

CHAPTER 4

QUANTUM MECHANICS IN THREE DIMENSIONS

4.1 SCHRÖDINGER EQUATION IN SPHERICAL COORDINATES

The generalization to three dimensions is straightforward. Schrödinger's equation says

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi; \quad [4.1]$$

the Hamiltonian operator¹ H is obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

by the standard prescription (applied now to y and z , as well as x):

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial z}, \quad [4.2]$$

or

$$\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla, \quad [4.3]$$

¹Where confusion might otherwise occur, I have been putting "hats" on operators to distinguish them from the corresponding classical observables. I don't think there will be much occasion for ambiguity in this chapter, and the hats get to be cumbersome, so I am going to leave them off from now on.

for short. Thus

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi, \quad [4.4]$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad [4.5]$$

is the **Laplacian**, in Cartesian coordinates.

The potential energy V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$ and t . The probability of finding the particle in the infinitesimal volume $d^3\mathbf{r} = dx dy dz$ is $|\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$, and the normalization condition reads

$$\int |\Psi|^2 d^3\mathbf{r} = 1, \quad [4.6]$$

with the integral taken over all space. If the potential is independent of time, there will be a complete set of stationary states,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar}, \quad [4.7]$$

where the spatial wave function ψ_n satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V\psi_n = E_n \psi_n. \quad [4.8]$$

The general solution to the (time-dependent) Schrödinger equation is

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r})e^{-iE_n t/\hbar}, \quad [4.9]$$

with the constants c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$, in the usual way. (If the potential admits continuum states, then the sum in Equation 4.9 becomes an integral.)

*Problem 4.1

- (a) Work out all of the **canonical commutation relations** for components of the operators \mathbf{r} and \mathbf{p} : $[x, y]$, $[x, p_y]$, $[x, p_x]$, $[p_y, p_z]$, and so on. *Answer:*

$$[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0. \quad [4.10]$$

- (b) Show that

$$\frac{d}{dt}\langle \mathbf{r} \rangle = \frac{1}{m}\langle \mathbf{p} \rangle, \quad \text{and} \quad \frac{d}{dt}\langle \mathbf{p} \rangle = \langle -\nabla V \rangle. \quad [4.11]$$

(Each of these, of course, stands for *three* equations—one for each component.)

Hint: Note that Equation 3.148 is valid in three dimensions.

(c) Formulate Heisenberg's uncertainty principle in three dimensions. *Answer:*

$$\sigma_x \sigma_{p_x} \geq \hbar/2, \quad \sigma_y \sigma_{p_y} \geq \hbar/2, \quad \sigma_z \sigma_{p_z} \geq \hbar/2, \quad [4.12]$$

but there is no restriction on, say, $\sigma_x \sigma_{p_y}$.

4.1.1 Separation of Variables

Typically, the potential is a function only of the distance from the origin. In that case it is natural to adopt **spherical coordinates**, (r, θ, ϕ) (see Figure 4.1). In spherical coordinates the Laplacian takes the form²

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right). \quad [4.13]$$

In spherical coordinates, then, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V \psi = E \psi. \quad [4.14]$$

We begin by looking for solutions that are separable into products:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \quad [4.15]$$

Putting this into Equation 4.14, we have

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + V R Y = E R Y.$$

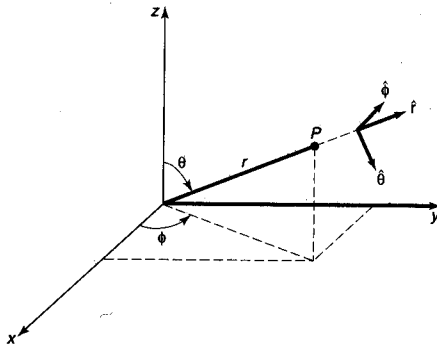


Figure 4.1: Spherical coordinates: radius r , polar angle θ , and azimuthal angle ϕ .

²In principle, this can be obtained by change of variables from the Cartesian expression (Equation 4.5). However, there are much more efficient ways of getting it; see, for instance, M. Boas, *Mathematical Methods in the Physical Sciences*, 2nd ed. (New York: John Wiley and Sons, Inc., 1983) Chapter 10, Section 9.

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Dividing by YR and multiplying by $-2mr^2/\hbar^2$:

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0.$$

★ The term in the first curly bracket depends only on r , whereas the remainder depends only on θ and ϕ ; accordingly, each must be a constant. For reasons that will appear in due course, I will write this "separation constant" in the form $l(l+1)$.³

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] = l(l+1); \quad [4.16]$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -l(l+1). \quad [4.17]$$

***Problem 4.2** Use separation of variables in Cartesian coordinates to solve the infinite cubical well (or "particle in a box"):

$$V(x, y, z) = \begin{cases} 0, & \text{if } x, y, z \text{ are all between } 0 \text{ and } a; \\ \infty, & \text{otherwise.} \end{cases}$$

- Find the stationary state wave functions and the corresponding energies.
- Call the distinct energies E_1, E_2, E_3, \dots , in order of increasing energy. Find E_1, E_2, E_3, E_4, E_5 , and E_6 . Determine the degeneracy of each of these energies (that is, the number of different states that share the same energy). Recall (Problem 2.42) that degenerate bound states do not occur in *one* dimension, but they are common in three dimensions.
- What is the degeneracy of E_{14} , and why is this case interesting?

4.1.2 The Angular Equation

Equation 4.17 determines the dependence of ψ on θ and ϕ ; multiplying by $Y \sin^2 \theta$, it becomes

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y. \quad [4.18]$$

³Note that there is no loss of generality here—at this stage l could be any complex number. Later on we'll discover that l must in fact be an *integer*, and it is in anticipation of that result that I express the separation constant in a way that looks peculiar now.

ff 63 You may have encountered this equation already—it occurs in the solution to Laplace's equation in classical electrodynamics. As always, we try separation of variables:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). = f g \text{ in Tipler} \quad [4.19]$$

Plugging this in, and dividing by $\Theta\Phi$, we find

$$\left\{ \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = 0.$$

The first term is a function only of θ , and the second is a function only of ϕ , so each must be a constant. This time I'll call the separation constant m^2 .⁴

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta = m^2; \quad [4.20]$$

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m^2. \quad [4.21]$$

The ϕ equation is easy:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}. \quad [4.22]$$

[Actually, there are *two* solutions: $\exp(im\phi)$ and $\exp(-im\phi)$, but we'll cover the latter by allowing m to run negative. There could also be a constant factor in front, but we might as well absorb that into Θ . Incidentally, in electrodynamics we would write the azimuthal function (Φ) in terms of sines and cosines, instead of exponentials, because electric potentials must be *real*. In quantum mechanics there is no such constraint, and the exponentials are a lot easier to work with.] Now, when ϕ advances by 2π , we return to the same point in space (see Figure 4.1), so it is natural to require that⁵

$$\Phi(\phi + 2\pi) = \Phi(\phi). \quad [4.23]$$

In other words, $\exp[im(\phi + 2\pi)] = \exp(im\phi)$, or $\exp(2\pi im) = 1$. From this it follows that m must be an *integer*:

$$m = 0, \pm 1, \pm 2, \dots \quad [4.24]$$

⁴Again, there is no loss of generality here since at this stage m could be any complex number; in a moment, though, we will discover that m must in fact be an *integer*. Beware: The letter m is now doing double duty, as *mass* and as the **azimuthal quantum number**. There is no graceful way to avoid this since both uses are standard. Some authors now switch to M or μ for mass, but I hate to change notation in midstream, and I don't think confusion will arise as long as you are aware of the problem.

⁵This is a more subtle point than it looks. After all, the *probability density* ($|\Phi|^2$) is single valued regardless of m . In Section 4.3 we'll obtain the condition on m by an entirely different—and more compelling—argument.

The θ equation,

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2] \Theta = 0, \quad [4.25]$$

may not be so familiar. The solution is

$$\Theta(\theta) = A P_l^m(\cos \theta), \quad [4.26]$$

where P_l^m is the **associated Legendre function**, defined by⁶

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x), \quad [4.27]$$

and $P_l(x)$ is the l th Legendre polynomial. We encountered the latter (Equation 3.91) as orthogonal polynomials on the interval $(-1, +1)$; for our present purposes it is more convenient to define them by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l. \quad [4.28]$$

For example,

$$P_0(x) = 1, \quad P_1(x) = \frac{1}{2} \frac{d}{dx} (x^2 - 1) = x,$$

$$P_2(x) = \frac{1}{4 \cdot 2} \left(\frac{d}{dx} \right)^2 (x^2 - 1)^2 = \frac{1}{2} (3x^2 - 1),$$

and so on. The first few Legendre polynomials were listed in Table 3.1. As the name suggests, $P_l(x)$ is a polynomial (of degree l) in x , and is even or odd according to the parity of l . But $P_l^m(x)$ is not, in general, a polynomial—if m is odd it carries a factor of $\sqrt{1-x^2}$:

$$P_2^0(x) = 1, \quad P_2^1(x) = (1-x^2)^{1/2} \frac{d}{dx} \left[\frac{1}{2} (3x^2 - 1) \right] = 3x \sqrt{1-x^2},$$

$$P_2^2(x) = (1-x^2) \left(\frac{d}{dx} \right) \left[\frac{1}{2} (3x^2 - 1) \right] = 3(1-x^2),$$

etc. [On the other hand, what we need is $P_l^m(\cos \theta)$, and $\sqrt{1-\cos^2 \theta} = \sin \theta$, so $P_l^m(\cos \theta)$ is always a polynomial in $\cos \theta$, multiplied—if m is odd—by $\sin \theta$. Some associated Legendre functions of $\cos \theta$ are listed in Table 4.1.]

