}{T} \geq 0 \tag{1.17d}$$

where $\mu^2 = g^2{\beta_e}^2 S(S+1)$ and N_V is the number of magnetic species per unit volume. Here C is called the Curie law 'constant'. The quantity $\kappa_m = 1 + \chi_m$ is called the *relative permeability* (compared to free space). Typically, for Eq. 1.17*c*, $\chi_m \approx 10^{-6}$.

The literature abounds in the use of the next-best approximation, the Curie–Weiss law

$$\chi = \frac{C}{T - T_c} \tag{1.17e}$$

where T_c is a semi-empirical parameter giving a measure of spin-spin interaction (e.g., exchange) present.

In addition, there is a smaller additive but negative and (almost) temperature-independent contribution to χ_m, arising from the reaction in the motion and distribution of all electrons (and to a lesser extent of all nuclei) in the bulk sample to the applied field **B**. Note that, by definition, paramagnetic samples have $\chi_m > 0$ whereas diamagnetic samples have $\chi_m < 0$.

An example of the simplest paramagnetic case is a dilute ensemble of free radicals, each with one unpaired electron and having zero orbital angular momentum. The experimental determination of χ_m yields only the product $N_V\mu^2$; to obtain μ one must determine N_V from other data. EPR measurements allow N_V and μ to be determined independently.

Subindex m will generally be suppressed throughout the rest of this book.

1.10 MAGNETIC ENERGIES AND STATES

Since the individual-particle magnetic energy U is proportional to the magnetic moment (Eqs. 1.14), the quantization of spin angular momentum in a specified direction leads to the quantization of the energy levels of a magnetic dipole in a magnetic field. If the direction **z** is chosen to be along **B**, application of the expression $U = -\mu_z B$ to a 'spin-only' system and substitution of $-g_e\beta_e M_S$ for μ_z give a set of energies

$$U = g_e\beta_e B M_S \tag{1.18}$$

For a single unpaired electron, the possible values of M_S are $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence the two possible values of μ_z are $\mp g_e\beta_e$ and the values of U are $\pm\frac{1}{2}g_e\beta_e B$ (Fig. 1.2). These are sometimes referred to as the *electronic Zeeman energies*.

Adjacent energy levels are separated by

$$\Delta U = U_{\text{upper}} - U_{\text{lower}} \tag{1.19a}$$

$$= g_e\beta_e B \tag{1.19b}$$

$$= -\gamma_e \hbar h$$

corresponding to $|\Delta M_S| = 1$. Note that, in this simplest case, Δ_U increases linearly with the magnetic field as shown in Fig. 1.2 (where now $M = M_S$).

The states of magnetic systems, as indicated earlier, are generally finite in number. If all the states in a set have the same energy, they are said to be *degenerate*. Each state is labeled with whatever set of quantum numbers is suitable. Thus, for an unpaired electron system, the quantum number M_S is required (Eq. 1.18). As we shall see in Chapter 2 (also Section A.5.4), the Dirac notation $|M_S\rangle$ (or $\langle M_S|$) is often used. For a single electron, since $M_S = +\frac{1}{2}$ or $-\frac{1}{2}$, the notation $|\alpha(e)\rangle$ and $|\beta(e)\rangle$ is found to be convenient. When there are several spin-bearing particles in a magnetic species, then quantum numbers for each particle may be needed to

specify the spin state of the system. For every transition, both the initial state and the final state must be specified by sets of quantum numbers.

In atomic and molecular systems, no more than two electrons can occupy a given spatial orbital. This is expressed by the Pauli exclusion principle, which arises from the fact that electrons act quantum-statistically as fermions. When two electrons occupy any given orbital, their spin components (M_S) always have opposite sign, and their magnetic moments cancel each other. Thus filled orbitals are ineffective with respect to spin magnetism. An EPR signal will be observed only when at least one orbital in a chemical species contains a single electron, that is, is a semi-occupied atomic or molecular orbital (SOMO).

1.11 INTERACTION OF MAGNETIC DIPOLES WITH ELECTROMAGNETIC RADIATION

Transitions between the two electronic Zeeman levels may be induced by an electromagnetic field $\mathbf{B}_1$ of the appropriate frequency ν such that the photon energy $h\nu$ matches[15] the energy-level separation ΔU. Then from Eqs. 1.19 one has

$$\Delta U = h\nu = g_e \beta_e B \tag{1.20}$$

where B designates the magnetic field that satisfies the resonance condition (Eq. 1.20). A more formal derivation of Eq. 1.20, valid for $S = \frac{1}{2}$, is deferred until Chapter 2. Even for systems with $S > \frac{1}{2}$, the conservation of angular momentum imposes a selection rule of $|\Delta M_S| = 1$ to such transitions because the photon has one unit ($\hbar h$) of angular momentum. Thus there is a second requirement, other than Eq. 1.20, that must be met for a transition to take place.

