

4.1 The Schrödinger Equation

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

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi; \quad (4.1)$$

the Hamiltonian operator $\hat{H}$ 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):

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}, \quad p_y \rightarrow -i\hbar \frac{\partial}{\partial y}, \quad p_z \rightarrow -i\hbar \frac{\partial}{\partial z}, \quad (4.2)$$

or

$$\boxed{\mathbf{p} \rightarrow -i\hbar \nabla,} \quad (4.3)$$

for short. Thus

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

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 V is independent of time, there will be a complete set of stationary states,

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

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

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi.} \quad (4.8)$$

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 the three-dimensional version of **Ehrenfest's theorem**,

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

(Each of these, of course, stands for *three* equations—one for each component.) *Hint:* First check that the “generalized” Ehrenfest theorem, Equation 3.73, 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, $\sigma_x \sigma_{p_y}$.

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

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

- (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 2.44), but in three dimensions they are very common.
 (c) What is the degeneracy of E_{14} , and why is this case interesting?

4.1.1 Spherical Coordinates

Most of the applications we will encounter involve **central potentials**, for which V is a function only of the distance from the origin, $V(\mathbf{r}) \rightarrow V(r)$. In that case it is natural to adopt **spherical coordinates**, (r, θ, ϕ) (Figure 4.1). In spherical coordinates the Laplacian takes the form¹

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

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

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

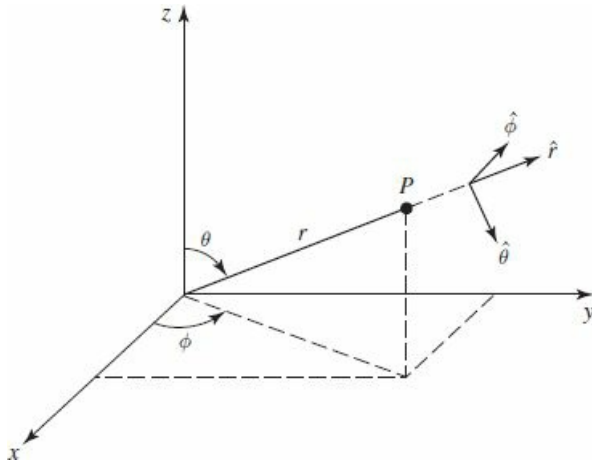


Figure 4.1: Spherical coordinates: radius r , polar angle θ , and azimuthal angle ϕ .

We begin by looking for solutions that are separable into products (a function of r times a function of θ and ϕ):

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

Putting this into Equation 4.14, we have

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

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

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

The term in the first curly bracket depends only on r , whereas the remainder depends only on θ and ϕ ; accordingly, each must be a constant. For reasons that will appear in due course,² I will write this “separation constant” in the form $\ell(\ell + 1)$:

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

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

Problem 4.3

- (a) Suppose $\psi(r, \theta, \phi) = Ae^{-r/a}$, for some constants A and a . Find E and $V(r)$, assuming $V(r) \rightarrow 0$ as $r \rightarrow \infty$.
- (b) Do the same for $\psi(r, \theta, \phi) = Ae^{-r^2/a^2}$, assuming $V(0) = 0$.

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:

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

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

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

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

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

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 time³ I'll call the separation constant m^2 :

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

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

The ϕ equation is easy:

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

Actually, there are *two* solutions: $\exp(im\phi)$ and $\exp(-im\phi)$, but we'll cover the latter by allowing m to run negative. There could also be a constant factor in front, but we might as well absorb that into Θ . Incidentally, in electrodynamics we would write the azimuthal function (Φ) in terms of sines and cosines, instead of exponentials, because electric fields are *real*. But there is no such constraint on the wave function, and 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 that⁴

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

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,

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

may not be so familiar. The solution is

$$\Theta(\theta) = AP_\ell^m(\cos \theta), \quad (4.26)$$

where P_ℓ^m is the associated Legendre function, defined by⁵

$$P_\ell^m(x) \equiv (-1)^m (1-x^2)^{m/2} \left(\frac{d}{dx} \right)^m P_\ell(x), \quad (4.27)$$

and $P_\ell(x)$ is the ℓ th Legendre polynomial, defined by the Rodrigues formula:

$$P_\ell(x) \equiv \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell. \quad (4.28)$$

For example,

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

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

and so on. The first few Legendre polynomials are listed in Table 4.1. As the name suggests, $P_\ell(x)$ is a polynomial (of degree ℓ) in x , and is even or odd according to the parity of ℓ . But $P_\ell^m(x)$ is not, in general, a polynomial⁶—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 $P_\ell^m(\cos \theta)$, and $\sqrt{1-\cos^2 \theta} = \sin \theta$, so $P_\ell^m(\cos \theta)$ 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.)

Table 4.1: The first few Legendre polynomials, $P_\ell(x)$: (a) functional form, (b) graph.

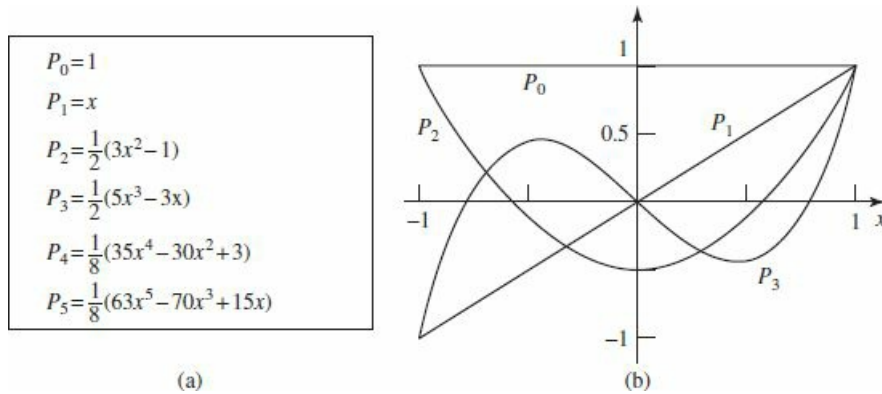
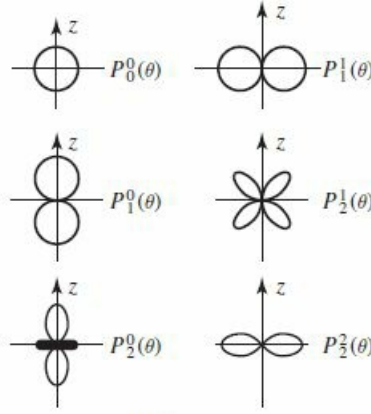


