

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):

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

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.

or

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

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:

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

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:*

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

where the indices stand for x , y , or z , and $r_x = x$, $r_y = y$, and $r_z = z$.

- (b) Confirm Ehrenfest's theorem for 3-dimensions:

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

(Each of these, of course, stands for *three* equations—one for each component.) *Hint:* First check that Equation 3.71 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

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

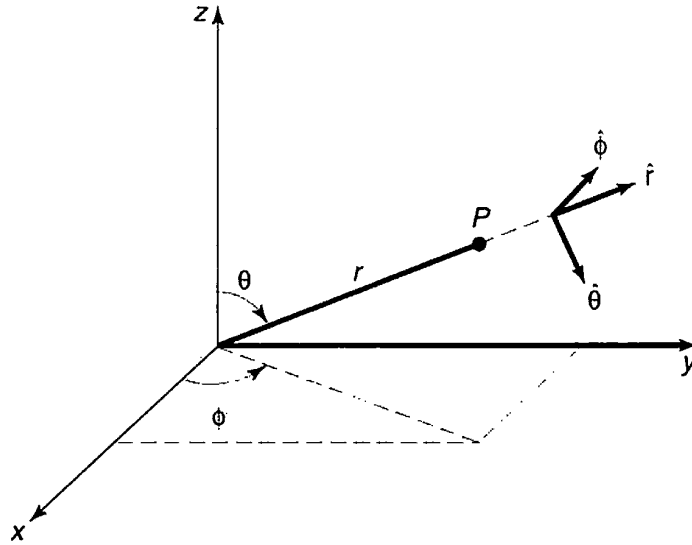
In spherical coordinates, then, the time-independent Schrödinger equation reads

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

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

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

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., (Wiley, New York, 1983), Chapter 10, Section 9.

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

Putting this into Equation 4.14, we have

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

Dividing by RY 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,³ I will write this “separation constant” in the form $l(l+1)$:

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

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

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.

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

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

- (a) Find the stationary states, and the corresponding energies.
- (b) 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 their degeneracies (that is, the number of different states that share the same energy). *Comment:* In *one* dimension degenerate bound states do not occur (see Problem 2.45), but in three dimensions they are very common.
- (c) 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:

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

You might recognize this equation—it occurs in the solution to Laplace’s equation in classical electrodynamics. As always, we try separation of variables:

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi). \quad [4.19]$$

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 time⁴ I’ll call the separation constant m^2 :

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

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

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 a separation constant. There is no graceful way to avoid this confusion, since both uses are standard. Some authors now switch to M or μ for mass, but I hate to change notation in mid-stream, and I don’t think confusion will arise, as long as you are aware of the problem.

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*:

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

The θ equation,

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

is not so simple. 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**, defined by the **Rodrigues formula**:

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

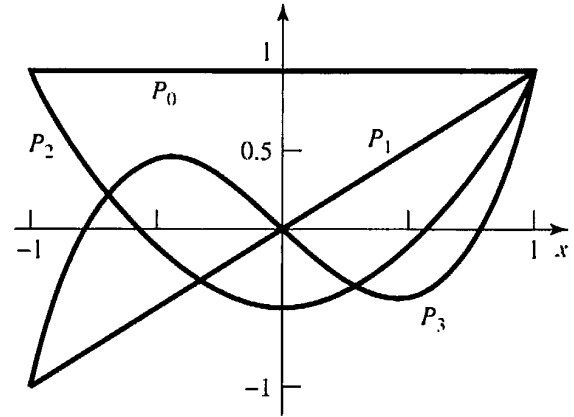
⁵This is more slippery than it looks. After all, the *probability density* ($|\Phi|^2$) is single-valued *regardless* of m . In Section 4.3 we'll obtain the condition on m by an entirely different—and more compelling—argument.

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: The first few Legendre polynomials, $P_l(x)$: (a) functional form, (b) graphs.

$P_0 = 1$
$P_1 = x$
$P_2 = \frac{1}{2}(3x^2 - 1)$
$P_3 = \frac{1}{2}(5x^3 - 3x)$
$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$
$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$

(a)



(b)

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 are listed in Table 4.1. 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 $\sqrt{1-x^2}$:

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

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

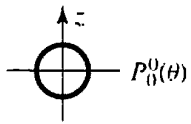
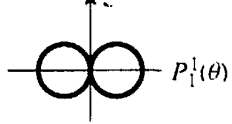
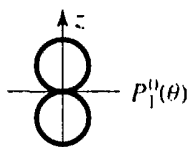
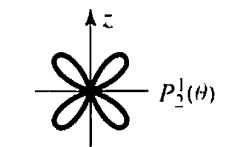
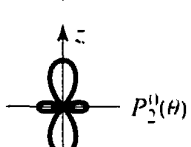
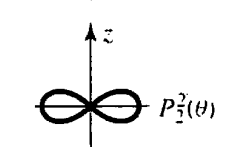


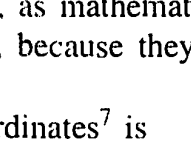
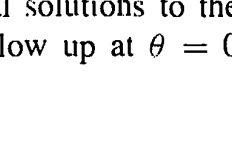
etc. (On the other hand, what we need is $P_l^m(\cos \theta)$, and $\sqrt{1-\cos^2 \theta} = \sin \theta$, so $P_l^m(\cos \theta)$ is always a polynomial in $\cos \theta$, multiplied—if m is odd—by $\sin \theta$. Some associated Legendre functions of $\cos \theta$ are listed in Table 4.2.)

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 :

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

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

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos \theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos \theta)$ (in these plots r tells you the magnitude of the function in the direction θ ; each figure should be rotated about the z -axis).

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3 \cos^2 \theta - 1)$		
$P_1^1 = \sin \theta$	$P_3^3 = 15 \sin \theta (1 - \cos^2 \theta)$		
$P_1^0 = \cos \theta$	$P_3^2 = 15 \sin^2 \theta \cos \theta$		
$P_2^2 = 3 \sin^2 \theta$	$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$		
$P_2^1 = 3 \sin \theta \cos \theta$	$P_3^0 = \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$		

(a)
(b)

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 $\theta = \pi$ (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 separately:

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

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

TABLE 4.3: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

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

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

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

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

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

In Table 4.3 I have listed the first few spherical harmonics. For historical reasons, l is called the **azimuthal quantum number**, and m the **magnetic quantum number**.

***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.

Problem 4.4 Show that

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

⁸The normalization factor is derived in Problem 4.54: ϵ (which is always 1 or -1) 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

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

satisfies the θ equation (Equation 4.25), for $l = m = 0$. This is the unacceptable “second solution”—what’s *wrong* with it?

***Problem 4.5** Use Equation 4.32 to construct $Y_l^l(\theta, \phi)$ and $Y_3^2(\theta, \phi)$. (You can take P_3^2 from Table 4.2, but you’ll have to work out P_l^l from Equations 4.27 and 4.28.) Check that they satisfy the angular equation (Equation 4.18), for the appropriate values of 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

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

This is called the **radial equation**;⁹ it is *identical in form* to the one-dimensional Schrödinger equation (Equation 2.5), except that the **effective potential**,

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

⁹Those m ’s are *masses*, of course—the separation constant m does not appear in the radial equation.

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

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

That's as far as we can go until a specific potential $V(r)$ is provided.

Example 4.1 Consider the **infinite spherical well**,

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

Find the wave functions and the allowed energies.

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

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

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

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

¹⁰Actually, all we require is that the wave function be *normalizable*, not that it be *finite*: $R(r) \sim 1/r$ at the origin *is* 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* (Plenum, New York, 1980), p. 351.

the same as for the one-dimensional infinite square well (Equation 2.27). Normalizing $u(r)$ yields $A = \sqrt{2/a}$; tacking on the angular part (trivial, 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:

$$u(r) = Arj_l(kr) + Brn_l(kr). \quad [4.45]$$

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,

$$\begin{aligned} j_0(x) &= \frac{\sin x}{x}; & n_0(x) &= -\frac{\cos x}{x}; \\ j_1(x) &= (-x) \frac{1}{x} \frac{d}{dx} \left(\frac{\sin x}{x} \right) = \frac{\sin x}{x^2} - \frac{\cos x}{x}; \\ j_2(x) &= (-x)^2 \left(\frac{1}{x} \frac{d}{dx} \right)^2 \frac{\sin x}{x} = x^2 \left(\frac{1}{x} \frac{d}{dx} \right) \frac{x \cos x - \sin x}{x^3} \\ &= \frac{3 \sin x - 3x \cos x - x^2 \sin x}{x^3}; \end{aligned}$$

and so on. The first few spherical Bessel and Neumann functions are listed in Table 4.4. For small x (where $\sin x = x - x^3/3! + x^5/5! - \dots$ and $\cos x = 1 - x^2/2 + x^4/4! - \dots$),

$$j_0(x) \approx 1; \quad n_0(x) \approx -\frac{1}{x}; \quad j_1(x) \approx \frac{x}{3}; \quad j_2(x) \approx \frac{x^2}{15};$$

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

$$R(r) = Aj_l(kr). \quad [4.47]$$

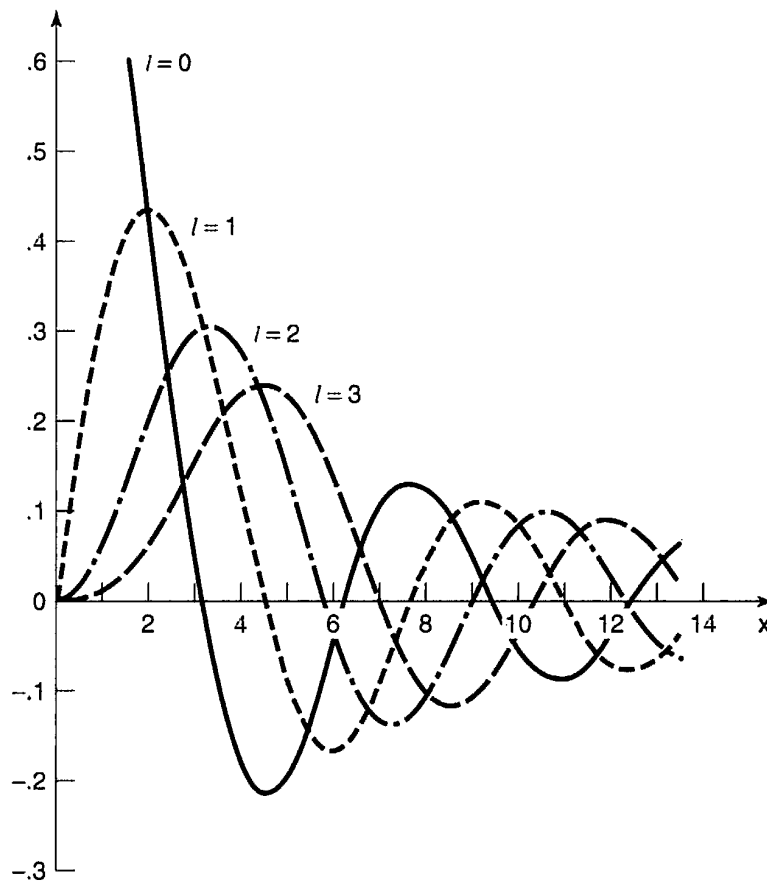
TABLE 4.4: The first few spherical Bessel and Neumann functions, $j_l(x)$ and $n_l(x)$; asymptotic forms for small x .

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

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

$$j_l(ka) = 0; \quad [4.48]$$

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.

**FIGURE 4.2:** Graphs of the first four spherical Bessel functions.

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

$$k = \frac{1}{a} \beta_{nl}. \quad [4.49]$$

where β_{nl} is the n th zero of the l th spherical Bessel function. The allowed energies, then, are given by

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2. \quad [4.50]$$

and the wave functions are

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l(\beta_{nl}r/a) Y_l^m(\theta, \phi). \quad [4.51]$$

with the constant A_{nl} to be determined by normalization. Each energy level is $(2l + 1)$ -fold degenerate, since there are $(2l + 1)$ different values of m for each value of l (see Equation 4.29).

Problem 4.7

- (a) From the definition (Equation 4.46), construct $n_1(x)$ and $n_2(x)$.
- (b) Expand the sines and cosines to obtain approximate formulas for $n_1(x)$ and $n_2(x)$, valid when $x \ll 1$. Confirm that they blow up at the origin.

