Chapter 6

Three-Dimensional Problems

6.1 Introduction

In this chapter we examine how to solve the Schrödinger equation for spinless particles moving in three-dimensional potentials. We carry out this study in two different coordinate systems: the Cartesian system and the spherical system.

First, working within the context of Cartesian coordinates, we study the motion of a particle in different potentials: the free particle, a particle in a (three-dimensional) rectangular potential, and a particle in a harmonic oscillator potential. This study is going to be a simple generalization of the one-dimensional problems presented in Chapter 4. Unlike the one-dimensional case, three-dimensional problems often exhibit degeneracy, which occurs whenever the potential displays symmetry.

Second, using spherical coordinates, we describe the motion of a particle in spherically symmetric potentials. After presenting a general treatment, we consider several applications ranging from the free particle and the isotropic harmonic oscillator to the hydrogen atom. We conclude the chapter by calculating the energy levels of a hydrogen atom when placed in a constant magnetic field; this gives rise to the Zeeman effect.

6.2 3D Problems in Cartesian Coordinates

We examine here how to extend Schrödinger's theory of one-dimensional problems (Chapter 4) to three dimensions.

6.2.1 General Treatment: Separation of Variables

The time-dependent Schrödinger equation for a spinless particle of mass m moving under the influence of a three-dimensional potential is

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(x, y, z, t) + \hat{V}(x, y, z, t)\Psi(x, y, z) = i\hbar\frac{\partial\Psi(x, y, z, t)}{\partial t}, \tag{6.1}$$

where $\vec{\nabla}^2$ is the Laplacian, $\vec{\nabla}^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. As seen in Chapter 4, the wave function of a particle moving in a time-independent potential can be written as a product of spatial and time components:

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar}, \tag{6.2}$$

where $\psi(x, y, z)$ is the solution to the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(x, y, z) + \hat{V}(x, y, z)\psi(x, y, z) = E\psi(x, y, z), \tag{6.3}$$

which is of the form $\hat{H}\psi = E\psi$.

This partial differential equation is generally difficult to solve. But, for those cases where the potential $\hat{V}(x, y, z)$ separates into the sum of three independent, one-dimensional terms (which should not be confused with a vector)

$$V(x, y, z) = V_x(x) + V_y(y) + V_z(z), \tag{6.4}$$

we can solve (6.3) by means of the technique of *separation of variables*. This technique consists of separating the three-dimensional Schrödinger equation (6.3) into three independent one-dimensional Schrödinger equations. Let us examine how to achieve this. Note that (6.3), in conjunction with (6.4), can be written as

$$\left[\hat{H}_x + \hat{H}_y + \hat{H}_z\right]\psi(x, y, z) = E\psi(x, y, z), \tag{6.5}$$

where $\hat{H}_x$ is given by

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x); \tag{6.6}$$

the expressions for $\hat{H}_y$ and $\hat{H}_z$ are analogous.

As $\hat{V}(x, y, z)$ separates into three independent terms, we can also write $\psi(x, y, z)$ as a product of three functions of a single variable each:

$$\psi(x, y, z) = X(x)Y(y)Z(z). \tag{6.7}$$

Substituting (6.7) into (6.5) and dividing by $X(x)Y(y)Z(z)$, we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + V_x(x)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + V_y(y)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} + V_z(z)\right] = E. \tag{6.8}$$

Since each expression in the square brackets depends on only one of the variables x, y, z, and since the sum of these three expressions is equal to a constant, E, each separate expression must then be equal to a constant such that the sum of these three constants is equal to E. For instance, the x-dependent expression is given by

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_x(x)\right]X(x) = E_xX(x). \tag{6.9}$$

Similar equations hold for the y and z coordinates, with

$$E_x + E_y + E_z = E. \tag{6.10}$$

The separation of variables technique consists in essence of reducing the three-dimensional Schrödinger equation (6.3) into three separate one-dimensional equations (6.9).

6.2.2 The Free Particle

In the simple case of a free particle, the Schrödinger equation (6.3) reduces to three equations similar to (6.9) with $V_x = 0$, $V_y = 0$, and $V_z = 0$. The x-equation can be obtained from (6.9):

$$\frac{d^2 X(x)}{dx^2} = -k_x^2 X(x), \tag{6.11}$$

where $k_x^2 = 2mE_x/\hbar^2$, and hence $E_x = \hbar^2 k_x^2/(2m)$. As shown in Chapter 4, the normalized solutions to (6.11) are plane waves

$$X(x) = \frac{1}{\sqrt{2\pi}} e^{ik_x x}. \tag{6.12}$$

Thus, the solution to the three-dimensional Schrödinger equation (6.3) is given by

$$\psi_{\vec{k}}(x, y, z) = (2\pi)^{-3/2} e^{ik_x x} e^{ik_y y} e^{ik_z z} = (2\pi)^{-3/2} e^{i\vec{k}\cdot\vec{r}}, \tag{6.13}$$

where $\vec{k}$ and $\vec{r}$ are the wave and position vectors of the particle, respectively. As for the total energy E, it is equal to the sum of the eigenvalues of the three one-dimensional equations (6.11):

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m}\vec{k}^2. \tag{6.14}$$

Note that, since the energy (6.14) depends only on the magnitude of $\vec{k}$, all different orientations of $\vec{k}$ (obtained by varying k_x, k_y, k_z) subject to the condition

$$|\vec{k}| = \sqrt{k_x^2 + k_y^2 + k_z^2} = constant \tag{6.15}$$

generate different eigenfunctions (6.13) without a change in the energy. As the total number of orientations of $\vec{k}$ which preserve its magnitude is infinite, the energy of a free particle is *infinitely degenerate*.

Note that the solutions to the time-dependent Schrödinger equation (6.1) are obtained by substituting (6.13) into (6.2):

$$\Psi_{\vec{k}}(\vec{r}, t) = \psi(\vec{r}) e^{-i\omega t} = (2\pi)^{-3/2} e^{i(\vec{k}\cdot\vec{r} - \omega t)}, \tag{6.16}$$

where $\omega = E/\hbar$; this represents a propagating wave with wave vector $\vec{k}$. The orthonormality condition of this wave function is expressed by

$$\int \Psi_{\vec{k}'}^*(\vec{r}, t)\Psi_{\vec{k}}(\vec{r}, t)\, d^3r = \int \psi_{\vec{k}'}^*(\vec{r})\psi_{\vec{k}}(\vec{r})\, d^3r = (2\pi)^{-3} \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d^3r = \delta(\vec{k} - \vec{k}'), \tag{6.17}$$

which can be written in Dirac's notation as

$$\langle \Psi_{\vec{k}'}(t) | \Psi_{\vec{k}}(t) \rangle = \langle \psi_{\vec{k}'} | \psi_{\vec{k}} \rangle = \delta(\vec{k} - \vec{k}'). \tag{6.18}$$

The free particle can be represented, as seen in Chapter 3, by a wave packet (a superposition of wave functions corresponding to the various wave vectors):

$$\Psi(\vec{r}, t) = (2\pi)^{-3/2} \int A(\vec{k}, t)\Psi_{\vec{k}}(\vec{r}, t)\, d^3k = (2\pi)^{-3/2} \int A(\vec{k}, t) e^{i(\vec{k}\cdot\vec{r} - \omega t)} d^3k, \tag{6.19}$$

where $A(\vec{k}, t)$ is the Fourier transform of $\Psi(\vec{r}, t)$:

$$A(\vec{k}, t) = (2\pi)^{-3/2} \int \Psi(\vec{r}, t) e^{-i(\vec{k}\cdot\vec{r}-\omega t)} d^3r. \tag{6.20}$$

As seen in Chapters 1 and 4, the position of the particle can be represented classically by the center of the wave packet.

6.2.3 The Box Potential

We are going to begin with the rectangular box potential, which has no symmetry, and then consider the cubic potential, which displays a great deal of symmetry, since the xyz axes are equivalent.

6.2.3.1 The Rectangular Box Potential

Consider first the case of a spinless particle of mass m confined in a *rectangular* box of sides $a,\ b,\ c$:

$$V(x, y, z) = \begin{cases} 0, & 0 < x < a,\ 0 < y < b,\ 0 < z < c, \\ \infty, & \text{elsewhere}, \end{cases} \tag{6.21}$$

which can be written as $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$, with

$$V_x(x) = \begin{cases} 0, & 0 < x < a, \\ \infty, & \text{elsewhere}; \end{cases} \tag{6.22}$$

the potentials $V_y(y)$ and $V_z(z)$ have similar forms.

The wave function $\psi(x, y, z)$ must vanish at the walls of the box. We have seen in Chapter 4 that the solutions for this potential are of the form

$$X(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x\pi}{a}x\right), \qquad n_x = 1, 2, 3, \ldots, \tag{6.23}$$

and the corresponding energy eigenvalues are

$$E_{n_x} = \frac{\hbar^2\pi^2}{2ma^2} n_x^2. \tag{6.24}$$

From these expressions we can write the normalized three-dimensional eigenfunctions and their corresponding energies:

$$\boxed{\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{abc}}\ \sin\left(\frac{n_x\pi}{a}x\right) \sin\left(\frac{n_y\pi}{b}y\right) \sin\left(\frac{n_z\pi}{c}z\right),} \tag{6.25}$$

$$\boxed{E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right).} \tag{6.26}$$

Table 6.1 Energy levels and their degeneracies for the cubic potential, with $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$.

$E_{n_x n_y n_z}/E_1$	$(n_x,\ n_y,\ n_z)$	g_n
3	(111)	1
6	(211), (121), (112)	3
9	(221), (212), (122)	3
11	(311), (131), (113)	3
12	(222)	1
14	(321), (312), (231), (213), (132), (123)	6

6.2.3.2 The Cubic Potential

For the simpler case of a *cubic* box of side L, the energy expression can be inferred from (6.26) by substituting $a = b = c = L$:

$$\boxed{E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2), \qquad n_x,\ n_y,\ n_z = 1, 2, 3, \ldots .} \tag{6.27}$$

The ground state corresponds to $n_x = n_y = n_z = 1$; its energy is given by

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2} = 3E_1, \tag{6.28}$$

where, as shown in Chapter 4, $E_1 = \pi^2\hbar^2/(2mL^2)$ is the zero-point energy of a particle in a one-dimensional box. Thus, the zero-point energy for a particle in a three-dimensional box is three times that in a one-dimensional box. The factor 3 can be viewed as originating from the fact that we are confining the particle symmetrically in all three dimensions.

The first excited state has three possible sets of quantum numbers $(n_x,\ n_y,\ n_z) = (2, 1, 1)$, $(1, 2, 1)$, $(1, 1, 2)$ corresponding to three different states $\psi_{211}(x, y, z)$, $\psi_{121}(x, y, z)$, and $\psi_{112}(x, y, z)$, where

$$\psi_{211}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right); \tag{6.29}$$

the expressions for $\psi_{121}(x, y, z)$ and $\psi_{112}(x, y, z)$ can be inferred from $\psi_{211}(x, y, z)$. Notice that all three states have the same energy:

$$E_{211} = E_{121} = E_{112} = 6\frac{\pi^2\hbar^2}{2mL^2} = 6E_1. \tag{6.30}$$

The first excited state is thus threefold *degenerate*.

Degeneracy occurs only when there is a symmetry in the problem. For the present case of a particle in a cubic box, there is a great deal of symmetry, since all three dimensions are equivalent. Note that for the rectangular box, there is no degeneracy since the three dimensions are not equivalent. Moreover, degeneracy did not exist when we treated one-dimensional problems in Chapter 4, for they give rise to only one quantum number.

The second excited state also has three different states, and hence it is threefold degenerate; its energy is equal to $9E_1$: $E_{221} = E_{212} = E_{122} = 9E_1$.

The energy spectrum is shown in Table 6.1, where every nth level is characterized by its energy, its quantum numbers, and its degeneracy g_n.

6.2.4 The Harmonic Oscillator

We are going to begin with the anisotropic oscillator, which displays no symmetry, and then consider the isotropic oscillator where the xyz axes are all equivalent.

6.2.4.1 The Anisotropic Oscillator

Consider a particle of mass m moving in a three-dimensional anisotropic oscillator potential

$$\hat{V}(\hat{x},\hat{y},\hat{z}) = \frac{1}{2}m\omega_x^2\hat{X}^2 + \frac{1}{2}m\omega_y^2\hat{Y}^2 + \frac{1}{2}m\omega_z^2\hat{Z}^2. \tag{6.31}$$

Its Schrödinger equation separates into three equations similar to (6.9):

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} + \frac{1}{2}m\omega_x x^2 X(x) = E_x X(x), \tag{6.32}$$

with similar equations for $Y(y)$ and $Z(z)$. The eigenenergies corresponding to the potential (6.31) can be expressed as

$$\boxed{E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y + \left(n_z + \frac{1}{2}\right)\hbar\omega_z,} \tag{6.33}$$

with $n_x, n_y, n_z = 0, 1, 2, 3, \ldots$. The corresponding stationary states are

$$\psi_{n_x n_y n_z}(x,y,z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z), \tag{6.34}$$

where $X_{n_x}(x)$, $Y_{n_y}(y)$, and $Z_{n_z}(z)$ are one-dimensional harmonic oscillator wave functions. These states are not degenerate, because the potential (6.31) has no symmetry (it is anisotropic).

6.2.4.2 The Isotropic Harmonic Oscillator

Consider now an *isotropic* harmonic oscillator potential. Its energy eigenvalues can be inferred from (6.33) by substituting $\omega_x = \omega_y = \omega_z = \omega$,

$$\boxed{E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega.} \tag{6.35}$$

Since the energy depends on the sum of n_x, n_y, n_z, any set of quantum numbers having the same sum will represent states of equal energy.

The ground state, whose energy is $E_{000} = 3\hbar\omega/2$, is not degenerate. The first excited state is threefold degenerate, since there are three different states, ψ_{100}, ψ_{010}, ψ_{001}, that correspond to the same energy $5\hbar\omega/2$. The second excited state is sixfold degenerate; its energy is $7\hbar\omega/2$.

In general, we can show that the degeneracy g_n of the nth excited state, which is equal to the number of ways the nonnegative integers n_x, n_y, n_z may be chosen to total to n, is given by

$$\boxed{g_n = \frac{1}{2}(n+1)(n+2),} \tag{6.36}$$

where $n = n_x + n_y + n_z$. Table 6.2 displays the first few energy levels along with their degeneracies.

Table 6.2 Energy levels and their degeneracies for an isotropic harmonic oscillator.

n	$2E_n/(\hbar\omega)$	$(n_x n_y n_z)$	g_n
0	3	(000)	1
1	5	(100), (010), (001)	3
2	7	(200), (020), (002) (110), (101), (011)	6
3	9	(300), (030), (003) (210), (201), (021) (120), (102), (012) (111)	10

Example 6.1 (Degeneracy of a harmonic oscillator)
Show how to derive the degeneracy relation (6.36).

Solution
For a fixed value of n, the degeneracy g_n is given by the number of ways of choosing n_x, n_y, and n_z so that $n = n_x + n_y + n_z$.

For a fixed value of n_x, the number of ways of choosing n_y and n_z so that $n_y + n_z = n - n_x$ is given by $(n - n_x + 1)$; this can be shown as follows. For a given value of n_x, the various permissible values of (n_y, n_z) are given by $(n_y, n_z) = (0, n - n_x)$, $(1, n - n_x - 1)$, $(2, n - n_x - 2)$, $(3, n - n_x - 3), \ldots, (n - n_x - 3, 3)$, $(n - n_x - 2, 2)$, $(n - n_x - 1, 1)$, and $(n - n_x, 0)$. In all, there are $(n - n_x + 1)$ sets of (n_y, n_z) so that $n_y + n_z = n - n_x$. Now, since the values of n_x can vary from 0 to n, the degeneracy is then given by

$$g_n = \sum_{n_x=0}^{n} (n - n_x + 1) = (n+1) \sum_{n_x=0}^{n} 1 - \sum_{n_x=0}^{n} n_x = (n+1)^2 - \frac{1}{2} n(n+1) = \frac{1}{2}(n+1)(n+2). \tag{6.37}$$

A more primitive way of calculating this series is to use Gauss's method: simply write the series $\sum_{n_x=0}^{n}(n - n_x + 1)$ in the following two equivalent forms:

$$g_n = (n+1) + n + (n-1) + (n-2) + \cdots + 4 + 3 + 2 + 1, \tag{6.38}$$

$$g_n = 1 + 2 + 3 + 4 + \cdots + (n-2) + (n-1) + n + (n+1). \tag{6.39}$$

Since both of these two series contain $(n + 1)$ terms each, a term by term addition of these relations yields

$$\begin{aligned} 2g_n &= (n+2) + (n+2) + (n+2) + \cdots + (n+2) + (n+2) + (n+2) \\ &= (n+1)(n+2); \end{aligned} \tag{6.40}$$

hence $g_n = \frac{1}{2}(n + 1)(n + 2)$.

6.3 3D Problems in Spherical Coordinates

6.3.1 Central Potential: General Treatment

In this section we study the structure of the Schrödinger equation for a particle of mass[1] M moving in a *spherically symmetric* potential

$$V(\vec{r}) = V(r), \tag{6.41}$$

which is also known as the *central* potential.

The time-independent Schrödinger equation for this particle, of momentum $-i\hbar\vec{\nabla}$ and position vector $\vec{r}$, is

$$\left[-\frac{\hbar^2}{2M}\nabla^2 + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}). \tag{6.42}$$

Since the Hamiltonian is spherically symmetric, we are going to use the spherical coordinates (r, θ, φ) which are related to their Cartesian counterparts by

$$x = r\sin\theta\cos\varphi, \qquad y = r\sin\theta\sin\varphi, \qquad z = r\cos\theta. \tag{6.43}$$

The Laplacian ∇^2 separates into a radial part ∇_r^2 and an angular part ∇_Ω^2 as follows (see Chapter 5):

$$\nabla^2 = \nabla_r^2 - \frac{1}{\hbar^2 r^2}\nabla_\Omega^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{\vec{L}}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\hat{\vec{L}}^2, \tag{6.44}$$

where $\hat{\vec{L}}$ is the orbital angular momentum with

$$\hat{\vec{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{6.45}$$

In spherical coordinates the Schrödinger equation therefore takes the form

$$\left[-\frac{\hbar^2}{2M}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2Mr^2}\hat{\vec{L}}^2 + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}). \tag{6.46}$$

The first term of this equation can be viewed as the *radial* kinetic energy

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{\partial^2}{\partial r^2}r = \frac{\hat{P}_r^2}{2M}, \tag{6.47}$$

since the radial momentum operator is given by the Hermitian form[2]

$$\hat{P}_r = \frac{1}{2}\left[\left(\frac{\vec{r}}{r}\right)\cdot\hat{\vec{P}} + \hat{\vec{P}}\cdot\left(\frac{\vec{r}}{r}\right)\right] = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \equiv -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r. \tag{6.48}$$

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[1] Throughout this section we will designate the mass of the particle by a capital M to avoid any confusion with the azimuthal quantum number m.

[2] Note that we can show that the commutator between the position operator, $\hat{r}$, and the radial momentum operator, $\hat{p}_r$, is given by: $[\hat{r},\ \hat{p}_r] = i\hbar$ (the proof is left as an exercise).

The second term $\hat{\vec{L}}^2/(2Mr^2)$ of (6.46) can be identified with the *rotational* kinetic energy, for this term is generated from a "pure" rotation of the particle about the origin (i.e., no change in the radial variable r, where Mr^2 is its moment of inertia with respect to the origin).

Now, since $\hat{\vec{L}}^2$ as shown in (6.45) does not depend on r, it commutes with both $\hat{V}(r)$ and the radial kinetic energy; hence it also commutes with the Hamiltonian $\hat{H}$. In addition, since $\hat{L}_z$ commutes with $\hat{\vec{L}}^2$, the three operators $\hat{H}$, $\hat{\vec{L}}^2$, and L_z mutually commute:

$$[\hat{H},\ \hat{\vec{L}}^2] = [\hat{H},\ \hat{L}_z] = 0. \tag{6.49}$$

Thus $\hat{H}$, $\hat{\vec{L}}^2$, and $\hat{L}_z$ have common eigenfunctions. We have seen in Chapter 5 that the simultaneous eigenfunctions of $\hat{\vec{L}}^2$ and $\hat{L}_z$ are given by the spherical harmonics $Y_{lm}(\theta, \varphi)$:

$$\hat{\vec{L}}^2 Y_{lm}(\theta, \varphi) \quad = \quad l(l+1)\hbar^2 Y_{lm}(\theta, \varphi), \tag{6.50}$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) \quad = \quad m\hbar Y_{lm}(\theta, \varphi). \tag{6.51}$$

Since the Hamiltonian in (6.46) is a sum of a radial part and an angular part, we can look for solutions that are products of a radial part and an angular part, where the angular part is simply the spherical harmonic $Y_{lm}(\theta, \varphi)$:

$$\psi(\vec{r}) = \langle \vec{r} \mid nlm \rangle = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi). \tag{6.52}$$

Note that the orbital angular momentum of a system moving in a central potential is conserved, since, as shown in (6.49), it commutes with the Hamiltonian.

