CHAPTER 6

SYSTEMS WITH MORE THAN ONE UNPAIRED ELECTRON

6.1 INTRODUCTION

Nearly all the species considered in previous chapters had only one unpaired electron (viz., $S = \frac{1}{2}$). In principle, an EPR spectrum is obtainable for any system with an odd number of electrons ($S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$). For systems with an even number of electrons ($S = 1, 2, 3, \ldots$), there is no such guarantee; however, as we shall see, many systems of the latter type are accessible to EPR spectroscopy.

We begin by considering the theory of systems with two unpaired electrons, initially ignoring all nuclear spins.¹ Such systems include (1) atoms or ions in the gas phase (e.g., oxygen atoms), (2) small molecules in the gas phase (e.g., O$_2$), (3) organic molecules containing two or more unpaired electrons (e.g., naphthalene excited to its metastable triplet state) in solid-state solutions and crystals, (4) inorganic molecules (e.g., CCO in rare-gas matrices), (5) ‘point’ defects in crystals containing more than one unpaired electron (e.g., the $F_\ell$ center in MgO), (6) biradicals in fluid solution and the solid state and (7) certain transition-group (e.g., V$^{3+}$ and Ni$^{2+}$) and rare-earth ions. Systems 1 and 2 are dealt with in Chapter 7.

In all chemical species, if the highest occupied electronic level is orbitally non-degenerate and is doubly occupied by electrons, the ground state must be a spin singlet (Fig. 6.1a). If one of these electrons is excited to an unoccupied orbital by absorption of a quantum of the appropriate energy (Fig. 6.1b), the system is still in a singlet state, since allowed transitions occur without change of multiplicity. However, the molecule may then undergo intersystem crossing to a metastable triplet state, with a change of spin (Fig. 6.1c). This process is attributed to the

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presence of spin-orbit coupling, molecular rotation and/or hyperfine interaction in the presence of an external field $B$. It is highly selective in populating the three sublevels; that is, the process leads to spin polarization.

A triplet ground state (Fig. 6.1d) requires, in view of the Pauli exclusion principle [1], that this state have at least a two-fold orbital degeneracy (or near degeneracy). Low-lying orbitals filled with electrons have been shown in Fig. 6.1 to emphasize that it is the set of highest occupied orbitals that is important in determining the multiplicity of the state.

### 6.2 Spin Hamiltonian for Two Interacting Electrons

For the case of two electrons there are four spin states. One way of representing these states is to construct simple product spin states (the *uncoupled representation*; Section B.6)

$$
\alpha(1)\alpha(2) \quad \alpha(1)\beta(2) \quad \beta(1)\alpha(2) \quad \beta(1)\beta(2)
$$  
Set (6.1)

In a paramagnetic center of moderate size, such that the two electrons interact appreciably, it is more advantageous to combine these configurations into combination states (the *coupled representation*) because the system separates in energy.
into a triplet state and a singlet state.\(^2\) These coupled functions are either *symmetric* or *antisymmetric* with respect to exchange of the electrons. The combination functions are (Section B.6)

\[
\begin{array}{c|c}
\text{Symmetric} & \text{Antisymmetric} \\
\hline
\alpha(1)\alpha(2) & \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
\beta(1)\beta(2) & \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\
\end{array}
\]

Set (6.2)

**Triplet state, \(S = 1\)**

**Singlet state, \(S = 0\)**

The multiplicity of the state with total spin \(S = 1\) is \(2S + 1 = 3\); hence it is called a *triplet state*. The state with \(S = 0\) analogously is called a *singlet state*. If the two electrons occupy the same spatial orbital, then only the antisymmetric or singlet state is possible because of the restrictions imposed by the Pauli exclusion principle [1]. However, if each electron occupies a different orbital, then both the singlet and triplet states exist.\(^3\)

### 6.2.1 Electron-Exchange Interaction

The singlet and triplet states are split apart in energy by the electron-exchange interaction, represented by the spin hamiltonian

\[
\hat{H}_{\text{exch}} = \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad \text{(6.3a)}
\]

\[
= \frac{1}{2}(\hat{S}_1^T \cdot \mathbf{J} \cdot \hat{S}_2 + \hat{S}_2^T \cdot \mathbf{J}^T \cdot \hat{S}_1) \quad \text{(6.3b)}
\]

where \(\hat{S}_1\) and \(\hat{S}_2\) are the electron-spin operators for electrons 1 and 2 (Section B.10 and Problem B.11). Indices \(i\) and \(j\) label spatial coordinates.

Here \(\mathbf{J}\) is a \(3 \times 3\) matrix that takes into account the electric (coulombic) interaction between the two unpaired electrons, but not the important magnetic interaction that is introduced in Section 6.2.2. Details concerning the theory of exchange-coupled systems are available in the literature [2–4].

For our purposes, we consider only the most important part of the exchange-energy operator (Eq. 6.3), that is, the isotropic part\(^4\)

\[
(\hat{H}_{\text{exch}})_{\text{iso}} = J_0 \hat{S}_1^T \cdot \hat{S}_2 \quad \text{(6.4)}
\]

where \(J_0 = \text{tr}(\mathbf{J})/3\) is the isotropic electron-exchange coupling constant, which to a first approximation is given [5] by the exchange integral

\[
J_0 = -2\left(\phi_a(1)\phi_b(2)\right) \frac{e^2}{4\pi\varepsilon_0 r} \left|\phi_a(2)\phi_b(1)\right| \quad \text{(6.5)}
\]

Here \(\phi_a\) and \(\phi_b\) are different normalized spatial molecular-orbital wavefunctions, evaluated while considering the electrons to be non-interacting, \(\varepsilon_0\) is the permittivity...
of the vacuum, and \( r \) is the inter-electron distance.\(^5\) Whether the singlet or the triplet state lies lower depends on the sign of \( J_0 \). The interaction between two hydrogen atoms is a textbook example; here \( J_0 > 0 \) and the singlet (bonding) state lies lowest. In the molecular-orbital description of \( \text{H}_2 \), \( J_0 \) is a major contribution to the total binding energy. If \( J_0 < 0 \), as is the case in some species, the triplet state has the lower energy (Fig. 6.2).

In analogy with the isotropic electron-nuclear hyperfine interaction (Eq. C.2b), Eq. 6.3 can be written as

\[
\hat{H}_{\text{exch}}^{\text{iso}} = J_0 \left[ \hat{S}_{1z} \hat{S}_{2z} + \frac{1}{2} (\hat{S}_{1+} \hat{S}_{2-} + \hat{S}_{1-} \hat{S}_{2+}) \right]
\]

Application of this operator to the spin wavefunctions shows that the singlet and triplet states are separated by the energy \( |J_0| \) (Fig. 6.2), with eigenfunctions as listed in set 6.2. Experimentally, one can observe which state (the singlet or triplet) is lower in energy by studying the EPR signal intensity (i.e., the spin-level populations) as the temperature approaches 0 K.

Note that \( J_0 \) is the analog of the isotropic hyperfine coupling parameter introduced in Eq. 2.39b. As pointed out, the four energy levels of the hydrogen atom are similarly split at zero field into a triplet and a singlet (Appendix C). There is also considerable analogy to the NMR isotropic spin-spin coupling constant \( J \). The magnitude of \( J_0 \) decreases with increasing \( r \) (Eq. 6.5), so that \( |J_0| \) is very small if the two electrons are on the average sufficiently far apart. In this case, if the exchange energy is not large compared to the magnetic dipolar interaction energy, then the two-electron system is called a biradical.

**FIGURE 6.2** The state energies of a system of two electrons exhibiting an exchange interaction, for \( J_0 < 0 \). When \( J_0 \) is positive, the singlet state lies lower in energy.
6.2.2 Electron-Electron Dipole Interaction

In addition to electron exchange, which splits the states into a singlet and a triplet, there exists another important interaction, also quadratic in the electron spin, namely, the anisotropic magnetic dipole-dipole interaction. This interaction causes the three-fold degeneracy of the triplet state to be removed even in zero magnetic field; the latter effect often is called zero-field splitting.

The dipole-dipole interaction for the coupling of two unpaired electrons is analogous to the corresponding interaction (Eq. 5.3) between electronic and nuclear magnetic dipoles, which gives rise to the anisotropic hyperfine interaction (Fig. 2.2); that is, the electron-spin electron-spin dipolar interaction is given by the hamiltonian

\[
\mathcal{H}_{ss}(\mathbf{r}) = \frac{\mu_0}{4\pi} \left[ \frac{\mathbf{\mu}_1 \cdot \mathbf{\mu}_2}{r^3} - \frac{3(\mathbf{\mu}_1 \cdot \mathbf{r})(\mathbf{\mu}_2 \cdot \mathbf{r})}{r^5} \right]
\]  

(6.7)

Here the inter-electron vector \( \mathbf{r} \) is defined as in Fig. 2.2 with \( \mathbf{\mu}_n \) replaced by \( \mathbf{\mu}_e \). The magnetic-moment operators may be replaced by the corresponding spin operators, to yield

\[
\mathcal{H}_{ss}(\mathbf{r}) = \frac{\mu_0}{4\pi} g_1 g_2 \beta_e^2 \left[ \frac{\hat{S}_1 \cdot \hat{S}_2}{r^3} - \frac{3(\hat{S}_1 \cdot \mathbf{r})(\hat{S}_2 \cdot \mathbf{r})}{r^5} \right]
\]  

(6.8)

where \( g_1 \) and \( g_2 \) are the g factors for electrons 1 and 2, taken here to be isotropic. Henceforth, for simplicity, we assume that \( g_1 = g_2 = g \). Expansion of the scalar products in Eq. 6.8 yields

\[
\mathcal{H}_{ss}(\mathbf{r}) = \frac{\mu_0 (g \beta_e)^2}{4\pi} \left[ (r^2 - 3x^2)\hat{S}_{1x}\hat{S}_{2x} + (r^2 - 3y^2)\hat{S}_{1y}\hat{S}_{2y} + (r^2 - 3z^2)\hat{S}_{1z}\hat{S}_{2z} - 3xy(\hat{S}_{1x}\hat{S}_{2y} + \hat{S}_{1y}\hat{S}_{2x}) - 3xz(\hat{S}_{1x}\hat{S}_{2z} + \hat{S}_{1z}\hat{S}_{2x}) - 3yz(\hat{S}_{1y}\hat{S}_{2z} + \hat{S}_{1z}\hat{S}_{2y}) \right]
\]  

(6.9)

Because the two electrons are coupled, it is more convenient to express \( \mathcal{H}_{ss} \) in terms of the total spin operator \( \hat{\mathbf{S}} \), defined by

\[
\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2
\]  

(6.10)

This is accomplished by expanding the appropriate operators, for example

\[
\hat{S}_{1x}^2 = (\hat{S}_{1x} + \hat{S}_{2x})^2 = \hat{S}_{1x}^2 + \hat{S}_{2x}^2 + \hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{2x}\hat{S}_{1x}
\]  

(6.11)

Note that \( \hat{S}_1 \) and \( \hat{S}_2 \) commute since they are operators for different particles. Hence

\[
\hat{S}_{1x}\hat{S}_{2x} = \frac{1}{2}\hat{S}_x^2 - \frac{1}{4}\hat{\mathbf{I}}_3
\]  

(6.12)

since the eigenvalues of \( \hat{S}_{1x}^2 \) and \( \hat{S}_{2x}^2 \) are both \( \frac{1}{2} \) (Section B.6). Similar expressions are obtained for the y and z terms. An expression for \( \hat{S}_{1x} \cdot \hat{S}_2 \) then follows (note
Eq. B.49). The circumflex about the unit matrix symbol signals that we are dealing with a three-dimensional quantum-mechanical space (i.e., the spin triplet state), rather than with ordinary 3-space.

Using the angular-momentum commutation relations (Eqs. B.12), the following transformation can be derived

\[
\hat{S}_{1x}\hat{S}_{2y} + \hat{S}_{2x}\hat{S}_{1y} = \frac{1}{2} (\hat{S}_{x}\hat{S}_{y} + \hat{S}_{y}\hat{S}_{x})
\]

with similar expressions for the \(xz\) and \(yz\) components.

Substitution of these expressions into Eq. 6.9, together with the identity \(r^2 = x^2 + y^2 + z^2\), yields

\[
\hat{H}_{ss}(r) = \frac{\mu_0 (g\beta_e)^2}{4\pi r^3} \left[ \frac{1}{2} \left( (r^2 - 3x^2)\hat{S}_x^2 + (r^2 - 3y^2)\hat{S}_y^2 + (r^2 - 3z^2)\hat{S}_z^2 - 3xy(\hat{S}_x\hat{S}_y + \hat{S}_y\hat{S}_x) - 3xz(\hat{S}_x\hat{S}_z + \hat{S}_z\hat{S}_x) - 3yz(\hat{S}_y\hat{S}_z + \hat{S}_z\hat{S}_y) \right) \right]
\]

The factor of \(\frac{1}{2}\) arises from the conversion from the \(S_1, S_2\) basis to the \(S\) basis. Because all matrix elements connecting the triplet and singlet manifolds are zero in \(\hat{H}_{ss}(r)\) as well as in \(\hat{S}\), one can switch from consideration of the full manifold to working separately with the triplet and singlet parts. The corresponding dipolar energy for the latter (\(S = 0\)) is, of course, zero.