Problem 4.8

- (a) Check that $Ar j_1(kr)$ satisfies the radial equation with $V(r) = 0$ and $l = 1$.
- (b) Determine graphically the allowed energies for the infinite spherical well, when $l = 1$. Show that for large n , $E_{n1} \approx (\hbar^2 \pi^2 / 2ma^2)(n + 1/2)^2$. *Hint:* First show that $j_1(x) = 0 \Rightarrow x = \tan x$. Plot x and $\tan x$ on the same graph, and locate the points of intersection.

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

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

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

Find the ground state, by solving the radial equation with $l = 0$. Show that there is no bound state 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 orbits around it, bound 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 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.)

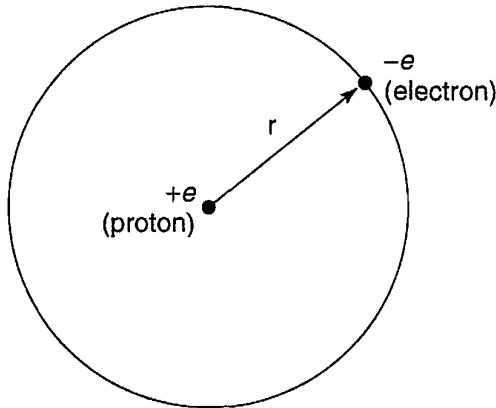


FIGURE 4.3: The hydrogen atom.

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.

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 is negative, 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 introduce

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

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 dominates;¹² approximately, then:

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

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).

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

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

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 :

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

Our problem is to determine the coefficients (c_0, c_1, c_2, \dots). Differentiating term by term:

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

[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 may object

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,

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

Inserting these into Equation 4.61, we have

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

Equating the coefficients of like powers yields

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j = 0.$$

or:

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

This recursion formula determines the coefficients, and hence the function $v(\rho)$: We start with c_0 (this becomes an overall constant, to be fixed eventually by normalization), and Equation 4.63 gives us c_1 ; putting this back in, we obtain c_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 says¹⁴

$$c_{j+1} \cong \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j.$$

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? Well, the reason for peeling off ρ^{l+1} is largely aesthetic: Without this, the sequence would begin with a long string of zeros (the first nonzero coefficient being c_{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 c_{j+2} , c_{j+1} , and c_j (try it!) and that is enormously more difficult to work with.

¹⁴You might ask why I don't drop the 1 in $j+1$ —after all, I am ignoring $2(l+1) - \rho_0$ in the numerator, and $2l+2$ in the denominator. In this approximation it would be fine to drop the 1 as well, but keeping it makes the argument a little cleaner. Try doing it without the 1, and you'll see what I mean.

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

$$c_j = \frac{2^j}{j!} c_0, \quad [4.64]$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho},$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}, \quad [4.65]$$

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

$$c_{(j_{\max}+1)} = 0. \quad [4.66]$$

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

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

Defining

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

(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

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

[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

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

is the so-called **Bohr radius**.¹⁵ It follows (again, from Equation 4.55) that

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

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

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j. \quad [4.76]$$

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:

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

¹⁵It is traditional to write the Bohr radius with a subscript: a_0 . But this is cumbersome and unnecessary, so I prefer to leave the subscript off.

Evidently the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in the ground state 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 $c_1 = 0$), so $v(\rho)$ is a constant (c_0), and

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a}. \quad [4.79]$$

Normalizing it, in accordance with Equation 4.31:

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|c_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |c_0|^2 \frac{a}{4} = 1,$$

so $c_0 = 2/\sqrt{a}$. Meanwhile, $Y_0^0 = 1/\sqrt{4\pi}$, and hence the ground state of hydrogen is

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

If $n = 2$ the energy is

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

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 $m = -1, 0$, or $+1$); evidently four different states share this same energy. If $l = 0$, the recursion relation (Equation 4.76) gives

$$c_1 = -c_0 \text{ (using } j = 0\text{), and } c_2 = 0 \text{ (using } j = 1\text{),}$$

so $v(\rho) = c_0(1 - \rho)$, and therefore

$$R_{20}(r) = \frac{c_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}. \quad [4.82]$$

[Notice that the expansion coefficients $\{c_j\}$ are completely different for different quantum numbers n and l .] If $l = 1$ the recursion formula terminates the series after a single term; $v(\rho)$ is a constant, and we find

$$R_{21}(r) = \frac{c_0}{4a^2} r e^{-r/2a}. \quad [4.83]$$

(In each case the constant c_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

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

and 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**.¹⁶ (The first few Laguerre polynomials are listed in Table 4.5; some associated Laguerre polynomials are given in Table 4.6. The first few radial wave functions are listed in Table 4.7, and plotted in Figure 4.4.) The normalized hydrogen wave functions are¹⁷

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

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. Notice that whereas the wave functions depend on all three quantum numbers, the *energies* (Equation 4.70) are determined by n alone. This is a peculiarity of the Coulomb potential; in the

¹⁶As usual, there are rival normalization conventions in the literature; I have adopted the most nearly standard one.

¹⁷If you want to see how the normalization factor is calculated, study (for example), L. Schiff, *Quantum Mechanics*, 2nd ed., (McGraw-Hill, New York, 1968), page 93.

TABLE 4.5: 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 4.6: Some associated Laguerre polynomials, $L_{q-p}^p(x)$.

$L_0^0 = 1$	$L_0^2 = 2$
$L_1^0 = -x + 1$	$L_1^2 = -6x + 18$
$L_2^0 = x^2 - 4x + 2$	$L_2^2 = 12x^2 - 96x + 144$
$L_0^1 = 1$	$L_0^3 = 6$
$L_1^1 = -2x + 4$	$L_1^3 = -24x + 96$
$L_2^1 = 3x^2 - 18x + 18$	$L_2^3 = 60x^2 - 600x + 1200$

case of the spherical well, you may recall, the energies depend also on l (Equation 4.50). The wave functions are mutually orthogonal:

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

This follows from the orthogonality of the spherical harmonics (Equation 4.33) and (for $n \neq n'$) from the fact that they are eigenfunctions of H with distinct eigenvalues.

Visualizing the hydrogen wave functions is not easy. Chemists like to draw “density plots,” in which the brightness of the cloud is proportional to $|\psi|^2$ (Figure 4.5). More quantitative (but perhaps harder to read) are surfaces of constant probability density (Figure 4.6).

***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.

TABLE 4.7: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

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

***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 $n = 5$, $l = 2$.
- (c) Find $v(\rho)$ again (for the case $n = 5$, $l = 2$), but this time get it from the recursion formula (Equation 4.76).

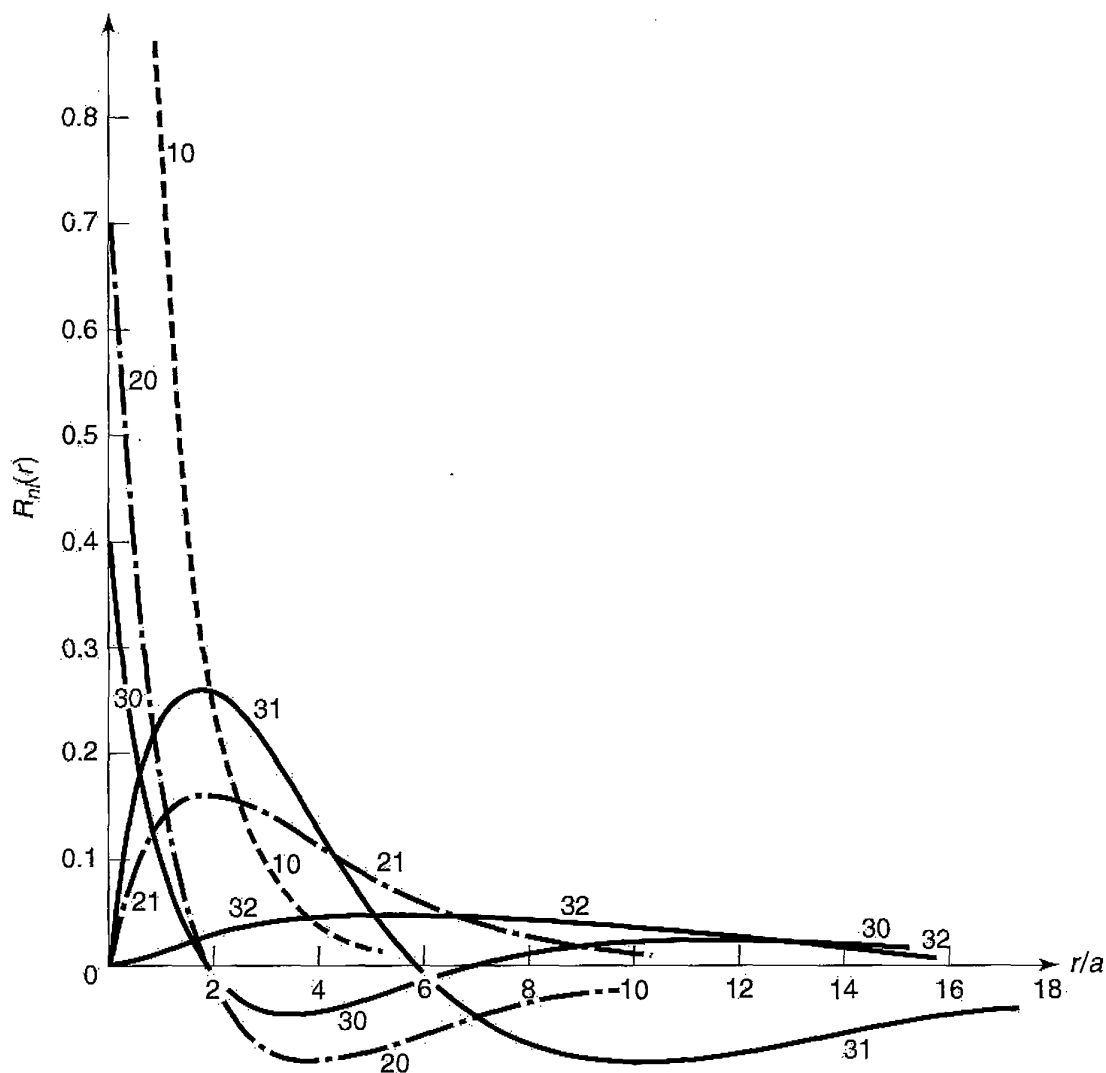


FIGURE 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

***Problem 4.13**

- Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius.
- Find $\langle x \rangle$ and $\langle x^2 \rangle$ for an electron in the ground state of hydrogen. *Hint:* This requires no new integration—note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.
- Find $\langle x^2 \rangle$ in the state $n = 2$, $l = 1$, $m = 1$. *Warning:* This state is *not* symmetrical in x , y , z . Use $x = r \sin \theta \cos \phi$.