Table 4.2: Some associated Legendre functions, $P_\ell^m(\cos \theta)$: (a) functional form, (b) graphs of $r = |P_\ell^m(\cos \theta)|$ (in these plots r tells you the magnitude of the function in the direction θ ; each figure should be rotated about the z axis).

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

(a)



(b)

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

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell. \quad (4.29)$$

But wait! Equation 4.25 is a second-order differential equation: It should have *two* linearly independent solutions, for *any old* values of ℓ and m . Where are all the other solutions? *Answer*: They *exist*, of course, as mathematical solutions to the equation, but they are *physically* unacceptable, because they blow up at $\theta = 0$ and/or $\theta = \pi$ (see Problem 4.5).

Now, the volume element in spherical coordinates⁷ is

$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi = r^2 \, dr \, d\Omega, \quad \text{where} \quad d\Omega \equiv \sin \theta \, d\theta \, d\phi, \quad (4.30)$$

so the normalization condition (Equation 4.6) becomes

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

It is convenient to normalize R and Y separately:

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

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

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}} e^{im\phi} P_\ell^m(\cos \theta), \quad (4.32)$$

As we shall prove later on, they are automatically orthogonal:

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

In Table 4.3 I have listed the first few spherical harmonics.

Table 4.3: *The first few spherical harmonics, $Y_\ell^m(\theta, \phi)$.*

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

- * **Problem 4.4** 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 4.5 Show that

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

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

Problem 4.6 Using Equation 4.32 and footnote 5, show that

$$Y_\ell^{-m} = (-1)^m (Y_\ell^m)^*.$$

- * **Problem 4.7** Using Equation 4.32, find $Y_\ell^\ell(\theta, \phi)$ 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 4.8** Starting from the Rodrigues formula, derive the orthonormality condition for Legendre polynomials:

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

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:

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

This simplifies if we change variables: Let

$$u(r) \equiv r R(r), \quad (4.36)$$

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

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

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**,

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

contains an extra piece, the so-called **centrifugal term**, $(\hbar^2/2m)[\ell(\ell + 1)/r^2]$. 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**,

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

Find the wave functions and the allowed energies.

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

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

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}. \quad (4.42)$$

Our problem is to solve Equation 4.41, subject to the boundary condition $u(a) = 0$. The case $\ell = 0$ is easy:

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

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

$$E_{N0} = \frac{N^2 \pi^2 \hbar^2}{2ma^2}, \quad (N = 1, 2, 3, \dots) \quad (4.43)$$

(same as for the one-dimensional infinite square well, Equation 2.30). Normalizing $u(r)$ yields $A = \sqrt{2/a}$:

$$u_{N0} = \sqrt{\frac{2}{a}} \sin\left(\frac{N\pi r}{a}\right). \quad (4.44)$$

Notice that the radial wave function has $N - 1$ nodes (or, if you prefer, N “lobes”).

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

$$u(r) = Ar j_\ell(kr) + Br n_\ell(kr), \quad (4.45)$$

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

$$j_\ell(x) \equiv (-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\sin x}{x}; \quad n_\ell(x) \equiv -(-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\cos x}{x}. \quad (4.46)$$

For example,

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

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

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

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, $B_\ell = 0$, and hence

$$R(r) = A j_\ell(kr). \quad (4.47)$$

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

$$j_\ell(ka) = 0; \quad (4.48)$$

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. But (unfortunately for us) they are not located at nice sensible points (such as multiples of π); they have to be computed numerically.¹¹ At any rate, the boundary condition requires that

$$k = \frac{1}{a} \beta_{N\ell}, \quad (4.49)$$

where $\beta_{N\ell}$ is the N th zero of the ℓ th spherical Bessel function. The allowed energies, then, are given by

$$E_{N\ell} = \frac{\hbar^2}{2ma^2} \beta_{N\ell}^2. \quad (4.50)$$

It is customary to introduce the **principal quantum number**, n , which simply orders the allowed energies, starting with 1 for the ground state (see Figure 4.3). The wave functions are

$$\psi_{n\ell m}(r, \theta, \phi) = A_{n\ell} j_\ell\left(\beta_{N\ell} \frac{r}{a}\right) Y_\ell^m(\theta, \phi), \quad (4.51)$$

with the constant $A_{n\ell}$ to be determined by normalization. As before, the wave function has $N - 1$ radial nodes.¹²

Table 4.4 The first few spherical Bessel and Neumann functions, $j_\ell(x)$ and $n_\ell(x)$; asymptotic forms for small x .

