

20.4 Hyperfine Splitting

As our first physical application, we will consider hyperfine splitting. For this example the construction of eigenstates of total angular momentum is simple and was considered earlier. We will discuss here some of the general features of addition of angular momentum, leaving the study of complete sets of observables to our second example, the case of spin-orbit

coupling. Since both of these phenomena are considered in the context of the hydrogen atom, let us recall the basics of this system.

We learned in section 11.3 that the hydrogen atom bound state spectrum consists of states with energies E_n , where

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}, \quad n = 1, 2, \dots, \quad a_0 = \frac{\hbar^2}{me^2}. \quad (20.4.1)$$

For each value $n \geq 1$, we have the following ℓ multiplets of orbital angular momentum:

$$\ell = 0, 1, \dots, n-1. \quad (20.4.2)$$

A simple computation shows that this gives a total of n^2 states (ignoring the degeneracy due to the electron spin). So at each n , we have a degenerate n^2 -dimensional space \mathcal{H}_n of energy eigenstates that can be written as the direct sum of angular momentum multiplets:

$$\mathcal{H}_n = (\ell = n-1) \oplus (\ell = n-2) \oplus \dots \oplus (\ell = 0). \quad (20.4.3)$$

The hydrogen Hamiltonian takes the form

$$\hat{H}^{(0)} = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{e^2}{r}, \quad (20.4.4)$$

where, in the spirit of perturbation theory, we consider this to be the unperturbed Hamiltonian, whose spectrum is well known.

Turning to hyperfine splitting, the simple hydrogen atom Hamiltonian $\hat{H}^{(0)}$ receives a small correction because both the proton and the electron have magnetic dipole moments. The proton magnetic dipole creates a magnetic field. The contribution to the Hamiltonian is the energy of the electron dipole in the magnetic field created by the proton. Recall from section 17.5 that the proton and electron dipole moments are

$$\hat{\boldsymbol{\mu}}_p = \frac{g_p e}{2m_p c} \hat{\mathbf{S}}_p, \quad g_p \simeq 5.59, \quad \hat{\boldsymbol{\mu}}_e = -\frac{e}{m_e c} \hat{\mathbf{S}}_e. \quad (20.4.5)$$

The extra term ΔH in the Hamiltonian is

$$\delta H = -\hat{\boldsymbol{\mu}}_e \cdot \hat{\mathbf{B}}_p = \frac{e}{m_e c} \hat{\mathbf{S}}_e \cdot \hat{\mathbf{B}}_p, \quad (20.4.6)$$

where $\hat{\mathbf{B}}_p$ is the magnetic field at the electron due to the proton dipole. This magnetic field is an operator (thus the hat) because it is proportional to the proton magnetic moment operator. The magnetic field of a magnetic dipole contains two terms:

$$\hat{\mathbf{B}}_p = \frac{1}{r^3} [3\mathbf{n}(\mathbf{n} \cdot \hat{\boldsymbol{\mu}}_p) - \hat{\boldsymbol{\mu}}_p] + \frac{8\pi}{3} \hat{\boldsymbol{\mu}}_p \delta(\mathbf{r}), \quad (20.4.7)$$

with \mathbf{n} the unit vector pointing from the proton to the electron. The first term is the familiar piece that falls off like $1/r^3$. The second term is a delta function contribution at the position of the dipole, required for the magnetic field of the dipole to have the correct integral over space.

We choose to work out the hyperfine correction for the $n = 1$, $\ell = 0$ ground states $|\psi_{100}\rangle$ of the hydrogen atom, a set of four states because we must include the electron and proton spin degrees of freedom. We will now show that for such states the familiar $1/r^3$ term in $\hat{\mathbf{B}}_p$ does *not* contribute an energy correction. For this term, using (20.4.6), the Hamiltonian contribution $\delta H'$ is given by

$$\delta H' \sim \frac{1}{3} \hat{\mathbf{S}}_e \cdot [3\mathbf{n}(\mathbf{n} \cdot \hat{\mathbf{S}}_p) - \hat{\mathbf{S}}_p] = \frac{1}{3} [3(\mathbf{n} \cdot \hat{\mathbf{S}}_e)(\mathbf{n} \cdot \hat{\mathbf{S}}_p) - \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p], \quad (20.4.8)$$