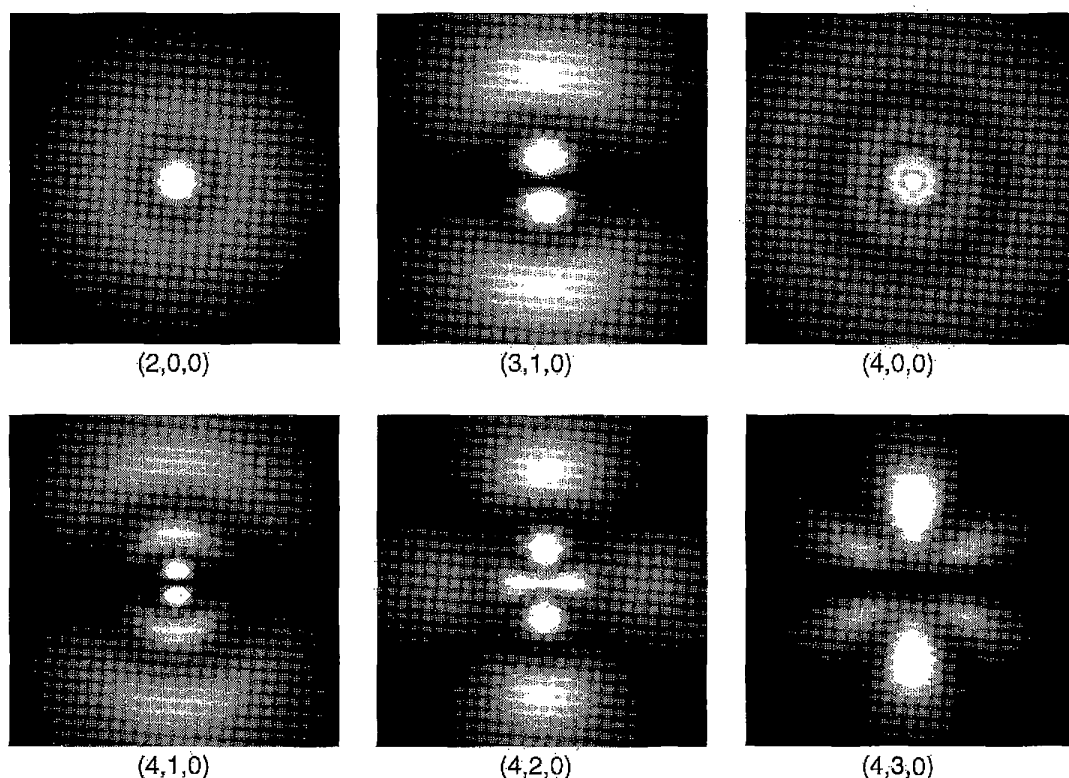


FIGURE 4.5: Density plots for the hydrogen wave functions (n, l, m) . Imagine each plot to be rotated about the (vertical) z axis. Printed by permission using “Atom in a Box,” v1.0.8, by Dauger Research. You can make your own plots by going to the Web site <http://dauger.com>.

Problem 4.14 What is the *most probable* value of r , in the ground state of hydrogen? (The answer is *not* zero!) *Hint:* First you must figure out the probability that the electron would be found between r and $r + dr$.

Problem 4.15 A hydrogen atom starts out in the following linear combination of the stationary states $n = 2, l = 1, m = 1$ and $n = 2, l = 1, m = -1$:

$$\Psi(\mathbf{r}, 0) = \frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1}).$$

- Construct $\Psi(\mathbf{r}, t)$. Simplify it as much as you can.
 - Find the expectation value of the potential energy, $\langle V \rangle$. (Does it depend on t ?) Give both the formula and the actual number, in electron volts.
-

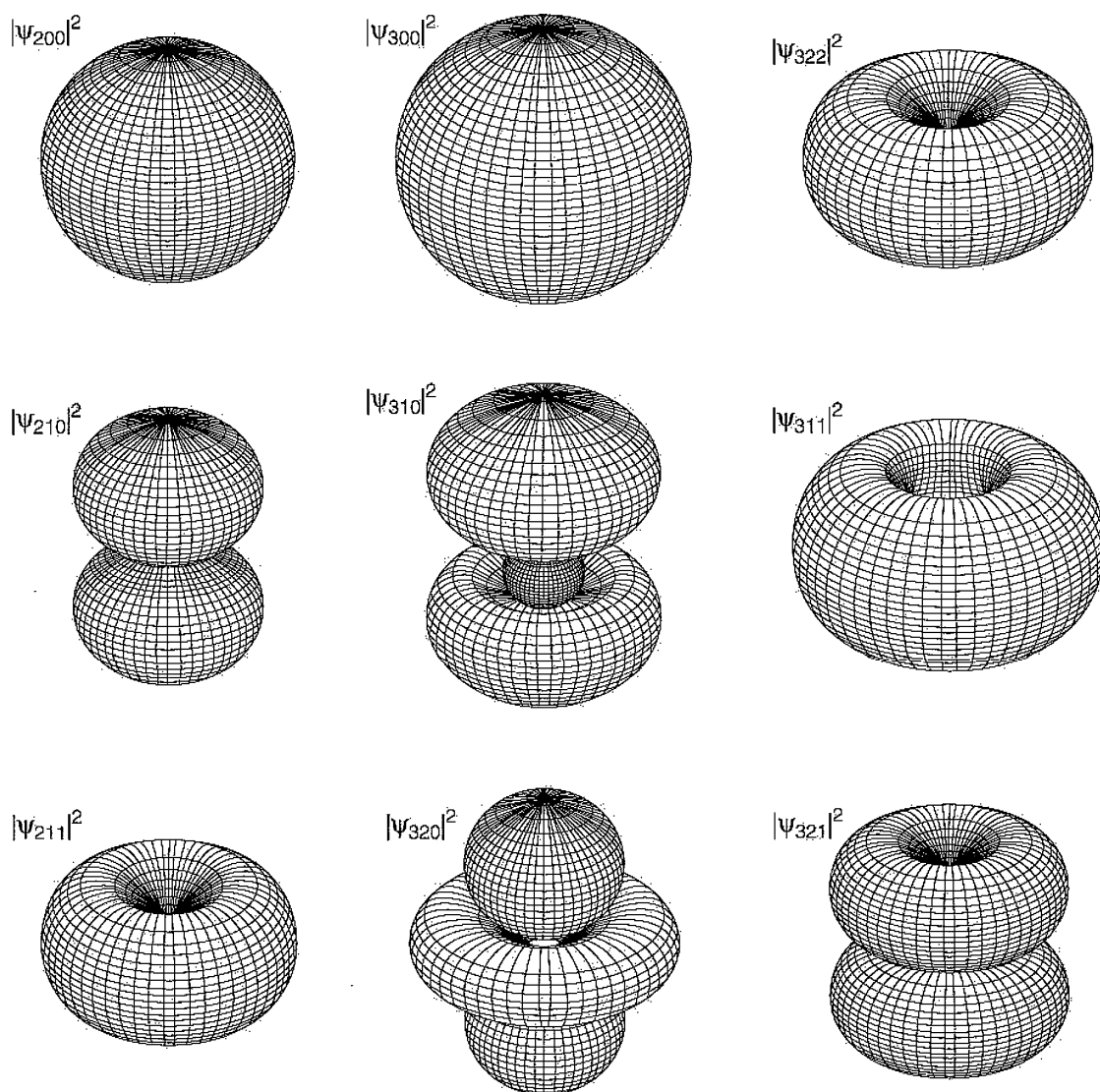


FIGURE 4.6: Surfaces of constant $|\psi|^2$ for the first few hydrogen wave functions. Reprinted by permission from Siegmund Brandt and Hans Dieter Dahmen, *The Picture Book of Quantum Mechanics*, 3rd ed., Springer, New York (2001).

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), the electron 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.¹⁸ 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**,¹⁹ 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

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

is known as the **Rydberg constant**. 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 4.7). (At room temperature, most hydrogen atoms are in the ground state; to obtain the emission spectrum you must first populate the various excited states; typically this is done by passing an electric spark through the gas.)

***Problem 4.16** 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, $Z = 3$

¹⁸By 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.

¹⁹The 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.

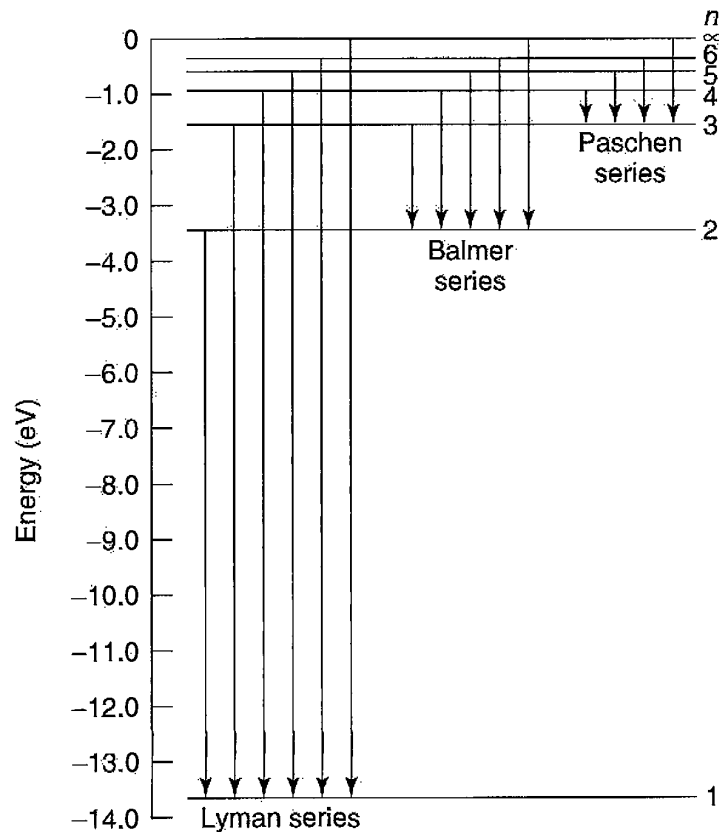


FIGURE 4.7: Energy levels and transitions in the spectrum of hydrogen.

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 $Z = 3$? *Hint:* There's nothing much to *calculate* here—in the potential (Equation 4.52) $e^2 \rightarrow Ze^2$, so all you have to do is make the same substitution in all the final results.

Problem 4.17 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,” a_g , for this system? Work out the actual number.
- 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 $n = \sqrt{r_o/a_g}$. From this, estimate the quantum number n of the earth.

- (d) 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? (Express your answer in light years—is the remarkable answer²⁰ a coincidence?)

4.3 ANGULAR MOMENTUM

As we have seen, the stationary states of the hydrogen atom are labeled by three quantum numbers: n , l , and m . The principal quantum number (n) determines the energy of the state (Equation 4.70); as it turns out, l and m are related to the orbital angular momentum. In the classical theory of central forces, energy and angular momentum are the fundamental conserved quantities, and it is not surprising that angular momentum plays a significant (in fact, even *more* important) role in the quantum theory.

Classically, 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,

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

The corresponding quantum operators are obtained by the standard prescription $p_x \rightarrow -i\hbar\partial/\partial x$, $p_y \rightarrow -i\hbar\partial/\partial y$, $p_z \rightarrow -i\hbar\partial/\partial z$. In the following section we'll obtain the eigenvalues of the angular momentum operators by a purely algebraic technique reminiscent of the one we used in Chapter 2 to get the allowed energies of the harmonic oscillator; it is all based on the clever exploitation of commutation relations. After that we will turn to the more difficult problem of determining the eigenfunctions.

4.3.1 Eigenvalues

The operators L_x and L_y do not commute; in fact²¹

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]. \end{aligned} \quad [4.97]$$

²⁰Thanks to John Meyer for pointing this out.

²¹Note that all the operators we encounter in quantum mechanics (footnote 15, Chapter 1) are *distributive* with respect to addition: $A(B + C) = AB + AC$. In particular, $[A, B + C] = [A, B] + [A, C]$.

From the canonical commutation relations (Equation 4.10) we know that the only operators here that *fail* to commute are x with p_x , y with p_y , and z with p_z . So the two middle terms drop out, leaving

$$[L_x, L_y] = yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z. \quad [4.98]$$

Of course, we could have started out with $[L_y, L_z]$ or $[L_z, L_x]$, but there is no need to calculate these separately—we can get them immediately by cyclic permutation of the indices ($x \rightarrow y, y \rightarrow z, z \rightarrow x$):

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y. \quad [4.99]$$

These are the fundamental commutation relations for angular momentum; everything else follows from them.

