CHAPTER 2

MAGNETIC INTERACTION BETWEEN PARTICLES

2.1 INTRODUCTION

The first dipolar interaction to be considered is that of the electron-spin magnetic dipole with that of nuclei in its vicinity. It was noted in Chapter 1 that some nuclei possess an intrinsic spin angular momentum. The spin quantum number \( I \) of these nuclei is found to have one of the values \( \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots \), with a corresponding multiplicity of nuclear-spin states given by \( 2I + 1 \). Analogous to the electron case, there is a magnetic moment associated with the nuclear-spin angular momentum. The spins and magnetic moments of various nuclei are listed in Table H.4. For the present the discussion is restricted to species containing one unpaired electron (\( S = \frac{1}{2} \)), although much of this chapter applies equally well to species containing more than one unpaired electron (\( S > \frac{1}{2} \)).

The simplest system exhibiting nuclear hyperfine interaction is the hydrogen atom, which we first consider in a qualitative fashion. The details of the origin of the hyperfine interaction and the calculation of energy levels are discussed later in this chapter. The EPR spectrum of a hydrogen atom is shown in Fig. 1.4. As already mentioned in Section 1.12, instead of a single line characterized by \( B = h \nu / g \beta_e \) with \( g = 2.0022 \), one observes a pair of lines, which implies the presence of more than two spin energy levels. Since the proton has a spin \( I = \frac{1}{2} \), \( M_I \) has two allowed values: \( M_I = \pm \frac{1}{2} \). Hence at each position of the electron, there is one of
two possible local fields (Section 1.12.1) at which resonance occurs, that is

\[ B = B' - aM_I + \cdots = B' + \frac{a}{2} + \cdots \]  

(2.1)

where \( aM_I \) is \( B_{\text{local}} \) at the electron, and where \( B' = h\nu/g\beta_e \) is the would-be resonant field if the hyperfine parameter \( a \) were zero.\(^2\) In addition, there is a series of terms (indicated by \( \ldots \) in Eq. 2.1) of the form \( a^q/B^{q-1} \) with \( q = 2, 3, \ldots \). These become less and less important as \( B' \) increases relative to \( a \). These extra terms are considered later (Eq. 3.2; also Chapters 5 and 6, as well as Appendix C). For the free hydrogen atom, \( a = 50.684 \text{ mT} \), whereas at 9.5 GHz the spacing of the hyperfine doublet is 50.970 mT. We see here that, with such a large splitting, the above-mentioned correction is substantial. For most species (say, organic free radicals) the hyperfine parameters encountered are less than 1 mT (and \( g \approx g_e \)); hence the additional terms are sufficiently small that the spacing between hyperfine lines is well approximated by the parameter \( a \).

The astute observer may notice that there are four possible EPR transitions in Fig. 2.1 for the one-nucleus \((I = \frac{1}{2})\) system. Two of the transitions involve simultaneous nuclear-spin flips (shown as dashed lines in Fig. 1.4). For the free hydrogen atom these have negligibly small EPR transition probabilities as compared to the

\[ \text{FIGURE 2.1 Energy levels of a system with one unpaired electron and one magnetic nucleus with } I = \frac{1}{2} \text{ (e.g., the free hydrogen atom) as a function of magnetic field. The dashed-line transition would be observed if } a_0 \text{ were zero. The observed fixed-frequency spectrum (Section C.1.6 and Fig. 1.4) may be accounted for if the allowed transitions shown as solid lines are both drawn with the same length, since } h\nu \text{ is constant.} \]
pure transitions (solid lines in Fig. 2.1). Here, then, only two EPR transitions are observed. In general, however, with other hydrogen-containing radicals, for which only relatively small hyperfine interactions are involved, all four EPR lines can be present. This subject is considered in Chapter 5 and Appendix C.

2.2 THEORETICAL CONSIDERATIONS OF THE HYPERFINE INTERACTION

If the electron and nuclear magnetic dipoles were to behave classically and a substantial externally applied static magnetic field $B$ ($\|z\|$) were present so as to align them, then the energy of dipole-dipole interaction (Section 5.2) between them would be given by the following approximate expression:\(^3\)

$$U_{\text{dipolar}} = -\frac{\mu_0}{4\pi} \frac{3 \cos^2 \theta - 1}{r^3} \mu_n \mu_{ez} = -B_{\text{local}} \mu_{ez}$$  (2.2)

Here the components of the electron and nuclear dipole moments along the applied magnetic field $B$ are $\mu_{ez}$ and $\mu_{nz}$. The dipoles are separated by the distance $r$, and $\theta$ is the angle between $B$ and the line joining the two dipoles. This classical system is shown in Fig. 2.2. Depending on the value of $\theta$, the local field $B_{\text{local}}$ caused by the nucleus at the electron can either aid or oppose the external magnetic field. From Eq. 2.2 and Fig. 2.2 it is apparent that $B_{\text{local}}$, arising from the nucleus, depends markedly on the instantaneous value of $\theta$ (and of $r$).

It is clear from Eq. 2.2 that as the inter-particle distance $r$ approaches zero, the interaction energy approaches infinity. This does not pose a problem, largely because the probability of this type of superposition of particles is suitably small. Further mathematical details of this pathological situation have been discussed by
Skinner and Weil [1]. This type of ‘contact’ interaction, to be explored in this section and the next, is important (but not huge) in most cases.

Since the electron is not localized at one position in space, the interaction energy $U_{\text{dipolar}}$ must be averaged over the electron probability distribution function. If all regions of $\theta$ are equally probable (as for an electron in an $s$ orbital centered on nucleus $n$), then the average local field at each $r$ is obtained by inserting the value of $\cos^2 \theta$ averaged over a sphere into Eq. 2.2.

\[
\langle \cos^2 \theta \rangle = \frac{\int_0^{2\pi} \int_0^\pi \cos^2 \theta \sin \theta \ d\theta \ d\phi}{\int_0^{2\pi} \int_0^\pi \sin \theta \ d\theta \ d\phi} = \frac{1}{3}
\] (2.3)

into Eq. 2.2. In spherical polar coordinates, $\sin \theta \ d\theta \ d\phi$ is the element of surface area on a sphere. Since $\langle \cos^2 \theta \rangle = \frac{1}{3}$, $B_{\text{local}}$ in Eq. 2.2 vanishes. Consequently, the classical action-at-a-distance dipolar interaction cannot be the origin of the hyperfine splitting in the hydrogen atom since the electron distribution in a 1s orbital is spherically symmetric.

