CHAPTER 17

STATIC FIELDS

17.1 Magnetic Fields

It is assumed that the electron (or hydrogen atom) is placed in a constant magnetic field $\mathbf{B}$ with vector potential

$$\mathbf{A} = \tfrac{1}{2}\mathbf{B} \times \mathbf{r}. \qquad (17.1\text{-}1)$$

Referring to the Schrödinger equation (15.2-32) the interaction terms that depend on the vector potential are

$$\frac{e}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2mc^2}A^2 + \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \nabla \times \mathbf{A}. \qquad (17.1\text{-}2)$$

When $\mathbf{A}$ has form (17.1-1), $\nabla \cdot \mathbf{A}$ is identically zero as a result of which

$$\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}. \qquad (17.1\text{-}3)$$

We shall confine our attention, initially, to effects which are linear in $\mathbf{B} = \nabla \times \mathbf{A}$; hence the Hamiltonian describing the interaction with the field is

$$\mathcal{H}_m = \frac{e}{mc}\mathbf{A} \cdot \mathbf{p} + \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \mathbf{B}. \qquad (17.1\text{-}4)$$

But

$$\mathbf{A} \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \times \mathbf{r} \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot \mathbf{r} \times \mathbf{p} = \tfrac{1}{2}\hbar\mathbf{B} \cdot \mathbf{L} \qquad (17.1\text{-}5)$$

in which $\mathbf{L}$ is the orbital angular momentum operator. With the replacement of $\boldsymbol{\sigma}$ by $2\mathbf{S}$ and substitution of (17.1-5) into (17.1-4) we have

$$\mathcal{H}_m = \frac{e\hbar}{2mc}\mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}) = \beta\mathbf{B} \cdot (\mathbf{L} + 2\mathbf{S}). \qquad (17.1\text{-}6)$$

The positive constant

$$\beta = \frac{e\hbar}{2mc} = 9.27 \times 10^{-21} \quad \text{erg/G}$$

$$= 9.27 \times 10^{-24} \text{ J/T}. \qquad (17.1\text{-}7)$$

is known as the *Bohr magneton*.

Equation (17.1-6) may also be written as

$$\mathcal{H}_m = -\boldsymbol{\mu}_L \cdot \mathbf{B} - \boldsymbol{\mu}_S \cdot \mathbf{B} \qquad (17.1\text{-}8)$$

where

$$\boldsymbol{\mu}_L = -\beta\mathbf{L}; \qquad \boldsymbol{\mu}_S = -2\beta\mathbf{S}. \qquad (17.1\text{-}9)$$

The resemblance of (17.1-8) to the classical expression for the energy of a magnetic dipole in a magnetic field suggests that $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_S$ be interpreted as magnetic moment operators associated with $\mathbf{L}$ and $\mathbf{S}$, respectively. The minus signs in (17.1-9) are due to the negative charge on the electron. Note that the factor of 2 appears in the relation between $\boldsymbol{\mu}_S$ and $\mathbf{S}$ and is absent in the relation between $\boldsymbol{\mu}_L$ and $\mathbf{L}$. The latter has a classical analog but the former does not. Actually, the factor of 2 is slightly erroneous; higher order corrections show that

$$\boldsymbol{\mu}_S = -g_e\beta\mathbf{S} \qquad (17.1\text{-}10)$$

with

$$g_e = 2.0023; \qquad (17.1\text{-}11)$$

although in most cases it is sufficient to set $g_e = 2$.