Notice that L_x , L_y , and L_z are *incompatible* observables. According to the generalized uncertainty principle (Equation 3.62),

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

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 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 3.64 to simplify the commutators; note also that *any* operator commutes with *itself*.) It follows, of course, that L^2 also commutes with L_y and L_z :

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

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

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

The 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 $L_{\pm} f$: 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 $\mu \pm \hbar$. We call L_+ the "raising" operator, because it *increases* the eigenvalue of L_z by \hbar , and L_- 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 4.8). 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

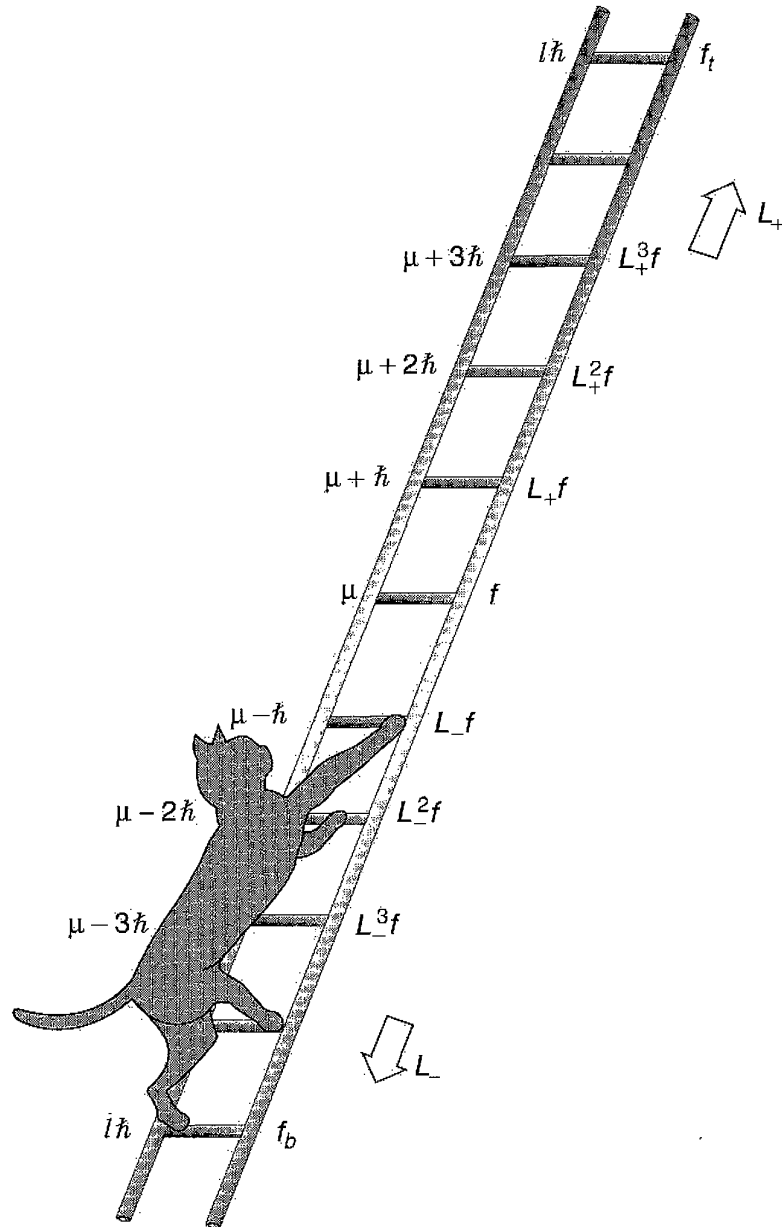


FIGURE 4.8: The “ladder” of angular momentum states.

to reach a state for which the z -component exceeds the *total*, and that cannot be.²² There must exist a “top rung,” f_t , such that²³

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

²²Formally, $\langle L^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$, but $\langle L_x^2 \rangle = \langle f | L_x^2 f \rangle = \langle L_x f | L_x f \rangle \geq 0$ (and likewise for L_y), so $\lambda = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \mu^2 \geq \mu^2$.

²³Actually, all we can conclude is that $L_+ f_t$ is *not normalizable*—its norm could be *infinite*, instead of zero. Problem 4.18 explores this alternative.

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

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

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

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

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 would be 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”).

Some people like to illustrate this result with the diagram in Figure 4.9 (drawn for the case $l=2$). The arrows are supposed to represent possible angular momenta—in units of \hbar they all have the same length $\sqrt{l(l+1)}$ (in this case $\sqrt{6} = 2.45$), and their z components are the allowed values of m ($-2, -1, 0, 1, 2$). Notice that the magnitude of the vectors (the radius of the sphere) is *greater* than the maximum z component! (In general, $\sqrt{l(l+1)} > l$, except for the “trivial” case $l=0$.) Evidently you can’t get the angular momentum to point perfectly along the z direction. At first, this sounds absurd. “Why can’t I just *pick* my axes so that z points along the direction of the angular momentum vector?” Well, to do this you would have to know all three components simultaneously, and the

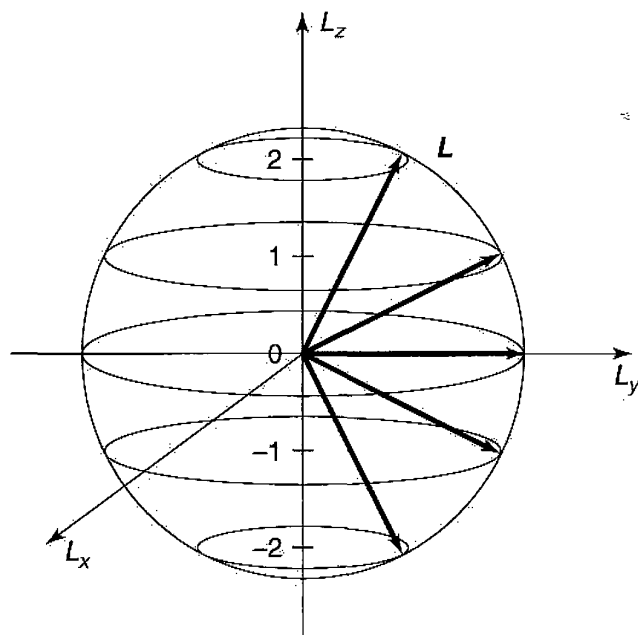


FIGURE 4.9: Angular momentum states (for $l=2$).

uncertainty principle (Equation 4.100) says that's impossible. "Well, all right, but surely once in a while, by good fortune, I will just *happen* to aim my z -axis along the direction of \mathbf{L} ." No, no! You have missed the point. It's not merely that you don't *know* all three components of \mathbf{L} ; there simply *aren't* three components—a particle just cannot *have* a determinate angular momentum vector, any more than it can simultaneously have a determinate position and momentum. If L_z has a well-defined value, then L_x and L_y do *not*. It is misleading even to *draw* the vectors in Figure 4.9—at best they should be smeared out around the latitude lines, to indicate that L_x and L_y are indeterminate.

I hope you're impressed: By *purely algebraic means*, starting with the fundamental commutation relations for angular momentum (Equation 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 begin with the punch line: $f_l^m = Y_l^m$ —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). And I can now tell you why the spherical harmonics are orthogonal: They are eigenfunctions of hermitian operators (L^2 and L_z) belonging to distinct eigenvalues (Theorem 2, Section 3.3.1).

***Problem 4.18** 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 L_y are *observables*, you may assume they are hermitian ... but *prove* it if you like); then use Equation 4.112. *Answer:*

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

Note what happens at the top and bottom of the ladder (i.e., when you apply L_+ to f_l^l or L_- to f_l^{-l}).

***Problem 4.19**

(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 obtain $[L_z, L_x] = i\hbar L_y$ 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 4.20

- (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, is:²⁴

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

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

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

²⁴George Arfken and Hans-Jürgen Weber, *Mathematical Methods for Physicists*, 5th ed., Academic Press, Orlando (2000), Section 2.5.

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

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

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

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

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

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

In particular (Problem 4.21(a)):

$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right), \quad [4.131]$$

and hence (Problem 4.21(b)):

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad [4.132]$$

We are now in a position to determine $f_l^m(\theta, \phi)$. It's an eigenfunction of L^2 , with eigenvalue $\hbar^2 l(l+1)$:

$$L^2 f_l^m = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] f_l^m = \hbar^2 l(l+1) f_l^m.$$

But this is precisely the “angular equation” (Equation 4.18). And it's also an eigenfunction of L_z , with the eigenvalue $m\hbar$:

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

but this is equivalent to the azimuthal equation (Equation 4.21). We have already solved this system of equations: The result (appropriately normalized) is the spherical harmonic, $Y_l^m(\theta, \phi)$. *Conclusion:* Spherical harmonics *are* 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 :

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

Incidentally, we can use Equation 4.132 to rewrite the Schrödinger equation (Equation 4.14) more compactly:

$$\frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \psi + V\psi = E\psi.$$

There is a curious final 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 separation of variables yielded eigenfunctions only for *integer* values (Equation 4.29). You might suppose 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 4.21**

- (a) Derive Equation 4.131 from Equation 4.130. *Hint:* Use a test function; otherwise you're likely to drop some terms.
 - (b) Derive Equation 4.132 from Equations 4.129 and 4.131. *Hint:* Use Equation 4.112.
-

***Problem 4.22**

- (a) What is $L_+ Y_l^l$? (No calculation allowed!)
 - (b) Use the result of (a), together with Equation 4.130 and 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 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 4.25).²⁵ 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 relations:²⁶

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

It follows (as before) that the eigenvectors of S^2 and S_z satisfy²⁷

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

²⁵For a contrary interpretation, see Hans C. Ohanian, “What is Spin?”, *Am. J. Phys.* **54**, 500 (1986).

²⁶We shall take these as *postulates* for the theory of spin; the analogous formulas for *orbital* angular momentum (Equation 4.99) were *derived* from the known form of the operators (Equation 4.96). In a more sophisticated treatment they can both be obtained from rotational invariance in three dimensions (see, for example, Leslie E. Ballentine, *Quantum Mechanics: A Modern Development*, World Scientific, Singapore (1998), 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.

²⁷Because the eigenstates of spin are not *functions*, I will use 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).

and

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

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.²⁸

Problem 4.25 If the electron were 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 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) would a point on the "equator" be moving? Does this model make sense? (Actually, the radius of the electron is known experimentally to be much less than r_c , but this only makes matters worse.)

²⁸Indeed, in a mathematical sense, spin 1/2 is the simplest possible nontrivial quantum system, for it admits just two basis states. In place of an infinite-dimensional Hilbert space, with all its subtleties and complications, we find ourselves working in an ordinary 2-dimensional vector space; in place of unfamiliar differential equations and fancy functions, we are confronted with 2×2 matrices and 2-component vectors. For this reason, some authors *begin* quantum mechanics with the study of spin. (An outstanding example is John S. Townsend, *A Modern Approach to Quantum Mechanics*, University Books, Sausalito, CA, 2000.) But the price of mathematical simplicity is conceptual abstraction, and I prefer not to do it that way.

4.4.1 Spin 1/2

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**):

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

with

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

representing spin up, and

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

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

$$\mathbf{S}^2 \chi_+ = \frac{3}{4} \hbar^2 \chi_+ \quad \text{and} \quad \mathbf{S}^2 \chi_- = \frac{3}{4} \hbar^2 \chi_-. \quad [4.142]$$

If we write \mathbf{S}^2 as a matrix with (as yet) undetermined elements,

$$\mathbf{S}^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix},$$

then the first equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4} \hbar^2 \\ 0 \end{pmatrix},$$

so $c = (3/4)\hbar^2$ and $e = 0$. The second equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4} \hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4} \hbar^2 \end{pmatrix},$$

so $d = 0$ and $f = (3/4)\hbar^2$. *Conclusion:*

$$\mathbf{S}^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad [4.143]$$

Similarly,

$$\mathbf{S}_z \chi_+ = \frac{\hbar}{2} \chi_+, \quad \mathbf{S}_z \chi_- = -\frac{\hbar}{2} \chi_-, \quad [4.144]$$

from which it follows that

$$\mathbf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad [4.145]$$

Meanwhile, Equation 4.136 says

$$\mathbf{S}_+ \chi_- = \hbar \chi_+, \quad \mathbf{S}_- \chi_+ = \hbar \chi_-, \quad \mathbf{S}_+ \chi_+ = \mathbf{S}_- \chi_- = 0,$$

so

$$\mathbf{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \mathbf{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad [4.146]$$

Now $S_{\pm} = S_x \pm iS_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$, and hence

$$\mathbf{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad [4.147]$$

Since \mathbf{S}_x , \mathbf{S}_y , and \mathbf{S}_z all carry a factor of $\hbar/2$, it is tidier to write $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$, where

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

[4.148]

These are the famous **Pauli spin matrices**. Notice that \mathbf{S}_x , \mathbf{S}_y , \mathbf{S}_z , and \mathbf{S}^2 are all *hermitian* (as they *should* be, since they represent observables). On the other hand, \mathbf{S}_+ and \mathbf{S}_- are *not* hermitian—evidently they are not observable.