An understanding of the actual origin of the hyperfine interaction in the hydrogen atom may be obtained by examining the radial dependence of the hydrogen 1s orbital shown in Fig. 2.3. One notes that the 1s electron density at the nucleus (here taken to be a mathematical point) is non-zero; it is precisely this non-zero density that gives rise to the hyperfine interaction. It is clear from Fig. 2.3 that only electrons in $s$ orbitals have a non-zero probability density at the nucleus; $p$, $d$, $f$, ... orbitals all have nodes at the nucleus. On the other hand, electrons in 2s, 3s, ... orbitals also have a non-zero electron density at the nucleus and give rise to such hyperfine interactions. From Table H.4, column 7, the hyperfine interactions for valence $s$ electrons of some atoms are seen to attain very large values. By virtue of the spherical symmetry of $s$ orbitals, the hyperfine interaction in these cases is, of course, isotropic.

Fermi [3] has shown that for systems with one electron the magnetic energy for the isotropic interaction is given approximately by

\[
U_{\text{iso}} = -\frac{2\mu_0}{3} |\psi(0)|^2 \mu_{ez} \mu_{nz}
\] (2.4)

when the applied field $B (||z)$ is sufficiently large. Here $\psi(0)$ represents the electron wavefunction evaluated at the point nucleus. For example, the hydrogen atom ground-state wavefunction is given by

\[
\psi_{1s}(r) = \left( \frac{1}{\pi r_b^3} \right)^{1/2} \exp \left( -\frac{r}{r_b} \right)
\] (2.5)

where $r_b$ is the radius of the first Bohr orbit (52.9 pm). Using the probability density $|\psi_{1s}(0)|^2 = 1/\pi r_b^3$, one can then calculate a value of $U_{\text{iso}}$ with the aid of Eq. 2.4. This calculation, which provides an excellent approximation to the actual value, is the subject of Problem 2.3. In Section 2.4, we relate $U_{\text{iso}}$ to the hyperfine parameter $a$. Detailed consideration of hyperfine anisotropy is deferred to Chapter 5.
It is worthwhile noting that the above considerations hold for the hydrogen atom in its electronic ground state. EPR studies of the atom in any of its (infinite number of) excited states are, in principle, feasible and would yield different but analogous results. The same wealth of states is at hand for any of the molecular species treated in this book. Unless otherwise stated, only the electronic (and vibrational) ground state is dealt with. For examples of excited-state EPR, see Sections 6.3.4 and 6.3.5.

2.3 ANGULAR-MOMENTUM AND ENERGY OPERATORS

Before considering further details of the hyperfine interaction, it is instructive to introduce operator methods for determining the energies of a system of interest. In this chapter, we examine some relatively simple problems so that the reader
may become familiar with these techniques, which are also applicable to more complicated systems. The algebraic manipulation of operators is briefly described in Section A.2. General properties of spin operators are given in Appendix B. Their application to the hydrogen atom and to radicals of type RH₂, which exhibits hyperfine interaction with two equivalent protons, is given in Appendix C.

2.3.1 Spin Operators and Hamiltonians

For a system having discrete energy levels described by well-defined quantum numbers, it is always possible to write an eigenvalue equation; that is, if \( \hat{A} \) is the operator appropriate to the property under study, the eigenvalue equation (Eq. A.9) is

\[
\hat{A}\psi_k = \lambda_k \psi_k \tag{2.6}
\]

Here \( \lambda_k \) represents an eigenvalue of a state (labeled \( k \)) for which the eigenfunction is \( \psi_k \).

The topic of primary interest in EPR is the quantization of spin angular momentum. Hence one seeks a spin operator that operates on a function describing a spin state, causing it to be multiplied by a constant characteristic of that state. For a system with electron spin \( S = \frac{1}{2} \), the two states (\( k = 1,2 \)) are characterized by the quantum numbers \( M_S = \pm \frac{1}{2} \). These measure the components \( M_S \) of angular momentum along the direction \( z \) of the magnetic field, corresponding to the operator \( \hat{S}_z \). Thus, if \( \hat{S} \) is the angular-momentum operator, then its \( z \) component obeys Eq. 2.6, written as

\[
\hat{S}_z \phi_e = M_S \phi_e \tag{2.7}
\]

For simplicity here and below we omit the index \( k \). The factor \( M_S \) is called the eigenvalue of the operator \( \hat{S}_z \) and \( \phi_e(M_S) \) is the corresponding eigenfunction. We adopt the notation \( \alpha(e) = \phi_e(M_S = +\frac{1}{2}) \) and \( \beta(e) = \phi_e(M_S = -\frac{1}{2}) \), so that

\[
\hat{S}_z \alpha(e) = +\frac{1}{2} \alpha(e) \tag{2.8a}
\]

\[
\hat{S}_z \beta(e) = -\frac{1}{2} \beta(e) \tag{2.8b}
\]

Note that the angular momentum is taken in units of \( h \).

Similar expressions pertain to the nuclear-spin operator \( \hat{I}_z \) for a nucleus with nuclear spin \( I = \frac{1}{2} \) and \( z \) component \( M_I \):

\[
\hat{I}_z \alpha(n) = +\frac{1}{2} \alpha(n) \tag{2.9a}
\]

\[
\hat{I}_z \beta(n) = -\frac{1}{2} \beta(n) \tag{2.9b}
\]

The symbolism for the representation of an eigenfunction can readily be simplified. Since the functions are distinguished by their quantum numbers, one may enclose these numbers in a distinctive way to represent the function. Dirac suggested the notation \( |k \rangle \) for an eigenfunction \( \psi_k \). (A function represented in such a way is
called a ‘ket’; see Sections A.5.4 and B.4.) Then Eqs. 2.8 and 2.9 may be rewritten as

\[ \hat{S}_z |\alpha(e)\rangle = +\frac{1}{2} |\alpha(e)\rangle \]  
(2.10a)

\[ \hat{S}_z |\beta(e)\rangle = -\frac{1}{2} |\beta(e)\rangle \]  
(2.10b)

and

\[ \hat{I}_z |\alpha(n)\rangle = +\frac{1}{2} |\alpha(n)\rangle \]  
(2.11a)

\[ \hat{I}_z |\beta(n)\rangle = -\frac{1}{2} |\beta(n)\rangle \]  
(2.11b)