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

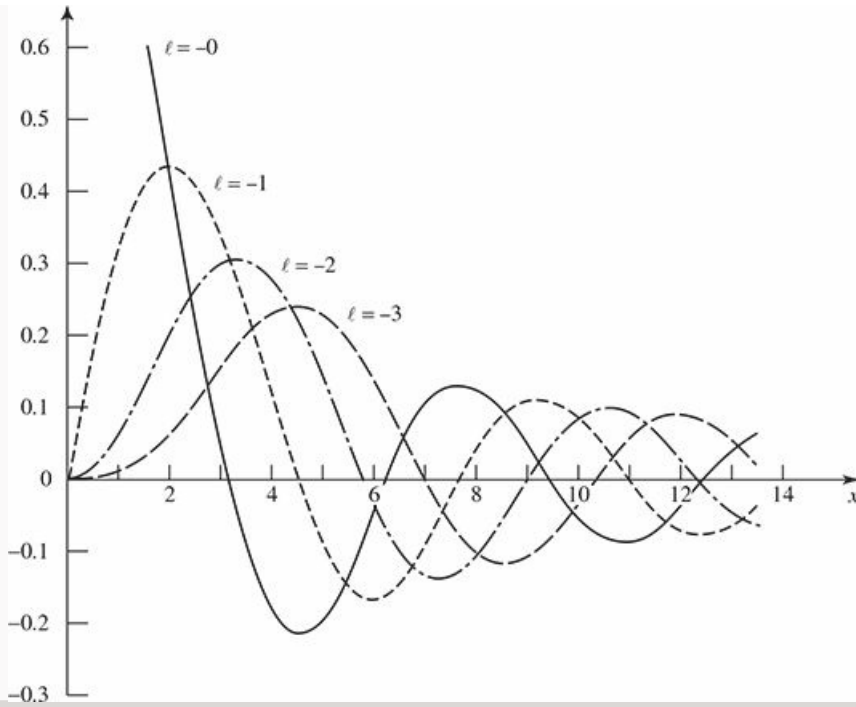


Figure 4.2: Graphs of the first four spherical Bessel functions.

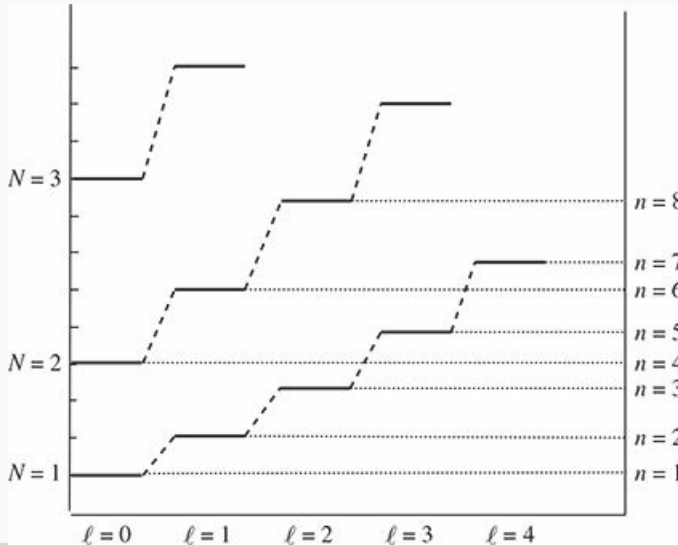


Figure 4.3: Energy levels of the infinite spherical well (Equation 4.50). States with the same value of N are connected by dashed lines.

Notice that the energy levels are $(2\ell + 1)$ -fold degenerate, since there are $(2\ell + 1)$ different values of m for each value of ℓ (see Equation 4.29). This is the degeneracy to be expected for a spherically symmetric potential, since m does not appear in the radial equation (which determines the energy). But in some cases (most famously the hydrogen atom) there is *extra* degeneracy, due to coincidences in the energy levels not attributable to spherical symmetry alone. The deeper reason for such “accidental” degeneracy is intriguing, as we shall see in Chapter 6.

Problem 4.9

- (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 4.10

- (a) Check that $Arj_1(kr)$ satisfies the radial equation with $V(r) = 0$ and $\ell = 1$.
- (b) Determine graphically the allowed energies for the infinite spherical well, when $\ell = 1$. 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.

**

Problem 4.11 A particle of mass m is placed in a *finite* spherical well:

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

Find the ground state, by solving the radial equation with $\ell = 0$. 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 (mass m_e , charge $-e$) that orbits around it, bound by the mutual attraction of opposite charges (see Figure 4.4). From Coulomb's law, the potential energy of the electron¹³ (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

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

(The effective potential—the term in square brackets—is shown in Figure 4.5.) Our problem is to solve this equation for $u(r)$, and determine the allowed energies. 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 want to refer back to Section 2.3.2 for a more complete explanation.) Incidentally, the Coulomb potential (Equation 4.52) admits *continuum* states (with $E > 0$), describing electron-proton scattering, as well as discrete *bound* states, representing the hydrogen atom, but we shall confine our attention to the latter.¹⁴

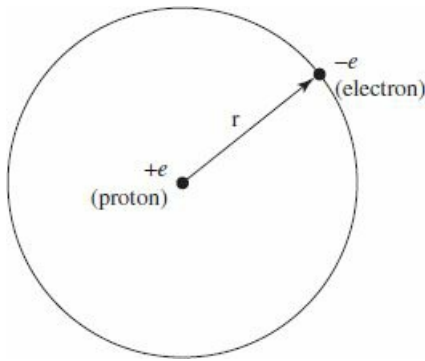


Figure 4.4: The hydrogen atom.

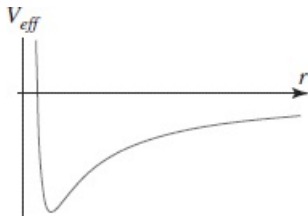


Figure 4.5: The effective potential for hydrogen (Equation 4.53), if $\ell > 0$.

4.2.1 The Radial Wave Function

Our first task is to tidy up the notation. Let

$$\kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar}. \quad (4.54)$$

(For bound states, E is negative, so κ is *real*.) Dividing Equation 4.53 by E , we have

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

This suggests that we introduce

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{m_e e^2}{2\pi \epsilon_0 \hbar^2 \kappa}, \quad (4.55)$$

so that

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

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

$$u(\rho) = A e^{-\rho} + B e^{\rho}, \quad (4.57)$$

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

$$u(\rho) \sim A e^{-\rho}, \quad (4.58)$$

for large ρ . On the other hand, as $\rho \rightarrow 0$ the centrifugal term dominates;¹⁵ approximately, then:

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

The general solution (check it!) is

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

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

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

for small ρ .