Let us briefly think in terms of absorption and emission of individual photons by our unpaired-electron system. The photon has its spin component ($\pm \hbar h$) along or opposed to its direction of motion [38]. This corresponds to right and left circular polarization see App. D. The photon has no magnetic moment. For absorption, depending on its direction of approach relative to the axis of the electron spin, it can deliver either energy $h\nu$ and angular momentum (photon type σ) or merely energy (photon type π). To meet the energy requirement of Eq. 1.20, several photons can cooperate, but only one of type σ can be involved, in order to match the condition of total (photon + electron) angular-momentum conservation. The situation is shown in Fig. 1.10. Such two-frequency EPR experiments are not routine but have been carried out, for instance, using the stable organic free radical DPPH (see Section F.2.2 and Ref. 39). In the vast majority of EPR experiments, only a single photon (of type σ) is involved in each transition excited. We shall now restrict ourselves to considerations of such transitions. However, in more recent EPR work, multi-quantum phenomena have become ever more evident and important. These effects (e.g., development of new EPR lines) appear as the excitation field intensity B_1 is increased.

It is of organizational value to distinguish between experimental techniques that provide EPR signal intensities that are linear in B_1, the usual case, and those that are

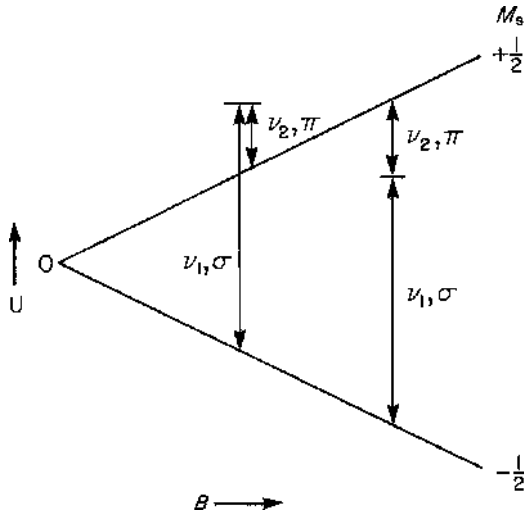

FIGURE 1.10 Energy levels for a $S = \frac{1}{2}$ system, as a function of applied magnetic field B, showing the (unusual) transitions induced when two excitation fields with two distinct frequencies are present. Photon types σ and π are discussed in the text.

not. The latter types include resonance line saturation, harmonic generation, multiquantum transitions, spin decoupling, intermodulation and longitudinal detection (some of which will be discussed later in this book).

The transitions between the Zeeman levels require a change in the orientation of the electron magnetic moment. Hence transitions can occur only if the electromagnetic radiation can cause such a reorientation. To make transitions possible, the electromagnetic radiation must be polarized such that the oscillating magnetic field has a component *perpendicular* to the static magnetic field (justification for this statement is given in Section C.1.4). The requirement of a suitable oscillating perpendicular magnetic field (i.e., σ photons) is easily met at microwave frequencies. If we apply the electromagnetic radiation polarized such that its oscillating magnetic field $\mathbf{B}_1$ is oriented parallel to the static magnetic field $\mathbf{B}$, then the effect of the radiation would merely cause an oscillation at frequency ν in the *energies* of the Zeeman levels. Generally no *reorientation* of the electron magnetic moment would occur. In this case no transitions are possible, unless certain other conditions (to be discussed; e.g., in Appendix C) are met.

From Eq. 1.20 one may infer that there are two approaches to the detection of resonant energy absorption (or emission) by a paramagnetic sample. In the first case, the separation of the Zeeman levels is fixed by holding the magnetic field constant; the microwave frequency is then varied until a resonant absorption is found. In the second case the microwave frequency is fixed; the magnetic field is then varied. Until recently, the second method has been the one of choice, because experimentally it was relatively easy to vary the field B (i.e., the current

in an electromagnet) but difficult and expensive to obtain microwave sources with wide frequency variability. The latter situation still holds; however, with the advent of pulsed microwave sources, it is now routine to work at fixed **B** and to utilize Fourier-transformation techniques to attain EPR spectra over modest frequency ranges. This subject is discussed in Section 11.4.

Everything that has been said about the electron-spin energy levels and transitions is also applicable to nuclear-spin systems. The nuclear Zeeman levels are given by an expression analogous to Eq. 1.18, namely, $U = -g_n\beta_n B M_I$; g_n is the nuclear g factor,[16] β_n is the nuclear magneton, and M_I is the component of the nuclear-spin angular-momentum vector in the z direction. In analogy to the electron-spin case, only dipolar transitions for which $|\Delta M_I| = 1$ (and I is unchanged) are allowed; hence

$$\Delta U = h\nu = |g_n|\beta_n B \tag{1.21}$$

The corresponding spectroscopic phenomenon for nuclei is commonly referred to as *nuclear magnetic resonance* (NMR).

