

## 16.1 Central potentials

In this chapter we will consider the stationary states of a particle of mass  $\mu$  moving in three dimensions. (As we discussed in [Section 14.2](#), this may in fact represent a relative position degree of freedom of a system of two or more particles, in which case  $\mu$  is the reduced mass.) For a stationary state with energy  $E$ , the wave function  $\psi(\vec{r})$  must satisfy

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + U(\vec{r})\psi = E\psi. \quad (\text{Re 11.28})$$

We wish to find the possible eigenvalues  $E$  and the corresponding wave functions  $\psi$  for a given potential function  $U(\vec{r})$ . In fact, our focus will be even narrower, in two important respects. First, we will consider only *bound* stationary states, which are normalizable. Second, we will assume that the potential is a *central potential*  $U(r)$  that depends only on the distance  $r$  from the coordinate origin. Even in such a restricted context, solving [Eq. 11.28](#) is a matter of considerable physical interest!

Since the potential energy function depends only on  $r$ , it makes sense to do our analysis in spherical coordinates  $(r, \theta, \phi)$ , as defined in [Eq. 12.21](#) and [12.22](#).<sup>1</sup> In spherical coordinates, the Laplacian operator is

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}. \quad (16.1)$$

**Exercise 16.1** From the definition of the Laplacian in Cartesian coordinates ([Eq. 11.27](#)) and the partial derivatives in [Eq. 12.23](#), derive [Eq. 16.1](#).

We recognize part of this as the position representation of the orbital angular momentum operator  $L^2$ :

$$L^2 : \psi \rightarrow -\hbar^2 \left( \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \right). \quad (\text{Re 12.28})$$

We can draw the following conclusions:

<sup>1</sup> This is an excellent time to review the discussion of spherical coordinates and orbital angular momentum in [Section 12.2](#).

- For a central potential  $U(r)$ , the Hamiltonian of the particle in the position representation depends only on the angular coordinates  $\theta$  and  $\phi$  via the orbital angular momentum operator  $L^2$ .
- Both  $L^2$  and  $L_z$ , which depend only on the angular coordinates, commute with the Hamiltonian for the particle. Thus, we can find energy eigenstates that are also eigenstates of these angular momentum operators.

This simplifies our problem considerably. In [Section 12.2](#) we established that the eigenstates of  $L^2$  and  $L_z$  have wave functions of the form  $R(r) Y_{lm}(\theta, \phi)$ , where  $Y_{lm}$  is a spherical harmonic function. Given a function of this form, [Eq. 11.28](#) becomes an equation for the radial function  $R(r)$ :

$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} R \right] + U(r)R = ER. \quad (16.2)$$

Solving this ordinary differential equation will yield the stationary state wave functions and associated energy eigenvalues.

**Exercise 16.2** What happened to the spherical harmonic  $Y_{lm}(\theta, \phi)$  in [Eq. 16.2](#)?

What can we say about the functions  $R(r)$  and the energies  $E$  that solve [Eq. 16.2](#)? Both may depend on the  $L^2$  quantum number  $l$ , which appears in the equation. However, the  $L_z$  quantum number  $m$  does not appear in the equation, so we conclude that neither  $R(r)$  nor  $E$  depends on  $m$ . For a given  $l$ , there may be many possible solutions to [Eq. 16.2](#), which we can designate by a third radial quantum number  $n$ . The energy eigenstates  $|nlm\rangle$  have wave functions

$$\langle r, \theta, \phi | nlm \rangle = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi), \quad (16.3)$$

and energies  $E_{nl}$  (independent of  $m$ ). The radial equation becomes

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR_{nl}}{dr} \right) + \frac{2\mu}{\hbar^2} \left( E_{nl} - U(r) - \frac{l(l+1)\hbar^2}{2\mu r^2} \right) R_{nl} = 0. \quad (16.4)$$

We can simplify this even further. First, we note that the term  $\frac{l(l+1)\hbar^2}{2\mu r^2}$ , though derived from the kinetic energy term in the Hamiltonian, formally appears like an  $l$ -dependent term in the potential energy. A potential of this form would provide a force pushing away from the origin, so that we call it the *centrifugal term*. We define the *effective potential*  $U_{\text{eff}}(r)$  to be the sum of the real potential energy and the centrifugal term:

$$U_{\text{eff}}(r) = U(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}, \quad (16.5)$$

(see [Fig. 16.1](#)). Rather than working with the function  $R_{nl}(r)$  directly, it is sometimes easier to consider  $u_{nl}(r) = rR_{nl}(r)$ . This simplifies the derivatives somewhat.