The energies \( U_k \) of systems, for which \( M_S \) and \( M_I \) are precise measures of components of electronic and nuclear-spin angular momentum, are obtained from the time-independent Schrödinger equation

\[ \hat{H}_e \phi_{ek} = U_{ek} \phi_{ek} \]  
(2.12)

\[ \hat{H}_n \phi_{nk} = U_{nk} \phi_{nk} \]  
(2.13)

Here the hamiltonian operator \( \hat{H} \) (which we consider commutes with \( \hat{S}_z \) as well as with \( \hat{I}_z \)) is the operator for the total energy. The index \( k \) is any one of the labels of the eigenstates of the system. The importance of Eqs. 2.12 and 2.13, taken together with Eqs. 2.8 and 2.9, is that the same \( \phi_k \) is an eigenfunction of the \( z \) component of the spin angular momentum and of the energy \(^7 \) (Section A.2.2).

Hence

\[ \hat{H}_e |\alpha(e)\rangle = U_{\alpha(e)} |\alpha(e)\rangle \]  
(2.14a)

\[ \hat{H}_e |\beta(e)\rangle = U_{\beta(e)} |\beta(e)\rangle \]  
(2.14b)

and

\[ \hat{H}_n |\alpha(n)\rangle = U_{\alpha(n)} |\alpha(n)\rangle \]  
(2.15a)

\[ \hat{H}_n |\beta(n)\rangle = U_{\beta(n)} |\beta(n)\rangle \]  
(2.15b)

It is often useful to express \( \hat{H} \) in a special reduced form. In general, the hamiltonian operator of a system is a function of the positions and momenta of all particles present (the spatial part), and of their intrinsic angular momenta (the spin part). Of necessity, since the hamiltonian contains spin operators, it is represented by a matrix (in quantum-mechanical state space) that is generated from angular-momentum matrices (Section B.5). Since the rules for setting these up are straightforward, it
is possible to construct the matrix $\mathcal{H}$ for any system, as long as one knows which spins (electrons and nuclei) are present.

The energy eigenvalues are obtained by integrating over all spatial variables to yield numerical parameters, leaving the spin part of the hamiltonian operator intact. The resulting entity, consisting of parameters and spin operators, is called a spin hamiltonian. This approach has proved to be very valuable, in that it enables measurement by magnetic-resonance techniques of the parameters $g$, $D$, $A$, ... to be introduced later. These can be tabulated in the scientific literature and can be used to reproduce the original EPR spectra in detail. Theoretical analysis, to interpret the parameters in terms of the spatial behavior of the electrons and nuclei, can be carried out separately, possibly at a later date as appropriate mathematical tools evolve. Thus spin-hamiltonian parameter sets can be regarded as storehouses of quantitative information about atoms and molecules. We use the same symbol $\hat{H}$ for the hamiltonian and the spin hamiltonian, but we take care with the explicit nomenclature to distinguish which of these is being considered.

As we shall see (Chapters 4–6), the spin-hamiltonian concept is especially suitable for description of EPR line positions and relative intensities of paramagnetic species in solids, but is also of major use in liquids. While originally developed for use with transition ions located in a symmetric environment (in certain salts), the spin hamiltonian is now utilized with all EPR-detectable species, inorganic and organic.

To obtain the energy values $U(B)$, in terms of the various parameters, one must solve the secular determinant of dimension $(2S + 1)P,(2I + 1)$. For sufficiently simple small determinants, this can be done analytically to yield algebraic equations for the eigenvalues. (e.g., see the solution of the hamiltonian matrix $\hat{H}$ for the hydrogen atom in Appendix C.) Failing that, when the numerical parameters in $\hat{H}$ are available, one can always diagonalize it numerically by computer to obtain the possible values of $U(B)$.

### 2.3.2 Electronic and Nuclear Zeeman Interactions

The first problem we treat with spin-operator methods is the interaction of an electron or a nucleus with a static magnetic field taken along some direction $z$, that is, we re-derive the resonance equation (Eq. 1.19) for a system with $S = \frac{1}{2}$ and also for a system with $I = \frac{1}{2}$. In operator form, Eq. 1.14b becomes

$$\hat{H} = -B^T \cdot \hat{\mu}$$

$$= -B \hat{\mu}_e \tag{2.16a}$$

$$= -B \hat{\mu}_n \tag{2.16b}$$

where we have chosen axis $z$ along $B$. We now use operator relations between the magnetic moment and the spin angular momentum. The electron magnetic-moment operator $\hat{\mu}_e$ is proportional to the electron-spin operator $\hat{S}_z$ (Eq. 1.9). Similarly $\hat{\mu}_n$ is
proportional to the nuclear-spin operator $\hat{I}_z$. Thus
\[
\hat{\mu}_{ez} = \gamma_e \hat{S}_z = -g \beta_e \hat{S}_z \tag{2.17}
\]
\[
\hat{\mu}_{nz} = \gamma_n \hat{I}_z = +g_n \beta_n \hat{I}_z \tag{2.18}
\]
The extension of Eqs. 2.17 and 2.18 leads to the definition of the electron and nuclear *spin-hamiltonian operators*
\[
\hat{\mathcal{H}}_e = +g \beta_e B \hat{S}_z \tag{2.19}
\]
\[
\hat{\mathcal{H}}_n = -g_n \beta_n B \hat{I}_z \tag{2.20}
\]
Note that the only operators in spin hamiltonians are those of spin. We shall find this type of formulation very useful in more complex situations. Now application of the spin hamiltonians of Eqs. 2.19 and 2.20 to the spin state functions (also called eigenfunctions) has the following results
\[
\hat{\mathcal{H}}_e |\alpha(e)\rangle = +g \beta_e B \hat{S}_z |\alpha(e)\rangle = +\frac{1}{2} g \beta_e B |\alpha(e)\rangle \tag{2.21a}
\]
and
\[
\hat{\mathcal{H}}_e |\beta(e)\rangle = +g \beta_e B \hat{S}_z |\beta(e)\rangle = -\frac{1}{2} g \beta_e B |\beta(e)\rangle \tag{2.21b}
\]
Similarly
\[
\hat{\mathcal{H}}_n |\alpha(n)\rangle = -g_n \beta_n B \hat{I}_z |\alpha(n)\rangle = -\frac{1}{2} g_n \beta_n B |\alpha(n)\rangle \tag{2.22a}
\]
and
\[
\hat{\mathcal{H}}_n |\beta(n)\rangle = -g_n \beta_n B \hat{I}_z |\beta(n)\rangle = +\frac{1}{2} g_n \beta_n B |\beta(n)\rangle \tag{2.22b}
\]
One may infer from Eqs. 2.21 and 2.22 that
\[
U_{\alpha(e)} = +\frac{1}{2} g \beta_e B \tag{2.23a}
\]
\[
U_{\beta(e)} = -\frac{1}{2} g \beta_e B \tag{2.23b}
\]
and
\[
U_{\alpha(n)} = -\frac{1}{2} g_n \beta_n B \tag{2.24a}
\]
\[
U_{\beta(n)} = +\frac{1}{2} g_n \beta_n B \tag{2.24b}
\]
Thus
\[
\Delta U_e = U_{\alpha(e)} - U_{\beta(e)} = g\beta_0 B = h\nu_e
\]
(2.25)
\[
\Delta U_n = U_{\beta(n)} - U_{\alpha(n)} = g_n\beta_n B = h\nu_n
\]
(2.26)

