20.8 HydrogenAtomandHiddenSymmetry

Our goal here is to give an algebraic derivation of the bound state spectrum of the unperturbed hydrogen atom Hamiltonian $\hat{H}^{(0)}$. The electron spin will play no role here and will be suppressed. For simplicity of notation, we will write the Hamiltonian as $\hat{H}$:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{e^2}{r}. \tag{20.8.1}$$

For this Hamiltonian, the orbital angular momentum operators $\hat{L}$ are conserved:

$$[\hat{H}, \hat{\mathbf{L}}] = 0, \qquad \hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar\hat{\mathbf{L}}. \tag{20.8.2}$$

The bound state spectrum of the Hamiltonian consists of states with energies $E_n = -\frac{e^2}{2a_0}\frac{1}{n^2}$ with $n = 1, 2, \ldots$. For each value $n \geq 1$, we have the degenerate n^2-dimensional space $\mathcal{H}_n$ described as a direct sum of ℓ multiplets with values ranging from zero to $n-1$: $\mathcal{H}_n = (\ell = n-1) \oplus (\ell = n-2) \oplus \cdots \oplus (\ell = 0)$.

The algebraic derivation of the spectrum makes use of another conserved vector, the Runge-Lenz vector operator $\hat{R}$ defined in (19.8.18):

$$\hat{\mathbf{R}} \equiv \frac{1}{2me^2}(\hat{\mathbf{p}} \times \hat{\mathbf{L}} - \hat{\mathbf{L}} \times \hat{\mathbf{p}}) - \frac{\hat{\mathbf{r}}}{r}. \tag{20.8.3}$$

As written this operator is manifestly Hermitian. It is also conserved, as it too commutes with the Hamiltonian (problem 19.10):

$$[\hat{H}, \hat{\mathbf{R}}] = 0. \tag{20.8.4}$$

Two rewritings of $\hat{R}$ are possible using the identity $\hat{\mathbf{p}}\times\hat{L} = -\hat{L}\times\hat{\mathbf{p}} + 2i\hbar\hat{\mathbf{p}}$ obtained in (19.2.2). These are

$$\hat{\mathbf{R}} = \frac{1}{me^2}(\hat{\mathbf{p}} \times \hat{\mathbf{L}} - i\hbar\hat{\mathbf{p}}) - \frac{\hat{\mathbf{r}}}{r} = \frac{1}{me^2}(-\hat{\mathbf{L}} \times \hat{\mathbf{p}} + i\hbar\hat{\mathbf{p}}) - \frac{\hat{\mathbf{r}}}{r}. \tag{20.8.5}$$

If $\hat{\mathbf{R}}$ and $\hat{\mathbf{L}}$ are conserved, all of their scalar products are conserved too since the Hamiltonian would commute with them using the derivation property of commutators. We are already familiar with the Casimir $\hat{\mathbf{L}}^2$ that in fact commutes with all $\hat{L}_i$. Let us consider now $\hat{\mathbf{R}}^2$, which must be a conserved scalar. Its evaluation gives (19.8.20):

$$\hat{\mathbf{R}}^2 = 1 + \frac{2\hat{H}}{me^4}(\hat{\mathbf{L}}^2 + \hbar^2). \tag{20.8.6}$$

Notice that $\hat{H}$, which appears on the above right-hand side, can be moved, if desired, to the right of the parentheses, as it commutes with $\hat{L}$. The right-hand side is indeed a conserved scalar. We now look into $\hat{R}\cdot\hat{L}$, which must also be conserved. Classically, $\hat{R}\cdot\hat{L}$ vanishes since $\hat{R}$ lies on the plane of the orbit (along the major axis of the ellipse), while $\hat{L}$ is orthogonal to the plane of the orbit. The dot product of the quantum operators also vanishes, as we now confirm. First recall that

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{L}} = 0, \quad \hat{\mathbf{p}} \cdot \hat{\mathbf{L}} = 0. \tag{20.8.7}$$

Using these and the first equality in (20.8.5), we find

$$\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = \frac{1}{me^2}(\hat{\mathbf{p}}\times\hat{\mathbf{L}})\cdot\hat{\mathbf{L}}. \tag{20.8.8}$$

