

## 20.6 Spin-Orbit Coupling

The hydrogen atom Hamiltonian we have used so far is nonrelativistic. It is a good description of the spectrum because an estimate of the typical electron velocity  $v$  gives  $v/c \simeq \alpha \simeq 1/137$  (problem 11.4). Relativistic corrections are of interest, and they determine the so-called fine-structure of the hydrogen atom, in which some of the degeneracies we have encountered are removed. These corrections can be derived systematically using the relativistic Dirac equation of the electron. Such analysis gives three correction terms to the Hamiltonian: one called, perhaps redundantly, the relativistic correction, a second called spin-orbit, and a third called the Darwin correction. We will study these three in detail in chapter 25. In this section we preview the spin-orbit interaction to further develop our

understanding of addition of angular momentum. A complete and systematic analysis of hydrogen will be conducted in chapter 25.

Spin-orbit couplings are a relativistic interaction affecting the particle's spin as it moves inside a potential. While this coupling is relevant in a variety of settings, including the motion of electrons in semiconductors, it is most familiar in atomic physics. Indeed, for hydrogen it refers to a correction to the Hamiltonian that can be interpreted as an interaction of the electron magnetic moment with the magnetic field the electron experiences as it travels around the proton. This magnetic field is itself a relativistic effect: the proton only creates an electric field  $\mathbf{E}$ , but any particle moving with some velocity  $\mathbf{v}$  in an electric field  $\mathbf{E}$  will observe a magnetic field  $\mathbf{B}$  of the form

$$\mathbf{B} \simeq \mathbf{E} \times \frac{\mathbf{v}}{c} \sim \frac{e}{c} \frac{\mathbf{r} \times \mathbf{v}}{r^3}, \quad (20.6.1)$$

when  $|\mathbf{v}| \ll c$ . Since  $\mathbf{r} \times \mathbf{v} \sim \mathbf{L}$ , we conclude that the magnetic field at the electron is proportional to the orbital angular momentum of the electron. Since the magnetic dipole of the electron is proportional to its spin, the extra coupling  $-\hat{\mu} \cdot \mathbf{B}$  in the Hamiltonian is proportional to  $\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$ . The spin and orbital operators commute, so the order in which they are multiplied is irrelevant. If we kept track of the constant factors, we would get a result that is well known to be off by a factor of two. This error arises because one must implement a further *Thomas correction*, a subtle effect present because the electron rest frame is not inertial. A complete derivation would take us far afield, so here we will just state the resulting correction to the Hamiltonian and explore some of the consequences. One finds that,

spin-orbit correction:  $\delta H = \frac{e^2 \hbar^2}{2m^2 c^2 r^3} \frac{1}{\hbar^2} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}.$

(20.6.2)

To estimate the magnitude  $\delta E$  of this correction, we set  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} / \hbar^2 \sim 1$  and  $r \sim a_0$  to find

$$\delta E \sim \frac{e^2 \hbar^2}{m^2 c^2 a_0^3} = \frac{e^8}{\hbar^4 c^4} \cdot mc^2 = \alpha^4 (mc^2). \quad (20.6.3)$$

Since the ground state energy is of order  $\alpha^2(mc^2)$ , the fine structure of the hydrogen atom is in effect a factor  $\alpha^2 \approx 1/19,000$  smaller than the scale of the energy levels!

Consider the  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  factor in  $\delta H$ . As we discussed for hyperfine splitting, this operator product is a tensor product  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \sum_i L_i \otimes S_i$ . This time we define the total angular momentum

$$\hat{\mathbf{J}} \equiv \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (20.6.4)$$

or more precisely,  $\hat{J}_i \equiv \hat{L}_i \otimes \mathbb{1} + \mathbb{1} \otimes \hat{S}_i$ . The computation of  $\hat{\mathbf{J}}^2$  is completely analogous to the computation we did earlier and gives  $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 \otimes \mathbb{1} + 2 \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \mathbb{1} \otimes \hat{\mathbf{S}}^2$ , which leads to the useful