The eigenspinors of \mathbf{S}_z are (of course):

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

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,

$$|a|^2 + |b|^2 = 1 \quad [4.150]$$

(i.e., the spinor must be *normalized*).²⁹

²⁹People often say that $|a|^2$ is the “probability that the particle is in the spin-up state,” but this is sloppy language; what they *mean* is that if you *measured* S_z , $|a|^2$ is the probability you’d get $\hbar/2$. See footnote 16 in Chapter 3.

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 \mathbf{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 \mathbf{S}_x are

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

As the eigenvectors of a hermitian matrix, they span the space; the generic spinor χ (Equation 4.139) can be expressed as a linear combination of them:

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

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 4.2 Suppose a spin-1/2 particle is in the state

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

What are the probabilities of getting $+\hbar/2$ and $-\hbar/2$, if you measure S_z and S_x ?

Solution: Here $a = (1+i)/\sqrt{6}$ and $b = 2/\sqrt{6}$, so for S_z the probability of getting $+\hbar/2$ is $|(1+i)/\sqrt{6}|^2 = 1/3$, and the probability of getting $-\hbar/2$ is $|2/\sqrt{6}|^2 = 2/3$. For S_x the probability of getting $+\hbar/2$ is $(1/2)|(3+i)/\sqrt{6}|^2 = 5/6$, and

the probability of getting $-\hbar/2$ is $(1/2)|(-1+i)/\sqrt{6}|^2 = 1/6$. Incidentally, 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:

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

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 fifty-fifty 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 ; $\hbar/2$." 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 ." 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 layman, the philosopher, or the classical physicist, a statement of the form "this particle doesn't have a well-defined position" (or momentum, or 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 4.26

- (a) Check that the spin matrices (Equations 4.145 and 4.147) obey the fundamental commutation relations for angular momentum, Equation 4.134.
- (b) Show that the Pauli spin matrices (Equation 4.148) satisfy the product rule

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

where the indices stand for x , y , or z , and ϵ_{jkl} is the **Levi-Civita** symbol: +1 if $jkl = 123, 231$, or 312 ; -1 if $jkl = 132, 213$, or 321 ; 0 otherwise.

***Problem 4.27** 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} . (*Note:* These sigmas are standard deviations, not Pauli matrices!)
- (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 4.28** 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 4.29**

- (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. *Note:* a and b need not be real!

(c) If you measured S_y^2 , what values might you get, and with what probabilities?

****Problem 4.30** Construct the matrix \mathbf{S}_r representing the component of spin angular momentum along an arbitrary direction \hat{r} . Use spherical coordinates, for which

$$\hat{r} = \sin \theta \cos \phi \hat{i} + \sin \theta \sin \phi \hat{j} + \cos \theta \hat{k}. \quad [4.154]$$

Find the eigenvalues and (normalized) eigenspinors of \mathbf{S}_r . *Answer:*

$$\chi_+^{(r)} = \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}; \quad \chi_-^{(r)} = \begin{pmatrix} e^{-i\phi} \sin(\theta/2) \\ -\cos(\theta/2) \end{pmatrix}. \quad [4.155]$$

Note: You're always free to multiply by an arbitrary phase factor—say, $e^{i\phi}$ —so your answer may not *look* exactly the same as mine.

Problem 4.31 Construct the spin matrices (\mathbf{S}_x , \mathbf{S}_y , and \mathbf{S}_z) for a particle of spin 1. *Hint:* How many eigenstates of S_z are there? Determine the action of S_z , S_+ , and S_- on each of these states. Follow the procedure used in the text for spin 1/2.

4.4.2 Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, $\boldsymbol{\mu}$, is proportional to its spin angular momentum, \mathbf{S} :

$$\boldsymbol{\mu} = \gamma \mathbf{S}; \quad [4.156]$$

the proportionality constant, γ , is called the **gyromagnetic ratio**.³⁰ When a magnetic dipole is placed in a magnetic field \mathbf{B} , it experiences a torque, $\boldsymbol{\mu} \times \mathbf{B}$, which

³⁰See, for example, D. Griffiths, *Introduction to Electrodynamics*, 3rd ed. (Prentice Hall, Upper Saddle River, NJ, 1999), page 252. Classically, the gyromagnetic ratio of an object whose charge and mass are identically distributed is $q/2m$, where q is the charge and m is the mass. For reasons that are fully explained only in relativistic quantum theory, the gyromagnetic ratio of the electron is (almost) exactly *twice* the classical value: $\gamma = -e/m$.

tends to line it up parallel to the field (just like a compass needle). The energy associated with this torque is³¹

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}, \quad [4.157]$$

so the Hamiltonian of a spinning charged particle, at rest³² in a magnetic field \mathbf{B} , is

$$H = -\gamma \mathbf{B} \cdot \mathbf{S}. \quad [4.158]$$

Example 4.3 Larmor precession: Imagine a particle of spin 1/2 at rest in a uniform magnetic field, which points in the z -direction:

$$\mathbf{B} = B_0 \hat{k}. \quad [4.159]$$

The Hamiltonian (Equation 4.158), in matrix form, is

$$\mathbf{H} = -\gamma B_0 \mathbf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad [4.160]$$

The eigenstates of \mathbf{H} are the same as those of \mathbf{S}_z :

$$\begin{cases} \chi_+, & \text{with energy } E_+ = -(\gamma B_0 \hbar)/2, \\ \chi_-, & \text{with energy } E_- = +(\gamma B_0 \hbar)/2. \end{cases} \quad [4.161]$$

Evidently the energy is lowest when the dipole moment is parallel to the field—just as it would be classically.

Since the Hamiltonian is time-independent, the general solution to the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = \mathbf{H} \chi, \quad [4.162]$$

can be expressed in terms of the stationary states:

$$\chi(t) = a \chi_+ e^{-iE_+ t/\hbar} + b \chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{pmatrix}.$$

³¹Griffiths (footnote 30), page 281.

³²If the particle is allowed to *move*, there will also be kinetic energy to consider; moreover, it will be subject to the Lorentz force ($q\mathbf{v} \times \mathbf{B}$), which is not derivable from a potential energy function, and hence does not fit the Schrödinger equation as we have formulated it so far. I'll show you later on how to handle this (Problem 4.59), but for the moment let's just assume that the particle is free to *rotate*, but otherwise stationary.

The constants a and b are determined by the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix},$$

(of course, $|a|^2 + |b|^2 = 1$). With no essential loss of generality³³ I'll write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, where α is a fixed angle whose physical significance will appear in a moment. Thus

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}. \quad [4.163]$$

To get a feel for what is happening here, let's calculate the expectation value of \mathbf{S} , as a function of time:

$$\begin{aligned} \langle S_x \rangle &= \chi(t)^\dagger \mathbf{S}_x \chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{-i\gamma B_0 t/2} & \sin(\alpha/2)e^{i\gamma B_0 t/2} \end{pmatrix} \\ &\quad \times \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t). \end{aligned} \quad [4.164]$$

Similarly,

$$\langle S_y \rangle = \chi(t)^\dagger \mathbf{S}_y \chi(t) = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t), \quad [4.165]$$

and

$$\langle S_z \rangle = \chi(t)^\dagger \mathbf{S}_z \chi(t) = \frac{\hbar}{2} \cos \alpha. \quad [4.166]$$

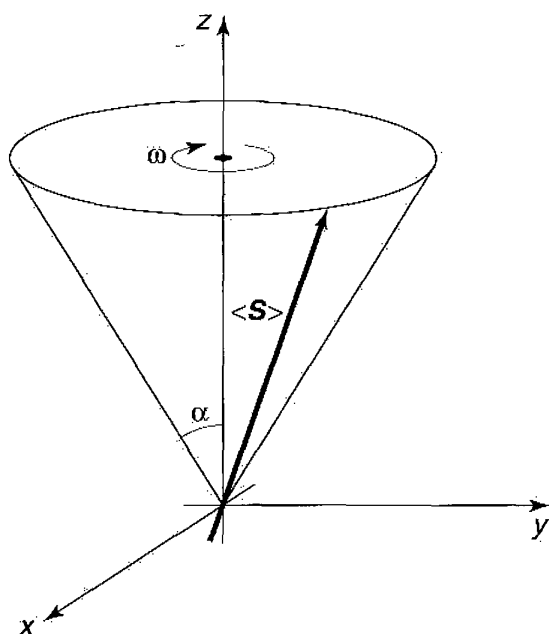
Evidently $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z -axis, and precesses about the field at the **Larmor frequency**

$$\omega = \gamma B_0, \quad [4.167]$$

just as it would classically³⁴ (see Figure 4.10). No *surprise* here—Ehrenfest's theorem (in the form derived in Problem 4.20) guarantees that $\langle \mathbf{S} \rangle$ evolves according to the classical laws. But it's nice to see how this works out in a specific context.

³³This does assume that a and b are *real*; you can work out the general case if you like, but all it does is add a constant to t .

³⁴See, for instance, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, 1964), Volume II, Section 34-3. Of course, in the classical case it is the angular momentum vector itself, not just its expectation value, that precesses around the magnetic field.

FIGURE 4.10: Precession of $\langle \mathbf{S} \rangle$ in a uniform magnetic field.

Example 4.4 The Stern-Gerlach experiment: In an *inhomogeneous* magnetic field, there is not only a *torque*, but also a *force*, on a magnetic dipole:³⁵

$$\mathbf{F} = \nabla(\boldsymbol{\mu} \cdot \mathbf{B}). \quad [4.168]$$

This force can be used to separate out particles with a particular spin orientation, as follows. Imagine a beam of relatively heavy neutral atoms,³⁶ traveling in the y direction, which passes through a region of inhomogeneous magnetic field (Figure 4.11)—say,

$$\mathbf{B}(x, y, z) = -\alpha x \hat{i} + (B_0 + \alpha z) \hat{k}, \quad [4.169]$$

where B_0 is a strong uniform field and the constant α describes a small deviation from homogeneity. (Actually, what we'd *like* is just the z component, but unfortunately that's impossible—it would violate the electromagnetic law $\nabla \cdot \mathbf{B} = 0$; like it or not, an x component comes along for the ride.) The force on these atoms is

$$\mathbf{F} = \gamma \alpha (-S_x \hat{i} + S_z \hat{k}).$$

³⁵Griffiths. (footnote 30), page 258. Note that \mathbf{F} is the negative gradient of the energy (Equation 4.157).

³⁶We make them neutral so as to avoid the large-scale deflection that would otherwise result from the Lorentz force, and heavy so we can construct localized wave packets and treat the motion in terms of classical particle trajectories. In practice, the Stern-Gerlach experiment doesn't work, for example, with a beam of free electrons.

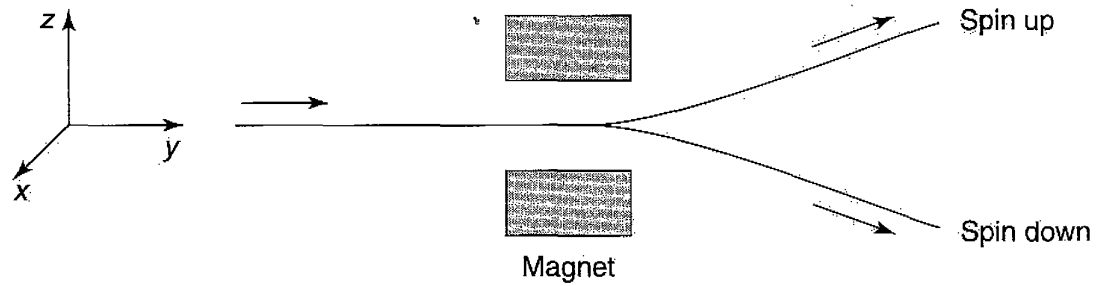


FIGURE 4.11: The Stern-Gerlach apparatus.

But because of the Larmor precession about B_0 , S_x oscillates rapidly, and *averages* to zero; the *net* force is in the z direction:

$$F_z = \gamma \alpha S_z, \quad [4.170]$$

and the beam is deflected up or down, in proportion to the z component of the spin angular momentum. *Classically* we'd expect a *smear* (because S_z would not be quantized), but in fact the beam splits into $2s + 1$ separate streams, beautifully demonstrating the quantization of angular momentum. (If you use silver atoms, for example, all the inner electrons are paired, in such a way that their spin and orbital angular momenta cancel. The net spin is simply that of the outermost—unpaired—electron, so in this case $s = 1/2$, and the beam splits in two.)