The radial wave function $R_{nl}(r)$ has yet to be found. The quantum number n is introduced to identify the eigenvalues of $\hat{H}$:

$$\hat{H} \mid nlm \rangle = E_n \mid nlm \rangle. \tag{6.53}$$

Substituting (6.52) into (6.46) and using the fact that $\psi_{nlm}(r, \theta, \varphi)$ is an eigenfunction of $\hat{\vec{L}}^2$ with eigenvalue $l(l+1)\hbar^2$, then dividing through by $R_{nl}(r)Y_{lm}(\theta, \varphi)$ and multiplying by $2Mr^2$, we end up with an equation where the radial and angular degrees of freedom are separated:

$$\left[-\hbar^2 \frac{r}{R_{nl}} \frac{\partial^2}{\partial r^2}(rR_{nl}) + 2Mr^2(V(r) - E)\right] + \left[\frac{\hat{\vec{L}}^2 Y_{lm}(\theta, \varphi)}{Y_{lm}(\theta, \varphi)}\right] = 0. \tag{6.54}$$

The terms inside the first square bracket are independent of θ and φ and those of the second are independent of r. They must then be separately equal to constants and their sum equal to zero. The second square bracket is nothing but (6.50), the eigenvalue equation of $\hat{\vec{L}}^2$; hence it is equal to $l(l+1)\hbar^2$. As for the first bracket, it must be equal to $-l(l+1)\hbar^2$; this leads to an equation known as the *radial equation* for a central potential:

$$\boxed{-\frac{\hbar^2}{2M}\frac{d^2}{dr^2}(rR_{nl}(r)) + \left[V(r) + \frac{l(l+1)\hbar^2}{2Mr^2}\right](rR_{nl}(r)) = E_n\,(rR_{nl}(r))\,.} \tag{6.55}$$

Note that (6.55), which gives the energy levels of the system, does not depend on the azimuthal quantum number m. Thus, the energy E_n is $(2l+1)$-fold *degenerate*. This is due to the fact that, for a given l, there are $(2l+1)$ different eigenfunctions ψ_{nlm} (i.e., $\psi_{nl\ -l}$, $\psi_{nl\ -l+1}, \ldots, \psi_{nl\ l-1}$, $\psi_{nl\ l}$) which correspond to the same eigenenergy E_n. This degeneracy property is peculiar to central potentials.

Note that (6.55) has the structure of a one-dimensional equation in r,

$$-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2}+\left[V(r)+\frac{l(l+1)\hbar^2}{2Mr^2}\right]U_{nl}(r)=E_nU_{nl}(r), \tag{6.56}$$

or

$$\boxed{-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2}+V_{\mathit{eff}}(r)U_{nl}(r)=E_nU_{nl}(r),} \tag{6.57}$$

whose solutions give the energy levels of the system. The wave function $U_{nl}(r)$ is given by

$$U_{nl}(r)=rR_{nl}(r) \tag{6.58}$$

and the potential by

$$V_{\mathit{eff}}(r)=V(r)+\frac{l(l+1)\hbar^2}{2Mr^2}, \tag{6.59}$$

which is known as the *effective* or *centrifugal* potential, where $V(r)$ is the central potential and $l(l+1)\hbar^2/2Mr^2$ is a repulsive or centrifugal potential, associated with the orbital angular momentum, which tends to repel the particle away from the center. As will be seen later, in the case of atoms, $V(r)$ is the Coulomb potential resulting from the attractive forces between the electrons and the nucleus. Notice that although (6.57) has the structure of a one-dimensional eigenvalue equation, it differs from the one-dimensional Schrödinger equation in one major aspect: the variable r cannot have negative values, for it varies from $r=0$ to $r\to+\infty$. We must therefore require the wave function $\psi_{nlm}(r,\theta,\varphi)$ to be finite for all values of r between 0 and ∞, notably for $r=0$. But if $R_{nl}(0)$ is finite, $rR_{nl}(r)$ must vanish at $r=0$, i.e.,

$$\lim_{r\to 0}[rR_{nl}(r)]=U_{nl}(0)=0. \tag{6.60}$$

Thus, to make the radial equation (6.57) equivalent to a one-dimensional eigenvalue problem, we need to assume that the particle's potential is given by the effective potential $V_{\mathit{eff}}(r)$ for $r>0$ and by an infinite potential for $r\leq 0$.

For the eigenvalue equation (6.57) to describe bound states, the potential $V(r)$ must be attractive (i.e., negative) because $l(l+1)\hbar^2/(2Mr^2)$ is repulsive. Figure 6.1 shows that, as l increases, the depth of $V_{\mathit{eff}}(r)$ decreases and its minimum moves farther away from the origin. The farther the particle from the origin, the less bound it will be. This is due to the fact that as the particle's angular momentum increases, the particle becomes less and less bound.

In summary, we want to emphasize the fact that, for spherically symmetric potentials, the Schrödinger equation (6.46) reduces to a trivial angular equation (6.50) for $\hat{\vec{L}}^2$ and to a one-dimensional radial equation (6.57).

Remark

When a particle has orbital and spin degrees of freedom, its total wave function $\mid\Psi\rangle$ consists of a product of two parts: a spatial part, $\psi(\vec{r})$, and a spin part, $\mid s,\ m_s\rangle$; that is, $\mid\Psi\rangle=\mid\psi\rangle\mid s,\ m_s\rangle$. In the case of an electron moving in a central field, besides the quantum numbers

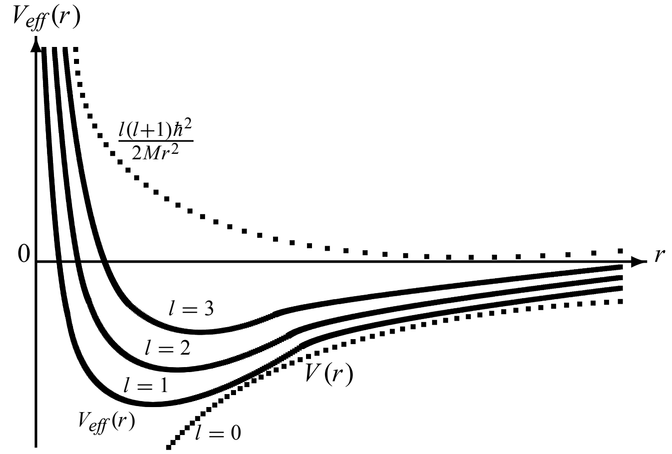

Figure 6.1 The effective potential $V_{eff}(r) = V(r)+\hbar^2 l(l+1)/(2Mr^2)$ corresponding to several values of l: $l = 0, 1, 2, 3$; $V(r)$ is an attractive central potential, while $\hbar^2 l(l+1)/(2Mr^2)$ is a repulsive (centrifugal) potential.

n, l, m_l, a complete description of its state would require a fourth quantum number, the spin quantum number m_s: $\mid nlm_l m_s\rangle = \mid nlm_l\rangle \mid s,\ m_s\rangle$; hence

$$\Psi_{n,l,m_l,m_s}(\vec{r}) = \psi_{nlm_l}(\vec{r}) \mid s,\ m_s\rangle = R_{nl}(r)Y_{lm_l}(\theta,\varphi) \mid s,\ m_s\rangle. \qquad (6.61)$$

Since the spin does not depend on the spatial degrees of freedom, the spin operator does not act on the spatial wave function $\psi_{nlm_l}(\vec{r})$ but acts only on the spin part $|s,\ m_s\rangle$; conversely, $\hat{\vec{L}}$ acts only the spatial part.

6.3.2 The Free Particle in Spherical Coordinates

In what follows we want to apply the general formalism developed above to study the motion of a free particle of mass M and energy $E_k = \hbar^2 k^2/(2M)$, where k is the wave number ($k = |\vec{k}|$). The Hamiltonian $\hat{H} = -\hbar^2\nabla^2/(2M)$ of a free particle commutes with $\hat{\vec{L}}^2$ and $\hat{L}_z$. Since $V(r) = 0$ the Hamiltonian of a free particle is *rotationally invariant*. The free particle can then be viewed as a special case of central potentials. We have shown above that the radial and angular parts of the wave function can be separated, $\psi_{klm}(r,\theta,\varphi) = \langle r\theta\varphi \mid klm\rangle = R_{kl}(r)Y_{lm}(\theta,\varphi)$.

The radial equation for a free particle is obtained by setting $V(r) = 0$ in (6.55):

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}(rR_{kl}(r)) + \frac{l(l+1)\hbar^2}{2Mr^2}R_{kl}(r) = E_k R_{kl}(r), \qquad (6.62)$$

which can be rewritten as

$$-\frac{1}{r}\frac{d^2}{dr^2}(rR_{kl}(r)) + \frac{l(l+1)}{r^2}R_{kl}(r) = k^2 R_{kl}(r), \qquad (6.63)$$

where $k^2 = 2ME_k/\hbar^2$.

Table 6.3 First few spherical Bessel and Neumann functions.

Bessel functions $j_l(r)$	Neumann functions $n_l(r)$
$j_0(r) = \frac{\sin r}{r}$	$n_0(r) = -\frac{\cos r}{r}$
$j_1(r) = \frac{\sin r}{r^2} - \frac{\cos r}{r}$	$n_1(r) = -\frac{\cos r}{r^2} - \frac{\sin r}{r}$
$j_2(r) = \left(\frac{3}{r^3} - \frac{1}{r}\right)\sin r - \frac{3\cos r}{r^2}$	$n_2(r) = -\left(\frac{3}{r^3} - \frac{1}{r}\right)\cos r - \frac{3}{r^2}\sin r$

Using the change of variable $\rho = kr$, we can reduce this equation to

$$\frac{d^2\mathcal{R}_l(\rho)}{d\rho^2} + \frac{2}{\rho}\frac{d\mathcal{R}_l(\rho)}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]\mathcal{R}_l(\rho) = 0, \tag{6.64}$$

where $\mathcal{R}_l(\rho) = \mathcal{R}_l(kr) = R_{kl}(r)$. This differential equation is known as the *spherical Bessel equation*. The general solutions to this equation are given by an independent linear combination of the *spherical Bessel functions* $j_l(\rho)$ and the *spherical Neumann functions* $n_l(\rho)$:

$$\mathcal{R}_l(\rho) = A_l j_l(\rho) + B_l n_l(\rho), \tag{6.65}$$

where $j_l(\rho)$ and $n_l(\rho)$ are given by

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\sin\rho}{\rho}, \qquad n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\cos\rho}{\rho}. \tag{6.66}$$

The first few spherical Bessel and Neumann functions are listed in Table 6.3 and their shapes are displayed in Figure 6.2.

Expanding $\sin\rho/\rho$ and $\cos\rho/\rho$ in a power series of ρ, we see that the functions $j_l(\rho)$ and $n_l(\rho)$ reduce for small values of ρ (i.e., near the origin) to

$$j_l(\rho) \simeq \frac{2^l l!}{(2l+1)!}\rho^l, \qquad n_l(\rho) \simeq -\frac{(2l)!}{2^l l!}\rho^{-l-1}, \qquad \rho \ll 1, \tag{6.67}$$

and for large values of ρ to

$$j_l(\rho) \simeq \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right), \qquad n_l(\rho) \simeq -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right), \qquad \rho \gg 1. \tag{6.68}$$

Since the Neumann functions $n_l(\rho)$ diverge at the origin, and since the wave functions ψ_{klm} are required to be finite everywhere in space, the functions $n_l(\rho)$ are unacceptable solutions to the problem. Hence only the spherical Bessel functions $j_l(kr)$ contribute to the eigenfunctions of the free particle:

$$\psi_{klm}\,(r, \theta, \psi) = j_l(kr)Y_{lm}(\theta, \varphi), \tag{6.69}$$

where $k = \sqrt{2ME_k}/\hbar$. As shown in Figure 6.2, the amplitude of the wave functions becomes smaller and smaller as r increases. At large distances, the wave functions are represented by spherical waves.

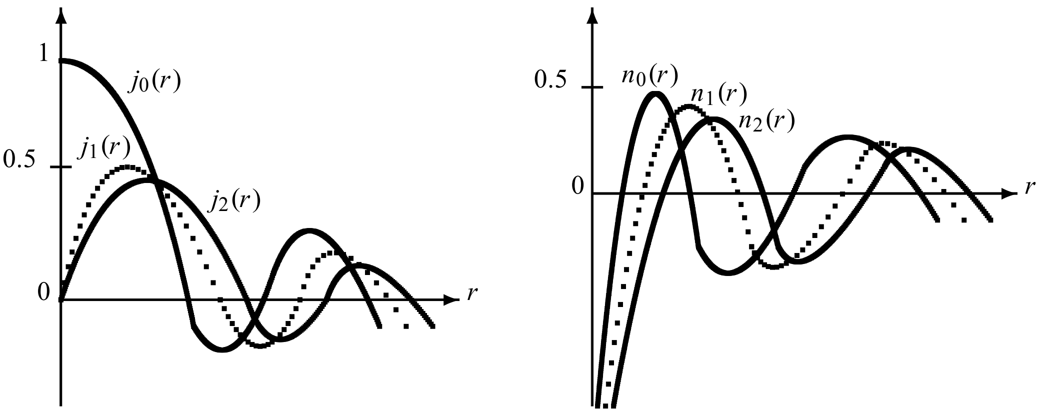

Figure 6.2 Spherical Bessel functions $j_l(r)$ and spherical Neumann functions $n_l(r)$; only the Bessel functions are finite at the origin.

Note that, since the index k in $E_k = \hbar^2 k^2/(2M)$ varies *continuously*, the energy spectrum of a free particle is *infinitely degenerate*. This is because all orientations of $\vec{k}$ in space correspond to the same energy.

Remark

We have studied the free particle within the context of Cartesian and spherical coordinate systems. Whereas the energy is given in both coordinate systems by the same expression, $E_k = \hbar^2 k^2/(2M)$, the wave functions are given in Cartesian coordinates by *plane waves* $e^{i\vec{k}\cdot\vec{r}}$ (see (6.13)) and in spherical coordinates by *spherical waves* $j_l(kr)Y_{lm}(\theta, \varphi)$ (see (6.69)). We can, however, show that both sets of wave functions are equivalent, since we can express a plane wave $e^{i\vec{k}\cdot\vec{r}}$ in terms of spherical wave states $j_l(kr)Y_{lm}(\theta, \varphi)$. In particular, we can generate plane waves from a linear combination of spherical states that have the same k but different values of l and m:

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm}\, j_l(kr)Y_{lm}(\theta, \varphi). \tag{6.70}$$

The problem therefore reduces to finding the expansion coefficients a_{lm}. For instance, in the case where $\vec{k}$ is along the z-axis, $m = 0$, we can show that

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l\, (2l+1) j_l\, (kr) P_l(\cos\theta), \tag{6.71}$$

where $P_l(\cos\theta)$ are the Legendre polynomials, with $Y_{l0}(\theta, \varphi) \sim P_l(\cos\theta)$. The wave functions $\psi_{klm}(r, \theta, \varphi) = j_l(kr)Y_{lm}(\theta, \varphi)$ describe a free particle of energy E_k, with angular momentum l, but they give no information on the linear momentum $\vec{p}$ (ψ_{klm} is an eigenstate of $\hat{H}$, $\hat{\vec{L}}^2$, and $\hat{L}_z$ but not of $\hat{\vec{P}}$). On the other hand, the plane wave $e^{i\vec{k}\cdot\vec{r}}$ which is an eigenfunction of $\hat{H}$ and $\hat{\vec{P}}$, but not of $\hat{\vec{L}}^2$ nor of $\hat{L}_z$, gives no information about the particle's angular momentum. That is, plane waves describe states with well-defined linear momenta but poorly defined angular momenta. Conversely, spherical waves describe states with well-defined angular momenta but poorly defined linear momenta.

6.3.3 The Spherical Square Well Potential

Consider now the problem of a particle of mass M in an attractive square well potential

$$V(r) = \begin{cases} -V_0, & r < a, \\ 0, & r > a. \end{cases} \tag{6.72}$$

Let us consider the cases $0 < r < a$ and $r > a$ separately.

6.3.3.1 Case where $0 < r < a$

Inside the well, $0 < r < a$, the time-independent Schrödinger equation for this particle can be obtained from (6.55):

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}(rR_l(r)) + \frac{l(l+1)\hbar^2}{2Mr^2}R_l(r) = (E + V_0)R_l(r). \tag{6.73}$$

Using the change of variable $\rho = k_1 r$, where k_1 is now given by $k_1 = \sqrt{2M(E+V_0)}/\hbar$, we see that (6.73) reduces to the spherical Bessel differential equation (6.64). As in the case of a free particle, the radial wave function must be finite everywhere, and is given as follows in terms of the spherical Bessel functions $j_l(k_1 r)$:

$$R_l(r) = Aj_l(k_1 r) = Aj_l\left(\frac{\sqrt{2M(E+V_0)}}{\hbar}r\right), \qquad \text{for} \qquad r < a, \tag{6.74}$$

where A is a normalization constant.

6.3.3.2 Case where $r > a$

Outside the well, $r > a$, the particle moves freely; its Schrödinger equation is (6.62):

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}(rR_{kl}(r)) + \frac{l(l+1)\hbar^2}{2Mr^2}R_{kl}(r) = E_k R_{kl}(r) \qquad (r > a). \tag{6.75}$$

Two possibilities arise here, depending on whether the energy is negative or positive.

- The negative energy case corresponds to bound states (i.e., to a discrete energy spectrum). The general solutions of (6.75) are similar to those of (6.63), but k is now an imaginary number; that is, we must replace k by ik_2 and, hence, the solutions are given by linear combinations of $j_l(ik_2 r)$ and $n_l(ik_2 r)$:

  $$R_l(ik_2 r) = B\left[j_l(ik_2 r) \pm n_l(ik_2 r)\right], \tag{6.76}$$

  where B is a normalization constant, with $k_2 = \sqrt{-2ME}/\hbar$. **Note:** Linear combinations of $j_l(\rho)$ and $n_l(\rho)$ can be expressed in terms of the *spherical Hankel functions* of the first kind, $h_l^{(1)}(\rho)$, and the second kind, $h_l^{(2)}(\rho)$, as follows:

  $$h_l^{(1)}(\rho) = j_l(\rho) + in_l(\rho), \tag{6.77}$$

  $$h_l^{(2)}(\rho) = j_l(\rho) - in_l(\rho) = \left(h_l^{(1)}(\rho)\right)^*. \tag{6.78}$$

The first few spherical Hankel functions of the first kind are

$$h_0^{(1)}(\rho) = -i\frac{e^{i\rho}}{\rho}, \quad h_1^{(1)}(\rho) = -\left(\frac{1}{\rho} + \frac{i}{\rho^2}\right)e^{i\rho}, \quad h_2^{(1)}(\rho) = \left(\frac{i}{\rho} - \frac{3}{\rho^2} - \frac{3i}{\rho^3}\right)e^{i\rho}. \tag{6.79}$$

The asymptotic behavior of the Hankel functions when $\rho \to \infty$ can be inferred from (6.68):

$$h_l^{(1)}(\rho) \to -\frac{i}{\rho}e^{i(\rho - l\pi/2)}, \qquad h_l^{(2)}(\rho) \to \frac{i}{\rho}e^{-i(\rho - l\pi/2)}. \tag{6.80}$$

The solutions that need to be retained in (6.76) must be finite everywhere. As can be inferred from Eq (6.80), only the Hankel functions of the first kind $h_l^{(1)}(ik_2r)$ are finite at large values of r (the functions $h_l^{(2)}(ik_2r)$ diverge for large values of r). Thus, the wave functions outside the well that are physically meaningful are those expressed in terms of the Hankel functions of the first kind (see (6.76)):

$$R_l(ik_2r) = Bh_l^{(1)}\left(i\frac{\sqrt{-2ME}}{\hbar}r\right) = Bj_l\left(i\frac{\sqrt{-2ME}}{\hbar}r\right) + iBn_l\left(i\frac{\sqrt{-2ME}}{\hbar}r\right). \tag{6.81}$$

The continuity of the radial function and its derivative at $r = a$ yields

$$\frac{1}{h_l^{(1)}(ik_2r)}\frac{dh_l^{(1)}(ik_2r)}{dr}\bigg|_{r=a} = \frac{1}{j_l(k_1r)}\frac{dj_l(k_1r)}{dr}\bigg|_{r=a}. \tag{6.82}$$

For the $l = 0$ states, this equation reduces to

$$-k_2 = k_1\cot(k_1a). \tag{6.83}$$

This continuity condition is analogous to the transcendental equation we obtained in Chapter 4 when we studied the one-dimensional finite square well potential.

- The positive energy case corresponds to the continuous spectrum (unbound or scattering states), where the solution is asymptotically oscillatory. The solution consists of a linear combination of $j_l(k'r)$ and $n_l(k'r)$, where $k' = \sqrt{2ME}/\hbar$. Since the solution must be finite everywhere, the continuity condition at $r = a$ determines the coefficients of the linear combination. The particle can move freely to infinity with a finite kinetic energy $E = \hbar^2k'^2/(2M)$.

