10.2 Hyperfine structure of hydrogen

The most important interactions in an atom are the Coulomb interactions between the electrons and the nuclear charge. [The latter charge is sometimes called the nuclear monopole ($E0$) moment.] However, additional couplings exist between the electrons and higher magnetic and electric multipole moments of the nucleus. These couplings are responsible for hyperfine structure (hfs) observed in atomic spectra. If the nucleus has spin $I \geq 1/2$, it can possess a magnetic dipole moment μ_I. Also, if $J \geq 1/2$, a nonzero magnetic field B_e is generated at the nucleus from electron spin and orbital motion. The coupling of μ_I to B_e causes magnetic dipole ($M1$) hfs, which is the most significant contribution to hfs. If $I \geq 1$, the nucleus can possess an electric quadrupole ($E2$) moment, and if $J \geq 1$, the electronic charge distribution generates a nonzero electric field gradient at the nucleus. The coupling of the quadrupole moment and the electric field gradient produces an additional ($E2$) hfs energy shift. Smaller still but observable

nonetheless in a few cases is magnetic octupole (M3) hfs, which requires $I \geq 3/2$, $J \geq 3/2$. Note that static moments $E0$, $E2$, $E4$, ... and $M1$, $M3$, ... are allowed, but static moments $E1$, $E3$, ... and $M2$, $M4$, ... are forbidden by space-inversion and time-reversal symmetries, a point to be discussed later.

In this section we confine ourselves to a discussion of $M1$ hfs in the hydrogen atom. Here the perturbation Hamiltonian is

$$H_{hfs} = -\mu_p \cdot B_e \tag{10.20}$$

where $\mu_p = g_p \mu_N I$ is the proton spin magnetic moment operator. Let the position of the electron with respect to the nucleus be r_e, and define $r = -r_e$. Now

$$B_e = \nabla \times A_e \tag{10.21}$$

where in atomic units

$$A_e = \frac{\mu_e \times r}{r^3} = -\mu_e \times \nabla \left(\frac{1}{r} \right) \tag{10.22}$$

In the analysis of hyperfine structure, there is a fundamental difference between s-states and states with $\ell > 0$. For s-states, the wave functions of which are spherically symmetric and non-zero at the origin, calculation of B_e requires special attention because A_e is singular at $r = 0$. No such difficulty occurs for states with $\ell > 0$ because these wave functions vanish at the origin. In the latter case, we can assume that $r \neq 0$ when using (10.21) and (10.22) to find B_e. We start our analysis with the simpler case $\ell > 0$. The identity

$$\nabla \times (a \times b) = a(\nabla \cdot b) - b(\nabla \cdot a) + (b \cdot \nabla)a - (a \cdot \nabla)b$$

and the fact that the electron spin magnetic moment μ_s is a fixed quantity independent of the coordinates imply that the magnetic field B_{es} generated by μ_s is

$$B_{es} = \nabla \times A_{es} = \frac{1}{4\pi} \left[(\mu_s \cdot \nabla) \nabla \left(\frac{1}{r} \right) - \mu_s \nabla^2 \left(\frac{1}{r} \right) \right] \tag{10.23}$$

The second term on the right-hand side of (10.23) vanishes for $r \neq 0$, and the first term is

$$B_{e,s}^{\ell>0}(0) = \left(\frac{3\mu_s \cdot rr}{r^5} - \frac{\mu_s}{r^3} \right) \tag{10.24}$$

In addition, there exists a contribution μ_ℓ / r^3 to $B_e^{\ell>0}$ arising from orbital motion of the electron, where $\mu_\ell = -\mu_B L = -\mu_B (r_e \times p)$. Altogether for $\ell > 0$ we have

$$B_e^{\ell>0}(0) = \frac{3(\mu_s \cdot r)r}{r^5} - \frac{\mu_s}{r^3} + \frac{\mu_\ell}{r^3} \tag{10.25}$$