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (20.6.5)$$

**Complete set of commuting observables (CSCO)** Let us now consider the CSCO suitable for the spin-orbit supplemented hydrogen Hamiltonian. For the unperturbed hydrogen atom Hamiltonian  $\hat{H}^{(0)}$ , the complete set of observables is

$$\{\hat{H}^{(0)}, \hat{\mathbf{L}}^2, \hat{L}_z\}. \quad (20.6.6)$$

Recall that  $[\hat{H}^{(0)}, \hat{L}_i] = 0$ , so all the operators here commute. Suppose we now consider the spin of the electron but *do not* change the Hamiltonian. In this case the list would be enlarged to

$$\{\hat{H}^{(0)}, \hat{\mathbf{L}}^2, \hat{L}_z, \hat{\mathbf{S}}^2, \hat{S}_z\}. \quad (20.6.7)$$

Since  $\hat{H}^{(0)}$  contains no spin operator,  $[\hat{H}^{(0)}, \hat{S}_i] = 0$  trivially. Moreover, since  $\hat{L}_i$ 's and  $\hat{S}_j$ 's commute, all operators on the list commute. Let us now consider the case when the full Hamiltonian  $\hat{H}$  includes the spin-orbit correction:

$$\hat{H} = \hat{H}^{(0)} + \delta H, \quad \delta H \sim \frac{1}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}. \quad (20.6.8)$$

With this new Hamiltonian, the list of commuting observables must be rethought. Consider first the list

$$\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \dots\}, \quad (20.6.9)$$

where the dots indicate additional operators we may be able to add. Notice that so far all is good since both  $\hat{L}^2$  and  $\hat{S}^2$  commute with  $\hat{H}^{(0)}$  and with  $\delta H$  and thus with  $\hat{H}$ . This is because  $\delta H$  is built from  $\hat{L}_i$  and  $\hat{S}_i$  operators that commute with  $\hat{L}^2$  and  $\hat{S}^2$ .  $\delta H$  also contains  $r$ , but  $r$  commutes with any  $\hat{L}_i$  and commutes trivially with any  $\hat{S}_i$ . Neither  $\hat{L}_i$  nor  $\hat{S}_i$ , for any value of  $i$ , can be added to the list above because

$$[\hat{L}_i, \hat{L} \cdot \hat{S}] \neq 0, \text{ and } [\hat{S}_i, \hat{L} \cdot \hat{S}] \neq 0, \quad (20.6.10)$$

as one can quickly check. Since the separate spin and orbital angular momenta no longer are conserved (they don't commute with the new Hamiltonian), we should consider the total angular momentum  $\hat{J} = \hat{L} + \hat{S}$ . Can we add  $\hat{J}^2$  to the list? Well,

$$\begin{aligned} [\hat{J}^2, \hat{H}^{(0)}] &= 0, \quad \text{since } \hat{H}^{(0)} \text{ commutes with all } \hat{L}_i, \hat{S}_i, \\ [\hat{J}^2, \hat{L}^2] &= 0, \quad \text{since } \hat{L}^2 \text{ commutes with all } \hat{L}_i, \hat{S}_i, \\ [\hat{J}^2, \hat{S}^2] &= 0, \quad \text{since } \hat{S}^2 \text{ commutes with all } \hat{L}_i, \hat{S}_i, \\ [\hat{J}^2, \hat{L} \cdot \hat{S}] &= [\hat{J}^2, \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)] = 0, \text{ using (20.6.5),} \\ [\hat{J}^2, f(r)] &= 0, \quad \text{since } \hat{L}_i \text{ and } \hat{S}_i \text{ commute with } r. \end{aligned} \quad (20.6.11)$$

The last two lines imply that  $\hat{J}^2$  commutes with  $\delta H$ , and therefore it commutes with  $\hat{H}$ . So, yes, we can add  $\hat{J}^2$  to the list. The new list is

$$\{\hat{H}, \hat{L}^2, \hat{S}^2, \hat{J}^2, \dots\}. \quad (20.6.12)$$

We can try now to add some  $\hat{J}_i$ . You can see that  $\hat{J}_i$  commutes with  $\hat{H}^{(0)}$ ,  $\hat{L}^2$ ,  $\hat{S}^2$ , and  $\hat{J}^2$ , the last one by the Casimir property. Moreover,

$$[\hat{J}_i, \hat{L} \cdot \hat{S}] = [\hat{J}_i, \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)] = 0. \quad (20.6.13)$$

Since  $[\hat{J}_i, f(r)] = 0$  by the same arguments as before, we can add one  $\hat{J}_i$  to the list. Note that we have demonstrated that  $\hat{J}_i$ , for all  $i$ , commutes with the new Hamiltonian:

$$[\hat{J}_i, \hat{H}] = 0, \quad (20.6.14)$$

confirming that the total angular momentum is conserved in the presence of the spin-orbit correction. Following convention, we add  $\hat{J}_z$  to find our final list, which we claim is a CSCO:

CSCO for spin-orbit coupling:  $\{\hat{H}, \hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z\}$ .