Nuclear spins and magnetic moments are very important in EPR studies; the interactions of the unpaired electron(s) with magnetic nuclei give rise to the rich hyperfine structure that characterizes many EPR spectra.

1.12 CHARACTERISTICS OF THE SPIN SYSTEMS

1.12.1 The *g* Factor

It should be noted that the actual field at each spin species is not necessarily only the magnetic field $\mathbf{B}_{\text{ext}}$ applied externally to the sample. In addition to this, there may exist local fields $\mathbf{B}_{\text{local}}$ that add vectorially to the external field to produce the total field $\mathbf{B}_{\text{eff}}$ effective at the electron being considered. Thus [35, Eq. 3.104]

$$\mathbf{B}_{\text{eff}} = \mathbf{B} + \mathbf{B}_{\text{local}} \tag{1.22}$$

where the subindex ext has been suppressed (as is the usual practice). There are two types of local field: (1) those that are induced by **B**, and hence have a magnitude dependent on **B**; and (2) those that are permanent and independent of **B** except in their orientation.

For the moment consider only the first type, that is, the induced contribution to $\mathbf{B}_{\text{local}}$. Field B in Eq. 1.20 in principle should be replaced by B_{eff}; in practice it is much more convenient to retain the *external* magnetic field B. Then g_e must be replaced by a *variable g factor* (Section 4.8) that can and does deviate from g_e (according to the strength of $\mathbf{B}_{\text{local}}$). Thus we can write Eq. 1.22 as

$$\mathbf{B}_{\text{eff}} = (1 - \sigma)\mathbf{B} \tag{1.23a}$$

$$= (g/g_e)\mathbf{B} \tag{1.23b}$$

where σ is the EPR analog of the 'chemical shift' parameter σ_n used in NMR spectroscopy ($0 \leq \sigma^2 \ll 1$) and where g is the effective Zeeman factor used by EPR spectroscopists.[17] For now, we shall speak as if each magnetic species has a single unique g factor; however, we shall soon see that in fact each material exhibits a range of g factors. Many free radicals and some transition ions do have $g \approx g_e$, but there are many systems (e.g., many transition ions) that show marked deviations from this value (in some rare cases, g can be negative).

We note that incorporation of the generalized g factor into the magnetic moment (Eqs. 1.16–1.20) allows for a variable g to take account of field-induced local magnetic fields. For example, these local fields often arise from the orbital motion of the unpaired electron.

If it were not for the variation in g and the additional line structure contributed to $\mathbf{B}_{\text{local}}$ by various neighbor dipoles, EPR spectra would be very dull and uninteresting, consisting of a single line with $g = g_e$. In practice, these factors cause a multiplicity of fascinating and useful phenomena observable in EPR spectroscopy.

In most paramagnetic systems, there are so-called 'zero-field' terms in the energy that cause the resonance energy to be

$$h\nu = g\beta_e B + \text{terms} \tag{1.24}$$

At times, it is convenient to use an effective g parameter $g_{\text{eff}}(B)$ defined as

$$g_{\text{eff}} \equiv h\nu/(\beta_e B) \tag{1.25a}$$

$$= g + \text{terms}/(g\beta_e) \tag{1.25b}$$

We note that this type of g value (often found in the literature) is dependent on the magnetic field used (i.e., on the microwave frequency) and thus is far from being a constant (e.g., see Chapter 6).

There are many examples of systems for which the g factor is sufficiently distinctive to provide a reasonable identification of the paramagnetic species. Consider the spectrum of x-irradiated MgO (a cubic crystalline material) shown in Fig. 1.11 for a resonant frequency $\nu = 9.41756$ GHz. We seek to establish the origin of the very intense line to the right of the center of the spectrum. The weaker lines arise from Co^{2+} with effective spin $S' = \frac{1}{2}$, for which $g = 4.2785$ in this (isotropic) medium; the octet multiplicity of lines in this spectrum is due to magnetic (hyperfine) interaction with the ^{59}Co nucleus (100% natural abundance), which has spin $I = \frac{7}{2}$. This causes a type-2 contribution to $\mathbf{B}_{\text{local}}$. Substitution of the value 162.906 mT for the magnetic field B at the center of the intense line gives (using Table H.1) its electronic g factor as

$$g = \frac{h\nu}{\beta_e B} = \frac{(6.626069 \times 10^{-34}\ \text{J s})(9.41756 \times 10^{9}\ \text{s}^{-1})}{(9.27401 \times 10^{-24}\ \text{J T}^{-1})(0.162906\ \text{T})} = 4.1304 \tag{1.26}$$

where type-2 interactions are assumed (correctly) to be absent. A g factor of this size is unusual, and it gives an important clue as to the ion responsible for the intense