The resonance equation (Eq. 2.25) corresponds to transitions between the states \( |\beta(e)\rangle \) and \( |\alpha(e)\rangle \) (an EPR transition) and the next resonance equation (Eq. 2.26) (considering \( g_n > 0 \)) corresponds to transitions between the states \( |\alpha(n)\rangle \) and \( |\beta(n)\rangle \) (an NMR transition). Here \( h\nu_e \) and \( h\nu_n \) are the photon energies that stimulate the electronic and nuclear transitions.

A general procedure for determining the energy \( U \) from a given hamiltonian involves multiplication of both sides of Eq. 2.12 (and similarly Eq. 2.13) from the left by \( f_k/C_3 \)
\[
\int f_k/C_3 \hat{H} f_k \, d\tau = U_k \int f_k/C_3 f_k \, d\tau
\]
(2.28)
Hence
\[
U_k = \frac{\int f_k/C_3 \hat{H} f_k \, d\tau}{\int f_k/C_3 f_k \, d\tau}
\]
(2.29)
If the spatial functions \( f_k \) are normalized, that is, if they satisfy the condition
\[
\int f_k/C_3 f_k \, d\tau = 1
\]
(2.30)
then
\[
U_k = \int f_k/C_3 \hat{H} f_k \, d\tau
\]
(2.31)
One can say that the expectation value \( \langle \hat{H} \rangle \) is \( U_k \) for the energy of the system in its \( k \)th state.

It is appropriate to rewrite Eqs. 2.27–2.31 in the Dirac notation used in Eqs. 2.14 and 2.15. The symbol appropriate to multiplication from the left by \( f_k/C_3 \) is \( \langle \phi_k \rangle \) (Dirac called this function a ‘bra’). When \( \langle \phi_k \rangle \) is combined with the ket \( |\phi_k\rangle \), integration over the full range of all variables is implied. Thus the combination \( \langle \phi_k | \phi_k \rangle \), that is, \( bra[|]ket \), suggests the origin of the notation. Then Eq. 2.28 becomes
\[
\langle \phi_k | \hat{H} | \phi_k \rangle = U_k \langle \phi_k | \phi_k \rangle
\]
(2.32)
For normalized functions, Eq. 2.30 is

$$\langle \phi_k | \phi_k \rangle = 1$$  \hspace{1cm} (2.33)

and hence Eq. 2.31 is

$$U_k = \langle \phi_k | \hat{T} | \phi_k \rangle$$  \hspace{1cm} (2.34)

We see that the energy $U_k$ is the kth diagonal element of matrix $\hat{T}$. In dealing with spin hamiltonians, the bra-ket notation is the appropriate one, since there are no spatial variables to be integrated for spin states.

For the electronic and nuclear-spin states of our simple problem (Section 2.3.1), one writes

$$U_{\alpha(e)} = \langle \alpha(e) | \hat{T}_e | \alpha(e) \rangle = +\frac{1}{2} g \beta_e B$$  \hspace{1cm} (2.35a)

$$U_{\beta(e)} = \langle \beta(e) | \hat{T}_e | \beta(e) \rangle = -\frac{1}{2} g \beta_e B$$  \hspace{1cm} (2.35b)

and

$$U_{\alpha(n)} = \langle \alpha(n) | \hat{T}_n | \alpha(n) \rangle = -\frac{1}{2} g \beta_n B$$  \hspace{1cm} (2.36a)

$$U_{\beta(n)} = \langle \beta(n) | \hat{T}_n | \beta(n) \rangle = +\frac{1}{2} g \beta_n B$$  \hspace{1cm} (2.36b)

At this point, the reader who is interested in eigenfunctions and their manipulation may wish to turn to Section A.2.2, where the problem of a particle in a ring is considered in terms of both the angular-momentum operator and the energy operator.

### 2.3.3 Spin Hamiltonian Including Isotropic Hyperfine Interaction

Let us now consider the effects of the isotropic hyperfine interaction, deferring the anisotropic interaction until Chapter 5. The appropriate spin-hamiltonian operator may be obtained from Eq. 2.4 by replacing the classical magnetic moments by their corresponding operators (Eqs. 2.17 and 2.18). Following the same procedure as in the preceding section, one obtains the result

$$\hat{H}_{\text{iso}} = \frac{2\mu_0}{3} g \beta_e \beta_n |\psi(0)|^2 \hat{S}_z \hat{I}_z$$  \hspace{1cm} (2.37)

The factor multiplying $\hat{S}_z \hat{I}_z$ often is called the isotropic hyperfine coupling ‘constant’

$$A_0 = \frac{2\mu_0}{3} g \beta_e \beta_n |\psi(0)|^2$$  \hspace{1cm} (2.38)
which measures the magnetic interaction energy (in joules) between the electron and the nucleus. Hence Eq. 2.37 becomes

$$\hat{H}_{\text{iso}} = A_0 \hat{S}_z \hat{I}_z$$  \hspace{1cm} (2.39a)