But we now notice that

$$(\hat{\mathbf{p}}\times\hat{\mathbf{L}})\cdot\hat{\mathbf{L}} = \epsilon_{ijk}\hat{p}_j\hat{L}_k\hat{L}_i = \hat{p}_j\epsilon_{jki}\hat{L}_k\hat{L}_i = \hat{p}_j(\hat{\mathbf{L}}\times\hat{\mathbf{L}})_j = \hat{\mathbf{p}}\cdot i\hbar\hat{\mathbf{L}} = 0. \tag{20.8.9}$$

As a result, we have shown that

$$\boxed{\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = 0.} \tag{20.8.10}$$

The Runge-Lenz vector $\hat{\mathbf{R}}$ is a vector under rotations. This we know without any computation since it is built using cross products from $\hat{\mathbf{p}}$ and $\hat{\mathbf{L}}$, which are both vectors under rotations. Therefore we must find that

$$[\hat{L}_i, \hat{R}_j] = i\hbar\epsilon_{ijk}\hat{R}_k. \tag{20.8.11}$$

Recall (19.2.20), which states that for any vector $\hat{\mathbf{u}}$ under rotations, $\hat{\mathbf{L}}\times\hat{\mathbf{u}} + \hat{\mathbf{u}}\times\hat{\mathbf{L}} = 2i\hbar\,\hat{\mathbf{u}}$. It follows that

$$\hat{\mathbf{L}}\times\hat{\mathbf{R}} + \hat{\mathbf{R}}\times\hat{\mathbf{L}} = 2i\hbar\hat{\mathbf{R}}. \tag{20.8.12}$$

Exercise 20.4. *Show that* $\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = \hat{\mathbf{L}}\cdot\hat{\mathbf{R}}$. *Thus, both* $\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = 0$ *and* $\hat{\mathbf{L}}\cdot\hat{\mathbf{R}} = 0$.

In order to understand the commutator of two $\hat{\mathbf{R}}$ operators, we need a simple result: The commutator of two conserved operators is a conserved operator. To prove this consider two conserved operators $\hat{S}_1$ and $\hat{S}_2$:

$$[\hat{S}_1, \hat{H}] = [\hat{S}_2, \hat{H}] = 0. \tag{20.8.13}$$

The Jacobi identity (5.2.9) applied to the operators $\hat{S}_1$, $\hat{S}_2$, and $\hat{H}$ reads

$$[[\hat{S}_1, \hat{S}_2], \hat{H}] + [[\hat{H}, \hat{S}_1], \hat{S}_2] + [[\hat{S}_2, \hat{H}], \hat{S}_1] = 0. \tag{20.8.14}$$

The second term on the left-hand side vanishes by conservation of $\hat{S}_1$ and the third by conservation of $\hat{S}_2$. It follows that $[\,[\hat{S}_1, \hat{S}_2\,], \hat{H}] = 0$, which establishes the conservation of the commutator $[\hat{S}_1, \hat{S}_2]$. This result tells us that the commutator $[\hat{R}_i, \hat{R}_j]$ must be some conserved object. We can focus, equivalently, on the cross product of two $\hat{\mathbf{R}}$s that encodes the commutator. We must have

$$\hat{\mathbf{R}} \times \hat{\mathbf{R}} = (\cdots) \text{ “conserved vector,”} \tag{20.8.15}$$

where the dots represent some conserved scalar. Since $\hat{L}$ and $\hat{\mathbf{R}}$ are conserved vectors, the possible vectors on the right-hand side are $\hat{L}$, $\hat{\mathbf{R}}$, and $\hat{L} \times \hat{\mathbf{R}}$. To narrow down the options, we examine the behavior of various vectors under the parity transformation $\hat{\mathbf{r}} \to -\hat{\mathbf{r}}$. Under this transformation we must have

$$\hat{\mathbf{p}} \to -\hat{\mathbf{p}}, \quad \hat{\mathbf{L}} \to \hat{\mathbf{L}}, \quad \hat{\mathbf{R}} \to -\hat{\mathbf{R}}. \tag{20.8.16}$$