It is important to distinguish between a magnetic moment operator $\boldsymbol{\mu}$ such as $\boldsymbol{\mu}_L$ or $\boldsymbol{\mu}_S$ defined by (17.1-9) from the quantity μ known as "the magnetic moment." The orbital magnetic moment μ_L is defined as

$$\mu_L = \langle l\, m_l = l | \mu_z^{L} | l\, m_l = l \rangle \qquad (17.1\text{-}12)$$

where μ_z^{L} is the z component of $\boldsymbol{\mu}_L$. From (17.1-9),

$$\mu_L = -\beta\langle l\, m_l = l | L_z | l\, m_l = l \rangle = -\beta l. \qquad (17.1\text{-}13)$$

Similarly, the spin magnetic moment μ_S is given by

$$\mu_S = \langle s\, m_s = s | \mu_z^{S} | s\, m_s = s \rangle$$
$$= -\beta g_e \langle s\, m_s = s | S_z | s\, m_s = s \rangle$$
$$= -\beta g_e s = -\tfrac{1}{2}\beta g_e \approx -\beta. \qquad (17.1\text{-}14)$$

In other words, the absolute value of the spin magnetic moment of the electron is one Bohr magneton.

In place of (17.1-9) we may now write

$$\boldsymbol{\mu}_L = \frac{\mu_L}{l}\,\mathbf{L}; \qquad \boldsymbol{\mu}_S = \frac{\mu_S}{s}\,\mathbf{S} = 2\mu_S\mathbf{S}. \qquad (17.1\text{-}15)$$

It is convenient, although not essential, to assume that the coordinate system has been chosen so that the z axis coincides with the direction of $\mathbf{B}$. In that case (17.1-6) simplifies to

$$\mathscr{H}_m = \beta B(L_z + 2S_z) \qquad (17.1\text{-}16)$$

where $B = B_z$. We shall now divide the discussion of magnetic field effects into two parts: "weak" fields and "strong" fields. The scale is set by the spin-orbit interaction energy. If the changes in energy due to the application of a magnetic field are small compared with the spin-orbit coupling energy, the field is said to be "weak"; otherwise it is strong. The "weak" field case is the regime of the ordinary *Zeeman effect* while the "strong" field case corresponds to the *Paschen–Back* effect.

When the fields are "weak" it is presumed that the effects of spin-orbit coupling have already been taken into account so that the eigenstates are described in the coupled representation $|lsjm\rangle$. We shall therefore be interested in matrix elements of $\mathscr{H}_m$ in this basis set. Furthermore, the assumption of a "weak" field implies that individual terms like $^2S_{1/2}$, $^2P_{1/2}$, $^2P_{3/2}$, etc., are sufficiently isolated so that attention can be confined to matrix elements which are diagonal in l, s, and j. To evaluate such matrix elements we apply the Landé formula (6.3-19):

$$\langle lsjm'|L_z + 2S_z|lsjm\rangle = \frac{\langle lsjm|(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{J}|lsjm\rangle}{j(j+1)}\langle lsjm'|J_z|lsjm\rangle. \quad (17.1\text{-}17)$$

But

$$\langle lsjm'|J_z|lsjm\rangle = m\,\delta_{m'm} \qquad (17.1\text{-}18)$$

and

$$(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{J} = (\mathbf{J} + \mathbf{S})\cdot\mathbf{J} = J^2 + \mathbf{S}\cdot\mathbf{J}.$$

Since

$$\mathbf{L} = \mathbf{J} - \mathbf{S}, \qquad L^2 = J^2 + S^2 - 2\mathbf{S}\cdot\mathbf{J},$$

and

$$\mathbf{S}\cdot\mathbf{J} = \tfrac{1}{2}(J^2 + S^2 - L^2),$$

we have

$$(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{J} = \tfrac{3}{2}J^2 + \tfrac{1}{2}(S^2 - L^2).$$