⁶Notice that $P_l^{-m} = P_l^m$. Some authors adopt a different sign convention for negative values of m ; see Boas (footnote 2) p. 505.

Table 4.1: Some associated Legendre functions, $P_l^m(\cos \theta)$.

$P_1^1 = \sin \theta$	$P_3^3 = 15 \sin^3 \theta$
$P_1^0 = \cos \theta$	$P_3^2 = 15 \sin^2 \theta \cos \theta$
$P_2^2 = 3 \sin^2 \theta$	$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$
$P_2^1 = 3 \sin \theta \cos \theta$	$P_3^0 = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$
$P_2^0 = \frac{1}{2} (3 \cos^2 \theta - 1)$	

Notice that l must be a nonnegative integer for the Rodrigues formula to make any sense; moreover, if $|m| > l$, then Equation 4.27 says $P_l^m = 0$. For any given l , then, there are $(2l + 1)$ possible values of m :

$$l = 0, 1, 2, \dots; m = -l, -l + 1, \dots, -1, 0, 1, \dots, l - 1, l. \quad [4.29]$$

But wait! Equation 4.25 is a second-order differential equation: It should have *two* linearly independent solutions, for *any old* values of l and m . Where are all the *other* solutions? *Answer:* They *exist*, of course, as mathematical solutions to the equation, but they are *physically* unacceptable because they blow up at $\theta = 0$ and/or $\theta = \pi$, and do not yield normalizable wave functions (see Problem 4.4).

Now, the volume element in spherical coordinates⁷ is

$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi, \quad [4.30]$$

so the normalization condition (Equation 4.6) becomes

$$\int |\psi|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \sin \theta \, d\theta \, d\phi = 1.$$

It is convenient to normalize R and Y individually:

$$\int_0^\infty |R|^2 r^2 \, dr = 1 \quad \text{and} \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta \, d\theta \, d\phi = 1. \quad [4.31]$$

The normalized angular wave functions⁸ are called **spherical harmonics**:

⁷See, for instance, Boas, (footnote 2), Chapter 5, Section 4.

⁸The normalization factor is derived in Problem 4.47. The ϵ factor is chosen for consistency with the notation we will be using in the theory of angular momentum; it is reasonably standard, though some older books use other conventions. Notice that

$$Y_l^{-m} = (-1)^m Y_l^m.$$

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1.10

add (4.31)

2

Table 4.2: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$
$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta), \quad [4.32]$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal, so

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$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}. \quad [4.33]$$

In Table 4.2-I have listed the first few spherical harmonics.

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***Problem 4.3** Use Equations 4.27, 4.28, and 4.32 to construct Y_0^0 and Y_2^1 . Check that they are normalized and orthogonal. 4.23
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Problem 4.4 Show that

$$\Theta(\theta) = A \ln[\tan(\theta/2)]$$

satisfies the θ equation (Equation 4.25) for $l = m = 0$. This is the unacceptable "second solution"—what's wrong with it?

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***Problem 4.5** Using Equation 4.32, find $Y_l^l(\theta, \phi)$ and $Y_3^2(\theta, \phi)$. Check that they satisfy the angular equation (Equation 4.18), for the appropriate values of the parameters l and m .

****Problem 4.6** Starting from the Rodrigues formula, derive the orthonormality condition for Legendre polynomials:

$$\int_{-1}^1 P_l(x) P_{l'}(x) dx = \left(\frac{2}{2l+1}\right) \delta_{ll'}. \quad [4.34]$$

Hint: Use integration by parts.

4.1.3 The Radial Equation

Notice that the angular part of the wave function, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials; the actual *shape* of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$, which is determined by Equation 4.16:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E]R = l(l+1)R. \quad [4.35]$$

This equation simplifies if we change variables: Let

$$u(r) \equiv rR(r), \quad [4.36]$$

so that $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = rd^2u/dr^2$, and hence

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu. \quad [4.37]$$

This is called the **radial equation**⁹; it is *identical in form* to the one-dimensional Schrödinger equation (Equation 2.4), except that the effective potential,

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}, \quad [4.38]$$

contains an extra piece, the so-called **centrifugal term**, $(\hbar^2/2m)[l(l+1)/r^2]$. It tends to throw the particle outward (away from the origin), just like the centrifugal (pseudo-) force in classical mechanics. Meanwhile, the normalization condition (Equation 4.31) becomes

$$\int_0^\infty |u|^2 dr = 1. \quad [4.39]$$

We cannot proceed further until a specific potential is provided.

Example. Consider the **infinite spherical well**,

$$V(r) = \begin{cases} 0, & \text{if } r < a; \\ \infty, & \text{if } r > a. \end{cases} \quad [4.40]$$

Outside the well the wave function is zero; inside the well the radial equation says

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u, \quad [4.41]$$

⁹Those m 's are *masses*, of course—the radial equation makes no reference to the azimuthal quantum number m .

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}, \quad [4.42]$$

as usual. Our problem is to solve this equation, subject to the boundary condition $u(a) = 0$. The case $l = 0$ is easy:

$$\frac{d^2u}{dr^2} = -k^2u \Rightarrow u(r) = A \sin(kr) + B \cos(kr).$$

But remember, the actual radial wave function is $R(r) = u(r)/r$, and $[\cos(kr)]/r$ blows up as $r \rightarrow 0$. So¹⁰ we must choose $B = 0$. The boundary condition then requires $\sin(ka) = 0$, and hence $ka = n\pi$, for some integer n . The allowed energies are evidently

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \dots), \quad [4.43]$$

the same as for the one-dimensional infinite square well (Equation 2.23). Normalizing $u(r)$ yields $A = \sqrt{2/a}$; inclusion of the angular part (constant, in this instance, since $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$), we conclude that

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}. \quad [4.44]$$

[Notice that the stationary states are labeled by *three quantum numbers*, n , l , and m : $\psi_{nlm}(r, \theta, \phi)$. The *energy*, however, depends only on n and l : E_{nl} .]

The general solution to Equation 4.41 (for an arbitrary integer l) is not so familiar:

$$u(r) = Ar j_l(kr) + Br n_l(kr), \quad [4.45]$$

where $j_l(x)$ is the **spherical Bessel function** of order l , and $n_l(x)$ is the **spherical Neumann function** of order l . They are defined as follows:

$$j_l(x) \equiv (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x}; \quad n_l(x) \equiv -(-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x}. \quad [4.46]$$

For example,

$$j_0(x) = \frac{\sin x}{x}; \quad n_0(x) = -\frac{\cos x}{x};$$

$$j_1(x) = (-x) \frac{1}{x} \frac{d}{dx} \left(\frac{\sin x}{x} \right) = \frac{\sin x}{x^2} - \frac{\cos x}{x};$$

¹⁰Actually, all we require is that the wave function be *normalizable*, not that it be *finite*: $R(r) \sim 1/r$ at the origin *would* be normalizable (because of the r^2 in Equation 4.31). For a more compelling proof that $B = 0$, see R. Shankar, *Principles of Quantum Mechanics* (New York: Plenum, 1980), p. 351.

$$n_1(x) = -(-x) \frac{1}{x} \frac{d}{dx} \left(\frac{\cos x}{x} \right) = -\frac{\cos x}{x^2} - \frac{\sin x}{x};$$

and so on. The first few spherical Bessel and Neumann functions are listed in Table 4.3. Notice that for small x (where $\sin x \approx x - x^3/3! + x^5/5! - \dots$ and $\cos x \approx 1 - x^2/2 + x^4/4! - \dots$),

$$j_0(x) \approx 1; \quad n_0(x) \approx \frac{1}{x}; \quad j_1(x) \approx \frac{x}{3}; \quad n_1(x) \approx -\frac{1}{x^2};$$

etc. The point is that the Bessel functions are finite at the origin, but the Neumann functions blow up at the origin. Accordingly, we must have $B_l = 0$, and hence

$$R(r) = A j_l(kr). \tag{4.47}$$

There remains the boundary condition, $R(a) = 0$. Evidently k must be chosen such that

$$j_l(ka) = 0; \tag{4.48}$$

that is, (ka) is a zero of the l^{th} -order spherical Bessel function. Now the Bessel functions are oscillatory (see Figure 4.2); each one has an infinite number of zeros. But (unfortunately, for us) they are not located at nice sensible points (such as n , or $n\pi$, or something); they have to be computed numerically.¹¹ At any rate, the boundary condition requires that

$$k = \frac{1}{a} \beta_{nl}, \tag{4.49}$$

Table 4.3: The first few spherical Bessel and Neumann functions, $j_l(x)$ and $n_l(x)$.

$j_0 = \frac{\sin x}{x}$	$n_0 = -\frac{\cos x}{x}$
$j_1 = \frac{\sin x}{x^2} - \frac{\cos x}{x}$	$n_1 = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$
$j_2 = \left(\frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3}{x^2} \cos x$	$n_2 = -\left(\frac{3}{x^3} - \frac{1}{x} \right) \cos x - \frac{3}{x^2} \sin x$
$j_l \rightarrow \frac{x^l}{(2l+1)!!}, \quad n_l \rightarrow -\frac{(2l-1)!!}{x^{l+1}}, \quad \text{for } x \ll 1.$	

¹¹Abramowitz and Stegun, eds., *Handbook of Mathematical Functions* (New York: Dover, 1965), Chapter 10, provides an extensive listing.