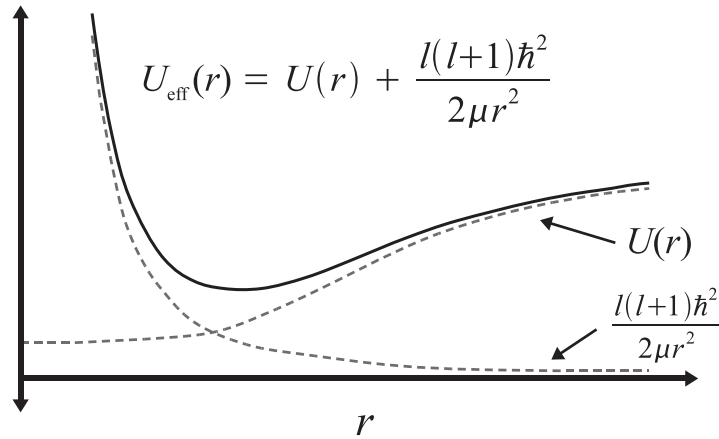


Fig. 16.1

The effective potential is the sum of  $U(r)$  and the centrifugal term, which depends on the angular momentum quantum number  $l$ . For  $l > 0$  there is an infinite “centrifugal barrier” at  $r = 0$ .

**Exercise 16.3** Show that  $\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR_{nl}}{dr} \right) = \frac{1}{r} \frac{d^2 u_{nl}}{dr^2}$ .

We arrive at the equation

$$\frac{d^2 u_{nl}}{dr^2} + \frac{2\mu}{\hbar^2} (E_{nl} - U_{\text{eff}}(r)) u_{nl} = 0. \quad (16.6)$$

This is exactly the same as the energy eigenvalue equation for a 1-D particle moving in the effective potential  $U_{\text{eff}}$ . (Compare it with Eq. 11.17 and 15.4.)

What boundary conditions does the function  $u_{nl}$  satisfy? The wave function is bounded at the origin, so we know that  $u_{nl}(r) \rightarrow 0$  as  $r \rightarrow 0$ . As far as the function  $u_{nl}$  is concerned, there is an impenetrable “wall” at  $r = 0$ . The boundary condition as  $r \rightarrow \infty$  requires slightly more thought. Since the bound state is normalized,

$$\iiint |\psi_{nlm}|^2 dV = \iiint |R_{nl}|^2 |Y_{lm}|^2 r^2 \sin \theta d\phi d\theta dr = 1, \quad (16.7)$$

where the integration includes all of 3-D space. The angular integrals are done by recognizing that the spherical harmonics have the normalization

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta |Y_{lm}|^2 = 1. \quad (16.8)$$

Thus, our wave function normalization becomes

$$\int_0^\infty |R_{nl}|^2 r^2 dr = \int_0^\infty |u_{nl}|^2 dr = 1. \quad (16.9)$$

We conclude from this that  $u_{nl}(r) \rightarrow 0$  as  $r \rightarrow \infty$ .

Because there are boundary conditions on  $u_{nl}$  in both directions, we expect the spectrum of possible energy eigenvalues  $E_{nl}$  to be discrete. See the discussion in Section 15.2.

We conclude our general discussion with a bit of nomenclature borrowed from atomic physics. The values  $l = 0, 1, 2, 3, \dots$  for the  $L^2$  quantum number may be denoted by the

letters S, P, D, F, etc. A state with  $l = 0$  is called an S-state, one with  $l = 1$  is called a P-state, and so on.

The S-states of a particle in a central potential are special in a couple of ways. First of all, since the spherical harmonic  $Y_{00}$  is a constant, these states have radially symmetric wave functions. Also, the effective potential  $U_{\text{eff}}(r)$  for an S-state has no centrifugal term. Because such a term can only increase the energy of a state, it follows that the ground state of a particle in a central potential is always an S-state.

**Exercise 16.4** Prove the last assertion by showing that, for any energy eigenstate having  $l \neq 0$ , there is an S-state with a lower expectation value  $\langle E \rangle$  for its energy.

## 16.2 The isotropic oscillator

When exploring a new set of ideas, it is often useful to apply those ideas to a problem for which the answer is already known. For a particle moving in a central potential, we have a perfect example: the isotropic harmonic oscillator. In the isotropic oscillator, the potential energy function is

$$U(\vec{r}) = \frac{\mu\omega^2}{2}r^2 = \frac{\mu\omega^2}{2}(x^2 + y^2 + z^2). \quad (16.10)$$

This is at the same time both a central potential and a potential of the form  $U_x(x) + U_y(y) + U_z(z)$ . The three Cartesian coordinates are non-interacting degrees of freedom, each of which is a 1-D harmonic oscillator with classical frequency  $\omega$ . We can construct independent ladder operators  $a_x$ ,  $a_y$ , and  $a_z$ , with corresponding number operators

$$n_x = a_x^\dagger a_x, \quad n_y = a_y^\dagger a_y, \quad n_z = a_z^\dagger a_z. \quad (16.11)$$

The Hamiltonian for the system is

$$H = \hbar\omega \left( n_x + \frac{1}{2} \mathbf{1} \right) + \hbar\omega \left( n_y + \frac{1}{2} \mathbf{1} \right) + \hbar\omega \left( n_z + \frac{1}{2} \mathbf{1} \right). \quad (16.12)$$