Equation 6.14 can be converted into a spin-hamiltonian form by suitable integration; it can then be written more conveniently in matrix form as

\[
\hat{H}_{ss} = \frac{\mu_0 (g\beta_e)^2}{8\pi} \begin{bmatrix}
\hat{S}_x \\
\hat{S}_y \\
\hat{S}_z
\end{bmatrix} \cdot \begin{bmatrix}
\frac{r^2 - 3x^2}{r^5} \\
\frac{-3xy}{r^5} \\
\frac{-3xz}{r^5}
\end{bmatrix} \cdot \begin{bmatrix}
\hat{s}_x \\
\hat{s}_y \\
\hat{s}_z
\end{bmatrix}
\]

\[
= \hat{S}^T \cdot \mathbf{D} \cdot \hat{S} \quad \text{for} \quad S = 0, 1 \tag{6.15a}
\]

\[
= \hat{S}_1^T \cdot \mathbf{D} \cdot \hat{S}_2 + \hat{S}_2^T \cdot \mathbf{D} \cdot \hat{S}_1 \quad (= 2\hat{S}_1^T \cdot \mathbf{D} \cdot \hat{S}_2) \tag{6.15b}
\]

Note that \(\hat{S}_1^T \cdot \mathbf{D} \cdot \hat{S}_1 = \hat{S}_2^T \cdot \mathbf{D} \cdot \hat{S}_2 = 0\). The last form results from the interchangeability of the individual spins \(S_1, S_2\). Operator \(\hat{H}_{ss}\) is sometimes called the ‘electronic quadrupole spin hamiltonian’. As before, the angular brackets indicate that the elements of the parameter matrix \(\mathbf{D}\) are averages over the electronic spatial wavefunction. As with the matrices encountered in Chapters 4 and 5, \(\mathbf{D}\) can be diagonalized, to
The diagonal elements of $\mathbf{D}$ are $D_x$, $D_y$ and $D_z$. By convention, $D_z$ is taken to be the principal value with the largest absolute magnitude and $D_y$ has the smallest absolute magnitude when $D_x \neq D_y$, producing a set ordered in energy.

We see from the sum of the diagonal elements of Eq. 6.15a that $\mathbf{D}$ is a matrix with a trace of zero:

$$\text{tr}(\mathbf{D}) = D_x + D_y + D_z = 0 \quad (6.16)$$

In the principal-axis system of $\mathbf{D}$, Eq. 6.15b becomes

$$\hat{\mathbf{H}}_{ss} = D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2 \quad (6.17)$$

As always, the principal-axis system is defined by the details of the interaction giving rise to the $3 \times 3$ matrix. The axes lie on symmetry elements, for example, along molecular symmetry axes when such are present.

The dipole-dipole coupling between the two unpaired electrons is not the only interaction that can lead to a spin-hamiltonian term of the form of Eq. 6.15b. Coupling between the electron spin and the electronic orbital angular momentum (Section 4.8) gives rise to a term of the same form (Eq. 6.15b), as does the generalized anisotropic exchange interaction [8].

The effective spin hamiltonian for two interacting electrons, obtained by adding Eqs. 6.4 and 6.15b to the electron Zeeman term, is

$$\hat{\mathbf{H}} = g\beta_e \mathbf{B} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^T \cdot \mathbf{D} \cdot \hat{\mathbf{S}} + \frac{1}{2} J_0 \left[ \hat{S}^2 - \frac{2}{3} \hat{1}_3 \right] \quad (6.18)$$

where the form of the last term arises from the vector cosine sum rule (Eq. B.49). If $J_0 < 0$ and $|J_0| \gg k_b T$, only the lower ($S = 1$) state is populated. Conversely, if $J_0 \gg k_b T$, only the diamagnetic ($S = 0$) state is thermally populated. Furthermore, since the exchange term of Eq. 6.18 contributes only a common constant to the energy of each of the three triplet states, it is neglected in the next section.

### 6.3 Systems with $S = 1$ (Triplet States)

From our previous discussion we see that the spin hamiltonian for an $S = 1$ state is

$$\hat{\mathbf{H}} = g\beta_e \mathbf{B}^T \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^T \cdot \mathbf{D} \cdot \hat{\mathbf{S}} \quad (6.19a)$$

If $\mathbf{D}$ is expressed in its principal-axis system, Eq. 6.19a may be written as

$$\hat{\mathbf{H}} = g\beta_e \mathbf{B}^T \cdot \hat{\mathbf{S}} + D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2 \quad (6.19b)$$
Note that, although there are actually two unpaired electrons (each \( S = \frac{1}{2} \)) in the triplet molecule, we use an effective spin \( S' = 1 \) to describe its magnetic properties, with the singlet ignored. Thus, while there really are four spin states, only three are active. The use of an effective spin, one that generates the multiplicity needed for the states considered, is common and convenient in magnetic resonance. For one, it allows a simple formulation of the spin hamiltonian describing the system.

### 6.3.1 Spin Energies and Eigenfunctions

It is often convenient to use the eigenfunctions \( |M_S\rangle = |+1\rangle, |0\rangle \) and \( |-1\rangle \) of \( \hat{S}_Z \) as a basis set (Fig. 6.2); these are the eigenfunctions of \( \hat{\mathbf{H}} \) (Eq. 6.19b) in the limit as \( B \to 0 \). However, they are not eigenfunctions of \( \hat{\mathbf{H}}_{ss} \) (Eqs. 6.15b and 6.17). Hence it is necessary to set up the spin-hamiltonian matrix for \( \hat{\mathbf{H}} \) and find its energy eigenvalues and eigenstates. For present purposes, it is not necessary to know how the principal-axis system is oriented but only that it exists. Equation 6.19b can be written as

\[
\hat{\mathbf{H}} = g \beta_e (B_X \hat{S}_X + B_Y \hat{S}_Y + B_Z \hat{S}_Z) + D_X \hat{S}_X^2 + D_Y \hat{S}_Y^2 + D_Z \hat{S}_Z^2 \quad (6.19c)
\]

If we take the quantization axis for \( \hat{\mathbf{S}} \) along principal axis \( Z \), then the required spin matrices are those given in Eq. B.77. Substitution of these into Eq. 6.19c with subsequent matrix addition and multiplication yields spin-hamiltonian matrix

\[
\mathbf{H} = \begin{pmatrix}
|+1\rangle & |0\rangle & |-1\rangle \\
\begin{pmatrix}
g \beta_e B_Z + \frac{1}{3} D \\
\frac{1}{\sqrt{2}} g \beta_e (B_X - iB_Y) \\
\frac{1}{\sqrt{2}} (D_X - D_Y)
\end{pmatrix} & \begin{pmatrix}
g \beta_e B_Z + \frac{1}{3} D \\
\frac{1}{\sqrt{2}} g \beta_e (B_X + iB_Y) \\
\frac{1}{\sqrt{2}} g \beta_e (B_X - iB_Y)
\end{pmatrix} & \begin{pmatrix}
g \beta_e B_Z + \frac{1}{3} D \\
\frac{1}{\sqrt{2}} g \beta_e (B_X + iB_Y) \\
-g \beta_e B_Z + \frac{1}{3} D
\end{pmatrix}
\end{pmatrix}
\]

where \( D/3 = (D_X + D_Y)/2 + D_Z \). The secular determinant (Eq. A.69a) is obtained from \( \mathbf{H} \) by subtracting energy \( U \) from all diagonal elements. Setting the corresponding determinant equal to zero, one obtains

\[
\begin{vmatrix}
g \beta_e B_Z + \frac{1}{2} D_Z - U & \frac{1}{\sqrt{2}} g \beta_e (B_X - iB_Y) & \frac{1}{2} (D_X - D_Y) \\
\frac{1}{\sqrt{2}} g \beta_e (B_X + iB_Y) & -D_Z - U & \frac{1}{\sqrt{2}} g \beta_e (B_X - iB_Y) \\
\frac{1}{2} (D_X - D_Y) & \frac{1}{\sqrt{2}} g \beta_e (B_X + iB_Y) & -g \beta_e B_Z + \frac{1}{2} D_Z - U
\end{vmatrix} = 0 \quad (6.21)
\]
Here Eq. 6.16 has been used to simplify terms. The situation is especially simple when \( B \parallel Z \). Then \( B_X = B_Y = 0 \), and Eq. 6.21 becomes

\[
\begin{pmatrix}
g\beta_e B_Z + \frac{1}{2} D_Z - U & 0 & \frac{1}{2} (D_X - D_Y) \\
0 & -D_Z - U & 0 \\
\frac{1}{2} (D_X - D_Y) & 0 & -g\beta_e B_Z + \frac{1}{2} D_Z - U
\end{pmatrix} = 0 \quad (6.22)
\]

The solution \( U = -D_Z \) is obtained by inspection. Expansion of the remaining 2 \( \times \) 2 determinant gives the other two energies as

\[
U_{X,Y} = \frac{1}{2} \{ D_Z \pm \sqrt{[4g^2\beta_e^2 B_Z^2 + (D_X - D_Y)^2]^{1/2}} \} \quad (6.23)
\]

In zero magnetic field, the energies are

\[
\begin{align*}
U_X &= \frac{1}{2} [D_Z - (D_X - D_Y)] = -D_X \\
U_Y &= \frac{1}{2} [D_Z + (D_X - D_Y)] = -D_Y \\
U_Z &= -D_Z
\end{align*} \quad (6.24a, b, c)
\]

Thus \( |U_Z| > |U_X| \geq |U_Y| \) at \( B = 0 \), in accordance with our convention (Section 6.2.2). We note that the zero in energy lies between the smallest and the largest principal \( D \) values, and that all the degeneracy is removed except in the uniaxial case. In the literature, the notation \( \chi = -D_X \), \( \gamma = -D_Y \) and \( Z = -D_Z \) has sometimes been used.

Since the trace of \( D \) is zero, only two independent energy parameters are required. It is common to designate these as

\[
\begin{align*}
D &= \frac{3}{2} D_Z \\
E &= \frac{1}{2} (D_X - D_Y)
\end{align*} \quad (6.25a, b)
\]

Useful expressions for \( D \) and \( E \) are obtainable from the matrix \( D \) in Eq. 6.15a taken in its principal-axis system and will be given later, by Eqs. 6.41 and 9.18a, b. Note that \( D \) and \( E \) are analogous to the hyperfine parameters \( b_0 \) and \( c_0 \) of Eqs. 5.9b, c. Equations 6.24 can now be written as

\[
\begin{align*}
U_X &= \frac{1}{3} D - E \\
U_Y &= \frac{1}{3} D + E \\
U_Z &= -\frac{2}{3} D
\end{align*} \quad (6.26a, b, c)
Thus, by our convention, if $D > 0$, then $E < 0$. In terms of $D$ and $E$, the spin-hamiltonian operator (Eq. 6.19b) becomes

$$\hat{H}_n = g\beta_e B^T \cdot \hat{S} + D(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2)$$  \hspace{1cm} (6.27)$$

It is important to note that the values of $D$ and $E$ are not unique. They depend on which axis is chosen as $Z$. The convention [9] already stated (see text after Eq. 6.15) ensures that $|D|/3 \geq |E|$. One often is ignorant of the absolute signs of $D$ and $E$ since the EPR line positions depend only on their relative signs. Thus the values quoted for $D$ and $E$ often are absolute magnitudes. The sign of $D$ can be determined from relative intensity measurements of EPR lines at low temperatures [10], by optically detected EPR [11], from static magnetic susceptibility data [12], or possibly by comparison with other spin-hamiltonian parameters (e.g., hyperfine and quadrupolar). The sign of $E$ depends on the specific assignment of the axes $X$ and $Y$ and thus has no physical meaning except in terms of the convention that we have chosen. It is sometimes convenient to express $D$ and $E$ in magnetic-field units, that is, $D' = D / g_e \beta_e$ and $E' = E / g_e \beta_e$. It is not uncommon to express these parameters in cm$^{-1}$, that is, by defining $D = D' \hbar c$ and $E = E' \hbar c$.

The energies of the three states as a function of magnetic field are plotted in Fig. 6.3 for $B$ parallel to $Z$. Here it is assumed that $D > 0$. When $D < 0$, the states at zero field are reversed in their energy order. For systems with uniaxial

![FIGURE 6.3 The state energies and corresponding eigenfunctions (high-field labels) as a function of applied magnetic field $B$ for a system of spin $S = 1$ and $B || Z$, shown for $D > 0$ and $E = 0$. The two primary transitions, of type $\Delta M_S = \pm 1$, are indicated for a constant-frequency spectrum. When $E \neq 0$, then the degeneracy at $B = 0$ is lifted, and the corresponding energies vary non-linearly with $B$ (Eqs. 6.30).](image-url)
symmetry one has $D_X = D_Y$ and hence $E = 0$ (Fig. 6.3). When $E \neq 0$, for systems with rhombic symmetry, all three states are non-degenerate at zero field. For naphthalene in its lowest triplet state (Section 6.3.4), the energies and transitions are shown in Figs. 6.4a–c for $B$ parallel to $X$, $Y$ and $Z$. The lowest-field transition in each figure is of the ‘$\Delta M_S = \pm 2$’ type, as explained in Section 6.3.2. Note that this nomenclature is tainted, since $M_S$ is not a strictly valid quantum number at low magnetic fields.

The eigenfunctions (kets) of $\hat{H}$ (Eq. 6.19b) are linear combinations of the kets $|M_S\rangle = |+1\rangle$, $|0\rangle$ and $|-1\rangle$. The coefficients are obtained by substitution of the eigenvalues of Eq. 6.24 into the determinant 6.21 and solving the corresponding secular equations (e.g., as in Section A.5.5). The coefficients depend on the magnitude of $B$. It is convenient to define an auxiliary ‘mixing’ angle $\gamma = \frac{1}{2} \tan^{-1}(E\beta_0/B)$.

Consider the situation $B$ parallel to the principal axis $Z$ with $D > 0$. The upper state $[\sin \gamma |-1\rangle - \cos \gamma |+1\rangle]$ becomes $T_X$ (e.g., Eq. 6.28a) at

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure6.4}
\caption{Spin system energies $(U + 2D/3)/\hbar c$ as a function of applied magnetic field $B$ for naphthalene in its lowest triplet state (which lies $\sim 21,000$ cm$^{-1}$ above the singlet ground state), measured at $T = 77$ K. Clearly, $D > 0$. The transition at lowest field in each case is allowed only for the microwave magnetic field $B_1$ parallel to $B$. We note that it is relatively isotropic as compared to the usual EPR transitions. The latter yielded $D = 0.1003(6)$ and $E = -0.0137(2)$ cm$^{-1}$. (a) $B \parallel X$; (b) $B \parallel Y$; (c) $B \parallel Z$. The resonance magnetic fields at $\nu = 9.272$ GHz are indicated vertically, in gauss. The proton hyperfine energies are ignored. [After C. A. Hutchison Jr., B. W. Mangum, \textit{J. Chem. Phys.}, \textbf{34}, 908 (1961).]}\end{figure}
\[ B = 0 \ (\gamma = -\pi/4, \text{if } E < 0), \] whereas the other mixed state \(|\cos \gamma \left| -1 \right> - \sin \gamma \left| +1 \right>\) is \(T_y\) (e.g., Eq. 6.28b) at \(B = 0\). Note that the upper two levels merge at \(B = 0\) for uniaxial symmetry (\(E = 0\)), and that the high-field states (\(\gamma = 0\)) are usually renormalized to be \(|+1\rangle\) and \(|-1\rangle\) (highest and lowest energies).