- (b) Determine graphically the allowed energies for the infinite spherical well when $l = 1$. Show that for large n , $E_{n1} \approx (\hbar^2 \pi^2 / 2ma^2)(n + 1/2)^2$.

****Problem 4.9** A particle of mass m is placed in a finite spherical well:

$$V(r) = \begin{cases} 0, & \text{if } r \leq a; \\ V_0, & \text{if } r > a. \end{cases}$$

Find the ground state by solving the radial equation with $l = 0$. Show that there is no bound state at all if $V_0 a^2 < \pi^2 \hbar^2 / 8m$.

4.2 THE HYDROGEN ATOM

The hydrogen atom consists of a heavy, essentially motionless proton (we may as well put it at the origin) of charge e , together with a much lighter electron (charge $-e$) that circles around it, held in orbit by the mutual attraction of opposite charges (see Figure 4.3). From Coulomb's law, the potential energy (in SI units) is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}, \quad [4.52]$$

and the radial equation (Equation 4.37) says

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu. \quad [4.53]$$

Our problem is to solve this equation for $u(r)$ and determine the allowed electron energies E . The hydrogen atom is such an important case that I'm not going to hand you the solutions this time—we'll work them out in detail by the method we used in the analytical solution to the harmonic oscillator. (If any step in this process is unclear, you may wish to refer back to Section 2.3.2 for a more complete explanation.) Incidentally, the Coulomb potential (Equation 4.52) admits *continuum* states (with $E > 0$), describing electron-proton scattering, as well as discrete *bound* states, representing the hydrogen atom, but we shall confine our attention to the latter.

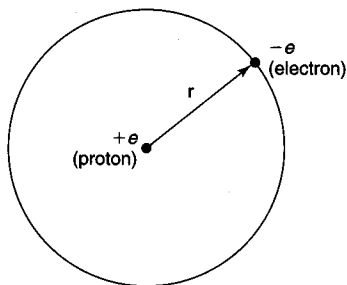


Figure 4.3: The hydrogen atom.

4.2.1 The Radial Wave Function

Our first task is to tidy up the notation. Let

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}. \quad [4.54]$$

(For bound states, $E < 0$, so κ is real.) Dividing Equation 4.53 by E , we have

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \frac{1}{\kappa r} + \frac{l(l+1)}{(\kappa r)^2} \right] u.$$

This suggests that we let

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}, \quad [4.55]$$

so that

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u. \quad [4.56]$$

Next we examine the asymptotic form of the solutions. As $\rho \rightarrow \infty$, the constant term in the brackets dominates, so (approximately)

$$\frac{d^2 u}{d\rho^2} = u.$$

The general solution is

$$u(\rho) = Ae^{-\rho} + Be^{\rho}, \quad [4.57]$$

but e^{ρ} blows up (as $\rho \rightarrow \infty$), so $B = 0$. Evidently,

$$u(\rho) \sim Ae^{-\rho} \quad [4.58]$$

for large ρ . On the other hand, as $\rho \rightarrow 0$ the centrifugal term dominates¹²; approximately, then,

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u.$$

The general solution (check it!) is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l},$$

but ρ^{-l} blows up (as $\rho \rightarrow 0$), so $D = 0$. Thus

$$u(\rho) \sim C\rho^{l+1} \quad [4.59]$$

¹²This argument does not apply when $l = 0$ (although the conclusion, Equation 4.59, is in fact valid for that case too). But never mind: All I am trying to do is provide some *motivation* for a change of variables (Equation 4.60.)

for small ρ .

The next step is to peel off the asymptotic behavior, introducing the new function $v(\rho)$:

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho), \quad [4.60]$$

in the hope that $v(\rho)$ will turn out to be simpler than $u(\rho)$. The first indications are not auspicious:

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1-\rho)v + \rho \frac{dv}{d\rho} \right],$$

and

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho} \left\{ \left[-2l - 2 + \rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1-\rho) \frac{dv}{d\rho} + \rho \frac{d^2v}{d\rho^2} \right\}.$$

In terms of $v(\rho)$, then, the radial equation (Equation 4.56) reads

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0. \quad [4.61]$$

Finally, we assume the solution, $v(\rho)$, can be expressed as a power series in ρ :

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j. \quad [4.62]$$

Our problem is to determine the coefficients (a_0, a_1, a_2, \dots). Differentiating term by term,

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j.$$

[In the second summation I have renamed the "dummy index": $j \rightarrow j+1$. If this troubles you, write out the first few terms explicitly, and *check* it. You might say that the sum should now begin at $j = -1$, but the factor $(j+1)$ kills that term anyway, so we might as well start at zero.] Differentiating again,

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1}.$$

Inserting these into Equation 4.61, we have

$$\begin{aligned} & \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j \\ & - 2 \sum_{j=0}^{\infty} j a_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} a_j \rho^j = 0. \end{aligned}$$

Equating the coefficients of like powers yields

$$j(j+1)a_{j+1} + 2(l+1)(j+1)a_{j+1} - 2ja_j + [\rho_0 - 2(l+1)]a_j = 0,$$

or

$$a_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} a_j. \quad [4.63]$$

This recursion formula determines the coefficients, and hence the function $v(\rho)$: We start with $a_0 = A$ (this becomes an overall constant, to be fixed eventually by normalization), and Equation 4.63 gives us a_1 ; putting this back in, we obtain a_2 , and so on.¹³

Now let's see what the coefficients look like for **large J** (this corresponds to large ρ , where the higher powers dominate). In this regime the recursion formula says

$$a_{j+1} \cong \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j,$$

so

$$a_j \cong \frac{2^j}{j!} A. \quad [4.64]$$

Suppose for a moment that this were the *exact* result. Then

$$v(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho},$$

and hence

$$u(\rho) = A \rho^{l+1} e^{\rho}, \quad [4.65]$$

which blows up at large ρ . The positive exponential is precisely the asymptotic behavior we *didn't* want in Equation 4.57. (It's no accident that it reappears here; after all, it *does* represent the asymptotic form of *some* solutions to the radial equation—they just don't happen to be the ones we're interested in, because they aren't normalizable.) There is only one way out of this dilemma: *The series must terminate*. There must occur some maximal integer, j_{\max} , such that

$$a_{j_{\max}+1} = 0 \quad [4.66]$$

(and beyond which all coefficients vanish automatically). Evidently (Equation 4.63)

$$2(j_{\max} + l + 1) - \rho_0 = 0.$$

¹³You might wonder why I didn't use the series method directly on $u(\rho)$ —why factor out the asymptotic behavior before applying this procedure? The reason for peeling off ρ^{l+1} is largely aesthetic: Without this, the sequence would begin with a long string of zeroes (the first nonzero coefficient being a_{l+1}); by factoring out ρ^{l+1} we obtain a series that starts out with ρ^0 . The $e^{-\rho}$ factor is more critical—if you *don't* pull that out, you get a three-term recursion formula involving a_{j+2} , a_{j+1} , and a_j (try it!), and that is enormously more difficult to work with.

Defining

$$n \equiv j_{\max} + l + 1 = n' + l \quad [4.67]$$

(the so-called **principal quantum number**), we have

$$\rho_0 = 2n. \quad [4.68]$$

But ρ_0 determines E (Equations 4.54 and 4.55):

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}, \quad [4.69]$$

so the allowed energies are

HW - Show

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots \quad [4.70]$$

This is the famous **Bohr formula**—by any measure the most important result in all of quantum mechanics. Bohr obtained it in 1913 by a serendipitous mixture of inapplicable classical physics and premature quantum theory (the Schrödinger equation did not come until 1924).

Combining Equations 4.55 and 4.68, we find that

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an}, \quad [4.71]$$

where

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \quad [4.72]$$

HW - Show

is the so-called **Bohr radius**. It follows (again, from Equation 4.55) that

$$\rho = \frac{r}{an}. \quad [4.73]$$

Evidently the spatial wave functions for hydrogen are labeled by three quantum numbers (n , l , and m):

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi), \quad [4.74]$$

where (referring back to Equations 4.36 and 4.60)

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho), \quad [4.75]$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - l - 1$ in ρ , whose coefficients are determined (up to an overall normalization factor) by the recursion formula

$$v = \sum q_j \rho^j \quad a_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} a_j. \quad [4.76]$$

The **ground state** (that is, the state of lowest energy) is the case $n = 1$; putting in the accepted values for the physical constants, we get

$$E_1 = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}. \quad [4.77]$$

Evidently the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in order to ionize the atom) is 13.6 eV. Equation 4.67 forces $l = 0$, whence also $m = 0$ (see Equation 4.29), so

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi). \quad [4.78]$$

The recursion formula truncates after the first term (Equation 4.76 with $j = 0$ yields $a_1 = 0$), so $v(\rho)$ is a constant (a_0) and

$$R_{10}(r) = \frac{a_0}{a} e^{-r/a}. \quad [4.79]$$

Normalizing it, in accordance with Equation 4.31,

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|a_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |a_0|^2 \frac{a}{4} = 1,$$

so $a_0 = 2/\sqrt{a}$. Meanwhile, $Y_0^0 = 1/\sqrt{4\pi}$, so

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}. \quad [4.80]$$

If $n = 2$ the energy is

$$\text{4x degenerate} \quad E_2 = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV}; \quad [4.81]$$

this is the first excited state—or rather, *states*, since we can have either $l = 0$ (in which case $m = 0$) or $l = 1$ (with $m = -1, 0, \text{ or } +1$), so there are actually four different states that share this energy. If $l = 0$, the recursion relation (Equation 4.76) gives

$$a_1 = -a_0 \text{ (using } j = 0\text{), and } a_2 = 0 \text{ (using } j = 1\text{),}$$

so $v(\rho) = a_0(1 - \rho)$, and hence

$$R_{20}(r) = \frac{a_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}. \quad [4.82]$$

If $l = 1$ the recursion formula terminates the series after a single term, so $v(\rho)$ is a constant, and we find

$$R_{21}(r) = \frac{a_0}{4a^2} r e^{-r/2a}. \quad [4.83]$$

(In each case the constant a_0 is to be determined by normalization—see Problem 4.11.)