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

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

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

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

and

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

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

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

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,

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

Inserting these into Equation 4.61,

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

Equating the coefficients of like powers yields

$$j(j + 1) c_{j+1} + 2(\ell + 1)(j + 1) c_{j+1} - 2j c_j + [\rho_0 - 2(\ell + 1)] c_j = 0,$$

or:

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

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.¹⁶

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 says¹⁷

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j,$$

so

$$c_j \approx \frac{2^j}{j!} c_0. \quad (4.64)$$

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

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

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 escape from this dilemma: *The series must terminate*. There must occur some integer N such that

$$c_{N-1} \neq 0 \quad \text{but} \quad c_N = 0 \quad (4.66)$$

(beyond this all coefficients vanish automatically).¹⁸ In that case Equation 4.63 says

$$2(N + \ell) - \rho_0 = 0.$$

Defining

$$n \equiv N + \ell, \quad (4.67)$$

we have

$$\rho_0 = 2n. \quad (4.68)$$

But ρ_0 determines E (Equations 4.54 and 4.55):

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{m_e e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}, \quad (4.69)$$

so the allowed energies are

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

This is the famous **Bohr formula**—by any measure the most important result in all of quantum mechanics. Bohr obtained it in 1913 by a serendipitous mixture of inapplicable classical physics and premature quantum theory (the Schrödinger equation did not come until 1926).

Combining Equations 4.55 and 4.68, we find that

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

where

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m} \quad (4.72)$$

is the so-called **Bohr radius**.¹⁹ It follows (again, from Equation 4.55) that

$$\rho = \frac{r}{an}. \quad (4.73)$$

The spatial wave functions are labeled by three quantum numbers (n , ℓ , and m):²⁰

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell}^m(\theta, \phi), \quad (4.74)$$

where (referring back to Equations 4.36 and 4.60)

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v(\rho), \quad (4.75)$$

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

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

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:²¹

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

In other words, the **binding energy** of hydrogen (the amount of energy you would have to impart to the electron in its ground state in order to ionize the atom) is 13.6 eV. Equation 4.67 forces $\ell = 0$, 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

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

If $n = 2$ the energy is

$$E_2 = \frac{-13.6 \text{ eV}}{4} = -3.40 \text{ eV}; \quad (4.81)$$

this is the first excited state—or rather, *states*, since we can have either $\ell = 0$ (in which case $m = 0$) or $\ell = 1$ (with $m = -1, 0$, or $+1$); evidently four different states share this same energy. If $\ell = 0$, the recursion relation (Equation 4.76) gives

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

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 $\ell = 1$ 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 4.13.)

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

$$\ell = 0, 1, 2, \dots, n-1, \quad (4.84)$$

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

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

In Figure 4.6 I plot the energy levels for hydrogen. Notice that different values of ℓ carry the same energy (for a given n)—contrast the infinite spherical well, Figure 4.3. (With Equation 4.67, ℓ dropped out of sight, in the derivation of the allowed energies, though it does still affect the wave functions.) This is what gives rise to the “extra” degeneracy of the Coulomb potential, as compared to what you would expect from spherical symmetry alone ($n^2 = 1, 4, 9, 16, \dots$, as opposed to $(2\ell + 1) = 1, 3, 5, 7, \dots$).

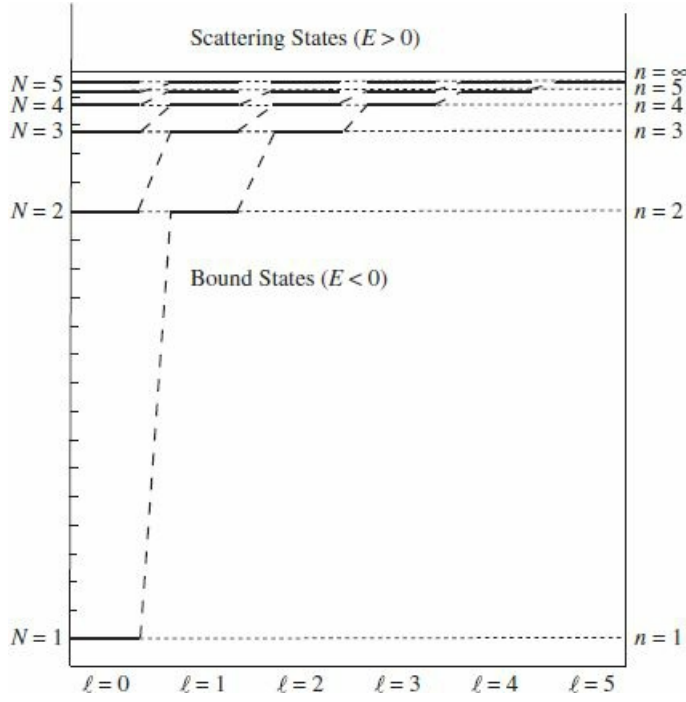


Figure 4.6: Energy levels for hydrogen (Equation 4.70); $n = 1$ is the ground state, with $E_1 = -13.6$ eV; an infinite number of states are squeezed in between $n = 5$ and $n = \infty$; $E_\infty = 0$ separates the bound states from the scattering states. Compare Figure 4.3, and note the extra (“accidental”) degeneracy of the hydrogen energies.

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

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

where

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

is an **associated Laguerre polynomial**, and

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

is the q th **Laguerre polynomial**.²² 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 4.7.) The normalized hydrogen wave functions are²³

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

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. The wave functions are mutually orthogonal:

$$\int \psi_{n\ell m}^* \psi_{n'\ell'm'} r^2 dr d\Omega = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}. \quad (4.90)$$

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 $\hat{H}$ with distinct eigenvalues.