In the limit as \(B \to 0\) with \(B\) parallel to the principal axis \(Z\), the zero-field triplet eigenfunctions [13] are

\[ |T_x\rangle = \frac{1}{\sqrt{2}}(|-1\rangle - |+1\rangle) \]  \[ |T_y\rangle = \frac{i}{\sqrt{2}}(|-1\rangle + |+1\rangle) \]  \[ |T_z\rangle = |0\rangle \]

Note that the zero-field functions \(|T_x\rangle\), \(|T_y\rangle\) and \(|T_z\rangle\) are the same linear combinations of angular-momentum eigenfunctions as for the orbital functions for \(\ell = 1\) (Fig. 4.9); that is, they transform like \(p\) orbitals. Here each of the three eigenstates corresponds to a situation in which the spin angular momentum vector lies in one of the three principal planes (e.g., XY) of \(D\).

It is sometimes convenient to choose the functions in Eqs. 6.28 as the basis set, since they are the eigenfunctions of \(\hat{H}_{ss}\) at zero field. In the presence of a magnetic field, the spin-hamiltonian matrix then becomes (note Problem 6.2)

\[
\mathcal{H} = \begin{bmatrix}
-D_X & -ig\beta_x B_Z & +ig\beta_y B_Y \\
+ig\beta_x B_Z & -D_Y & -ig\beta_z B_X \\
-ig\beta_y B_Y & +ig\beta_z B_X & -D_Z
\end{bmatrix}
\]

From this it is clear that when \(B\) is parallel to \(X\), or \(Y\), or \(Z\), the energy of the corresponding state has its zero-field value, and is independent of \(B\).

For \(B\) along \(Z\), one has \(U_z = -2D/3\) and, using Eqs. 6.16 and 6.25, one again finds Eq. 6.23, now written in the form

\[ U_{xy} = \frac{1}{2}D \pm \left[E^2 + (g\beta_x B)^2\right]^{1/2} \]

Clearly, when \(B \parallel Z\), the eigenfunctions of the spin hamiltonian are of the form \(b_1|T_x\rangle + ib_2|T_y\rangle, ib_2|T_x\rangle + b_1|T_y\rangle\) and \(|T_z\rangle\). The coefficients \(b_1\) and \(b_2\) are real, depend on \(B\) [10] and are not difficult to obtain (e.g., Problem 6.4). Alternatively, the eigenfunctions can, of course, be written in terms of the \(|M_3\rangle\) set.

When \(B\) is sufficiently large in magnitude compared to \(D\) and is parallel to \(Z\), the off-diagonal elements in the spin-hamiltonian matrix 6.20 can be neglected. Then
the eigenstates $|M_S\rangle$ of $\hat{S}_z$ are eigenstates of the spin Hamiltonian of Eq. 6.19b. Hence the spin energies can be labeled by the value of $M_S$.

As stated above, in the special case in which $\mathbf{B}$ lies along any one of the three principal axes, there exists an exact analytic solution, valid for all field positions of the primary ($\Delta M_S = +1$) EPR lines. For example, if $\mathbf{B} \parallel \mathbf{Z}$, Eqs. 6.26c and 6.30 give the energy separations corresponding to the two allowed $\Delta M_S = +1$ lines as

$$U_X - U_Z = h\nu = +D + [E^2 + (g\beta_e B_{ax})^2]^{1/2}$$

$$U_Z - U_Y = h\nu = -D + [E^2 + (g\beta_e B_{ay})^2]^{1/2}$$

(6.31a)

(6.31b)

where $B_{ax}$ corresponds to the transition at lower field and $B_{ay}$ to that at higher field when $D > 0$ (and vice versa for $D < 0$). These are valid above the level-crossing region visible in Fig. 6.3; that is, the square-root term dominates over $|D|$. One can then derive from Eqs. 6.31 the exact and general expression

$$|D| = \frac{(g\beta_e)^2}{4h\nu}(B_{hZ}^2 - B_{\ell Z}^2)$$

(6.32a)

valid for either sign of $D$. Here the subindices $h$ and $\ell$ denote the higher and lower resonant fields. Similarly, for $\mathbf{B} \parallel \mathbf{X}$

$$|D - 3E| = \frac{(g\beta_e)^2}{2h\nu}(B_{hx}^2 - B_{\ell x}^2)$$

(6.32b)

and for $\mathbf{B} \parallel \mathbf{Y}$

$$|D + 3E| = \frac{(g\beta_e)^2}{2h\nu}(B_{hy}^2 - B_{\ell y}^2)$$

(6.32c)

Equations 6.32 are very useful for obtaining the zero-field parameters $|D|$ and $|E|$, especially for statistically randomly oriented samples (Section 6.3.3). Note the simplification when $E = 0$.

One possible problem with the previous considerations is that the $D$ principal-axis directions in the single crystal may not yet be known. Another is that the assumption that $g$ is isotropic, made above, is not appropriate.

From the secular equation for the $S = 1$ spin-Hamiltonian matrix (Eq. 6.29) generalized for anisotropic $g$, one can obtain in general a cubic equation in energy eigenvalues $U$, valid for any direction of $\mathbf{B}$. It is possible to derive an exact equation from this giving the magnetic fields of the magnetic-resonance transitions, all observed at each crystal orientation always at the same constant frequency [14,15] to yield the
useful anisotropic parameter \( g^2 d_1 \) (see Eq. 6.55b) as

\[
\mathbf{n}^T \cdot \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g}^T \cdot \mathbf{n} = \frac{\text{det}(\mathbf{D})}{(\beta_c B)^2} + \\
\pm \frac{1}{3^{3/2}} \left[ \frac{(\hbar v)^2 - \text{tr}(\mathbf{D}^2) - (g\beta_c B)^2}{(\beta_c B)^2} \right] \times \\
[(2g\beta_c B)^2 - (\hbar v)^2 + 2\text{tr}(\mathbf{D}^2)]^{1/2}
\]  

(6.33)

where \( \mathbf{n} \) is the unit vector along \( \mathbf{B} \), and \( g = (\mathbf{n}^T \cdot \mathbf{g} \cdot \mathbf{g}^T \cdot \mathbf{n})^{1/2} \) (Eq. 4.12). Here field \( B \) is the resonant field for both \( |\Delta M_S| = 1 \) transitions as well as the \( |\Delta M_S| = 2 \) transition. Only the left-hand side of Eq. (6.33) depends on the field orientation. Having measured frequency \( v \) and the sets of magnetic fields \( B \) (i.e., at each of various orientations), it is then possible to arrive at the unknown matrices \( \mathbf{D} \) and \( \mathbf{g} \), using numerical fitting techniques.

An easier to visualize but approximate technique for arriving at \( \mathbf{D} \) from experimental data is available from perturbation theory, valid when the electron Zeeman energy \( g\beta_c B \) is sufficiently large compared to \( |D| \). We can utilize such an expression (Eq. 6.54) for the spin-hamiltonian energies, to obtain the transition energies in the approximate forms

\[
U(0) - U(-1) = g\beta_c B_h - \frac{3}{2} d_1 + \\
\frac{1}{4g\beta_c B_h} \left[ d_2 - \frac{3}{2} d_1^2 + \frac{1}{2} \left[ \text{tr}(\mathbf{D}^2) - 2d_{-1}\text{det}(\mathbf{D}) \right] \right] + \cdots
\]  

(6.34a)

\[
U(+1) - U(0) = g\beta_c B_\ell + \frac{3}{2} d_1 + \\
\frac{1}{4g\beta_c B_h} \left[ d_2 - \frac{3}{2} d_1^2 + \frac{1}{2} \left[ \text{tr}(\mathbf{D}^2) - 2d_{-1}\text{det}(\mathbf{D}) \right] \right] + \cdots
\]  

(6.34b)

where \( d_n = \mathbf{n}^T \cdot \mathbf{g} \cdot \mathbf{D}^n \cdot \mathbf{g}^T \cdot \mathbf{n} / g^2 \) and \( B_h \) and \( B_\ell \) are the magnetic fields of the higher- and lower-field transitions.\(^9\) By simple manipulation, one may obtain the expression

\[
\Delta B = B_h - B_\ell 
\]  

(6.35a)

\[
= \frac{3d_1}{g\beta_c} - \frac{1}{4g^2\beta_c} \left( \frac{1}{B_h} - \frac{1}{B_\ell} \right) \times \\
\left[ d_2 - \frac{3}{2} d_1^2 + \frac{1}{2} \left[ \text{tr}(\mathbf{D}^2) - 2d_{-1}\text{det}(\mathbf{D}) \right] \right] + \cdots
\]  

(6.35b)

for the field separation between the \( \Delta M_S = \pm 1 \) transitions, valid at any field orientation.\(^10\) We see that in the first approximation, for isotropic \( g \), one has
\[ B_B - B_e \approx 3n^T \cdot D \cdot n / g \beta_c \text{;} \] that is, one obtains the magnitude of \( D \) projected along \( n \). It is thus possible, by measuring the field separations at various directions \( n \), to arrive directly at a first approximation to \( D \). This matrix may then be refined by using Eq. 6.33 or Eq. 6.35. In practice, matrix \( D \) (and simultaneously all other spin-hamiltonian parameters: \( g \), sets of \( A_i \) and \( P_i \), etc.) is obtained numerically by computer fitting of the observed line positions.

Note that, while Eqs. 6.33–6.35 in this section assume that \( B \neq 0 \), it is quite feasible to do EPR studies at \( B = 0 \). This is possible whenever zero-field spin energy-level splittings exist and can be connected by matching photon energies \( h \nu \) of an applied excitation field \( B_1 \) (Appendix E).

In certain systems, the literature routinely contains citations of effective \( g \) values, as defined in Chapter 1. A prominent example is the high-spin Fe\textsuperscript{3+} \( 3d^5 \) EPR peak found in many circumstances in various glasses, which occurs at ‘\( g = 4.3 \)’ (e.g., see Refs. 16–20), when measured at X band. Its presence is a useful indicator of the presence of this ion, and indicates some aspects of its surroundings. However, the reality here is that this ‘\( g \)’ takes on this value because of the presence of sizable zero-field electronic quadrupole energy (parameters \( D \) and \( E \); see Eqs. 6.25) in addition to the electron-spin Zeeman term, and is frequency-dependent. The actual \( g \) value is very close to being isotropic, nearly at \( g_e \). This situation is in sharp contrast with the occurrence of a true \( g \) value of 4.13 (∼30/7 in theory) for low-spin (effective \( S = \frac{1}{2} \)) Fe\textsuperscript{3+} \( 3d^7 \) in octahedral sites (see Fig. 1.11).

### 6.3.2 ‘\( \Delta M_S = \pm 2 \)’ Transitions

At high fields, where the quantum numbers \( M_S = +1, 0 \) and \(-1 \) are meaningful in that they correspond to the eigenfunctions of the spin hamiltonian, a ‘\( \Delta M_S = \pm 2 \)’ transition is not allowed. However, at low fields, the eigenfunctions become linear combinations of the high-field states (Eqs. 6.28) and quantum numbers \( M_S \) are no longer strictly applicable. Thus the usual \( \Delta M_S = \pm 1 \) selection rule does not apply. The ‘\( \Delta M_S = \pm 2 \)’ transition is permitted for the microwave field \( B_1 \) parallel to the static field \( B \). This can be shown by taking the \( \hat{S}_c \) matrix element for the states

\[
c_2|-1\rangle + c_1|+1\rangle \quad \text{and} \quad -i[c_1^*|-1\rangle - c_2^*|+1\rangle]
\]

between which the ‘\( \Delta M_S = \pm 2 \)’ transition occurs (Fig. 6.4 and Problem 6.4). As we saw, the coefficients are functions of angle \( \gamma \). One also finds that, when \( B \) is at an arbitrary orientation relative to the principal axes of \( D \), the \(|+1\rangle, |0\rangle \) and \(|-1\rangle \) states are all mixed by the spin-spin interaction. Hence ‘\( \Delta M_S = \pm 2 \)’ transitions can be seen in a normal EPR cavity [21] (i.e., with the microwave field perpendicular to the static field). These are single-photon transitions. Since the non-zero parts of the intensity arise from the same states (e.g., \(|+1\rangle \) and \(|+1\rangle \)) on both sides of the transition matrix element, it follows that no net angular momentum change in the
spin system is involved (π transition: see Appendix D). Note that the state |0⟩ does not enter into the mechanism.

The position of the low-field side of the ‘ΔMₜ = ±2’ transition in randomly oriented solids does not correspond to that of the low-field X, Y or Z components from Fig. 6.4 but rather occurs at a turning point Bₘᵦ [21,22].

As we have seen, the angular dependence of all the (single-photon) lines in the triplet spectrum for any fixed frequency ν is given [14, 23] by all the non-negative real solutions for B of Eq. 6.33. This holds for the ΔMₜ = ±2 transition. Then, for isotropic g, the minimum possible value

\[ B_{\text{min}} = \frac{1}{2g\beta_e} [(hv)^2 - 2(Dx^2 + Dy^2 + Dz^2)]^{1/2} \]  
\[ B_{\text{min}} = \frac{1}{g\beta_e} \left[ \frac{(hv)^2}{4} - \frac{D^2 + 3E^2}{3} \right]^{1/2} \]  

of the resonant field occurs when the square-root factor in Eq. 6.33 becomes zero. The orientation of the direction B at which Bₘᵦ is achieved is not generally a principal axis of D. Note that the low-field edge of the derivative line for a randomly oriented triplet system can be used to estimate \( D^* \equiv (D^2 + 3E^2)^{1/2} \), which is a measure of the root-mean-square zero-field splitting. In some cases, D and E can be approximately determined if the shape of the ‘ΔMₜ = ±2’ line is analyzed [24]. However, if the zero-field splitting parameters are sufficiently large compared with the microwave photon energy \( h ν \), no ‘ΔMₜ = 2’ transition can occur. In any case, the preceding equations make no prediction about the intensity of such a transition.