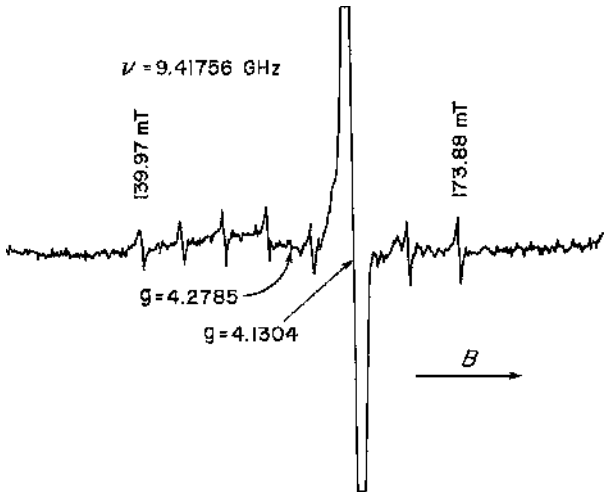

FIGURE 1.11 First-derivative EPR spectrum of Fe^{+} and Co^{2+} in MgO at 4.2 K, with microwave frequency 9.41756 GHz. The Fe^{+} spectrum consists of a single intense line at $g = 4.1304$ ($B = 162.906$ mT), while the Co^{2+} spectrum is an octet at $g = 4.2785$ arising from hyperfine splitting from the ^{59}Co nucleus, which has $I = \frac{7}{2}$. (Adapted from a spectrum supplied by Mr. F. Dravnieks.)

line. It is generally observed that isoelectronic ions (i.e., ions that have the same electronic configuration) in environments of similar symmetry have similar g factors. An ion that is isoelectronic with the $3d^7$ Co^{2+} ion is Fe^{+}. Considering the large deviation of both the g factors 4.2785 and 4.1304 from the free-electron g factor $g_e = 2.0023$, the two g factors may be considered similar enough to arise from isoelectronic ions. Hence the intense line is assigned to Fe^{+}. The disappearance of the Fe^{+} line (but not the Co^{2+} spectrum) on heating the crystal to 400 K is consistent with expectation for an unstable oxidation state. It should be mentioned that EPR lines for both the Fe^{+} and the Fe^{3+} ions may be observed in these crystals. It is typical of isoelectronic ions in an environment of similar symmetry that their EPR spectra are observable under comparable conditions. Neither Co^{2+} nor Fe^{+} exhibit a resonance line at 77 K, yet one does find strong absorption for both at 20 K and lower. This similarity is confirmatory evidence for the identification of Fe^{+}. Inability to see lines at room temperatures or even at 77 K is shown in Chapter 10 to be due to excessive broadening of lines as a result of their very short relaxation times (τ_1). One of the joys of EPR spectroscopy is that advanced quantum theory can predict (usually after the fact) what is observed. This is so for the g values of the $3d^7$ ions just described [40].

Media yielding EPR spectra that are truly isotropic[18] are relatively rare. They do include all cubic crystalline materials not distorted by impurities or external forces. As stated above, dilute liquid solutions of low viscosity effectively act as magnetically isotropic systems. Their isotropic behavior is the result of rapid, random

reorientation of the solute molecules. When such solutions are cooled sufficiently or even frozen, the EPR spectrum may consist of only a broad band. Such rigid solutions are 'isotropic', in that changing the sample orientation relative to the magnetic field **B** does not alter the EPR spectrum. However, the individual species responsible for it may well have anisotropic magnetic properties. It is with single-crystal systems that EPR reveals anisotropy, that is, dependence of the line positions and splittings on the crystal orientation relative to the magnetic field **B**.

It is *not* necessary to have an indefinitely large number of parameters to describe an anisotropic property quantitatively, in all directions. As stated earlier (Section 1.4), six parameters suffice. For our purposes, any physical system is deemed to have three mutually perpendicular inherent directions (principal axes) such that these, together with the results (principal values) measured along these directions, completely describe the anisotropic property. This is true for EPR line positions and splittings. Analogous statements may be made about other magnetic and optical properties (e.g., magnetic susceptibility, optical absorption behavior, or refractive index) of an anisotropic crystal.[19] The basic reason for this proliferation of parameters is that, for a general crystal orientation, the response is in a direction *different* from that of the applied stimulus.

Specifically, the simple resonance expression $B = h\nu/g\beta_e$ (Eqs. 1.20 and 1.24) with a single numerical value of parameter g is applicable only to systems that behave isotropically (and require no other types of energy terms). With anisotropic systems, variability of g with orientation relative to **B** is required. Thus (Eq. 1.23) the magnetic field $\mathbf{B}_{\text{eff}}$ effective on $\hat{\mathbf{S}}$ generally differs in direction from that of **B**. Furthermore, the resonant field value is a function of the field orientation relative to the crystal (or molecular) axes. For some purposes, it is convenient to append subscripts on g to specify the field orientation defining it. If the principal axes of the paramagnetic entity are labeled X, Y and Z,[20] g_X is to be interpreted for our simple case as $h\nu/\beta_e B_X$, that is, the g factor for **B** along the X axis of the magnetic entity. A detailed treatment of anisotropy in EPR spectra is developed in Chapters 4–6.