Table 4.5: *The first few Laguerre polynomials.*

$L_0(x)$	=	1
$L_1(x)$	=	$-x + 1$
$L_2(x)$	=	$\frac{1}{2}x^2 - 2x + 1$
$L_3(x)$	=	$-\frac{1}{6}x^3 + \frac{3}{2}x^2 - 3x + 1$
$L_4(x)$	=	$\frac{1}{24}x^4 - \frac{2}{3}x^3 + 3x^2 - 4x + 1$
$L_5(x)$	=	$-\frac{1}{120}x^5 + \frac{5}{24}x^4 - \frac{5}{3}x^3 + 5x^2 - 5x + 1$
$L_6(x)$	=	$\frac{1}{720}x^6 - \frac{1}{20}x^5 + \frac{5}{8}x^4 - \frac{10}{3}x^3 + \frac{15}{2}x^2 - 6x + 1$

Table 4.6: *Some associated Laguerre polynomials.*

$L_0^0(x)$	=	1	$L_0^2(x)$	=	1
$L_1^0(x)$	=	$-x + 1$	$L_1^2(x)$	=	$-x + 3$
$L_2^0(x)$	=	$\frac{1}{2}x^2 - 2x + 1$	$L_2^2(x)$	=	$\frac{1}{2}x^2 - 4x + 6$
$L_0^1(x)$	=	1	$L_0^3(x)$	=	1
$L_1^1(x)$	=	$-x + 2$	$L_1^3(x)$	=	$-x + 4$
$L_2^1(x)$	=	$\frac{1}{2}x^2 - 3x + 3$	$L_2^3(x)$	=	$\frac{1}{2}x^2 - 5x + 10$

Table 4.7: *The first few radial wave functions for hydrogen, $R_{n\ell}(r)$.*

$R_{10} = 2a^{-3/2} \exp(-r/a)$
$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a} \right) \exp(-r/2a)$ $R_{21} = \frac{1}{2\sqrt{6}} a^{-3/2} \left(\frac{r}{a} \right) \exp(-r/2a)$
$R_{30} = \frac{2}{3\sqrt{3}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a} \right)^2 \right) \exp(-r/3a)$ $R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a} \right) \left(\frac{r}{a} \right) \exp(-r/3a)$ $R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a} \right)^2 \exp(-r/3a)$
$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a} \right)^2 - \frac{1}{192} \left(\frac{r}{a} \right)^3 \right) \exp(-r/4a)$ $R_{41} = \frac{5}{16\sqrt{15}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a} \right)^2 \right) \left(\frac{r}{a} \right) \exp(-r/4a)$ $R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a} \right) \left(\frac{r}{a} \right)^2 \exp(-r/4a)$ $R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a} \right)^3 \exp(-r/4a)$

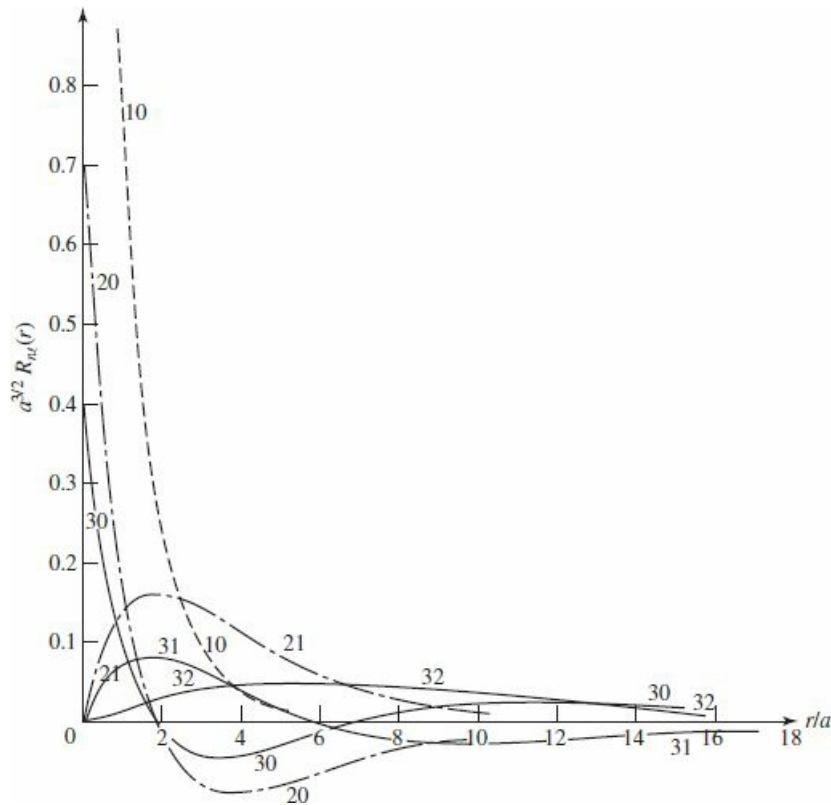


Figure 4.7: Graphs of the first few hydrogen radial wave functions, $R_{n\ell}(r)$.

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 4.8). More quantitative (but perhaps harder to decipher) are surfaces of constant probability density (Figure 4.9). The quantum numbers n , ℓ , and m can be identified from the nodes of the wave function. The number of radial nodes is, as always, given by $N - 1$ (for hydrogen this is $n - \ell - 1$). For each radial node the wave function vanishes on a sphere, as can be seen in Figure 4.8. The quantum number m counts the number of nodes of the real (or imaginary) part of the wave function in the ϕ direction. These nodes are planes containing the z axis on which the real or imaginary part of ψ vanishes.²⁴ Finally, $\ell - m$ gives the number of nodes in the θ direction. These are cones about the z axis on which ψ vanishes (note that a cone with opening angle $\pi/2$ is the $x - y$ plane itself).