recalling that $\hat{\boldsymbol{\mu}}_p \sim \hat{\mathbf{S}}_p$. To assess the contribution of $\delta H'$, we must evaluate its expectation value on the proton-electron ground states. Happily, we do not need to calculate much to see that it vanishes. The expectation value calculation involves both the spatial part and the spin part of the proton-electron states. Focus on the spatial part of the computation, which requires integration over all of space of $\delta H'$, multiplied by the norm squared of the spatial wave function $\langle \mathbf{r} | \psi_{100} \rangle$. Being just a function of r , the wave function does not affect the angular part of the integration. The angular integral is in fact the integral over the direction of the radial unit vector \mathbf{n} , and therefore it is proportional to

$$\int d\Omega [3(\mathbf{n} \cdot \hat{\mathbf{S}}_e)(\mathbf{n} \cdot \hat{\mathbf{S}}_p) - \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p] = 3\hat{S}_{e,i}\hat{S}_{p,j} \int d\Omega n_i n_j - 4\pi \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = 0, \quad (20.4.9)$$

where we used $\int d\Omega = 4\pi$, and the last equality follows because in fact

$$\int d\Omega n_i n_j = \frac{4\pi}{3} \delta_{ij}. \quad (20.4.10)$$

To show this, note that, by rotational symmetry, $\int d\Omega n_1^2 = \int d\Omega n_2^2 = \int d\Omega n_3^2$. Since $n_1^2 + n_2^2 + n_3^2 = 1$, the sum of these integrals has value 4π , and each integral is equal to $\frac{4\pi}{3}$, consistent with the above claim for $i = j$. When $i \neq j$, the integral vanishes, again, by symmetry considerations. Consider, for example, the integral $\int d\Omega n_x n_y$. For each point on the unit sphere with coordinates (n_x, n_y, n_z) and contributing to the integral, there is a point $(-n_x, n_y, n_z)$ that gives exactly a canceling contribution. Thus, the integral vanishes. Having shown that (20.4.10) holds, we have demonstrated that the $1/r^3$ term in the magnetic field does not contribute to the energy correction.

It follows that the relevant δH arises from the second term in the magnetic field (20.4.7), and it is given by

$$\delta H = \frac{e}{mc} \hat{\mathbf{S}}_e \cdot \frac{8\pi}{3} \hat{\boldsymbol{\mu}}_p \delta(\mathbf{r}) = \frac{4\pi}{3} \frac{g_p e^2}{m_p m_e c^2} \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p \delta(\mathbf{r}). \quad (20.4.11)$$

In this situation, the Hamiltonian $\hat{H}^{(0)}$ before inclusion of the perturbation is the hydrogen atom Hamiltonian that depends on the spin degrees of freedom of neither the electron nor the proton. Since each particle can be in either of two states, up or down, we have four degenerate energy eigenstates that share a common spatial wave function, the ground state $|\psi_{100}\rangle$, but differ on the spin degrees of freedom:

$$|\psi_{100}\rangle \otimes |\uparrow\uparrow\rangle, \quad |\psi_{100}\rangle \otimes |\uparrow\downarrow\rangle, \quad |\psi_{100}\rangle \otimes |\downarrow\uparrow\rangle, \quad |\psi_{100}\rangle \otimes |\downarrow\downarrow\rangle. \quad (20.4.12)$$

Before we include the perturbation δH , these states are all degenerate with energy equal to the ground state energy of the hydrogen atom. As discussed in case 2 of section 20.3, we can get the perturbed energies if we find new basis states, linear combinations of the above states for which the matrix $[\delta H]$ is diagonal. Let us denote these “good” basis states as

$$|\psi_{100}\rangle |s_i\rangle, \quad i = 1, 2, 3, 4, \quad (20.4.13)$$

where the $|s_i\rangle$ are some yet *undetermined* combinations of the spin states for the proton-electron pair. The matrix elements δH_{ij} are given by

$$\begin{aligned}
\delta H_{ij} &= \langle \psi_{100} | \langle s_i | \delta H | \psi_{100} \rangle | s_j \rangle, \\
&= \frac{4\pi}{3} \frac{g_p e^2}{m_p m_e c^2} \int d^3x |\psi_{100}(r)|^2 \delta(\mathbf{r}) \langle s_i | \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p | s_j \rangle, \\
&= \frac{4\pi}{3} \frac{g_p e^2}{m_p m_e c^2} |\psi_{100}(0)|^2 \langle s_i | \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p | s_j \rangle, \\
&= \frac{4g_p e^2}{3m_p m_e c^2 a_0^3} \langle s_i | \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p | s_j \rangle,
\end{aligned} \tag{20.4.14}$$