We now turn our attention to s-states and make use of the following picture: let an imaginary sphere be centered on the proton, with radius R larger than the proton radius but much smaller than the Bohr radius a_0. Because $R \ll a_0$,

$$\psi_{ns}(r_e) = \psi_{ns}(0)$$

is an excellent approximation for the spatial wave function at all points inside the sphere. Outside the sphere, $\psi_{ns}(r_e)$ does vary with r_e when the latter becomes comparable with a_0, but in any event, $\psi_{ns}(r_e)$ is spherically symmetric everywhere. Because the electron has a spin magnetic moment, there exists a magnetic moment density or magnetization

$$M(r_e) = \mu_s |\psi_{ns}(r_e)|^2$$

Using subscripts i and o to denote the interior and exterior of the sphere, respectively, we note that inside the sphere of radius R, the magnetization is uniform with value

$$M_i = \mu_s |\psi_{ns}(0)|^2$$

Outside the sphere, M_o is spherically symmetric everywhere, although it also varies with r_e when the latter becomes comparable with a_0. Thus M_o gives no contribution to $B_e(0)$; however, from elementary magnetostatics, we have

$$B_e^{\ell=0}(0) = \frac{8\pi}{3} M_i = \frac{8\pi}{3}\mu_s |\psi_{ns}(0)|^2 \qquad (10.2)$$

Taking (10.25) and (10.26) into account, we write the hfs Hamiltonian (10.20) as

$$H_{\text{hfs}} = \left[-\frac{8\pi}{3}\mu_p \cdot \mu_s \delta^3(r) \right]_{\ell=0} + \left[\left(\frac{\mu_p \cdot \mu_s}{r^3} - \frac{3\mu_p \cdot r \mu_s \cdot r}{r^5} \right) - \frac{\mu_p \cdot \mu_\ell}{r^3} \right]_{\ell>0} \qquad (10.$$

The first bracketed term on the right-hand side of (10.27) is sometimes called the *contact interaction*. In the Dirac theory, the derivation of (10.27) is actually more transparent, as will see in Chapter 21. Equation (10.27) was first derived by E. Fermi in 1930 using the Dirac theory.

We now calculate the first-order hyperfine energies of s-states in hydrogen. Noting that

$$\mu_p = g_p \frac{\alpha}{2m_p} I = g_p \mu_B \frac{m_e}{m_p} I$$

where $g_p = 5.58$ and I is the nuclear spin, and employing the contact interaction term in (10. we obtain

$$\Delta E_{\text{hfs}}^{(1)}(ns) = \frac{8\pi}{3} g_p g_s \mu_B^2 \frac{m_e}{m_p} \langle ns | \delta^3(r) | ns \rangle \langle I \cdot S \rangle \qquad (1($$

In atomic units, $\langle ns | \delta^3(r) | ns \rangle = 1/\pi n^3$ and $\mu_B = \alpha/2$. Thus (10.28) becomes

$$\Delta E_{\text{hfs}}^{(1)}(ns) = a\langle I \cdot S \rangle \tag{10.29}$$

where

$$a = \frac{2}{3n^3} g_p g_s \alpha^2 \frac{m_e}{m_p} \tag{10.30}$$

The total atomic angular-momentum operator, including nuclear spin, is defined as $F = I + J$. Also, $i = 1/2$ for the proton, and $j = s = 1/2$ for the s-states; thus $f = 1$ or 0. The $f = 1$ multiplet contains three components: $m_F = 1, 0,$ and -1, whereas the $f = 0$ state is a singlet with $m_F = 0$. In the absence of hfs interaction, all four components are degenerate. However, because

$$\langle I \cdot S \rangle = \frac{f(f+1) - i(i+1) - s(s+1)}{2} = \frac{f(f+1)}{2} - \frac{3}{4}$$

(10.29) yields

$$\Delta E_{\text{hfs}}^{(1)}(ns, f = 1) = \frac{a}{4}$$
$$\Delta E_{\text{hfs}}^{(1)}(ns, f = 0) = -\frac{3a}{4} \tag{10.31}$$

for a hyperfine splitting between $f = 1$ and $f = 0$ of

$$\delta = a = \frac{2}{3n^3} g_p g_s \alpha^2 \frac{m_e}{m_p} \tag{10.32}$$

Note that even when H_{hfs} is included, the three m_F components of $f = 1$ remain degenerate in the absence of an external magnetic field. However, when such a field is imposed, the degeneracy is lifted by the Zeeman effect, to be discussed in the next section.