6.3.4 The Isotropic Harmonic Oscillator

The radial Schrödinger equation for a particle of mass M in an isotropic harmonic oscillator potential

$$V(r) = \frac{1}{2}M\omega^2r^2 \tag{6.84}$$

is obtained from (6.57):

$$-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2} + \left[\frac{1}{2}M\omega^2r^2 + \frac{l(l+1)\hbar^2}{2Mr^2}\right]U_{nl}(r) = EU_{nl}(r). \tag{6.85}$$

We are going to solve this equation by examining the behavior of the solutions at the asymptotic limits (at very small and very large values of r). On the one hand, when $r \to 0$, the E and $M\omega^2r^2/2$ terms become too small compared to the $l(l+1)\hbar^2/2Mr^2$ term. Hence, when $r \to 0$, Eq. (6.85) reduces to

$$-\frac{\hbar^2}{2M}\frac{d^2U(r)}{dr^2} + \frac{l(l+1)\hbar^2}{2Mr^2}U(r) = 0; \tag{6.86}$$

the solutions of this equation are of the form $U(r) \sim r^{l+1}$. On the other hand,when $r \to \infty$, the E and $l(l+1)\hbar^2/2Mr^2$ terms become too small compared to the $M\omega^2r^2/2$ term; hence, the asymptotic form of (6.85) when $r \to \infty$ is

$$-\frac{\hbar^2}{2M}\frac{d^2U(r)}{dr^2} + \frac{1}{2}M\omega^2r^2U(r) = 0, \tag{6.87}$$

which admits solutions of type $U(r) \sim e^{-M\omega r^2/2\hbar}$. Combining (6.86) and (6.87), we can write the solutions of (6.85) as

$$U(r) = f(r)r^{l+1}e^{-M\omega r^2/2\hbar}, \tag{6.88}$$

where $f(r)$ is a function of r. Substituting this expression into (6.85), we obtain an equation for $f(r)$:

$$\frac{d^2f(r)}{dr^2} + 2\left(\frac{l+1}{r} - \frac{M\omega}{\hbar}r\right)\frac{df(r)}{dr} + \left[\frac{2ME}{\hbar^2} - (2l+3)\frac{M\omega}{\hbar}\right]f(r) = 0. \tag{6.89}$$

Let us try a power series solution

$$f(r) = \sum_{n=0}^{\infty} a_n r^n = a_0 + a_1 r + a_2 r^2 + \cdots + a_n r^n + \cdots. \tag{6.90}$$

Substituting this function into (6.89), we obtain

$$\sum_{n=0}^{\infty}\left\{n(n-1)a_nr^{n-2} + 2\left(\frac{l+1}{r} - \frac{M\omega}{\hbar}r\right)na_nr^{n-1} + \left[\frac{2ME}{\hbar^2} - (2l+3)\frac{M\omega}{\hbar}\right]a_nr^n\right\} = 0, \tag{6.91}$$

which in turn reduces to

$$\sum_{n=0}^{\infty}\left\{n(n+2l+1)a_nr^{n-2} + \left[-\frac{2M\omega}{\hbar}n + \frac{2ME}{\hbar^2} - (2l+3)\frac{M\omega}{\hbar}\right]a_nr^n\right\} = 0. \tag{6.92}$$

For this equation to hold, the coefficients of the various powers of r must vanish separately. For instance, when $n = 0$ the coefficient of r^{-2} is indeed zero:

$$0 \cdot (2l+1)a_0 = 0. \tag{6.93}$$

Note that a_0 need not be zero for this equation to hold. The coefficient of r^{-1} corresponds to $n = 1$ in (6.92); for this coefficient to vanish, we must have

$$1 \cdot (2l+2)a_1 = 0. \tag{6.94}$$

Since $(2l + 2)$ cannot be zero, because the quantum number l is a positive integer, a_1 must vanish.

The coefficient of r^n results from the relation

$$\sum_{n=0} \left\{ (n+2)(n+2l+3)a_{n+2} + \left[\frac{2ME}{\hbar^2} - \frac{M\omega}{\hbar}(2n+2l+3) \right] a_n \right\} r^n = 0, \tag{6.95}$$

which leads to the recurrence formula

$$(n+2)(n+2l+3)a_{n+2} = \left[\frac{-2ME}{\hbar^2} + \frac{M\omega}{\hbar}(2n+2l+3) \right] a_n. \tag{6.96}$$

This recurrence formula shows that all coefficients a_n corresponding to odd values of n are zero, since $a_1 = 0$ (see (6.94)). The function $f(r)$ must therefore contain only even powers of r:

$$f(r) = \sum_{n=0}^{\infty} a_{2n} r^{2n} = \sum_{n'=0,2,4,\cdots}^{\infty} a_{n'} r^{n'}, \tag{6.97}$$

where all coefficients a_{2n}, with $n \geq 1$, are proportional to a_0.

Now note that when $n \to +\infty$ the function $f(r)$ diverges, for it behaves asymptotically like e^{r^2}. To obtain a finite solution, we must require the series (6.97) to stop at a maximum power $r^{n'}$; hence it must be *polynomial*. For this, we require $a_{n'+2}$ to be zero. Thus, setting $a_{n'+2} = 0$ into the recurrence formula (6.96) and since $a_{n'} \neq 0$, we obtain at once the *quantization condition*

$$2\frac{M}{\hbar^2} E_{n'l} - \frac{M\omega}{\hbar}(2n' + 2l + 3) = 0, \tag{6.98}$$

or

$$E_{n'l} = \left(n' + l + \frac{3}{2} \right) \hbar\omega, \tag{6.99}$$

where n' is even (see (6.97)). Denoting n' by $2N$, where $N = 0, 1, 2, 3, \ldots$, we rewrite this energy expression as

$$\boxed{E_n = \left(n + \frac{3}{2} \right) \hbar\omega \qquad (n = 0, 1, 2, 3, \ldots),} \tag{6.100}$$

where $n = n' + l = 2N + l$.

The ground state, whose energy is $E_0 = \frac{3}{2}\hbar\omega$, is not degenerate; the first excited state, $E_1 = \frac{5}{2}\hbar\omega$, is threefold degenerate; and the second excited state, $E_2 = \frac{7}{2}\hbar\omega$, is sixfold degenerate (Table 6.4). As shown in the following example, the degeneracy relation for the nth level is given by

$$\boxed{g_n = \frac{1}{2}(n+1)(n+2).} \tag{6.101}$$

This expression is in agreement with (6.36) obtained for an isotropic harmonic oscillator in Cartesian coordinates.

Finally, since the radial wave function is given by $R_{nl}(r) = U_{nl}(r)/r$, where $U_{nl}(r)$ is listed in (6.88) with $f(r)$ being a polynomial in r^{2l} of degree $(n - l)/2$, the total wave function for the isotropic harmonic oscillator is

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi) = \frac{U_{nl}(r)}{r} Y_{lm}(\theta, \varphi) = r^l f(r) Y_{lm}(\theta, \varphi) e^{-M\omega r^2/2\hbar}, \tag{6.102}$$

Table 6.4 Energy levels E_n and degeneracies g_n for an isotropic harmonic oscillator.

n	E_n	Nl	m	g_n
0	$\frac{3}{2}\hbar\omega$	0 0	0	1
1	$\frac{5}{2}\hbar\omega$	0 1	$\pm 1, 0$	3
2	$\frac{7}{2}\hbar\ \omega$	1 0	0	6
		0 2	$\pm 2, \pm 1, 0$	
3	$\frac{9}{2}\hbar\omega$	1 1	$\pm 1, 0$	10
		0 3	$\pm 3, \pm 2, \pm 1, 0$	

where l takes only odd or only even values. For instance, the ground state corresponds to $(n, l, m) = (0, 0, 0)$; its wave function is

$$\psi_{000}(r, \theta, \varphi) = R_{00}(r)Y_{00}(\theta, \varphi) = \frac{2}{\sqrt{\sqrt{\pi}}}\left(\frac{M\omega}{\hbar}\right)^{3/4} e^{-M\omega r^2/2\hbar}Y_{00}(\theta, \varphi). \tag{6.103}$$

The (n, l, m) configurations of the first, second, and third excited states can be determined as follows. The first excited state has three degenerate states: $(1, 1, m)$ with $m = -1, 0, 1$. The second excited states has 6 degenerate states: $(2, 0, 0)$ and $(2, 2, m)$ with $m = -2, -1, 0, 1, 2$. The third excited state has 10 degenerate states: $(3, 1, m)$ with $m = -1, 0, 1$ and $(3, 3, m)$ where $m = -3, -2, -1, 0, 1, 2, 3$. Some of these wave functions are given by

$$\psi_{11m}(r, \theta, \varphi) = R_{11}(r)Y_{1m}(\theta, \varphi) = \sqrt{\frac{8}{3\sqrt{\pi}}}\left(\frac{M\omega}{\hbar}\right)^{5/4} re^{-M\omega r^2/2\hbar}Y_{1m}(\theta, \varphi), \tag{6.104}$$

$$\psi_{200}(r, \theta, \varphi) = R_{20}(r)Y_{00}(\theta, \varphi) = \sqrt{\frac{8}{3\sqrt{\pi}}}\left(\frac{M\omega}{\hbar}\right)^{3/4}\left(\frac{3}{2} - \frac{M\omega}{\hbar}r^2\right)e^{-M\omega r^2/2\hbar}Y_{00}(\theta, \varphi), \tag{6.105}$$

$$\psi_{31m}(r, \theta, \varphi) = R_{31}(r)Y_{1m}(\theta, \varphi) = \frac{4}{\sqrt{15\sqrt{\pi}}}\left(\frac{M\omega}{\hbar}\right)^{7/4} r^2e^{-M\omega r^2/2\hbar}Y_{1m}(\theta, \varphi). \tag{6.106}$$

Example 6.2 (Degeneracy relation for an isotropic oscillator)
Prove the degeneracy relation (6.101) for an isotropic harmonic oscillator.

Solution
Since $n = 2N + l$ the quantum numbers n and l must have the same parity. Also, since the isotropic harmonic oscillator is spherically symmetric, its states have definite parity[3]. In addition, since the parity of the states corresponding to a central potential is given by $(-1)^l$, the

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[3] Recall from Chapter 4 that if the potential of a system is symmetric, $V(x) = V(-x)$, the states of the system must be either odd or even.

quantum number l (hence n) can take only even or only odd values. Let us consider separately the cases when n is even or odd.

First, when n is even the degeneracy g_n of the nth excited state is given by

$$g_n = \sum_{l=0,2,4,\ldots}^{n}(2l+1) = \sum_{l=0,2,4,\ldots}^{n} 1 \; + \; 2\sum_{l=0,2,4,\ldots}^{n} l = \frac{1}{2}(n+2) + \frac{n(n+2)}{2} = \frac{1}{2}(n+1)(n+2). \quad (6.107)$$

A more explicit way of obtaining this series consists of writing it in the following two equivalent forms:

$$g_n = 1+5+9+13+\cdots+(2n-7)+(2n-3)+(2n+1), \quad (6.108)$$

$$g_n = (2n+1)+(2n-3)+(2n-7)+(2n-11)+\cdots+13+9+5+1. \quad (6.109)$$

We then add them, term by term, to get

$$2g_n = (2n+2)+(2n+2)+(2n+2)+(2n+2)+\cdots+(2n+2) = (2n+2)\left(\frac{n}{2}+1\right). \quad (6.110)$$

This relation yields $g_n = \frac{1}{2}(n+1)(n+2)$, which proves (6.101) when n is even.

Second, when n is odd, a similar treatment leads to

$$g_n = \sum_{l=1,3,5,7,\ldots}^{n}(2l+1) = \sum_{l=1,3,5,7,\ldots}^{n} 1 \; + \; 2\sum_{l=1,3,5,7,\ldots}^{n} l = \frac{1}{2}(n+1)+\frac{1}{2}(n+1)^2 = \frac{1}{2}(n+1)(n+2), \quad (6.111)$$

which proves (6.101) when n is odd. Note that this degeneracy relation is, as expected, identical with the degeneracy expression (6.36) obtained for a harmonic oscillator in Cartesian coordinates.

6.3.5 The Hydrogen Atom

The hydrogen atom consists of an electron and a proton. For simplicity, we will ignore their spins. The wave function then depends on six coordinates $\vec{r}_e(x_e, y_e, z_e)$ and $\vec{r}_p(x_p, y_p, z_p)$, where $\vec{r}_e$ and $\vec{r}_p$ are the electron and proton position vectors, respectively. According to the probabilistic interpretation of the wave function, the quantity $|\Psi(\vec{r}_e, \vec{r}_p, t)|^2 d^3r_e\, d^3r_p$ represents the probability that a simultaneous measurement of the electron and proton positions at time t will result in the electron being in the volume element d^3r_e and the proton in d^3r_p.

The time-dependent Schrödinger equation for the hydrogen atom is given by

$$\left[-\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r)\right]\Psi(\vec{r}_e,\ \vec{r}_p,\ t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}_e,\ \vec{r}_p,\ t), \quad (6.112)$$

where ∇_p^2 and ∇_e^2 are the Laplacians with respect to the proton and the electron degrees of freedom, with $\nabla_p^2 = \partial^2/\partial x_p^2 + \partial^2/\partial y_p^2 + \partial^2/\partial z_p^2$ and $\nabla_e^2 = \partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2$, and where $V(r)$ is the potential (interaction) between the electron and the proton. This interaction, which depends only on the distance that separates the electron and the proton $\vec{r} = \vec{r}_e - \vec{r}_p$, is given by the Coulomb potential:

$$V(r) = -\frac{e^2}{r}. \quad (6.113)$$

Note: Throughout this text, we will be using the CGS units for the Coulomb potential where it is given by $V(r) = -e^2/r$ (in the MKS units, however, it is given by $V(r) = -e^2/(4\pi\varepsilon_0 r)$).

Since V does not depend on time, the solutions of (6.112) are stationary; hence, they can be written as follows:

$$\Psi(\vec{r}_e, \vec{r}_p, t) = \chi(\vec{r}_e, \vec{r}_p)e^{-iEt/\hbar}, \tag{6.114}$$

where E is the total energy of the electron–proton system. Substituting this into (6.112), we obtain the time-independent Schrödinger equation for the hydrogen atom:

$$\left[-\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{|\vec{r}_e - \vec{r}_p|}\right]\chi(\vec{r}_e, \vec{r}_p) = E\chi(\vec{r}_e, \vec{r}_p). \tag{6.115}$$

6.3.5.1 Separation of the Center of Mass Motion

Since V depends only on the relative distance r between the electron and proton, instead of the coordinates $\vec{r}_e$ and $\vec{r}_p$ (position vectors of the electron and proton), it is more appropriate to use the coordinates of the center of mass, $\vec{R} = X\vec{i} + Y\vec{j} + Z\vec{k}$, and the relative coordinates of the electron with respect to the proton, $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$. The transformation from $\vec{r}_e$, $\vec{r}_p$ to $\vec{R}$, $\vec{r}$ is given by

$$\vec{R} = \frac{m_e\vec{r}_e + m_p\vec{r}_p}{m_e + m_p}, \qquad \vec{r} = \vec{r}_e - \vec{r}_p. \tag{6.116}$$

We can verify that the Laplacians ∇_e^2 and ∇_p^2 are related to

$$\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}, \qquad \nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{6.117}$$

as follows:

$$\frac{1}{m_e}\nabla_e^2 + \frac{1}{m_p}\nabla_p^2 = \frac{1}{M}\nabla_R^2 + \frac{1}{\mu}\nabla_r^2, \tag{6.118}$$

where

$$M = m_e + m_p, \qquad \mu = \frac{m_e m_p}{m_e + m_p} \tag{6.119}$$

are the total and reduced masses, respectively The time-independent Schrödinger equation (6.115) then becomes

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\Psi_E(\vec{R}, \vec{r}) = E\ \Psi_E(\vec{R}, \vec{r}), \tag{6.120}$$

where $\Psi_E(\vec{R}, \vec{r}) = \chi(\vec{r}_e, \vec{r}_p)$. Let us now solve this equation by the separation of variables; that is, we look for solutions of the form

$$\Psi_E(\vec{R}, \vec{r}) = \Phi(\vec{R})\psi(\vec{r}), \tag{6.121}$$

where $\Phi(\vec{R})$ and $\psi(\vec{r})$ are the wave functions of the CM and of the relative motions, respectively. Substituting this wave function into (6.120) and dividing by $\Phi(\vec{R})\psi(\vec{r})$, we obtain

$$\left[-\frac{\hbar^2}{2M}\frac{1}{\Phi(\vec{R})}\nabla_R^2\Phi(\vec{R})\right] + \left[-\frac{\hbar^2}{2\mu}\frac{1}{\psi(\vec{r})}\nabla_r^2\psi(\vec{r}) + V(r)\right] = E. \tag{6.122}$$

The first bracket depends only on $\vec{R}$ whereas the second bracket depends only on $\vec{r}$. Since $\vec{R}$ and $\vec{r}$ are independent vectors, the two expressions of the left hand side of (6.122) must be separately constant. Thus, we can reduce (6.122) to the following two separate equations:

$$-\frac{\hbar^2}{2M}\nabla_R^2\Phi(\vec{R}) = E_R\Phi(\vec{R}), \tag{6.123}$$

$$-\frac{\hbar^2}{2\mu}\nabla_r^2\psi(\vec{r}) + V(r)\psi(\vec{r}) = E_r\psi(\vec{r}), \tag{6.124}$$

with the condition

$$E_R + E_r = E. \tag{6.125}$$

We have thus reduced the Schrödinger equation (6.120), which involves two variables $\vec{R}$ and $\vec{r}$, into two separate equations (6.123) and (6.124) each involving a single variable. Note that equation (6.123) shows that the center of mass moves like a free particle of mass M. The solution to this kind of equation was examined earlier in this chapter; it has the form

$$\Phi(\vec{R}) = (2\pi)^{-3/2}e^{i\vec{k}\cdot\vec{R}}, \tag{6.126}$$

where $\vec{k}$ is the wave vector associated with the center of mass. The constant $E_R = \hbar^2k^2/(2M)$ gives the kinetic energy of the center of mass in the lab system (the total mass M is located at the origin of the center of mass coordinate system).

The second equation (6.124) represents the Schrödinger equation of a fictitious particle of mass μ moving in the central potential $-e^2/r$.

We should note that the total wave function $\Psi_E(\vec{R},\vec{r}) = \Phi(\vec{R})\psi(\vec{r})$ is seldom used. When the hydrogen problem is mentioned, this implicitly refers to $\psi(\vec{r})$ and E_r. That is, the hydrogen wave function and energy are taken to be given by $\psi(\vec{r})$ and E_r, not by Ψ_E and E.

6.3.5.2 Solution of the Radial Equation for the Hydrogen Atom

The Schrödinger equation (6.124) for the relative motion has the form of an equation for a central potential. The wave function $\psi(\vec{r})$ that is a solution to this equation is a product of an angular part and a radial part. The angular part is given by the spherical harmonic $Y_{lm}(\theta,\varphi)$. The radial part $R(r)$ can be obtained by solving the following radial equation:

$$-\frac{\hbar^2}{2\mu}\frac{d^2U(r)}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right]U(r) = EU(r), \tag{6.127}$$

where $U(r) = rR(r)$. To solve this radial equation, we are going to consider first its asymptotic solutions and then attempt a power series solution.

(a) Asymptotic behavior of the radial wave function

For very small values of r, (6.127) reduces to

$$-\frac{d^2U(r)}{dr^2} + \frac{l(l+1)}{r^2}U(r) = 0, \tag{6.128}$$

whose solutions are of the form

$$U(r) = Ar^{l+1} + Br^{-l}, \tag{6.129}$$

where A and B are constants. Since $U(r)$ vanishes at $r = 0$, the second term r^{-l}, which diverges at $r = 0$, must be discarded. Thus, for small r, the solution is

$$U(r) \sim r^{l+1}. \tag{6.130}$$

Now, in the limit of very large values of r, we can approximate (6.127) by

$$\frac{d^2U(r)}{dr^2} + \frac{2\mu E}{\hbar^2}U(r) = 0. \tag{6.131}$$

Note that, for bound state solutions, which correspond to the states where the electron and the proton are bound together, the energy E must be negative. Hence the solutions to this equation are of the form $U(r) \sim e^{\pm\lambda r}$ where $\lambda = \sqrt{2\mu(-E)}/\hbar$. Only the minus sign solution is physically acceptable, since $e^{\lambda r}$ diverges for large values of r. So, for large values of r, $U(r)$ behaves like

$$U(r) \longrightarrow e^{-\lambda r}. \tag{6.132}$$

The solutions to (6.127) can be obtained by combining (6.130) and (6.132):

$$U(r) = r^{l+1}f(r)e^{-\lambda r}, \tag{6.133}$$

where $f(r)$ is an r-dependent function. Substituting (6.133) into (6.127) we end up with a differential equation that determines the form of $f(r)$:

$$\frac{d^2 f}{dr^2} + 2\left(\frac{l+1}{r} - \lambda\right)\frac{df}{dr} + 2\left[\frac{-\lambda(l+1) + \mu e^2/\hbar^2}{r}\right]f(r) = 0. \tag{6.134}$$

(b) Power series solutions for the radial equation

As in the case of the three-dimensional harmonic oscillator, let us try a power series solution for (6.134):

$$f(r) = \sum_{k=0}^{\infty} b_k r^k, \tag{6.135}$$

which, when inserted into (6.134), yields

$$\sum_{k=0}^{\infty}\left\{k(k+2l+1)b_k r^{k-2} + 2\left[-\lambda(k+l+1) + \frac{\mu e^2}{\hbar^2}\right]b_k r^{k-1}\right\} = 0. \tag{6.136}$$

This equation leads to the following recurrence relation (by changing k to $k-1$ in the last term):

$$k(k+2l+1)b_k = 2\left[\lambda(k+l) - \frac{\mu e^2}{\hbar^2}\right]b_{k-1}. \tag{6.137}$$

In the limit of large values of k, the ratio of successive coefficients,

$$\frac{b_k}{b_{k-1}} = \frac{2\left[\lambda(k+l) - \mu e^2/\hbar^2\right]}{k(k+2l+1)}, \tag{6.138}$$

is of the order of

$$\frac{b_k}{b_{k-1}} \longrightarrow \frac{2\lambda}{k}. \tag{6.139}$$

This is the behavior of an exponential series, since the ratio of successive coefficients of the relation $e^{2x} = \sum_{k=0}^{\infty}(2x)^k/k!$ is given by

$$\frac{2^k}{k!}\frac{(k-1)!}{2^{k-1}} = \frac{2}{k}. \tag{6.140}$$

That is, the asymptotic behavior of (6.135) is

$$f(r) = \sum_{k=0}^{\infty} b_k r^k \longrightarrow e^{2\lambda r}; \tag{6.141}$$

hence the radial solution (6.133) becomes

$$U(r) = r^{l+1} e^{2\lambda r} e^{-\lambda r} = r^{l+1} e^{\lambda r}. \tag{6.142}$$

But this contradicts (6.133): for large values of r, the asymptotic behavior of the physically acceptable radial function (6.133) is given by $e^{-\lambda r}$ while that of (6.142) by $e^{\lambda r}$; the form (6.142) is thus physically unacceptable.