When $B$ is along an arbitrary direction (or absent), $\hat{H}_{\text{iso}}$ should be expressed in its most general form

$$\hat{H}_{\text{iso}} = A_0 \hat{S}^T \cdot \hat{I}$$  \hspace{1cm} (2.39b)

Often the hyperfine coupling constant is given as $A_0/h$ in frequency units (MHz). It may also be expressed in magnetic-field units (Table H.4) and is then called the *hyperfine splitting* constant $a_0 = A_0/g_e \beta_e$. Strictly speaking, Eq. 2.37 should be written with the factor $\hat{S}^T \cdot \hat{I}$ in place of $\hat{S}_z \hat{I}_z$; however, it is shown in Section C.1.7 that when the hyperfine interaction $A_0$ is small compared to the electron Zeeman interaction $g_e B$, Eq. 2.37 is adequate.

The spin-hamiltonian operator for the hydrogen atom (and other isotropic systems with one electron and one nucleus with $I = 1/2$) is obtained by adding Eqs. 2.19, 2.20 and 2.39:

$$\hat{H} = g \beta_e B \hat{S}_z - g_n \beta_n B \hat{I}_z + A_0 \hat{I}_z \hat{S}_z$$  \hspace{1cm} (2.40)

This is valid when $B$ is sufficiently large. We note that the hyperfine term destroys the independence of the electron and nuclear spins. If more than one magnetic nucleus interacts with the electron, the terms in $\hat{I}_z$ are additive. Thus, summing over all nuclei yields

$$\hat{H} = g \beta_e B \hat{S}_z - \sum_i g_n \beta_n B \hat{I}_z + \sum_i A_{0i} \hat{S}_z \hat{I}_z$$  \hspace{1cm} (2.41)

The nuclear Zeeman energy (the second term) has been included in Eqs. 2.40 and 2.41 but has little effect on the transition energies, since the contributions from this term tend to cancel when the hyperfine terms (third terms on the right) are relatively large (e.g., in the hydrogen atom). This is not the case when the second and third terms give contributions of similar magnitude in anisotropic systems (Section 5.3.2.1).

### 2.4 ENERGY LEVELS OF A SYSTEM WITH ONE UNPAIRED ELECTRON AND ONE NUCLEUS WITH $I = 1/2$

This is the simplest case exhibiting hyperfine interaction, for which the hydrogen atom is the prototype. Since the eigenvalues $M_S$ of $\hat{S}_z$ are $+\frac{1}{2}$ and those of $\hat{I}_z$ are $M_I = +\frac{1}{2}$, there are four possible composite spin states; the kets are

$$|\alpha(e), \alpha(n)\rangle \quad |\alpha(e), \beta(n)\rangle \quad |\beta(e), \alpha(n)\rangle \quad |\beta(e), \beta(n)\rangle$$
Application of the spin operators \( \hat{S}_z \) and \( \hat{I}_z \) gives the following results

\[
\hat{S}_z |\alpha(e), \alpha(n)\rangle = +\frac{1}{2} |\alpha(e), \alpha(n)\rangle \quad (2.42a)
\]

\[
\hat{I}_z |\alpha(e), \alpha(n)\rangle = +\frac{1}{2} |\alpha(e), \alpha(n)\rangle \quad (2.42b)
\]

and so on for the other six combinations.

The energies of these states are obtained by evaluating expressions analogous to Eqs. 2.35 and 2.36; for example

\[
U_{\alpha(e), \alpha(n)} = \langle \alpha(e), \alpha(n) | \hat{\mathcal{H}} | \alpha(e), \alpha(n) \rangle
\]

\[
= \langle \alpha(e), \alpha(n) | g\beta_e B \hat{S}_z - g_n \beta_n B \hat{I}_z + A_0 \hat{I}_z \hat{S}_z + \cdots | \alpha(e), \alpha(n) \rangle
\]

\[
= +\frac{1}{2} g\beta_e B - \frac{1}{2} g_n \beta_n B + \frac{1}{2} A_0 + \cdots \quad (2.43a)
\]

Similarly

\[
U_{\alpha(e), \beta(n)} = +\frac{1}{2} g\beta_e B + \frac{1}{2} g_n \beta_n B - \frac{1}{2} A_0 + \cdots \quad (2.43b)
\]

\[
U_{\beta(e), \alpha(n)} = -\frac{1}{2} g\beta_e B - \frac{1}{2} g_n \beta_n B - \frac{1}{2} A_0 + \cdots \quad (2.43c)
\]

\[
U_{\beta(e), \beta(n)} = -\frac{1}{2} g\beta_e B + \frac{1}{2} g_n \beta_n B + \frac{1}{2} A_0 + \cdots \quad (2.43d)
\]

where the ellipses (\( \cdots \)) indicate terms that have been left implicit (Section 3.6). Neglecting these gives the so-called first-order energies. For the present case of \( S = I = \frac{1}{2} \), the mathematical energy problem has been solved exactly, as a function of the field \( B \), by Breit and Rabi [4]. The solution (Appendix C) can be expanded as an infinite series, the first terms of which are given explicitly in Eqs. 2.43. The energy levels are shown in Fig. 2.4a for a moderately high magnetic field, including the EPR transitions observable by scanning the frequency \( v \).

From these quantitative expressions for the energy levels, valid for sufficiently large \( B \), we note the (near) equality of splitting of each nuclear doublet. Second, we note that the ordering (\( M_I \)) of the levels is reversed in the lower set of levels as compared with the upper set. Since the one unit (\( h \)) of angular momentum in the absorbed photon is used to change the angular momentum of the electron, no change in the angular momentum of the nucleus is possible. However, in some cases it may be possible for more than one photon to be absorbed. We also note that, in the limit of \( B = 0 \), energy-level splittings arising from the hyperfine term remain, so that zero-field transitions at specific frequencies are observable when a suitable excitation magnetic field \( B_1 \) is applied. A notable example of this is the 1420 MHz emission from atomic hydrogen in outer space (see Sections 7.8 and C.1 and Problem 2.3).