Finally, it should be mentioned that for significantly high power levels (large \( B_1 \)), double-quantum (two-photon) transitions are observable [25,26]. These are between states |±1⟩, and occur near \( g = 2 \).

### 6.3.3 Randomly Oriented Triplet Systems

Triplet molecules in liquid solution are difficult to detect. While the rotational motions do tend to remove the zero-field splittings (D), very rapid tumbling is required to do so, and the associated spin-lattice relaxation (\( τ_1 \) much shorter than for \( S = \frac{1}{2} \) radicals) broadens the lines [27].

Few triplet systems have been investigated in the oriented solid state. This arises largely from the difficulties of preparing single crystals of adequate size with well-defined orientation of guest molecules at an appropriate concentration. The observation of a ‘ΔMₜ = ±2’ line in the region of \( g \approx 4 \) was the stimulus for the detection of triplet states in numerous non-oriented systems [24]. The relatively large amplitude of the ‘ΔMₜ = ±2’ lines is associated with their small anisotropy. Subsequently, it was recognized [23] that even for non-oriented systems one can detect the ordinary \( ΔMₜ = ±1 \) transitions at ‘turning points’. General conditions for the occurrence
of off-axis extra lines in the EPR powder (and glass phase) patterns have been derived, using third-order perturbation theory applied to $S > \frac{1}{2}$ systems [30].

It is instructive to mention that high-quality triplet-state EPR lines can be obtained from aromatic molecules (e.g., anthracene-$d_{10}$) dissolved in low-density stretched polyethylene films [31]. These molecules then occur oriented within the film. The photo-excited spectra are strongly anisotropic, as becomes evident by placing $\mathbf{B}$ along various different directions relative to the stretch axis. The parameters obtained are consistent with those derived from single-crystal measurements.

For simplicity, we now consider an ensemble of triplet-state molecules randomly oriented in a solid matrix. From an evaluation of $d_1$ in Eqs. 6.35, the field separation $\Delta B$ of the two allowed $\Delta M_S = \pm 1$ transitions to a first approximation (with isotropic $g$) is seen to be given by

$$\Delta B = B_h - B_L = \frac{3}{g\beta_e} [D_x \sin^2 \theta \cos^2 \phi + D_y \sin^2 \theta \sin^2 \phi + D_z \cos^2 \theta]^{1/2}$$  \hspace{1cm} (6.37a)

$$= \frac{1}{g\beta_e} [D(3 \cos^2 \theta - 1) + 3E \sin^2 \theta \cos 2\phi]^{1/2}$$  \hspace{1cm} (6.37b)

where $\theta$ is the polar angle (between $\mathbf{B}$ and axis $\mathbf{Z}$ of a given molecule) and $\phi$ is the azimuthal angle. If $\bar{B}$ is the average field ($B_h + B_L$)/2, then the orientation dependence of each line is given by

$$B_h - \bar{B} = \bar{B} - B_L = \frac{1}{2g\beta_e} [D(3 \cos^2 \theta - 1) + 3E \sin^2 \theta \cos^2 \phi]^{1/2}$$  \hspace{1cm} (6.38)

as can be derived from Eqs. 6.34.

For the uniaxial case, as the field changes its orientation from $\theta = 0^\circ$ to $\theta = 90^\circ$, the line positions relative to $\bar{B}$ change from $|D|/g\beta_e$ to $-|D|/2g\beta_e$. By applying an analysis similar to that given in Sections 4.7 and 5.7, we can express the probability distribution for a given upper-field transition as follows:

$$P(B_h) \propto \frac{g\beta_e}{6|D \cos \theta|}$$  \hspace{1cm} (6.39)

The calculated shapes for the $\Delta M_S = \pm 1$ lines are given in Fig. 6.5. The separation between the outer vertical lines in Fig. 6.5a (which represents the theoretical lineshape) is approximately $2|D|/g\beta_e$, while that between the two inner lines is $|D|/g\beta_e$. The high-field portion of the triphenylbenzene di-anion (I) spectrum in Fig. 6.6 shows a satisfying correspondence with the derivative spectrum in Fig. 6.5b. Note that the triplet powder pattern (for $\Delta M_S = \pm 1$) tends to consist of equal, but oppositely signed, contributions, just as was the
case for the hyperfine-dominated spectra (see Figs. 5.10 and 5.11), for analogous reasons.

\[
\begin{align*}
\text{(I) triphenylbenzene dianion} \\
\end{align*}
\]

The analysis can readily be extended to a randomly oriented triplet system with \( E \neq 0 \). The theoretical lineshape is given in Fig. 6.7a, and the derivative spectrum is given in Fig. 6.7b. The separation of outermost lines is again \( 2|D|/g\beta_e \), whereas that of the intermediate and inner pairs is \( (|D + 3E|)/g\beta_e \) and \( (|D - 3E|)/g\beta_e \). There is a close correspondence between Figs. 6.7b and 6.8, which gives the spectrum of the first excited triplet state of naphthalene in a rigid, non-oriented (‘glassy’) matrix at 77 K. The compound used was actually \( \text{C}_{10}\text{D}_8 \) instead of \( \text{C}_{10}\text{H}_8 \) so as to minimize linewidth contributions from unresolved hyperfine splittings. The pairs of lines correspond with those given in Fig. 6.4 for a single crystal. In the \( g = 2 \) region an additional line is seen at high microwave power. This line has been identified as a double-quantum transition [25]. For observations of the \( \Delta M_S = \pm 1 \) lines in the random non-oriented sample, one requires a far greater EPR spectrometer sensitivity than for an equivalent concentration in a single crystal. In the former case, only a small fraction of all molecules in the triplet state contribute to any of the observable derivative lines. The \( \Delta M_S = \pm 1 \) lines are seen to be weak compared with the \( \Delta M_S = \pm 2 \) line.

For rigid media in which the geometric configurations of host and guest molecules are markedly dissimilar, the linewidths in the triplet spectrum may be many times broader than in cases where host and guest are very similar (specifically, diphenylmethylene \( \text{C}_5\text{H}_5-\text{C}-\text{C}_5\text{H}_5 \) in diphenyldiazomethane \( \text{C}_6\text{H}_4-\text{C}(\text{N}_2)-\text{C}_6\text{H}_4 \) shows a linewidth of 1.7 mT; in \( n \)-pentane \( \text{CH}_3(\text{CH}_2)_{3}\text{CH}_3 \) the linewidth is 9.4 mT [32]). Thus in a dissimilar host-matrix system, it appears likely that a range of solute-solvent configurations is tolerated; the various configurations display a distribution of \( D \) and \( E \) values.

In nonrigid media, EPR absorption for triplet-state systems is not observed unless \( |D| \) and \( E \) are sufficiently small. If intramolecular spin-spin interactions are modulated at a rapid rate because of molecular reorientations, one expects
a spread in the components of $D$. Since the trace of $D$ is zero, the contribution of the term $\hat{S}^T \cdot D \cdot \hat{S}$ may become negligible. Two limiting cases may be considered:

1. When $|D|$ and $|E|$ are large, the modulations of the spin-spin interaction lead to so short a spin lifetime that the averaged spectrum has undetectably broad lines.

2. When $|D|$ and $|E|$ are very small, the line-broadening effects in non-rigid media are also small. In the absence of hyperfine splitting, one sees a single line, as if the spectrum were due to a system with $S = \frac{1}{2}$.

FIGURE 6.5  (a) Theoretical EPR absorption spectrum for a randomly oriented triplet system (with $E = 0$) for a given value of $D$ and $v$ (taking $g = g_e$). A zero linewidth is assumed. The solid curve $B$ corresponds to the curve of Fig. 4.7a; the solid curve $A$ represents a reflection of $B$ about the central field $B_0$. The central (small dash) trough is the sum of $A$ and $B$. Compare with Fig. 5.10 ($\xi = 10$). (b) First-derivative curve computed from (a) after assuming a non-zero linewidth. Only the field region corresponding to $\Delta M_S = \pm 1$ is shown. The points marked $x$ correspond to the resonant field values when the magnetic field is oriented along $Z$ (cusp-shaped lines) or perpendicular to $Z$. [After E. Wasserman, L. C. Snyder, W. A. Yager, J. Chem. Phys., 41, 1763 (1964).] Note and tentatively explain the difference between the idealized first-derivative spectrum shown here, and the one depicted in Fig. 5.11.
A system that may be an example of case 2 is the set of four ions shown below [structure II; \( R \) could be \( \text{C(CH}_3)_3 \)]. Here two ketyl radical anions (formed by reaction of carbonyl compounds and an alkali metal) are bound by two alkali ions to form a quartet cluster [33].

\[
\text{\begin{align*}
\text{R} & \quad \text{Na}^+ \\
\text{C} & \quad \text{O}^- \\
\text{R} & \quad \text{Na}^+ \\
\text{II}
\end{align*}}
\]

Such systems have very small \( D \) values (0.007–0.015 cm\(^{-1}\)), in solid CH\(_3\)DMF at 77 K. At room temperature, in liquid DMF, they show a seven-component composite spectrum (intensity ratios: 1:2:3:4:3:2:1) arising from two equivalent alkali (\(^{23}\text{Na}, I = \frac{2}{2}\)) nuclei, with each proton-split component looking just as if the second ketyl unit were not present [34].

### 6.3.4 Photo-excited Triplet-State Entities

We have now developed the theory necessary to interpret the EPR spectra of triplet (\( S = 1 \)) systems and are thus in a position to examine specific examples of the application of EPR to these systems.
There is a very wide range of possibilities for triplet systems. We begin in this section with the most important category, namely, the large number of systems that are diamagnetic ($S = 0$) in the ground state but have relatively long-lived
excited triplet states generated by steady-state or flash irradiation. Thereafter we consider thermally excited triplet entities and, finally, ground-state triplet species.

After irradiation with visible or ultraviolet light, many aromatic hydrocarbons in rigid solutions at low temperature exhibit excited states of unusually long lifetime—some of the order of minutes, as manifested by the long-lived glow (phosphorescence) remaining after turning off the incident light. This behavior is the result of the existence of a metastable state, which is populated via other excited states. G. N. Lewis et al. [35] postulated in 1941 that this long-lived state is a spin triplet state and that direct excitation to, or emission from, this state is spin-forbidden (to first approximation). Following Lewis’ prediction, magnetic-susceptibility experiments on excited aromatic molecules in rigid media yielded results in qualitative accord with the triplet nature of the state. That is, on irradiation there is an increase in paramagnetism; this decays on cessation of irradiation, with the same decay rate constant as that of phosphorescence.

Aromatic hydrocarbons have been the focus of much of the early EPR triplet work, partly because of their availability and stability, their well-defined π-electron systems, and their long triplet lifetimes (no heavy atoms). It is relatively easy to prepare magnetically dilute systems containing small amounts of the molecules of interest in a diamagnetic optically inert medium. Thus specific photo-excitation of the molecules from their diamagnetic (singlet) ground states to populate their (lowest) triplets should allow study by EPR. However, a number of early experiments failed to detect such triplets. One reason for the initial failures is the marked anisotropy of the EPR line positions, arising from the dipolar interaction between the two electrons coupled to give \( S = 1 \). A second reason is the low sensitivity of the spectrometers at the time (1950–1955) when these first attempts were made.

FIGURE 6.8 EPR spectrum at 9.08 GHz of photo-excited triplet perdeuteronaphthalene (C\(_{10}\)D\(_{8}\)) in a glassy mixture (‘EPA’) of hydrocarbon solvents at 77 K. Lines in the region of \( g = 2 \) arise from free radicals (\( S = \frac{1}{2} \)) and from double-quantum transitions. [After W. A. Yager, E. Wasserman, R. M. R. Cramer, J. Chem. Phys., 37, 1148 (1962).]
Once the cause of the earlier failures was recognized, a successful observation of the lowest excited triplet state of naphthalene was achieved by irradiating single crystals of durene \((1,2,4,5\text{-tetramethylbenzene})\) containing a small fraction of naphthalene.\(^{13}\) Since the two molecules are similar in shape, the naphthalene directly replaces durene in the lattice.

Optical studies indicate that the singlet-triplet splitting in naphthalene is \(\sim 20,000 \text{ cm}^{-1}\), and hence that \(J_0\) is large enough to ensure that the singlet excited state does not affect the magnetic properties of the system. Note that the EPR spectrum of a triplet system yields no explicit information about the exchange parameter(s). An electronic energy diagram, patterned after the one originated by A. Jablonski in 1933, is shown in Fig. 6.9.

The EPR spectra observed for naphthalene are precisely in accord with the expectations for a system with \(S = 1\). The positions of EPR lines for the three principal-axis orientations of the field are given in Figs. 6.4\(a\)–\(c\). It was found \(^{[10,37]}\) that \(D = 0.1003 \text{ cm}^{-1}\), \(E = -0.0137 \text{ cm}^{-1}\) \((D' = 107.3 \text{ mT} \text{ and } E' = -14.7 \text{ mT})\), and \(g\) (isotropic) = 2.0030. The principal-axis system for \(D\), as related to the molecular frame, is shown in Figs. 6.4 and 6.9. The lines in the vicinity of \(h\nu/2g\beta_s\) were considered in Section 6.3.2. The zero-field splitting parameters shown above are relatively small. This is consistent with the Pauli exclusion

\[\begin{align*}
\text{S}_2 & \quad \text{T}_2 \\
\text{S}_1 & \quad \text{T}_1 \\
\text{S}_0 & \quad \text{T}_0
\end{align*}\]

\(\text{Singlet S=0 manifold} \quad \text{Triplet S=1 manifold}\)

\(10^{-9}\text{s} \quad 1.2\text{s} \quad 2.0\text{s} \quad 4.0\text{s} \quad 1.4\text{s}

\(\text{fluorescence} \quad \text{phosphorescence} \sim 21,000 \text{ cm}^{-1}\)

\(Y \quad 1 \quad 2 \quad X \quad 6 \quad 5 \quad 4 \quad 3 \quad \text{D}_{2h}\)

**FIGURE 6.9** The lowest electronic singlet and triplet energy levels of naphthalene, showing photon absorption, fluorescence and phosphorescence transitions and their mean lifetimes, as well as radiation-less transitions (wavy lines). The zero-field splittings of the lowest triplet are indicated at the right.
principle and the coulombic repulsion between the two mobile unpaired electrons, which causes them to stay apart, decreasing the dipolar interaction energy and hence $|D|$. The line positions as a function of orientation for triplet naphthalene in a single crystal of durene, for the magnetic field oriented in the $xy$, $xz$ and $yz$ planes of the crystal, are shown in Fig. 6.10. The spectra include contributions from the two types of sites in the unit cell, one of which (site 1) is scanned in its $D$ principal planes. The reader is urged to interpret the angular-dependence

![Diagram](attachment:image.png)

**FIGURE 6.10** Angular dependence of the resonant field (at 9.7 GHz) for triplet naphthalene in durene, as a function of rotation with $B$ in several planes for the two symmetry-related molecules (the planes are defined in Fig. 6.4). Hyperfine effects are ignored. [After C. A. Hutchison Jr., B. W. Mangum, *J. Chem. Phys.*, 34, 908 (1961).]
curves and to extract the zero-field splitting parameters $D$ and $E$ (Problems 6.5 and 6.6).