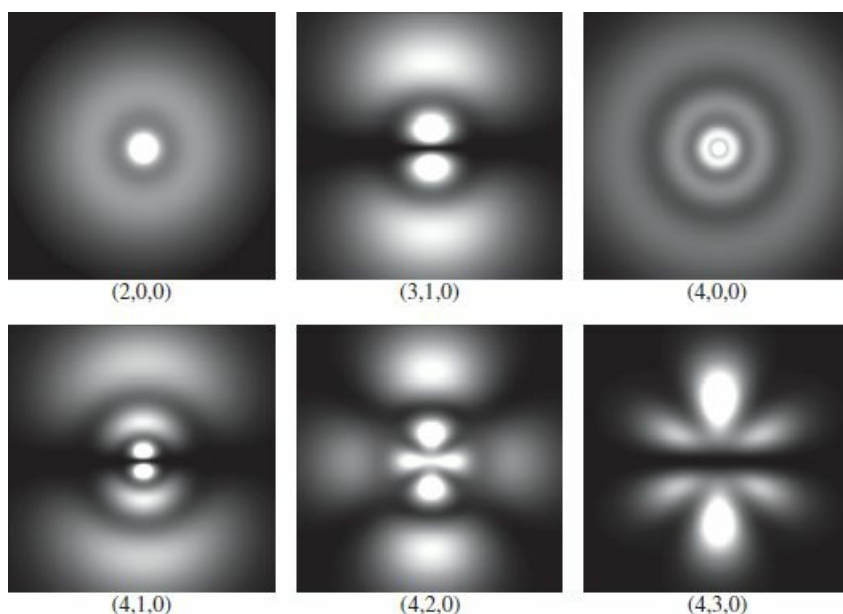


Figure 4.8: Density plots for the first few hydrogen wave functions, labeled by (n, ℓ, m) . Printed by permission using “Atom in a Box” by Dauger Research. You can make your own plots by going to: <http://dauger.com>.

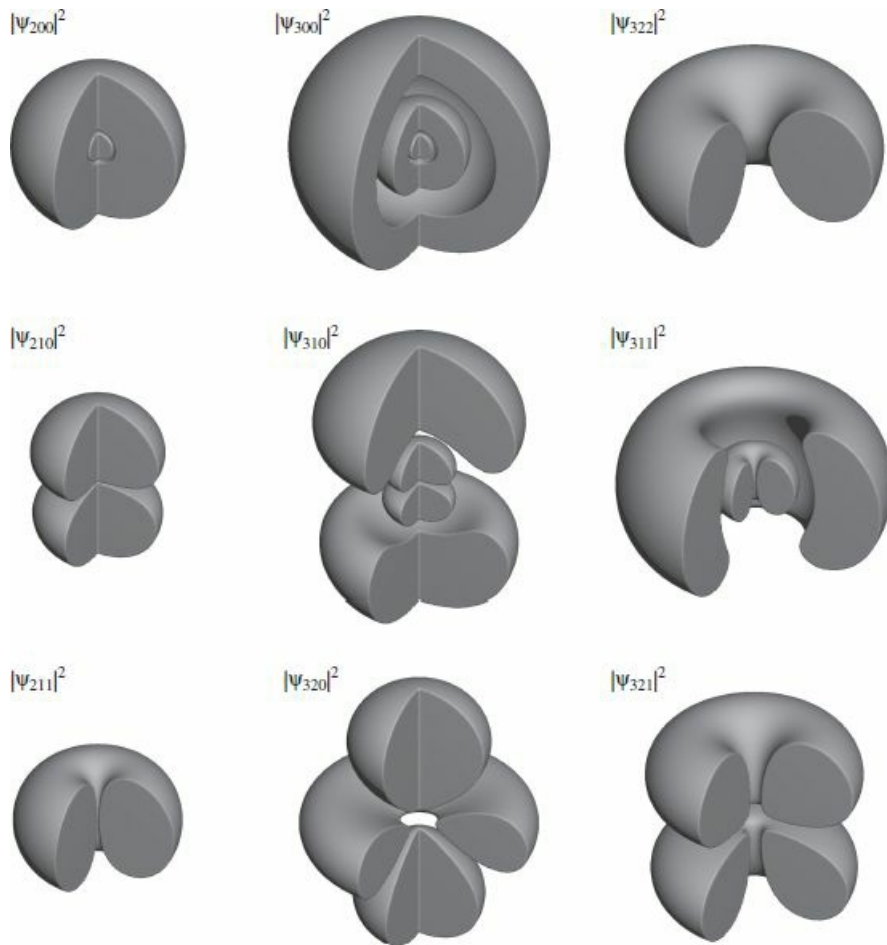


Figure 4.9: Shaded regions indicate significant electron density ($|\psi|^2 > 0.25/\text{nm}^3$) for the first few hydrogen wave functions. The region $0 < \phi < \pi/2$ has been cut away; $|\psi|^2$ has azimuthal symmetry in all cases.

* **Problem 4.12** Work out the radial wave functions R_{30} , R_{31} , and R_{32} , using the recursion formula (Equation 4.76). Don't bother to normalize them.

* **Problem 4.13**

- Normalize R_{20} (Equation 4.82), and construct the function ψ_{200} .
- Normalize R_{21} (Equation 4.83), and construct ψ_{211} , ψ_{210} , and ψ_{21-1} .

* **Problem 4.14**

- Using Equation 4.88, work out the first four Laguerre polynomials.
- Using Equations 4.86, 4.87, and 4.88, find $v(\rho)$, for the case $n = 5$, $\ell = 2$.
- Find $v(\rho)$ again (for the case $n = 5$, $\ell = 2$), but this time get it from the recursion formula (Equation 4.76).

*

Problem 4.15

- (a) 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.
- (b) 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.
- (c) Find $\langle x^2 \rangle$ in the state $n = 2, \ell = 1, m = 1$. *Hint:* this state is *not* symmetrical in x, y, z . Use $x = r \sin \theta \cos \phi$.