The stationary states for this system are eigenstates of the total number operator  $N = n_x + n_y + n_z$ . This operator has eigenvalues  $N = 0, 1, 2, \dots$

There is some degeneracy in this system, of course. We can give a specific basis of stationary states by choosing the joint eigenstates  $|n_x, n_y, n_z\rangle$  of the three Cartesian coordinate number operators. Then

$$H |n_x, n_y, n_z\rangle = \left( N + \frac{3}{2} \right) \hbar\omega |n_x, n_y, n_z\rangle, \quad (16.13)$$

where  $N = n_x + n_y + n_z$ . The degeneracies associated with the various energy levels – that is, the dimensions of the eigenspaces associated with each energy – can be worked out simply by enumerating the  $(n_x, n_y, n_z)$  combinations for each given  $N$ . For  $N = 0, 1, 2, 3, \dots$  the corresponding degeneracies are 1, 3, 6, 10,  $\dots$

**Exercise 16.5** Confirm these results and find the degeneracy for  $N = 4$ .

So much for the Cartesian analysis. The isotropic oscillator is also a central potential, so that we should be able to find energy eigenstates that are also eigenstates of the angular momentum operators  $L^2$  and  $L_z$ . The eigenstates can be labeled  $|nlm\rangle$ , where  $n$  is a radial quantum number and  $l$  and  $m$  are angular momentum quantum numbers. Our previous analysis immediately yields the following facts:

- $L^2 |nlm\rangle = l(l+1)\hbar^2 |nlm\rangle$ , and  $L_z |nlm\rangle = m\hbar |nlm\rangle$ .
- The energy of the state  $|nlm\rangle$  is  $E_{nl}$ , which depends only on  $n$  and  $l$ . Since we already know from Eq. 16.13 that the energy is determined by the total quantum number  $N$ , we infer that this  $N$  is a function of  $n$  and  $l$ .
- The energy is not dependent on the  $L_z$  quantum number  $m$ . This leads to some degeneracy in the energy levels. There may also be additional degeneracy – that is, distinct values of  $n$  and  $l$  might yield the same  $E_{nl}$ .
- The state  $|nlm\rangle$  will have a wave function of the form  $R_{nl}(r) Y_{lm}(\theta, \phi)$ , where the radial function  $R_{nl}$  is a solution to the radial equation, Eq. 16.4.

We could now proceed by solving this radial differential equation (Eq. 16.4) directly. In fact, we will follow exactly this strategy for the Coulomb potential in the next section. This time, however, it is more interesting to approach the problem algebraically.

The Cartesian coordinates and momenta can be written in terms of the corresponding ladder operators. Thus,

$$x = \sqrt{\frac{\hbar}{2\mu\omega}} (a_x + a_x^\dagger) \quad \text{and} \quad p_x = -i\sqrt{\frac{\hbar\mu\omega}{2}} (a_x - a_x^\dagger), \quad (16.14)$$

with similar expressions for the other two coordinates.

**Exercise 16.6** Derive Eq. 16.14 from the analysis of the harmonic oscillator in Section 13.2.

The components of the angular momentum are  $L_x = yp_z - zp_y$ , etc. We can therefore write the angular momentum operators in terms of the Cartesian ladder operators.

**Exercise 16.7** Use Eq. 16.14 (and the corresponding relations for the other coordinates) to show

$$\begin{aligned} L_x &= i\hbar (a_y a_z^\dagger - a_y^\dagger a_z), \\ L_y &= i\hbar (a_z a_x^\dagger - a_z^\dagger a_x), \\ L_z &= i\hbar (a_x a_y^\dagger - a_x^\dagger a_y). \end{aligned} \quad (16.15)$$

From these, we could work out a lengthy expression for  $L^2$ . But it is easier to postpone the algebra for a bit. We first establish two useful elementary facts about ladder operators.

**Exercise 16.8** Suppose  $a$  and  $a^\dagger$  are the ladder operators for an oscillator, and  $n = a^\dagger a$  is the corresponding number operator. From the commutation relation  $[a, a^\dagger] = \mathbf{1}$ , show that (a)  $[a^2, a^\dagger] = 2a$ ; and (b)  $(a^\dagger)^2 a^2 = n^2 - n$ .