(c) Energy quantization

To obtain physically acceptable solutions, the series (6.135) *must terminate at a certain power* N; hence the function $f(r)$ becomes a *polynomial* of order N:

$$f(r) = \sum_{k=0}^{N} b_k r^k. \tag{6.143}$$

This requires that all coefficients b_{N+1}, b_{N+2}, b_{N+3}, ... have to vanish. When $b_{N+1} = 0$ the recurrence formula (6.137) yields

$$\lambda(N + l + 1) - \frac{\mu e^2}{\hbar^2} = 0. \tag{6.144}$$

Since $\lambda = \sqrt{-2\mu E/\hbar^2}$ and using the notation

$$n = N + l + 1, \tag{6.145}$$

where n is known as the *principal* quantum number and N as the *radial* quantum number, we can infer the energy

$$E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}, \tag{6.146}$$

which in turn can be written as

$$\boxed{E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{e^2}{2a_0}\frac{1}{n^2},} \tag{6.147}$$

because (from Bohr theory of the hydrogen atom) the Bohr radius is given by $a_0 = \hbar^2/(\mu e^2)$ and hence $\mu/\hbar^2 = 1/(e^2 a_0)$. Note that we can write λ in terms of a_0 as follows:

$$\lambda = \sqrt{-2\frac{\mu}{\hbar^2}E_n} = \sqrt{2\frac{1}{e^2 a_0}\frac{e^2}{2a_0 n^2}} = \frac{1}{n a_0}. \tag{6.148}$$

Since $N = 0, 1, 2, 3, \ldots$, the allowed values of n are nonzero integers, $n = l+1, l+2, l+3, \ldots$. For a given value of n, the orbital quantum number l can have values only between 0 and $n-1$ (i.e., $l = 0, 1, 2, \ldots, n-1$).

Remarks

- Note that (6.147) is similar to the energy expression obtained from the Bohr quantization condition, discussed in Chapter 1. It can be rewritten in terms of the Rydberg constant $\mathcal{R} = m_e e^4/(2\hbar^2)$ as follows:

$$E_n = -\frac{m_p}{m_p + m_e}\frac{\mathcal{R}}{n^2}, \tag{6.149}$$

  where $\mathcal{R} = 13.6\,\text{eV}$. Since the ratio m_e/m_p is very small ($m_e/m_p \ll 1$), we can approximate this expression by

$$E_n = -\left(1 + \frac{m_e}{m_p}\right)^{-1}\frac{\mathcal{R}}{n^2} \simeq -\left(1 - \frac{m_e}{m_p}\right)\frac{\mathcal{R}}{n^2}. \tag{6.150}$$

  So, if we consider the proton to be infinitely more massive than the electron, we recover the energy expression as derived by Bohr: $E_n = -\mathcal{R}/n^2$.

- **Energy of hydrogen-like atoms:** How does one obtain the energy of an atom or ion with a nuclear charge Ze but which has only one electron[4]? Since the Coulomb potential felt by the single electron due to the charge Ze is given by $V(r) = -Ze^2/r$, the energy of the electron can be inferred from (6.147) by simply replacing e^2 with Ze^2:

$$E_n = -\frac{m_e(Ze^2)^2}{2\hbar^2}\frac{1}{n^2} = -\frac{Z^2 E_0}{n^2}, \tag{6.151}$$

  where $E_0 = e^2/(2a_0) = 13.6\,\text{eV}$; in deriving this relation, we have assumed that the mass of the nucleus is infinitely large compared to the electronic mass.

(d) Radial wave functions of the hydrogen atom

The radial wave function $R_{nl}(r)$ can be obtained by inserting (6.143) into (6.133),

$$R_{nl}(r) = \frac{1}{r}U_{nl}(r) = A_{nl} r^l e^{-\lambda r}\sum_{k=0}^{N} b_k r^k = A_{nl} r^l e^{-r/na_0}\sum_{k=0}^{N} b_k r^k, \tag{6.152}$$

since, as shown in (6.148), $\lambda = 1/(na_0)$; A_{nl} is a normalization constant.

How does one determine the expression of $R_{nl}(r)$? This issue reduces to obtaining the form of the polynomial $r^l\sum_{k=0}^{N} b_k r^k$ and the normalization constant A_{nl}. For this, we are going to explore two methods: the first approach follows a straightforward calculation and the second makes use of special functions.

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[4] For instance, $Z = 1$ refers to H, $Z = 2$ to He^{+}, $Z = 3$ to Li^{2+}, $Z = 4$ to Be^{3+}, $Z = 5$ to B^{4+}, $Z = 6$ to C^{5+}, and so on.

(i) First approach: straightforward calculation of $R_{nl}(r)$

This approach consists of a straightforward construction of $R_{nl}(r)$; we are going to show how to construct only the first few expressions. For instance, if $n = 1$ and $l = 0$ then $N = 0$. Since $N = n - l - 1$ and $\lambda = 1/(na_0)$ we can write (6.152) as

$$R_{10}(r) = A_{10}e^{-r/a_0}\sum_{k=0}^{0} b_k r^k = A_{10}b_0 e^{-r/a_0}, \tag{6.153}$$

where $A_{10}b_0$ can be obtained from the normalization of $R_{10}(r)$: using $\int_0^\infty x^n e^{-ax}\,dx = n!/a^{n+1}$, we have

$$1 = \int_0^\infty r^2\,|R_{10}(r)|^2\,dr = A_{10}^2 b_0^2 \int_0^\infty r^2 e^{-2r/a_0} dr = A_{10}^2 b_0^2 \frac{a_0^3}{4}; \tag{6.154}$$

hence $A_{10} = 1$ and $b_0 = 2\,(a_0)^{-3/2}$. Thus, $R_{10}(r)$ is given by

$$R_{10}(r) = 2\,(a_0)^{-3/2}\,e^{-r/a_0}. \tag{6.155}$$

Next, let us find $R_{20}(r)$. Since $n = 2, l = 0$ we have $N = 2 - 0 - 1 = 1$ and

$$R_{20}(r) = A_{20}e^{-r/2a_0}\sum_{k=0}^{1} b_k r^k = A_{20}(b_0 + b_1 r)e^{-r/2a_0}. \tag{6.156}$$

From (6.138) we can express b_1 in terms of b_0 as

$$b_1 = \frac{2\lambda(k + l) - 2/a_0}{k(k + 2l + 1)} b_0 = -\frac{1}{2a_0} b_0 = -\frac{1}{a_0\sqrt{a_0^3}}, \tag{6.157}$$

because $\lambda = 1/(2a_0)$, $k = 1$, and $l = 0$. So, substituting (6.157) into (6.156) and normalizing, we get $A_{20} = 1/(2\sqrt{2})$; hence

$$R_{20}(r) = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}. \tag{6.158}$$

Continuing in this way, we can obtain the expression of any radial wave function $R_{nl}(r)$; note that, knowing $b_0 = 2\,(a_0)^{-3/2}$, we can use the recursion relation (6.138) to obtain all other coefficients $b_2, b_3, \ldots$.

(ii) Second approach: determination of $R_{nl}(r)$ by means of special functions

The polynomial $r^l \sum_{k=0}^{N} b_k r^k$ present in (6.152) is a polynomial of degree $N + l$ or $n - 1$ since $n = N + l + 1$. This polynomial, which is denoted by $L_k^N(r)$, is known as the *associated Laguerre polynomial*; it is a solution to the Schrödinger equation (6.134). The solutions to differential equations of the form (6.134) were studied by Laguerre long before the birth of quantum mechanics. The associated Laguerre polynomial is defined, in terms of the *Laguerre polynomials* of order k, $L_k(r)$, by

$$L_k^N(r) = \frac{d^N}{dr^N}L_k(r), \tag{6.159}$$

where

$$L_k(r) = e^r \frac{d^k}{dr^k}(r^k e^{-r}). \tag{6.160}$$

Table 6.5 First few Laguerre polynomials and associated Laguerre polynomials.

Laguerre polynomials $L_k(r)$	Associated Laguerre polynomials $L_k^N(r)$
$L_0 = 1$	
$L_1 = 1 - r$	$L_1^1 = -1$
$L_2 = 2 - 4r + r^2$	$L_2^1 = -4 + 2r, \quad L_2^2 = 2$
$L_3 = 6 - 18r + 9r^2 - r^3$	$L_3^1 = -18 + 18r - 3r^2,\ L_3^2 = 18 - 6r,\ L_3^3 = -6$
$L_4 = 24 - 96r + 72r^2 - 16r^3 + r^4$	$L_4^1 = -96 + 144r - 48r^2 + 4r^3$
	$L_4^2 = 144 - 96r + 12r^2,\ L_4^3 = 24r - 96,\ L_4^4 = 24$
$L_5 = 120 - 600r + 600r^2 - 200r^3 + 25r^4 - r^5$	$L_5^1 = -600 + 1200r - 600r^2 + 100r^3 - 5r^4$
	$L_5^2 = 1200 - 1200r + 300r^2 - 20r^3$
	$L_5^3 = -1200 + 600r - 60r^2,\ L_5^4 = 600 - 120r$
	$L_5^5 = -120$

The first few Laguerre polynomials are listed in Table 6.5.

We can verify that $L_k(r)$ and $L_k^N(r)$ satisfy the following differential equations:

$$r\frac{d^2L_k(r)}{dr^2} + (1-r)\frac{dL_k(r)}{dr} + kL_k(r) = 0, \tag{6.161}$$

$$r\frac{d^2L_k^N(r)}{dr^2} + (N+1-r)\frac{dL_k^N(r)}{dr} + (k-N)L_k^N(r) = 0. \tag{6.162}$$

This last equation is identical to the hydrogen atom radial equation (6.134). The proof goes as follows. Using a change of variable

$$\rho = 2\lambda r = 2\frac{\sqrt{-2\mu E}}{\hbar}r, \tag{6.163}$$

along with the fact that $a_0 = \hbar^2/(\mu e^2)$ (Bohr radius), we can show that (6.134) reduces to

$$\rho\frac{d^2g(\rho)}{d\rho^2} + [(2l+1)+1-\rho]\frac{dg(\rho)}{d\rho} + [(n+l)-(2l+1)]\,g(\rho) = 0, \tag{6.164}$$

where $f(r) = g(\rho)$. In deriving (6.164), we have used the fact that $1/\lambda a_0 = n$ (see (6.148)). Note that equations (6.162) and (6.164) are identical; the solutions to (6.134) are thus given by the associated Laguerre polynomials $L_{n+l}^{2l+1}(2\lambda r)$.

The radial wave function of the hydrogen atom is then given by

$$R_{nl}(r) = N_{nl}\left(\frac{2r}{na_0}\right)^l e^{-r/na_0}L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right), \tag{6.165}$$

where N_{nl} is a constant obtained by normalizing the radial function $R_{nl}(r)$:

$$\int_0^\infty r^2R_{nl}^2(r)\,dr = 1. \tag{6.166}$$

Table 6.6 The first few radial wave functions $R_{nl}(r)$ of the hydrogen atom.

$R_{10}(r) = 2a_0^{-3/2} e^{-r/a_0}$	$R_{21}(r) = \frac{1}{\sqrt{6a_0^3}} \frac{r}{2a_0} e^{-r/2a_0}$
$R_{20}(r) = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$	$R_{31}(r) = \frac{8}{9\sqrt{6a_0^3}} \left(1 - \frac{r}{6a_0}\right) \left(\frac{r}{3a_0}\right) e^{-r/3a_0}$
$R_{30}(r) = \frac{2}{3\sqrt{3a_0^3}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$R_{32}(r) = \frac{4}{9\sqrt{30a_0^3}} \left(\frac{r}{3a_0}\right)^2 e^{-r/3a_0}$

Using the normalization condition of the associated Laguerre functions

$$\int_0^\infty e^{-\rho} \rho^{2l} \left[L_{n+l}^{2l+1}(\rho)\right]^2 \rho^2 d\rho = \frac{2n\left[(n+l)!\right]^3}{(n-l-1)!}, \tag{6.167}$$

where $\rho = 2\lambda r = 2r/(na_0)$, we can show that N_{nl} is given by

$$N_{nl} = -\left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}. \tag{6.168}$$

The wave functions of the hydrogen atom are given by

$$\boxed{\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi),} \tag{6.169}$$

where the radial functions $R_{nl}(r)$ are

$$\boxed{R_{nl}(r) = -\left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right).} \tag{6.170}$$

The first few radial wave functions are listed in Table 6.6; as shown in (6.155) and (6.158), they are identical with those obtained from a straightforward construction of $R_{nl}(r)$. The shapes of some of these radial functions are plotted in Figure 6.3.

(e) Properties of the radial wave functions of hydrogen

The radial wave functions of the hydrogen atom behave as follows (see Figure 6.3):

- They behave like r^l for small r.
- They decrease exponentially at large r, since L_{n+l}^{2l+1} is dominated by the highest power, r^{n-l-1}.
- Each function $R_{nl}(r)$ has $n - l - 1$ radial nodes, since $L_{n+l}^{2l+1}(\rho)$ is a polynomial of degree $n - l - 1$.

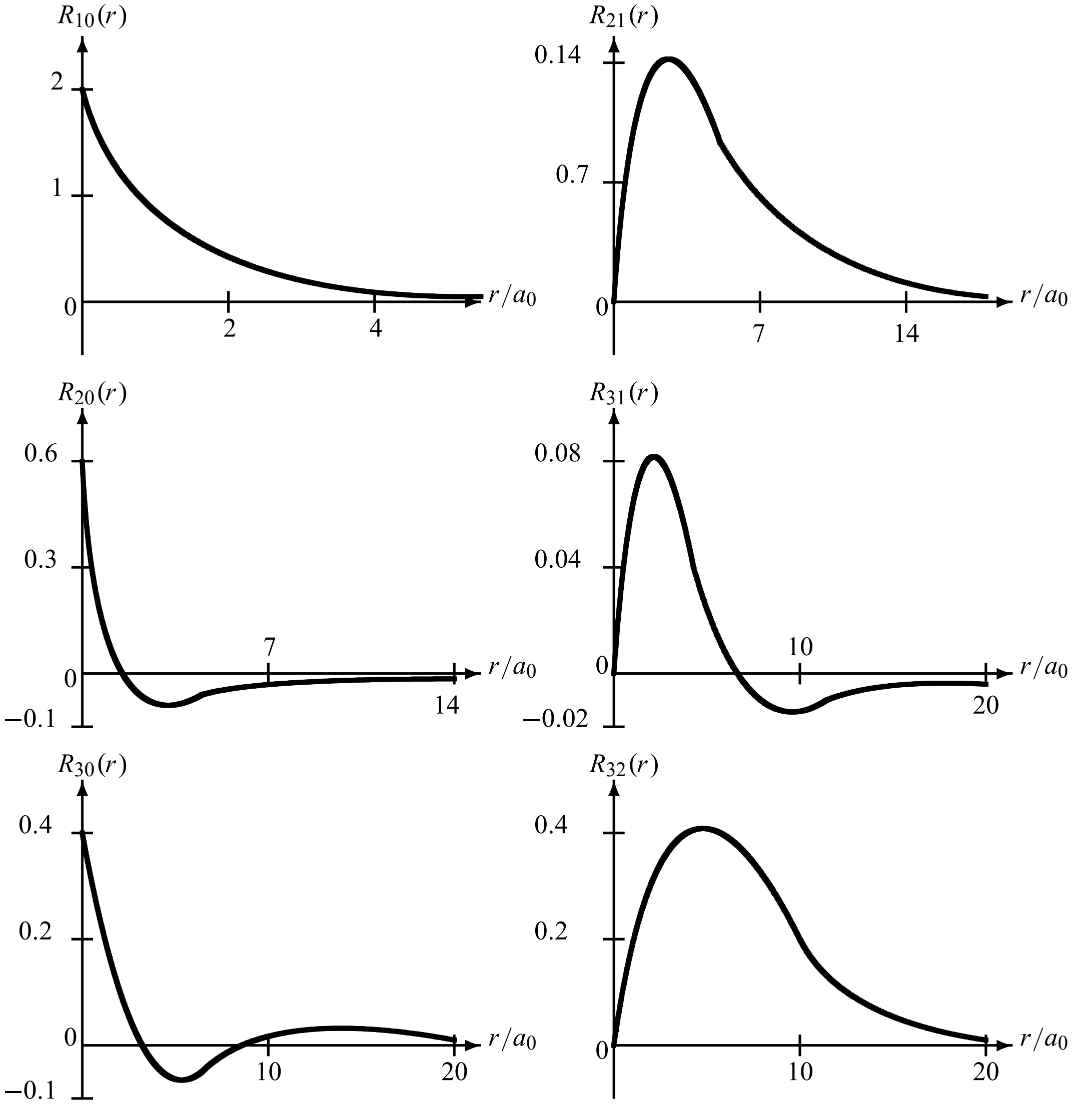

Figure 6.3 The first few radial wave functions $R_{nl}(r)$ for hydrogen; the radial length is in units of the Bohr radius $a_0 = \hbar^2/(\mu e^2)$. Notice that $R_{nl}(r)$ has $(n - l - 1)$ nodes.

Table 6.7 Hydrogen energy levels and their degeneracies when the electron's spin is ignored.

n	l	Orbitals	m	g_n	E_n
1	0	s	0	1	$-e^2/(2a_0)$
2	0	s	0	4	$-e^2/(8a_0)$
	1	p	$-1, 0, 1$		
3	0	s	0	9	$-e^2/(18a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
4	0	s	0	16	$-e^2/(32a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
	3	f	$-3, -2, -1, 0, 1, 2, 3$		
5	0	s	0	25	$-e^2/(50a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
	3	f	$-3, -2, -1, 0, 1, 2, 3$		
	4	g	$-4, -3, -2, -1, 0, 1, 2, 3, 4$		

6.3.5.3 Degeneracy of the Bound States of Hydrogen

Besides being independent of m, which is a property of central potentials (see (6.55)), the energy levels (6.147) are also independent of l. This *additional degeneracy* in l is not a property of central potentials, but a *particular feature of the Coulomb potential*. In the case of central potentials, the energy E usually depends on two quantum numbers: one radial, n, and the other orbital, l, giving E_{nl}.

The total quantum number n takes only nonzero values $1, 2, 3, \ldots$. As displayed in Table 6.7, for a given n, the quantum l number may vary from 0 to $n-1$; and for each l, m can take $(2l+1)$ values: $m = -l, -l+1, \ldots, l-1, l$. The degeneracy of the state n, which is specified by the total number of different states associated with n, is then given by (see Example 6.3 on page 364)

$$\boxed{g_n = \sum_{l=0}^{n-1}(2l+1) = n^2.} \tag{6.171}$$

Remarks

- The state of every hydrogenic electron is specified by three quantum numbers (n, l, m), called the single-particle state or *orbital*, $|nlm\rangle$. According to the spectroscopic notation, the states corresponding to the respective numerical values $l = 0, 1, 2, 3, 4, 5, \ldots$ are called the s, p, d, f, g, h, ... states; the letters s, p, d, f refer to sharp, principal, diffuse, and fundamental labels, respectively (as the letters g, h, ... have yet to be assigned labels, the reader is free to guess how to refer to them!). Hence, as shown in Table 6.7, for a given n an s-state has 1 orbital $|n00\rangle$, a p-state has 3 orbitals $|n1m\rangle$ corresponding to $m = -1, 0, 1$, a d-state has 5 orbitals $|n2m\rangle$ corresponding to $m = -2, -1, 0, 1, 2$, and so on.