Problem 4.16 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 4.17 Calculate $\langle z \hat{H} z \rangle$, in the ground state of hydrogen. *Hint:* This takes two pages and six integrals, or four lines and no integrals, depending on how you set it up. To do it the quick way, start by noting that $[z, [H, z]] = 2zHz - Hz^2 - z^2H$.²⁵

Problem 4.18 A hydrogen atom starts out in the following linear combination of the stationary states $n = 2, \ell = 1, m = 1$ and $n = 2, \ell = 1, m = -1$:

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

- (a) Construct $\Psi(\mathbf{r}, t)$. Simplify it as much as you can.
- (b) 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.

4.2.2 The Spectrum of Hydrogen

In principle, if you put a hydrogen atom into some stationary state $\Psi_{n\ell m}$, it should stay there forever. However, if you *tickle* it slightly (by collision with another atom, say, or by shining light on it), the atom may undergo a **transition** to some other stationary state—either by *absorbing* energy, and moving up to a higher-energy state, or by *giving off* energy (typically in the form of electromagnetic radiation), and moving down.²⁶ 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**,²⁷ 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

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

where

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

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 $\mathcal{R}$ 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 4.10). (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.)

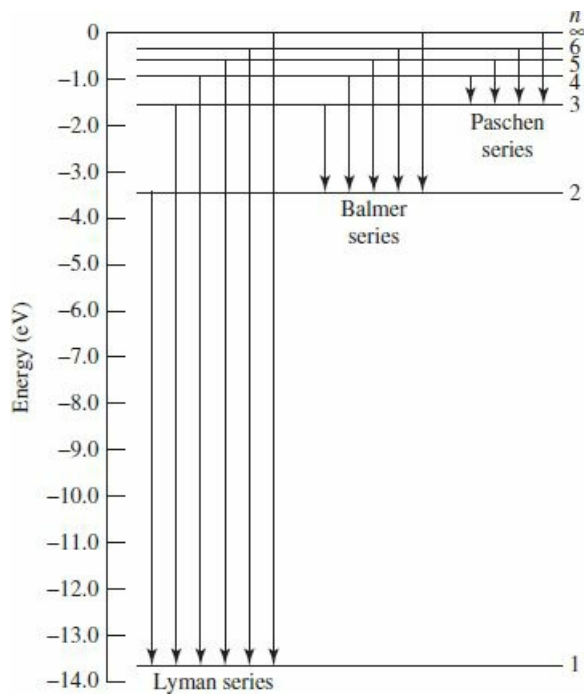


Figure 4.10: Energy levels and transitions in the spectrum of hydrogen.

* **Problem 4.19** A **hydrogenic atom** consists of a single electron orbiting a nucleus with Z protons. ($Z = 1$ would be hydrogen itself, $Z = 2$ is ionized helium, $Z = 3$ is doubly ionized lithium, and so on.) Determine the Bohr energies $E_n(Z)$, the binding energy $E_1(Z)$, the Bohr radius $a(Z)$, and the Rydberg constant $\mathcal{R}(Z)$ 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 4.20 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_E 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.
- 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 answer²⁸ 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); 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 an 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,²⁹

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

The corresponding quantum operators³⁰ 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 this section we'll obtain the eigenvalues of the 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 fact

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

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 ($x \rightarrow y, y \rightarrow z, z \rightarrow x$):

$$\boxed{[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y.} \quad (4.99)$$

These are the fundamental commutation relations for angular momentum; everything 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 3.65 to reduce the commutators; of course, *any* operator commutes with *itself*.) It follows 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

$$L_{\pm} \equiv L_x \pm i L_y. \quad (4.105)$$

Its commutator with L_z is

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

so

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

Also (from Equation 4.102)

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

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

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

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 4.11). To ascend the ladder we apply the raising operator, and to descend, the lowering operator. But this process cannot go on forever: Eventually we're going to reach a state for which the z -component exceeds the *total*, and that cannot be.³¹ There must exist a “top rung”, f_t , such that³²

$$L_+ f_t = 0. \quad (4.110)$$

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

$$L_z f_t = \hbar\ell f_t; \quad L^2 f_t = \lambda f_t. \quad (4.111)$$

Now,

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

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

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

and hence

$$\lambda = \hbar^2 \ell (\ell + 1). \quad (4.113)$$

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

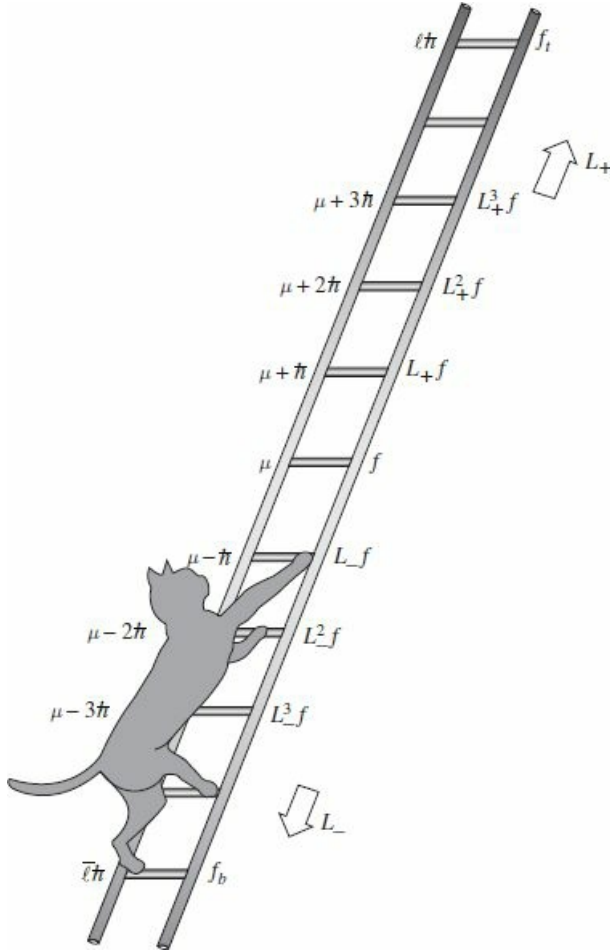


Figure 4.11: The “ladder” of angular momentum states.

