In the quantum-mechanical picture, shielding shifts the energy of the S state below that of the P states, thus ensuring that, in the absence of an imposed field, the atom is spherical and has no dipole moment. An electric field deprives L^2 of its status as a constant of motion because the field can apply a torque to the atom. Shielding is a very weak effect in hydrogen (because it relies on the vacuum's virtual electrons and positrons), so the S state lies very little below the P states and in even a weak electric field this offset becomes irrelevant. The lowest-energy state becomes $(|200\rangle + |210\rangle)/\sqrt{2}$. This is not an eigenket of L^2 but it is an eigenket of L_z with eigenvalue zero. Thus its angular momentum is perpendicular to the field, as we expect from the classical picture of a Kepler ellipse with its major axis parallel to **E**. Figure 10.1 shows that in this state the charge distribution comprises a dense cloud around the origin and an extended cloud centred on $R = 0$, $z \simeq -3a_0$. We can think of these clouds as arising from the pericentre and apocentre, respectively, of eccentric orbits that have their major axes roughly aligned with the negative z-axis. The integral $\int \mathrm{d}^3\mathbf{x}, z|\psi|^2 = -3a_0$, so in this state the atom has dipole moment $P = +3ea_0$.

10.1.3 Effect of an external magnetic field

When an atom is placed in a magnetic field, the wavelengths of lines in its spectrum change slightly. Much of quantum mechanics emerged from attempts to understand this phenomenon. We now use perturbation theory to explain it.

In Chapter 9 we discussed the motion of a free particle in a uniform magnetic field. Our starting point was the Hamiltonian (9.1), which governs the motion of a free particle of mass m and charge Q in the magnetic field produced by the vector potential $\mathbf{A}$. This is the Hamiltonian of a free particle, $p^2/2m$, with $\mathbf{p}$ replaced by $\mathbf{p} - Q\mathbf{A}$. Hence we can incorporate the effects of a magnetic field on a hydrogen atom by replacing $\mathbf{p}_\mathrm{n}$ and $\mathbf{p}_\mathrm{e}$ in the gross-structure Hamiltonian (8.1) with $\mathbf{p}_\mathrm{n} - e\mathbf{A}$ and $\mathbf{p}_\mathrm{e} + e\mathbf{A}$, respectively.

The magnitude of $\mathbf{A}$ is gauge dependent, and we should choose a gauge that makes $|e\mathbf{A}|$ small relative to $|\mathbf{p}|$. Since atoms are very small, it should be satisfactory to treat the magnetic field $\mathbf{B}$ as uniform within an atom, so a possible choice is $\mathbf{A} = \frac{1}{2}\mathbf{B}\times\mathbf{x}$ (page 255). We saw in §9.3.1 that shifting the coordinate origin along a vector $\mathbf{a}$ so $\mathbf{x} \to \mathbf{x}' = \mathbf{x} - \mathbf{a}$ and $\mathbf{A} \to \mathbf{A}' = \frac{1}{2}\mathbf{B}\times\mathbf{x}'$ amounts to a gauge transformation. It is clear that the values taken by $\mathbf{A}$ within the atom will be minimised if we place take the coordinate origin at the atom's centre of mass, so we will do this.

With $Z = 1$ the kinetic-energy term in the Hamiltonian then becomes

$$\begin{aligned} H_\mathrm{KE} &\equiv \frac{(\mathbf{p}_\mathrm{n} - \frac{1}{2}e\mathbf{B}\times\mathbf{x}_\mathrm{n})^2}{2m_\mathrm{n}} + \frac{(\mathbf{p}_\mathrm{e} + \frac{1}{2}e\mathbf{B}\times\mathbf{x}_\mathrm{e})^2}{2m_\mathrm{e}} \\ &= \frac{p_\mathrm{n}^2}{2m_\mathrm{n}} + \frac{p_\mathrm{e}^2}{2m_\mathrm{e}} + e\left(\mathbf{B}\times\mathbf{x}_\mathrm{e}\cdot\frac{\mathbf{p}_\mathrm{e}}{2m_\mathrm{e}} - \mathbf{B}\times\mathbf{x}_\mathrm{n}\cdot\frac{\mathbf{p}_\mathbf{n}}{2m_\mathrm{n}}\right) + \mathrm{O}(|\mathbf{B}|^2), \end{aligned} \tag{10.20}$$

where we have taken advantage of the fact that $\mathbf{p}\cdot\mathbf{B}\times\mathbf{x} = \mathbf{B}\times\mathbf{x}\cdot\mathbf{p}$ because this triple scalar product involves only products of orthogonal components of $\mathbf{x}$ and $\mathbf{p}$, which commute with each other. Moreover, we can exploit the usual symmetry of a scalar triple product to replace $\mathbf{B}\times\mathbf{x}\cdot\mathbf{p}$ by $\mathbf{B}\cdot\mathbf{x}\times\mathbf{p}$.

