1 Revision of Section 18.5: The role of spin

We now discuss the role that the spin of an electron plays in the analysis of the hydrogen atom. An electron is a spin 1/2 particle. As discussed in Section 17.8, this statement means that the Hilbert space for an electron is $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$, where $\mathbb{C}^2$ carries an irreducible projective representation of $\mathsf{SO}(3)$. Up to now, we have neglected the spin in our calculations. The reason for this omission is simple: to first approximation, the spin plays no role in the structure of hydrogen. Specifically, in the simplest model of a hydrogen atom with spin, the Hamiltonian is simply $\hat{H} \otimes I$, where $\hat{H}$ is the hydrogen-atom Hamiltonian (18.7) acting on $L^2(\mathbb{R}^3)$. For any $n > 0$, we can obtain a basis of eigenvectors for $\hat{H} \otimes I$ with eigenvalue E_n by taking vectors of the form $\psi_{n,l,m} \otimes e_j$, where the $\psi_{n,l,m}$'s are as in (18.10) and where $\{e_1, e_2\}$ forms a basis for $\mathbb{C}^2$. That is to say, the eigenvalues for $\hat{H} \otimes I$ are the same as those for $\hat{H}$, but each eigenspace for $\hat{H} \otimes I$ has twice the dimension of the eigenspace for $\hat{H}$.

Let us consider, as an example, the states with $n = 3$ and $l = 1$, which are referred to as "$3p$ states" in the traditional chemistry notation. If we neglect spin entirely, even in the description of the Hilbert space, we obtain a three-dimensional space, for which we may choose a basis $\{\psi_1, \psi_2, \psi_3\}$. If we incorporate the spin into the description of the Hilbert space, but take our Hamiltonian to be simply $\hat{H} \otimes I$, then the three-dimensional space of $3p$ states becomes a six-dimensional space, spanned by vectors of the form $\psi_j \otimes e_k$, where $j = 1, 2, 3$ and $k = 1, 2$.

Now, as we discussed in Section 17.8, the natural action of the rotation group on the full Hilbert space $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ is one in which the rotation group acts in the usual way on $L^2(\mathbb{R}^3)$ and acts projectively on $\mathbb{C}^2$. At the level of the Lie algebra $\mathsf{so}(3)$ of $\mathsf{SO}(3)$, this means we consider the action of the total angular momentum operators $\hat{L}_j = \hat{J}_j \otimes I + I \otimes S_j$, where the S_j's are the spin angular momentum operators introduced in Section 17.8. Although the action of $\mathsf{SO}(3)$ on the span of the ψ_j's inside $L^2(\mathbb{R}^3)$ is irreducible, the projective action of $\mathsf{SO}(3)$ on the span of the $\psi_j \otimes e_k$'s is not irreducible. Rather, by the results of Section 17.9, this six-dimensional space decomposes as a direct sum of irreducible representations of dimensions two and four.

At the moment, this decomposition is merely a curiosity. Since all the vectors in the span of the $\psi_j \otimes e_k$'s have the same eigenvalue for $\hat{H} \otimes I$, we have apparently not gained much from decomposing the space into irreducible pieces. The benefit of this decomposition comes when we consider a more realistic model of hydrogen. Specifically, we will discuss the "fine structure" of hydrogen, which is a model that adds three correction terms to the simple-minded Hamiltonian $\hat{H} \otimes I$. (There are still other correction terms one can consider, which make up the "hyperfine structure" of hydrogen.)

Space does not permit us to examine the correction terms in detail. We focus on the role that rotational symmetry, as implemented through representation theory, plays in the analysis. Recall (Theorem 18.3) that the simple-minded Hamiltonian $\hat{H}$ has eigenvalues of the form $E_n = -R/n^2$, where $R = \mu Q^4/(2\hbar^2)$ is the Rydberg constant, with the associated eigenspaces (Corollary 18.5) hav-

ing dimension n^2. The operator $\hat{H} \otimes I$ then has eigenvalues E_n with eigenspaces of dimension $2n^2$. When we add in the correction terms, the $2n^2$-dimensional eigenspace will split into several eigenspaces with different eigenvalues. In particular, the six-dimensional space of $3p$ states will split into a two-dimensional space with one eigenvalue and a four-dimensional space with a different eigenvalue.