- If we take into account the spin of the electron, the state of every electron will be specified by four quantum numbers (n, l, m_l, m_s), where $m_s = \pm\frac{1}{2}$ is the z-component of the spin of the electron. Hence the complete wave function of the hydrogen atom must be equal to the product of a space part or orbital $\psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r)Y_{lm_l}(\theta, \varphi)$, and a spin part $\left|\frac{1}{2},\ m_s\right\rangle$:

$$\Psi_{nlm_lm_s}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi)\left|\frac{1}{2},\ \pm\frac{1}{2}\right\rangle = R_{nl}(r)Y_{lm_l}(\theta, \varphi)\left|\frac{1}{2},\ \pm\frac{1}{2}\right\rangle. \qquad (6.172)$$

Using the spinors from Chapter 5 we can write the spin-up wave function as

$$\Psi_{nlm_l\frac{1}{2}}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi)\left|\frac{1}{2},\ \frac{1}{2}\right\rangle = \psi_{nlm_l}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \psi_{nlm_l} \\ 0 \end{pmatrix}, \qquad (6.173)$$

and the spin-down wave function as

$$\Psi_{nlm_l-\frac{1}{2}}(\vec{r}) = \psi_{nlm_l}(r, \theta, \varphi)\left|\frac{1}{2},\ -\frac{1}{2}\right\rangle = \psi_{nlm_l}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ \psi_{nlm_l} \end{pmatrix}. \qquad (6.174)$$

For instance, the spin-up and spin-down *ground state* wave functions of hydrogen are given by

$$\Psi_{100\frac{1}{2}}(\vec{r}) = \begin{pmatrix} \psi_{100} \\ 0 \end{pmatrix} = \begin{pmatrix} (1/\sqrt{\pi})a_0^{-3/2}e^{-r/a_0} \\ 0 \end{pmatrix}, \qquad (6.175)$$

$$\Psi_{100-\frac{1}{2}}(\vec{r}) = \begin{pmatrix} 0 \\ \psi_{100} \end{pmatrix} = \begin{pmatrix} 0 \\ (1/\sqrt{\pi})a_0^{-3/2}e^{-r/a_0} \end{pmatrix}. \qquad (6.176)$$

- When spin is included the degeneracy of the hydrogen's energy levels is given by

$$2\sum_{l=0}^{n-1}(2l + 1) = 2n^2, \qquad (6.177)$$

since, in addition to the degeneracy (6.171), each level is doubly degenerate with respect to the spin degree of freedom. For instance, the ground state of hydrogen is doubly degenerate since $\Psi_{100\ \frac{1}{2}}(\vec{r})$ and $\Psi_{100\ -\frac{1}{2}}(\vec{r})$ correspond to the same energy $-13.6\,\text{eV}$. Similarly, the first excited state is eightfold degenerate ($2(2)^2 = 8$) because the eight states $\Psi_{200\ \pm\frac{1}{2}}(\vec{r})$, $\Psi_{211\ \pm\frac{1}{2}}(\vec{r})$, $\Psi_{210\ \pm\frac{1}{2}}(\vec{r})$, and $\Psi_{21-1\ \pm\frac{1}{2}}(\vec{r})$ correspond to the same energy $-13.6/4\,\text{eV} = -3.4\,\text{eV}$.

6.3.5.4 Probabilities and Averages

When a hydrogen atom is in the stationary state $\psi_{nlm}(r, \theta, \varphi)$, the quantity $|\psi_{nlm}(r,\ \theta,\ \varphi)|^2\, d^3r$ represents the probability of finding the electron in the volume element d^3r, where

$d^3r = r^2 \sin\theta\, dr\, d\theta\, d\varphi$. The probability of finding the electron in a spherical shell located between r and $r + dr$ (i.e., a shell of thickness dr) is given by

$$\begin{aligned} P_{nl}(r)\, dr &= \left(\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, |\psi_{nlm}(r,\theta,\varphi)|^2\right) r^2 dr \\ &= |R_{nl}(r)|^2 r^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} Y_{lm}^*(\theta,\varphi) Y_{lm}(\theta,\varphi)\, d\varphi \\ &= |R_{nl}(r)|^2 r^2 dr. \end{aligned} \tag{6.178}$$

If we integrate this quantity between $r = 0$ and $r = a$, we obtain the probability of finding the electron in a sphere of radius a centered about the origin. Hence integrating between $r = 0$ and $r = \infty$, we would obtain 1, which is the probability of finding the electron somewhere in space.

Let us now specify the average values of the various powers of r. Since $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$, we can see that the average of r^k is independent of the azimuthal quantum number m:

$$\begin{aligned} \langle nlm|r^k|nlm\rangle &= \int r^k |\psi_{nlm}(r,\theta,\varphi)|^2 r^2 \sin\theta\, dr\, d\theta\, d\varphi \\ &= \int_0^{\infty} r^{k+2}|R_{nl}(r)|^2 dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} Y_{lm}^*(\theta,\varphi) Y_{lm}(\theta,\varphi)\, d\varphi \\ &= \int_0^{\infty} r^{k+2}|R_{nl}(r)|^2 dr \\ &= \langle nl \mid r^k|nl\rangle. \end{aligned} \tag{6.179}$$

Using the properties of Laguerre polynomials, we can show that (Problem 6.2, page 370)

$$\langle nl|\, r|nl\rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right] a_0, \tag{6.180}$$

$$\langle nl|\, r^2 \mid nl\rangle = \frac{1}{2}n^2\left[5n^2 + 1 - 3l\,(l+1)\right] a_0^2, \tag{6.181}$$

$$\langle nl|r^{-1}|nl\rangle = \frac{1}{n^2\, a_0}, \tag{6.182}$$

$$\langle nl|r^{-2}|nl\rangle = \frac{2}{n^3(2l\, + 1)a_0^2}, \tag{6.183}$$

where a_0 is the Bohr radius, $a_0 = \hbar^2/(\mu e^2)$. The averages (6.180) to (6.183) can be easily derived from Kramers' recursion relation (Problem 6.3, page 371):

$$\frac{k+1}{n^2}\langle nl|r^k|nl\rangle - (2k+1)a_0\langle nl|r^{k-1}|nl\rangle + \frac{ka_0^2}{4}\left[(2l+1)^2 - k^2\right]\langle nl|r^{k-2}|nl\rangle = 0. \tag{6.184}$$

Equations (6.180) and (6.182) reveal that $1/\langle r\rangle$ and $\langle 1/r\rangle$ are not equal, but are of the same order of magnitude:

$$\langle r\rangle \sim n^2 a_0. \tag{6.185}$$

This relation is in agreement with the expression obtained from the Bohr theory of hydrogen: the quantized radii of circular orbits for the hydrogen atom are given by $r_n = n^2 a_0$. We will show in Problem 6.6 page 375 that the Bohr radii for circular orbits give the locations where the probability density of finding the electron reaches its maximum.

Next, using the expression (6.182) for $\langle r^{-1}\rangle$, we can obtain the average value of the Coulomb potential

$$\langle V(r)\rangle = -e^2\left\langle\frac{1}{r}\right\rangle = -\frac{e^2}{a_0}\frac{1}{n^2}, \tag{6.186}$$

which, as specified by (6.147), is equal to twice the total energy:

$$E_n = \frac{1}{2}\langle V(r)\rangle = -\frac{e^2}{2a_0}\frac{1}{n^2}. \tag{6.187}$$

This is known as the Virial theorem, which states that if $V(\alpha r) = \alpha^n V(r)$, the average expressions of the kinetic and potential energies are related by

$$\langle T\rangle = \frac{n}{2}\langle V(r)\rangle. \tag{6.188}$$

For instance, in the case of a Coulomb potential $V(\alpha r) = \alpha^{-1}V(r)$, we have $\langle T\rangle = -\frac{1}{2}\langle V\rangle$; hence $E = -\frac{1}{2}\langle V\rangle + \langle V\rangle = \frac{1}{2}\langle V\rangle$.

Example 6.3 (Degeneracy relation for the hydrogen atom)

Prove the degeneracy relation (6.171) for the hydrogen atom.

Solution

The energy $E_n = -e^2/(2a_0n^2)$ of the hydrogen atom (6.147) does not depend on the orbital quantum number l or on the azimuthal number m; it depends only on the principal quantum number n. For a given n, the orbital number l can take $n-1$ values: $l = 0, 1, 2, 3, \ldots, n-1$; while for each l, the azimuthal number m takes $2l+1$ values: $m = -l, -l+1, \ldots, l-1, l$. Thus, for each n, there exist g_n different wave functions $\psi_{nlm}(\vec{r})$, which correspond to the same energy E_n, with

$$g_n = \sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l \; + \; \sum_{l=0}^{n-1} 1 = n(n-1) + n = n^2. \tag{6.189}$$

Another way of finding this result consists of writing $\sum_{l=0}^{n-1}(2l+1)$ in the following two equivalent forms:

$$g_n = 1 + 3 + 5 + 7 + \cdots + (2n-7) + (2n-5) + (2n-3) + (2n-1), \tag{6.190}$$
$$g_n = (2n-1) + (2n-3) + (2n-5) + (2n-7) + \cdots + 7 + 5 + 3 + 1, \tag{6.191}$$

and then add them, term by term:

$$2g_n = (2n) + (2n) + (2n) + (2n) + \cdots + (2n) + (2n) + (2n) + (2n). \tag{6.192}$$

Since there are n terms (because l can take n values: $l = 0, 1, 2, 3, \ldots, n-1$), we have $2g_n = n(2n)$; hence $g_n = n^2$.

6.3.6 Effect of Magnetic Fields on Central Potentials

As discussed earlier (6.55), the energy levels of a particle in a central potential do not depend on the azimuthal quantum number m. This degeneracy can be lifted if we place the particle in a uniform magnetic field $\vec{B}$ (if $\vec{B}$ is uniform, its spatial derivatives vanish).

6.3.6.1 Effect of a Magnetic Field on a Charged Particle

Consider a particle of mass μ and charge q which, besides moving in a central potential $V(r)$, is subject to a uniform magnetic field $\vec{B}$.

From the theory of classical electromagnetism, the vector potential corresponding to a uniform magnetic field may be written as $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$ since, using the relation $\vec{\nabla} \times (\vec{C} \times \vec{D}) = \vec{C}(\vec{\nabla} \cdot \vec{D}) - \vec{D}(\vec{\nabla} \cdot \vec{C}) + (\vec{D} \cdot \vec{\nabla})\vec{C} - (\vec{C} \cdot \vec{\nabla})\vec{D}$, we have

$$\vec{\nabla} \times \vec{A} = \frac{1}{2}\vec{\nabla} \times (\vec{B} \times \vec{r}) = \frac{1}{2}\left[\vec{B}(\vec{\nabla} \cdot \vec{r}) - (\vec{B} \cdot \vec{\nabla})\vec{r}\right] = \frac{1}{2}\left[3\vec{B} - \vec{B}\right] = \vec{B}, \tag{6.193}$$

where we have used $\vec{\nabla} \cdot \vec{B} = 0$, $(\vec{r} \cdot \vec{\nabla})\vec{B} = 0$, $\vec{\nabla} \cdot \vec{r} = 3$, and $(\vec{B} \cdot \vec{\nabla})\vec{r} = \vec{B}$. When the charge is placed in a magnetic field $\vec{B}$, its linear momentum becomes $\vec{p} \to \vec{p} - (q/c)\vec{A}$, where c is the speed of light. The Hamiltonian of the particle is thus given by (see (6.124))

$$\hat{H} = \frac{1}{2\mu}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 + V(r) = \hat{H}_0 - \frac{q}{2\mu c}\left(\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}\right) + \frac{q^2}{2\mu c^2}\vec{A}^2, \tag{6.194}$$

where $\hat{H}_0 = \vec{p}^{\,2}/(2\mu) + V(r)$ is the Hamiltonian of the particle when the magnetic field $\vec{B}$ is not present. The term $\vec{p} \cdot \vec{A}$ can be calculated by analogy with the commutator $[\hat{p},\ \hat{F}(x)] = -i\hbar d\hat{F}(x)/dx$:

$$(\vec{p} \cdot \vec{A}) \mid \psi\rangle = -i\hbar(\vec{\nabla} \cdot \vec{A}) \mid \psi\rangle - i\hbar\vec{A} \cdot \vec{\nabla} \mid \psi\rangle = -i\hbar(\vec{\nabla} \cdot \vec{A}) \mid \psi\rangle + \vec{A} \cdot \vec{p} \mid \psi\rangle. \tag{6.195}$$

We see that, whenever $\vec{\nabla} \cdot \vec{A} = 0$ is valid (the Coulomb gauge), $\vec{A} \cdot \vec{p}$ is equal to $\vec{p} \cdot \vec{A}$:

$$\vec{p} \cdot \vec{A} - \vec{A} \cdot \vec{p} = -i\hbar(\vec{\nabla} \cdot \vec{A}) = 0 \qquad \Longrightarrow \qquad \vec{A} \cdot \vec{p} = \vec{p} \cdot \vec{A}. \tag{6.196}$$

On the other hand, since $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$, we have

$$\vec{A} \cdot \vec{p} = \frac{1}{2}(\vec{B} \times \vec{r}) \cdot \vec{p} = \frac{1}{2}\vec{B} \cdot (\vec{r} \times \vec{p}) = \frac{1}{2}\vec{B} \cdot \vec{L}, \tag{6.197}$$

where $\hat{\vec{L}}$ is the orbital angular momentum operator of the particle. Now, a combination of (6.196) and (6.197) leads to $\vec{p} \cdot \vec{A} = \vec{A} \cdot \vec{p} = \frac{1}{2}\vec{B} \cdot \hat{\vec{L}}$ which, when inserted in the Hamiltonian (6.194), yields

$$\hat{H} = \hat{H}_0 - \frac{q}{\mu c}\vec{A} \cdot \vec{p} + \frac{q^2}{2\mu c^2}\vec{A}^2 = \hat{H}_0 - \frac{q}{2\mu c}\vec{B} \cdot \hat{\vec{L}} + \frac{q^2}{2\mu c^2}\vec{A}^{\,2} = \hat{H}_0 - \vec{\mu}_L \cdot \vec{B} + \frac{q^2}{2\mu c^2}\vec{A}^{\,2}, \tag{6.198}$$

where

$$\vec{\mu}_L = \frac{q}{2\mu c}\vec{L} = \frac{\mu_B}{\hbar}\vec{L} \tag{6.199}$$

is called the *orbital magnetic dipole moment* of the charge q and $\mu_B = q\hbar/(2\mu c)$ is known as the *Bohr magneton*; as mentioned in Chapter 5, $\vec{\mu}_L$ is due to the orbiting motion of the charge about the center of the potential. The term $-\vec{\mu}_L \cdot \vec{B}$ in (6.198) represents the energy resulting from the interaction between the particle's orbital magnetic dipole moment $\vec{\mu}_L = q\vec{L}/(2\mu c)$ and the magnetic field $\vec{B}$. We should note that if the charge q had an intrinsic spin $\vec{S}$, its spinning motion would give rise to a magnetic dipole moment $\vec{\mu}_S = q\vec{S}/(2\mu c)$ which, when interacting with an external magnetic field $\vec{B}$, would in turn generate an energy term $-\vec{\mu}_S \cdot \vec{B}$ that must be added to the Hamiltonian. This issue will be discussed further in Chapter 7.

Finally, using the relation $(\vec{C} \times \vec{D}) \cdot (\vec{E} \times \vec{F}) = (\vec{C} \cdot \vec{E})(\vec{D} \cdot \vec{F}) - (\vec{C} \cdot \vec{F})(\vec{D} \cdot \vec{E})$, and since $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$, we have

$$\vec{A}^{\,2} = \frac{1}{4}(\vec{B} \times \vec{r}) \cdot (\vec{B} \times \vec{r}) = \frac{1}{4}\left[B^2 r^2 - (\vec{B} \cdot \vec{r})^2\right]. \tag{6.200}$$

We can thus write (6.198) as

$$\boxed{\hat{H} = \frac{1}{2\mu}\vec{p}^{\,2} + V(r) - \frac{q}{2\mu c}\vec{B} \cdot \hat{\vec{L}} + \frac{q^2}{8\mu c^2}\left[B^2 r^2 - (\vec{B} \cdot \vec{r})^2\right].} \tag{6.201}$$

This is the Hamiltonian of a particle of mass μ and charge q moving in a central potential $V(r)$ under the influence of a uniform magnetic field $\vec{B}$.

6.3.6.2 The Normal Zeeman Effect ($\vec{S} = 0$)

When a hydrogen atom is placed in an external uniform magnetic field, its energy levels get shifted. This energy shift is known as the *Zeeman effect.*

In this study *we ignore the spin* of the hydrogen's electron. The Zeeman effect *without the spin* of the electron is called the *normal* Zeeman effect. When the spin of the electron is considered, we get what is called the *anomalous* Zeeman effect, to be examined in Chapter 9 since its study requires familiarity with the formalisms of addition of angular momenta and perturbation theory, which will be studied in Chapters 7 and 9, respectively.

For simplicity, we take $\vec{B}$ along the z-direction: $\vec{B} = B\hat{z}$. The Hamiltonian of the hydrogen atom when subject to such a magnetic field can be obtained from (6.201) by replacing q with the electron's charge $q \to -e$,

$$\hat{H} = \frac{1}{2\mu}\vec{p}^{\,2} - \frac{e^2}{r} + \frac{e}{2\mu c}B\hat{L}_z + \frac{e^2 B^2}{8\mu c^2}\left(x^2 + y^2\right) = \hat{H}_0 + \frac{e}{2\mu c}B\hat{L}_z + \frac{e^2 B^2}{8\mu c^2}\left(x^2 + y^2\right), \tag{6.202}$$

where $\hat{H}_0 = \vec{p}^2/(2\mu) - e^2/r$ is the atom's Hamiltonian in the absence of a magnetic field. We can ignore the quadratic term $e^2 B^2(x^2 + y^2)/(8\mu c^2)$; it is too small for a one-electron atom even when the field $\vec{B}$ is strong; then (6.202) reduces to

$$\hat{H} = \hat{H}_0 + \frac{B\mu_B}{\hbar}\hat{L}_z, \tag{6.203}$$

where $\mu_B = e\hbar/(2\mu c) = 9.2740 \times 10^{-24}\,\mathrm{J\,T^{-1}} = 5.7884 \times 10^{-5}\,\mathrm{eV\,T^{-1}}$ is the Bohr magneton; the electron's orbital magnetic dipole moment, which results from the orbiting motion of the electron about the proton, would be given by $\vec{\mu}_L = -e\vec{B}/(2\mu c)$. Since $\hat{H}_0$ commutes with $\hat{L}_z$, the operators $\hat{H}$, $\hat{L}_z$, and $\hat{H}_0$ mutually commute; hence they possess a set of common eigenfunctions: $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta,\ \varphi)$. The eigenvalues of (6.203) are

$$E_{nlm} = \langle nlm \mid \hat{H} \mid nlm\rangle = \langle nlm \mid \hat{H}_0 \mid nlm\rangle + \frac{B\mu_B}{\hbar}\langle nlm \mid \hat{L}_z \mid nlm\rangle \tag{6.204}$$

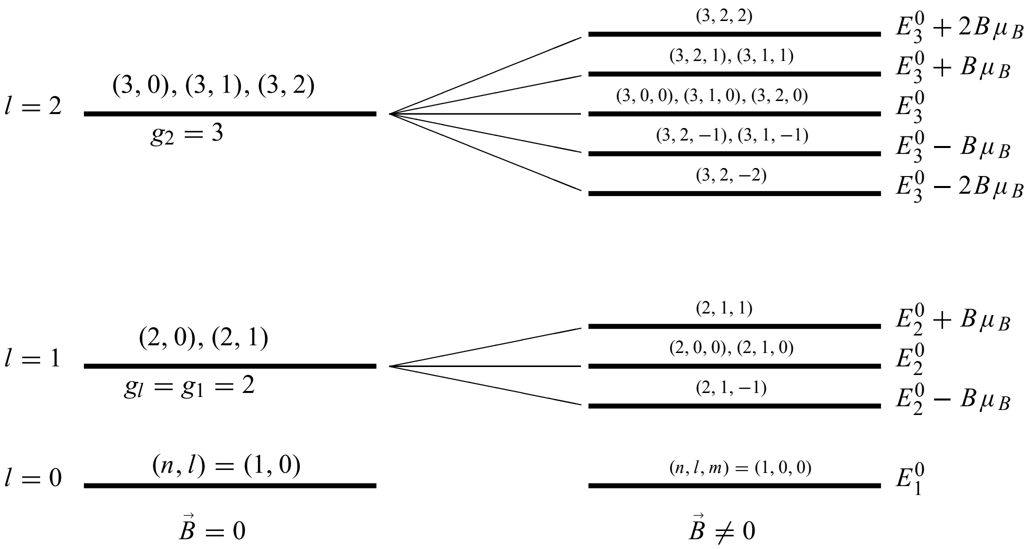

Figure 6.4 Normal Zeeman effect in hydrogen. (Left) When $\vec{B} = 0$ the energy levels are degenerate with respect to l and m. (Right) When $\vec{B} \neq 0$ the degeneracy with respect to m is removed, but the degeneracy with respect to l persists; $\mu_B = e\hbar/(2\mu c)$.

or

$$E_{nlm} = E_n^0 + m\mu_B B = E_n^0 + m\hbar\omega_L, \tag{6.205}$$

where E_n^0 are the hydrogen's energy levels $E_n^0 = -\mu e^4/(2\hbar^2 n^2)$ (6.147) and ω_L is called the *Larmor frequency*:

$$\omega_L = \frac{eB}{2\mu c}. \tag{6.206}$$

So when a hydrogen atom is placed in a uniform magnetic field, and if we ignore the spin of the electron, the atom's spherical symmetry will be broken: each level with angular momentum l will split into $(2l + 1)$ equally spaced levels (Figure 6.4), where the spacing is given by $\Delta E = \hbar\omega_L = B\mu_B$; the spacing is independent of l. This *equidistant* splitting of the levels is known as the *normal* Zeeman effect. The splitting leads to transitions which are restricted by the selection rule: $\Delta m = -1, 0, 1$. Transitions $m' = 0 \longrightarrow m = 0$ are not allowed.