Therefore

$$\langle lsjm|(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{J}|lsjm\rangle = \langle lsjm|\tfrac{3}{2}J^2 + \tfrac{1}{2}(S^2 - L^2)|lsjm\rangle$$
$$= \tfrac{3}{2}j(j+1) + \tfrac{1}{2}s(s+1) - \tfrac{1}{2}l(l+1),$$

$$\frac{\langle lsjm|(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{J}|lsjm\rangle}{j(j+1)} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

$$\equiv g_J = \text{Landé } g \text{ factor.} \qquad (17.1\text{-}19)$$

Substituting (17.1-18) and (17.1-19) into (17.1-17) we obtain

$$\langle lsjm'|L_z + 2S_z|lsjm\rangle = g_J m\,\delta_{m'm} \qquad (17.1\text{-}20)$$

which indicates that only diagonal elements are nonzero. Hence the energies in a "weak" magnetic field are given by

$$E_m = \beta g_J B m. \qquad (17.1\text{-}21)$$

These are known as the *Zeeman levels* with energies proportional to the magnetic quantum number m. Thus, the effect of the magnetic field has been to remove the m-degeneracy.

The Landé g factor (17.1-19) may also be written as

$$g_J = 1 + (g_e - 1)\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \qquad (17.1\text{-}22)$$

to permit the use of the more exact value of g_e given by (17.1-11).

It is now possible to define a total magnetic moment operator $\boldsymbol{\mu}_J$ by

$$\boldsymbol{\mu}_J = -\beta g_J \mathbf{J} \qquad (17.1\text{-}23)$$

which contains (17.1-9) as special cases. Corresponding to (17.1-12)–(17.1-14) we have, for the total magnetic moment

$$\mu_J = \langle jm = j|\mu_z{}^J|jm = j\rangle = -g_J\beta\langle jm = j|J_z|jm = j\rangle = -\beta g_J j. \quad (17.1\text{-}24)$$

Hence (17.1-23) may be written as

$$\boldsymbol{\mu}_J = (\mu_J/j)\mathbf{J},$$

and, in terms of $\boldsymbol{\mu}_J$, the magnetic Hamiltonian (17.1-6) is

$$\mathscr{H}_m = -\boldsymbol{\mu}_J \cdot \mathbf{B} \qquad (17.1\text{-}25)$$

which then leads directly to (17.1-21). Also, on comparing (17.1-25) with (17.1-8), it is seen that

$$\boldsymbol{\mu}_J = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S. \qquad (17.1\text{-}26)$$
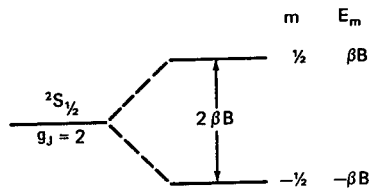
FIG. 17.1 Splitting of $^2S_{1/2}$ in a weak magnetic field.

For an electron in an s state ($^2S_{1/2}$), $l = 0$, $s = \frac{1}{2}$, $j = \frac{1}{2}$, $g_J = 2$ so that the energies, from (17.1-21) are

$$E_m = \pm \beta B \qquad (17.1\text{-}27)$$

as shown in Fig. 17.1. The energy separations in $^2P_{1/2}$ and $^2P_{3/2}$ are

$$E_m(^2P_{1/2}) = \pm\tfrac{1}{3}\beta B$$
$$E_m(^2P_{3/2}) = \pm 2\beta B, \pm\tfrac{2}{3}\beta B \qquad (17.1\text{-}28)$$
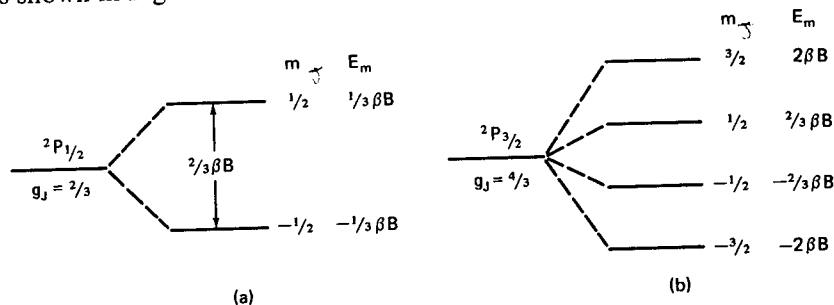
as shown in Fig. 17.2.