For arbitrary n , the possible values of l (consistent with Equation 4.67) are

$$l = 0, 1, 2, \dots, n - 1. \quad [4.84]$$

For each l , there are $(2l + 1)$ possible values of m (Equation 4.29), so the total degeneracy of the energy level E_n is

$$d(n) = \sum_{l=0}^{n-1} (2l + 1) = n^2. \quad [4.85]$$

The polynomial $v(\rho)$ (defined by the recursion formula, Equation 4.76) is a function well known to applied mathematicians; apart from normalization, it can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho), \quad [4.86]$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \quad [4.87]$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q) \quad [4.88]$$

is the q th **Laguerre polynomial**.¹⁴ (The first few Laguerre polynomials are listed in Table 4.4; some associated Laguerre polynomials are given in Table 4.5. The first few radial wave functions are listed in Table 4.6 and plotted in Figure 4.4.) The normalized hydrogen wave functions are¹⁵

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta, \phi). \quad [4.89]$$

¹⁴As usual, there are rival normalization conventions in the literature; I have adopted the most nearly standard one.

¹⁵If you want to see how the normalization factor is calculated, study (for example), L. Schiff, *Quantum Mechanics*, 2nd ed. (New York: McGraw-Hill, 1968), page 93.

Table 4.4: The first few Laguerre polynomials, $L_q(x)$.

$$L_0 = 1$$

$$L_1 = -x + 1$$

$$L_2 = x^2 - 4x + 2$$

$$L_3 = -x^3 + 9x^2 - 18x + 6$$

$$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$$

$$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$$

$$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$$

Table 4.5: Some associated Laguerre polynomials, $L_{q-p}^p(x)$.

$$L_0^0 = 1$$

$$L_0^2 = 2$$

$$L_1^0 = -x + 1$$

$$L_1^2 = -6x + 18$$

$$L_2^0 = x^2 - 4x + 2$$

$$L_2^2 = 12x^2 - 96x + 144$$

$$L_0^1 = 1$$

$$L_0^3 = 6$$

$$L_1^1 = -2x + 4$$

$$L_1^3 = -24x + 96$$

$$L_2^1 = 3x^2 - 18x + 18$$

$$L_2^3 = 60x^2 - 600x + 1200$$

They are not pretty, but don't complain—this is one of the very few realistic systems that can be solved at all, in exact closed form. As we will prove later on, they are mutually orthogonal:

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta dr d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}. \quad [4.90]$$

***Problem 4.10** Work out the radial wave functions R_{30} , R_{31} , and R_{32} , using the recursion formula (Equation 4.76). Don't bother to normalize them.

***Problem 4.11**

(a) Normalize R_{20} (Equation 4.82), and construct the function ψ_{200} .

(b) Normalize R_{21} (Equation 4.83), and construct ψ_{211} , ψ_{210} , and ψ_{21-1} .

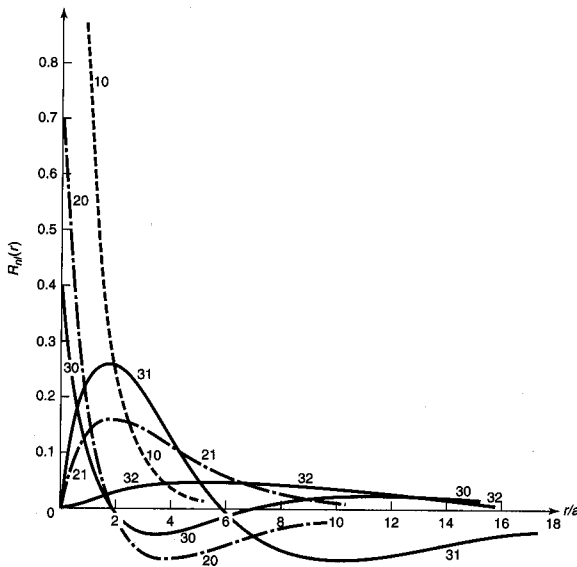
***Problem 4.12**

(a) Using Equation 4.88, work out the first four Laguerre polynomials.

(b) Using Equations 4.86, 4.87, and 4.88, find $v(\rho)$ for the case $n = 5$, $l = 2$.

Table 4.6: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$R_{10} = 2a^{-3/2} e^{-r/a}$
$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) \exp\left(-\frac{r}{a}/2\right)$
$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp\left(-\frac{r}{a}/2\right)$
$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right) \exp\left(-\frac{r}{a}/3\right)$
$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp\left(-\frac{r}{a}/3\right)$
$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp\left(-\frac{r}{a}/3\right)$
$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3\right) \exp\left(-\frac{r}{a}/4\right)$
$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a}\right)^2\right) \frac{r}{a} \exp\left(-\frac{r}{a}/4\right)$
$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a}\right) \left(\frac{r}{a}\right)^2 \exp\left(-\frac{r}{a}/4\right)$
$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp\left(-\frac{r}{a}/4\right)$


Figure 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

4.2.2 The Spectrum of Hydrogen

In principle, if you put a hydrogen atom into some stationary state Ψ_{nlm} , it should stay there forever. However, if you *tickle* it slightly (by collision with another atom, say, or by shining light on it), then the atom may undergo a **transition** to some other stationary state—either by *absorbing* energy and moving up to a higher-energy state, or by *giving off* energy (typically in the form of electromagnetic radiation) and moving down.¹⁶ In practice such perturbations are *always* present; transitions (or, as they are sometimes called, “quantum jumps”) are constantly occurring, and the result is that a container of hydrogen gives off light (photons), whose energy corresponds to the *difference* in energy between the initial and final states:

$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right). \quad [4.91]$$

Now, according to the **Planck formula**,¹⁷ the energy of a photon is proportional to its frequency:

$$E_\gamma = h\nu. \quad [4.92]$$

Meanwhile, the *wavelength* is given by $\lambda = c/\nu$, so

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad [4.93]$$

where

$$R \equiv \frac{m}{4\pi c\hbar^3} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}. \quad [4.94]$$

R is known as the **Rydberg constant**, and Equation 4.93 is the **Rydberg formula** for the spectrum of hydrogen. It was discovered empirically in the nineteenth century, and the greatest triumph of Bohr’s theory was its ability to account for this result—and to calculate R in terms of the fundamental constants of nature. Transitions to the ground state ($n_f = 1$) lie in the ultraviolet; they are known to spectroscopists as the **Lyman series**. Transitions to the first excited state ($n_f = 2$) fall in the visible region; they constitute the **Balmer series**. Transitions to $n_f = 3$ (the **Paschen series**) are in the infrared, and so on (see Figure 4.5). (At room temperature, most hydrogen atoms are in the ground state; to obtain the emission spectrum, you must first pump them up into the various excited states; typically this is done by passing an electric spark through the gas.)

¹⁶By its nature, this involves a time-dependent interaction, and the details will have to wait for Chapter 9; for our present purposes the actual mechanism involved is immaterial.

¹⁷The photon is a quantum of electromagnetic radiation; it’s a relativistic object if there ever was one, and therefore outside the scope of nonrelativistic quantum mechanics. It will be useful in a few places to speak of photons and to invoke the Planck formula for their energy, but please bear in mind that this is external to the theory we are developing.

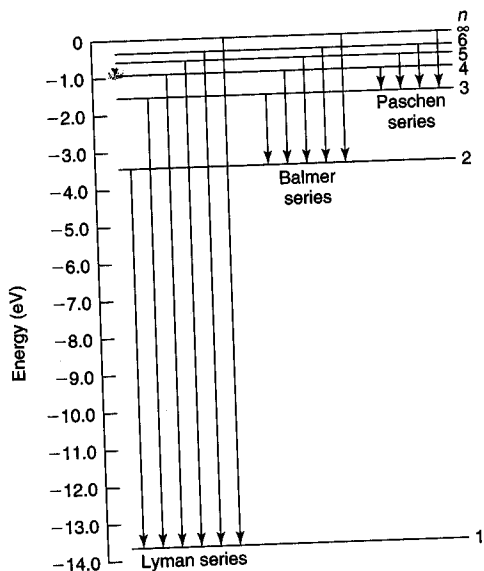


Figure 4.5: Energy levels and transitions in the spectrum of hydrogen.

Problem 4.16 Consider the earth-sun system as a gravitational analog to the hydrogen atom.

- What is the potential energy function (replacing Equation 4.52)? (Let m be the mass of the earth and M the mass of the sun.)
- What is the "Bohr radius" for this system? Work out the actual numerical value.
- Write down the gravitational "Bohr formula", and, by equating E_n to the classical energy of a planet in a circular orbit of radius r_o , show that $n = \sqrt{r_o/a}$. From this, estimate the quantum number n of the earth.
- Suppose the earth made a transition to the next lower level ($n - 1$). How much energy (in Joules) would be released? What would the wavelength of the emitted photon (or, more likely, graviton) be?