Next, we define a *radial ladder operator*  $A$  by

$$A = a_x^2 + a_y^2 + a_z^2. \quad (16.16)$$

Why define  $A$  in this way? Intuitively, the Cartesian ladder operators appear in a “Pythagorean” way in this definition. More crucially, this operator commutes with all of the angular momentum components:

$$[L_x, A] = [L_y, A] = [L_z, A] = 0. \quad (16.17)$$

**Exercise 16.9** Choose one of these commutators and confirm that it is zero.

It follows that  $[L^2, A] = 0$  as well. The operator  $A$  has a definite effect on the energy – or, equivalently, on the total quantum number  $N$ . Suppose  $|\psi\rangle$  is an eigenstate of  $N$  with eigenvalue  $N$ . Then  $A|\psi\rangle$  and  $A^\dagger|\psi\rangle$  are also  $N$ -eigenstates.

$$NA|\psi\rangle = (N-2)A|\psi\rangle \quad \text{and} \quad NA^\dagger|\psi\rangle = (N+2)A^\dagger|\psi\rangle. \quad (16.18)$$

We can see this in two distinct ways. The first would begin by calculating the commutator  $[N, A] = -2A$ , and then proceed from there. The second way to see this is simply to note that  $A$  involves *squares* of the Cartesian ladder operators. Thus, every term in  $A$  has the effect of changing the sum  $N = n_x + n_y + n_z$  by exactly  $-2$ . The opposite is of course true for  $A^\dagger$ .

Now we can derive a compact expression for  $L^2$ . We leave the detailed algebra for [Problem 16.4](#), and here simply state the final result:

$$L^2 = \hbar^2 \left( N(N+1) - A^\dagger A \right). \quad (16.19)$$

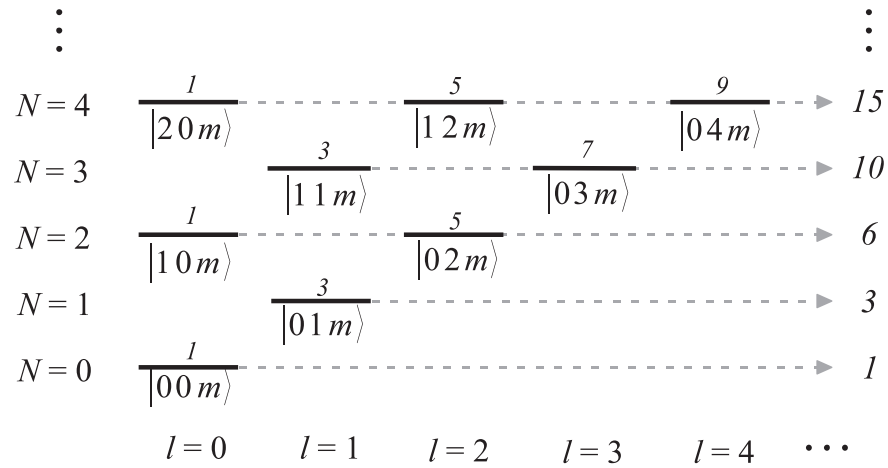
It is now straightforward to construct the states  $|nlm\rangle$ . For each choice of  $l$  and  $m$ , there is a “ladder” of states  $|0lm\rangle$ ,  $|1lm\rangle$ ,  $|2lm\rangle$ , and so on. Each state is an eigenstate of  $N$  (and thus the total energy) with eigenvalue  $N$ . Adjacent rungs of each ladder are connected by the  $A$  and  $A^\dagger$  operators. The bottom “rung” of each ladder is defined by  $A|0lm\rangle = 0$ . What is the value of  $N$  for this state? We find that

$$\begin{aligned} L^2|0lm\rangle &= \hbar^2 N(N+1)|0lm\rangle - \hbar^2 A^\dagger A|0lm\rangle, \\ l(l+1)\hbar^2|0lm\rangle &= N(N+1)\hbar^2|0lm\rangle. \end{aligned} \quad (16.20)$$

It follows that, for the bottom rung state,  $N = l$ . By applying  $A^\dagger$  (and normalizing as necessary) we obtain  $|1lm\rangle$ ,  $|2lm\rangle$  and so on. Each time we apply  $A^\dagger$ , we increase  $N$  by 2. Thus  $N = 2n + l$ , and the energy is

$$E_{nl} = \left( N + \frac{3}{2} \right) \hbar\omega = \left( 2n + l + \frac{3}{2} \right) \hbar\omega. \quad (16.21)$$

How does the overall pattern of energy levels, including degeneracy, compare with the pattern we found using Cartesian coordinates? [Figure 16.2](#) shows the arrangement. There is a “ladder” of different values of  $n$  for each  $l$ , and each rung of this ladder corresponds to  $2l + 1$  degenerate basis states differing in  $m$ . These are arranged according to the quantum number  $N = 2n + l$ . Thus, states on the same horizontal line (same  $N$ ) have the same energy.



**Fig. 16.2** Energy levels  $|nlm\rangle$  of the isotropic oscillator in 3-D, showing the degeneracy for each combination of  $n$  and  $l$ . At the right are the degeneracies for each  $N = 2n + 1$ .

The total degeneracy for each  $N$ -value is exactly as we found in the Cartesian analysis. (The eigenstates  $|nlm\rangle$  are, however, generally superpositions of the various Cartesian  $|n_x, n_y, n_z\rangle$  states. Some of the details are worked out in [Problem 16.5](#).)