Now, that argument was purely *classical*, up to the very final step; “force” has no place in a proper quantum calculation, and you might therefore prefer the following approach to the same problem.³⁷ We examine the process from the perspective of a reference frame that moves along with the beam. In this frame the Hamiltonian starts out zero, turns on for a time T (as the particle passes through the magnet), and then turns off again:

$$H(t) = \begin{cases} 0, & \text{for } t < 0, \\ -\gamma(B_0 + \alpha z)S_z, & \text{for } 0 \leq t \leq T, \\ 0, & \text{for } t > T. \end{cases} \quad [4.171]$$

(I ignore the pesky x component of \mathbf{B} , which—for reasons indicated above—is irrelevant to the problem.) Suppose the atom has spin $1/2$, and starts out in the state

$$\chi(t) = a\chi_+ + b\chi_-, \quad \text{for } t \leq 0.$$

³⁷This argument follows L. Ballentine (footnote 26) Section 9.1.

While the Hamiltonian acts, $\chi(t)$ evolves in the usual way:

$$\chi(t) = a\chi_+e^{-iE_+t/\hbar} + b\chi_-e^{-iE_-t/\hbar}, \quad \text{for } 0 \leq t \leq T,$$

where (from Equation 4.158)

$$E_{\pm} = \mp\gamma(B_0 + \alpha z)\frac{\hbar}{2}, \quad [4.172]$$

and hence it emerges in the state

$$\chi(t) = \left(ae^{i\gamma T B_0/2} \chi_+ \right) e^{i(\alpha\gamma T/2)z} + \left(be^{-i\gamma T B_0/2} \chi_- \right) e^{-i(\alpha\gamma T/2)z}, \quad [4.173]$$

(for $t \geq T$). The two terms now carry *momentum* in the z direction (see Equation 3.32); the spin-up component has momentum

$$p_z = \frac{\alpha\gamma T\hbar}{2}, \quad [4.174]$$

and it moves in the plus- z direction; the spin-down component has the opposite momentum, and it moves in the minus- z direction. Thus the beam splits in two, as before. (Note that Equation 4.174 is consistent with the earlier result (Equation 4.170), for in this case $S_z = \hbar/2$, and $p_z = F_z T$.)

The Stern-Gerlach experiment has played an important role in the philosophy of quantum mechanics, where it serves both as the prototype for the preparation of a quantum state and as an illuminating model for a certain kind of quantum measurement. We tend casually to assume that the *initial* state of a system is *known* (the Schrödinger equation tells us how it subsequently evolves)—but it is natural to wonder how you get a system into a particular state in the first place. Well, if you want to prepare a beam of atoms in a given spin configuration, you pass an unpolarized beam through a Stern-Gerlach magnet, and select the outgoing stream you are interested in (closing off the others with suitable baffles and shutters). Conversely, if you want to *measure* the z component of an atom's spin, you send it through a Stern-Gerlach apparatus, and record which bin it lands in. I do not claim that this is always the most *practical* way to do the job, but it is *conceptually* very clean, and hence a useful context in which to explore the problems of state preparation and measurement.

Problem 4.32 In Example 4.3:

- (a) If you measured the component of spin angular momentum along the x direction, at time t , what is the probability that you would get $+\hbar/2$?

- (b) Same question, but for the y component.
 (c) Same, for the z component.

****Problem 4.33** An electron is at rest in an oscillating magnetic field

$$\mathbf{B} = B_0 \cos(\omega t) \hat{k},$$

where B_0 and ω are constants.

- (a) Construct the Hamiltonian matrix for this system.
 (b) The electron starts out (at $t = 0$) in the spin-up state with respect to the x -axis (that is: $\chi(0) = \chi_+^{(x)}$). Determine $\chi(t)$ at any subsequent time. *Beware:* This is a time-dependent Hamiltonian, so you cannot get $\chi(t)$ in the usual way from stationary states. Fortunately, in this case you can solve the time-dependent Schrödinger equation (Equation 4.162) directly.
 (c) Find the probability of getting $-\hbar/2$, if you measure S_x . *Answer:*

$$\sin^2 \left(\frac{\gamma B_0}{2\omega} \sin(\omega t) \right).$$

- (d) What is the minimum field (B_0) required to force a complete flip in S_x ?

4.4.3 Addition of Angular Momenta

Suppose now that we have *two* spin-1/2 particles—for example, the electron and the proton in the ground state³⁸ of hydrogen. Each can have spin up or spin down, so there are four possibilities in all:³⁹

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow, \quad [4.175]$$

where the first arrow refers to the electron and the second to the proton. *Question:* What is the *total* angular momentum of the atom? Let

$$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}. \quad [4.176]$$

³⁸I put them in the ground state so there won't be any *orbital* angular momentum to worry about.

³⁹More precisely, each particle is in a *linear combination* of spin up and spin down, and the composite system is in a *linear combination* of the four states listed.

Each of these four composite states is an eigenstate of S_z —the z components simply *add*:

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} + S_z^{(2)}) \chi_1 \chi_2 = (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_1 \chi_1) \chi_2 + \chi_1 (\hbar m_2 \chi_2) = \hbar(m_1 + m_2) \chi_1 \chi_2, \end{aligned}$$

(note that $S^{(1)}$ acts only on χ_1 , and $S^{(2)}$ acts only on χ_2 ; this notation may not be elegant, but it does the job). So m (the quantum number for the composite system) is just $m_1 + m_2$:

$$\uparrow\uparrow: m = 1;$$

$$\uparrow\downarrow: m = 0;$$

$$\downarrow\uparrow: m = 0;$$

$$\downarrow\downarrow: m = -1.$$

At first glance, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to $+s$, so it appears that $s = 1$ —but there is an “extra” state with $m = 0$. One way to untangle this problem is to apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$, using Equation 4.146:

$$\begin{aligned} S_-(\uparrow\uparrow) &= (S_-^{(1)} \uparrow) \uparrow + \uparrow (S_-^{(2)} \uparrow) \\ &= (\hbar \downarrow) \uparrow + \uparrow (\hbar \downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow). \end{aligned}$$

Evidently the three states with $s = 1$ are (in the notation $|s\ m\rangle$):

$$\left\{ \begin{array}{l} |1\ 1\rangle = \uparrow\uparrow \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle = \downarrow\downarrow \end{array} \right\} \quad s = 1 \text{ (triplet).} \quad [4.177]$$

(As a check, try applying the lowering operator to $|1\ 0\rangle$; what *should* you get? See Problem 4.34(a).) This is called the **triplet** combination, for the obvious reason. Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{ |0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet).} \quad [4.178]$$

(If you apply the raising or lowering operator to *this* state, you'll get *zero*. See Problem 4.34(b).)

I claim, then, that the combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration. To *confirm* this, I need to prove that the triplet states are eigenvectors of S^2 with eigenvalue $2\hbar^2$, and the singlet is an eigenvector of S^2 with eigenvalue 0. Now,

$$S^2 = (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \cdot (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}. \quad [4.179]$$

Using Equations 4.145 and 4.147, we have

$$\begin{aligned} \mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} (\uparrow\downarrow) &= (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow) \\ &= \left(\frac{\hbar}{2} \downarrow\right) \left(\frac{\hbar}{2} \uparrow\right) + \left(\frac{i\hbar}{2} \downarrow\right) \left(\frac{-i\hbar}{2} \uparrow\right) + \left(\frac{\hbar}{2} \uparrow\right) \left(\frac{-\hbar}{2} \downarrow\right) \\ &= \frac{\hbar^2}{4} (2 \downarrow\uparrow - \uparrow\downarrow). \end{aligned}$$

Similarly,

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} (\downarrow\uparrow) = \frac{\hbar^2}{4} (2 \uparrow\downarrow - \downarrow\uparrow).$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |10\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow + 2 \uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4} |10\rangle, \quad [4.180]$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |00\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow - 2 \uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4} |00\rangle. \quad [4.181]$$

Returning to Equation 4.179 (and using Equation 4.142), we conclude that

$$S^2 |10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2 \frac{\hbar^2}{4} \right) |10\rangle = 2\hbar^2 |10\rangle, \quad [4.182]$$

so $|10\rangle$ is indeed an eigenstate of S^2 with eigenvalue $2\hbar^2$; and

$$S^2 |00\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2 \frac{3\hbar^2}{4} \right) |00\rangle = 0, \quad [4.183]$$

so $|00\rangle$ is an eigenstate of S^2 with eigenvalue 0. (I will leave it for you to confirm that $|11\rangle$ and $|1-1\rangle$ are eigenstates of S^2 , with the appropriate eigenvalue—see Problem 4.34(c).)

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: If you combine spin s_1 with spin s_2 , what total spins s can you get?⁴⁰ The answer⁴¹ is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$ —or $(s_2 - s_1)$, if $s_2 > s_1$ —in integer steps:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|. \quad [4.184]$$

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.) For example, if you package together a particle of spin 3/2 with a particle of spin 2, you could get a total spin of 7/2, 5/2, 3/2, or 1/2, depending on the configuration. Another example: If a hydrogen atom is in the state ψ_{nlm} , the net angular momentum of the electron (spin plus orbital) is $l + 1/2$ or $l - 1/2$; if you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is $l + 1$, l , or $l - 1$ (and l can be achieved in two distinct ways, depending on whether the electron alone is in the $l + 1/2$ configuration or the $l - 1/2$ configuration).

The combined state $|s\ m\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1\ m_1\rangle|s_2\ m_2\rangle$:

$$|s\ m\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1\ m_1\rangle |s_2\ m_2\rangle \quad [4.185]$$

(because the z components *add*, the only composite states that contribute are those for which $m_1 + m_2 = m$). Equations 4.177 and 4.178 are special cases of this general form, with $s_1 = s_2 = 1/2$ (I used the informal notation $\uparrow = |\frac{1}{2}\ \frac{1}{2}\rangle$, $\downarrow = |\frac{1}{2}\ (-\frac{1}{2})\rangle$). The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**. A few of the simplest cases are listed in Table 4.8.⁴² For example, the shaded column of the 2×1 table tells us that

$$|3\ 0\rangle = \frac{1}{\sqrt{5}}|2\ 1\rangle|1\ -1\rangle + \sqrt{\frac{3}{5}}|2\ 0\rangle|1\ 0\rangle + \frac{1}{\sqrt{5}}|2\ -1\rangle|1\ 1\rangle.$$

In particular, if two particles (of spin 2 and spin 1) are at rest in a box, and the *total* spin is 3, and its z component is 0, then a measurement of $S_z^{(1)}$ could return the value \hbar (with probability 1/5), or 0 (with probability 3/5), or $-\hbar$ (with probability

⁴⁰I say *spins*, for simplicity, but either one (or both) could just as well be *orbital* angular momentum (for which, however, we would use the letter l).

⁴¹For a proof you must look in a more advanced text; see, for instance, Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloë, *Quantum Mechanics*, (Wiley, New York, 1977), Vol. 2, Chapter X.

⁴²The general formula is derived in Arno Bohm, *Quantum Mechanics: Foundations and Applications*, 2nd ed., (Springer, 1986), p. 172.

These tables also work the other way around:

$$|s_1 m_1\rangle |s_2 m_2\rangle = \sum_s C_{m_1 m_2 m}^{s_1 s_2 s} |s m\rangle. \quad [4.186]$$

For example, the shaded row in the $3/2 \times 1$ table tells us that

$$|\frac{3}{2} \frac{1}{2}\rangle|10\rangle = \sqrt{\frac{3}{5}}|\frac{5}{2} \frac{1}{2}\rangle + \sqrt{\frac{1}{15}}|\frac{3}{2} \frac{1}{2}\rangle - \sqrt{\frac{1}{3}}|\frac{1}{2} \frac{1}{2}\rangle,$$

If you think this is starting to sound like mystical numerology, I don't blame you. We will not be using the Clebsch-Gordan tables much in the rest of the book, but I wanted you to know where they fit into the scheme of things, in case you encounter them later on. In a mathematical sense this is all applied **group theory**—what we are talking about is the decomposition of the direct product of

two irreducible representations of the rotation group into a direct sum of irreducible representations (you can quote that, to impress your friends).