The first follows because parity must preserve the commutator of $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$, the second from $\hat{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$, and the third from the expression for $\hat{\mathbf{R}}$ in terms of $\hat{\mathbf{r}}$, $\hat{\mathbf{p}}$, and $\hat{L}$. Since the left-hand side of (20.8.15) does not change sign under the parity transformation, neither should the right-hand side. Note now that there are no parity-odd conserved scalars; the only candidate, **R**·**L**, vanishes. On the other hand, there are parity-even conserved scalars, such as the Hamiltonian itself. Thus, the conserved vector must be parity even. From our choices $\hat{L}$, $\hat{\mathbf{R}}$, and $\hat{L} \times \hat{\mathbf{R}}$, we can only have $\hat{L}$. We must therefore have $\hat{\mathbf{R}} \times \hat{\mathbf{R}} = (\cdots)\hat{L}$, with the expression in parentheses a conserved parity-even scalar. A calculation (problem 20.13) gives

$$\hat{\mathbf{R}} \times \hat{\mathbf{R}} = i\hbar\left(-\frac{2\hat{H}}{me^4}\right)\hat{\mathbf{L}}. \tag{20.8.17}$$

This completes the determination of all commutators relevant to $\hat{L}$ and $\hat{\mathbf{R}}$.

Now we come to the main point. We will derive algebraically the characterization of the subspaces of degenerate energy eigenstates. For this we will focus on one such subspace $\mathcal{H}_\nu$, at some energy E_ν, where ν is a parameter to be specified below. We will look at our operators *in that subspace*. Indeed, since both $\hat{L}$ and $\hat{\mathbf{R}}$ are conserved, $\mathcal{H}_\nu$ is invariant under the action of these operators. In our operator relations (20.8.6) and (20.8.17), we are actually allowed to replace $\hat{H}$ by the energy E_ν, given that $\hat{H}$, which commutes with $\hat{L}$, can be brought to the right, directly in front of the states. We then have

$$\hat{H} \rightarrow E_\nu = -\frac{me^4}{2\hbar^2}\frac{1}{\nu^2}, \quad \nu \in \mathbb{R}, \tag{20.8.18}$$

where we have written E_ν in terms of a unit-free, real constant ν, to be determined. The rest of the factors, except for a convenient factor of two, provide the right units. Of course, we know that the correct answer for these energies emerges if ν is a positive integer. This, however, is something we will be able to derive. It follows from the above equation that we can set

$$-\frac{2\hat{H}}{me^4} = \frac{1}{\hbar^2\nu^2}. \tag{20.8.19}$$

We can use this expression to simplify our key relations (20.8.17) and (20.8.6):

$$\begin{aligned} \hat{\mathbf{R}} \times \hat{\mathbf{R}} &= i\hbar\,\frac{1}{\hbar^2\nu^2}\,\hat{\mathbf{L}}, \\ \hat{\mathbf{R}}^2 &= 1 - \frac{1}{\hbar^2\nu^2}\,(\hat{\mathbf{L}}^2 + \hbar^2). \end{aligned} \tag{20.8.20}$$

A few further rearrangements give

$$\boxed{\begin{aligned} (\hbar\nu\hat{\mathbf{R}}) \times (\hbar\nu\hat{\mathbf{R}}) &= i\hbar\,\hat{\mathbf{L}}, \\ \hat{\mathbf{L}}^2 + \hbar^2\nu^2\hat{\mathbf{R}}^2 &= \hbar^2(\nu^2 - 1). \end{aligned}} \tag{20.8.21}$$

These are clear and simple algebraic relations between our operators. The first one shows that $\hbar\nu_{\hat{\mathbf{R}}}$ has the units of angular momentum and sort of behaves like one, except that the operator to the right is not $\hbar\nu_{\hat{\mathbf{R}}}$ but rather $\hat{L}$.

Our next step is to show that with the help of $\hat{L}$ and $\hat{\mathbf{R}}$ we can construct two independent, commuting algebras of angular momentum. Of course, it is clear that $\hat{L}$ is an algebra of angular momentum. But by using suitable linear combinations of $\hat{L}$ and $\hat{\mathbf{R}}$, we will obtain two such algebras. Indeed, define $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ as follows:

$$\begin{aligned} \hat{\mathbf{J}}_1 &\equiv \tfrac{1}{2}(\hat{\mathbf{L}} + \hbar\nu\hat{\mathbf{R}}), \\ \hat{\mathbf{J}}_2 &\equiv \tfrac{1}{2}(\hat{\mathbf{L}} - \hbar\nu\hat{\mathbf{R}}). \end{aligned} \tag{20.8.22}$$

We can also solve for $\hat{L}$ and $\hbar\nu_{\hat{\mathbf{R}}}$ in terms of $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$:

$$\begin{aligned} \hat{\mathbf{L}} &= \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2, \\ \hbar\nu\hat{\mathbf{R}} &= \hat{\mathbf{J}}_1 - \hat{\mathbf{J}}_2. \end{aligned} \tag{20.8.23}$$

It is important to realize that $\hat{L}$ is nothing but the sum of $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$. It is the total angular momentum.