We neglect the terms that are $\mathrm{O}(|\mathbf{B}|^2)$ on the grounds that when the field is weak enough for the $\mathrm{O}(|\mathbf{B}|)$ terms to be small compared to the terms in the gross-structure Hamiltonian, the $\mathrm{O}(|\mathbf{B}|^2)$ terms are negligible. With this approximation, the magnetic field's contribution to the Hamiltonian is

$$H_B \equiv e\mathbf{B}\cdot\left(\mathbf{x}_\mathrm{e}\times\frac{\mathbf{p}_\mathrm{e}}{2m_\mathrm{e}} - \mathbf{x}_\mathrm{n}\times\frac{\mathbf{p}_\mathbf{n}}{2m_\mathrm{n}}\right). \tag{10.21}$$

Now we need to express H_B in terms of the centre-of-mass coordinate $\mathbf{X}$ and the position $\mathbf{r}$ of the reduced particle. From the definitions (8.3) we have

$$\mathbf{x}_\mathrm{e} = \mathbf{X} + \frac{m_\mathrm{n}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r} \quad\text{and}\quad \mathbf{x}_\mathrm{n} = \mathbf{X} - \frac{m_\mathrm{e}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r}. \tag{10.22}$$

Equation (8.4) and the corresponding equation for $\partial/\partial\mathbf{x}_\mathrm{n}$ imply that

$$\mathbf{p}_\mathrm{e} = \frac{m_\mathrm{e}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{p}_\mathbf{X} + \mathbf{p}_\mathbf{r} \quad\text{and}\quad \mathbf{p}_\mathrm{n} = \frac{m_\mathrm{n}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{p}_\mathbf{X} - \mathbf{p}_\mathbf{r}, \tag{10.23}$$

where $\mathbf{p}_\mathbf{X}$ is the momentum associated with the centre-of-mass coordinate $\mathbf{X}$, while $\mathbf{p}_\mathbf{r}$ is the momentum of the reduced particle. In terms of the new variables

$$\begin{aligned} H_B &= \tfrac{1}{2}e\mathbf{B}\cdot\left(\frac{\mathbf{x}_\mathrm{e}\times\mathbf{p}_\mathrm{e}}{m_\mathrm{e}} - \frac{\mathbf{x}_\mathrm{n}\times\mathbf{p}_\mathbf{n}}{m_\mathrm{n}}\right)\\ &= \tfrac{1}{2}e\mathbf{B}\cdot\left\{\left(\mathbf{X}+\frac{m_\mathrm{n}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r}\right)\times\left(\frac{1}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{p}_\mathbf{X}+\frac{1}{m_\mathrm{e}}\mathbf{p}_\mathbf{r}\right)\right.\\ &\qquad\left.-\left(\mathbf{X}-\frac{m_\mathrm{e}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r}\right)\times\left(\frac{1}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{p}_\mathbf{X}-\frac{1}{m_\mathrm{n}}\mathbf{p}_\mathbf{r}\right)\right\}. \end{aligned} \tag{10.24}$$

When we multiply out the brackets, the terms with $\mathbf{X}\times\mathbf{p}_\mathbf{X}$ will cancel and what remains is

$$\begin{aligned} H_B = \tfrac{1}{2}e\mathbf{B}\cdot\Bigg\{&\left(\frac{1}{m_\mathrm{e}}+\frac{1}{m_\mathrm{n}}\right)\mathbf{X}\times\mathbf{p}_\mathbf{r} + \frac{1}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r}\times\mathbf{p}_\mathbf{X}\\ &+\frac{m_\mathrm{n}/m_\mathrm{e}-m_\mathrm{e}/m_\mathrm{n}}{m_\mathrm{e}+m_\mathrm{n}}\mathbf{r}\times\mathbf{p}_\mathbf{r}\Bigg\}. \end{aligned} \tag{10.25}$$