For the naphthalene triplet state in a durene single crystal, with $B$ along the $X$ or $Y$ principal axes, a $1:4:6:4:1$ quintet can be resolved at 77 K [38]. By employing variously deuterated samples, it was determined that the hyperfine splitting $a = 0.561$ mT arises from the 1,4,5,8 protons and $a = 0.229$ mT from the 2,3,6,7 protons (these values refer to $B \parallel Z$). These hyperfine splittings are very similar to those of the naphthalene anion considered in Chapter 3 (Fig. 3.8) (see Section 9.2.2 for further discussion).

Benzene itself has been studied by EPR [39, 40]. The data indicate that the molecule in its lowest triplet state no longer has $D_{6h}$ symmetry; that is, it is distorted. There is interconversion among the (three) energy-equivalent configurations, as is evident from the linewidth behavior. Such transfer of the triplet excitation, here intramolecular, is a general phenomenon. Thus diffusion of such triplet excitons [41] can populate triplet states in molecules that were not originally excited by the ultraviolet irradiation. For example, the EPR signal of phenanthrene can decrease while that of naphthalene increases after irradiation in biphenyl crystals doped with both [42].

There exist inorganic systems that display photo-excited metastable triplet states with optical and magnetic properties closely analogous to those of the aromatic $\pi$ systems. We consider the $d^0$ transition ions (e.g., $V^{5+}$, $Cr^{6+}$, $Mn^{7+}$, $Mo^{6+}$) in oxides [43]; for example, the $V_{O_4}^{3-}$ ion in $YVO_4$ or in $Ba_3(VO_4)_2$, which, while diamagnetic in its singlet ground state, exhibits an EPR spectrum when illuminated. Presumably the optical excitation shifts electrons into the previously empty $d$ shell with accompanying distortion of the already elongated oxygen tetrahedron (Fig. 6.11). Studies of EPR at various frequencies (4–23 GHz) and magnetic fields (including $B = 0$) have yielded electronic quadrupole ($D$) splittings (and mean lifetimes) of the lowest triplet levels (Fig. 6.12) for the vanadate ion dilute (4%) in $YPO_4$ at 1.2 K [44]. Note the magnitude of the zero-field splittings as compared to those found for the delocalized $p$ electrons in aromatic systems. These sensitive measurements, yielding the spin-hamiltonian parameters $g, D$ and an estimate of $A(\text{V}^{51})$ (Fig. 6.11), were carried out by means of optical detection of the EPR signals. Here square-wave modulation at 300 Hz of excitation field $B_1$ results in modulation of the phosphorescence detected synchronously at the same frequency (Chapter 12).

6.3.5 Thermally Accessible Triplet Entities

Sections 6.3.4 and 6.3.6 of this chapter deal with systems in which the triplet state of interest is a photo-excited state or the ground state. In either case we tacitly assume that the separation of the triplet state from a nearby singlet state is large enough so that one need not consider mixing of the two states. An additional interesting case is that in which the singlet-triplet separation is small enough to make the triplet state thermally accessible but still not so small as to cause serious mixing of states. The singlet-triplet separation is approximately $|J_0|$, where the exchange
FIGURE 6.11 The structure of the YPO$_4$ unit cell, showing a V$^{5+}$ ion having replaced a P$^{5+}$ ion at the center. For the ground-state singlet, the local symmetry is $D_{2d}$ (as in pure YPO$_4$), featuring two reflection planes ($ac$ and $bc$) intersecting at two-fold axis $c$. It is believed that distortion removes one such plane in the lowest triplet state. Axes $X$, $Y$, $Z$ indicate the principal axes of $D$, with axis $Z$ normal to the remaining reflection plane and axis $Y$ along a V–O direction. Axes $X_g$, $Y_g$, $Z_g$ denote the principal axes of $g$. [After W. Barendswaard, R. T. Weber, J. H. van der Waals, *J. Chem. Phys.*, 87, 3731 (1987).]

FIGURE 6.12 The zero-field splitting of the lowest $S = 1$ state of V$^{5+}$ in YPO$_4$ at 1.2 K, also giving the mean lifetime of each level. The sign of $D$ here was taken to be positive; if it were negative, then the order of the levels would be reversed. The $X$, $Y$, $Z$ labeling follows this book's convention [W. Barenwaard, R. T. Weber, J. H. van der Waals, *J. Chem. Phys.*, 87, 3731 (1987)].
interaction between two electrons is given by \( J_0 \hat{S}_1^\times \hat{S}_2 \) (Eqs. 6.3–6.5). When the triplet lies higher than the singlet \( (J_0 > 0) \), the relative population of the triplet state is governed by the Boltzmann factor \( 3 \exp[-J_0/k_BT] \). In general, for a given population of a paramagnetic state, the intensity \( \mathcal{I} \) of EPR absorption is given by a Curie-law (Eq. 1.16 and Section 10.3.4) dependence, that is, \( \mathcal{I} \propto 1/T \). The integrated intensity \( \mathcal{I} \) of EPR absorption arising from a thermally excited triplet state should depend on temperature as

\[
\mathcal{I} \propto T^{-1} [3 + \exp(J_0/k_BT)]^{-1}
\]

(6.40)

Thus a study of the temperature dependence of the EPR intensity (i.e., area \( \mathcal{A} \); see Section E.1) permits a determination of the value of \( J_0 \).

A clear-cut example of a thermally accessible triplet state is provided by the \( F_t \) ‘point’ defect in MgO [45]. This center is thought to be a neutral trivacancy, that is, a missing linear \((O—Mg—O)^2\) fragment replaced by two electrons. It gives no EPR spectrum at very low temperatures, unless ultraviolet (uv)-irradiated. Alternatively, a spectrum is generated by warming above 4 K. This indicates that the triplet state for the two electrons lies above the singlet so that \( J_0 > 0 \). An analysis of the temperature dependence yields \( T_0 = 56(7) \) cm\(^{-1}\cdot{}^{14}\). At arbitrary orientations of the magnetic field, the EPR spectrum consists of six lines (pairs of \( \Delta M_S = \pm 1 \) transitions, one for each of the three distinct orientations of the \((O^2—Mg^{2+}—O^2\) axes in the cubic crystal). The 300 K line positions as a function of rotation in the (001) and (110) planes are shown in Fig. 6.13. An analysis of these data reveals that \( D' = 30.7 \) mT and \( E = 0 \), with \( g = 2.0030(5) \). From Eqs. 6.41 or 9.18a, the average interelectronic distance is found to be 4.5 Å; this compares well with the relevant oxygen-oxygen distance of 4.2 Å in MgO [45].

![FIGURE 6.13](image)

Another interesting example is the observation of a triplet EPR spectrum in powdered samples of Fremy’s salt, represented here by $K_4[(SO_3)_2NO]_2$ to emphasize its spin-paired dimeric structure [46]. Here $D = +0.076$ cm$^{-1}$ and $E = +0.0044$ cm$^{-1}$. The area of the half-field peak was found to increase exponentially (Eq. 6.40) with temperature (250–350 K), yielding the singlet-triplet gap energy $J_0 = 2180$ cm$^{-1}$. Since no hyperfine ($^{14}$N) splitting is observed, this spectrum has been assigned to a triplet exciton, which is an excited state that migrates rapidly through the crystal lattice.

6.3.6 Ground-State Triplet Entities

A triplet species need be no larger than an atom if it has an appropriate set of degenerate orbitals. The list of ground-state triplet atoms includes C, O, Si, S, Ti and Ni. The two most prominent ground-state triplet diatomic molecules are O$_2$ and S$_2$ (Chapter 7).

6.3.6.1 Carbenes and Nitrenes The H–C–H fragment (methylene or ‘carbene’) is one of the simplest molecular systems, and the triplet nature of its ground state has been established spectroscopically. The EPR spectrum of methylene has been reported (Table 6.1) for both CH$_2$ and CD$_2$. For the former, $D = 0.69$ cm$^{-1}$ and $E = 0.003$ cm$^{-1}$; for the latter, $D = 0.75$ cm$^{-1}$ and $E = 0.011$ cm$^{-1}$. The difference presumably arises from the effect of zero-point vibration. Many substituted methylenes have also been studied (Table 6.1). The non-zero value of $E$ for some of these molecules indicates that for them there is

| Molecule | $|D|$ (cm$^{-1}$) | $|E|$ (cm$^{-1}$) | Reference |
|----------|-----------------|-----------------|-----------|
| H–C–H    | 0.69            | 0.003           | $^a$       |
| D–C–D    | 0.75            | 0.011           | $^a$       |
| H–C–C≡N  | 0.8629          | 0               | $^b$       |
| H–C–CF$_3$ | 0.712          | 0.021           | $^c$       |
| H–C–C$_3$H$_4$ | 0.5150 | 0.0251         | $^d$       |
| H–C–C≡C≡C–H | 0.6256   | 0               | $^b$       |
| H–C–C≡C–CH$_3$ | 0.6263 | 0               | $^b$       |
| H–C–C≡C–C$_6$H$_5$ | 0.5413 | 0.0035         | $^b$       |
| C$_6$H$_5$–C–C$_6$H$_5$ | 0.4055 | 0.0194 | $^d$       |
| N≡C–C–C≡N  | 1.002          | <0.002          | $^e$       |
| N=C≡N     | 1.52           | <0.002          | $^e$       |


no axis of symmetry of order 3 or greater; this indicates that the molecules are non-
linear. For such systems, the maximum number of peaks (six $\Delta M_S = \pm 1$ transitions)
is expected in the glass-phase EPR spectrum, just as for naphthalene in the excited
triplet state (Figs. 6.7 and 6.8). When the system is nearly uniaxial, the parameter $E$
may be so small that one may only be able to set an upper limit for its value. An
increase in the extent of the conjugated system attached to the methylene carbon
atom may lead to a decrease in the parameter $D$ as is evident from Table 6.1.

Figure 6.14 shows the energy-level diagrams for the fluorenylidene molecule
(III) [47]. The molecule is generated in its ground triplet state by irradiation of
diazofluorene at 77 K. It is thus to be regarded as a derivative of methylene. If
the zero-field splitting $D$ is large compared with $hn$ for a microwave quantum,
only certain of the lines allowed by the selection rules are observed. When $B$
is parallel to axis $X$ or $Y$, only one transition is observed for $\nu \approx 9.7$ GHz. Since the ordi-
nate in Fig. 6.14 is expressed in gigahertz, the frequency required to cause a
transition between adjacent levels is immediately apparent from it. For $B \parallel Z$,
three transitions are expected and are observed. Two of these are between the
levels designated by $|0\rangle$ and $|-1\rangle$. Note (Fig. 6.14c) that the ‘$\Delta M_S = \pm 2$’ transition
occurs at an intermediate value of the magnetic field. The parameters measured,$|D| = 0.4078$ and $|E| = 0.0283 \text{ cm}^{-1}$, are appreciably larger than those of naphtha-
lene, as expected (Section 6.3.4). The reader should compare the resulting tran-
sitions allowed at X band (Figs. 6.4 and 6.14).

![Figure 6.14](image)

**FIGURE 6.14**  Energy levels of the fluorenylidene molecule (III) in its triplet ground state
as a function of applied magnetic field (measured in proton NMR fluxmeter frequency units).
The EPR transitions indicated are at $\sim 9.7$ GHz. (a) $B \parallel X$; (b) $B \parallel Y$; (c) $B \parallel Z$. Here $|D| = 0.4078$ and $|E| = 0.0283 \text{ cm}^{-1}$. [After C. A. Hutchison Jr., G. A. Pearson, *J. Chem.
Phys.*, 47, 520 (1967).]

(III) fluorenylidene
Another organic triplet species of considerable experimental and theoretical interest is trimethylenemethane (IV), which can be represented as

![Diagram of trimethylenemethane]

This free radical, TMM,\textsuperscript{15} can be prepared by $\gamma$ irradiation of methylenecyclopropane. EPR studies [49] reveal that it is a triplet ground-state species, rather than a biradical; that is, $|J_0|$ is relatively large compared to $|D|$, and parameter $J_0$ is negative (see Fig. 6.2). The radical has four $\pi$ electrons, and is close to uniaxial (planar with symmetry $D_{3h}$) as inferred from the parameters $D = 0.0248 \text{ cm}^{-1}$ and $E < 0.003 \text{ cm}^{-1}$ at 77 K. The temperature dependence of these parameters, and of the proton hyperfine matrix (six equivalent protons, principal values $A_i/h$ of $-14$, $-38$ and $-26 \text{ MHz}$) suggests that anisotropic rotational effects occur. Because the proton nuclear Zeeman term is not small compared to the hyperfine values in this anisotropic system, all four hyperfine transitions per proton are observed (Section 5.3.2.1). The relative sign of $D$ and $A_i$, obtainable from the EPR data, discloses that $D$ is positive.