## 16.3 Hydrogen

In the hydrogen atom, a single electron of charge  $-e$  moves around a nucleus (generally a proton), bound by the Coulomb attraction between them. Generalizing slightly, we consider a nucleus of arbitrary charge  $+Ze$ , where  $Z$  is the atomic number.<sup>2</sup> The potential energy function of the system is

$$U(r) = -\frac{kZe^2}{r}, \quad (16.22)$$

where  $r$  is the distance between the nucleus and the electron (the magnitude of the relative position vector) and the Coulomb constant is  $k = 8.99 \times 10^9 \text{ N m}^2/\text{C}^2$ . What are the stationary bound states and the corresponding energies for this system?

Note that  $U(r) < 0$ , with  $U(r) \rightarrow 0$  as  $r \rightarrow \infty$ . Thus, the bound stationary states will be the energy eigenstates having  $E < 0$ . From our general analysis in [Section 16.1](#), we know that we can make sure the eigenstates are at the same time eigenstates of  $L^2$  and  $L_z$ . The wave functions are of the form  $R(r)Y_{lm}(\theta, \phi)$ , where  $R(r)$  satisfies the radial equation

$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} R \right] + U(r)R = ER, \quad (\text{Re } 16.2)$$

<sup>2</sup> Thus, our analysis will cover H atoms,  $\text{He}^+$  ions,  $\text{Li}^{++}$  ions, etc.

where  $\mu$  is the relative mass of the electron with respect to the nucleus, which is nearly equal to the electron mass. This leads to

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left( E + \frac{kZe^2}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right) R = 0. \quad (16.23)$$

Since the energy is negative,  $E = -|E|$ .

To work with this equation, we employ a trick we previously used in our discussion of the quantum circular billiard system in [Section 11.5](#). We use combinations of the parameters in [Eq. 16.23](#) to construct a dimensionless radial coordinate  $\rho$ :

$$\rho = \alpha r = \sqrt{\frac{8\mu |E|}{\hbar^2}} r. \quad (16.24)$$

[Equation 16.23](#) can now be rewritten

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2} R + \left( \frac{\lambda}{\rho} - \frac{1}{4} \right) R = 0, \quad (16.25)$$

where the dimensionless parameter  $\lambda$  is

$$\lambda = \frac{kZe^2}{\hbar} \sqrt{\frac{\mu}{2|E|}}. \quad (16.26)$$

**Exercise 16.10** Confirm that the coordinate  $\rho$  and the parameter  $\lambda$  are both dimensionless. Then verify [Eq. 16.25](#).

[Equation 16.25](#) has two “kinetic” terms involving derivatives of  $R$  and three “potential” terms. To learn more about its solutions, we will consider how they behave when the coordinate  $\rho$  is very small or very large.

First, suppose that  $\rho \ll 1$ . Then the centrifugal potential term will dominate (provided  $l > 0$ ) and the other two will be negligible. If we suppose that the solution is given by a power series  $R = \sum_n c_n \rho^n$ , then the first non-zero term  $c_s \rho^s$  also dominates. Then

$$\begin{aligned} \frac{d^2 R}{d\rho^2} &= s(s-1)c_s \rho^{s-2}, \\ \frac{2}{\rho} \frac{dR}{d\rho} &= 2s c_s \rho^{s-2}, \\ \frac{l(l+1)}{\rho^2} R &= l(l+1)c_s \rho^{s-2}, \end{aligned} \quad (16.27)$$

and therefore

$$(s(s+1) - l(l+1)) c_s \rho^{s-2} = 0. \quad (16.28)$$

Either  $s = l$  or  $s = -(l+1)$ . The second possibility, however, would mean that  $R$  diverges as  $\rho \rightarrow 0$ , so we exclude it. We conclude that  $R \propto \rho^l$  close to the origin.<sup>3</sup>

<sup>3</sup> This is a pretty general fact, and should hold whenever the potential  $V(r)$  is “less singular” than  $1/\rho^2$ .



Next, consider what happens when  $\rho \rightarrow \infty$ . Then the only non-negligible terms from Eq. 16.25 yield

$$\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0. \quad (16.29)$$

The independent solutions of this equations are  $\exp(\rho/2)$  and  $\exp(-\rho/2)$ . The first solution cannot apply, because for a bound state we must have  $R \rightarrow 0$  as  $\rho \rightarrow \infty$ .

All of this motivates us to write the general solution in the form

$$R = \rho^l f(\rho) \exp\left(-\frac{\rho}{2}\right), \quad (16.30)$$

where  $f(\rho)$  is an as-yet-undetermined function. Equation 16.25 becomes an equation for  $f$ .