(20.6.15)

We will confirm that all eigenstates can be labeled uniquely by eigenvalues of the above operators.

**Computation of the perturbation** We will look into the simplest example. Since we want some nonvanishing angular momentum, we will take  $\ell = 1$ . The lowest-energy states with  $\ell = 1$  have principal quantum number  $n = 2$ . The  $\ell = 1$  multiplet has three states  $|1, m\rangle$ , with  $m = \pm 1$  and  $m = 0$ . Since the spin of the electron can be either up or down, we have a total of *six states*. The states can be written as

$$R_{2,1}(r) |1, m\rangle \otimes |\tfrac{1}{2}, m_s\rangle, \quad \text{with } m = \pm 1, 0, \quad m_s = \pm \tfrac{1}{2}. \quad (20.6.16)$$

Here,  $|\tfrac{1}{2}, m_s\rangle$  is the spin state, and  $|1, m\rangle$  is the angular state, whose explicit coordinate form is  $Y_{1,m}(\theta, \phi) = \langle \theta \phi | 1, m \rangle$ . Finally,  $R_{n\ell}(r)$ , with  $n = 2$  and  $\ell = 1$ , denotes the radial wave function, which is common for all six states above. These states are degenerate in the original hydrogen atom Hamiltonian, but the degeneracy will be partially removed by spin-orbit correction to the Hamiltonian. To find the energy corrections, we need to find a basis  $|i\rangle$ ,  $i = 1, \dots, 6$ , formed by linear combinations of the above states such that the matrix  $\langle i | \delta H | j \rangle$  is diagonal, in which case the energy shift of  $|i\rangle$  is simply  $\langle i | \delta H | i \rangle$ . The six states in (20.6.16), apart from the  $R_{2,1}(r)$  factor, are the tensor product of an  $\ell = 1$  multiplet and an  $s = 1/2$  multiplet. They are in fact  $1 \otimes \tfrac{1}{2}$ . This makes our work in the previous section useful. Since we know that

$$1 \otimes \tfrac{1}{2} = \tfrac{3}{2} \oplus \tfrac{1}{2}, \quad (20.6.17)$$

the states will break down into multiplets  $\tfrac{3}{2}$  and  $\tfrac{1}{2}$  of the total angular momentum  $\hat{J}$ .

The uncoupled states (20.6.16) are *all* eigenstates of  $\hat{L}^2$  and  $\hat{S}^2$  with eigenvalues  $\hbar^2 \ell(\ell + 1)$ , with  $\ell = 1$ , and  $\hbar^2 s(s + 1)$ , with  $s = 1/2$ , respectively. Any linear combinations of these states are still eigenstates of  $\hat{L}^2$  and  $\hat{S}^2$ . This includes the particular linear combinations that will be eigenstates of  $\hat{J}^2$ . Therefore, we see that the basis of  $(\hat{J}^2, \hat{J}_z)$  eigenstates are

in fact eigenstates of all the operators in the above CSCO, except for  $\hat{H}$ . Crucially, as we will see below,  $\hat{H}$  is diagonal in the subspace spanned by this basis.