From Eq. 6.15a (D diagonal) and Eq. 6.25a, it is easily shown that

$$D = \frac{3\mu_0}{16\pi} g^2 \beta^2_e (r^{-3}) (1 - 3 \cos^2 \theta)$$  \hspace{1cm} (6.41)

Here angle $\theta$ is the angle between the inter-electron (spin) vector $r$ and the principal axis $Z$ of $D$. It is evident that the sign of $D$ is determined solely by $(1 - 3 \cos^2 \theta)$. If the dipoles were fixed at two points (in which case $r/r = Z$ and $\frac{1}{2} D_Z = -D_Y = -D_X$), Eq. 6.41 would yield $D = -(3 \mu_0/8\pi) g^2 \beta^2_e (r^{-3})$, that is, $D$ would be negative. For a triplet-state atom not in an electric field, the spherical symmetry dictates that $D = 0$. In non-spherical systems, $D$ can be negative or positive. The latter sign occurs in binuclear triplet species when the internuclear axis is perpendicular to $Z$, as dictated by the unpaired-electron distribution. In trimethylenemethane (IV), the two unpaired electrons can be considered as being equally distributed at three points (carbons) in a plane normal to the symmetry axis, so that $D > 0$.

6.3.6.2 Dianions of Symmetric Aromatic Hydrocarbons A molecule may have a ground triplet state in its neutral, cationic or anionic form. Here there is one unpaired electron in each of a pair of degenerate orbitals. Thus, as is shown in Fig. 6.1d, the lowest-energy state (ground state) is that corresponding to single occupation with parallel spins of the highest two occupied levels.

Degenerate orbital energy levels are found in molecules with an $n$-fold ($n \geq 3$) axis of symmetry. Molecules of this type do not necessarily have a triplet ground
state. The situation depends on the sign of the electron-exchange integral (Eq. 6.5). If $J_0$ is positive, then the singlet state lies lower. This is the case, for instance, in the coronene di-anion with alkali counterions (V) [49,50].

![Coronene di-anion](image)

(V) coronene di-anion

Occurrence of one electron in each of two degenerate orbitals of symmetrically substituted benzenes may be achieved if the di-anion can be formed. Triplet ground states have been demonstrated for symmetric molecules such as the 1,3,5-triphenylbenzene (I) and triphenylene di-anions (VI).

![Triphenylene di-anion](image)

(VI) triphenylene di-anion

These ions possess degenerate antibonding orbitals, analogous to those shown in Fig. 6.15 for the hypothetical benzene di-anion (note Table 9A.2). For the triphenylbenzene di-anion (ground triplet state, Fig. 6.6) $D$ is less ($\overline{D} = 0.042 \text{ cm}^{-1}$) than that of the neutral excited triplet-state molecule ($\overline{D} = 0.111 \text{ cm}^{-1}$) [51]. The orbital occupation is very different for these two cases; calculations show that in the excited triplet molecule, there is a greater interaction (leading to a larger $D$ value) between two electrons in the ‘paired’ bonding and antibonding orbitals than between two electrons in the antibonding orbitals of the ground-state di-anion.

6.3.6.3 Inorganic Triplet Species Other than $O_2$ and $S_2$ (considered in Chapter 7) and some transition-ion complexes, there are not many stable inorganic molecules that exist in a triplet ground state. Some unstable species can be trapped in low-temperature matrices. Excellent examples are the isoelectronic molecules CCO
and CNN, prepared by reaction of C atoms with CO or N\textsubscript{2} with subsequent trapping in a frozen rare-gas matrix at 4 K [52]. Both of these molecules have large values of $D$ ($D = 0.7392$ cm\(^{-1}\) for CCO and $D = 1.1590$ cm\(^{-1}\) for CNN in solid neon) such that $D > h\nu$ at X band. Thus only one transition is seen in each case. The \(^{13}\)C and \(^{14}\)N hyperfine parameters are also reported. The fact that $E = 0$ indicates that these molecules are linear.

Another quite different example of a ground-state triplet is the quasi-tetrahedral [AlO\textsubscript{4}]\(^{+}\) ‘point’ defect in a quartz single crystal [53]. This center is believed to contain two electron holes forming a triplet spin system in which the two unpaired electrons are \(~0.265\) nm apart on adjacent (and symmetry-related) oxygens in the AlO\textsubscript{4} entity. For this center at \(~35\) K, $D' = -69.8$ mT and $E' = 6.3$ mT. These values are in very good agreement with those calculated on the basis of a model placing an unpaired-electron population of 0.76 in two oxygen 2p orbitals perpendicular to the Al—O—Si plane. As expected [3], the hyperfine matrix from the central \(^{27}\)Al ion is accurately approximated by $A = (A_1 + A_2)/2$, where matrices $A_i$ ($i = 1, 2$) stem from the corresponding radicals ($S = \frac{1}{2}$) centered on the two oxygens. Similarly, $g = (g_1 + g_2)/2$. The hyperfine splittings arising from the low-abundance isotope \(^{29}\)Si, that is, from outer silicon atoms bonded to the oxygens, are half as large as the corresponding ones from the $S = \frac{1}{2}$ species.

Various transition ions provide examples of $S = 1$ systems, for example, V\textsuperscript{3+} and Ni\textsuperscript{2+} in the 3d series (Chapter 8). The latter ion, dilute in K\textsubscript{2}MgF\textsubscript{4} where it is in a Mg\textsuperscript{2+} site surrounded by a slightly distorted octahedron of F\textsuperscript{—} ions, yielded $D = -0.425$ cm\(^{-1}\) and $E = -0.065$ cm\(^{-1}\) (with isotropic $g = 2.275$) at 1.6 K [54].

6.4 INTERACTING RADICAL PAIRS

The earliest EPR work in this specialty area is that done by Bleaney and Bowers [55] and also by Kumagai et al. [56], on cupric acetate monohydrate, in which Cu\textsuperscript{2+} 3d\(^{1}\) ions, each influenced by the local electric field, also interact pairwise and reveal an
effective electron spin of \( S = 1 \) \((g_\perp = 2.08 \text{ and } g_\parallel = 2.42)\) at 90 K. The electronic quadrupolar parameters are \( D/\hbar c = 0.34 \text{ cm}^{-1} \) and \( E/\hbar c = 0.01 \text{ cm}^{-1} \). There are \( 5 \times 5 \) orbital states, with a singlet lowest, each such state with spin degeneracy of \( 2 \times 2 \) (neglecting nuclear Cu spins; these do, however, give rise to observed hyperfine structure). The resulting ground state is a singlet (diamagnetic), while the lowest excited state is a triplet. The latter becomes appreciably populated even at quite low temperatures (>50 K) and gives rise to the observed EPR spectrum. The splitting \( J_0/\hbar c \) (about \( +300 \text{ cm}^{-1} \); see Eq. 6.4) between the singlet and triplet states, as determined from the temperature dependence of the EPR intensity, is caused primarily by the electronic exchange interaction. Thus, here, \( |J_0| \gg g \beta B \). The anisotropy of the \( g \) value indicates presence of appreciable spin-orbit interaction.

In the case of strongly coupled spin = 1/2 identical pairs with nuclear spins, such as described above, the hyperfine coupling parameters have magnitudes half as large as the corresponding values for the single entities.

The case of weakly coupled radical pairs \((|J_0| \ll g \beta B)\) has been successfully treated by Itoh et al. [57]. Here the singlet and triplet are mixed by the Zeeman and hyperfine interactions, and \( J_0 \) can be evaluated from the EPR line positions. This has been done for pairs of RR'C–NO free radicals created by irradiation of single crystals of glyoximes [57]; for \( R = R' = \text{CH}_3 \), \( J_0/\hbar c = +0.200 \text{ cm}^{-1} \).

Obviously, far more detail on the spin-pair systems will be sought. Thus, the exact distances between the pair units, in both the singlet and triplet states, will be welcomed, as will the orientations of these axes within the crystals. Advanced techniques, such as ELDOR in ESE studies (see Chapters 11 and 12), are expected to be helpful in such efforts [58].

### 6.5 Biradicals

As indicated above, a biradical is a molecule containing two unpaired electrons that, on the average, are so far apart that interactions between them are sufficiently weak and energy classification into a singlet and a triplet manifold is not useful. More generally, this category includes radical pairs, in which the spins are located on close but separate species.

The border region between triplet-state species and biradicals is, of course, nebulous, as it is set by the magnitudes of \( D \) and \( E \) compared to that of the singlet-triplet energy separation. We note that as \( D \) and \( E \rightarrow 0 \), the half-field transition remains pretty well in place (see Eq. 6.36b), but declines rapidly in intensity. For triplet states, \(|D/\hbar c|\) typically is in the range \( 0.1–2.5 \text{ cm}^{-1} \) (Section 6.3), but it is this magnitude compared to that of exchange energy parameter \( J_0 \) which is the crucial factor. Thus TMM previously discussed has a triplet ground state with \( D/\hbar c \sim +0.025 \text{ cm}^{-1} \), while \( J_0/\hbar c \) is estimated to be \(-5000 \text{ cm}^{-1}\) [59].

Consider a biradical composed of two identical molecular fragments, each containing one unpaired electron as well as one magnetic nucleus giving rise to hyperfine splitting. We consider the isotropic case. The spin hamiltonian appropriate
to this system is $[60,61]^{16}$

$$\hat{H} = g\beta_e B(\hat{S}_{1z} + \hat{S}_{2z}) + A_0(\hat{S}_1^T \cdot \hat{I}_1 + \hat{S}_2^T \cdot \hat{I}_2) + J_0\hat{S}_1^T \cdot \hat{S}_2 \quad (6.42)$$

Here we consider the biradical to exist in liquid solution so that the anisotropies arising from $g$, $D$ and $T$ are averaged to zero. We neglect the effect of the nuclear Zeeman terms, the cross-hyperfine interactions, and the nucleus-nucleus spin couplings. If $|A_0| \ll g\beta_e B$, then the hyperfine terms may be taken to first order only, and Eq. 6.42 can be approximated as

$$\hat{H} = g\beta_e B(\hat{S}_{1z} + \hat{S}_{2z}) + J_0\hat{S}_1^T \cdot \hat{S}_2 \quad (6.43)$$

where $B \parallel z$.

First, consider the limiting case where $|J_0| \gg |A_0|$. The zero-order spin hamiltonian is then

$$\hat{H}_0 = g\beta_e B(\hat{S}_{1z} + \hat{S}_{2z}) + J_0\hat{S}_1^T \cdot \hat{S}_2 \quad (6.44a)$$

which can be expanded (Section C.1) to yield

$$\hat{H}_0 = g\beta_e B(\hat{S}_{1z} + \hat{S}_{2z}) + J_0\left[\hat{S}_{1z}\hat{S}_{2z} + \frac{1}{2}(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+})\right] \quad (6.44b)$$

The appropriate eigenfunctions are

$$|1, 1\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (6.45a)$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}} \left( \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \left| -\frac{1}{2}, \frac{1}{2} \right\rangle \right) \quad (6.45b)$$

$$|1, -1\rangle = \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle \quad (6.45c)$$

$$|0, 0\rangle = \frac{1}{\sqrt{2}} \left( \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \left| -\frac{1}{2}, \frac{1}{2} \right\rangle \right) \quad (6.45d)$$

The quantum numbers in the right-hand set of kets (uncoupled representation) refer to the eigenvalues of $\hat{S}_{1z}$ and $\hat{S}_{2z}$, whereas those on the left (coupled representation) refer to the quantum numbers $S$ and $M_S$ arising from $\hat{S}_z^2$ and $\hat{S}_z$, where $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$.
The energies to first order (in $A_0$ and $J_0$; note and compare Figs. 6.2 and 6.15, in which $A_0$ is neglected) are

\begin{align}
U_{1,+1}^{(1)} &= +g\beta_e B + J_0/4 + A_0^i M_1/2 \\
U_{1,0}^{(1)} &= +J_0/4 \\
U_{1,-1}^{(1)} &= -g\beta_e B + J_0/4 - A_0^i M_1/2 \\
U_{0,0}^{(1)} &= -3J_0/4
\end{align}

(6.46a) (6.46b) (6.46c) (6.46d)

Here $^iM_I = M_1 + M_2$. The only allowed EPR transitions are $|1, \pm 1\rangle \leftrightarrow |1,0\rangle$, which are degenerate at a transition energy of $g\beta_e B + A_0^i M_I/2$ and are independent of $J_0$. In the case of $I_1 = I_2 = 1$, the first-order spectrum would consist of five lines separated by $|a_0|/2$ (where $a_0 = A_0/g_e\beta_e$) with intensity ratios 1–2–3–2–1, since $^iM_I = -2, \ -1, \ 0, \ +1, \ +2$. An example of this case is the EPR spectrum of the biradical tetramethyl-2,2,5,5-pyrroldioneazine-3 dioxyl1,1 (VII), shown in Fig. 6.16a, where the line separation is only 0.740 mT so that $a_0^i(14N) = 1.480$ mT [62].

**FIGURE 6.16** (a) X-band EPR spectrum of biradical VII showing interaction of both unpaired electrons with nitroxide $^{14}$N nuclei. The spacing is $|a_0|/2$, where $|a_0| = 1.480$ mT is the spacing for the corresponding monoradical (one NO group replaced by NH). [After R. M. Dupeyre, H. Lemaire, A. Rassat, *J. Am. Chem. Soc.*, 87, 3771 (1965).] (b) X-band EPR spectrum of the biradical VIII, in which the nitroxide groups are isolated from each other. The hyperfine splitting (1.56 mT) is just the same as that of the corresponding monoradical. This is an illustration of the case $|J_0| \ll |A_0|$. [After R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, P. Rey, *Bull. Soc. Chim. France*, No. 11, 3290 (1965).]
Now consider the second limiting case, of $|J_0| \ll |A_0|$. The zero-order spin hamiltonian is

$$\hat{H}_0 = g\beta_e B(\hat{S}_{1z} + \hat{S}_{2z}) + A_0[\hat{S}_{1z}\hat{I}_{1z} + \hat{S}_{2z}\hat{I}_{2z}] \quad (6.47)$$

This operator is separable into two parts

$$\hat{H}_0(1) = g\beta_e B\hat{S}_{1z} + A_0\hat{S}_{1z}\hat{I}_{1z} \quad (6.48a)$$
$$\hat{H}_0(2) = g\beta_e B\hat{S}_{2z} + A_0\hat{S}_{2z}\hat{I}_{2z} \quad (6.48b)$$

The eigenfunctions of $\hat{H}_0(1)$ are

$$|+\frac{1}{2}, M_f(1)\rangle \quad \text{and} \quad \lvert -\frac{1}{2}, M_f(1)\rangle$$

with eigenvalues

$$U_{+1/2}^{(0)} = +g\beta_e B/2 + A_0 M_f(1)/2 \quad (6.49a)$$
$$U_{-1/2}^{(0)} = -g\beta_e B/2 - A_0 M_f(1)/2 \quad (6.49b)$$

One obtains analogous results for $\hat{H}_0(2)$. Thus this case may be considered as two non-interacting systems with $S = \frac{1}{2}$. When $I = 1$, the first-order EPR spectrum consists of three lines separated by $|a_0|$. An example of this case is shown in Fig. 6.16b, where the biradical is di(tetramethyl-2,2,6,6-piperidinyl-4

(VII) tetramethyl-2,2,5,5-pyrrolidoneazine-3 dioxyk-1,1'}
oxyl-1)terephthalate (VIII).