The normal Zeeman effect has removed the degeneracy of the levels only partially; the degeneracy with respect to l remains. For instance, as shown in Figure 6.4, the following levels are still degenerate: $E_{nlm} = E_{200} = E_{210}$, $E_{32,-1} = E_{31,-1}$, $E_{300} = E_{310} = E_{320}$, and $E_{321} = E_{311}$. That is, the degeneracies of the levels corresponding to the same n and m but different values of l are not removed by the normal Zeeman effect: $E_{nl'm} = E_{nlm}$ with $l' \neq l$.

The results of the normal Zeeman effect, which show that each energy level splits into an *odd* number of $(2l + 1)$ equally spaced levels, disagree with the experimental observations. For instance, every level in the hydrogen atom actually splits into an *even* number of levels. This suggests that the angular momentum is not integer but half-integer. This disagreement is due to the simplifying assumption where the spin of the electron was ignored. A proper treatment, which includes the electron spin, confirms that the angular momentum is not purely orbital but includes a spin component as well. This leads to the splitting of each level into an *even*[5] number of $(2j+1)$ unequally spaced energy levels. This effect, known as the *anomalous* Zeeman effect, is in full agreement with experimental findings.

6.4 Concluding Remarks

An important result that needs to be highlighted in this chapter is the solution of the Schrödinger equation for the hydrogen atom. Unlike Bohr's semiclassical model, which is founded on piecemeal assumptions, we have seen how the Schrödinger equation yields the energy levels systematically and without ad hoc arguments, the quantization of the energy levels comes out naturally as a by-product of the formalism, not as an unjustified assumption: it is a consequence of the boundary conditions which require the wave function to be finite as $r \to \infty$; see (6.144) and (6.147). So we have seen that by solving a single differential equation—the Schrödinger equation—we obtain all that we need to know about the hydrogen atom. As such, the Schrödinger equation has delivered on the promise made in Chapter 1: namely, a theory that avoids the undesired aspects of Bohr's model—its hand-waving, ad hoc assumptions—while preserving its good points (i.e., the expressions for the energy levels, the radii, and the transition relations).

6.5 Solved Problems

Problem 6.1

Consider a spinless particle of mass m which is moving in a three-dimensional potential

$$V(x,y,z) = \begin{cases} \frac{1}{2}m\omega^2 z^2, & 0 < x < a,\ 0 < y < a, \\ \infty, & \text{elsewhere.} \end{cases}$$

(a) Write down the total energy and the total wave function of this particle.

(b) Assuming that $\hbar\omega > 3\pi^2\hbar^2/(2ma^2)$, find the energies and the corresponding degeneracies for the ground state and first excited state.

(c) Assume now that, in addition to the potential $V(x,y,z)$, this particle also has a negative electric charge $-q$ and that it is subjected to a constant electric field ϵ directed along the z-axis. The Hamiltonian along the z-axis is thus given by

$$\hat{H}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + \frac{1}{2}m\omega^2 z^2 - q\epsilon z.$$

Derive the energy expression E_{n_z} for this particle and also its total energy $E_{n_x n_y n_z}$. Then find the energies and the corresponding degeneracies for the ground state and first excited state.

Solution

(a) This three-dimensional potential consists of three independent one-dimensional potentials: (i) a potential well along the x-axis, (ii) a potential well along the y-axis, and (iii) a

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[5] When spin is included, the electron's total angular momentum j would be half-integer; $(2j+1)$ is then an even number.

harmonic oscillator along the z-axis. The energy must then be given by

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2\right) + \hbar\omega\left(n_z + \frac{1}{2}\right) \tag{6.207}$$

and the wave function by

$$\psi_{n_x n_y n_z}(x, y, z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z) = \frac{2}{a}\sin\left(\frac{\pi n_x}{a}x\right)\sin\left(\frac{\pi n_y}{a}y\right)Z_{n_z}, \tag{6.208}$$

where $Z_{n_z}(z)$ is the wave function of a harmonic oscillator which, as shown in Chapter 4, is given in terms of the Hermite polynomial $H_{n_z}\left(\frac{z}{z_0}\right)$ by

$$Z_{n_z}(z) = \frac{1}{\sqrt{\sqrt{\pi}2^{n_z}n_z!z_0}}e^{-z^2/2z_0^2}H_{n_z}\left(\frac{z}{z_0}\right), \tag{6.209}$$

with $z_0 = \sqrt{\pi\hbar/(m\omega)}$.

(b) The energy of the ground state is given by

$$E_{110} = \frac{\pi^2\hbar^2}{ma^2} + \frac{\hbar\omega}{2} \tag{6.210}$$

and the energy of the first excited state is given by

$$E_{120} = E_{210} = \frac{5\pi^2\hbar^2}{2ma^2} + \frac{\hbar\omega}{2}. \tag{6.211}$$

Note that, while the ground state is not degenerate, the first excited state is twofold degenerate. We should also mention that, since $\hbar\omega > 3\pi^2\hbar^2/(2ma^2)$, we have $E_{120} < E_{111}$, or

$$E_{111} = \frac{\pi^2\hbar^2}{ma^2} + \frac{3\hbar\omega}{2} = E_{120} + \hbar\omega - \frac{3\pi^2\hbar^2}{2ma^2}, \tag{6.212}$$

and hence the first excited state is given by E_{120} and not by E_{111}.

(c) To obtain the energies for

$$\hat{H}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + \frac{1}{2}m\omega^2 z^2 - q\epsilon z, \tag{6.213}$$

we need simply to make the change of variable $\lambda = z - q\epsilon/(m\omega^2)$; hence $dz = d\lambda$. The Hamiltonian $\hat{H}_z$ then reduces to

$$\hat{H}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\lambda^2} + \frac{1}{2}m\omega^2\lambda^2 - \frac{q^2\epsilon^2}{2m\omega^2}. \tag{6.214}$$

This suggestive form implies that the energy eigenvalues of $\hat{H}_z$ are those of a harmonic oscillator that are shifted downwards by an amount equal to $q^2\epsilon^2/(2m\omega^2)$:

$$E_{n_z} = \langle n_z|\hat{H}_z|n_z\rangle = \hbar\omega\left(n_z + \frac{1}{2}\right) - \frac{q^2\epsilon^2}{2m\omega^2}. \tag{6.215}$$

As a result, the total energy is now given by

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2\right) + \hbar\omega\left(n_z + \frac{1}{2}\right) - \frac{q^2\epsilon^2}{2m\omega^2}. \tag{6.216}$$

The energies of the ground and first excited states are

$$E_{110} = \frac{\pi^2\hbar^2}{ma^2} + \frac{\hbar\omega}{2} - \frac{q^2\epsilon^2}{2m\omega^2}, \qquad E_{120} = E_{210} = \frac{5\pi^2\hbar^2}{2ma^2} + \frac{\hbar\omega}{2} - \frac{q^2\epsilon^2}{2m\omega^2}. \tag{6.217}$$

Problem 6.2

Show how to obtain the expressions of: (a) $\langle nl|r^{-2}|nl\rangle$ and (b) $\langle nl|r^{-1}|nl\rangle$; that is, prove (6.183) and (6.182).

Solution

The starting point is the radial equation (6.127),

$$-\frac{\hbar^2}{2\mu}\frac{d^2U_{nl}(r)}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right]U_{nl}(r) = E_n U_{nl}(r), \tag{6.218}$$

which can be rewritten as

$$\frac{U''_{nl}(r)}{U_{nl}(r)} = \frac{l(l+1)}{r^2} - \frac{2\mu e^2}{\hbar^2}\frac{1}{r} + \frac{\mu^2 e^4}{\hbar^4 n^2}, \tag{6.219}$$

where $U_{nl}(r) = rR_{nl}(r)$, $U''_{nl}(r) = d^2U_{nl}(r)/dr^2$, and $E_n = -\mu e^4/(2\hbar^2 n^2)$.

(a) To find $\langle r^{-2}\rangle_{nl}$, let us treat the orbital quantum number l as a continuous variable and take the first l derivative of (6.219):

$$\frac{\partial}{\partial l}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right] = \frac{2l+1}{r^2} - \frac{2\mu^2 e^4}{\hbar^4 n^3}, \tag{6.220}$$

where we have the fact that n depends on l since, as shown in (6.145), $n = N + l + 1$; thus $\partial n/\partial l = 1$. Now since $\int_0^\infty U_{nl}^2(r)\,dr = \int_0^\infty r^2 R_{nl}^2(r)\,dr = 1$, multiplying both sides of (6.220) by $U_{nl}^2(r)$ and integrating over r we get

$$\int_0^\infty U_{nl}^2(r)\frac{\partial}{\partial l}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right]dr = (2l+1)\int_0^\infty U_{nl}^2(r)\frac{1}{r^2}dr - \frac{2\mu^2 e^4}{\hbar^4 n^3}\int_0^\infty U_{nl}^2(r)\,dr, \tag{6.221}$$

or

$$\int_0^\infty U_{nl}^2(r)\frac{\partial}{\partial l}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right]dr = (2l+1)\left\langle nl\left|\frac{1}{r^2}\right|nl\right\rangle - \frac{2\mu^2 e^4}{\hbar^4 n^3}. \tag{6.222}$$

The left-hand side of this relation is equal to zero, since

$$\int_0^\infty U_{nl}^2(r)\frac{\partial}{\partial l}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right]dr = \int_0^\infty U_{nl}(r)\frac{\partial U''_{nl}(r)}{\partial l}dr - \int_0^\infty U''_{nl}(r)\frac{\partial U_{nl}(r)}{\partial l}dr = 0. \tag{6.223}$$

We may therefore rewrite (6.222) as

$$(2l+1)\left\langle nl\left|\frac{1}{r^2}\right|nl\right\rangle = \frac{2\mu^2 e^4}{\hbar^4 n^3}; \tag{6.224}$$

hence

$$\left\langle nl \left| \frac{1}{r^2} \right| nl \right\rangle = \frac{2}{n^3(2l+1)a_0^2}, \tag{6.225}$$

since $a_0 = \hbar^2/(\mu e^2)$.

(b) To find $\langle r^{-1} \rangle_{nl}$ we need now to treat the electron's charge e as a continuous variable in (6.219). The first e-derivative of (6.219) yields

$$\frac{\partial}{\partial e}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right] = -\frac{4\mu e}{\hbar^2}\frac{1}{r} + \frac{4\mu^2 e^3}{\hbar^4 n^2}. \tag{6.226}$$

Again, since $\int_0^\infty U_{nl}^2(r)\,dr = 1$, multiplying both sides of (6.226) by $U_{nl}^2(r)$ and integrating over r we obtain

$$\int_0^\infty U_{nl}^2(r)\frac{\partial}{\partial e}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right]dr = -\frac{4\mu e}{\hbar^2}\int_0^\infty U_{nl}^2(r)\frac{1}{r}dr + \frac{4\mu^2 e^3}{\hbar^4 n^2}\int_0^\infty U_{nl}^2(r)\,dr, \tag{6.227}$$

or

$$\int_0^\infty U_{nl}^2(r)\frac{\partial}{\partial e}\left[\frac{U''_{nl}(r)}{U_{nl}(r)}\right]dr = -\frac{4\mu e}{\hbar^2}\left\langle nl \left| \frac{1}{r} \right| nl \right\rangle + \frac{4\mu^2 e^3}{\hbar^4 n^2}. \tag{6.228}$$

As shown in (6.223), the left-hand side of this is equal to zero. Thus, we have

$$\frac{4\mu e}{\hbar^2}\left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{4\mu^2 e^3}{\hbar^4 n^2} \quad \Longrightarrow \quad \left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{1}{n^2 a_0}, \tag{6.229}$$

since $a_0 = \hbar^2/(\mu e^2)$.

Problem 6.3

(a) Use Kramers' recursion rule (6.184) to obtain expressions (6.180) to (6.182) for $\langle nl|r^{-1}|nl\rangle$, $\langle nl|r|nl\rangle$, and $\langle nl|r^2|nl\rangle$.

(b) Using (6.225) for $\langle nl|r^{-2}|nl\rangle$ and combining it with Kramers' rule, obtain the expression for $\langle nl|r^{-3}|nl\rangle$.

(c) Repeat (b) to obtain the expression for $\langle nl|r^{-4}|nl\rangle$.

Solution

(a) First, to obtain $\langle nl\,|r^{-1}|\,nl\rangle$, we need simply to insert $k = 0$ into Kramers' recursion rule (6.184):

$$\frac{1}{n^2}\left\langle nl \left| r^0 \right| nl \right\rangle - a_0\left\langle nl \left| r^{-1} \right| nl \right\rangle = 0; \tag{6.230}$$

hence

$$\left\langle nl \left| \frac{1}{r} \right| nl \right\rangle = \frac{1}{n^2 a_0}. \tag{6.231}$$

Second, an insertion of $k = 1$ into (6.184) leads to the relation for $\langle nl\,|r|\,nl\rangle$:

$$\frac{2}{n^2}\langle nl\,|r|\,nl\rangle - 3a_0\left\langle nl \left| r^0 \right| nl \right\rangle + \frac{a_0^2}{4}\left[(2l+1)^2 - 1\right]\left\langle nl \left| r^{-1} \right| nl \right\rangle = 0, \tag{6.232}$$

and since $\langle nl\,|r^{-1}|\,nl\rangle = 1/(n^2 a_0)$, we have

$$\langle nl\,|r|\,nl\rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right]a_0. \tag{6.233}$$

Third, substituting $k = 2$ into (6.184) we get

$$\frac{3}{n^2}\left\langle nl\left|r^2\right|nl\right\rangle - 5a_0\left\langle nl\left|r\right|nl\right\rangle + \frac{a_0^2}{2}\left[(2l+1)^2 - 4\right]\left\langle nl\left|r^0\right|nl\right\rangle = 0, \tag{6.234}$$

which when combined with $\langle nl\left|r\right|nl\rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right]a_0$ yields

$$\boxed{\left\langle nl\left|r^2\right|nl\right\rangle = \frac{1}{2}n^2\left[5n^2 + 1 - 3l(l+1)\right]a_0^2.} \tag{6.235}$$

We can continue in this way to obtain any positive power of r: $\left\langle nl\left|r^k\right|nl\right\rangle$.

(b) Inserting $k = -1$ into Kramers' rule,

$$0 + a_0\left\langle nl\left|r^{-2}\right|nl\right\rangle - \frac{1}{4}\left[(2l+1)^2 - 1\right]a_0^2\left\langle nl\left|r^{-3}\right|nl\right\rangle, \tag{6.236}$$

we obtain

$$\left\langle nl\left|\frac{1}{r^3}\right|nl\right\rangle = \frac{1}{l(l+1)a_0}\left\langle nl\left|\frac{1}{r^2}\right|nl\right\rangle, \tag{6.237}$$

where the expression for $\left\langle nl\left|r^{-2}\right|nl\right\rangle$ is given by (6.225); thus, we have

$$\boxed{\left\langle nl\left|\frac{1}{r^3}\right|nl\right\rangle = \frac{2}{n^3 l(l+1)(2l+1)a_0^3}.} \tag{6.238}$$

(c) To obtain the expression for $\left\langle nl\left|r^{-4}\right|nl\right\rangle$ we need to substitute $k = -2$ into Kramers' rule:

$$-\frac{1}{n^2}\left\langle nl\left|r^{-2}\right|nl\right\rangle + 3a_0\left\langle nl\left|r^{-3}\right|nl\right\rangle - \frac{a_0^2}{2}\left[(2l+1)^2 - 4\right]\left\langle nl\left|r^{-4}\right|nl\right\rangle = 0. \tag{6.239}$$

Inserting (6.225) and (6.238) for $\left\langle nl\left|r^{-2}\right|nl\right\rangle$ and $\left\langle nl\left|r^{-3}\right|nl\right\rangle$, we obtain

$$\boxed{\left\langle nl\left|\frac{1}{r^4}\right|nl\right\rangle = \frac{4\left[3n^2 - l(l+1)\right]}{n^5 l(l+1)(2l+1)\left[(2l+1)^2 - 4\right]a_0^4}.} \tag{6.240}$$

We can continue in this way to obtain any negative power of r: $\left\langle nl\left|r^{-k}\right|nl\right\rangle$.

Problem 6.4

An electron is trapped inside an infinite spherical well $V(r) = \begin{cases} 0, & r < a, \\ +\infty, & r > a. \end{cases}$

(a) Using the radial Schrödinger equation, determine the bound eigenenergies and the corresponding normalized radial wave functions for the case where the orbital angular momentum of the electron is zero (i.e., $l = 0$).

(b) Show that the lowest energy state for $l = 7$ lies above the second lowest energy state for $l = 0$.

(c) Calculate the probability of finding the electron in a sphere of radius $a/2$, and then in a spherical shell of thickness $a/2$ situated between $r = a$ and $r = 3a/2$.

Solution

(a) Since $V(r) = 0$ in the region $r \leq a$, the radial Schrödinger equation (6.57) becomes

$$-\frac{\hbar^2}{2m}\left[\frac{d^2U_{nl}(r)}{dr^2} - \frac{l(l+1)}{r^2}U_{nl}(r)\right] = EU_{nl}(r), \tag{6.241}$$

where $U_{nl}(r) = rR_{nl}(r)$. For the case where $l = 0$, this equation reduces to

$$\frac{d^2U_{n0}(r)}{dr^2} = -k_n^2U_{n0}(r), \tag{6.242}$$

where $k_n^2 = 2mE_n/\hbar^2$. The general solution to this differential equation is given by

$$U_{n0}(r) = A\cos(k_nr) + B\sin(k_nr) \tag{6.243}$$

or

$$R_{n0}(r) = \frac{1}{r}\left(A\cos(k_nr) + B\sin(k_nr)\right). \tag{6.244}$$

Since $R_{n0}(r)$ is finite at the origin or $U_{n0}(0) = 0$, the coefficient A must be zero. In addition, since the potential is infinite at $r = a$ (rigid wall), the radial function $R_{n0}(a)$ must vanish:

$$R_{n0}(a) = B\frac{\sin k_na}{a} = 0; \tag{6.245}$$

hence $ka = n\pi$, $n = 1, 2, 3, \ldots$. This relation leads to

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2. \tag{6.246}$$

The normalization of the radial wave function $R(r)$, $\int_0^a |R_{n0}(r)|^2r^2dr = 1$, leads to

$$\begin{aligned}1 &= |B|^2\int_0^a \frac{1}{r^2}\sin^2(k_nr)r^2dr = \frac{|B|^2}{k_n}\int_0^{k_na}\sin^2\rho\, d\rho = \frac{|B|^2}{k_n}\left(\frac{\rho}{2} - \frac{\sin 2\rho}{4}\right)\Bigg|_{\rho=0}^{\rho=k_na}\\ &= \frac{1}{2}|B|^2a;\end{aligned} \tag{6.247}$$

hence $B = \sqrt{2/a}$. The normalized radial wave function is thus given by

$$R_{n0}(r) = \sqrt{\frac{2}{a}}\frac{1}{r}\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}r\right). \tag{6.248}$$

(b) For $l = 7$ we have

$$E_1(l = 7) > V_{eff}(l = 7) = \frac{56\hbar^2}{2ma^2} = \frac{28\hbar^2}{ma^2}. \tag{6.249}$$

The second lowest state for $l = 0$ is given by the 3s state; its energy is

$$E_2(l = 0) = \frac{2\pi^2\hbar^2}{ma^2}, \tag{6.250}$$

since $n = 2$. We see that

$$E_1(l = 7) > E_2(l = 0). \tag{6.251}$$

(c) Since the probability of finding the electron in the sphere of radius a is equal to 1, the probability of finding it in a sphere of radius $a/2$ is equal to $1/2$.

As for the probability of finding the electron in the spherical shell between $r = a$ and $r = 3a/2$, it is equal to zero, since the electron cannot tunnel through the infinite potential from $r < a$ to $r > a$.

Problem 6.5

Find the $l = 0$ energy and wave function of a particle of mass m that is subject to the following central potential $V(r) = \begin{cases} 0, & a < r < b, \\ \infty, & \text{elsewhere.} \end{cases}$

Solution

This particle moves between two concentric, hard spheres of radii $r = a$ and $r = b$. The $l = 0$ radial equation between $a < r < b$ can be obtained from (6.57):

$$\frac{d^2U_{n0}(r)}{dr^2} + k^2U_{n0}(r) = 0, \tag{6.252}$$

where $U_{n0}(r) = rR_{n0}(r)$ and $k^2 = 2mE/\hbar^2$. Since the solutions of this equation must satisfy the condition $U_{n0}(a) = 0$, we may write

$$U_{n0}(r) = A\sin[k(r - a)]; \tag{6.253}$$

the radial wave function is zero elsewhere, i.e., $U_{n0}(r) = 0$ for $0 < r < a$ and $r > b$.