where we recalled that $|\psi_{100}(0)|^2 = 1/(\pi a_0^3)$. Therefore, we have

$$\delta H_{ij} = \Delta E \langle s_i | \frac{1}{\hbar^2} \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p | s_j \rangle, \tag{20.4.15}$$

where ΔE is the energy scale relevant to hyperfine splitting:

$$\Delta E \equiv \frac{4e^2 g_p}{3m_p m_e c^2} \frac{\hbar^2}{a_0^3}. \tag{20.4.16}$$

If the states $|s_i\rangle$ are chosen properly, the matrix $\langle s_i | \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p | s_j \rangle$ is diagonal and so is $[\delta H]$.

To make progress, let us relate the operator product $\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p$ to the total spin angular momentum. This product is a tensor product of operators:

$$\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p \equiv \hat{S}_{e,1} \otimes \hat{S}_{p,1} + \hat{S}_{e,2} \otimes \hat{S}_{p,2} + \hat{S}_{e,3} \otimes \hat{S}_{p,3} = \sum_i \hat{S}_{e,i} \otimes \hat{S}_{p,i}. \tag{20.4.17}$$

We now define the total spin operator $\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_e + \hat{\mathbf{S}}_p$, or more precisely,

$$\hat{S}_i \equiv \hat{S}_{e,i} \otimes \mathbb{1} + \mathbb{1} \otimes \hat{S}_{p,i}. \tag{20.4.18}$$

As we have seen, the \hat{S}_i operators satisfy the algebra of angular momentum. It is now a simple computation to expand $\hat{\mathbf{S}}^2$:

$$\begin{aligned}
\hat{\mathbf{S}}^2 &= \sum_i \hat{S}_i \hat{S}_i = \sum_i (\hat{S}_{e,i} \otimes \mathbb{1} + \mathbb{1} \otimes \hat{S}_{p,i}) (\hat{S}_{e,i} \otimes \mathbb{1} + \mathbb{1} \otimes \hat{S}_{p,i}) \\
&= \sum_i (\hat{S}_{e,i} \hat{S}_{e,i} \otimes \mathbb{1} + 2 \hat{S}_{e,i} \otimes \hat{S}_{p,i} + \mathbb{1} \otimes \hat{S}_{p,i} \hat{S}_{p,i}) \\
&= \hat{\mathbf{S}}_e^2 \otimes \mathbb{1} + 2 \sum_i \hat{S}_{e,i} \otimes \hat{S}_{p,i} + \mathbb{1} \otimes \hat{\mathbf{S}}_p^2.
\end{aligned} \tag{20.4.19}$$

Given our definition of $\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p$, the above result is in fact

$$\hat{\mathbf{S}}^2 = \hat{\mathbf{S}}_e^2 \otimes \mathbb{1} + 2 \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p + \mathbb{1} \otimes \hat{\mathbf{S}}_p^2. \tag{20.4.20}$$

With a little abuse of notation, one simply writes

$$\hat{\mathbf{S}}^2 = \hat{\mathbf{S}}_e^2 + 2 \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p + \hat{\mathbf{S}}_p^2. \quad (20.4.21)$$

This expression is the “obvious” result for the square of the sum of two commuting operators. We have derived it to ensure you understand how the tensor product works on each term, but next time you should write it directly. We then have the useful rewriting:

$$\boxed{\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = \frac{1}{2}(\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_e^2 - \hat{\mathbf{S}}_p^2).} \quad (20.4.22)$$

This shows the relevance of the total spin angular momentum: we can effectively trade $\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p$ for $\hat{\mathbf{S}}^2$ because the other operators $\hat{\mathbf{S}}_e^2$ and $\hat{\mathbf{S}}_p^2$ on the right-hand side are simply multiples of the identity: $\hat{\mathbf{S}}_e^2 = \hat{\mathbf{S}}_p^2 = \frac{3}{4}\hbar^2 \mathbb{1}$. Given this, the operator whose matrix elements we are considering in (20.4.15) is

$$\frac{1}{\hbar^2} \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = \frac{1}{2} \left(\frac{1}{\hbar^2} \hat{\mathbf{S}}^2 - \frac{3}{2} \mathbb{1} \right). \quad (20.4.23)$$