A truly isotropic system is one for which

$$g_X = g_Y = g_Z \tag{1.27}$$

On the other hand, for paramagnetic species in a liquid system of low viscosity, the measured (apparently isotropic) g factor is to be regarded as an effective value averaged over all orientations.

It is important to distinguish between a *space-averaged* and a *time-averaged* quantity. In the case of the paramagnetic species in solution, *each* entity exhibits a time-averaged response, and hence the resultant spectral line is narrow. However, if the averaging is spatial, as would be the case if a crystal were ground into a powder, each center exhibits its own resonance position, depending on its orientation, and the resultant spectrum is broad since the resonance is an envelope representing a weighted distribution of all possible resonance fields.

We now comment on the functional dependences of parameters, such as g factors and hyperfine splitting factors a, which describe the paramagnetic species and that

are needed to characterize EPR spectra. These parameters (often called 'constants') are functions of many factors (temperature, pressure, solvent or crystal surroundings; impurity content of the host; nature of the molecular or lattice vibrations in solid media, presence of any externally applied electric fields; etc.). These do not show any dependence on B for the usual magnetic fields applied. In principle, all these variables should be specified when values of parameters are reported. Further parameters, namely, those that describe the inherent lineshapes (lineshape function, linewidth and other 'moments') and the intensity of (area below) each line (which is proportional to the concentration of the paramagnetic species in the sample) must also be given. These, of course, depend in part on the instrumental settings.

The primary variables in EPR spectroscopy are either the magnetic field B or the frequency ν of the continuously applied exciting radiation.[21] When B is scanned at various fixed values of ν, the Zeeman terms (g factors) yield line positions proportional to B, whereas splittings of hyperfine multiplets tend to be independent of B.

Clearly, to obtain an EPR spectrum having appreciable intensity requires the presence of a large number of unpaired-electron species in the sample (Sections 4.6 and F.2.2). On the other hand, if the spin concentration in the sample is too high, the spins interact appreciably with each other, and this alters the nature of the EPR spectrum observed. The realm between these limits, which we term the 'magnetically dilute sample', is the one dealt with throughout most of this book. In other words, we consider each paramagnetic species to act independently of all others (but see Chapters 6 and 9).

1.12.2 Characteristics of Dipolar Interactions

As discussed earlier, if the interaction of unpaired electrons with externally applied homogeneous magnetic fields were the only effect operative, then all EPR spectra would consist of one line. The primary information to be garnered from these spectra would be the line positions, that is, the g factors. The EPR technique would thus provide rather limited information. Fortunately, other interactions can produce spectra rich in line components, offering a wealth of detailed information about the species studied.

Specifically, the magnetic-resonance spectrum of a dipole is very sensitive to the orientation of all other nearby magnetic dipoles (electronic or nuclear). These dipoles generate local magnetic fields that add vectorially and contribute to the local field $\mathbf{B}_{\text{local}}$ in Eq. 1.22. This local field is of the second type, that is, either independent of the applied field (but not its direction) or only weakly dependent on it. An important characteristic of these neighboring dipoles is that the magnitude and direction of the local-field contribution depend on the spin state of the center containing the dipole. Consequently, the EPR spectrum is split into a number of lines, each corresponding to a specific set of spin states.

In EPR the unpaired electron may interact with neighboring nuclear-dipole moments with a resulting splitting of the resonance. This interaction, and the resulting splitting, is called nuclear *hyperfine interaction* and *hyperfine splitting*. The term

'hyperfine splitting' was first used in atomic spectroscopy to designate the splitting of certain lines as a result of such an interaction with magnetic nuclei. The hyperfine interaction may be either isotropic (orientation-independent) or anisotropic (dependent on the orientation of **B** with respect to a molecular axis). As we shall see, an anisotropic hyperfine interaction can be accompanied by a significant isotropic component, and both are measurable. Hyperfine interactions with one or more magnetic nuclei are dealt with in Chapters 2, 3 and 5.

If there are two or more unpaired electrons in sufficiently close proximity, similar splittings (often called *fine structure*) may occur. This case is discussed in Chapter 6. A high concentration of species with one or more unpaired electrons results in intermolecular interactions of the dipoles that usually leads to line broadening.

Since the electron magnetic moment is much larger than that of nuclei, electron-electron dipolar interactions (when present) are usually very strong and dominate the spectral features. This leads to complications in the EPR spectra, discussion of which we defer until later (Chapter 6). For this reason, and also because the preponderance of EPR work has been carried out on species containing only one unpaired electron, we shall first treat those species in which the dominant feature is hyperfine interaction.