***Problem 4.17** A **hydrogenic atom** consists of a single electron orbiting a nucleus with Z protons. ($Z = 1$ would be hydrogen itself, $Z = 2$ is ionized helium, $Z = 3$ is doubly ionized lithium, and so on.) Determine the Bohr energies $E_n(Z)$, the binding energy $E_1(Z)$, the Bohr radius $a(Z)$, and the Rydberg constant $R(Z)$ for a hydrogenic atom. (Express your answers as appropriate multiples of the hydrogen values.) Where in the electromagnetic spectrum would the Lyman series fall, for $Z = 2$ and $Z = 3$?

4.3 ANGULAR MOMENTUM

In classical mechanics, the angular momentum of a particle (with respect to the origin) is given by the formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad [4.95]$$

which is to say,

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad \text{and} \quad L_z = xp_y - yp_x. \quad [4.96]$$

The corresponding quantum operators are obtained by the standard prescription (Equation 4.2):

$$\begin{aligned} L_x &= \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad L_y = \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \\ L_z &= \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \end{aligned} \quad [4.97]$$

In the following sections we will deduce the eigenvalues and eigenfunctions of these operators.

4.3.1 Eigenvalues

L_x and L_y do not commute; in fact [providing a test function, $f(x, y, z)$, for them to act upon]:

$$\begin{aligned} [L_x, L_y]f &= \left(\frac{\hbar}{i}\right)^2 \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) f \right. \\ &\quad \left. - \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) f \right\} \\ &= \left(\frac{\hbar}{i}\right)^2 \left\{ y \frac{\partial}{\partial z} \left(z \frac{\partial f}{\partial x} \right) - y \frac{\partial}{\partial z} \left(x \frac{\partial f}{\partial z} \right) \right. \\ &\quad \left. - z \frac{\partial}{\partial y} \left(z \frac{\partial f}{\partial x} \right) + z \frac{\partial}{\partial y} \left(x \frac{\partial f}{\partial z} \right) - z \frac{\partial}{\partial x} \left(y \frac{\partial f}{\partial z} \right) \right. \\ &\quad \left. + z \frac{\partial}{\partial x} \left(z \frac{\partial f}{\partial y} \right) + x \frac{\partial}{\partial z} \left(y \frac{\partial f}{\partial z} \right) - x \frac{\partial}{\partial z} \left(z \frac{\partial f}{\partial y} \right) \right\} \\ &= \left(\frac{\hbar}{i}\right)^2 \left(y \frac{\partial f}{\partial x} + yz \frac{\partial^2 f}{\partial z \partial x} - yx \frac{\partial^2 f}{\partial z^2} - z^2 \frac{\partial^2 f}{\partial y \partial x} + zx \frac{\partial^2 f}{\partial y \partial z} \right. \\ &\quad \left. - zy \frac{\partial^2 f}{\partial x \partial z} + z^2 \frac{\partial^2 f}{\partial x \partial y} + xy \frac{\partial^2 f}{\partial z^2} - x \frac{\partial f}{\partial y} - xz \frac{\partial^2 f}{\partial z \partial y} \right). \end{aligned}$$

do 4.20 instead

All the terms cancel in pairs (by virtue of the equality of cross-derivatives) except two:

$$[L_x, L_y]f = \left(\frac{\hbar}{i}\right)^2 \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y}\right) f = i\hbar L_z f,$$

and we conclude (dropping the test function)

$$[L_x, L_y] = i\hbar L_z. \quad [4.98]$$

By cyclic permutation of the indices it follows also that

$$[L_y, L_z] = i\hbar L_x \quad \text{and} \quad [L_z, L_x] = i\hbar L_y. \quad [4.99]$$

From these fundamental commutation relations the entire theory of angular momentum can be deduced.

Evidently L_x , L_y , and L_z are *incompatible* observables. According to the generalized uncertainty principle (Equation 3.139),

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle\right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2,$$

or

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|. \quad [4.100]$$

It would therefore be futile to look for states that are simultaneously eigenfunctions of L_x and of L_y . On the other hand, the *square* of the *total* angular momentum,

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2, \quad [4.101]$$

does commute with L_x :

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_y (-i\hbar L_z) + (-i\hbar L_z) L_y + L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= 0. \end{aligned}$$

(I used Equation 3.142 and the fact that *any* operator commutes with *itself*.¹⁸) It follows, of course, that L^2 also commutes with L_y and L_z :

$$[L^2, L_x] = 0, \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0, \quad [4.102]$$

¹⁸Note that all the operators we encounter in quantum mechanics (see footnote 8, Chapter 1) are **linear**, in the sense that $\hat{A}(f+g) = \hat{A}f + \hat{A}g$, and therefore *distributive* with respect to addition: $\hat{A}(\hat{B} + \hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}$. In particular, $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$.

or, more compactly,

$$[L^2, \mathbf{L}] = 0. \quad [4.103]$$

So L^2 is compatible with each component of \mathbf{L} , and we can hope to find simultaneous eigenstates of L^2 and (say) L_z :

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f. \quad [4.104]$$

We'll use a "ladder operator" technique, very similar to the one we applied to the harmonic oscillator back in Section 2.3.1. Let

$$L_{\pm} \equiv L_x \pm iL_y. \quad [4.105]$$

Its commutator with L_z is

$$[L_z, L_{\pm}] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar(L_x \pm iL_y),$$

so

$$[L_z, L_{\pm}] = \pm\hbar L_{\pm}. \quad [4.106]$$

And, of course,

$$[L^2, L_{\pm}] = 0. \quad [4.107]$$

I claim that if f is an eigenfunction of L^2 and L_z , so also is $L_{\pm}f$. For Equation 4.107 says

$$L^2(L_{\pm}f) = L_{\pm}(L^2 f) = L_{\pm}(\lambda f) = \lambda(L_{\pm}f), \quad [4.108]$$

so $L_{\pm}f$ is an eigenfunction of L^2 , with the same eigenvalue λ , and Equation 4.106 says

$$\begin{aligned} L_z(L_{\pm}f) &= (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f = \pm\hbar L_{\pm}f + L_{\pm}(\mu f) \\ &= (\mu \pm \hbar)(L_{\pm}f), \end{aligned} \quad [4.109]$$

so $L_{\pm}f$ is an eigenfunction of L_z with the *new* eigenvalue $\mu \pm \hbar$. L_+ is called the "raising" operator because it *increases* the eigenvalue of L_z by \hbar , and L_- is called the "lowering" operator because it *lowers* the eigenvalue by \hbar .

For a given value of λ , then, we obtain a "ladder" of states, with each "rung" separated from its neighbors by one unit of \hbar in the eigenvalue of L_z (see Figure 4.6). To ascend the ladder we apply the raising operator, and to descend, the lowering operator. But this process cannot go on forever: Eventually we're going to reach a state for which the z -component exceeds the *total*, and that cannot be (see Problem 4.18). So there must exist a "top rung," f_i , such that¹⁹

$$L_+ f_i = 0. \quad [4.110]$$

¹⁹Actually, all we can conclude is that $L_+ f_i$ is *not normalizable*—its norm could be *infinite*, instead of zero. Problem 4.19 eliminates this alternative.

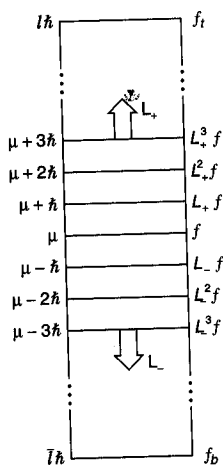


Figure 4.6: The "ladder" of angular momentum states.

Let $\hbar l$ be the eigenvalue of L_z at this top rung (the appropriateness of the letter l will appear in a moment):

$$L_z f_l = \hbar l f_l; \quad L^2 f_l = \lambda f_l. \quad [4.111]$$

Now

$$\begin{aligned} L_{\pm} L_{\mp} &= (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) \\ &= L^2 - L_z^2 \mp i(\hbar L_z), \end{aligned}$$

or, putting it the other way around,

$$L^2 = L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z. \quad [4.112]$$

It follows that

$$L^2 f_l = (L_- L_+ + L_z^2 + \hbar L_z) f_l = (0 + \hbar^2 l^2 + \hbar^2 l) f_l = \hbar^2 l(l+1) f_l,$$

and hence

$$\lambda = \hbar^2 l(l+1). \quad [4.113]$$

This tells us the eigenvalue of L^2 in terms of the maximum eigenvalue of L_z .

Meanwhile, there is also (for the same reason) a *bottom* rung, f_b , such that

$$L_- f_b = 0. \quad [4.114]$$

Let $\hbar \bar{l}$ be the eigenvalue of L_z at this bottom rung:

$$L_z f_b = \hbar \bar{l} f_b; \quad L^2 f_b = \lambda f_b. \quad [4.115]$$

Using Equation 4.112, we have

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \hbar^2 \bar{l}(\bar{l}-1) f_b,$$

and therefore

$$\lambda = \hbar^2 \bar{l}(\bar{l} - 1). \quad [4.116]$$

Comparing Equations 4.113 and 4.116, we see that $l(l + 1) = \bar{l}(\bar{l} - 1)$, so either $\bar{l} = l + 1$ (which is absurd—the bottom rung is higher than the top rung!), or else

$$\bar{l} = -l. \quad [4.117]$$

Evidently the eigenvalues of L_z are $m\hbar$, where m (the appropriateness of this letter will also be clear in a moment) goes from $-l$ to $+l$ in N integer steps. In particular, it follows that $l = -l + N$, and hence $l = N/2$, so l must be *an integer or a half-integer*. The eigenfunctions are characterized by the numbers l and m :

$$L^2 f_l^m = \hbar^2 l(l + 1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m, \quad [4.118]$$

where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l + 1, \dots, l - 1, l. \quad [4.119]$$

For a given value of l , there are $2l + 1$ different values of m (i.e., $2l + 1$ “rungs” on the “ladder”).