Moreover, since the radial function must vanish at $r = b$, $U_{n0}(b) = 0$, we have

$$A\sin[k(b - a)] = 0 \quad \Longrightarrow \quad k(b - a) = n\pi, \qquad n = 1, 2, 3, \ldots. \tag{6.254}$$

Coupled with the fact that $k^2 = 2mE/(\hbar^2)$, this condition leads to the energy

$$E_n = \frac{\hbar^2k^2}{2m} = \frac{\pi^2\hbar^2}{2m(a - b)^2}, \qquad n = 1, 2, 3, \ldots. \tag{6.255}$$

We can normalize the radial function (6.253) to obtain the constant A:

$$\begin{aligned} 1 &= \int_a^b r^2R_{n0}^2(r)dr = \int_a^b U_{n0}^2(r)dr = A^2\int_a^b \sin^2[k(r - a)]\,dr \\ &= \frac{A^2}{2}\int_a^b \{1 - \cos[2k(r - a)]\}\,dr = \frac{b - a}{2}A^2; \end{aligned} \tag{6.256}$$

hence $A = \sqrt{2/(b - a)}$. Since $k_n = n\pi/(b - a)$ the normalized radial function is given by

$$R_{n0}(r) = \frac{1}{r}U_{n0}(r) = \begin{cases} \sqrt{\frac{2}{b-a}}\frac{1}{r}\sin[\frac{n\pi(r-a)}{b-a}], & a < r < b, \\ 0, & \text{elsewhere.} \end{cases} \tag{6.257}$$

To obtain the total wave function $\psi_{nlm}(\vec{r})$, we need simply to divide the radial function by a $1/\sqrt{4\pi}$ factor, because in this case of $l = 0$ the wave function $\psi_{n00}(r)$ depends on no angular degrees of freedom, it depends only on the radius:

$$\psi_{n00}(r) = \frac{1}{\sqrt{4\pi}} R_{n0}(r) = \begin{cases} \sqrt{\frac{2}{4\pi(b-a)}}\frac{1}{r}\sin[\frac{n\pi(r-a)}{b-a}], & a < r < b, \\ 0, & \text{elsewhere.} \end{cases} \tag{6.258}$$

Problem 6.6

(a) For the following cases, calculate the value of r at which the radial probability density of the hydrogen atom reaches its maximum: (i) $n = 1, l = 0, m = 0$; (ii) $n = 2, l = 1, m = 0$; (iii) $l = n - 1, m = 0$.

(b) Compare the values obtained with the Bohr radius for circular orbits.

Solution

(a) Since the radial wave function for $n = 1$ and $l = 0$ is $R_{10}(r) = 2a_0^{-3/2}e^{-r/a_0}$, the probability density is given by

$$P_{10}(r) = r^2|R_{10}(r)|^2 = \frac{4}{a_0^3}r^2e^{-2r/a_0}. \tag{6.259}$$

(i) The maximum of $P_{10}(r)$ occurs at r_1:

$$\left.\frac{dP_{10}(r)}{dr}\right|_{r=r_1} = 0 \implies 2r_1 - \frac{2r_1^2}{a_0} = 0 \implies r_1 = a_0. \tag{6.260}$$

(ii) Similarly, since $R_{21}(r) = 1/(2\sqrt{6}a_0^{5/2})re^{-r/2a_0}$, we have

$$P_{21}(r) = r^2|R_{21}(r)|^2 = \frac{1}{24a_0^5}r^4e^{-r/a_0}. \tag{6.261}$$

The maximum of the probability density is given by

$$\left.\frac{dP_{21}(r)}{dr}\right|_{r=r_2} = 0 \implies 4r_2^3 - \frac{r_2^4}{a_0} = 0 \implies r_2 = 4a_0. \tag{6.262}$$

(iii) The radial function for $l = n - 1$ can be obtained from (6.170):

$$R_{n(n-1)}(r) = -\left(\frac{2}{na_0}\right)^{3/2}\frac{1}{\sqrt{2n[(2n-1)!]^3}}\left(\frac{2r}{na_0}\right)^{(n-1)}e^{-r/na_0}L_{2n-1}^{2n-1}\left(\frac{2r}{na_0}\right). \tag{6.263}$$

From (6.159) and (6.160) we can verify that the associated Laguerre polynomial L_{2n-1}^{2n-1} is a *constant*, $L_{2n-1}^{2n-1}(y) = -(2n-1)!$. We can thus write $R_{n(n-1)}(r)$ as $R_{n(n-1)}(r) = A_nr^{n-1}e^{-r/na_0}$, where A_n is a constant. Hence the probability density is given by

$$P_{n(n-1)}(r) = r^2|R_{n(n-1)}(r)|^2 = A_n^2r^{2n}e^{-2r/na_0}. \tag{6.264}$$

The maximum of the probability density is given by

$$\left.\frac{dP_{n(n-1)}(r)}{dr}\right|_{r=r_n} = 0 \implies 2nr_n^{2n-1} - \frac{2r_n^{2n}}{na_0} = 0 \implies r_n = n^2a_0. \tag{6.265}$$

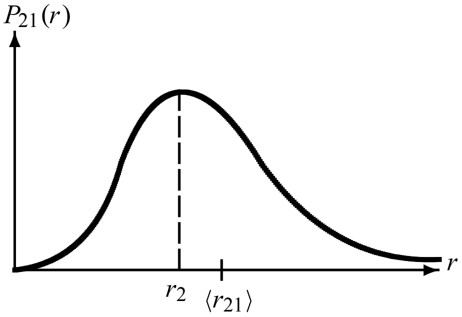

Figure 6.5 The probability density $P_{21}(r) = r^4 e^{-r/a_0}/(24a_0^5)$ is asymmetric about its maximum $r_2 = 4a_0$; the average of r is $\langle r_{21}\rangle = 5a_0$ and the width of the probability density is $\Delta r_{21} = \sqrt{5}a_0$.

(b) The values of r_n displayed in (6.260), (6.262), and (6.265) are nothing but the Bohr radii for circular orbits, $r_n = n^2 a_0$. The Bohr radius $r_n = n^2 a_0$ gives the position of maximum probability density for an electron in a hydrogen atom.

Problem 6.7

(a) Calculate the expectation value $\langle r\rangle_{21}$ for the hydrogen atom and compare it with the value r at which the radial probability density reaches its maximum for the state $n = 2, l = 1$.

(b) Calculate the width of the probability density distribution for r.

Solution

(a) Since $R_{21}(r) = re^{-r/2a_0}/\sqrt{24a_0^5}$ the average value of r in the state $R_{21}(r)$ is

$$\langle r\rangle_{21} = \frac{1}{24a_0^5}\int_0^\infty r^5 e^{-r/a_0}dr = \frac{a_0}{24}\int_0^\infty u^5 e^{-u}du = \frac{120a_0}{24} = 5a_0; \tag{6.266}$$

in deriving this relation we have made use of $\int_0^\infty x^n e^{-x}dx = n!$.

The value r at which the radial probability density reaches its maximum for the state $n = 2$, $l = 1$ is given by $r_2 = 4a_0$, as shown in (6.262).

What makes the results $r_2 = 4a_0$ and $\langle r\rangle_{21} = 5a_0$ different? The reason that $\langle r\rangle_{21}$ is different from r_2 can be attributed to the fact that the probability density $P_{21}(r)$ is asymmetric about its maximum, as shown in Figure 6.5. Although the most likely location of the electron is at $r_0 = 4a_0$, the average value of the measurement of its location is $\langle r\rangle_{21} = 5a_0$.

(b) The width of the probability distribution is given by $\Delta r = \sqrt{\langle r^2\rangle_{21} - \langle r\rangle_{21}^2}$, where the expectation value of r^2 is

$$\langle r^2\rangle_{21} = \int_0^\infty r^4 R_{21}^2(r)dr = \frac{1}{24a_0^5}\int_0^\infty r^6 \exp\left(-\frac{1}{a_0}r\right)dr = \frac{6!a_0^7}{24a_0^5} = 30a_0^2. \tag{6.267}$$

Thus, the width of the probability distribution shown in Figure 6.5 is given by

$$\Delta r_{21} = \sqrt{\langle r^2\rangle_0 - \langle r\rangle_0^2} = \sqrt{30a_0^2 - (5a_0)^2} = \sqrt{5}a_0. \tag{6.268}$$

Problem 6.8

The operators associated with the radial component of the momentum p_r and the radial coordinate r are denoted by $\hat{P}_r$ and $\hat{R}$, respectively. Their actions on a radial wave function $\psi_{(r)}$ are given by $\hat{P}_r\psi(\vec{r}) = -i\hbar(1/r)(\partial/\partial r)(r\psi(\vec{r}))$ and $\hat{R}\psi(\vec{r}) = r\psi(\vec{r})$.

(a) Find the commutator $[\hat{P}_r, \hat{R}]$ and $\Delta P_r \Delta r$, where $\Delta r = \sqrt{\langle \hat{R}^2\rangle - \langle \hat{R}\rangle^2}$ and $\Delta P_r = \sqrt{\langle \hat{P}_r^2\rangle - \langle \hat{P}_r\rangle^2}$.

(b) Show that $\hat{P}_r^2 = -(\hbar^2/r)(\partial^2/\partial r^2)r$.

Solution

(a) Since $\hat{R}\psi(\vec{r}) = r\psi(\vec{r})$ and

$$\hat{P}_r\psi(\vec{r}) = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}\left(r\psi(\vec{r})\right) = -i\hbar\frac{1}{r}\psi(\vec{r}) - i\hbar\frac{\partial\psi(\vec{r})}{\partial r}, \tag{6.269}$$

and since

$$\hat{P}_r(\hat{R}\psi(\vec{r})) = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\psi(\vec{r})\right) = -2i\hbar\psi(\vec{r}) - i\hbar r\frac{\partial\psi(\vec{r})}{\partial r}, \tag{6.270}$$

the action of the commutator $[\hat{P}_r, \hat{R}]$ on a function $\psi(\vec{r})$ is given by

$$\begin{aligned}[\hat{P}_r,\ \hat{R}]\psi(\vec{r}) &= -i\hbar\left[\frac{1}{r}\frac{\partial}{\partial r}r,\ \hat{R}\right]\psi(\vec{r}) = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\psi(\vec{r})\right) + i\hbar\frac{\partial}{\partial r}\left(r\psi(\vec{r})\right)\\ &= -2i\hbar\psi(\vec{r}) - i\hbar r\frac{\partial\psi(\vec{r})}{\partial r} + i\hbar\psi(\vec{r}) + i\hbar r\frac{\partial\psi(\vec{r})}{\partial r}\\ &= -i\hbar\psi(\vec{r}).\end{aligned} \tag{6.271}$$

Thus, we have

$$[\hat{P}_r,\ \hat{R}] = -i\hbar. \tag{6.272}$$

Using the uncertainty relation for a pair of operators $\hat{A}$ and $\hat{B}$, $\Delta A\Delta B \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|$, we can write

$$\Delta P_r\Delta r \geq \frac{1}{2}\left|\left\langle[\hat{P}_r, \hat{R}]\right\rangle\right|, \tag{6.273}$$

or

$$\Delta P_r\Delta r \geq \frac{\hbar}{2}. \tag{6.274}$$

(b) The action of $\hat{P}_r^2$ on $\psi(\vec{r})$ gives

$$\hat{P}_r^2\psi(\vec{r}) = -\hbar^2\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{1}{r}\frac{\partial}{\partial r}(r\psi)\right] = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi(\vec{r})); \tag{6.275}$$

hence

$$\hat{P}_r^2 = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}(r). \tag{6.276}$$

Problem 6.9

Find the number of s bound states for a particle of mass m moving in a delta potential $V(r) = -V_0\delta(r-a)$ where $V_0 > 0$. Discuss the existence of bound states in terms of the size of a. Find the normalized wave function of the bound state(s).

Solution
The $l = 0$ radial equation can be obtained from (6.57):

$$\frac{d^2U_{n0}(r)}{dr^2} + \left[\frac{2mV_0}{\hbar^2}\delta(r-a) - k^2\right]U_{n0}(r) = 0, \tag{6.277}$$

where $U_{nl}(r) = U_{n0}(r) = rR_{n0}(r)$ and $k^2 = -2mE/\hbar^2$, since we are looking here at the bound states only, $E < 0$. The solutions of this equation are

$$U_{n0}(r) = \begin{cases} U_{n0_1}(r) = Ae^{kr} + Be^{-kr}, & 0 < r < a, \\ U_{n0_2}(r) = Ce^{-kr}, & r > a. \end{cases} \tag{6.278}$$

The energy eigenvalues can be obtained from the boundary conditions. As the wave function vanishes at $r = 0$, $U_{n0}(0) = 0$, we have $A + B = 0$ or $B = -A$; hence $U_{n0_1}(r) = D\sinh kr$:

$$U_{n0}(r) = D\sinh kr, \qquad 0 < r < a, \tag{6.279}$$

with $D = 2A$. The continuity condition at $r = a$ of $U_{n0}(r)$, $U_{n0_1}(a) = U_{n0_2}(a)$, leads to

$$D\sinh ka = Ce^{-ka}. \tag{6.280}$$

To obtain the discontinuity condition for the first derivative of $U_{n0}(r)$ at $r = a$, we need to integrate (6.277):

$$\lim_{\varepsilon\to a}\left[U'_{n0_2}(a+\varepsilon) - U'_{n0_1}(a-\varepsilon)\right] + \frac{2mV_0}{\hbar^2}U_{n0_2}(a) = 0 \tag{6.281}$$

or

$$-kCe^{-ka} - kD\cosh ka + \frac{2mV_0}{\hbar^2}Ce^{-ka} = 0. \tag{6.282}$$

Taking $Ce^{-ka} = D\sinh ka$, as given by (6.280), and substituting it into (6.282), we get

$$-k\sinh ka - k\cosh ka + \frac{2mV_0}{\hbar^2}\sinh ka = 0; \tag{6.283}$$

hence

$$\gamma\coth\gamma = \frac{2mV_0}{\hbar^2}a - \gamma, \tag{6.284}$$

where $\gamma = ka$.

The energy eigenvalues are given by the intersection of the curves $f(\gamma) = \gamma\coth\gamma$ and $g(\gamma) = 2mV_0a/\hbar^2 - \gamma$. As shown in Figure 6.6, if $a < \hbar^2/(2mV_0)$ then no bound state solution can exist, since the curves of $f(\gamma)$ and $g(\gamma)$ do not intersect. But if $a > \hbar^2/(2mV_0)$ the curves intersect only once; hence there is one bound state. We can summarize these results as follows:

$$a < \frac{\hbar^2}{2mV_0} \Longrightarrow \text{no bound states}, \tag{6.285}$$

$$a > \frac{\hbar^2}{2mV_0} \Longrightarrow \text{only one bound state.} \tag{6.286}$$

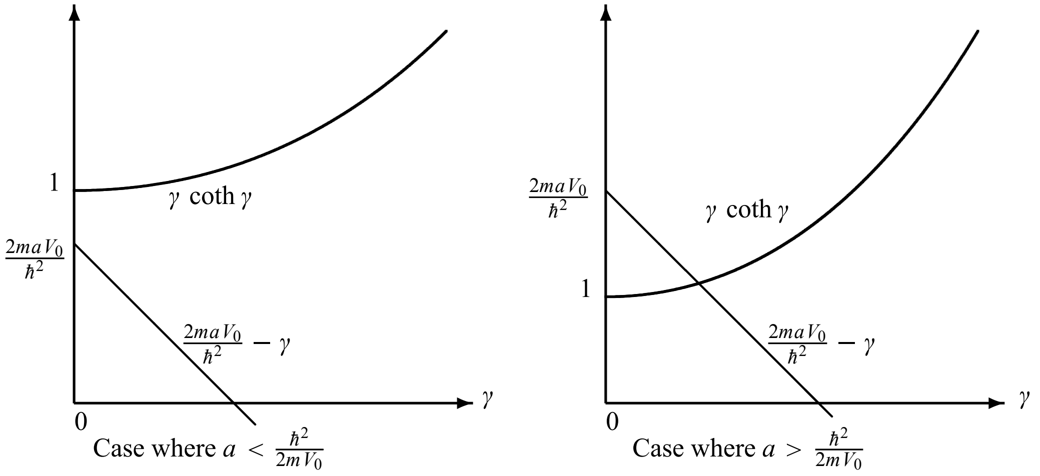

Figure 6.6 Graphical solutions of $f(\gamma) = g(\gamma)$, with $\gamma = ka$, $f(\gamma) = \gamma \coth\gamma$, and $g(\gamma) = 2mV_0a/\hbar^2 - \gamma$. If $a < \hbar^2/(2mV_0)$ there is no bound state. If $a > \hbar^2/(2mV_0)$ there is one bound state.

The radial wave function is given by

$$R_{n0}(r) = \frac{1}{r}U_{n0}(r) = \begin{cases} (D/r)\sinh kr, & 0 < r < a, \\ (C/r)e^{-kr}, & r > a. \end{cases} \tag{6.287}$$

The normalization of this function yields

$$\begin{aligned} 1 &= \int_0^\infty r^2 R_{n0}^2(r)\,dr = \int_0^\infty U_{n0}^2(r)\,dr \\ &= D^2 \int_0^a \sinh^2 kr\,dr + C^2 \int_a^\infty e^{-2kr}dr = \frac{D^2}{2}\int_0^a [\cosh 2kr - 1]\,dr + \frac{C^2}{2k}e^{-2ka} \\ &= D^2\left[\frac{1}{4k}\sinh 2ka - \frac{a}{2}\right] + \frac{C^2}{2k}e^{-2ka}. \end{aligned} \tag{6.288}$$

From (6.280) we have $Ce^{-ka} = D\sinh ka$, so we can rewrite this relation as

$$1 = D^2\left[\frac{1}{4k}\sinh 2ka - \frac{a}{2}\right] + \frac{D^2}{2k}\sinh^2 ka = D^2\left[\frac{\sinh 2ka + 2\sinh^2 ka}{4k} - \frac{a}{2}\right]; \tag{6.289}$$

hence

$$D = \frac{2\sqrt{k}}{\sqrt{\sinh 2ka + 2\sinh^2 ka - 2ak}}. \tag{6.290}$$

The normalized wave function is thus given by $\psi_{nlm}(r) = \psi_{n00}(r) = (1/\sqrt{4\pi})R_{n0}(r)$ or

$$\psi_{n00}(r) = \frac{\sqrt{k}}{\sqrt{\pi\sinh 2ka + 2\pi\sinh^2 ka - 2\pi ak}} \begin{cases} (1/r)\sinh(kr), & 0 < r < a, \\ (1/r)\sinh(ka)e^{-k(r-a)}, & r > a. \end{cases} \tag{6.291}$$

Problem 6.10

Consider the $l = 0$ states of a bound system of two quarks having the same mass m and interacting via $V(r) = kr$.

(a) Using the Bohr model, find the speed, the radius, and the energy of the system in the case of circular orbits. Determine also the angular frequency of the radiation generated by a transition of the system from an energy state n to m.

(b) Solve the Schrödinger equation for the central potential $V(r) = kr$ for the two-quark system and find the expressions for the energy and the radial function $R_{nl}(r)$. Compare the energy with the value obtained in (a).

(c) Use the expressions derived in (a) and (b) to calculate the four lowest energy levels of a bottom–antibottom (bottomonium) quark system with $k = 15\,\text{GeV fm}^{-1}$; the mass–energy of a bottom quark is $mc^2 = 4.4\,\text{GeV}$.