FIG. 17.2 Splitting of (a) $^2P_{1/2}$ and (b) $^2P_{3/2}$ in a weak magnetic field.

As the strength of the field is increased to the point where the splitting is comparable to the spin-orbit coupling, it is no longer legitimate to isolate a single term with a specific value of j. In place of (17.1-6), the Hamiltonian must now include both the spin orbit interaction and the magnetic field term:

$$\mathcal{H}_m' = \xi(r)\mathbf{L}\cdot\mathbf{S} + \beta B(L_z + 2S_z). \qquad (17.1\text{-}29)$$

Matrix elements are most conveniently calculated in the $|lsm_lm_s\rangle$ representation, since then

$$\langle l'sm_l'm_s'|L_z + 2S_z|lsm_lm_s\rangle = (m_l + 2m_s)\delta_{l'l}\delta_{m_l'm_l}\delta_{m_s'm_s} \qquad (17.1\text{-}30)$$

and

$$\langle l'sm_l'm_s'|\mathbf{L}\cdot\mathbf{S}|lsm_lm_s\rangle = \langle l'sm_l'm_s'| -L_{+1}S_{-1} + L_0S_0 - L_{-1}S_{+1}|lsm_lm_s\rangle. \qquad (17.1\text{-}31)$$

	$\left|1\,\tfrac{1}{2}\right\rangle$	$\left|1\,-\tfrac{1}{2}\right\rangle$	$\left|0\,\tfrac{1}{2}\right\rangle$	$\left|0\,-\tfrac{1}{2}\right\rangle$	$\left|-1\,\tfrac{1}{2}\right\rangle$	$\left|-1\,-\tfrac{1}{2}\right\rangle$
$\left\langle 1\,\tfrac{1}{2}\right|$	$\tfrac{1}{2}\xi_{nl} + 2\beta B$					
$\left\langle 1\,-\tfrac{1}{2}\right|$		$-\tfrac{1}{2}\xi_{nl}$	$\tfrac{1}{\sqrt{2}}\xi_{nl}$			
$\left\langle 0\,\tfrac{1}{2}\right|$		$\tfrac{1}{\sqrt{2}}\xi_{nl}$	βB			
$\left\langle 0\,-\tfrac{1}{2}\right|$				$-\beta B$	$\tfrac{1}{\sqrt{2}}\xi_{nl}$	
$\left\langle -1\,\tfrac{1}{2}\right|$				$\tfrac{1}{\sqrt{2}}\xi_{nl}$	$-\tfrac{1}{2}\xi_{nl}$	
$\left\langle -1\,-\tfrac{1}{2}\right|$						$\tfrac{1}{2}\xi_{nl} - 2\beta B$

For the 2p manifold, the matrix elements of $\mathbf{L}\cdot\mathbf{S}$ have already been calculated (Table 16.5). Adding the magnetic field interaction from (17.1-30), the results are those shown in Table 17.1. The secular equation, therefore, factors into

$$\left(2\beta B + \tfrac{1}{2}\xi_{nl} - E\right) = 0 \qquad m_l = 1,\ m_s = \tfrac{1}{2}$$

$$\begin{vmatrix} -\tfrac{1}{2}\xi_{nl} - E & \tfrac{1}{\sqrt{2}}\xi_{nl} \\ \tfrac{1}{\sqrt{2}}\xi_{nl} & \beta B - E \end{vmatrix} = 0 \qquad m_l = 1, 0,\ m_s = \mp\tfrac{1}{2}$$

$$\qquad\qquad (17.1\text{-}32)$$

$$\begin{vmatrix} -\beta B - E & \tfrac{1}{\sqrt{2}}\xi_{nl} \\ \tfrac{1}{\sqrt{2}}\xi_{nl} & -\tfrac{1}{2}\xi_{nl} - E \end{vmatrix} = 0 \qquad m_l = 0, -1,\ m_s = \pm\tfrac{1}{2}$$