We now claim that the operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ commute with each other. This is quickly confirmed by direct computation:

$$\begin{aligned} [\hat{J}_{1i}, \hat{J}_{2j}] &= \tfrac{1}{4}\,[\hat{L}_i + \hbar\nu\hat{R}_i,\, \hat{L}_j - \hbar\nu\hat{R}_j\,] \\ &= \tfrac{1}{4}\big(\, i\hbar\,\epsilon_{ijk}\hat{L}_k - \hbar\nu[\hat{L}_i, \hat{R}_j] - \hbar\nu[\hat{L}_j, \hat{R}_i] - i\hbar\,\epsilon_{ijk}\hat{L}_k\,\big) \;=\; 0, \end{aligned} \tag{20.8.24}$$

where we note that the first and last terms on the right-hand side cancel each other out, and the second and third terms also cancel each other out using (20.8.11). Now we want to show that $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ are indeed angular momenta. We check both operators at the same time using the notation $\hat{\mathbf{J}}_\pm$, with $+$ for $\hat{\mathbf{J}}_1$ and $-$ for $\hat{\mathbf{J}}_2$:

$$\begin{aligned} \hat{\mathbf{J}}_\pm \times \hat{\mathbf{J}}_\pm &= \tfrac{1}{4}(\hat{\mathbf{L}} \pm \hbar\nu\hat{\mathbf{R}}) \times (\hat{\mathbf{L}} \pm \hbar\nu\hat{\mathbf{R}}) \\ &= \tfrac{1}{4}\big(i\hbar\hat{\mathbf{L}} + i\hbar\hat{\mathbf{L}} \pm (\hat{\mathbf{L}} \times \hbar\nu\hat{\mathbf{R}} + \hbar\nu\hat{\mathbf{R}} \times \hat{\mathbf{L}})\big) \\ &= \tfrac{1}{4}(2i\hbar\hat{\mathbf{L}} \pm 2i\hbar\hbar\nu\hat{\mathbf{R}}) \\ &= i\hbar\tfrac{1}{2}(\hat{\mathbf{L}} \pm \hbar\nu\hat{\mathbf{R}}) = i\hbar\hat{\mathbf{J}}_\pm. \end{aligned} \tag{20.8.25}$$

In the first step, we used the first equation in (20.8.21), and in the second step, we used (20.8.12). In summary, we have confirmed that $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ are indeed two commuting angular momentum operators:

$$\begin{aligned} \hat{\mathbf{J}}_1 \times \hat{\mathbf{J}}_1 &= i\hbar\hat{\mathbf{J}}_1, \\ \hat{\mathbf{J}}_2 \times \hat{\mathbf{J}}_2 &= i\hbar\hat{\mathbf{J}}_2, \\ [\,\hat{\mathbf{J}}_1, \hat{\mathbf{J}}_2\,] &= 0. \end{aligned} \tag{20.8.26}$$

The constraint $\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = 0$ gives us crucial information on the angular momenta. Using (20.8.23) and the commutativity of $\hat{\mathbf{J}}_1$ with $\hat{\mathbf{J}}_2$, we find that

$$(\hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2)\cdot(\hat{\mathbf{J}}_1 - \hat{\mathbf{J}}_2) = 0 \quad\Rightarrow\quad \hat{\mathbf{J}}_1^2 = \hat{\mathbf{J}}_2^2. \tag{20.8.27}$$

Both angular momenta have the same "magnitude" on the subspace $\mathcal{H}_\nu$ of degenerate energy eigenstates. Let us look at $\hat{\mathbf{J}}_1^2$. Again, using $\hat{\mathbf{R}} \cdot \hat{\mathbf{L}} = 0$ and the second of (20.8.21), we find

$$\hat{\mathbf{J}}_1^2 \;=\; \tfrac{1}{4}\left(\hat{\mathbf{L}}^2 + \hbar^2\nu^2\hat{\mathbf{R}}^2\right) \;=\; \tfrac{1}{4}\,\hbar^2(\nu^2 - 1). \tag{20.8.28}$$

Note that the energy parameter ν determines the magnitude of $\hat{\mathbf{J}}_1^2$. This is our "eureka" moment: the quantization of angular momentum is going to imply the quantization of the energy!