The energies of these two allowed EPR transitions are

\[
\Delta U_1 = U_{\alpha(e), \alpha(n)} - U_{\beta(e), \alpha(n)} = g\beta_e B + \frac{1}{2} A_0 + \cdots \quad (2.44a)
\]

\[
\Delta U_2 = U_{\alpha(e), \beta(n)} - U_{\beta(e), \beta(n)} = g\beta_e B - \frac{1}{2} A_0 + \cdots \quad (2.44b)
\]
Note that the nuclear Zeeman terms cancel out. We examine these two EPR transitions under two conditions: constant magnetic field and constant frequency.

1. **Constant Magnetic Field \( B \).** When the frequency is swept and \( A_0 = 0 \), a single transition occurs at a frequency \( n = \hbar / g_e B \) (see the dashed transition mark in Fig. 2.4a). For non-zero hyperfine interaction, transitions occur at the two frequencies

\[
\begin{align*}
\nu_k &= \hbar^{-1}(g \beta_e B + \frac{1}{2} A_0 + \cdots) \quad (M_I = \frac{1}{2}) \quad (2.45a) \\
\nu_m &= \hbar^{-1}(g \beta_e B - \frac{1}{2} A_0 + \cdots) \quad (M_I = -\frac{1}{2}) \quad (2.45b)
\end{align*}
\]

(see transitions marked \( k \) and \( m \) in Fig. 2.4a). Note that each of the two transitions occurs between levels of identical \( M_I \) value. This corresponds to the selection rules \( \Delta M_S = \pm 1, \Delta M_I = 0 \) for EPR absorption. \(^{12}\)
2. Constant Microwave Frequency $\nu$. Here the magnetic field is swept slowly. When $A_0 = 0$, a single transition occurs at the resonant magnetic field $B' = \hbar \nu / g \beta_e$ (see the dashed transition in Fig. 2.4b). With $A_0 \neq 0$, EPR transitions occur at the two magnetic fields

\[ B_k = \hbar \nu / g \beta_e - A_0 / 2g \beta_e \cdots \quad (M_I = +\frac{1}{2}) \]  
\[ B_m = \hbar \nu / g \beta_e + A_0 / 2g \beta_e \cdots \quad (M_I = -\frac{1}{2}) \]  
(see transitions marked $k$ and $m$ in Fig. 2.4b).

The resonance equation becomes

\[ h \nu = g \beta_e B + A_0 M_I + \cdots = g \beta_e [B + (g_e / g) a_0 M_I] + \cdots \]  
(2.47)

Here

\[ a_0 = A_0 / g_e \beta_e \]  
(2.48)

is the hyperfine splitting constant (in magnetic-field units), and the factor $g_e / g$ represents the chemical shift correction (Eq. 1.22b). To first order, the hyperfine splitting is $(g_e / g) a_0$. For many free radicals, $g$ is sufficiently close to $g_e$ to allow neglect of the deviation from unity of the ratio $g / g_e$ in Eq. 2.47.

Finally, we note that with this chemical system, the other type of magnetic-resonance transition (i.e., NMR) also occurs. There are two pure NMR transitions, in which the electron-spin direction remains unaltered, but the nuclear-spin flips. Of more interest for our purposes are the electron-nuclear double-resonance (ENDOR) experiments, in which the two appropriate excitation magnetic fields are applied simultaneously (Chapter 12). A major advantage of this technique is the simplification of spectra, which facilitates analysis and measurement of spectral parameters for all unpaired-electron systems in which nuclear spins are present.

2.5 ENERGY LEVELS OF A SYSTEM WITH $S = \frac{1}{2}$ AND $I = 1$

The $^2$H (deuterium) atom is a simple example of a system with $S = \frac{1}{2}$ and $I = 1$. As in Section 2.4, the energy levels are computed using the spin-hamiltonian operator $\hat{H}$ (Eq. 2.40). There are now six spin states, which are represented by $|M_S, M_I\rangle$

\[
|+\frac{1}{2}, +1\rangle \quad |-\frac{1}{2}, -1\rangle \\
|+\frac{1}{2}, 0\rangle \quad |-\frac{1}{2}, 0\rangle \\
|+\frac{1}{2}, -1\rangle \quad |-\frac{1}{2}, +1\rangle
\]
These energies, given to first order by expressions analogous to Eqs. 2.43 (using the appropriate matrix elements—Section B.10), are

\[
\begin{align*}
U_{+1/2, +1} &= \frac{1}{2} g \beta_e B - g_n \beta_n B + \frac{1}{2} A_0 \\
U_{+1/2, 0} &= \frac{1}{2} g \beta_e B \\
U_{+1/2, -1} &= \frac{1}{2} g \beta_e B + g_n \beta_n B - \frac{1}{2} A_0 \\
U_{-1/2, +1} &= -\frac{1}{2} g \beta_e B + g_n \beta_n B + \frac{1}{2} A_0 \\
U_{-1/2, 0} &= -\frac{1}{2} g \beta_e B \\
U_{-1/2, -1} &= -\frac{1}{2} g \beta_e B - g_n \beta_n B - \frac{1}{2} A_0
\end{align*}
\]

(2.49)

By virtue of the selection rules \(\Delta M_S = \pm 1\) and \(\Delta M_I = 0\), there are three allowed EPR transitions. These are depicted in Fig. 2.5a; a typical first-derivative spectrum in an increasing magnetic field is shown in Fig. 2.5b. A spectrum of the deuterium atom trapped in crystalline quartz is shown as the middle three lines in Fig. 2.6 [5].

Under conditions of constant microwave frequency, transitions to first order occur at the resonant fields

\[
B_k = \frac{h \nu}{g \beta_e} - \frac{g_e}{g} a_0, \quad B_l = \frac{h \nu}{g \beta_e}, \quad B_m = \frac{h \nu}{g \beta_e} + \frac{g_e}{g} a_0
\]

(2.50)

**FIGURE 2.5**  
(a) Energy levels and allowed EPR transitions at constant field for an \(S = \frac{1}{2}\), \(I = 1\) atom (e.g., deuterium), for which \(A_0 > 0\); (b) simulated constant-frequency spectrum.
for $M_I = +1, 0$ and $-1$. These lines are of equal intensity since there is no coincidence of states, that is, all states are non-degenerate.