$$\left(\tfrac{1}{2}\xi_{nl} - 2\beta B - E\right) = 0 \qquad m_l = -1,\ m_s = -\tfrac{1}{2}$$
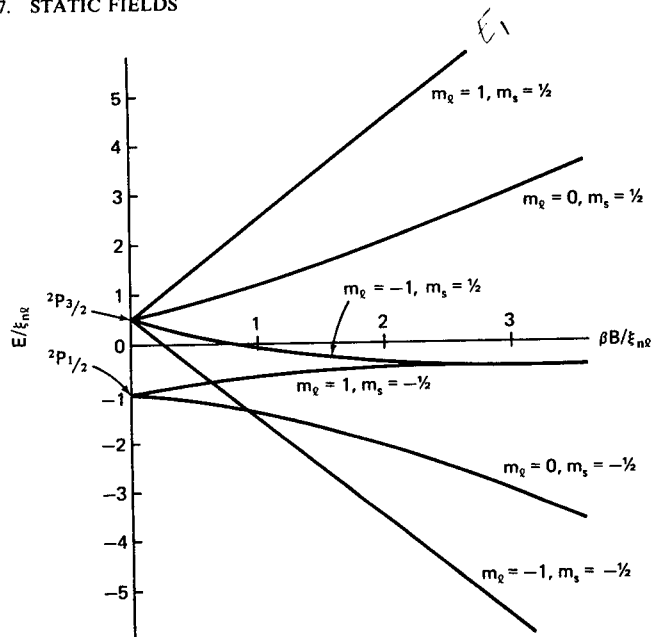
FIG. 17.3   Transition from a weak to a strong magnetic field for a ^2P term.

from which the energy eigenvalues are readily calculated. They are

$$\frac{E_1}{\xi_{nl}} = 2\frac{\beta B}{\xi_{nl}} + \frac{1}{2},$$

$$\frac{E_{2,3}}{\xi_{nl}} = \frac{1}{2}\left\{\left(\frac{\beta B}{\xi_{nl}} - \frac{1}{2}\right) \pm \left[\left(\frac{\beta B}{\xi_{nl}}\right)^2 + \left(\frac{\beta B}{\xi_{nl}}\right) + \frac{9}{4}\right]^{1/2}\right\},$$

$$\frac{E_{4,5}}{\xi_{nl}} = \frac{1}{2}\left\{-\left(\frac{\beta B}{\xi_{nl}} + \frac{1}{2}\right) \pm \left[\left(\frac{\beta B}{\xi_{nl}}\right)^2 - \left(\frac{\beta B}{\xi_{nl}}\right) + \frac{9}{4}\right]^{1/2}\right\}, \quad (17.1\text{-}33)$$

$$\frac{E_6}{\xi_{nl}} = -2\frac{\beta B}{\xi_{nl}} + \frac{1}{2}.$$

These energies are plotted in Fig. 17.3. A few special cases are of interest.

$\beta B \gg \xi_{nl}$:   This is the *Paschen–Back* region. In this approximation the energies conform to the expression

$$E_m = \beta B(m_l + 2m_s). \quad (17.1\text{-}34)$$

$\beta B \ll \xi_{nl}$:   If we confine ourselves to linear terms in βB, the reduction of (17.1-33) gives

$$E_1 = \tfrac{1}{2}\xi_{nl} + 2\beta B, \qquad E_2 = \tfrac{1}{2}\xi_{nl} + \tfrac{2}{3}\beta B, \qquad E_3 = -\xi_{nl} + \tfrac{1}{3}\beta B,$$
$$E_4 = \tfrac{1}{2}\xi_{nl} - \tfrac{2}{3}\beta B, \qquad E_5 = -\xi_{nl} - \tfrac{1}{3}\beta B, \qquad E_6 = \tfrac{1}{2}\xi_{nl} - 2\beta B. \quad (17.1\text{-}35)$$