I hope you're impressed: By *purely algebraic means*, starting with the fundamental commutation relations (Equations 4.98 and 4.99), we have determined the eigenvalues of L^2 and L_z —without ever seeing the eigenfunctions themselves! We turn now to the problem of constructing the eigenfunctions, but I should warn you that this is a much messier business. Just so you know where we're headed, I'll tell you the punch line before we begin: $f_l^m = Y_l^m$ —the eigenfunctions of L^2 and L_z are nothing but the old spherical harmonics, which we came upon by a quite different route in Section 4.1.2 (that's why I chose the letters l and m , of course).

Problem 4.18

- (a) Prove that if f is simultaneously an eigenfunction of L^2 and of L_z (Equation 4.104), the square of the eigenvalue of L_z cannot exceed the eigenvalue of L^2 . *Hint:* Examine the expectation value of L^2 .
- (b) As it turns out (see Equations 4.118 and 4.119), the square of the eigenvalue of L_z never even *equals* the eigenvalue of L^2 (except in the special case $l = m = 0$). Comment on the implications of this result. Show that it is enforced by the uncertainty principle (Equation 4.100), and explain how the special case gets away with it.

***Problem 4.19** The raising and lowering operators change the value of m by one unit:

$$L_{\pm} f_l^m = (A_l^m) f_l^{m \pm 1}, \quad [4.120]$$

where A_l^m is some constant. *Question:* What is A_l^m , if the eigenfunctions are to be *normalized*? *Hint:* First show that L_{\mp} is the Hermitian conjugate of L_{\pm} (since L_x

and therefore

$$\lambda = \hbar^2 \bar{l}(\bar{l} - 1). \quad [4.116]$$

Comparing Equations 4.113 and 4.116, we see that $l(l + 1) = \bar{l}(\bar{l} - 1)$, so either $\bar{l} = l + 1$ (which is absurd—the bottom rung is higher than the top rung!), or else

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Evidently the eigenvalues of L_z are $m\hbar$, where m (the appropriateness of this letter will also be clear in a moment) goes from $-l$ to $+l$ in N integer steps. In particular, it follows that $l = -l + N$, and hence $l = N/2$, so l must be *an integer or a half-integer*. The eigenfunctions are characterized by the numbers l and m :

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where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l + 1, \dots, l - 1, l. \quad [4.119]$$

For a given value of l , there are $2l + 1$ different values of m (i.e., $2l + 1$ “rungs” on the “ladder”).

I hope you're impressed: By *purely algebraic means*, starting with the fundamental commutation relations (Equations 4.98 and 4.99), we have determined the eigenvalues of L^2 and L_z —without ever seeing the eigenfunctions themselves! We turn now to the problem of constructing the eigenfunctions, but I should warn you that this is a much messier business. Just so you know where we're headed, I'll tell you the punch line before we begin: $f_l^m = Y_l^m$ —the eigenfunctions of L^2 and L_z are nothing but the old spherical harmonics, which we came upon by a quite different route in Section 4.1.2 (that's why I chose the letters l and m , of course).

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- As it turns out (see Equations 4.118 and 4.119), the square of the eigenvalue of L_z never even *equals* the eigenvalue of L^2 (except in the special case $l = m = 0$). Comment on the implications of this result. Show that it is enforced by the uncertainty principle (Equation 4.100), and explain how the special case gets away with it.

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where A_l^m is some constant. *Question:* What is A_l^m , if the eigenfunctions are to be *normalized*? *Hint:* First show that L_{\mp} is the Hermitian conjugate of L_{\pm} (since L_x

and L_y are observables, you may assume they are Hermitian, but prove it if you like); then use Equation 4.112. Answer:

$$A_l^m = \hbar \sqrt{l(l+1) - m(m \pm 1)}. \quad [4.121]$$

Note what happens at the top and bottom of the ladder.

→ *Problem 4.20

- (a) Starting with the canonical commutation relations for position and momentum, Equation 4.10, work out the following commutators:

$$\begin{aligned} [L_z, x] &= i\hbar y, & [L_z, y] &= -i\hbar x, & [L_z, z] &= 0 \\ [L_z, p_x] &= i\hbar p_y, & [L_z, p_y] &= -i\hbar p_x, & [L_z, p_z] &= 0. \end{aligned} \quad [4.122]$$

- (b) Use these results to rederive Equation 4.98 directly from Equation 4.96.
 (c) Evaluate the commutators $[L_z, r^2]$ and $[L_z, p^2]$ (where, of course, $r^2 = x^2 + y^2 + z^2$ and $p^2 = p_x^2 + p_y^2 + p_z^2$).
 (d) Show that the Hamiltonian $H = (p^2/2m) + V$ commutes with all three components of \mathbf{L} , provided that V depends only on r . (Thus H , L^2 , and L_z are mutually compatible observables.)

**Problem 4.21

- (a) Prove that for a particle in a potential $V(\mathbf{r})$ the rate of change of the expectation value of the orbital angular momentum \mathbf{L} is equal to the expectation value of the torque:

$$\frac{d}{dt} \langle \mathbf{L} \rangle = \langle \mathbf{N} \rangle,$$

where

$$\mathbf{N} = \mathbf{r} \times (-\nabla V).$$

(This is the rotational analog to Ehrenfest's theorem.)

- (b) Show that $d\langle \mathbf{L} \rangle / dt = 0$ for any spherically symmetric potential. (This is one form of the quantum statement of **conservation of angular momentum**.)

4.3.2 Eigenfunctions

First of all we need to rewrite L_x , L_y , and L_z in spherical coordinates. Now $\mathbf{L} = (\hbar/i)(\mathbf{r} \times \nabla)$, and the gradient, in spherical coordinates, is²⁰

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}; \quad [4.123]$$

²⁰George Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Orlando, FL: Academic Press, 1985), Section 2.5.

meanwhile, $\mathbf{r} = r\hat{r}$, so

$$\mathbf{L} = \frac{\hbar}{i} \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + (\hat{r} \times \hat{\phi}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

But $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$ (see Figure 4.1), and hence

$$\mathbf{L} = \frac{\hbar}{i} \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right). \quad [4.124]$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their Cartesian components:

$$\hat{\theta} = (\cos \theta \cos \phi)\hat{i} + (\cos \theta \sin \phi)\hat{j} - (\sin \theta)\hat{k}; \quad [4.125]$$

$$\hat{\phi} = -(\sin \phi)\hat{i} + (\cos \phi)\hat{j}. \quad [4.126]$$

Thus

$$\mathbf{L} = \frac{\hbar}{i} \left[(-\sin \phi \hat{i} + \cos \phi \hat{j}) \frac{\partial}{\partial \theta} - (\cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

Evidently,

$$L_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad [4.127]$$

$$L_y = \frac{\hbar}{i} \left(+\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad [4.128]$$

and

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \quad [4.129]$$

We shall also need the raising and lowering operators:

$$L_{\pm} = L_x \pm iL_y = \frac{\hbar}{i} \left[(-\sin \phi \pm i \cos \phi) \frac{\partial}{\partial \theta} - (\cos \phi \pm i \sin \phi) \cot \theta \frac{\partial}{\partial \phi} \right].$$

But $\cos \phi \pm i \sin \phi = e^{\pm i\phi}$, so

$$L_{\pm} = \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right). \quad [4.130]$$

We are now in a position to determine $f_l^m(\theta, \phi)$ (I'll drop the subscript and superscript for now). It's an eigenfunction of L_z , with eigenvalue $\hbar m$:

$$L_z f = \frac{\hbar}{i} \frac{\partial f}{\partial \phi} = \hbar m f,$$

so

$$f = g(\theta) e^{im\phi}. \quad [4.131]$$

[Here $g(\theta)$ is a constant of integration, as far as ϕ is concerned, but it can still depend on θ .] And f is also an eigenfunction of L^2 (which we'll write in terms of L_{\pm} and L_z , using Equation 4.112), with eigenvalue $\hbar^2 l(l+1)$:

$$\begin{aligned} L^2 f &= (L_+ L_- + L_z^2 - \hbar L_z) f \\ &= \hbar e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) (-\hbar e^{-i\phi}) \left(\frac{\partial f}{\partial \theta} - i \cot \theta \frac{\partial f}{\partial \phi} \right) - \hbar^2 \frac{\partial^2 f}{\partial \phi^2} - \frac{\hbar^2}{i} \frac{\partial f}{\partial \phi} \\ &= \hbar^2 l(l+1) f. \end{aligned}$$