The hyperfine transition between $f = 1$ and $f = 0$ in the ground state of hydrogen is used in high-precision atomic clocks and is also extremely important in radioastronomy, where it is observed in absorption and emission. The quantity $a = 1.4204$ GHz (wavelength $= 21$ cm) has actually been measured to a precision of more than 12 significant figures using hydrogen maser techniques and is one of the most accurately determined physical quantities. For a precise comparison between theory and experiment, (10.32) with $g_s = 2$ is not accurate enough. The most important correction to a is the g-factor anomaly a_e in $g_s = 2(1 + a_e)$. In addition, there are small but important effects resulting from finite proton mass, proton recoil, relativistic electron motion, and so on. When all these corrections are included, theory and experiment agree, but the theoretical uncertainty, about 1 part per million (1 ppm), is much larger than the experimental uncertainty.

The hyperfine energies of states with $\ell > 0$ are derived from the second bracketed term on the right-hand side of (10.27). Assuming that $g_s = 2, g_\ell = 1$, it can be shown with the aid of the Wigner-Eckart theorem (see Section 7.12) that

$$\Delta E_{\text{hfs}}^{(1)}\left(n, \ell > 0, j, f\right) = \alpha^2 \frac{m_e}{m_p} g_p \frac{\ell(\ell+1)\left[f(f+1)-i(i+1)-j(j+1)\right]}{4j(j+1)}\left\langle \frac{1}{r^3}\right\rangle$$

$$= \alpha^2 \frac{m_e}{m_p} g_p \frac{\left[f(f+1)-i(i+1)-j(j+1)\right]}{2n^3(2\ell+1)j(j+1)} \qquad (10.33)$$

10.3 Zeeman effect

In the presence of an external magnetic field $\boldsymbol{B} = B_0\hat{z}$, the Hamiltonian for a hydrogenic atom is

$$H = \frac{1}{2\mu}\left(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\right)^2 - \frac{Z}{r} + H_{fs} + H_{hfs} + g_s\mu_B \boldsymbol{S}\cdot\boldsymbol{B} - g_p\mu_N \boldsymbol{I}\cdot\boldsymbol{B} \qquad (10.34)$$

where $H_{fs} = H_{\text{Darwin}} + H_1 + H_{so}$ and the external vector potential A can be chosen as

$$A = \frac{B_0}{2}\left(x\hat{y} - y\hat{x}\right)$$

to give $\boldsymbol{B} = \nabla \times \boldsymbol{A}$. Ignoring the distinction between the reduced mass μ and m_e, we expand the first term on the right-hand side of (10.34)

$$\frac{1}{2m_e}\left(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\right)^2 = \frac{p^2}{2m_e} + \frac{e}{2m_ec}\left(\boldsymbol{A}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{A}\right) + \frac{e^2}{2m_ec^2}A^2 \qquad (10.35)$$

Because $\nabla\cdot\boldsymbol{A} = 0$, $\boldsymbol{p}\cdot\boldsymbol{A} = \boldsymbol{A}\cdot\boldsymbol{p} - i\nabla\cdot\boldsymbol{A} = \boldsymbol{A}\cdot\boldsymbol{p}$. Also,

$$\boldsymbol{A}\cdot\boldsymbol{p} = B_0\left(xp_y - yp_x\right)/2 = B_0L_z/2$$

where $\boldsymbol{L} = \left(\boldsymbol{r} \times \boldsymbol{p}\right)$. Thus (10.34) becomes

$$H = H_0 + H_{fs} + H_{hfs} + g_\ell\mu_B\boldsymbol{L}\cdot\boldsymbol{B} + g_s\mu_B\boldsymbol{S}\cdot\boldsymbol{B} - g_p\mu_N\boldsymbol{I}\cdot\boldsymbol{B} + \frac{\alpha^2}{2}A^2 \qquad (10.36)$$