Since both $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ commute with the Hamiltonian, the degenerate subspace $\mathcal{H}_\nu$ must furnish a *simultaneous* representation of both of these angular momenta! All states in the subspace carry the same value of $\hat{\mathbf{J}}_1^2$ and carry the same value of $\hat{\mathbf{J}}_2^2$. So all states are simultaneously in some (irreducible) representation j_1 of $\hat{\mathbf{J}}_1$ and in some (irreducible) representation j_2 of $\hat{\mathbf{J}}_2$. The equality $\hat{\mathbf{J}}_1^2 = \hat{\mathbf{J}}_2^2$, however, implies $j_1 = j_2 \equiv j$. We thus have

$$\hat{\mathbf{J}}_1^2 = \hat{\mathbf{J}}_2^2 = \tfrac{1}{4}\hbar^2(\nu^2 - 1) = \hbar^2 j(j+1). \tag{20.8.29}$$

Since j is an angular momentum, it is quantized: $2j \in \mathbb{Z}$. Solving for ν in terms of j, we now get the quantized energies:

$$\nu^2 = 1 + 4j(j+1) = 4j^2 + 4j + 1 = (2j+1)^2 \quad\Rightarrow\quad \nu \;=\; 2j+1. \tag{20.8.30}$$

Note that as anticipated, the energy is determined by the value of j. This shows that in fact each subspace $\mathcal{H}_\nu$ of degenerate energy eigenstates cannot carry more than one value of j. As j runs over all possible values, ν takes all positive integer values and thus can be indentified with the principal quantum number n:

$$\begin{aligned} j \;&=\; 0,\ \tfrac{1}{2},\ 1,\ \tfrac{3}{2}, \ldots, \\ n \equiv \nu \;=\; 2j+1 \;&=\; 1,\ 2,\ 3,\ 4, \ldots. \end{aligned} \tag{20.8.31}$$

We have recovered the quantization of the energy levels in the hydrogen atom!

What is the structure of the degenerate subspace $\mathcal{H}_n$, with $n = 2j + 1$? We already know that each state must be an eigenstate of $\hat{\mathbf{J}}_1^2$ with eigenvalue $\hbar^2 j(j + 1)$ and *at the same time* an eigenstate of $\hat{\mathbf{J}}_2^2$ with the same eigenvalue. Since the two angular momenta are independent, the space can be described as a tensor product of a space that carries the representation j of $\hat{\mathbf{J}}_1$ with a space that carries the representation j of $\hat{\mathbf{J}}_2$. The degenerate subspace must be a $j \otimes j$ vector space. A little elaboration helps make this clear. Consider the set of basis states we are speaking about: the states spanning $\mathcal{H}_{2j+1}$. Since they are all $\hat{\mathbf{J}}_1^2$ eigenstates of eigenvalue $\hbar^2 j(j+1)$, they must form a *collection* of j multiplets. Therefore, the full set of basis states can be organized in the form

$$\left\{ |j, m_1\rangle \otimes |\varphi_1\rangle, \ \ldots, \ |j, m_1\rangle \otimes |\varphi_k\rangle \right\}, \quad -j \leq m_1 \leq j. \tag{20.8.32}$$

Here k is an integer to be determined, and the $|\varphi_i\rangle$ states, with $i = 1, \ldots, k$, are fixed, independent of the value of m_1. In this way, we have k j multiplets of $\hat{\mathbf{J}}_1$, each tensored with a different $|\varphi\rangle$ state. Focus now on the second angular momentum $\hat{\mathbf{J}}_2$. Since all basis states in the space are $\hat{\mathbf{J}}_2^2$ eigenstates and the $\hat{\mathbf{J}}_2$ operators do not act on the $|j, m_1\rangle$ states, each of the $|\varphi\rangle$ states must be a state in a j multiplet of $\hat{\mathbf{J}}_2$. Since a j multiplet has $2j + 1$ basis states, the construction of the whole space requires choosing $k = 2j + 1$ and letting

$$|\varphi_1\rangle = |j, j\rangle, \ \ldots, \ |\varphi_{2j+1}\rangle = |j, -j\rangle. \tag{20.8.33}$$