But in view of Equation 4.131, $\partial f / \partial \theta = e^{im\phi} dg/d\theta$ and $\partial f / \partial \phi = im e^{im\phi} g$, so

$$\begin{aligned} -e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) (e^{i(m-1)\phi}) \left(\frac{dg}{d\theta} + mg \cot \theta \right) + m^2 g e^{im\phi} - m g e^{im\phi} \\ = e^{im\phi} \left[-\frac{d}{d\theta} \left(\frac{dg}{d\theta} + mg \cot \theta \right) + (m-1) \cot \theta \left(\frac{dg}{d\theta} + mg \cot \theta \right) \right. \\ \left. + m(m-1)g \right] = l(l+1)g e^{im\phi}. \end{aligned}$$

Canceling $e^{im\phi}$,

$$\begin{aligned} -\frac{d^2 g}{d\theta^2} - m \frac{dg}{d\theta} \cot \theta + mg \csc^2 \theta + (m-1) \cot \theta \frac{dg}{d\theta} + m(m-1)(1 + \cot^2 \theta)g \\ = -\frac{d^2 g}{d\theta^2} - \cot \theta \frac{dg}{d\theta} + m^2 g \csc^2 \theta = l(l+1)g, \end{aligned}$$

or, multiplying through by $-\sin^2 \theta$:

$$\sin^2 \theta \frac{d^2 g}{d\theta^2} + \sin \theta \cos \theta \frac{dg}{d\theta} - m^2 g = -l(l+1) \sin^2 \theta g.$$

This is a differential equation for $g(\theta)$; it can be written in a more familiar form:

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dg}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2]g = 0. \quad [4.132]$$

But this is precisely the equation for the θ -dependent part, $\Theta(\theta)$, of $Y_l^m(\theta, \phi)$ (compare Equation 4.25). Meanwhile, the ϕ -dependent part of f (to wit, $e^{im\phi}$) is identical to $\Phi(\phi)$ (Equation 4.22). Conclusion: The *spherical harmonics are precisely the (normalized) eigenfunctions of L^2 and L_z* .

When we solved the Schrödinger equation by separation of variables, in Section 4.1, we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 , and L_z :

✱

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi. \quad [4.133]$$

But there is a curious twist to this story, for the *algebraic* theory of angular momentum permits l (and hence also m) to take on *half-integer* values (Equation 4.119), whereas the *analytic* method yielded eigenfunctions only for *integer* values (Equation 4.29). You might reasonably guess that the half-integer solutions are spurious, but it turns out that they are of profound importance, as we shall see in the following sections.

***Problem 4.22**

- (a) What is $L_+ Y_l^l$? (No calculation allowed!)
- (b) Use the result of (a), together with the fact that $L_z Y_l^l = \hbar l Y_l^l$, to determine $Y_l^l(\theta, \phi)$, up to a normalization constant.
- (c) Determine the normalization constant by direct integration. Compare your final answer to what you got in Problem 4.5.

Problem 4.23 In Problem 4.3 you showed that

$$Y_2^1(\theta, \phi) = -\sqrt{15/8\pi} \sin\theta \cos\theta e^{i\phi}.$$

Apply the raising operator to find $Y_2^2(\theta, \phi)$. Use Equation 4.121 to get the normalization.

Problem 4.24

- (a) Prove that the spherical harmonics are orthogonal (Equation 4.33). *Hint:* This requires no calculation, if you invoke the appropriate theorem.
- (b) Prove the orthogonality of the hydrogen wave functions $\psi_{nlm}(r, \theta, \phi)$ (Equation 4.90).

Problem 4.25 Two particles of mass m are attached to the ends of a massless rigid rod of length a . The system is free to rotate in three dimensions about the center (but the center point itself is fixed).

- (a) Show that the allowed energies of this **rigid rotor** are

$$E_n = \frac{\hbar^2 n(n+1)}{ma^2}, \quad \text{for } n = 0, 1, 2, \dots$$

Hint: First express the (classical) energy in terms of the total angular momentum.

- (b) What are the normalized eigenfunctions for this system? What is the degeneracy of the n th energy level?

4.4 SPIN

In classical mechanics, a rigid object admits two kinds of angular momentum: **orbital** ($\mathbf{L} = \mathbf{r} \times \mathbf{p}$), associated with the motion of the center of mass, and **spin** ($\mathbf{S} = I\boldsymbol{\omega}$), associated with motion about the center of mass. For example, the earth has orbital angular momentum attributable to its annual revolution around the sun, and spin angular momentum coming from its daily rotation about the north-south axis. In the classical context this distinction is largely a matter of convenience, for when you come right down to it, \mathbf{S} is nothing but the sum total of the “orbital” angular momenta of all the rocks and dirt clods that go to make up the earth, as they circle around the axis. But an analogous thing happens in quantum mechanics, and here the distinction is absolutely fundamental. In addition to orbital angular momentum, associated (in the case of hydrogen) with the motion of the electron around the nucleus (and described by the spherical harmonics), the electron also carries *another* form of angular momentum, which has nothing to do with motion in space (and which is not, therefore, described by any function of the position variables r, θ, ϕ) but which is somewhat analogous to classical spin (and for which, therefore, we use the same word). It doesn't pay to press this analogy too far: The electron (as far as we know) is a structureless point particle, and its spin angular momentum cannot be decomposed into orbital angular momenta of constituent parts (see Problem 4.26).²¹ Suffice it to say that elementary particles carry **intrinsic** angular momentum (\mathbf{S}) in addition to their “extrinsic” angular momentum (\mathbf{L}).

The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum, beginning with the fundamental commutation relations²²:

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y. \quad [4.134]$$

It follows (as before) that the eigenvectors of S^2 and S_z satisfy²³

$$S^2|s m\rangle = \hbar^2 s(s+1)|s m\rangle; \quad S_z|s m\rangle = \hbar m|s m\rangle; \quad [4.135]$$

and

$$S_{\pm}|s m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}|s(m \pm 1)\rangle, \quad [4.136]$$

²¹For a contrary interpretation, see Hans C. Ohanian, “What is Spin?”, *Am. J. Phys.* **54**, 500 (1986).

²²We shall take these as *postulates* for the theory of spin; the analogous formulas for *orbital* angular momentum (Equations 4.98 and 4.99) were *derived* from the known form of the operators (Equation 4.97). In a more sophisticated treatment they can both be obtained from the rotational invariance of the three-dimensional world [see, for example, Leslie E. Ballentine, *Quantum Mechanics* (Englewood Cliffs, NJ: Prentice Hall, 1990), Section 3.3]. Indeed, these fundamental commutation relations apply to *all* forms of angular momentum, whether spin, orbital, or the combined angular momentum of a composite system, which could include some spin and some orbital.

²³Because the eigenstates of spin are not *functions*, I revert to the “ket” notation for them. (I could have done the same in Section 4.3, writing $|l m\rangle$ in place of Y_l^m , but in that context the function notation seems more natural.) By the way, I'm running out of letters, so I'll use m for the eigenvalue of S_z , just as I did for L_z (some authors write m_l and m_s at this stage, just to be absolutely clear).

where $S_{\pm} \equiv S_x \pm iS_y$. But this time the eigenvectors are *not* spherical harmonics (they're not functions of θ and ϕ at all), and there is no a priori reason to exclude the half-integer values of s and m :

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s + 1, \dots, s - 1, s. \quad [4.137]$$

It so happens that every elementary particle has a *specific and immutable* value of s , which we call the **spin** of that particular species: pi mesons have spin 0; electrons have spin 1/2; photons have spin 1; deltas have spin 3/2; gravitons have spin 2; and so on. By contrast, the *orbital* angular momentum quantum number l (for an electron in a hydrogen atom, say) can take on any (integer) value you please, and will change from one to another when the system is perturbed. But s is *fixed*, for any given particle, and this makes the theory of spin comparatively simple.²⁴

Problem 4.26 If the electron is a classical solid sphere, with radius

$$r_c = \frac{e^2}{4\pi\epsilon_0 mc^2}, \quad [4.138]$$

(the so-called **classical electron radius**, obtained by assuming that the electron's mass is attributable to energy stored in its electric field, via the Einstein formula $E = mc^2$), and its angular momentum is $(1/2)\hbar$, then how fast (in m/s) is a point on the "equator" moving? Does this model for spin make sense? (Actually, the radius of the electron is known experimentally to be much less than r_c , but this only makes matters worse.)

$\frac{E^2}{2} = \frac{4}{3}\pi r^3$

4.4.1 Spin 1/2

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By far the most important case is $s = 1/2$, for this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. Moreover, once you understand spin 1/2, it is a simple matter to work out the formalism for any higher spin. There are just *two* eigenstates: $|\frac{1}{2} \frac{1}{2}\rangle$, which we call **spin up** (informally, \uparrow), and $|\frac{1}{2} (-\frac{1}{2})\rangle$, which we call **spin down** (\downarrow). Using these as basis vectors, the general state of a spin-1/2 particle can be expressed as a two-element column matrix (or **spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-, \quad [4.139]$$

²⁴Indeed, in a mathematical sense, spin 1/2 is the simplest possible nontrivial quantum system, for it admits just two possible states. In place of an infinite-dimensional Hilbert space, with all its subtleties and complications, we find ourselves working in an ordinary two-dimensional vector space; in place of unfamiliar differential equations and fancy functions, we are confronted with 2×2 matrices and two-component vectors. For this reason, some authors *begin* quantum mechanics with a treatment of the spin-1/2 system. But the price of mathematical simplicity is conceptual abstraction, and I prefer not to do it that way.