Here $H_0 = \left(p^2/2m_e\right) + V$, and $g_\ell = 1$ is the orbital g-value. Later in this section we discuss the final term on the right-hand side of (10.36). For the present, we ignore it and concentrate on the remaining perturbing terms. In particular, for the ground state of hydrogen, we are concerned with the Zeeman effect of the hyperfine structure and thus with the third, fifth, and sixth terms of (10.36). Here the perturbing Hamiltonian is

$$H' = a\boldsymbol{I}\cdot\boldsymbol{S} + g_s\mu_B B_0 S_z - g_p\mu_N B_0 I_z \qquad (10.37)$$

Defining the positive constants $k_1 = g_s \mu_B B_0$ and $k_2 = g_p \mu_N B_0$, where $k_1 \gg k_2$, we write (10.37) as

$$H' = a\mathbf{I} \cdot \mathbf{S} + k_1 S_z - k_2 I_z$$
$$= \frac{a}{2}[I_+ S_- + I_- S_+] + a I_z S_z + k_1 S_z - k_2 I_z \tag{10.38}$$

In the absence of H', the ground-state components $f = 1$ $(m_F = 1, 0, -1)$ and $f = 0$, $m_F = 0$ are degenerate. Hence we may choose any convenient orthonormal linear combinations of these components as a basis for the perturbation matrix of H'. We arbitrarily choose the four basis states:

$$u_{1s} \cdot \left\{ \alpha_e \alpha_p,\ \beta_e \beta_p,\ \alpha_e \beta_p,\ \beta_e \alpha_p \right\} \tag{10.39}$$

where u_{1s} is the spatial wave function, and as usual, α (β) signifies spin up (down). With rows and columns in the same order as (10.39), the perturbation matrix is

$$\langle H' \rangle = \begin{pmatrix} \dfrac{a}{4} + \dfrac{k_1 - k_2}{2} & 0 & 0 & 0 \\[2ex] 0 & \dfrac{a}{4} - \dfrac{k_1 - k_2}{2} & 0 & 0 \\[2ex] 0 & 0 & -\dfrac{a}{4} + \dfrac{k_1 + k_2}{2} & \dfrac{a}{2} \\[2ex] 0 & 0 & \dfrac{a}{2} & -\dfrac{a}{4} - \dfrac{k_1 + k_2}{2} \end{pmatrix} \tag{10.40}$$

The eigenvalues

$$\lambda_1 = \frac{a}{4} + \frac{k_1 - k_2}{2} \tag{10.41}$$

and

$$\lambda_{-1} = \frac{a}{4} - \frac{k_1 - k_2}{2} \tag{10.42}$$

correspond to the $f = 1$ states $\alpha_e \alpha_p$ $(m_F = 1)$ and $\beta_e \beta_p$ $(m_F = -1)$, respectively, and are linear in B_0 with opposite slopes. To find the other two eigenvalues, we diagonalize the 2×2 submatrix in the lower right-hand corner of (10.40). Its secular determinant is