**Exercise 16.11** Show that Eq. 16.25 becomes

$$\frac{d^2 f}{d\rho^2} + \left(\frac{2(l+1)}{\rho} - 1\right) \frac{df}{d\rho} + \left(\frac{\lambda - (l+1)}{\rho}\right) f = 0. \quad (16.31)$$

We solve this equation by letting  $f(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$ . Equation 16.31 implies a recursion relation for the series coefficients  $a_j$ :

$$a_{j+1} = \frac{j + (l+1) - \lambda}{(j+1)(j+2(l+1))} a_j. \quad (16.32)$$

**Exercise 16.12** Check this. Along the way, you will do some “reindexing” of the sums. For example, you have to rewrite the second derivative term

$$\sum_{j=0}^{\infty} j(j-1) a_j \rho^{j-2} \quad \text{as} \quad \sum_{j=0}^{\infty} (j+1)j a_{j+1} \rho^{j-1}. \quad (16.33)$$

Explain why this is okay.

As  $k \rightarrow \infty$ , both  $\lambda$  and  $l$  become negligible. Then  $a_{j+1} \approx a_j/j$ . But this is the same asymptotic recursion relation for  $f(\rho) = \exp(\rho)$ . This looks like a serious problem, since it would mean that  $R \rightarrow \infty$  as  $\rho \rightarrow \infty$ , which is impossible for a normalized wave function.

The only way to avoid this unphysical disaster is to posit that the series for  $f(\rho)$  *terminates* at some point – that is, to insist that  $f(\rho)$  is a polynomial of finite degree. Then there exists an integer  $j$  such that  $j + (l+1) - \lambda = 0$ . This amounts to a restriction on the possible values of  $\lambda$ , namely that  $\lambda = n$ , for some integer  $n \geq l+1$ . We call  $n$  the *principal quantum number* for the system, and then rewrite Eq. 16.26 as

$$n^2 = \left(\frac{kZe^2}{\hbar}\right)^2 \frac{\mu}{2|E|}. \quad (16.34)$$

The bound state energy  $E = -|E|$  depends only on the principal quantum number  $n$ . We can write

$$E_n = - \left( \frac{\mu k^2 Z^2 e^4}{2\hbar^2} \right) \frac{1}{n^2}. \quad (16.35)$$

The boundary condition that  $R \rightarrow 0$  as  $\rho \rightarrow \infty$  forces the energy levels of the atom to be quantized according to Eq. 16.35.

**Exercise 16.13** For the actual hydrogen atom,  $Z = 1$ . Show that the constant factor in Eq. 16.35 has a value of 13.6 eV. Write down the energies of the lowest five levels of the atom, and sketch an energy-level diagram.

We can make things look a little simpler by defining a characteristic length, the *Bohr radius*  $a$ , to be

$$a = \frac{\hbar^2}{\mu k Z e^2}. \quad (16.36)$$

Then the dimensionless radial coordinate is  $\rho = 2r/na$  and

$$E_n = - \frac{kZe^2}{2a} \frac{1}{n^2}. \quad (16.37)$$

Let us summarize our results. In addition to angular momentum quantum numbers  $l$  and  $m$ , the hydrogen wave function has a principal quantum number  $n$ . We can have  $n = 1, 2, 3, \dots$ , and for a given value of  $n$  the angular momentum quantum number  $l = 0, \dots, n-1$ . As usual,  $m$  ranges over  $-l, \dots, l$ . The radial function  $R_{nl}$  depends on the quantum numbers  $n$  and  $l$ , but not  $m$ . Thus, we will have  $R_{10}, R_{20}, R_{21}, R_{30}$ , and so on. The energy eigenvalue of the state depends only on  $n$ , according to Eq. 16.35 (or 16.37). The general form of the radial function is

$$R_{nl} = A \left( \frac{r}{a} \right)^l \left( \text{polynomial in } \left( \frac{r}{a} \right) \right) \exp \left( -\frac{r}{na} \right), \quad (16.38)$$

where  $A$  is a normalization constant,  $a$  is the Bohr radius, and the polynomial function<sup>4</sup> has degree  $n - (l + 1)$ .

We can obtain a good deal of qualitative information simply by inspecting Eq. 16.38. The asymptotic ( $r \rightarrow \infty$ ) drop-off rate is determined by  $n$ , so that wave functions with higher  $n$  decrease more slowly with  $r$ . On the other hand, the behavior of the wave function near the origin is strongly influenced by  $l$ . For larger values of  $l$ , the wave function is shifted outward, away from the origin. This makes excellent sense, because a larger orbital angular momentum means a higher “centrifugal barrier” in the effective potential.

<sup>4</sup> These polynomials are well known in mathematical physics. For  $l = 0$  they are the so-called Laguerre polynomials, and for  $l > 0$  they are the associated Laguerre polynomials.