(1)

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \uparrow \quad [4.140]$$

representing spin up, and

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \downarrow \quad [4.141]$$

for spin down. Meanwhile, the spin operators become 2×2 matrices, which we can work out by noting their effect on χ_+ and χ_- : Equation 4.135 says

$$S^2 \chi_+ = \frac{3}{4} \hbar^2 \chi_+; \quad S^2 \chi_- = \frac{3}{4} \hbar^2 \chi_-; \quad S_z \chi_+ = \frac{\hbar}{2} \chi_+; \quad S_z \chi_- = -\frac{\hbar}{2} \chi_-; \quad [4.142]$$

and Equation 4.136 gives

$$S_+ \chi_- = \hbar \chi_+; \quad S_- \chi_+ = \hbar \chi_-; \quad S_+ \chi_+ = S_- \chi_- = 0. \quad [4.143]$$

Now, $S_{\pm} = S_x \pm i S_y$, so

$$S_x = \frac{1}{2}(S_+ + S_-) \quad \text{and} \quad S_y = \frac{1}{2i}(S_+ - S_-), \quad [4.144]$$

and it follows that

$$S_x \chi_+ = \frac{\hbar}{2} \chi_-; \quad S_x \chi_- = \frac{\hbar}{2} \chi_+; \quad S_y \chi_+ = -\frac{\hbar}{2i} \chi_-; \quad S_y \chi_- = \frac{\hbar}{2i} \chi_+. \quad [4.145]$$

Thus

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}; \quad [4.146]$$

while

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad [4.147]$$

It's a little tidier to divide off the factor of $\hbar/2$: $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$, where

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad [4.148]$$

These are the famous **Pauli spin matrices**. Notice that S_x , S_y , S_z , and S^2 are all *Hermitian* (as they should be, since they represent observables). On the other hand, S_+ and S_- are *not* Hermitian—evidently they are not observable.

The eigenspinors of S_z are (of course)

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (\text{eigenvalue } +\frac{\hbar}{2}); \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (\text{eigenvalue } -\frac{\hbar}{2}). \quad [4.149]$$

If you measure S_z on a particle in the general state χ (Equation 4.139), you could get $+\hbar/2$, with probability $|a|^2$, or $-\hbar/2$, with probability $|b|^2$. Since these are the only possibilities,

$$|a|^2 + |b|^2 = 1 \tag{4.150}$$

(i.e., the spinor must be normalized).²⁵

But what if, instead, you chose to measure S_x ? What are the possible results and what are their respective probabilities? According to the generalized statistical interpretation, we need to know the eigenvalues and eigenspinors of S_x . The characteristic equation is

$$\begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 = \left(\frac{\hbar}{2}\right)^2 \Rightarrow \lambda = \pm \frac{\hbar}{2}.$$

Not surprisingly, the possible values for S_x are the same as those for S_z . The eigenspinors are obtained in the usual way:

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow \begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

so $\beta = \pm\alpha$. Evidently the (normalized) eigenspinors of S_x are

$$\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \text{ (eigenvalue } +\frac{\hbar}{2}\text{); } \chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \text{ (eigenvalue } -\frac{\hbar}{2}\text{).} \tag{4.151}$$

As the eigenvectors of a Hermitian matrix, they span the space; the generic spinor χ can be expressed as a linear combination of them:

$$\chi = \left(\frac{a+b}{\sqrt{2}}\right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}}\right) \chi_-^{(x)}. \tag{4.152}$$

If you measure S_x , the probability of getting $+\hbar/2$ is $(1/2)|a+b|^2$, and the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$. (You should check for yourself that these probabilities add up to 1.)

Example. Suppose a spin 1/2 particle is in the state

$$\chi = \frac{1}{\sqrt{6}} \begin{pmatrix} 1+i \\ 2 \end{pmatrix}.$$

If you measure S_z , the probability of getting $+\hbar/2$ is $|(1+i)/\sqrt{6}|^2 = 1/3$, and the probability of getting $-\hbar/2$ is $|2/\sqrt{6}|^2 = 2/3$. If you measure S_x , the probability of

²⁵People often say that $|a|^2$ is the "probability that the particle is in the spin-up state", but this is sloppy language; the particle is in state χ —not χ_+ —and what the speaker really means is that if you measured S_z , $|a|^2$ is the probability you'd get $\hbar/2$, which is an entirely different assertion.

getting $+\hbar/2$ is $(1/2)|(3+i)/\sqrt{6}|^2 = 5/6$, and the probability of getting $-\hbar/2$ is $(1/2)|(-1+i)/\sqrt{6}|^2 = 1/6$. Evidently the *expectation* value of S_x is

$$\frac{5}{6} \left(+\frac{\hbar}{2} \right) + \frac{1}{6} \left(-\frac{\hbar}{2} \right) = \frac{\hbar}{3},$$

which we could also have obtained more directly:

$$\langle S_x \rangle = \chi^\dagger S_x \chi = \left(\frac{1-i}{\sqrt{6}} \quad \frac{2}{\sqrt{6}} \right) \begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix} \begin{pmatrix} (1+i)/\sqrt{6} \\ 2/\sqrt{6} \end{pmatrix} = \frac{\hbar}{3}.$$

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[S_x] [S_z]

I'd like now to walk you through an imaginary measurement scenario involving spin 1/2, because it serves to illustrate in very concrete terms some of the abstract ideas we discussed back in Chapter 1. Let's say we start out with a particle in the state χ_+ . If someone asks, "What is the z-component of that particle's spin angular momentum?", we could answer unambiguously: $+\hbar/2$. For a measurement of S_z is certain to return that value. But if our interrogator asks instead, "What is the x-component of that particle's spin angular momentum?", we are obliged to equivocate: If you measure S_x , the chances are 50-50 of getting either $\hbar/2$ or $-\hbar/2$. If the questioner is a classical physicist, or a "realist" (in the sense of Section 1.2), he will regard this as an inadequate—not to say impertinent—response: "Are you telling me that you *don't know* the true state of that particle?" On the contrary; I know *precisely* what the state of the particle is: χ_+ . "Well, then, how come you can't tell me what the x-component of its spin is?" Because it simply *does not have* a particular x-component of spin. Indeed, it *cannot*, for if both S_x and S_z were well defined, the uncertainty principle would be violated.

At this point our challenger grabs the test tube and *measures* the x-component of its spin; let's say he gets the value $+\hbar/2$. "Aha!" (he shouts in triumph), "You *lied!* This particle has a perfectly well-defined value of S_x : It's $\hbar/2$." Well, sure—it does *now*, but that doesn't prove it *had* that value, prior to your measurement. "You have obviously been reduced to splitting hairs. And anyway, what happened to your uncertainty principle? I now know both S_x and S_z ." I'm sorry, but you do *not*: In the course of your measurement, you altered the particle's state; it is now in the state $\chi_+^{(x)}$, and whereas you know the value of S_x , you no longer know the value of S_z . "But I was extremely careful not to disturb the particle when I measured S_x ." ²⁶ Very well, if you don't believe me, *check it out*: Measure S_z , and see what you get. (Of course, he *may* get $+\hbar/2$, which will be embarrassing to my case—but if we repeat this whole scenario over and over, half the time he will get $-\hbar/2$.)

To the layperson, the philosopher, or the classical physicist, a statement of the form "this particle doesn't have a well-defined position" (or momentum, or

²⁶Neils Bohr was anxious to track down the *mechanism* by which the measurement of S_x inevitably destroys the value of S_z , in gedanken experiments of this sort. His famous debates with Einstein include many delightful examples, showing in detail how experimental constraints serve to enforce the uncertainty principle.

x -component of spin angular momentum, or whatever) sounds vague, incompetent, or (worst of all) profound. It is none of these. But its precise meaning is, I think, almost impossible to convey to anyone who has not studied quantum mechanics in some depth. If you find your own comprehension slipping, from time to time (if you *don't*, you probably haven't understood the problem), come back to the spin-1/2 system: It is the simplest and cleanest context for thinking through the conceptual paradoxes of quantum mechanics.

Problem 4.27

- (a) Check that the spin matrices (Equation 4.147) obey the fundamental commutation relation for angular momentum: $[S_x, S_y] = i\hbar S_z$.
- (b) Show that the Pauli spin matrices satisfy

$$\sigma_j \sigma_k = \delta_{jk} + i \sum_l \epsilon_{jkl} \sigma_l, \quad [4.153]$$

where the indices stand for x , y , or z .

***Problem 4.28** An electron is in the spin state

$$\chi = A \begin{pmatrix} 3i \\ 4 \end{pmatrix}.$$

- (a) Determine the normalization constant A .
- (b) Find the expectation values of S_x , S_y , and S_z .
- (c) Find the “uncertainties” σ_{S_x} , σ_{S_y} , and σ_{S_z} .
- (d) Confirm that your results are consistent with all three uncertainty principles (Equation 4.100 and its cyclic permutations—only with S in place of L , of course).

***Problem 4.29** For the most general normalized spinor χ (Equation 4.139), compute $\langle S_x \rangle$, $\langle S_y \rangle$, $\langle S_z \rangle$, $\langle S_x^2 \rangle$, $\langle S_y^2 \rangle$, and $\langle S_z^2 \rangle$. Check that $\langle S_x^2 \rangle + \langle S_y^2 \rangle + \langle S_z^2 \rangle = \langle S^2 \rangle$.

***Problem 4.30**

- (a) Find the eigenvalues and eigenspinors of S_y .
- (b) If you measured S_y on a particle in the general state χ (Equation 4.139), what values might you get, and what is the probability of each? Check that the probabilities add up to 1.
- (c) If you measured S_y^2 , what values might you get and with what probability?
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