$$\begin{vmatrix} -\dfrac{a}{4} + \dfrac{k_1 + k_2}{2} - \lambda & \dfrac{a}{2} \\[2ex] \dfrac{a}{2} & -\dfrac{a}{4} - \dfrac{k_1 + k_2}{2} - \lambda \end{vmatrix} = 0$$
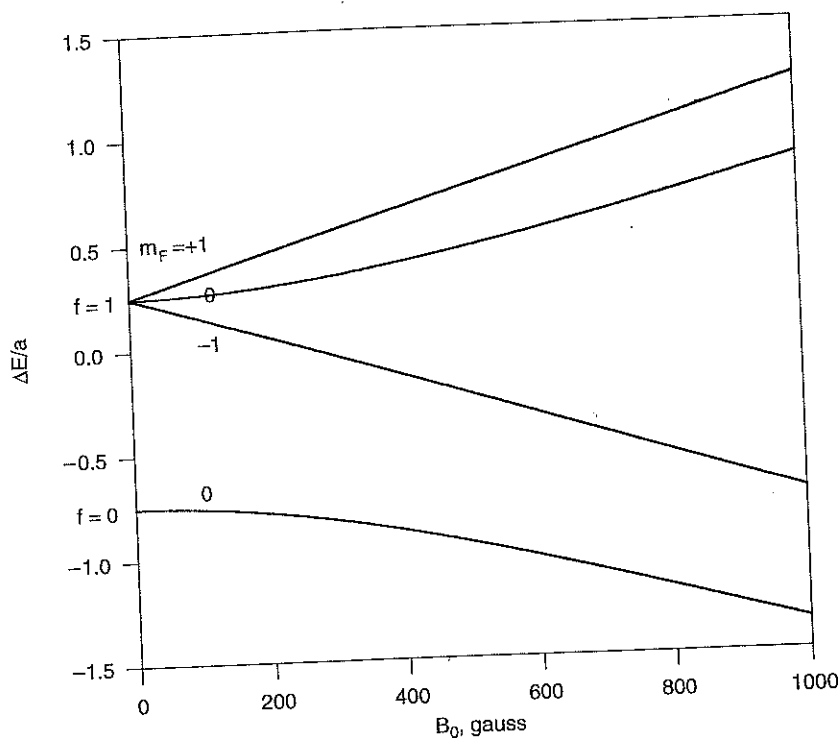
Figure 10.2   Zeeman effect of the hyperfine structure of the $1^2s_{1/2}$ state of hydrogen.

which yields

$$\left(\lambda + \frac{a}{4}\right)^2 = \left(\frac{k_1 + k_2}{2}\right)^2 + \frac{a^2}{4} \tag{10.43}$$

We define $x = (k_1 + k_2)/a$ and find from (10.43) that the two eigenvalues are

$$\lambda_\pm = -\frac{a}{4} \pm \frac{a}{2}\sqrt{1 + x^2} \tag{10.44}$$

Because x is proportional to B_0, we have $\lambda_+ (B_0 = 0) = a/4$, $\lambda_- (B_0 = 0) = -3a/4$. Thus $\lambda_\pm (B_0 = 0)$ obviously correspond to the states $f = 1, m_F = 0$, and $f = 0, m_F = 0$, respectively. Wher $0 < x \ll 1$, $\sqrt{1 + x^2} \approx 1 + x^2/2$; hence, for small x, $\lambda_\pm$ vary quadratically with x. However, wher $x \gg 1$, $\sqrt{1 + x^2} \approx x$ and $\lambda_\pm$ are linear in x with opposite slopes. Figure 10.2 shows the four eigen values plotted as a function of B_0.

It remains to find the eigenvectors corresponding to $\lambda_\pm$. These can be expressed as

$$\psi_\pm = a_\pm(x)\alpha_e\beta_p + b_\pm(x)\beta_e\alpha_p \tag{10.45}$$

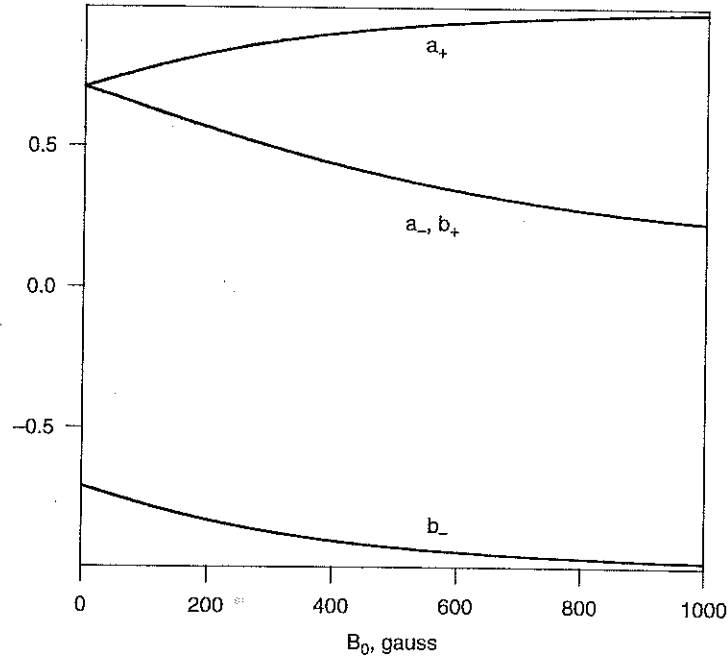The coefficients $a_\pm(x), b_\pm(x)$ are found from the eigenvalue equation