Here $\mathbb{1}$ is the identity matrix in the four-dimensional tensor product space. It follows from this result that

$$\delta H_{ij} = \frac{1}{2} \Delta E \langle s_i | \left(\frac{1}{\hbar^2} \hat{\mathbf{S}}^2 - \frac{3}{2} \mathbb{1} \right) | s_j \rangle. \quad (20.4.24)$$

This matrix is diagonal when the states $|s_i\rangle$ are eigenstates of the total spin $\hat{\mathbf{S}}^2$! Those total spin eigenstates thus define a good basis, and the diagonal elements of this matrix are the energy shifts, as we discussed in the previous section. We have seen that the four states in the tensor product of two spin one-half particles combine into a triplet ($s = 1$) and a singlet ($s = 0$). Thus, we take $|s_i\rangle$ with $i = 1, 2, 3$ to be the triplet and $|s_4\rangle$ to be the singlet:

$$|s_1\rangle = |\uparrow\uparrow\rangle, \quad |s_2\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |s_3\rangle = |\downarrow\downarrow\rangle; \quad |s_4\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (20.4.25)$$

Any state of the triplet $s = 1$ is an $(\frac{1}{\hbar^2} \hat{\mathbf{S}}^2 - \frac{3}{2})$ eigenstate with eigenvalue one-half:

$$\left(\frac{1}{\hbar^2} \hat{\mathbf{S}}^2 - \frac{3}{2} \right) |s_i\rangle = \left(2 - \frac{3}{2} \right) |s_i\rangle = \frac{1}{2} |s_i\rangle, \quad i = 1, 2, 3. \quad (20.4.26)$$

Moreover, the singlet $s = 0$ is an $(\frac{1}{\hbar^2}\hat{\mathbf{S}}^2 - \frac{3}{2})$ eigenstate with eigenvalue $-\frac{3}{2}$:

$$\left(\frac{1}{\hbar^2}\hat{\mathbf{S}}^2 - \frac{3}{2}\right)|s_4\rangle = \left(0 - \frac{3}{2}\right)|s_4\rangle = -\frac{3}{2}|s_4\rangle. \quad (20.4.27)$$

Therefore, the matrix $[\delta H]$ in (20.4.24) takes the form

$$[\delta H] = \begin{pmatrix} \frac{1}{4}\Delta E & 0 & 0 & 0 \\ 0 & \frac{1}{4}\Delta E & 0 & 0 \\ 0 & 0 & \frac{1}{4}\Delta E & 0 \\ 0 & 0 & 0 & -\frac{3}{4}\Delta E \end{pmatrix}. \quad (20.4.28)$$

The three states on the triplet are pushed up $\frac{1}{4}\Delta E$, and the singlet is pushed down $\frac{3}{4}\Delta E$. The total split between the two sets of states is ΔE , which is now identified as the magnitude of the hyperfine splitting of the ground state of the hydrogen atom (figure 20.1).