These are precisely the energies obtained on the basis of (16.3-12) for the spin-orbit interaction with $l = 1$ and (17.1-21) for the splitting in a "weak" magnetic field. The correlations between the "weak" field and "strong" field levels are shown in Fig. 17.4. Note that states with the same value of $m (= m_l + m_s)$ do not cross. A further point is that the "weak" field case is best described in the coupled representation as evidenced by the fact that m is a "good" quantum number. In a classical sense this means that the orbital and spin angular momenta are coupled to produce a total angular momentum and it is the latter which precesses about the applied magnetic field. On the other hand, when the field is "strong," the "good" quantum numbers are m_l and m_s. This is in the uncoupled representation and corresponds, classically, to the orbital angular momentum and the spin angular momentum *individually* precessing about the field (Fig. 17.5).

A further point to note is that, when an atom is subjected to a magnetic field, the Hamiltonian is no longer invariant under all three-dimensional rotations but only under rotations about an axis parallel to the magnetic field. In other words, the symmetry has been reduced from $O^+(3)$ to C_∞. The consequence of this restriction in symmetry is that the Hamiltonian no longer commutes with J^2, although it commutes with J_z. Alternatively, it may be a said that, in a magnetic field, j is not a good quantum number but m is. When these features are fully realized, the field is regarded as "strong"
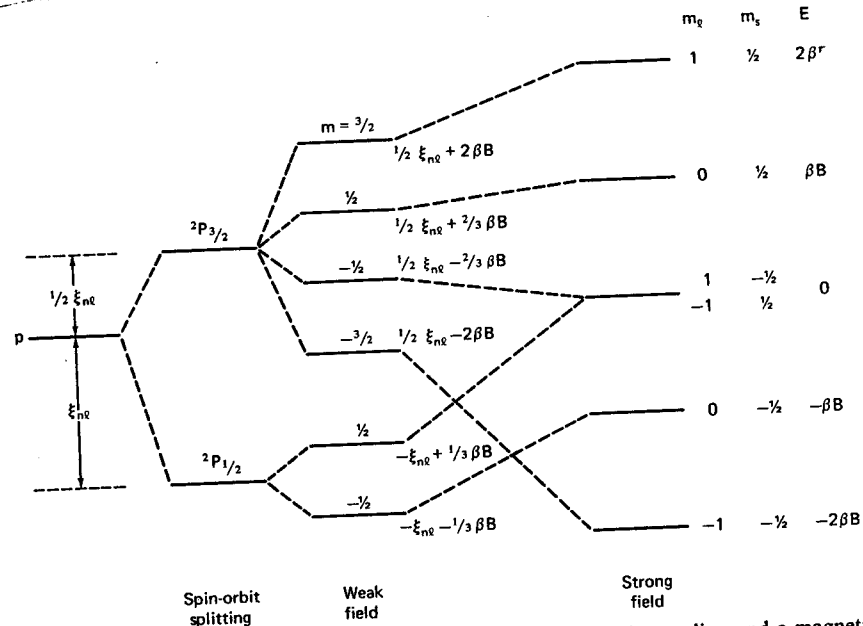

FIG. 17.4   Splitting of a p state under the influence of spin-orbit coupling and a magnetic field.
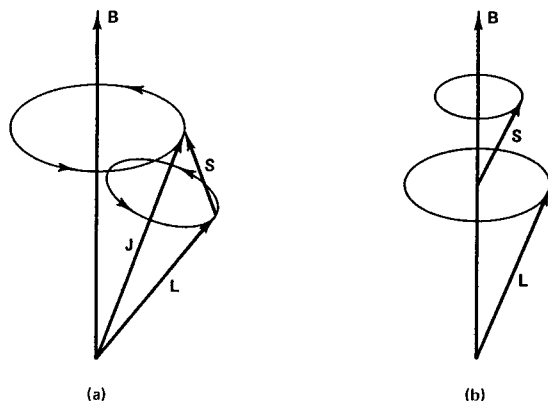
FIG. 17.5 Precession of **L, S, J** in (a) a weak and (b) a strong magnetic field.

and by the same token, a "weak" field is one for which, to a good approximation, j is still a good quantum number.