The extension to systems with $S = \frac{1}{2}$ and $I > 1$ is straightforward. For $I = \frac{3}{2}$, four transitions of equal intensity are observed. In general, for a single nucleus interacting with one unpaired electron, there are $2I + 1$ lines of equal intensity; adjacent lines are separated by the hyperfine splitting $a$.

In this chapter expressions have been obtained for the energy levels of systems in which a single electron interacts with one magnetic nucleus. In most free radicals the unpaired electron interacts with a number of magnetic nuclei.

For instance, when a hydrogen atom is trapped in a crystal structure in which its surrounding atoms have nuclear spins, then superhyperfine structure is resolved. In the case of CaF$_2$, there are eight nearest-neighbor F$^-$ ($I = \frac{1}{2}$) ions arranged at the corners of a cube, giving rise to such splittings (Fig. 2.7).

Examples of practical procedures for determining qualitative hyperfine splitting patterns, when more than one magnetic nucleus interacts with the unpaired electron, are given in the next chapter.

**FIGURE 2.6** X-band EPR spectrum of isotopically enriched atomic hydrogen trapped in x-irradiated $\alpha$-quartz at 95 K, presented in (almost pure) dispersion mode (Section F.3.5). The outer lines arise from $^1$H (Fig. 1.4) and the three inner lines, from $^2$H (Fig. 2.5). There are some unidentified lines present to the right of the central line. [After J. Isoya, J. A. Weil, P. H. Davis, *J. Phys. Chem. Solids*, 44, 335 (1983).]
2.6 SIGNS OF ISOTROPIC HYPERFINE COUPLING CONSTANTS

The sign of the hyperfine coupling constant determines the energy order of the zero-field levels. Thus for \( A_0 > 0 \) (e.g., atomic hydrogen — Fig. C.1a), the triplet \( |F = 1\rangle \) lies above the singlet \( |F = 0\rangle \). For \( A_0 < 0 \), the opposite would be true. Here the EPR spectrum is unaffected by the sign of \( A_0 \). However, in principle, at a sufficiently low field \( (B > 0) \) and temperature, the NMR spectrum would reveal the sign of \( A_0 \), since one of the two NMR lines would be of lower intensity.

For one-electron atoms, the hyperfine coupling is given by Eq. 2.38. Thus, in this simple case, the sign of \( g_n \) determines that of \( A_0 \). Physically, the sign of \( A_0 \) indicates whether the magnetic moments of the electron and nucleus tend to align parallel or antiparallel. Note that \( A_0 \) is a property of the spin system considered and does not depend on the direction or magnitude of any external magnetic fields present.

More generally, for multielectron systems, there is another factor, which takes into account a mutual unpairing interaction between the electrons; that is, an outer unpaired electron may cause inner electron pairs to exhibit spin polarization, either parallel or antiparallel to it. In molecules, there may be regions with either polarization. The net electron-spin polarization around any nucleus determines the sign of its \( A_0 \).

We can quantify these ideas by using a generalized expression

\[
A_0 = \frac{2\mu_0}{3}g_\beta g_n \beta_n \langle \rho_n \rangle
\]  

(2.51)

for the isotropic hyperfine interaction parameter at nucleus \( n \), appropriate for electronic state \( \psi \) of some atomic or molecular species. This allows us to take into account how each individual electron spin contributes at nucleus \( n \), with its direction.

![FIGURE 2.7](image-url) Room-temperature x-band EPR spectrum of interstitial hydrogen atoms in x-irradiated CaF\(_2\). The weak lines barely visible are ‘forbidden’, analogous to transitions \( b \) and \( c \) of Fig. 5.4. [The small central line arises from DPPH used as a \( g \) marker (Section F.4).] [After J. L. Hall, R. T. Schumacher, *Phys. Rev.*, 127, 1892 (1962).]
compared to the total electron-spin direction. In other words, expectation value 
\[ \langle \rho_s \rangle = \langle \psi | \hat{\rho}_s | \psi \rangle \] can contain both positive and negative contributions \[ | \delta_1^2 \] of individual 
electronic orbitals in \( \psi \) (Chapter 9); that is, it represents a competition at nucleus 
\( n \) between up-spin \( | \alpha \rangle_n \) and down-spin \( | \beta \rangle_n \) electrons. In the case of a single electron 
and nucleus, Eq. 2.51 reduces to Eq. 2.38. Finally, we note that \( \langle \rho_s \rangle \) represents a true 
density, having dimensions of volume\(^{-1}\). Thus \( \langle \rho_s \rangle \) is called the spin density, and is 
itself a probability density (see Note 9.1). Further details concerning this concept, 
and the spin-density operator \( \hat{\rho}_s \), are to be found in Chapters 5 and 9, as will the 
idea of unpaired-electron population.\(^{14}\)

Ordinary first-order EPR spectra yield only \( | A_0 | \), since peak-position terms \( A_0 M_I \) 
occur symmetrically with regard to \( \pm | M_I | \) (Figs. 2.4 and 3.1). Higher-order hyper-
fine correction terms (Section 3.6) can yield relative signs (i.e., of \( A_{0i}/A_{0j} \)) when 
more than one nucleus (i.e., \( i \) and \( j \)) is present and both give sufficiently large split-
tings. Various other circumstances and special techniques yielding sign information 
are discussed later in this book (see Sections 3.6, 5.2, 5.3.2, 6.7, 9.2.4–9.2.7 and 
10.5.5.1 and Problems 5.10 and 5.11).

2.7 DIPOLAR INTERACTIONS BETWEEN ELECTRONS

When two interacting spin moments arise from electrons, the ideas and theoretical 
aspects presented here remain valid. Of course, electrons are more mobile than 
nuclei and hence interact more readily so that exchange energy terms become 
important (Chapter 6). The magnitudes of the magnetic moments are about 2000 
times (i.e., \( \beta_e/\beta_n \)) greater for electrons due to the smaller electron mass, so that 
the dipolar interaction energy at any given inter-particle distance \( r \) (Eq. 2.2) 
is greater by this factor. The detailed discussion of systems with more than 
one unpaired electron is deferred to Chapter 6, in view of the complications cited 
above.