Figure 10.3 Coefficients $a_\pm$ and $b_\pm$ plotted versus B_0.

$$\begin{pmatrix} -\dfrac{a}{4}+\dfrac{ax}{2} & \dfrac{a}{2} \\[2ex] \dfrac{a}{2} & -\dfrac{a}{4}+\dfrac{ax}{2} \end{pmatrix}\begin{pmatrix} a_\pm \\[1ex] b_\pm \end{pmatrix} = \left(-\dfrac{a}{4}\pm\dfrac{a}{2}\sqrt{1+x^2}\right)\begin{pmatrix} a_\pm \\[1ex] b_\pm \end{pmatrix}$$

and from the normalization condition $a_\pm^2 + b_\pm^2 = 1$. We obtain

$$a_\pm = \frac{1}{\left[1+\left(x\mp\sqrt{1+x^2}\right)^2\right]^{1/2}} \tag{10.46a}$$

and

$$b_\pm = \frac{-\left(x\mp\sqrt{1+x^2}\right)}{\left[1+\left(x\mp\sqrt{1+x^2}\right)^2\right]^{1/2}} \tag{10.46b}$$

These coefficients are plotted versus B_0 in Figure 10.3.

Note that when $x=0$, $a_+ = a_- = 2^{-1/2}$ and $b_+ = -b_- = 2^{-1/2}$, but when $x \gg 1$, $a_+ \to 1$ and $a_- \to 0$, whereas $b_+ \to 0$ and $b_- \to -1$. These relations have a simple physical meaning. When B_0 is small ($x \ll 1$), the electron and proton spins are much more tightly coupled with one another by the hyperfine interaction than they are with the weak external field. Thus neither m_I nor m_J is a good quantum number; only f and m_F are well defined. For large B_0 ($x \gg 1$), the reverse is

(0.43)

10.44)

$_0 = 0)$
When
when
eigen-

10.45)

true: electron and proton spins separately precess about the strong external field, so neither f nor m_F is a good quantum number, but m_I and m_J become well defined.

The Zeeman effect for other hyperfine levels in hydrogen or in a multielectron atom is calculated according to similar principles. The main task is to diagonalize a perturbation matrix such as (10.40). For $I = 1/2$ and any J or for $J = \frac{1}{2}$ and any I, the matrix can be reduced to block diagonal form, where the submatrices are 2×2; hence only quadratic equations appear. In more complicated cases, the perturbation matrix is most easily diagonalized numerically by computer.

The Zeeman effect of fine-structure levels is calculated by the same method. For example, consider the $n = 2$, $\ell = 1$ states of ${}^4\text{He}^+$. Here the nuclear spin is zero, and there is no hyperfine structure. From (10.36), the relevant portion of the perturbing Hamiltonian is

$$H' = H_{fs} + g_\ell \mu_B \boldsymbol{L} \cdot \boldsymbol{B} + g_s \mu_B \boldsymbol{S} \cdot \boldsymbol{B} \tag{10.47}$$

and apart from an additive constant, $H_{fs} = \left(\alpha^2/3\right)\boldsymbol{L} \cdot \boldsymbol{S}$ in atomic units. The 6×6 perturbation matrix H' for $\ell = 1$, $s = 1/2$ is easily diagonalized.