***Problem 4.34**

- (a) Apply S_- to $|10\rangle$ (Equation 4.177), and confirm that you get $\sqrt{2}\hbar|1-1\rangle$.
 - (b) Apply S_{\pm} to $|00\rangle$ (Equation 4.178), and confirm that you get zero.
 - (c) Show that $|11\rangle$ and $|1-1\rangle$ (Equation 4.177) are eigenstates of S^2 , with the appropriate eigenvalue.
-

Problem 4.35 Quarks carry spin $1/2$. Three quarks bind together to make a **baryon** (such as the proton or neutron); two quarks (or more precisely a quark and an antiquark) bind together to make a **meson** (such as the pion or the kaon). Assume the quarks are in the ground state (so the *orbital* angular momentum is zero).

- (a) What spins are possible for baryons?
 - (b) What spins are possible for mesons?
-

Problem 4.36

- (a) A particle of spin 1 and a particle of spin 2 are at rest in a configuration such that the total spin is 3, and its z component is \hbar . If you measured the z component of the angular momentum of the spin-2 particle, what values might you get, and what is the probability of each one?
 - (b) An electron with spin down is in the state ψ_{510} of the hydrogen atom. If you could measure the total angular momentum squared of the electron alone (*not* including the proton spin), what values might you get, and what is the probability of each?
-

Problem 4.37 Determine the commutator of S^2 with $S_z^{(1)}$ (where $\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$). Generalize your result to show that

$$[S^2, \mathbf{S}^{(1)}] = 2i\hbar(\mathbf{S}^{(1)} \times \mathbf{S}^{(2)}). \quad [4.187]$$

Comment: Because $S_z^{(1)}$ does not commute with S^2 , we cannot hope to find states that are simultaneous eigenvectors of both. In order to form eigenstates of S^2 we

need *linear combinations* of eigenstates of $S_z^{(1)}$. This is precisely what the Clebsch-Gordan coefficients (in Equation 4.185) do for us. On the other hand, it follows by obvious inference from Equation 4.187 that the *sum* $S^{(1)} + S^{(2)}$ *does* commute with S^2 , which is a special case of something we already knew (see Equation 4.103).

FURTHER PROBLEMS FOR CHAPTER 4

✱Problem 4.38 Consider the **three-dimensional harmonic oscillator**, for which the potential is

$$V(r) = \frac{1}{2}m\omega^2 r^2. \quad [4.188]$$

(a) Show that separation of variables in cartesian coordinates turns this into three one-dimensional oscillators, and exploit your knowledge of the latter to determine the allowed energies. *Answer:*

$$E_n = (n + 3/2)\hbar\omega. \quad [4.189]$$

(b) Determine the degeneracy $d(n)$ of E_n .

✱✱✱Problem 4.39 Because the three-dimensional harmonic oscillator potential (Equation 4.188) is spherically symmetric, the Schrödinger equation can be handled by separation of variables in *spherical* coordinates, as well as cartesian coordinates. Use the power series method to solve the radial equation. Find the recursion formula for the coefficients, and determine the allowed energies. Check your answer against Equation 4.189.

✱✱Problem 4.40

(a) Prove the **three-dimensional virial theorem**:

$$2\langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle \quad [4.190]$$

(for stationary states). *Hint:* Refer to Problem 3.31.

(b) Apply the virial theorem to the case of hydrogen, and show that

$$\langle T \rangle = -E_n; \quad \langle V \rangle = 2E_n. \quad [4.191]$$

- (c) Apply the virial theorem to the three-dimensional harmonic oscillator (Problem 4.38), and show that in this case

$$\langle T \rangle = \langle V \rangle = E_n/2. \quad [4.192]$$

*****Problem 4.41** [Attempt this problem only if you are familiar with vector calculus.] Define the (three-dimensional) **probability current** by generalization of Problem 1.14:

$$\mathbf{J} \equiv \frac{i\hbar}{2m} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi). \quad [4.193]$$

- (a) Show that \mathbf{J} satisfies the **continuity equation**

$$\nabla \cdot \mathbf{J} = -\frac{\partial}{\partial t} |\Psi|^2, \quad [4.194]$$

which expresses local **conservation of probability**. It follows (from the divergence theorem) that

$$\int_{\mathcal{S}} \mathbf{J} \cdot d\mathbf{a} = -\frac{d}{dt} \int_{\mathcal{V}} |\Psi|^2 d^3\mathbf{r}, \quad [4.195]$$

where \mathcal{V} is a (fixed) volume and \mathcal{S} is its boundary surface. In words: The flow of probability out through the surface is equal to the decrease in probability of finding the particle in the volume.

- (b) Find \mathbf{J} for hydrogen in the state $n=2, l=1, m=1$. *Answer:*

$$\frac{\hbar}{64\pi m a^5} r e^{-r/a} \sin \theta \hat{\phi}.$$

- (c) If we interpret $m\mathbf{J}$ as the flow of *mass*, the angular momentum is

$$\mathbf{L} = m \int (\mathbf{r} \times \mathbf{J}) d^3\mathbf{r}.$$

Use this to calculate L_z for the state ψ_{211} , and comment on the result.

*****Problem 4.42** The (time independent) **momentum space wave function** in three dimensions is defined by the natural generalization of Equation 3.54:

$$\phi(\mathbf{p}) \equiv \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-i(\mathbf{p}\cdot\mathbf{r})/\hbar} \psi(\mathbf{r}) d^3\mathbf{r}. \quad [4.196]$$

- (a) Find the momentum space wave function for the ground state of hydrogen (Equation 4.80). *Hint:* Use spherical coordinates, setting the polar axis along the direction of \mathbf{p} . Do the θ integral first. *Answer:*

$$\phi(\mathbf{p}) = \frac{1}{\pi} \left(\frac{2a}{\hbar} \right)^{3/2} \frac{1}{[1 + (ap/\hbar)^2]^2}. \quad [4.197]$$

- (b) Check that $\phi(\mathbf{p})$ is normalized.
 (c) Use $\phi(\mathbf{p})$ to calculate $\langle p^2 \rangle$, in the ground state of hydrogen.
 (d) What is the expectation value of the kinetic energy in this state? Express your answer as a multiple of E_1 , and check that it is consistent with the virial theorem (Equation 4.191).
-

Problem 4.43

- (a) Construct the spatial wave function (ψ) for hydrogen in the state $n = 3$, $l = 2$, $m = 1$. Express your answer as a function of r , θ , ϕ , and a (the Bohr radius) *only*—no other variables (ρ , z , etc.) or functions (Y , v , etc.), or constants (A , c_0 , etc.), or derivatives, allowed (π is okay, and e , and 2, etc.).
 (b) Check that this wave function is properly normalized, by carrying out the appropriate integrals over r , θ , and ϕ .
 (c) Find the expectation value of r^s in this state. For what range of s (positive and negative) is the result finite?
-

Problem 4.44

- (a) Construct the wave function for hydrogen in the state $n = 4$, $l = 3$, $m = 3$. Express your answer as a function of the spherical coordinates r , θ , and ϕ .
 (b) Find the expectation value of r in this state. (As always, look up any nontrivial integrals.)
 (c) If you could somehow measure the observable $L_x^2 + L_y^2$ on an atom in this state, what value (or values) could you get, and what is the probability of each?
-

Problem 4.45 What is the probability that an electron in the ground state of hydrogen will be found *inside the nucleus*?

- (a) First calculate the *exact* answer, assuming the wave function (Equation 4.80) is correct all the way down to $r = 0$. Let b be the radius of the nucleus.

- (b) Expand your result as a power series in the small number $\epsilon \equiv 2b/a$, and show that the lowest-order term is the cubic: $P \approx (4/3)(b/a)^3$. This should be a suitable approximation, provided that $b \ll a$ (which it is).
- (c) Alternatively, we might assume that $\psi(r)$ is essentially constant over the (tiny) volume of the nucleus, so that $P \approx (4/3)\pi b^3 |\psi(0)|^2$. Check that you get the same answer this way.
- (d) Use $b \approx 10^{-15}$ m and $a \approx 0.5 \times 10^{-10}$ m to get a numerical estimate for P . Roughly speaking, this represents the “fraction of its time that the electron spends inside the nucleus.”

Problem 4.46

- (a) Use the recursion formula (Equation 4.76) to confirm that when $l = n - 1$ the radial wave function takes the form

$$R_{n(n-1)} = N_n r^{n-1} e^{-r/na},$$

and determine the normalization constant N_n by direct integration.

- (b) Calculate $\langle r \rangle$ and $\langle r^2 \rangle$ for states of the form $\psi_{n(n-1)m}$.
- (c) Show that the “uncertainty” in r (σ_r) is $\langle r \rangle / \sqrt{2n+1}$ for such states. Note that the fractional spread in r decreases, with increasing n (in this sense the system “begins to look classical,” with identifiable circular “orbits,” for large n). Sketch the radial wave functions for several values of n , to illustrate this point.

Problem 4.47 Coincident spectral lines.⁴³ According to the Rydberg formula (Equation 4.93) the wavelength of a line in the hydrogen spectrum is determined by the principal quantum numbers of the initial and final states. Find two distinct pairs $\{n_i, n_f\}$ that yield the *same* λ . For example, $\{6851, 6409\}$ and $\{15283, 11687\}$ will do it, but you’re not allowed to use those!

Problem 4.48 Consider the observables $A = x^2$ and $B = L_z$.

- (a) Construct the uncertainty principle for $\sigma_A \sigma_B$.
- (b) Evaluate σ_B in the hydrogen state ψ_{nlm} .
- (c) What can you conclude about $\langle xy \rangle$ in this state?

⁴³Nicholas Wheeler, “Coincident Spectral Lines” (unpublished Reed College report, 2001).

Problem 4.49 An electron is in the spin state

$$\chi = A \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix}.$$

- Determine the constant A by normalizing χ .
- If you measured S_z on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_z ?
- If you measured S_x on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_x ?
- If you measured S_y on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_y ?

*****Problem 4.50** Suppose two spin-1/2 particles are known to be in the singlet configuration (Equation 4.178). Let $S_a^{(1)}$ be the component of the spin angular momentum of particle number 1 in the direction defined by the unit vector \hat{a} . Similarly, let $S_b^{(2)}$ be the component of 2's angular momentum in the direction \hat{b} . Show that

$$\langle S_a^{(1)} S_b^{(2)} \rangle = -\frac{\hbar^2}{4} \cos \theta, \quad [4.198]$$

where θ is the angle between \hat{a} and \hat{b} .

*****Problem 4.51**

- Work out the Clebsch-Gordan coefficients for the case $s_1 = 1/2$, $s_2 = \text{anything}$. *Hint:* You're looking for the coefficients A and B in

$$|s\ m\rangle = A \left| \frac{1}{2} \ \frac{1}{2} \right\rangle |s_2\ (m - \frac{1}{2})\rangle + B \left| \frac{1}{2} \ (-\frac{1}{2}) \right\rangle |s_2\ (m + \frac{1}{2})\rangle,$$

such that $|s\ m\rangle$ is an eigenstate of S^2 . Use the method of Equations 4.179 through 4.182. If you can't figure out what $S_x^{(2)}$ (for instance) does to $|s_2\ m_2\rangle$, refer back to Equation 4.136 and the line before Equation 4.147. *Answer:*

$$A = \sqrt{\frac{s_2 \pm m + 1/2}{2s_2 + 1}}; \quad B = \pm \sqrt{\frac{s_2 \mp m + 1/2}{2s_2 + 1}},$$

where the signs are determined by $s = s_2 \pm 1/2$.

- Check this general result against three or four entries in Table 4.8.

Problem 4.52 Find the matrix representing S_x for a particle of spin $3/2$ (using, as always, the basis of eigenstates of S_z). Solve the characteristic equation to determine the eigenvalues of S_x .