It should be noted that it is possible to observe EPR transitions at zero magnetic field because often energy-level splittings caused by local magnetic fields of type 2 are present. All the fine-structure and hyperfine parameters, but not the g factors, can be measured by zero-field EPR [41], but of course one has no control over the level splittings. Thus the frequency of the excitation field $\mathbf{B}_1$ must be scanned to find the transitions, and this can be technically problematic.[22]

At this point, we can discern and summarize the major use of EPR spectroscopy. By measuring the spectral parameters of any paramagnetic species encountered, we can expect (in due time) not only to identify it, but also to deduce details of its structure, to characterize its location, orientation and surroundings, as well as to measure its concentration. It is a primary goal of this book to train the reader in the art and science of this capability.

1.13 PARALLEL-FIELD EPR

We have seen that, usually, the condition $\mathbf{B}_1 \perp \mathbf{B}$ must be met to excite EPR transitions. However, the situation $\mathbf{B}_1 \parallel \mathbf{B}$ in certain circumstances also leads to appreciable EPR lines.[23] A prime example, certain transitions of the hydrogen atom, is discussed in Appendix C. Here the transition (labeled F and M_F) is $|1, 0\rangle \leftrightarrow |0, 0\rangle$ and can be thought of as involving simultaneous and opposite flips of the electronic and nuclear spins, so that no angular-momentum transfer with the radiation field ($\mathbf{B}_1$) occurs. Another example, involving triplet-state molecules and 'half-field' transitions of type $|\Delta M_S| = 2$ (quantum number appropriate in the high-field limit) is to be found in Section 6.3.2; no nuclear spins are involved here. Both examples involve single-photon transitions.

Since the mid-1990s, parallel-field EPR has become better known and exploited. Thus, high-spin electron species with large zero-field parameters (D and E: see Chapter 6) can exhibit ordinary EPR transitions only at quite high fields, whereas parallel-field transitions are readily accessible and their analysis yields all the needed spin-hamiltonian parameters. This is so for transition-ion clusters (Cr_{12}, $S = 6$ [43]), exchange-coupled high-spin Fe^{3+} and nearby Cu^{2+} in beef heart cytochrome c oxidase [44], high-spin biological FeS clusters ($S \leq \frac{9}{2}$ [45]), and Mn^{3+} in oxidized manganese superoxide dismutase ($S = 2$ [46]). Obviously, parallel-mode EPR is having substantial impact in the study of biomedical systems.

1.14 TIME-RESOLVED EPR

Time-resolved EPR refers to the research area dedicated to the detection of spectra from magnetic species as soon as possible after their creation, say, by flash photolysis or pulse radiolysis (e.g., electron beams) [47–49]. Their immediate subsequent behavior also has been a prime topic of interest. The time scale achieved has been down to 10^{-7}s. Here one cannot scan or modulate the B field, but must sample a sufficiently large set of such fixed fields. ESE techniques also have been widely used. Clearly, highly efficient computer-based digital data storage and processing is a crucial aspect of such endeavors, and special instrumentation is required.

1.15 COMPUTEROLOGY

The electronic computer has, of course, had a huge impact on magnetic resonance spectroscopy, as it has everywhere else.

Solid-state devices and printed circuits form the backbone of all modern spectrometers. In EPR, they control and stabilize and scan and measure all magnetic fields and the excitation electromagnetic sources—continuous wave and pulsed. They control and set the sample temperatures, and the sequence of experiments can be computer-controlled; for example, automatic variation of single-crystal orientation can be done in the absence of the scientist. All spectra are stored digitally, and are displayed and adjusted at the operator's will.

Furthermore, virtually all the mathematics relevant to analysis of magnetic resonance is programmed and enabled on computers, allowing best-fit attainment of the parameters by comparison of the actual and simulated spectra (see Appendix F). Review articles covering spectral simulation are at hand [50,51].

One very important feature of EPR spectroscopy is that all parameters obtained experimentally can be made available and published, allowing generation of the spectra (line positions and relative intensities) at will. The actual modeling of these spin-hamiltonian data, using the increasingly advanced techniques of molecular quantum mechanics, can be done separately and later.

One negative aspect of all this computerology is that the EPR user is tempted to use the programs and to bypass the understanding in depth of the mathematical background. Hopefully the present text will help to assuage this situation.

1.16 EPR IMAGING

We cannot devote much space herein to the topic of EPR imaging, which is a developing sister to EPR spectroscopy. Certainly in the case of NMR, there has been a revolution where MRI has become a dominant applied aspect of that technique. With EPR imaging, there has been slow steady development. Some relevant references can be found herein in Section 13.6. It is as yet nebulous as to what the future holds for the importance of this technique, but the EPR community is hopeful.