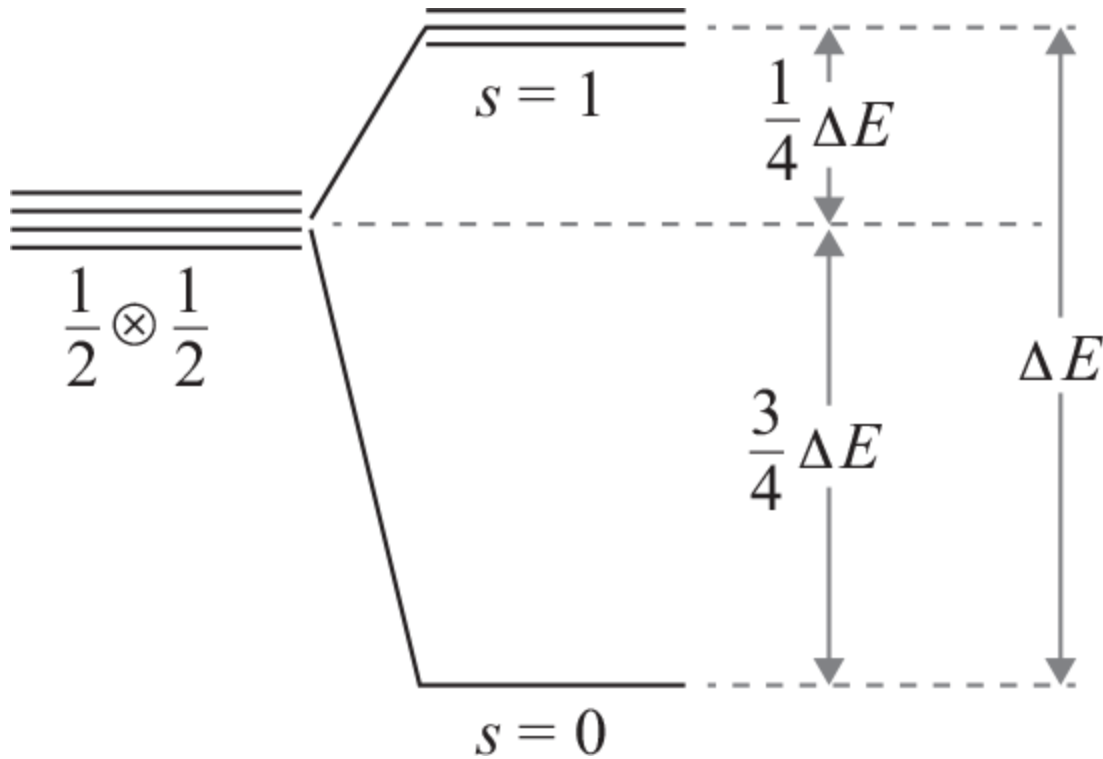


Figure 20.1

The hyperfine splitting of the electron-proton fourfold degenerate ground states $\frac{1}{2} \otimes \frac{1}{2}$ into a total-spin triplet, pushed up, and a total-spin singlet, pushed down.

Let us determine the value of ΔE , as given in (20.4.16):

$$\Delta E = \frac{4g_p e^2}{3m_p m_e c^2} \frac{\hbar^2}{a_0^3} = \frac{4g_p}{3m_p m_e c} \frac{e^2}{\hbar c} \left(\frac{\hbar}{a_0} \right)^3. \quad (20.4.29)$$

Recalling that $\alpha = \frac{e^2}{\hbar c}$, we see that

$$a_0 = \frac{\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c \alpha} \Rightarrow \frac{\hbar}{a_0} = m_e c \alpha. \quad (20.4.30)$$

This helps us rewrite ΔE in a clearer way:

$$\Delta E = \frac{4g_p}{3m_p m_e c} \alpha^4 m_e^3 c^3 = \frac{4}{3} g_p \left(\frac{m_e}{m_p} \right) \alpha^4 (m_e c^2). \quad (20.4.31)$$

Bohr's energy is of order $\alpha^2(m_e c^2)$ —that is, the rest energy of the electron times a suppression factor $\alpha^2 \simeq 1/19,000$. The spin-orbit correction, to be studied in section 20.6, is of order $\alpha^4(m_e c^2)$, thus suppressed relative to the Bohr energy by an additional factor of α^2 . Finally, hyperfine splitting is suppressed relative to spin-orbit by a factor $\frac{m_e}{m_p}$, of order one over two thousand. We quickly plug in the numbers:

$$\Delta E = \frac{4}{3} \cdot 5.59 \cdot \frac{1}{1,836} \cdot \left(\frac{1}{137} \right)^4 \cdot 511,000 \text{ eV} \simeq 5.88 \times 10^{-6} \text{ eV}. \quad (20.4.32)$$

In a transition from the triplet to the singlet, the energy ΔE is carried away by a photon of wavelength λ given by

$$\lambda = \frac{c}{\nu} = \frac{c}{\frac{\Delta E}{h}} = \frac{2\pi \hbar c}{\Delta E} = \frac{2\pi \cdot 197 \text{ MeV} \cdot \text{fm}}{5.88 \times 10^{-6} \text{ eV}} \simeq 21.1 \text{ cm}. \quad (20.4.33)$$

The corresponding photon frequency is $\nu = 1,420 \text{ MHz}$. This 21 cm spectral line was first observed by Harold Irving Ewen and Edward Purcell in 1951, who detected the emission of such photons from neutral hydrogen in the Milky Way. The hyperfine splitting is so small that even microwave background photons, of typical wavelength 2 mm, can easily excite the ground state into the triplet. The lifetime of the triplet state, however, is extremely long, about ten million years. As a result, the 21 cm line is extraordinarily sharp and very useful for astronomical Doppler shift measurements. The rotation curve of our galaxy has been calculated using the 21 cm line.