We note that the degeneracy in hydrogen between $2^2S_{1/2}$ and $2^2P_{1/2}$ has no effect on the computation performed above. Because of (17.1-29), matrix elements of $L_z + 2S_z$ between 2s and 2p vanish; the spin-orbit coupling matrix element (17.1-31) also vanishes unless $\Delta l = 0$.

Experiments in which photons are used to excite electronic transitions between magnetic substates are known as electron spin resonance (ESR) or electron paramagnetic resonance (EPR) experiments. For an s state the energies are given by (17.1-27); hence the photon energy must satisfy

$$\hbar\omega = 2\beta B \qquad (17.1-36)$$

and upon inserting numerical values for the constants, the photon frequency v is

$$v = \frac{\omega}{2\pi} = 2.80B\,\text{MHz}\ (s = \tfrac{1}{2},\ B\ \text{in gauss}). \qquad (17.1-37)$$

This relation is also applicable to a large number of free radicals.

The term in A^2 contained in (17.1-2) with **A** given by (17.1-1) is

$$\mathscr{H}_d = \frac{e^2}{2mc^2}\tfrac{1}{4}(\mathbf{B}\times\mathbf{r})\cdot(\mathbf{B}\times\mathbf{r}) = \frac{e^2}{8mc^2}B^2r^2\sin^2\theta \qquad (17.1-38)$$

where θ is the angle between **B** and **r**. For the ground state of hydrogen or any other spherically symmetric state the expectation value of (17.1-38) is

$$E_d = \frac{e^2}{8mc^2}B^2\langle r^2\rangle\,\overline{\sin^2\theta} = \frac{e^2}{12mc^2}B^2\langle r^2\rangle \qquad (17.1-39)$$

in which $\langle r^2\rangle$ is the expectation value of r^2, r is the distance of the electron from the nucleus and $\overline{\sin^2\theta}$ is a spherical average. The ratio of E_d in (17.1-39) to E_m in (17.1-21) at fields of the order of 10^4 gauss is approximately equal to $\alpha^2 = (e^2/\hbar c)^2 = (1/137)^2$.

For the magnetic moment we may take

$$\mu = -\frac{\partial E_d}{\partial B} = -\frac{e^2}{6mc^2}B\langle r^2\rangle \qquad (17.1-40)$$

from which we obtain the *diamagnetic susceptibility*

$$\chi_d = \frac{\mu}{B} = -\frac{e^2}{6mc^2}\langle r^2\rangle = -\tfrac{1}{6}\alpha^2 a_0\langle r^2\rangle \qquad (17.1-41)$$

where a_0 is the Bohr radius.

Diamagnetism arises as a consequence of the orbital motion of the electrons; hence it is a general property of all atoms and molecules. Paramagnetism, on the other hand, has its origin in the alignments of magnetic moments associated with orbital and spin angular momenta in an external magnetic field. Quite often, an electronic system may possess both a diamagnetic and paramagnetic susceptibility.

17.2 Electric Fields

Electric fields may also have an effect on the states of an atom. This is known as the Stark effect. The discussion in this section will be confined to hydrogen which is somewhat unique in this respect.

If the coordinate system is chosen so that the z axis coincides with the direction of the electric field, the Hamiltonian for the interaction is

$$\mathscr{H}_s = eEz = eEr\cos\theta. \qquad (17.2-1)$$

The situation of greatest physical interest is the one in which the splittings due to the Stark effect are large compared to the spin-orbit splittings. A numerical estimate of the required field will be given later. As in the case of high magnetic fields, the uncoupled representation is the appropriate one; we shall therefore calculate matrix elements of $\mathscr{H}_s$ in the $|nlsm_lm_s\rangle$ representation.