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NOTES

1. In truth, no one knows what an electron or a photon, and its spin, *really* is, but scientists and engineers can work wonderfully with these concepts. In relativistic quantum theory, it is postulated that the electron spin is a kind of orbital angular momentum associated with a very-high-frequency jitter motion (zitterbewegung) superimposed on its more classical 'time-averaged' trajectory [1,2]. The electron was discovered about 100 years ago, and has had a colorful history so far; for a good read, we recommend the book edited by Springford (see FURTHER READING).
2. An anectdotal colorful history of EPR has been included in an autobiography written by one of the prime sorcerers of its development [13] (see also Ref. 14).
3. The acronym EPR has more than 15 meanings. The predominant other use is the famed 'EPR paradox' of Einstein–Podolsky–Rosen (1935), which continues to be a source of fervent research regarding the root meaning of quantum mechanics. Often, the models used involve spatially separating two spin-paired electrons.
4. An example of a species showing transitions not appropriately described by the term *electron spin resonance* is O^{2-} in its ^1D state, which has two units of angular momentum about the internuclear axis but has zero spin angular momentum. Such entities may exhibit electron resonance in the gas phase (Chapter 7).
5. Mathematical operators are designated with a circumflex (e.g., $\hat{\mathcal{H}}$). A summary of the notation used herein for the symbols used can be found in Table I.1.
6. Many authors use the symbol T_1 for the spin-lattice relaxation time; we prefer the symbol τ_1 to avoid confusion with the symbol for temperature.
7. Note that $I = 0$ for all nuclei for which both the atomic mass number *and* the atomic number are *even*. If the atomic mass number is *even* and the atomic number *odd*, I is an integer (0, 1, 2, ...); if the atomic mass number is *odd*, I is a half-integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$).
8. When the directional aspects of quantities are of importance, we use vectors and designate these with **boldface** type. When only magnitudes or vector components are involved, we shall employ *italic* type. See Table I.1 herein.
9. Details about these quantities, as well as about the various systems of units used in the literature, may be found in the excellent treatise by Jackson [24]. The choice of which field quantity, **B** or **H**, is the more fundamental is a problematic and vexing one; see the classic book by Van Vleck [25].
10. In the quantum-mechanical treatment, **M** is the ensemble summation of the expectation value of the magnetic moment for each particle. Strictly speaking, Eq. 1.8 is not applicable as written, in that the right-hand sum should be replaced by the appropriate quantum-mechanical and statistical average of the operators μ_i [27].
11. The unfortunate IUPAC (International Union Pure and Applied Chemistry) recommendation of using the symbol μ_B for this quantity is not followed herein, since this latter symbol erroneously suggests the component of $\boldsymbol{\mu}$ along **B**. In cgs units, $\beta_e = |e|\hbar/2m_e c$.
12. The superscript "T" denotes taking the transpose of the vector; this operation is applicable when the vector specified is a row or column of components. The reader who is unfamiliar with these concepts or with scalar products is referred to Section A.4 and Table A.2.
13. For electric fields, the analogous equation $\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}$ is valid. Here **D** is the electrical displacement, **E** is the electric-field intensity (units of force/coulomb: $\mathrm{J\,C^{-}\,m^{-1}} = \mathrm{m\,s^{-1}\,T}$), and $\mathbf{P} = \mathbf{P}(\mathbf{E})$ is the electrical polarization. Electric susceptibilities are defined in exact analogy with the magnetic ones [25].

14. The volume magnetic susceptibility χ is an intensive (i.e., independent of sample amount) property and generally is anisotropic as well as dependent on the frequencies of any oscillating magnetic fields present (see Chapter 10). Here we have dropped the subscript m, which up to now has been used to indicate the medium. Scientists at times also use two related susceptibilities: $\chi_g \equiv \chi/\rho$ (where ρ is the mass density of the substance considered), and $\chi_M \equiv \chi_g m_M$ (where m_M denotes the molar mass of the substance considered). To convert from the older unrationalized cgs units to rationalized mksC (SI) units, multiply χ by 4π. Appropriate conversions between cgcC and mksC need, of course, also be done for all quantities. Susceptibility data in the literature should specify the type of χ at hand, whether it is rationalized or not, as well as (if relevant) the units used for ρ and m_M. Technically speaking, one should (in analogy with Eq. 1.13) utilize

$$\chi \equiv -\alpha \frac{g}{|g|} \frac{\partial M}{\partial H}\Big|_{H=0} \tag{1.28}$$

and also take into account anisotropy, perhaps via a series expansion of vector $\mathbf{M}$ in terms of $\mathbf{H}$, where the first term (i.e., linear in H) is $\boldsymbol{\chi} \cdot \mathbf{H}$, with tensor $\boldsymbol{\chi}$ independent of field magnitude H. We recall that, for electrons, we have $\alpha = -1$ and $g > 0$. Clearly also, by substituting $N_v \mu$ for $\mathbf{M}$, one can define and work with a molecular rather than a bulk magnetic susceptibility (e.g., see Ref. 34).