We will require matrix elements of H_B formed by squeezing the operator between states of the set $|\mathbf{p}_\mathbf{X}\rangle|n,l,m\rangle$ in which the atom has momentum $\mathbf{p}_\mathbf{X}$ and internal structure characterised by the usual quantum numbers n, l, m. Since we have placed the coordinate origin at the centre of mass, and we want the atom to be at rest in our coordinate system to the extent that the uncertainty relation allows, in the states of interest both $\langle \mathbf{X} \rangle = 0$ and $\langle \mathbf{p_X} \rangle = 0$. Consequently, the first two terms in our expression (10.25) for H_B, which involve $\mathbf{X}$ and $\mathbf{p_X}$, will not contribute to the relevant matrix elements, and we can take the perturbing Hamiltonian to be

$$H_B = \frac{e(m_\mathrm{n} - m_\mathrm{e})}{2m_\mathrm{e}m_\mathrm{n}}\mathbf{B}\cdot\mathbf{r}\times\mathbf{p_r} \simeq \frac{e\hbar}{2m_\mathrm{e}}\mathbf{B}\cdot\mathbf{L}, \qquad (10.26)$$

where $\mathbf{L} = \mathbf{r}\times\mathbf{p_r}/\hbar$ is the usual orbital angular momentum operator. If an atom has more than one unpaired ('valence') electron, each electron will contribute a term of this form to the overall Hamiltonian. We can fold these separate contributions into a single contribution H_B by interpreting $\mathbf{L}$ as the sum of the angular-momentum operators of the individual electrons.

For future reference, note that since $\mathbf{B}\cdot\mathbf{r}\times\mathbf{p_r} = \mathbf{B}\times\mathbf{r}\cdot\mathbf{p_r} = 2\mathbf{A}\cdot\mathbf{p_r}$, we can also write the perturbation introduced by a magnetic field in the form

$$H_B = \frac{e(m_\mathrm{n} - m_\mathrm{e})}{m_\mathrm{e}m_\mathrm{n}}\mathbf{A}\cdot\mathbf{p_r} \simeq \frac{e}{m_\mathrm{e}}\mathbf{A}\cdot\mathbf{p_r}. \qquad (10.27)$$

In §8.2.1 we discussed terms that must be added to hydrogen's gross-structure Hamiltonian to account for the effects of the electron's intrinsic dipole moment. We found that the coupling with an external field is generated by the Zeeman spin Hamiltonian (8.76). Adding this to the value of H_B given in equation (10.26), and orienting our coordinate system so that the z-axis is parallel to $\mathbf{B}$, we arrive at our final result, namely that a uniform magnetic field introduces a perturbation

$$H_{Bs} = \frac{e\hbar}{2m_\mathrm{e}}B(L_z + 2S_z) = \mu_\mathrm{B}B(J_z + S_z), \qquad (10.28)$$

where $\mathbf{S}$ is the sum of the spin operators of all the valence electrons.

The Hamiltonian formed by adding H_{Bs} to the gross-structure Hamiltonian (8.1) commutes with L^2, L_z, S^2 and S_z. Its eigenkets are simply the eigenkets of the gross-structure Hamiltonian upgraded to include eigenvalues of S^2 and S_z. The only difference from the situation we studied in §8.1 is that the energies of these eigenkets now depend on both L_z and S_z. Hence, each energy level of the gross-structure Hamiltonian is split by the magnetic field into as many sublevels as $m_l + 2m_s$ can take. For example, if $l = 0$ and $s = \frac{1}{2}$, there are two sublevels, while when $l = 1$ and $s = \frac{1}{2}$ there are five levels in which $m_l + 2m_s$ ranges between ± 2.

In practice the perturbation H_{Bs} always acts in conjunction with the spin–orbit perturbation H_SO of equation (8.77).[3] The general case in which H_{Bs} and H_SO are comparable, requires numerical solution. The extreme cases in which one operator is larger than the other can be handled analytically.

Paschen–Back effect In a sufficiently strong magnetic field, H_SO affects the atom much less than H_{Bs}, so H_SO simply perturbs the eigenkets

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[3] There is no spin–orbit coupling for an S state, but an allowed spectral line from an S state will connect to a P state for which there is spin–orbit coupling. Hence the frequencies of allowed transitions inevitably involve spin–orbit coupling.