It is convenient to replace $\cos\theta$ in (17.2-1) by $\sqrt{4\pi/3}\,Y_{10}$ so that we may make use of the theorem (1.2-29):

$$\langle l'm_{l'}|Y_{LM}|lm_l\rangle = (-1)^{m_{l'}}\sqrt{(2l'+1)(2L+1)(2l+1)/4\pi}$$

$$\times\begin{pmatrix} l' & L & l \\ -m_{l'} & M & m_l \end{pmatrix}\begin{pmatrix} l' & L & l \\ 0 & 0 & 0 \end{pmatrix}. \qquad (17.2-2)$$

The matrix element vanishes when $l' + L + l$ is odd, that is, when the integrand is of odd parity. In the present case $Y_{LM} = Y_{10}$ which means that the expectation value of $\mathcal{H}_s$ must vanish for any state in which l is a good quantum number. From this we conclude that there is no first-order splitting due to an electric field.

Although this conclusion is generally correct, it does not hold for hydrogen. The reason is that the energy in hydrogen, in first approximation, depends only on the principal quantum number n and not on l. Consider, for example, the case $n = 2$. This consists of four degenerate states: $l = 0, m_l = 0; l = 1, m_l = 0, \pm 1$. Within this manifold of states there will be nonvanishing matrix elements of Y_{10} between the state with $l = 0$ and states with $l = 1$. A first-order Stark effect in hydrogen is therefore expected.

To proceed with the calculation it is noted that

$$\begin{pmatrix} l' & L & l \\ -m_l' & M & m_l \end{pmatrix} = 0$$

unless $-m_l' + M + m_l = 0$. Since $M = 0, m_l$ and m_l' are equal. Moreover $m_l' = m_l = 0$ because one of the l values is zero. This leaves two nonzero matrix elements in (17.2-2) which are

$$\langle 00|Y_{10}|10\rangle = \langle 10|Y_{10}|00\rangle = 1/\sqrt{4\pi}. \tag{17.2-3}$$

Also, the matrix element of r taken between the 2s function and the radial part of the $2p_0$ wave function is given by

$$\langle 2s|r|R(2p_0)\rangle = \langle R(2p_0)|r|2s\rangle = \frac{9}{\sqrt{3}}\frac{a_0}{Z}. \tag{17.2-4}$$

Combining the results from (17.2-3) and (17.2-4), the Hamiltonian matrix is the one shown in Table 17.2 with eigenvalues

$$E_s = 3eEa_0/Z, \quad 0, \quad 0, \quad -3eEa_0/Z. \tag{17.2-5}$$

TABLE 17.2

Matrix Elements for the Stark Effect in Hydrogen with
$n = 2, s = \frac{1}{2}, m_s = m_s'$

	$|0\,0\rangle$	$|1\,0\rangle$	$|1\,1\rangle$	$|1\,-1\rangle$
$\langle 0\,0|$		$3eEa_0/Z$		
$\langle 1\,0|$	$3eEa_0/Z$			
$\langle 1\,1|$				
$\langle 1\,-1|$				

The two states with $m_l = 0$ are shifted up and down symmetrically while the states with $m_l = \pm 1$ are not affected by the electric field. Thus, the m degeneracy is only partially lifted.

In hydrogen, assuming $E = 10^4$ V cm^{-1} and $Z = 1$,

$$3eEa_0/Z = 1.3 \quad \text{cm}^{-1},$$

which is considerably larger than the fine structure splitting (Section 16.3 and Fig. 16.5).

It is seen that because of the degeneracy of states with different l and the same n there is a *linear* Stark effect in hydrogen. At very high field strengths a quadratic effect appears, superimposed upon the linear effect, and results in an asymmetric shift of energy levels.