15. The term *resonance condition* refers to the maximum in a spectral line. Strictly speaking, however, every system absorbs (and emits) electromagnetic radiation over the entire frequency range. Thus $g\beta_e B/h$ represents the peak of a line that (usually) drops off rapidly toward zero, as described by a lineshape function. For the same reason, no truly monochromatic source of radiation exists at a given frequency ν; that is, all sources emit over an infinite band.
16. In this book, we shall ignore the nuclear chemical shift σ_n as being negligible and take the effective nuclear Zeeman factor $g_n(1 - \sigma_n)$ to be simply g_n, i.e., that of the bare nucleus, as tabulated in Table H.4.
17. This effect can be viewed classically; magnetic moment $-g_e\beta_e\mathbf{S}$ induces a (usually) small magnetic moment in its surroundings.
18. By *isotropic*, we mean that reorienting the sample relative to $\mathbf{B}$ and $\mathbf{B}_1$ has no effect on the EPR spectrum.
19. Anisotropy causes recasting of Eq. 1.16 to become $\mathbf{M} = -\alpha(g/|g|)\boldsymbol{\chi}_m \cdot \mathbf{H}$. Here the magnetic susceptibility $\boldsymbol{\chi}_m$ is a 3×3 matrix, as is the relative permeability $\boldsymbol{\kappa}_m = \mathbf{1}_3 + \boldsymbol{\chi}_m$, where $\mathbf{1}_3$ is the 3×3 unit matrix.
20. Henceforth, x, y and z are used for laboratory-fixed axes and X, Y and Z for inherent axes fixed with respect to the paramagnetic species.
21. With pulsed sources of the stimulating electromagnetic radiation, it is *time* (length and spacing of pulses) that is important (Chapter 11). The time and frequency domains are interconvertible via Fourier transformation.
22. The time dependence of $\mathbf{B}_1$ usually is sinusoidal, at constant frequency, but in principle the frequency can be modulated or scanned linearly with time. In this book, we will not always state explicitly whether a given $\mathbf{B}_1$ (or its magnitude B_1) should be deemed to be time-dependent or just the constant amplitude. This aspect depends also on the coordinate system chosen; see discussion on 'rotating frame' in Section 10.3.3.

23. Parallel-field paramagnetic absorption has been investigated from the beginnings of EPR [42].

FURTHER READING

Appendix G contains a fairly complete list of books and monographs dealing with EPR and related topics. The texts in this field that appear below are especially recommended.

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PROBLEMS

1.1 (***a***) Draw a continuous-wave (cw) NMR spectrometer analogous to the cw EPR and optical spectrometers shown in Figs. 1.3*a* and 1.3*b*.
(***b***) Describe the functioning of those NMR components that are significantly different from their EPR analogs.
(***c***) Contrast the frequency and field regions that are routinely accessible to the two techniques. To be sure, cw NMR is close to obsolete, but nevertheless is conceptually useful. It has been replaced by pulsed NMR, which techniques also exist for EPR (Chapter 11), but that have not been as widely accepted and used in the latter.

1.2 What is the numerical value ℓ_z of the angular momentum of a classical electron rotating in a fixed circular orbit of 1 Bohr radius ($r = 0.0529$ nm) with a frequency ν of 10^{13} Hz? Note that the magnitude ν of the linear velocity of a rotating particle is given by $\nu = r\omega$, where $\omega = 2\pi\nu$ is called the *angular frequency*. Compare ℓ_z with $\hbar h$, the natural quantum-mechanical unit of angular momentum. Discuss the difference.

1.3 The separation of two lines (splitting) in a free-radical EPR spectrum is given as 75.0 MHz, and $g = 2.0050$. Express the splitting in mT and in cm^{-1}.

1.4 Is it possible to obtain EPR spectra with NMR equipment? Assuming $g = 2.0050$, what magnetic field would be required to observe EPR at $v = 400$ MHz?

1.5 A classical magnetic dipole placed in a static magnetic field precesses about the magnetic-field direction with an angular frequency $\omega = 2\pi v$ given by $\omega = \gamma B$. Consider the electron to be such a particle.
(***a***) What is the magnetogyric ratio for a free electron?
(***b***) At what frequency v does this dipole 'precess' in a field $B = 350.0$ mT?
(***c***) What would be the value of g for an electron trapped in a negative-ion vacancy in KBr ($g = 1.985$)?

1.6 Calculate the ratio of the resonant frequencies of a free electron and a free deuteron (^{2}H) in the same magnetic field.

1.7 Using the data in Table H.4, compute the NMR frequency for a proton at the magnetic field used in X-band EPR (9.5 GHz) (this is the basis of a popular gaussmeter for measuring magnetic-field strengths).

1.8 Explain why one might wish to perform an EPR experiment on an unpaired-electron system as well as to determine separately its static magnetic susceptibility by force measurements; that is, what is the difference in information provided by the two measurements?