In this way, the set of states in (20.8.32) becomes

$$\left\{ |j, m_1\rangle \otimes |j, j\rangle, \ \ldots, \ |j, m_1\rangle \otimes |j, -j\rangle \right\}, \quad -j \leq m_1 \leq j. \tag{20.8.34}$$

This is in fact the space spanned by

$$\left\{ |j, m_1\rangle \otimes |j, m_2\rangle \right\}, \quad -j \leq m_1, m_2 \leq j, \tag{20.8.35}$$

immediately recognized as $j \otimes j$. Note that this is the "minimal" solution for the space $\mathcal{H}_{2j+1}$. A direct sum of a number of $j \otimes j$ spaces would also be consistent with the algebraic constraints.

Therefore, assuming minimality, $\mathcal{H}_{n=2j+1}$ is the space $j \otimes j$:

$$\mathcal{H}_{n=2j+1} = j \otimes j, \quad \text{basis states} \quad |j; m_1\rangle \otimes |j; m_2\rangle, \quad -j \leq m_1, m_2 \leq j. \tag{20.8.36}$$

Since m_1 and m_2 each take $2j + 1$ values, the dimension of $\mathcal{H}_{n=2j+1}$ is $(2j + 1)^2 = n^2$. This is indeed the expected number of states that we have at this energy level. As we are familiar with, the tensor product breaks into a sum of representations of the *sum* of angular momenta. But the sum here is simply the conventional angular momentum $\hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 = \hat{\mathbf{L}}$. Since we know that

$$j \otimes j = 2j \oplus 2j - 1 \oplus \cdots \oplus 0, \tag{20.8.37}$$

the representations on the right-hand side are the ℓ multiplets that arise. Thus, the degenerate subspace is a direct sum of the ℓ values $(\ell = 2j) \oplus (\ell = 2j - 1) \oplus \cdots \oplus 0$. Recalling that $2j + 1 = n$, we have obtained

$$\mathcal{H}_n = (\ell = n-1) \oplus (\ell = n-2) \oplus \cdots \oplus (\ell = 0). \tag{20.8.38}$$

This is exactly the familiar set of ℓ multiplets at the degenerate subspace labeled by the principal quantum number n. This completes the algebraic derivation of the spectrum.

We should emphasize that the above analysis characterizes the *possible* subspaces $\mathcal{H}_n$ of degenerate energy eigenstates. These subspaces are labeled by the values of j in the infinite list $\{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots\}$. The algebraic analysis alone *cannot* tell us which values of j in the this list are used by the hydrogen atom. In physics, however, it is often the case that whatever is possible is in fact compulsory. So it is not surprising that all possible values of j actually appear in the hydrogen atom spectrum.

As the simplest nontrivial example of a degenerate subspace, consider $j = \frac{1}{2}$, which gives us $n = 2$. We then have $\mathcal{H}_2 = \frac{1}{2} \otimes \frac{1}{2} = \mathbf{1} \oplus \mathbf{0}$, where the right-hand side includes the triplet $\ell = 1$ and the singlet $\ell = 0$. The uncoupled basis states are of the form $|\frac{1}{2}, m_1\rangle \otimes |\frac{1}{2}, m_2\rangle$, and the four of them can be written briefly as $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$. The singlet and triplet are therefore

$$\ell = 1: \begin{cases} |1,1\rangle = |\uparrow\uparrow\rangle, \\ |1,0\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\big), \\ |1,-1\rangle = |\downarrow\downarrow\rangle, \end{cases} \qquad \ell = 0: \quad |0,0\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big). \tag{20.8.39}$$

These are the four states of the $n = 2$ energy level. Note that we have built them out of spin one-half states. These are mathematical entities not related in any way to elementary particle spin. The hydrogen atom Hamiltonian we have used assumes the electron and the proton are spinless. This is reminiscent of our discussion of the spectrum of the isotropic two-dimensional oscillator, at the end of section 19.7. There also, the energy levels of the oscillator formed representations of a “hidden” angular momentum and included representations with fractional angular momentum.