The intermediate case of $|J_0| \approx |A_0|$ gives rise to a complex group of lines. The intensity and position of these lines are a strong function of $|J_0/A_0|$ [63–65]. Thus $J_0$ can be extracted from the solution EPR spectrum.

The general case, when one encounters anisotropic parameters and where field $B$ is of arbitrary magnitude, can be dealt with using the spin hamiltonian

$$\hat{H} = \beta_e \mathbf{B} \cdot \mathbf{g}_1 \cdot \mathbf{S}_1 + \beta_e \mathbf{B} \cdot \mathbf{g}_2 \cdot \mathbf{S}_2 + \frac{1}{2} \mathbf{S}_1 \cdot \mathbf{J} \cdot \mathbf{S}_2 + \frac{1}{2} (\mathbf{S}_1 \cdot \mathbf{J} \cdot \mathbf{S}_2 + \text{h.c.})$$

+ nuclear terms as needed

(6.50)

The EPR line positions and relative intensities are obtainable from Eq. 6.50 by numerical (computer) solution. An example of the energy levels for such a case is depicted in Fig. 6.17.

**FIGURE 6.17** The energy levels $U(M_{S_1}, M_{S_2})$ as a function of applied magnetic field $B$ for a biradical system not containing any nuclear spin. The primary EPR transitions ($\Delta M_{S} = \pm 1$), involving the two $M_{S_1} = 0$ levels, are shown. No nuclear spins occur here. The spin-hamiltonian parameters (Eq. 6.50) used to generate the figure are taken from J. Isoya, W. C. Tennant, Y. Uchida, J. A. Weil, *J. Magn. Reson.*, 49, 489 (1982).
Note that the three matrices in Eq. 6.50 are attainable by computer analysis of single-crystal EPR rotational data, where $J$ includes the isotropic exchange parameter $J_0$ as well as the spin-spin dipolar interaction and anisotropic exchange.

### 6.6 SYSTEMS WITH $S > 1$

A few organic high-spin radicals are known. For instance, the assembly of the three diphenylhydrazyl groups (Section E.1.2) mounted meta to each other on a central 1,3,5-tricyanobenzene yields a stable triradical ($S = \frac{3}{2}$), exhibiting $\Delta M_S = \pm 1, \pm 2$ and $\pm 3$ transitions [66]. Perhaps the highest spin multiplicity known for organic molecules at this time is an undecet ground state, arising from the five sets of unpaired electrons formally located at five methylene carbons held between phenyl groups, in the meta-linked molecule $C_6H_5-C-(C_6H_4-C-C_6H_4-C-C_6H_5)_2C_6H_5$ (having $S = 5$) prepared and studied by EPR [67]. More accurately, five of the unpaired electrons are delocalized in a $\pi$ orbital; the other five occur in $\sigma$ non-bonding orbitals.

Monatomic high-spin species can be created (e.g., by irradiation procedures), and have been studied since the mid-1950s or 50. A good example is the nitrogen atom, whose electronic ground state ($S = \frac{3}{2}$) is $^4S_{3/2}$ (see Section B.7). Such atoms can be trapped and stabilized in solid matrices (e.g., in molecular nitrogen at low temperatures [68], in azides [69], and in fullerene cages [70]), in liquids (e.g., superfluid helium [71]), and in gas phase (see Section 7.2). For $N^0$, typical parameters are $g = 2.002$, $D = 0.010 \text{ cm}^{-1}$, $E = -0.002 \text{ cm}^{-1}$ (the latter two measured, of course, in solids) and $a_0(^{14}\text{N}) = 0.5 \text{ mT}$. Because of the high mobility of the atom, $D$ and $E$ are quite temperature-sensitive.

Numerous other inorganic systems offer high-spin ($S > 1$) species. These include clusters of adjacent unpaired electrons (i.e., of $F$ centers) in alkali halides. For instance, three $F$ centers forming an equilateral triangle in the (1,1,1) plane of a KCl crystal constitute an $S = \frac{3}{2}$ center, which has been studied by both EPR and ENDOR [72].

Clusters of transition atoms also lead to high-spin systems. Thus $\text{Mn}_2$ and $\text{Mn}_5$, in rare-gas matrices, are amenable to study by EPR [73]. For $\text{Mn}_2$, since the exchange parameter $J_0$ is negative ($J_0' = -11.0 \text{ T}$, i.e., antiferromagnetic coupling), this molecule features a diamagnetic ground state. However, higher spin states ($S = 1,2,3$) can be thermally populated and yield EPR spectra with characteristic $^{55}\text{Mn}$ ($I = \frac{5}{2}$) hyperfine structure. The pentamer cluster $\text{Mn}_5$ has a total spin $S = \frac{25}{2}$.

More recently, single-molecule magnets (SMMs) have been studied at very high frequencies (40–200 GHz). EPR spectroscopy has yielded information about the energy levels and power saturation behavior of molecular nanomagnet crystals, including ferric complexes (abbreviated ‘Fe$_8$’) and manganese complexes (abbreviated ‘Mn$_{12}$’) [74,75]). Both have effective spin: $S = 10$.

Clearly, the primary domain of high-spin species is that of transition ions (Chapter 8), which have been a fruitful source of EPR progress since the beginnings of this field.
6.7 HIGH-SPIN AND HIGH-FIELD ENERGY TERMS

For magnetic species with $S > 1$, additional terms (e.g., Eqs. 8.17) should be added to the spin hamiltonian (Eq. 6.18), at least in principle. These usually make only relatively small contributions to the total energy of the system but show up as corrections to the EPR line positions and intensities. They are not as simple as the terms in Eq. 6.18, since tensorial entities greater than rank 2 (not expressible as matrices) enter, and each term brings in a multitude of parameters to be obtained from the EPR data. Table 6.2 indicates what types of terms are in principle allowed. This table is a listing of what terms can be present for each value of $S$, ignoring nuclear-spin terms. The symbol $\hat{S}$ implies the possible presence of all three operators $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$. Operator $\hat{S}^2$ indicates the term $\hat{S}^2 = D \cdot \hat{S}$ discussed in this chapter. Similarly, the symbol $B$ here implies the possible presence of $B_x$, $B_y$ and $B_z$. Integers $n$, $n'$ and $n''$ are positive odd integers; thus $n = 1$ indicates the usual electron Zeeman term, and all other integers $n$ (and all $n'$, $n''$) are usually safely ignored (except in highly accurate measurements).

Column 2 in Table 6.2 includes the high-field situation (for any $S$) in which one considers that all spin-hamiltonian parameters are field-dependent. For instance, the Zeeman splitting factor can be written as the series

$$g = g^{(0)} + g^{(2)} B^2 + g^{(4)} B^4 + \cdots$$

(6.51)

Here $g^{(0)}$ is the usual $g$ factor, and the $g^{(2)}$ term describes an energy term having the form of components of $B^3 \hat{S}$ (e.g., $B_x \hat{S}_y \hat{S}_z$), which may become appreciable in the analysis of ultrahigh-field EPR spectra.

### Table 6.2 Possible Electron-Spin Magnetic-Field Terms in the Spin Hamiltonian

<table>
<thead>
<tr>
<th>$S$</th>
<th>$\hat{H}$ Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}$</td>
<td>$\hat{S}B^a$</td>
</tr>
<tr>
<td>1</td>
<td>$\hat{S}B^a$</td>
</tr>
<tr>
<td>$\frac{3}{2}$</td>
<td>$\hat{S}B^a$</td>
</tr>
<tr>
<td>2</td>
<td>$\hat{S}B^a$</td>
</tr>
<tr>
<td>$\frac{5}{2}$</td>
<td>$\hat{S}B^a$</td>
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<td>.</td>
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</table>

*The meaning of the symbols $\hat{S}$ and $B$ in this table are defined in the text (Sections 6.6 and 8.3). Exponents $n$, $n'$ and $n''$ generally are positive integers.*
In accordance with Table 6.2, a term of the form $B \hat{S}^3$ can occur for $S > 1$ [76–78]. With smaller $S$, for example, $S = \frac{1}{2}$, $\hat{S}^3$ can always be written as a linear combination of terms at most linear in $\hat{S}$. Terms of this type can arise from the product in perturbation theory of the normal Zeeman term $g_e \beta_e B \hat{T} \cdot \hat{S}$ and the square $(\hat{L}^T \cdot \hat{S})^2$ of the spin-orbit term [79]. For octahedral or tetrahedral symmetries, the additional terms have the form

$$g' \beta_e [B_\nu \hat{S}_\nu^3 + B_Y \hat{S}_Y^3 + B_Z \hat{S}_Z^3 - B_T \cdot \hat{S} (3 \hat{S}^T \cdot \hat{S} - \hat{I}) / 5]$$

Here the operator form of the last term is a notational formality: $\hat{S}^T \cdot \hat{S} = S(S + 1)$ and $\hat{I} = 1$. With lower symmetry, the number of $BS^3$-type terms increases, and there is proliferation of the parameters describing the effect [78]. Conversely, if description of an experimental spectrum requires such a term, this confirms the identification of an $S > \frac{1}{2}$ state. If there is a nucleus contributing splitting, an additional term of the form $\hat{S}^I \hat{I}$ may also be required.

The derivation and treatment of the terms in Table 6.2 are outside the scope of this book. The reader is referred to a variety of sources for this type of treatment [78, 80–86]. Note the special diagrammatic methods in Ref. 83.

### 6.8 The Spin Hamiltonian: A Summing Up

In the previous chapters, we focused on quantitative description of the Zeeman splittings ($g$), nuclear hyperfine and quadrupolar effects ($A, P$), and the electronic quadrupolar and high-spin interactions ($D, \ldots$). In general, these parameters can all occur simultaneously for any given paramagnetic species. Thus, to describe the EPR spectra (as well as other spectra, e.g., ENDOR), it is necessary to add together all possible terms into a single spin hamiltonian

$$\hat{H} = g \beta_e B^T \cdot \hat{S} + \sum_{i=1}^{N} (\hat{S}^T \cdot A_i \cdot \hat{I}_i + \beta_n B_i^T \cdot \hat{g}_i \cdot \hat{I}_i + \hat{I}_i^T \cdot P_i \cdot \hat{I}_i + \ldots)$$

encountered for any electron spin (composite or not) and $N$ nuclear spins, all contributing to the spectrum. Which terms must be included to analyze any given spectrum is a matter of judgment and experience, added to an understanding of the chemical system being investigated. The correct spin hamiltonian yields the observed positions and relative intensities of the lines, in the absence of dynamic effects (Chapter 10). However, exact energies and transition probabilities obtained by parameter fitting (i.e., repeated diagonalization of $\hat{H}$ by computer) are always possible, generally with some loss of intuitive understanding. One important mental exercise regarding Eq. 6.52 is to note which terms depend on $B$ and which do not (zero-field terms), since the choice of
spectral region (B region) selected to work in is significantly affected by this aspect.

Let us now discuss the signs associated with any parameter matrix \( Y \). The relative signs of the matrix elements \( Y_{ij} \) are all obtainable from the positions of the EPR lines. However, determination of the absolute sign (i.e., which of \( \pm Y \) is correct) may not always be possible. If several matrices (e.g., \( g, D, A, P \)) are important in the spin hamiltonian, the relative signs of some pairs may be available from the data, even though the absolute sign of the set is not. In some cases the relative signs of \( A \) and \( P \) for a particular nucleus may be fixed by the data, but not necessarily with respect to \( A \) and \( P \) of some other nucleus also exhibiting line splittings. Special auxiliary measurements may be needed (see Note 4 in Chapter 4 regarding matrix \( g \) and Section 6.3.1 for matrix \( D \)) to arrive at the most complete sign information.

In summary, determination of the signs of spin-hamiltonian parameters is a non-trivial task.

An approach to visualization of the energy terms arising from a given \( \hat{H} \) is to resort to a perturbation treatment. We now undertake a brief discussion of the results of this approximation technique.

Consider a simplified version of Eq. 6.52, namely

\[
\hat{H} = g_\beta B^T \cdot \hat{S} + \hat{S}^T \cdot D \cdot \hat{S} + \hat{S}^T \cdot A \cdot \hat{I}
\]  

(6.53)

of Eq. 6.52, incorporating the now familiar terms from Chapters 4 and 5. For sufficiently large field \( B \), the first term dominates (if \( M_S = 0 \)) and the other two can be treated as perturbations \[87, 88\]. The resulting single-nucleus second-order energy expressions, valid for any \( S \) and \( I \), and for any coordinate system are

\[
U(M_S, M_I) = g_\beta B M_S + \frac{1}{2} d_1 \left[ 3M_S^2 - S(S + 1) \right] + \\
\frac{1}{2} g_\beta B \left( d_2 - d_1^2 \right) \left[ 8M_S^2 + 1 - 4S(S + 1) \right] M_S + \\
\frac{1}{8} g_\beta B \left[ tr(D)^2 - 2d_2 + d_1^2 - 2d_{1-1} det(D) \right] \left[ 2S(S + 1) - 2M_S^2 - 1 \right] M_S + \\
KM_S M_I + \frac{1}{2} g_\beta B \left\{ \frac{1}{2} \left[ tr(A \cdot A^T) - k_1^2 \right] M_S - [I(I + 1) - M_I^2] \right\} - . \\
\frac{det(A)}{K} \left[ S(S + 1) - M_S^2 \right] M_I + \left( k_1^2 - K^2 \right) M_S M_I^2 + \\
2(e - d_1) K \left[ 3M_S^2 - S(S + 1) \right] M_I 
\]  

(6.54)
Here

\[ g^2 = n^T \cdot g \cdot g^T \cdot n \]  

(6.55a)

\[ d_n = n^T \cdot g \cdot D^n \cdot g^T \cdot n/g^2 \]  

(6.55b)

\[ K^2 = n^T \cdot g \cdot A \cdot A^T \cdot g^T \cdot n/g^2 \]  

(6.55c)

\[ k_1 = n^T \cdot g \cdot A \cdot A^T \cdot A \cdot A^T \cdot g^T \cdot n/g^2 K^2 \]  

(6.55d)

\[ e = n^T \cdot g \cdot \frac{1}{2} (D \cdot A \cdot A^T + A^T \cdot A \cdot D) \cdot g^T \cdot n/g^2 K^2 \]  

(6.55e)

and, as before, \( n = B/B \). Equation 6.55a is the same as Eq. 4.12. We note the presence in Eq. 6.54 of terms in \( B^{-1} \); higher-order perturbation treatment would give further terms, in \( B^{-2} \), and so on. The terms in \( d_{-1}, d_1, d_2, K, k_1 \) and \( e \) demonstrate the intermingling of the three spin-hamiltonian terms in Eq. 6.53 in arriving at the energy expression.