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

$$L_- f_b = 0. \quad (4.114)$$

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

$$L_z f_b = \hbar \bar{\ell} f_b; \quad L^2 f_b = \lambda f_b. \quad (4.115)$$

Using Equation 4.112, we have

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

and therefore

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

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

$$\bar{\ell} = -\ell. \quad (4.117)$$

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

$$\boxed{L^2 f_\ell^m = \hbar^2 \ell(\ell + 1) f_\ell^m; \quad L_z f_\ell^m = \hbar m f_\ell^m,} \quad (4.118)$$

where

$$\ell = 0, 1/2, 1, 3/2, \dots; \quad m = -\ell, -\ell + 1, \dots, \ell - 1, \ell. \quad (4.119)$$

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

Some people like to illustrate this with the diagram in Figure 4.12 (drawn for the case $\ell = 2$). The arrows are supposed to represent possible angular momenta (in units of $\hbar$)—they all have the same length $\sqrt{\ell(\ell + 1)}$ (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, $\sqrt{\ell(\ell + 1)} > \ell$, except for the “trivial” case $\ell = 0$.) 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 that you would have to know all three components simultaneously, and the 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 just *aren’t* three components—a particle simply 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 4.12—at best they should be smeared out around the latitude lines, to indicate that L_x and L_y are indeterminate.

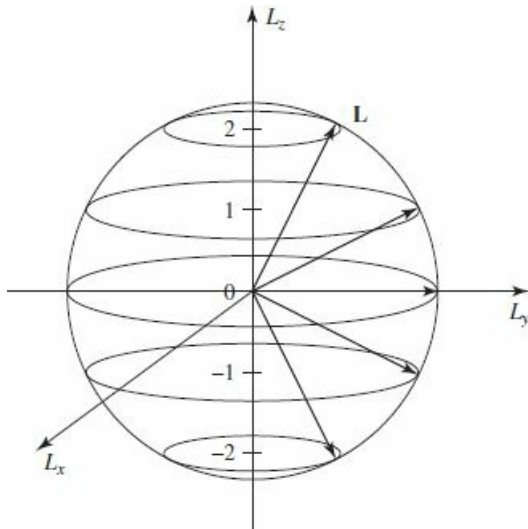


Figure 4.12: Angular momentum states (for $\ell = 2$).

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 let you in on the punch line: $f_\ell^m = Y_\ell^m$ —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 same letters ℓ and m , of course). And I can now explain 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 4.21** The raising and lowering operators change the value of m by one unit:

$$L_+ f_\ell^m = (A_\ell^m) f_\ell^{m+1}, \quad L_- f_\ell^m = (B_\ell^m) f_\ell^{m-1} \quad (4.120)$$

where A_ℓ^m and B_ℓ^m are constants. *Question:* What *are* they, 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:*

$$\begin{aligned} A_\ell^m &= \hbar \sqrt{\ell(\ell+1) - m(m+1)} = \hbar \sqrt{(\ell-m)(\ell+m+1)}, \\ B_\ell^m &= \hbar \sqrt{\ell(\ell+1) - m(m-1)} = \hbar \sqrt{(\ell+m)(\ell-m+1)}. \end{aligned} \quad (4.121)$$

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

- * **Problem 4.22**

- (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) Find 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 4.23

- (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, $\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla)$, and the gradient, in spherical coordinates, is:³³

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

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

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

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

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

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

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

So

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

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

and

$$\boxed{L_z = -i\hbar \frac{\partial}{\partial \phi}.} \quad (4.129)$$

We shall also need the raising and lowering operators:

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

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 4.24(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 4.24(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 $f_{\ell}^m(\theta, \phi)$. It's an eigenfunction of L^2 , with eigenvalue $\hbar^2 \ell(\ell + 1)$:

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

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

$$L_z f_{\ell}^m = -i\hbar \frac{\partial}{\partial \phi} f_{\ell}^m = \hbar m f_{\ell}^m,$$

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, $Y_{\ell}^m(\theta, \phi)$. *Conclusion:* Spherical harmonics *are* the 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 :

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

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: 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).³⁴ 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 4.24

- (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 4.25

- (a) What is $L_+ Y_\ell^\ell$? (No calculation allowed!)
- (b) Use the result of (a), together with Equation 4.130 and the fact that $L_z Y_\ell^\ell = \hbar \ell Y_\ell^\ell$, to determine $Y_\ell^\ell(\theta, \phi)$, up to a normalization constant.
- (c) Determine the normalization constant by direct integration. Compare your final answer to what you got in Problem 4.7.

Problem 4.26 In Problem 4.4 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 4.27 Two particles (masses m_1 and m_2) are attached to the ends of a massless rigid rod of length a . The system is free to rotate in three dimensions about the (fixed) center of mass.

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

$$E_n = \frac{\hbar^2}{2I} n(n+1), \quad (n = 0, 1, 2, \dots), \quad \text{where} \quad I = \frac{m_1 m_2}{(m_1 + m_2)} a^2$$

is the moment of inertia of the system. *Hint:* First express the (classical) energy in terms of the angular momentum.

- (b) What are the normalized eigenfunctions for this system? (Let θ and ϕ define the orientation of the rotor axis.) What is the degeneracy of the n th energy level?
- (c) What spectrum would you expect for this system? (Give a formula for the frequencies of the spectral lines.) *Answer:* $\nu_j = \hbar j / 2\pi I$, $j = 1, 2, 3, \dots$
- (d) Figure 4.13 shows a portion of the rotational spectrum of carbon monoxide (CO). What is the frequency separation ($\Delta\nu$) between adjacent lines? Look up the masses of ^{12}C and ^{16}O , and from m_1 , m_2 , and $\Delta\nu$ determine the distance between the atoms.