*****Problem 4.53** Work out the spin matrices for arbitrary spin s , generalizing spin $1/2$ (Equations 4.145 and 4.147), spin 1 (Problem 4.31), and spin $3/2$ (Problem 4.52).
Answer:

$$\mathbf{S}_z = \hbar \begin{pmatrix} s & 0 & 0 & \cdots & 0 \\ 0 & s-1 & 0 & \cdots & 0 \\ 0 & 0 & s-2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & \cdots & -s \end{pmatrix}$$

$$\mathbf{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & b_s & 0 & 0 & \cdots & 0 & 0 \\ b_s & 0 & b_{s-1} & 0 & \cdots & 0 & 0 \\ 0 & b_{s-1} & 0 & b_{s-2} & \cdots & 0 & 0 \\ 0 & 0 & b_{s-2} & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 & b_{-s+1} \\ 0 & 0 & 0 & 0 & \cdots & b_{-s+1} & 0 \end{pmatrix}$$

$$\mathbf{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -ib_s & 0 & 0 & \cdots & 0 & 0 \\ ib_s & 0 & -ib_{s-1} & 0 & \cdots & 0 & 0 \\ 0 & ib_{s-1} & 0 & -ib_{s-2} & \cdots & 0 & 0 \\ 0 & 0 & ib_{s-2} & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 0 & -ib_{-s+1} \\ 0 & 0 & 0 & 0 & \cdots & ib_{-s+1} & 0 \end{pmatrix}$$

where

$$b_j \equiv \sqrt{(s+j)(s+1-j)}.$$

*****Problem 4.54** Work out the normalization factor for the spherical harmonics, as follows. From Section 4.1.2 we know that

$$Y_l^m = B_l^m e^{im\phi} P_l^m(\cos \theta);$$

the problem is to determine the factor B_l^m (which I *quoted*, but did not derive, in Equation 4.32). Use Equations 4.120, 4.121, and 4.130 to obtain a recursion

relation giving B_l^{m+1} in terms of B_l^m . Solve it by induction on m to get B_l^m up to an overall constant, $C(l)$. Finally, use the result of Problem 4.22 to fix the constant. You may find the following formula for the derivative of an associated Legendre function useful:

$$(1-x^2)\frac{dP_l^m}{dx} = \sqrt{1-x^2}P_l^{m+1} - mxP_l^m. \quad [4.199]$$

Problem 4.55 The electron in a hydrogen atom occupies the combined spin and position state

$$R_{21} \left(\sqrt{1/3} Y_1^0 \chi_+ + \sqrt{2/3} Y_1^1 \chi_- \right).$$

- (a) If you measured the orbital angular momentum squared (L^2), what values might you get, and what is the probability of each?
- (b) Same for the z component of orbital angular momentum (L_z).
- (c) Same for the spin angular momentum squared (S^2).
- (d) Same for the z component of spin angular momentum (S_z).

Let $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$ be the *total* angular momentum.

- (e) If you measured J^2 , what values might you get, and what is the probability of each?
- (f) Same for J_z .
- (g) If you measured the *position* of the particle, what is the probability density for finding it at r, θ, ϕ ?
- (h) If you measured both the z component of the spin *and* the distance from the origin (note that these are compatible observables), what is the probability density for finding the particle with spin up and at radius r ?

*****Problem 4.56**

- (a) For a function $f(\phi)$ that can be expanded in a Taylor series, show that

$$f(\phi + \varphi) = e^{iL_z\varphi/\hbar} f(\phi)$$

(where φ is an arbitrary angle). For this reason, L_z/\hbar is called the **generator of rotations** about the z -axis. *Hint:* Use Equation 4.129, and refer to Problem 3.39.

More generally, $\mathbf{L} \cdot \hat{n}/\hbar$ is the generator of rotations about the direction \hat{n} , in the sense that $\exp(i\mathbf{L} \cdot \hat{n}\varphi/\hbar)$ effects a rotation through angle φ (in the right-hand sense) about the axis \hat{n} . In the case of *spin*, the generator of rotations is $\mathbf{S} \cdot \hat{n}/\hbar$. In particular, for spin 1/2

$$\chi' = e^{i(\boldsymbol{\sigma} \cdot \hat{n})\varphi/2} \chi \quad [4.200]$$

tells us how *spinors* rotate.

- (b) Construct the (2×2) matrix representing rotation by 180° about the x -axis, and show that it converts “spin up” (χ_+) into “spin down” (χ_-), as you would expect.
- (c) Construct the matrix representing rotation by 90° about the y -axis, and check what it does to χ_+ .
- (d) Construct the matrix representing rotation by 360° about the z -axis. If the answer is not quite what you expected, discuss its implications.
- (e) Show that

$$e^{i(\boldsymbol{\sigma} \cdot \hat{n})\varphi/2} = \cos(\varphi/2) + i(\hat{n} \cdot \boldsymbol{\sigma}) \sin(\varphi/2). \quad [4.201]$$

****Problem 4.57** The fundamental commutation relations for angular momentum (Equation 4.99) allow for half-integer (as well as integer) eigenvalues. But for *orbital* angular momentum only the integer values occur. There must be some *extra* constraint in the specific form $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ that excludes half-integer values.⁴⁴ Let a be some convenient constant with the dimensions of length (the Bohr radius, say, if we’re talking about hydrogen), and define the operators

$$\begin{aligned} q_1 &\equiv \frac{1}{\sqrt{2}} \left[x + (a^2/\hbar) p_y \right]; & p_1 &\equiv \frac{1}{\sqrt{2}} \left[p_x - (\hbar/a^2) y \right]; \\ q_2 &\equiv \frac{1}{\sqrt{2}} \left[x - (a^2/\hbar) p_y \right]; & p_2 &\equiv \frac{1}{\sqrt{2}} \left[p_x + (\hbar/a^2) y \right]. \end{aligned}$$

- (a) Verify that $[q_1, q_2] = [p_1, p_2] = 0$; $[q_1, p_1] = [q_2, p_2] = i\hbar$. Thus the q ’s and the p ’s satisfy the canonical commutation relations for position and momentum, and those of index 1 are compatible with those of index 2.
- (b) Show that

$$L_z = \frac{\hbar}{2a^2} (q_1^2 - q_2^2) + \frac{a^2}{2\hbar} (p_1^2 - p_2^2).$$

⁴⁴This problem is based on an argument in Ballentine (footnote 26), page 127.

- (c) Check that $L_z = H_1 - H_2$, where each H is the Hamiltonian for a harmonic oscillator with mass $m = \hbar/a^2$ and frequency $\omega = 1$.
- (d) We know that the eigenvalues of the harmonic oscillator Hamiltonian are $(n + 1/2)\hbar\omega$, where $n = 0, 1, 2, \dots$ (In the algebraic theory of Section 2.3.1 this follows from the form of the Hamiltonian and the canonical commutation relations). Use this to conclude that the eigenvalues of L_z must be integers.

Problem 4.58 Deduce the condition for minimum uncertainty in S_x and S_y (that is, equality in the expression $\sigma_{S_x}\sigma_{S_y} \geq (\hbar/2)|\langle S_z \rangle|$), for a particle of spin 1/2 in the generic state (Equation 4.139). *Answer:* With no loss of generality we can pick a to be real; then the condition for minimum uncertainty is that b is either pure real or else pure imaginary.

*****Problem 4.59** In classical electrodynamics the force on a particle of charge q moving with velocity \mathbf{v} through electric and magnetic fields \mathbf{E} and \mathbf{B} is given by the **Lorentz force law**:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad [4.202]$$

This force cannot be expressed as the gradient of a scalar potential energy function, and therefore the Schrödinger equation in its original form (Equation 1.1) cannot accommodate it. But in the more sophisticated form

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad [4.203]$$

there is no problem; the classical Hamiltonian⁴⁵ is

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\varphi, \quad [4.204]$$

where \mathbf{A} is the vector potential ($\mathbf{B} = \nabla \times \mathbf{A}$) and φ is the scalar potential ($\mathbf{E} = -\nabla\varphi - \partial\mathbf{A}/\partial t$), so the Schrödinger equation (making the canonical substitution $\mathbf{p} \rightarrow (\hbar/i)\nabla$) becomes

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - q\mathbf{A} \right)^2 + q\varphi \right] \Psi.$$

[4.205]

⁴⁵See, for example, H. Goldstein, C. P. Poole, and J. L. Safko, *Classical Mechanics*, 3rd ed., (Prentice Hall, Upper Saddle River, NJ, 2002), page 342.

(a) Show that

$$\frac{d\langle \mathbf{r} \rangle}{dt} = \frac{1}{m} \langle (\mathbf{p} - q\mathbf{A}) \rangle. \quad [4.206]$$

(b) As always (see Equation 1.32) we identify $d\langle \mathbf{r} \rangle/dt$ with $\langle \mathbf{v} \rangle$. Show that

$$m \frac{d\langle \mathbf{v} \rangle}{dt} = q\langle \mathbf{E} \rangle + \frac{q}{2m} \langle (\mathbf{p} \times \mathbf{B} - \mathbf{B} \times \mathbf{p}) \rangle - \frac{q^2}{m} \langle (\mathbf{A} \times \mathbf{B}) \rangle. \quad [4.207]$$

(c) In particular, if the fields \mathbf{E} and \mathbf{B} are *uniform* over the volume of the wave packet, show that

$$m \frac{d\langle \mathbf{v} \rangle}{dt} = q(\mathbf{E} + \langle \mathbf{v} \rangle \times \mathbf{B}), \quad [4.208]$$

so the *expectation value* of $\langle \mathbf{v} \rangle$ moves according to the Lorentz force law, as we would expect from Ehrenfest's theorem.

*****Problem 4.60** [Refer to Problem 4.59 for background.] Suppose

$$\mathbf{A} = \frac{B_0}{2}(x\hat{j} - y\hat{i}), \quad \text{and} \quad \varphi = Kz^2,$$

where B_0 and K are constants.

- (a) Find the fields \mathbf{E} and \mathbf{B} .
 (b) Find the allowed energies, for a particle of mass m and charge q , in these fields, *Answer:*

$$E(n_1, n_2) = (n_1 + \frac{1}{2})\hbar\omega_1 + (n_2 + \frac{1}{2})\hbar\omega_2, \quad (n_1, n_2 = 0, 1, 2, \dots), \quad [4.209]$$

where $\omega_1 \equiv qB_0/m$ and $\omega_2 \equiv \sqrt{2qK/m}$. *Comment:* If $K = 0$ this is the quantum analog to **cyclotron motion**; ω_1 is the classical cyclotron frequency, and it's a free particle in the z direction. The allowed energies, $(n_1 + \frac{1}{2})\hbar\omega_1$, are called **Landau Levels**.⁴⁶

*****Problem 4.61** [Refer to Problem 4.59 for background.] In classical electrodynamics the potentials \mathbf{A} and φ are not uniquely determined;⁴⁷ the *physical* quantities are the *fields*, \mathbf{E} and \mathbf{B} .

⁴⁶For further discussion see Ballentine (footnote 26) Section 11.3.

⁴⁷See, for example, Griffiths (footnote 30) Section 10.1.2.

(a) Show that the potentials

$$\varphi' \equiv \varphi - \frac{\partial \Lambda}{\partial t}, \quad \mathbf{A}' \equiv \mathbf{A} + \nabla \Lambda \quad [4.210]$$

(where Λ is an arbitrary real function of position and time) yield the same fields as φ and \mathbf{A} . Equation 4.210 is called a **gauge transformation**, and the theory is said to be **gauge invariant**.

(b) In quantum mechanics the potentials play a more direct role, and it is of interest to know whether the theory remains gauge invariant. Show that

$$\Psi' \equiv e^{iq\Lambda/\hbar} \Psi \quad [4.211]$$

satisfies the Schrödinger equation (4.205) with the gauge-transformed potentials φ' and \mathbf{A}' . Since Ψ' differs from Ψ only by a *phase factor*, it represents the same physical state,⁴⁸ and the theory is gauge invariant (see Section 10.2.3 for further discussion).

⁴⁸That is to say, $\langle \mathbf{r} \rangle$, $d\langle \mathbf{r} \rangle/dt$, etc. are unchanged. Because Λ depends on position, $\langle \mathbf{p} \rangle$ (with \mathbf{p} represented by the operator $(\hbar/i)\nabla$) *does* change, but as we found in Equation 4.206, \mathbf{p} does not represent the mechanical momentum ($m\mathbf{v}$) in this context (in lagrangian mechanics it is so-called **canonical momentum**).