Obviously, from the energy expression 6.54, it is now possible to derive anisotropic spectroscopic frequencies \( [U(M_{S0}, M_{I0}) - U(M_{S0}, M_{I0})]/h \) to be compared with experiment (e.g., see Eqs. 6.34). Similar perturbation techniques are available to derive transition moments, that is, relative intensities [89].

When more than one spin-bearing nucleus is present, there are naturally hyperfine terms in Eq. 6.53, for each nucleus, with resulting energy terms in Eq. 6.54 [90]. Even though no terms coupling the nuclear spins directly have been added to the spin hamiltonian (since such interaction energies are negligibly small), pair-wise cross-terms that depend on \( M_{Ii} \) and \( M_{Ij} \) will nevertheless occur in Eq. 6.54; these arise from electron-mediated dipolar interactions. As usual, for each nucleus with \( I > \frac{1}{2} \), quadrupole terms (Eq. 5.50) should be added to Eq. 6.53.

As more and more terms are included (e.g., nuclear-quadrupole energies [90]), the perturbation energy expressions become increasingly complicated and unwieldy. Clearly, also, the limited applicability of perturbation theory must be kept in mind. Nevertheless, Eq. 6.54 (or its variants) have proved very useful and yield important insights.

Finally, it should be pointed out that the general spin hamiltonian (Eq. 6.52), including all high-spin terms, can be formulated in a far more compact and mathematically elegant form, involving spherical-tensor operators [76,80–85,90]. Thus all the matrices (\( g, D, A, P, \ldots \)) can readily be expressed in terms of the relevant expansion coefficients. The higher-order terms (not formulatable in terms of \( 3 \times 3 \) matrices) are also easily presented. However, all too many different versions and notations regarding this operator structure appear in the literature.

### 6.9 Modeling the Spin-Hamiltonian Parameters

Since the mid-1990s with advent of ever more capable rapid computing systems, the accurate modeling of all the magnetic resonance parameters (e.g., \( g, A, P, D, \ldots \)) has become feasible, and thus there is now quite a burgeoning literature on this topic.
We can cite the text *Calculation of NMR and EPR Parameters* [91], which presents a nice overview. As specific examples, we can indicate the density functional theoretical (DFT) calculation of $g$ matrices, from first principles, say, for paramagnetic diatomic molecules and defect centers in crystalline quartz [92]. For the latter medium, the detailed structural configuration and the $^{17}\text{O}$, $^{27}\text{Al}$ and $^{29}\text{Si}$ hyperfine parameter matrices for the famed center $\text{[AlO}_4\text{]}^0$ have been very successfully calculated [93,94]. Years of such work by Ziegler and his group [95–97], and others, has borne much fruit; for instance, their inclusion of spin orbit coupling has indicated the general occurrence not only of spin singlet-triplet mixing but also the resulting appearance of non-zero spin density on the atoms even of diamagnetic molecules. Simultaneous inclusion of higher-order spin-orbit and spin-polarization effects in a relativistic calculation of electronic $g$ matrices were reported in 2005 [98].

**REFERENCES**

REFERENCES

NOTES

1. Most species containing two unpaired electrons have many other electrons. It is assumed that the spin states of the two electrons are not affected by the other electrons that occupy molecular orbitals, two paired electrons in each.

2. Note the analogous behavior of the $S = I = \frac{1}{2}$ system (Section C.1).

3. The very words ‘singlet’ and ‘triplet’ imply approximate (but most useful) labels, since all two-electron states in reality are mixtures of both.

4. Some authors [5] use the notation $-2\hat{J}_1^* \cdot \hat{S}_2$, and others [6] use $-\hat{J}_1^* \cdot \hat{S}_2$. Thus care must be taken to maintain self-consistency, correct numerical values.

5. We note that exchange is just one manifestation of the coulomb interaction between the electrons and is related to their capability to form a chemical bond.

6. There also exists an electron-spin electron-spin contact interaction, analogous to the Fermi contact interaction that is the mechanism of isotropic hyperfine interaction (Section 2.3.3). However, the magnitude of this term is very small [7]. To the extent that it is present, it contributes to $J_0$.

7. Of course, there is a zero-field splitting arising from the exchange interaction, which splits the singlet and triplet states. Also in the presence of hyperfine interaction there is a zero-field splitting (Section C.1.3), but this is far smaller than that of the dipolar zero-field splittings found in most systems with $S \geq 1$. 

REFERENCES

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8. For arbitrary orientations of $B$, these equations do not apply, since then none of the principal axes of $D$ correspond to the axis of quantization.

9. We consider $d_1 > 0$. When it is negative, $B_h$ and $B_l$ must be interchanged in Eqs. 6.34a,b.

10. Here we have assumed that $D > 0$; for $D < 0$, the field expression must be reversed.

11. We saw earlier that, in simple cases (Figs. 4.7, 4.8, 5.11, and 5.12), the first-derivative peaks in powder patterns occur at field locations for which the line positions are at extrema, which occur with the field $B$ along principal directions of matrix $g$ or $A$. In more complex cases, the peaks in powder spectra show up at field orientations where the line positions $B(\theta, \phi)$ are nearly constant with respect to field orientation [29–31]. These zero-slope positions of $B$, called ‘turning points’, are not necessarily linked to principal-axis locations of individual spin hamiltonian parameter matrices.

12. When matrices $g$ and $D$ are not coaxial, for example, for low-symmetry triplet species, the powder spectra can be considerably more complicated with not easily recognized patterns.

13. Use of dilute single crystals instead of pure naphthalene greatly lengthens the lifetime of the excited triplet state in a particular molecule. In the pure crystal, rapid migration of the triplet excitation usually leads to effective quenching. This technique has been used in some fundamental studies of the excitation of oriented molecules by polarized light [36].

14. The number in parentheses indicates the error in the last place(s).

15. The closely related cation free radical TMM$^+$ also has been studied in detail by EPR [48].

16. Note that, in analogy with the hyperfine interaction term (Eq. C.1), the dot product must be retained for the exchange term.

17. What types and forms of terms are actually allowed to occur in a general $\hat{H}$ is dictated by various physical principles. For a discussion of this, see Refs. 2, 78, and 80–86.

**FURTHER READING**


PROBLEMS

6.1 By substitution of the appropriate spin matrices, derive the spin hamiltonian matrix of Eq. 6.20. Express this in terms of $D$ and $E$.

6.2 (a) Obtain the spin matrices $S_x, S_y, S_z, S_x^2, S_y^2$ and $S_z^2$ using the triplet-state eigenfunctions given in Eqs. 6.28 as a basis set. (b) Use these $3 \times 3$ spin matrices to obtain the spin-hamiltonian matrix 6.29.

6.3 Show that the isotropic part of an electronic quadrupole matrix $D$ affects all spin levels (states $M_S$) equally, so that it generally can be ignored, since it cannot be measured spectroscopically.

6.4 Show that the $\hat{S}_x$ operator causes a transition between the spin states $c_2 |-1\rangle - c_1 |+1\rangle$ and $-i[c_1^*|-1\rangle + c_2^*|+1\rangle]$. Compare the intensity (at any field $B$) of this transition with that obtained using the $\hat{S}_x$ operator in the basis in which the spin hamiltonian matrix is diagonal (Hint: See Section C.1.4.). Thus justify the statements made in Section 6.3.2 concerning the relative orientation of the static and excitation magnetic fields required for observation of the ‘$\Delta M_S = \pm 2$’ transition.

6.5 Use the procedure outlined in Section 6.3.1 to extract the matrix $D$ for the naphthalene triplet in a single crystal of durene from the angular-dependence curves given in Fig. 6.10. Diagonalize $D$ and obtain the values of $D$ and $E$.

6.6 (a) Derive Eqs. 6.32 from Eqs. 6.31, and their analogs for $B \parallel X$ and for $B \parallel Y$. (b) Use the magnetic-field positions and microwave frequency from Fig. 6.4 to obtain $D$ and $E$ for the lowest triplet state of naphthalene, using Eqs. 6.32.

6.7 Show that on crystal rotation, in the case of uniaxial symmetry and at sufficiently high frequency $\nu$, the maximum field spacing between the $\Delta M_S = \pm 1$ transitions (for $S = 1$, $g = g_e$) is given by $\Delta B = 2|D|/g_e g_e = (3 \mu_0/4\pi)g_e g_e \langle r^{-3}\rangle = 5570.85 \langle r^{-3}\rangle$ with $B$ in mT and $r$ in Å.

6.8 Derive the matrix $D$ for the $F_1$ center in MgO, using the information given in the text and in Fig. 6.13.

6.9 The $V^0$ center produced by $x$ irradiation of MgO is an example of an $S = 1$ system in a local electric field of tetragonal symmetry. This defect consists of two positive holes (missing electrons) on opposite sides of a positive-ion vacancy, that is, the array $O^- \square O^-$ instead of $O^2- \square O^2-$. The spin hamiltonian for this system is Eq. 6.19b. For the case of $B \parallel Z$, where $Z$ is the tetragonal axis $\langle 001\rangle$ of the defect, the energy-level scheme and the allowed transitions for a system of this type are depicted in Fig. 6.3. The NMR proton resonance frequencies at the magnetic fields corresponding to
the two transitions shown occur at 13.3345 and 15.2680 MHz; 
\( \nu = 9.4174 \text{ GHz} \).
(a) Calculate the energies of the states in zero field and from these obtain the 
zero-field splitting.
(b) Write expressions for the energies of the two transitions.
(c) From these, find the value of \( D \).
(d) Obtain the value of \( g \) (here \( g_k \)).
(e) What feature of the spectrum could prove that in zero field the \( M_S = +1 \) 
states lie below the \( M_S = 0 \) state, rather than above it?
(f) The separation of the pair of lines is given approximately by
\[
\Delta B = (\mu_0 / 4 \pi) (3 \mu^2 / 2 g_e \beta_e) (r^{-3}) |3 \cos^2 \theta - 1|
\]
as one expects for interacting dipoles aligned by field \( B \). From this, calculate \( (r^{-3}) \) and hence estimate the separation of the two dipoles of spin \( \frac{1}{2} \) 
[99]. (The magnetic moment of a hole has the same absolute magnitude 
as that of the electron.)

6.10 The zero-field splitting parameters for the triplet exciton in anthracene are 
given as \( D = -0.0058 \) and \( E = 0.0327 \text{ cm}^{-1} \). The low value of \( D \) is decep-
tive, since (for this crystal-axis system) \( E > |D| \). After ascertaining the direction 
cosines of the axes of the anthracene molecules relative to the crystal 
axes [100], show that the parameters ascribable to the individual molecules 
are \( D = 0.0688 \) and \( E = -0.0081 \text{ cm}^{-1} \) [101].

6.11 Consider equations 6.36. In that context, can you justify the statement ‘There 
will be exactly four \( B \)-field orientations at which the lowest possible half-field 
line position \( B_{\text{min}} \) of a given triplet-state species occurs, if it occurs at all’? If 
so, do so and provide a critique citing at least five conditions that must be met 
for the statement to be valid.

6.12 Consider the proton hyperfine structure in the X-band EPR spectrum of triplet 
trimethylenemethane.
(a) Justify that 4096 hyperfine lines are to be expected for each of the two 
primary (\( \Delta M_S = \pm 1 \)) transitions.
(b) The isotropic proton splitting (in mT) is given (Chapter 9) by
\[
a_H \approx -2.46 \rho_{\pi}^a - 0.19 \rho_{\pi}^c \quad (6.56)
\]
at least approximately. Here the superindices \( a \) and \( c \) denote the adjacent 
and central carbon atoms. Using the relation
\[
3 \rho_{\pi}^a + \rho_{\pi}^c \approx 1 \quad (6.57)
\]
estimate the unpaired-electron populations \( \rho_{\pi} \) in the molecule [102].
Nitrogen atoms trapped at 77 K in irradiated potassium azide exhibit an EPR spectrum reproduced by the spin hamiltonian

\[ \hat{H} = \beta_z B^T \cdot g \cdot \hat{S} + D \hat{S}_Z^2 + E(\hat{S}_X^2 - \hat{S}_Y^2) + \hat{S}^T \cdot A \cdot \hat{I} \]  

(6.58)

with \( g = 2.001 \), \( D = +0.0143 \text{ cm}^{-1} \), \( E = -0.00199 \text{ cm}^{-1} \) and \( A = 0.00051 \text{ cm}^{-1} \) [103]. Parameters \( g \) and \( A \) are isotropic. What is the spin \( S \), and why? Draw semi-quantitatively the EPR spectrum expected at 9.2 GHz for the field orientation yielding the largest fine-structure splitting, including a field scale (mT).

The application of a scannable radiofrequency field \( B_1 \) to a sample containing molecules in a photo-excited triplet state can yield zero-field transitions detected directly in the transmitted light intensity. Such absorption-detected magnetic resonance in a photosynthetic reaction center at 12 K has yielded relatively strong absorptions in the 890 nm light, at frequencies \( v = 466 \) and 658 MHz, and a weaker one at 191 MHz [104]. Using Fig. 6.3, estimate values of \( |D|/h \) and \( |E|/h \) from these data.