The three correction terms in the fine-structure Hamiltonian are as follows: A "kinetic term," that incorporates relativity theory; the "Darwin term," which corrects for a simplistic treatment of the electron as a point particle; and the "spin–orbit coupling" term, which takes into account interactions between the ordinary angular momentum and the spin. We will not discuss the kinetic or Darwin terms further, except to note that all three terms have a crucial property: They respect the rotational symmetry of the problem. That is to say, each term commutes with the projective action of $\mathsf{SO}(3)$ on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$. Equivalently, each term commutes with the total angular momentum operators $\hat{L}_j$, $j = 1, 2, 3$. (These terms do not, however, commute with the Runge–Lenz vector.)

We label the kinetic, Darwin, and spin–orbit terms as $\hat{H}_1$, $\hat{H}_2$, and $\hat{H}_3$, respectively. The spin–orbit coupling term has the following form:

$$\hat{H}_3 \psi = C \frac{1}{r^3} (\hat{\mathbf{J}} \cdot \mathbf{S}) \psi,$$

where C is a certain constant and where $\hat{\mathbf{J}} \cdot \mathbf{S} = \hat{J}_1 \otimes S_1 + \hat{J}_2 \otimes S_2 + \hat{J}_3 \otimes S_3$. A key property of this term is that it is *not* of the form $A \otimes I$, where A is an operator on $L^2(\mathbb{R}^3)$. Rather, this operator couples together the ordinary angular momentum operators and the spin angular momentum operators. The operator $\hat{H}_3$ does not commute with the ordinary angular momentum operators $\hat{J}_j$, but it does commute—as do $\hat{H}_1$ and $\hat{H}_2$—with the total angular momentum operators $\hat{L}_j$.

We now consider the fine-structure Hamiltonian $\hat{H}_{\text{fs}}$ given by

$$\hat{H}_{\text{fs}} = \hat{H} \otimes I + \hat{H}_1 + \hat{H}_2 + \hat{H}_3.$$

Using the techniques of perturbation theory, one can approximate the eigenvectors and eigenvalues of $\hat{H}_{\text{fs}}$ as small perturbations of the eigenvectors and eigenvalues for $\hat{H} \otimes I$. While it is not possible to give a full account of perturbation theory here, we can describe the leading-order shift in the eigenvalues. (See, for example, Section 6.2 of [1]. Since the eigenvalues of the "unperturbed" Hamiltonian $\hat{H} \otimes I$ have multiplicity greater than one, we must use "degenerate perturbation theory.")

For simplicity, we restrict our attention to the $3p$ states. Let V denote the six-dimensional space spanned by the vectors $\psi_j \otimes e_k$ described above and let P_V denote the orthogonal projection from $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ onto V. Let $A : V \to V$ denote the "compression" of the correction terms into the space V. That is to say,

$$A\psi = P_V(\hat{H}_1 \psi + \hat{H}_2 \psi + \hat{H}_3 \psi), \quad \psi \in V.$$

Then according to the precepts of first-order eigenvalue perturbation theory, the approximate energy levels for $\hat{H}_{\text{fs}}$ coming from the $3p$ states are the numbers E of the form

$$E = E_3 + \lambda, \tag{1}$$

where $E_3 = -R/9$ is the eigenvalue for the unperturbed Hamiltonian $\hat{H} \otimes I$ and where λ is an eigenvalue for A.

Now, at last, we can understand the importance of the decomposition of the six-dimensional space V into a direct sum of irreducible subspaces—let us call them V_1 and V_2—of dimensions two and four. Since each of the correction terms $\hat{H}_j$ commutes with rotations, so does the operator A. Since V_1 and V_2 are *inequivalent* irreducible representations of $\mathsf{so}(3)$, it is not hard to show, using Schur's lemma, that A must leave the spaces V_1 and V_2 invariant. (See Exercise 1.) By Schur's lemma again, the restrictions of A to V_1 and to V_2 must be multiples of the identity, say $\lambda_1 I$ and $\lambda_2 I$. Thus, the possible values of λ in (1) are precisely λ_1 and λ_2.