Finally, we consider the last term on the right-hand side of (10.36); that is,

$$H_Q = \frac{\alpha^2}{2} A^2 = \frac{\alpha^2 B_0^2}{8}\left(x^2 + y^2\right) \tag{10.48}$$

This term is responsible for the quadratic Zeeman effect. It does not depend on S, L, J, or I and therefore does not cause any splittings between different magnetic sublevels of a zero-order eigenstate with given values of n and ℓ. Because $\langle x^2 + y^2 \rangle = 2\langle r^2 \rangle/3$ for s-states, the first-order energy shift in atomic units is

$$\Delta E_Q^{(1)} = \frac{\alpha^2 B_0^2}{12}\langle r^2 \rangle \tag{10.49}$$

Employing the formula

$$\langle r^2 \rangle = \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3\ell(\ell+1)\right] \tag{10.50}$$

we see that although $\Delta E_Q^{(1)}$ is very small for ordinary magnetic fields and low principal quantum numbers, it grows roughly in proportion to n^4 and thus becomes significant for $n \gg 1$. This is important in the case of a Rydberg atom, which is an atom (from almost anywhere in the periodic table) in which a valence electron is excited to a very high-lying state. The nucleus and remaining electrons form a compact core with effective charge $Z_{\text{eff}} = 1$, and the wave function of the valence electron is essentially hydrogenic with $n \gg 1$.

The positive-energy-shift quadratic in B_0 implies negative magnetic susceptibility; thus H_Q is directly related to diamagnetism. As is well known, this phenomenon arises from Lenz's law; if we apply an external magnetic field to an atom or a group of atoms by increasing the field from zero, the electron(s) experience a changing magnetic flux while the field is increasing. Thus, by Faraday's law, an electromagnetic force (emf) is generated that causes the electronic orbital currents to change. These incremental orbital currents generate an incremental magnetic field that is always opposite in direction to the applied field and generally much smaller in magnitude.

For illustration, we calculate the diamagnetic correction to the applied magnetic field at the origin of a hydrogen atom in its ground state. Such corrections are significant in high-precision nuclear magnetic resonance experiments and not merely for atomic hydrogen.

To start, we recall from equation (4.76) that in the presence of a vector potential A, the probability current density in atomic units for an electron is

$$j = \frac{1}{2i}\left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) + \alpha A \psi^* \psi$$

The electromagnetic current density is

$$j_{EM} = -ej = \frac{-1}{2i}\left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) - \alpha A \psi^* \psi \tag{10.51}$$

In (10.51), only the second term on the right-hand side is important for diamagnetism; thus, in what follows, we ignore the first term. The electromagnetic current density generates a new vector potential according to the well-known formula

$$A'(r) = \frac{1}{c}\int \frac{j_{EM}(r')}{|r - r'|}\, d^3r' = -\alpha^2 \int \frac{A(r')\rho(r')}{|r - r'|}\, d^3r' \tag{10.52}$$

where $\rho = \psi^* \psi$. The magnetic field generated by this vector potential is

$$B'(r) = \nabla \times A'(r) = \alpha^2 \int \frac{r - r'}{|r - r'|^3} \times A(r')\rho(r')\, d^3r'$$

Hence, at the origin,

$$B'(0) = -\alpha^2 \int \frac{r' \times A(r')}{r'^3}\rho(r')\, d^3r' \tag{10.53}$$

Because $A(r') = (B_0/2)(x'\hat{y} - y'\hat{x})$,

$$r' \times A(r') = \frac{B_0}{2}\left[-(x'z')\hat{x} - (y'z')\hat{y} + (x'^2 + y'^2)\hat{z}\right] \tag{10.54}$$

Only the third term on the right-hand side of (10.54) makes a nonzero contribution to the integral in (10.53). For the $1s$ state of hydrogen, it yields

$$B'(0) = -\frac{\alpha^2}{2} B_0 \hat{z} \int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r'\left(\frac{1}{\pi}\right)\exp(-2r')\, dr'$$
$$= -\frac{\alpha^2}{3} B(0) \tag{10.55}$$

As anticipated, the diamagnetic correction to the applied magnetic field B is proportional to B but in the opposite direction, and because $\alpha^2/3 = 1.78 \times 10^{-5}$, it is much smaller than B itself.