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NOTES

1. The average position of these lines (Fig. 1.4) corresponds to $g \approx 2$. This averaging procedure for obtaining the $g$ factor leads to an appreciable error when the separation of hyperfine lines is large, that is, $>1$ mT at $\nu = 10$ GHz (Section C.1.6).

2. Here we temporarily ignore (until Section 2.4) the small difference between $g$ and $g_e$. Subindex 0 indicates that we are dealing with an isotropic parameter; that is, the free hydrogen atom basically is spherically symmetric (and we neglect small deviations from this induced by $B$).

3. This equation is valid only if the applied field is much greater than the magnetic fields present at the two particles as a result of the hyperfine interaction (Section 5.3.2).

4. The average (expectation) value of a quantity $g(q)$ weighted by a probability function $P(q)$ is given by

$$\langle g \rangle = \frac{\int gP \, dq}{\int P \, dq} \quad (2.52)$$

Each integration is taken over the allowed range of $q$.

5. In addition to this assumption, throughout this book, we utilize the concepts of electron distributions (orbitals) as derived from non-relativistic quantum mechanics. The changes in viewpoint and (in general) small corrections obtained from relativistic (Dirac) theory are beyond the scope of this book (see Ref. 2).

6. Bare protons and neutrons are not point particles, but rather have non-zero size (radius $\approx 0.7 \times 10^{-3}$ nm). Each contains a complex mixture of quarks, which yields a total spin of $I = \frac{1}{2}$, and a very appreciable nuclear magnetic moment (see Appendix H). Electrons can travel through these (and all) nuclides.

7. This is a general property of linear operators $\hat{A}$ and $\hat{B}$ for which the commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is zero; that is, the operators commute (Section A.2).

8. It is often desirable to restructure the hamiltonian into a form that contains ‘pseudo-spin’ operators, formally describing sets of states and their energy levels, even in the absence of actual spins. These are also called ‘effective’ or ‘fictitious’ spins.

9. $\phi_k^*$ is the complex conjugate of $\phi_k$ (Section A.1).

10. In this book we use the convention that all parameters (e.g., $A_0$) in a spin hamiltonian are assumed to be in energy units. Division by $\hbar$ is required to convert to frequency units and by $g_eB_e$ to convert to magnetic-field units (e.g., mT or G).

11. Hydrogen atoms and other free radicals (e.g., methyl) can be obtained by (say) $\gamma$-irradiation of certain solids, and in some circumstances are quite stable even at room temperature (e.g., see Ref. 9).

12. The selection rules $\Delta M_S = 0, \Delta M_I = \pm 1$ apply in the case of NMR spectroscopy, that is, when the system is irradiated only at the nuclear resonance frequency.
13. For $I > \frac{1}{2}$ another energy term should be added in Eq. 2.40, and represents the nuclear electric quadrupole interaction (see Section 5.6). However, this does not affect the EPR lines of isotropic systems.

14. Spin densities and population distributions can be measured quantitatively by polarized neutron diffraction. Such work for nitroxide free radicals\(^{15}\) has been published by Schweizer and his group [6–8], and includes use of maximum-entropy reconstruction to generate projection maps.

15. Nitroxide is the name for species $\text{RR'N} \rightarrow \text{O} \leftrightarrow \text{RR'N}^+ \rightarrow \text{O}^-$, also known as the aminoxyl free radical. These and related numerous species (including nitric oxide $\text{N} \rightarrow \text{O}$ itself) are of major importance now in biomedical areas.

**FURTHER READING**


**PROBLEMS**

2.1  
\((a)\) Carry out the integrations indicated in Eq. 2.3 and verify the result.  
\((b)\) Compute $\langle \cos^2 \theta \rangle$ assuming that $\vec{\mu}_e$ and $\vec{\mu}_n$ are confined to a plane containing the magnetic field, for example, by setting $\phi = 0$. Assume that all values of $\theta$ are equally probable.

2.2  
Taking the value of $\mu_p$ for the hydrogen nucleus ($^1\text{H}$) from Table H.1, compute the local magnetic field at an electron 0.2 nm from a proton when $\theta = 0^\circ$ and again when $\theta = 90^\circ$. What assumption is made in applying Eq. 2.2?

2.3  
The experimental hyperfine coupling constant $A_0/h$ for the free hydrogen atom in its electronic ground state is 1420.40575 MHz, and $g = 2.0022838$. [The data were taken from MASER (microwave amplification by stimulated emission of radiation) experiments [10,11].] Compare the value of $A_0/h$ with that calculated using elementary quantum theory, that is, Eqs. 2.4 and 2.5. Can you give some reasons for the deviation (which can be represented by using a multiplicative correction factor $1 + \delta$ appended to Eq. 2.4)?

2.4  
The sodium nucleus ($^{23}\text{Na}$) has $I = \frac{3}{2}$.

\((a)\) Specify the possible spin eigenfunctions for the sodium atom in its electronic ground state ($^2S$).

\((b)\) Use the spin hamiltonian of Eq. 2.40 (neglecting the nuclear Zeeman term $\hat{H}_n$ therein) to derive expressions for the first-order energies of this spin system. What was assumed in using Eq. 2.40 and by neglecting $\hat{H}_n$?
(c) Derive expressions for the possible EPR transitions and draw energy-level diagrams similar to Figs. 2.4 and 2.5. Use $A_0$ taken from Table H.4 for this purpose.

2.5 Calculate the energy levels of a two-proton radical RH$_2$ (Section C.2) at sufficiently high magnetic fields, using the spin hamiltonian of Eq. 2.41. R is any suitable molecular group. Write the spin eigenfunctions as $|M_{S_i},M_I\rangle$, where $1M_I = M_{I_1} + M_{I_2}$ (where $M_{I_1}$ and $M_{I_2}$ are the quantum numbers for the $z$ components of the nuclear-spin angular momenta of protons 1 and 2). Plot the energy levels as a function of magnetic field (as in Problem 2.4) and indicate the allowed transitions and their relative intensities.

2.6 The EPR spectrum in Fig. 2.6 of hydrogen atoms trapped in a quartz crystal was taken at 9.94186 GHz. The $^1$H doublet lines occur at 326.857 and 378.913 mT. Estimate the line positions of the $^2$H triplet. Assume that $g = 2.002117$ for both species, and that high-field conditions pertain.