Here are the first few radial functions  $R_{nl}(r)$ :

$$\begin{aligned}
 R_{10}(r) &= 2 a^{-3/2} \exp(-r/a), \\
 R_{20}(r) &= \frac{1}{\sqrt{2}} a^{-3/2} \left( 1 - \frac{1}{2} \left( \frac{r}{a} \right) \right) \exp(-r/2a), \\
 R_{21}(r) &= \frac{1}{\sqrt{24}} a^{-3/2} \left( \frac{r}{a} \right) \exp(-r/2a), \\
 R_{30}(r) &= \frac{2}{\sqrt{27}} a^{-3/2} \left( 1 - \frac{2}{3} \left( \frac{r}{a} \right) + \frac{2}{27} \left( \frac{r}{a} \right)^2 \right) \exp(-r/3a), \\
 R_{31}(r) &= \frac{8}{27\sqrt{6}} a^{-3/2} \left( \frac{r}{a} \right) \left( 1 - \frac{1}{6} \left( \frac{r}{a} \right) \right) \exp(-r/3a), \\
 R_{32}(r) &= \frac{4}{81\sqrt{30}} a^{-3/2} \left( \frac{r}{a} \right)^2 \exp(-r/3a),
 \end{aligned} \tag{16.39}$$

where  $a$  is the Bohr radius from Eq. 16.36.

**Exercise 16.14** Compare the radial functions in Eq. 16.39 to the general form in Eq. 16.38 and identify each of the parts.

**Exercise 16.15** Why is there a factor of  $a^{-3/2}$  in each  $R_{nl}(r)$ . Hint: What are the units of the wave function?

**Exercise 16.16** Show that the radial function  $R_{20}$  is properly normalized.

Given the hydrogen stationary state wave functions  $R_{nl}(r)Y_{lm}(\theta, \phi)$ , we can compute various useful expectation values directly. However, many of these expectations can be found by other techniques, as we will now discuss.

## 16.4 Some expectations

Recall Eq. 16.6 for the radial function  $u_{nl}(r) = rR_{nl}(r)$ , which we repeat here in a slightly modified form:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u_{nl}}{dr^2} + U_{\text{eff}}(r)u_{nl} = E_{nl}u_{nl}. \tag{16.40}$$

As we saw, this is exactly the energy eigenvalue equation for a 1-D particle of mass  $\mu$  moving in the potential  $U_{\text{eff}}(r)$ , which for the hydrogen atom is

$$U_{\text{eff}}(r) = -\frac{kZe^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2}, \tag{16.41}$$

(see Eq. 16.5). The energy eigenvalues  $E_{nl}$  are given by Eq. 16.35.

Let  $|u_{nl}\rangle$  be the energy eigenstate of this equivalent 1-D problem. We can now apply the results of Section 15.7 to find certain expectation values for the hydrogen wave functions.

For instance, we can apply the Feynman–Hellmann theorem of Eq. 15.73 to the parameter  $Z$  and obtain

$$\langle u_{nl} | \left( -\frac{ke^2}{r} \right) | u_{nl} \rangle = - \left( \frac{\mu k^2 Z e^4}{\hbar^2} \right) \frac{1}{n^2}, \quad (16.42)$$

which in turn tells us that

$$\left\langle \frac{1}{r} \right\rangle = \left( \frac{\mu k Z e^2}{\hbar^2} \right) \frac{1}{n^2} = \frac{1}{n^2 a}. \quad (16.43)$$

**Exercise 16.17** Apply the Feynman–Hellmann theorem to the mass parameter  $\mu$  and obtain an expression for the average kinetic energy  $\langle K \rangle$ . (Remember, the physical kinetic energy includes one of the terms in the effective 1-D potential.)

We must apply the Feynman–Hellmann theorem with some care. For example, the angular momentum quantum number  $l$  appears as a parameter in Eq. 16.40. Applying the theorem to this parameter should yield an expectation value for  $\langle 1/r^2 \rangle$ . However, the energy  $E_{nl}$  is apparently independent of  $l$ , so we are tempted to conclude that  $\langle 1/r^2 \rangle = 0$  – a plainly absurd result. What has gone wrong?

The answer is subtle. When we solved the radial equation for the hydrogen atom, we found there must be an integer  $j$  (the degree of a polynomial) such that  $j + (l + 1) = \lambda$ , a dimensionless parameter related to the energy (defined in Eq. 16.26). The principal quantum number was the combination  $n = j + (l + 1)$ . If we now vary the  $l$  parameter continuously, the integer  $j$  remains unchanged, but not the combination  $n$ . Thus

$$\frac{dE}{dl} = -\frac{kZe^2}{2a} \frac{d}{dl} \left( \frac{1}{n^2} \right) = \frac{kZe^2}{a} \frac{1}{n^3}. \quad (16.44)$$

**Exercise 16.18** Verify this result. Then use it to show that

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2}{a^2} \frac{1}{(2l + 1)n^3}, \quad (16.45)$$

for a stationary state of the hydrogen atom.

These results can be extended in various ways. For example, suppose we wish to find the expectation  $\langle p^4 \rangle$  for the  $|nlm\rangle$  state of the hydrogen atom. At first, this seems very challenging. However, we can write this as

$$p^4 = (p^2)^2 = 4\mu^2 (H - U(r))^2, \quad (16.46)$$

with the Hamiltonian  $H$ .