To write the matrix elements clearly, it is convenient to factor out the  $r$  dependence of the basis states by writing

$$|i\rangle = R_{2,1}(r)|\underline{i}\rangle, \quad i=1, \dots, 6, \quad (20.6.18)$$

where  $|\underline{i}\rangle$  contains the angular and spin parts of the state. The matrix elements of interest are then written using the expression for  $\delta H$  in (20.6.2). Including only the spatial integral for the  $r$  dependence,

$$\begin{aligned} \delta H_{ij} \equiv \langle i | \delta H | j \rangle &= \frac{e^2 \hbar^2}{2m^2 c^2} \left[ \int_0^\infty r^2 dr |R_{2,1}(r)|^2 \frac{1}{r^3} \right] \frac{1}{\hbar^2} \langle \underline{i} | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | \underline{j} \rangle \\ &= \frac{e^2 \hbar^2}{2m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle_{\underline{i},1} \frac{1}{\hbar^2} \langle \underline{i} | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | \underline{j} \rangle. \end{aligned} \quad (20.6.19)$$

Here the subscripts 2, 1 on the expectation value indicate that one is using the  $R_{2,1}$  radial wave function. If the  $|\underline{i}\rangle$  are eigenstates of  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ , the matrix  $[\delta H]$  will be diagonal, and the diagonal elements are the energy shifts.

All the hard work has already been done. We just have to put the various pieces together. Begin with the simplification of  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  in (20.6.5), given that  $\ell = 1$  and  $s = \frac{1}{2}$ :

$$\begin{aligned} \frac{1}{\hbar^2} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} &= \frac{1}{2\hbar^2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) = \frac{1}{2\hbar^2} (\hat{\mathbf{J}}^2 - \hbar^2 \cdot 1 \cdot 2 - \hbar^2 \cdot \frac{1}{2} \cdot \frac{3}{2}) \\ &= \frac{1}{2} \left( \frac{1}{\hbar^2} \hat{\mathbf{J}}^2 - \frac{11}{4} \right). \end{aligned} \quad (20.6.20)$$

Additionally, the expectation value of  $1/r^3$  follows from (11.4.20):  $\langle 1/r^3 \rangle_{2,1} = 1/(24a_0^3)$ . From (20.6.19), we now get

$$\delta H_{ij} = \Delta E_0 \langle \underline{i} | \left( \frac{1}{\hbar^2} \hat{\mathbf{J}}^2 - \frac{11}{4} \right) | \underline{j} \rangle, \quad \text{with } \Delta E_0 \equiv \frac{e^2 \hbar^2}{96m^2 c^2 a_0^3}. \quad (20.6.21)$$

It is now clear that a good basis is one where the first four states are the states  $|j, m\rangle$  of the  $j = \frac{3}{2}$  multiplet, and the last two states are the states  $|j, m\rangle$  of the  $j = \frac{1}{2}$  multiplet. In that basis  $\delta H_{ij}$  is diagonal. More explicitly, letting the  $i, j$  and  $\underline{i}, \underline{j}$  labels denote the composite index  $j, m$ , we have

$$\begin{aligned}
\delta H_{j'm',jm} &= \Delta E_0 \langle j', m' | \left( \frac{1}{\hbar^2} \hat{\mathbf{J}}^2 - \frac{11}{4} \right) | j, m \rangle \\
&= \Delta E_0 \left( j(j+1) - \frac{11}{4} \right) \delta_{jj} \delta_{m'm}.
\end{aligned}
\tag{20.6.22}$$

The matrix is now manifestly diagonal, and the diagonal elements are the energy shifts. Calling  $\Delta E_{j,m}$  the energy shift of the state  $|j, m\rangle$ , equation (20.6.22) implies that

$$\Delta E_{j,m} = \Delta E_0 \left( j(j+1) - \frac{11}{4} \right), \tag{20.6.23}$$

and the shifts are  $m$  independent. Thus, the six states split into four  $j = \frac{3}{2}$  states that shift up together and two  $j = \frac{1}{2}$  states that shift down together:

$$\begin{aligned}
j = \frac{3}{2}: \quad \Delta E_{\frac{3}{2},m} &= \Delta E_0 \left( \frac{3}{2} \cdot \frac{5}{2} - \frac{11}{4} \right) = \Delta E_0, \\
j = \frac{1}{2}: \quad \Delta E_{\frac{1}{2},m} &= \Delta E_0 \left( \frac{1}{2} \cdot \frac{3}{2} - \frac{11}{4} \right) = -2 \Delta E_0.
\end{aligned}
\tag{20.6.24}$$

This is the final result for the spin-orbit correction to the  $n = 2$ ,  $\ell = 1$  levels of the hydrogen atom. The value of  $\Delta E_0$  is given in (20.6.21). This correction must be combined with other relativistic corrections to obtain the fine structure of hydrogen.