We may compute the values of λ_1 and λ_2 as follows: If ψ is any unit vector in V_1, then

$$\lambda_1 = \left\langle \psi, (\hat{H}_1 + \hat{H}_2 + \hat{H}_3)\psi \right\rangle.$$

To verify this formula, note that the orthogonal projection P_V is self-adjoint (Proposition A.57) and that ψ belongs to V. Thus,

$$\begin{aligned}
\left\langle \psi, (\hat{H}_1 + \hat{H}_2 + \hat{H}_3)\psi \right\rangle &= \left\langle P_V\psi, (\hat{H}_1 + \hat{H}_2 + \hat{H}_3)\psi \right\rangle \\
&= \left\langle \psi, P_V(\hat{H}_1 + \hat{H}_2 + \hat{H}_3)\psi \right\rangle \\
&= \langle \psi, A\psi \rangle \\
&= \lambda_1 \langle \psi, \psi \rangle \\
&= \lambda_1.
\end{aligned}$$

Of course, λ_2 may be computed similarly.

In working out the contribution of the spin–orbit term $\hat{H}_3$ to the above computation, it is helpful to relate the operator $\hat{\mathbf{J}} \cdot \mathbf{S}$ to the operator $\hat{\mathbf{L}}^2 := \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2$ by means of the identity

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{J}}^2 \otimes I + I \otimes \mathbf{S}^2 + 2\hat{\mathbf{J}} \cdot \mathbf{S}.$$

If we apply Proposition 17.8 to each of the operators $\hat{\mathbf{L}}^2$, $\hat{\mathbf{J}}^2$, and $\mathbf{S}^2$, we discover that V_1 and V_2 are eigenspaces for $\hat{\mathbf{J}} \cdot \mathbf{S}$. (See Section 6.3.2 of [1].)

Perturbation theory also gives an approximation to the eigenvectors for $\hat{H}_{\text{fs}}$. The eigenspaces of $\hat{H}_{\text{fs}}$ coming from the $3p$ states will consist of two-dimensional and four-dimensional spaces $\tilde{V}_1$ and $\tilde{V}_2$, which are "small perturbations" of V_1 and V_2. The spaces $\tilde{V}_1$ and $\tilde{V}_2$ will be irreducible invariant subspaces for the projective action of $\mathsf{SO}(3)$ on $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$.

For the interest of the reader, we record without proof the results of applying first-order perturbation theory to the energy levels of hydrogen. Let $V_{n,l}$ denote

the span of vectors $\psi_{n,l,m} \otimes e_k$, where m indexes a basis for the homogeneous harmonic polynomials of degree l and where $k = 1, 2$. (When $n = 3$ and $l = 1$, the space $V_{n,l}$ is the just the six-dimensional space V discussed above.) The associated eigenvalues of $\hat{H}_{\text{fs}}$, as approximated by first-order perturbation theory, are the numbers

$$E_n + E_n \frac{\alpha^2}{n} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right), \tag{2}$$

where $j = 1/2$ when $l = 0$ and $j = l - 1/2$ or $j = l + 1/2$ when $l > 0$. (See Section 6.3.2 of [1].)[1] Here, $E_n = -R/n^2$, as usual, and α is the so-called fine-structure constant, given by

$$\alpha = \frac{Q^2}{\hbar c} \tag{3}$$

where c is the speed of light. (The fine-structure constant is dimensionless, meaning that its numerical value is independent of the system of units being used. Its numerical value is approximately 1/137.)

Note that for each $n > 1$, there are several different allowed values of l and thus several different allowed values of j. Thus, the energy eigenspace for $\hat{H} \otimes I$ splits into several different eigenspaces with different eigenvalues. Because the shifts in the energy involve the quantity $\alpha^2 \approx 0.000053$, all of the perturbed energy levels are close to the unperturbed energy $E_n = -R/n^2$. Nevertheless, the splitting of the energy levels can be observed experimentally in sensitive measurements of hydrogen.

2 Exercise

1. Suppose V is a complex representation of a group or Lie algebra that decomposes as the direct sum of two *inequivalent* irreducible invariant subspaces V_1 and V_2. Let $A : V \to V$ be an interwining operator of V with itself. Using Schur's lemma, show that A must leave V_1 and V_2 invariant, and that the restrictions of A to V_1 and V_2 are multiples of the identity.

   Hint: The projection operators $P_1 : V \to V_1$ and $P_2 : V \to V_2$ are intertwining maps.

References

[1] D. J. Griffiths, Introduction to Quantum Mechanics, Second Edition, Cambridge University Press, 2016.

[1] Although Griffiths neglect the Darwin term in his computations, the contribution of this term is zero when $l > 0$, so that Griffiths' computations are valid except when $l = 0$.