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

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

the Hamiltonian operator[1] 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):

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

[1]Where 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

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

for short. Thus

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

where

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

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

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

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

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

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

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

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

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

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.)

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*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:*

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

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:

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

(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:*

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

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 form[2]

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

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

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

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

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \tag{4.15}$$

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[2] In 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.

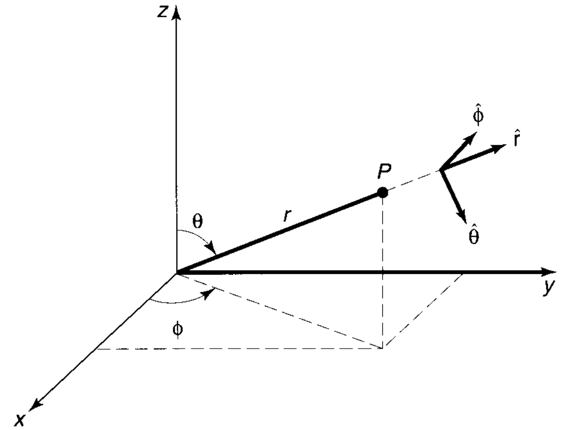

FIGURE 4.1: Spherical coordinates: radius r, polar angle θ, and azimuthal angle ϕ.

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 $l(l+1)$:

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

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

[3]Note 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"):

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

(a) Find the stationary states, and the corresponding energies.

(b) Call the distinct energies $E_1, E_2, E_3, \ldots$, 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:

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

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

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

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

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

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

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

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

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[4]Again, 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:

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

[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 that[5]

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

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*:

$$m = 0, \pm 1, \pm 2, \ldots . \qquad [4.24]$$

The θ equation,

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

is not so simple. The solution is

$$\Theta(\theta) = AP_l^m(\cos\theta), \qquad [4.26]$$

where P_l^m is the **associated Legendre function**, defined by[6]

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

and $P_l(x)$ is the lth **Legendre polynomial**, defined by the **Rodrigues formula**:

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

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[5] This 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.

[6] Notice 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.

$P_0 = 1$

$P_1 = x$

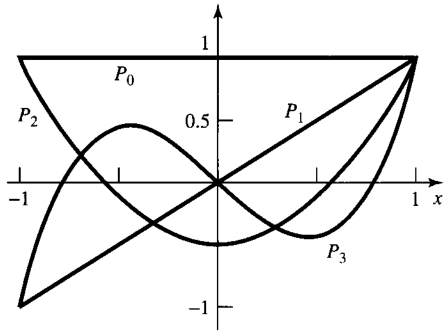
$P_2 = \frac{1}{2}(3x^2 - 1)$

$P_3 = \frac{1}{2}(5x^3 - 3x)$

$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$

$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$

(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:

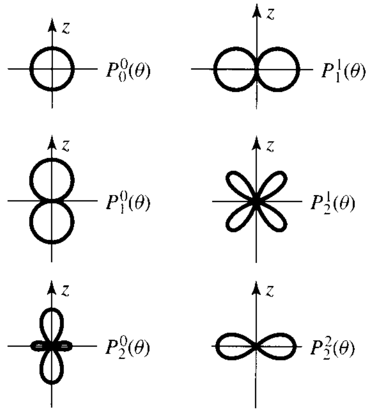
$$l = 0,\ 1,\ 2, \ldots; \quad m = -l,\ -l + 1,\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ l - 1,\ l. \quad [4.29]$$

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 coordinates[7] is

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

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:

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

[7] See, 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 functions[8] are called **spherical harmonics**:

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

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

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

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

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

[8]The 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

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

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:

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

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:

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

This equation simplifies if we change variables: Let

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

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

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

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,**

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

[9]Those 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

$$\int_0^\infty |u|^2\, dr = 1. \tag{4.39}$$

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

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

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

Find the wave functions and the allowed energies.

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

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

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}, \tag{4.42}$$

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

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

But remember, the actual radial wave function is $R(r) = u(r)/r$, and $[\cos(kr)]/r$ blows up as $r \to 0$. So[10] 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

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

[10]Actually, 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

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

[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:

$$u(r) = Arj_l(kr) + Brn_l(kr), \qquad [4.45]$$

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:

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

For example,

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

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

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

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

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

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

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

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

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

that is, (ka) is a zero of the lth-order spherical Bessel function. Now, the Bessel functions are oscillatory (see Figure 4.2); each one has an infinite number of zeros.

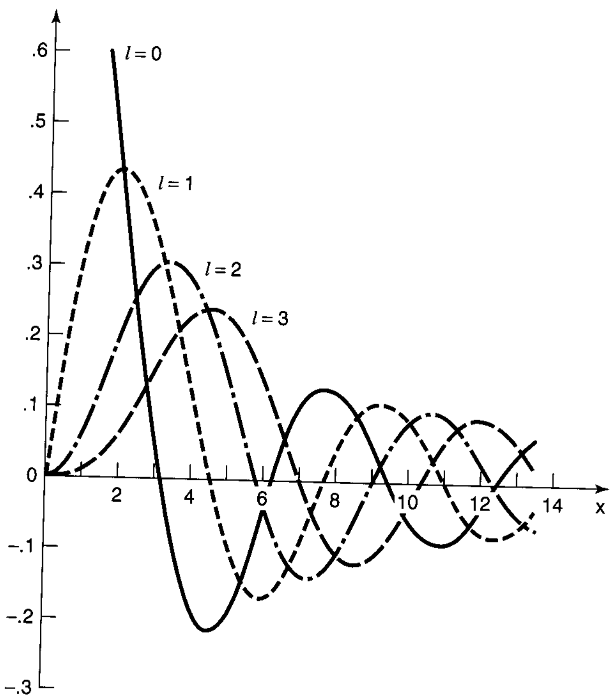


FIGURE 4.2: Graphs of the first four spherical Bessel functions.

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

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

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

$$E_{nl} = \frac{\hbar^2}{2ma^2}\beta_{nl}^2, \tag{4.50}$$

and the wave functions are

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

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 $Arj_1(kr)$ 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.

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