**Exercise 16.19** Show that for the state  $|nlm\rangle$ ,

$$\langle p^4 \rangle = 4\mu^2 \left( E_n^2 + 2kZe^2 E_n \left\langle \frac{1}{r} \right\rangle + k^2 Z^2 e^4 \left\langle \frac{1}{r^2} \right\rangle \right), \quad (16.47)$$

where  $E_n$  is given by Eq. 16.37. Do the algebra and write  $\langle p^4 \rangle$  in terms of physical constants and the quantum numbers  $n$  and  $l$ .

Finally, we mention an extremely useful fact about the  $|nlm\rangle$  states, called *Kramer's rule*, which relates the expectations  $\langle r^k \rangle$  for various integers  $k$ . The derivation of the rule is somewhat involved, so we will merely state the rule here without giving its proof.

$$\frac{k+1}{n^2} \langle r^k \rangle - (2k+1)a \langle r^{k-1} \rangle + \frac{k}{4} \left( (2l+1)^2 - k^2 \right) a^2 \langle r^{k-2} \rangle = 0. \quad (16.48)$$

**Exercise 16.20** Verify Kramer's rule for  $k = 0$ .

## Problems

**Problem 16.1** A free particle of mass  $\mu$  moves in a *spherical box* of radius  $R$ . The wave function  $\psi = 0$  for all  $r \geq R$ , but within the box its potential is  $U = 0$ . Find the ground state energy of this particle.

**Problem 16.2** A particle moves in three dimensions subject to a delta function potential  $U(\vec{r}) = -\epsilon \delta^3(\vec{r})$ . This is a radially symmetric potential, so its ground state should be an S state. Find the ground state and its energy. Are there any other bound states?

**Problem 16.3** In this problem we adapt the variational method of [Section 15.6](#) to finding the lowest-energy solutions of the radial equation ([Eq. 16.6](#)), which we interpret as the energy eigenvalue equation for a particle moving in one dimension subject to the effective potential  $U_{\text{eff}}(r)$ . Since the radial function  $R(r) = u(r)/r \propto r^l$  as  $r \rightarrow 0$ , we choose the test function

$$u_\alpha(r) = A_\alpha r^{l+1} e^{-\alpha r}, \quad (16.49)$$

for  $r \geq 0$ . We will consider only the cases  $l = 0, 1, 2$ .

- For each  $l$ , find  $A_\alpha$  so that  $u(r)$  is properly normalized.
- Calculate the expectation values for the kinetic and centrifugal terms in the equivalent 1-D Hamiltonian.
- Suppose the actual potential  $U(r) = kr^2/2$ , the isotropic oscillator potential. Use the variational method to estimate the minimum energies for S, P, and D states. Compare your results to the exact oscillator energies.
- Do the same for the hydrogen atom potential. (The  $l = 0$  result is actually correct. Why?)

**Problem 16.4** For the isotropic oscillator, show that the angular momentum operator  $L^2$  is given by

$$L^2 = \hbar^2 \left( N(N+1) - A^\dagger A \right), \quad (\text{Re 16.19})$$

where  $N$  and  $A$  are as defined in [Section 16.2](#).

**Problem 16.5** The isotropic oscillator has radial energy eigenstates  $|nlm\rangle$  which can be written in terms of Cartesian energy eigenstates  $|n_x, n_y, n_z\rangle$ .

- (a) Write the three radial states  $|01m\rangle$  as superpositions of the Cartesian states  $|1, 0, 0\rangle$ ,  $|0, 1, 0\rangle$ , and  $|0, 0, 1\rangle$ .
- (b) Write the radial states  $|10m\rangle$  and  $|02m\rangle$  as superpositions of Cartesian basis states.

**Problem 16.6** The size of the atomic nucleus is of the order of  $10^{-4}$  times the Bohr radius  $a$ , which is why we can regard it as a point charge in our analysis. Nuclear interactions only take place over very short ranges.

Some unstable nuclei decay by *electron capture*, in which an orbital electron is absorbed by the nucleus, transforming a proton into a neutron. (A neutrino is emitted in this process.) The captured electron essentially always comes from a 1S orbital state. Why?

**Problem 16.7** Tritium ( $^3\text{H}$ ) is an unstable isotope of hydrogen, which can undergo beta decay and become helium-3 ( $^3\text{He}$ ). The decay happens so fast that the wave function of the orbiting electron is unchanged. However, an energy eigenstate for  $^3\text{H}$  ( $Z = 1$ ) is not one for  $^3\text{He}$  ( $Z = 2$ ). Suppose the electron is in its ground state in the tritium atom immediately before the decay. Calculate the probability that it will be found in the ground state of the helium atom immediately afterwards.

**Problem 16.8** Use Kramer's rule to find  $\langle r \rangle$  for the  $|nlm\rangle$  state of hydrogen. Check the result for the  $|210\rangle$  state by doing the appropriate integral.