Solution

(a) Consider the two quarks to move circularly, much like the electron and proton in a hydrogen atom; we can write the force between them as

$$\mu\frac{v^2}{r} = \frac{dV(r)}{dr} = k, \tag{6.292}$$

where $\mu = m/2$ is the reduced mass. From the Bohr quantization condition of the orbital angular momentum, we have

$$L = \mu v r = n\hbar, \tag{6.293}$$

Multiplying (6.292) by (6.293), we end up with $\mu^2 v^3 = n\hbar k$ which yields the speed of the relative motion of the two-quark system:

$$v_n = \left(\frac{n\hbar k}{\mu^2}\right)^{1/3}. \tag{6.294}$$

The radius can be obtained from (6.293), $r_n = n\hbar/(\mu v_n)$; using (6.294) this leads to

$$r_n = \left(\frac{n^2\hbar^2}{\mu k}\right)^{1/3}. \tag{6.295}$$

We can obtain the total energy of the relative motion by adding the kinetic and potential energies:

$$E_n = \frac{1}{2}\mu v_n^2 + kr_n = \frac{3}{2}\left(\frac{n^2\hbar^2 k^2}{\mu}\right)^{1/3}. \tag{6.296}$$

In deriving this we have used the relations for v_n and r_n as given by (6.294) and (6.295), respectively. The angular frequency of the radiation generated by a transition from n to m is given by

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} = \frac{3}{2\hbar}\left(\frac{k^2}{\mu\hbar}\right)^{1/3}\left(n^{2/3} - m^{2/3}\right). \tag{6.297}$$

(b) The radial equation is given by (6.57):

$$-\frac{\hbar^2}{2\mu}\frac{d^2U_{nl}(r)}{dr^2} + \left[kr + \frac{l(l+1)\hbar^2}{2Mr^2}\right]U_{nl}(r) = E_n U_{nl}(r), \tag{6.298}$$

where $U_{nl}(r) = rR_{nl}(r)$. Since we are dealing with $l = 0$, we have

$$-\frac{\hbar^2}{2\mu}\frac{d^2U_{n0}(r)}{dr^2} + krU_{n0}(r) = E_nU_{n0}(r), \tag{6.299}$$

which can be reduced to

$$\frac{d^2U_{n0}(r)}{dr^2} - \frac{2\mu k}{\hbar^2}\left(r - \frac{E}{k}\right)U_{n0}(r) = 0. \tag{6.300}$$

Making the change of variable $x = (2\mu k/\hbar^2)^{1/3}(r - E/k)$, we can rewrite (6.300) as

$$\frac{d^2\phi_n(x)}{dx^2} - x\phi_n(x) = 0. \tag{6.301}$$

We have already studied the solutions of this equation in Chapter 4; they are given by the Airy functions $\mathrm{Ai}(x)$: $\phi(x) = B\mathrm{Ai}(x)$. The bound state energies result from the zeros of $\mathrm{Ai}(x)$. The boundary conditions on U_{nl} of (6.301) are $U_{nl}(r = 0) = 0$ and $U_{nl}(r \to +\infty) = 0$. The second condition is satisfied by the Airy functions, since $\mathrm{Ai}(x \to +\infty) = 0$. The first condition corresponds to $\phi[-(2\mu k/\hbar^2)^{1/3}E/k] = 0$ or to $\mathrm{Ai}[-(2\mu k/\hbar^2)^{1/3}E/k] = \mathrm{Ai}(R_n) = 0$, where R_n are the zeros of the Airy function.

The boundary condition $U_{nl}(r = 0) = 0$ then yields a discrete set of energy levels which can be expressed in terms of the Airy roots as follows:

$$\mathrm{Ai}\left[-\left(\frac{2\mu k}{\hbar^2}\right)^{1/3}\frac{E}{k}\right] = 0 \quad\Longrightarrow\quad -\left(\frac{2\mu k}{\hbar^2}\right)^{1/3}\frac{E_n}{k} = R_n; \tag{6.302}$$

hence

$$E_n = -\left(\frac{\hbar^2k^2}{2\mu}\right)^{1/3}R_n. \tag{6.303}$$

The radial function of the system is given by $R_{n0}(r) = (1/r)U_{n0}(r) = (B_n/r)\mathrm{Ai}(x)$ or

$$R_{n0}(r) = \frac{B_n}{r}\mathrm{Ai}(x) = \frac{B_n}{r}\mathrm{Ai}\left[\left(\frac{2\mu k}{\hbar^2}\right)^{1/3}r + R_n\right]. \tag{6.304}$$

The energy expression (6.303) has the same structure as the energy (6.296) derived from the Bohr model $E_n^B = \frac{3}{2}(n^2\hbar^2k^2/\mu)^{1/3}$; the ratio of the two expressions is

$$\frac{E_n}{E_n^B} = -\frac{2}{3}\frac{R_n}{(2n^2)^{1/3}}. \tag{6.305}$$

(c) In the following calculations we will be using $k = 15\,\mathrm{GeV\,fm^{-1}}$, $\mu c^2 = mc^2/2 = 2.2\,\mathrm{GeV}$, and $\hbar c = 197.3\,\mathrm{MeV\ fm}$. The values of the four lowest energy levels corresponding to the expression $E_n^B = \frac{3}{2}(n^2\hbar^2k^2/\mu)^{1/3}$, derived from the Bohr model, are

$$E_1^B = \frac{3}{2}\left(\frac{\hbar^2k^2}{\mu}\right)^{1/3} = 2.38\,\mathrm{GeV}, \qquad E_2^B = 2^{2/3}E_1^B = 3.77\,\mathrm{GeV}, \tag{6.306}$$

$$E_3^B = 3^{2/3}E_1^B = 4.95\,\mathrm{GeV}, \qquad E_4^B = 4^{2/3}E_1^B = 5.99\,\mathrm{GeV}. \tag{6.307}$$

Let us now calculate the exact energy levels. As mentioned in Chapter 4, the first few roots of the Airy function are given by $R_1 = -2.338$, $R_2 = -4.088$, $R_3 = -5.521$, $R_4 = -6.787$, so we can immediately obtain the first few energy levels:

$$E_1 = \left(\frac{\hbar^2 k^2}{2\mu}\right)^{1/3} R_1 = 2.94\,\text{GeV}, \qquad E_2 = \left(\frac{\hbar^2 k^2}{2\mu}\right)^{1/3} R_2 = 5.14\,\text{GeV}, \tag{6.308}$$

$$E_3 = \left(\frac{\hbar^2 k^2}{2\mu}\right)^{1/3} R_3 = 6.95\,\text{GeV}, \qquad E_4 = \left(\frac{\hbar^2 k^2}{2\mu}\right)^{1/3} R_4 = 8.54\,\text{GeV}. \tag{6.309}$$

Problem 6.11

Consider a system of two spinless particles of reduced mass μ that is subject to a finite, central potential well

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

where V_0 is positive. The purpose of this problem is to show how to find the minimum value of V_0 so that the potential well has one $l = 0$ bound state.

(a) Find the solution of the radial Schrödinger equation in both regions, $0 \le r \le a$ and $r > a$, in the case where the particle has zero angular momentum and its energy is located in the range $-V_0 < E < 0$.

(b) Show that the continuity condition of the radial function at $r = a$ can be reduced to a transcendental equation in E.

(c) Use this continuity condition to find the minimum values of V_0 so that the system has one, two, and three bound states.

(d) Obtain the results of (c) from a graphical solution of the transcendental equation derived in (b).

(e) Use the expression obtained in (c) to estimate a numerical value of V_0 for a deuteron nucleus with $a = 2 \times 10^{-15}$ m; a deuteron nucleus consists of a neutron and a proton.

Solution

(a) When $l = 0$ and $-V_0 < E < 0$ the radial equation (6.56),

$$-\frac{\hbar^2}{2\mu}\frac{d^2 U_{nl}(r)}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right] U_{nl}(r) = E_n U_{nl}(r), \tag{6.310}$$

can be written inside the well, call it region (1), as

$$U_n''(r)_1 + k_1^2 U_n(r)_1 = 0, \qquad 0 \le r \le a, \tag{6.311}$$

and outside the well, call it region (2), as

$$U_n''(r)_2 - k_2^2 U_n(r)_2 = 0, \qquad r > a, \tag{6.312}$$

where $U_n''(r) = d^2U_n(r)/dr^2$, $U_n(r)_1 = rR_n(r)_1$, $U_n(r)_2 = rR_n(r)_2$, $k_1 = \sqrt{2\mu(V_0 + E)/\hbar^2}$ and $k_2 = \sqrt{-2\mu E/\hbar^2}$. Since $U_n(r)_1$ must vanish at $r = 0$, while $U_n(r)_2$ has to be finite at $r \longrightarrow \infty$, the respective solutions of (6.311) and (6.312) are given by

$$U_n(r)_1 = A\sin(k_1 r), \qquad 0 \le r \le a, \tag{6.313}$$

$$U_n(r)_2 = Be^{-k_2 r}, \qquad r > a. \tag{6.314}$$

The corresponding radial functions are

$$R_n(r)_1 = A\frac{\sin(k_1 r)}{r}, \qquad R_n(r)_2 = B\frac{e^{-k_2 r}}{r}. \tag{6.315}$$

(b) Since the logarithmic derivative of the radial function is continuous at $r = a$, we can write

$$\frac{R_n'(a)_1}{R_n(a)_1} = \frac{R_n'(a)_2}{R_n(a)_2}. \tag{6.316}$$

From (6.315) we have

$$\frac{R_n'(a)_1}{R_n(a)_1} = k_1\cot(k_1 a) - \frac{1}{a}, \qquad \frac{R_n'(a)_2}{R_n(a)_2} = -k_2 - \frac{1}{a}. \tag{6.317}$$

Substituting (6.317) into (6.316) we obtain

$$-k_1\cot(k_1 a) = k_2 \tag{6.318}$$

or

$$\sqrt{\frac{2\mu}{\hbar^2}(V_0 + E)}\cot\left[\sqrt{\frac{2\mu}{\hbar^2}(V_0 + E)}a\right] = -\sqrt{-\frac{2\mu E}{\hbar^2}}, \tag{6.319}$$

since $k_1 = \sqrt{2\mu(V_0 + E)/\hbar^2}$ and $k_2 = \sqrt{-2\mu E/\hbar^2}$.

(c) In the limit $E \to 0$, the system has very few bound states; in this limit, equation (6.319) becomes

$$\sqrt{\frac{2\mu V_0}{\hbar^2}}\cot\left(\sqrt{\frac{2\mu V_0}{\hbar^2}}a\right) = 0, \tag{6.320}$$

which leads to $a\sqrt{2\mu V_{0n}/\hbar^2} = (2n + 1)\pi/2$; hence

$$V_{0n} = \frac{\pi^2\hbar^2}{8\mu a^2}(2n + 1)^2, \qquad n = 0, 1, 2, 3, \ldots. \tag{6.321}$$

Thus, the minimum values of V_0 corresponding to one, two, and three bound states are respectively

$$V_{00} = \frac{\pi^2\hbar^2}{8\mu a^2}, \qquad V_{01} = \frac{9\pi^2\hbar^2}{8\mu a^2}, \qquad V_{02} = \frac{25\pi^2\hbar^2}{8\mu a^2}. \tag{6.322}$$

(d) Using the notation $\alpha = ak_1$ and $\beta = ak_2$ we can, on the one hand, write

$$\alpha^2 + \beta^2 = \frac{2\mu a^2 V_0}{\hbar^2}, \tag{6.323}$$

and, on the other hand, reduce the transcendental equation (6.318) to

$$-\alpha\cot\alpha = \beta, \tag{6.324}$$

since $k_1 = \sqrt{2\mu(V_0 + E)/\hbar^2}$ and $k_2 = \sqrt{-2\mu E/\hbar^2}$.

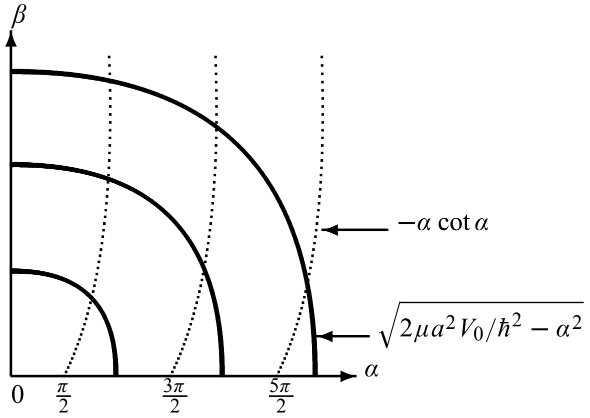

Figure 6.7 Graphical solutions for the finite, spherical square well potential: they are given by the intersection of the circle $\alpha^2 + \beta^2 = 2\mu a^2 V_0/\hbar^2$ with the curve of $-\alpha\cot\alpha$, where $\alpha^2 = 2\mu a^2(V_0 + E)/\hbar^2$ and $\beta^2 = -2\mu a^2 E/\hbar^2$, with $-V_0 < E < 0$.

As shown in Figure 6.7, when $\pi/2 < \alpha < 3\pi/2$, which in the limit of $E \to 0$ leads to

$$\frac{\pi^2\hbar^2}{8\mu a^2} < V_0 < \frac{9\pi^2\hbar^2}{8\mu a^2}, \tag{6.325}$$

there exists only one bound state, since the circle intersects only once with the curve $-\alpha\cot\alpha$. Similarly, there are two bound states if $3\pi/2 < \alpha < 5\pi/2$ or

$$\frac{9\pi^2\hbar^2}{8\mu a^2} < V_0 < \frac{25\pi^2\hbar^2}{8\mu a^2}, \tag{6.326}$$

and three bound states if $5\pi/2 < \alpha < 7\pi/2$:

$$\frac{25\pi^2\hbar^2}{8\mu a^2} < V_0 < \frac{49\pi^2\hbar^2}{8\mu a^2}. \tag{6.327}$$

(e) Since $m_p c^2 \simeq 938\,\text{MeV}$ and $m_n c^2 \simeq 940\,\text{MeV}$, the reduced mass of the deuteron is given by $\mu c^2 = (m_p c^2)(m_n c^2)/(m_p c^2 + m_n c^2) \simeq 469.5\,\text{MeV}$. Since $a = 2 \times 10^{-15}\,\text{m}$ the minimum value of V_0 corresponding to one bound state is

$$V_0 = \frac{\pi^2\hbar^2}{8\mu a^2} = \frac{\pi^2(\hbar c)^2}{8(\mu c^2)a^2} = \frac{\pi^2(197\,\text{MeV fm})^2}{8(469.5\,\text{MeV})(2 \times 10^{-15}\,\text{m})^2} \simeq 25.5\,\text{MeV}. \tag{6.328}$$

Problem 6.12

Calculate $\langle nl \mid \hat{P}^4 \mid nl\rangle$ in a stationary state $\mid nl\rangle$ of the hydrogen atom.

Solution

To calculate $\langle nl \mid \hat{P}^4 \mid nl\rangle$ we may consider expressing $\hat{P}^4$ in terms of the hydrogen's Hamiltonian. Since $\hat{H} = \hat{P}^2/(2m_e) - e^2/r$ we have $\hat{P}^2 = 2m_e(\hat{H} + e^2/r)$; hence

$$\begin{aligned}\langle nl \mid \hat{P}^4 \mid nl\rangle &= (2m_e)^2 \left\langle nl \left| \left(\hat{H} + \frac{e^2}{r}\right)^2 \right| nl \right\rangle \\ &= (2m_e)^2 \left\langle nl \left| \hat{H}^2 + \hat{H}\frac{e^2}{r} + \frac{e^2}{r}\hat{H} + \frac{e^4}{r^2} \right| nl \right\rangle \\ &= (2m_e)^2 \left[E_n^2 + E_n \left\langle nl \left| \frac{e^2}{r} \right| nl \right\rangle + \left\langle nl \left| \frac{e^2}{r} \right| nl \right\rangle E_n + \left\langle nl \left| \frac{e^4}{r^2} \right| nl \right\rangle \right],\end{aligned} \tag{6.329}$$

where we have used the fact that $\mid nl\rangle$ is an eigenstate of $\hat{H}$: $\hat{H} \mid nl\rangle = E_n \mid nl\rangle$ with $E_n = -e^2/(2a_0n^2) = -13.6\,\text{eV}/n^2$. The expectation values of $1/r$ and $1/r^2$ are given by (6.182) and (6.183), $\langle nl|r^{-1}|nl\rangle = 1/(n^2a_0)$ and $\langle nl|r^{-2}|nl\rangle = 2/[n^3(2l+1)a_0^2]$; we can thus rewrite (6.329) as

$$\begin{aligned}\langle nl \mid \hat{P}^4 \mid nl\rangle &= (2m_e)^2 \left[E_n^2 + 2E_n \left\langle nl \left| \frac{e^2}{r} \right| nl \right\rangle + \left\langle nl \left| \frac{e^4}{r^2} \right| nl \right\rangle \right] \\ &= (2m_eE_n)^2 \left[1 + \frac{2e^2}{E_n}\frac{1}{n^2\,a_0} + \frac{e^4}{E_n^2}\frac{2}{n^3(2l\ +1)a_0^2} \right] \\ &= (2m_eE_n)^2 \left[1 - 4 + \frac{8n}{2l+1} \right];\end{aligned} \tag{6.330}$$

in deriving the last relation we have used $E_n = -e^2/(2a_0n^2)$. Now, since $a_0 = \hbar^2/(m_ee^2)$, the energy E_n becomes $E_n = -e^2/(2a_0n^2) = -m_ee^4/(2\hbar^2n^2)$ which, when inserted into (6.330), leads to

$$\boxed{\langle nl \mid \hat{P}^4 \mid nl\rangle = \frac{m_e^4e^8}{\hbar^4n^4}\left[\frac{8n}{2l+1} - 3\right].} \tag{6.331}$$

6.6 Exercises

Exercise 6.1

A spinless particle of mass m is confined to move in the xy plane under the influence of a harmonic oscillator potential $\hat{V}(x, y) = \frac{1}{2}m\omega^2\left(\hat{x}^2 + \hat{y}^2\right)$ for all values of x and y.

(a) Show that the Hamiltonian $\hat{H}$ of this particle can be written as a sum of two familiar one-dimensional Hamiltonians, $\hat{H}_x$ and $\hat{H}_y$. Then show that $\hat{H}$ commutes with $\hat{L}_z = \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x$.

(b) Find the expression for the energy levels $E_{n_xn_y}$.

(c) Find the energies of the four lowest states and their corresponding degeneracies.

(d) Find the degeneracy g_n of the nth excited state as a function of the quantum number n ($n = n_x + n_y$).

(e) If the state vector of the nth excited state is $|n\rangle = |n_x\rangle|n_y\rangle$ or

$$\langle xy|n\rangle = \langle x|n_x\rangle\langle y|n_y\rangle = \psi_{n_x}(x)\psi_{n_y}(y),$$

calculate the expectation value of the operator $\hat{A} = \hat{x}^4 + \hat{y}^2$ in the state $|n\rangle$ as a function of the quantum numbers n_x and n_y.

Exercise 6.2
A particle of mass m moves in the xy plane in the potential

$$V(x, y) = \begin{cases} \frac{1}{2}m\omega^2 y^2 & \text{for all } y \text{ and } 0 < x < a, \\ +\infty, & \text{elsewhere.} \end{cases}$$

(a) Write down the time-independent Schrödinger equation for this particle and reduce it to a set of familiar one-dimensional equations.

(b) Find the normalized eigenfunctions and the eigenenergies.

Exercise 6.3
A particle of mass m moves in the xy plane in a two-dimensional rectangular well

$$V(x, y) = \begin{cases} 0, & 0 < x < a, \qquad 0 < y < b, \\ +\infty, & \text{elsewhere.} \end{cases}$$

By reducing the time-independent Schrödinger equation to a set of more familiar one-dimensional equations, find the normalized wave functions and the energy levels of this particle.

Exercise 6.4
Consider an anisotropic three-dimensional harmonic oscillator potential

$$V(x, y, z) = \frac{1}{2}m(\omega_x^2\, x^2 + \omega_y^2\, y^2 + \omega_z^2\, z^2).$$

(a) Evaluate the energy levels in terms of ω_x, ω_y, and ω_z.

(b) Calculate $[\hat{H},\ \hat{L}_z]$. Do you expect the wave functions to be eigenfunctions of $\hat{\vec{L}}^2$?

(c) Find the three lowest levels for the case $\omega_x = \omega_y = 2\omega_z/3$, and determine the degeneracy of each level.

Exercise 6.5
Consider a spinless particle of mass m which is confined to move under the influence of a three-dimensional potential

$$\hat{V}(x, y, z) = \begin{cases} 0 & \text{for } \ 0 < x < a,\ 0 < y < a,\ 0 < z < b, \\ +\infty & \text{elsewhere.} \end{cases}$$

(a) Find the expression for the energy levels $E_{n_x n_y n_z}$ and their corresponding wave functions.

(b) If $a = 2b$ find the energies of the five lowest states and their degeneracies.

Exercise 6.6
A particle of mass m moves in the three-dimensional potential

$$V(x, y, z) = \begin{cases} \frac{1}{2}m\omega^2 z^2 & \text{for } 0 < x < a,\ 0 < y < a, \text{ and } z > 0 \\ +\infty, & \text{elsewhere.} \end{cases}$$

(a) Write down the time-independent Schrödinger equation for this particle and reduce it to a set of familiar one-dimensional equations; then find the normalized wave function $\psi_{n_x n_y n_z}(x, y, z)$.

(b) Find the allowed eigenenergies of this particle and show that they can be written as: $E_{n_x n_y n_z} = E_{n_x n_y} + E_{n_z}$.

(c) Find the four lowest energy levels in the xy plane (i.e., $E_{n_x n_y}$) and their corresponding degeneracies.

Exercise 6.7

A particle of mass m moves in the potential $V(x, y, z) = V_1(x, y) + V_2(z)$ where

$$V_1(x, y) = \frac{1}{2}m\omega^2\left(x^2 + y^2\right), \qquad V_2(z) = \begin{cases} 0, & 0 \le z \le a, \\ +\infty, & \text{elsewhere.} \end{cases}$$

(a) Calculate the energy levels and the wave function of this particle.

(b) Let us now turn off $V_2(z)$ (i.e., m is subject only to $V_1(x, y)$). Calculate the degeneracy g_n of the nth energy level (note that $n = n_x + n_y$).

Exercise 6.8

Consider a muonic atom which consists of a nucleus that has Z protons (no neutrons) and a negative muon moving around it; the muon's charge is $-e$ and its mass is 207 times the mass of the electron, $m_{\mu^-} = 207m_e$. For a muonic atom with $Z = 6$, calculate

(a) the radius of the first Bohr orbit,

(b) the energy of the ground, first, and second excited states, and

(c) the frequency associated with the transitions $n_i = 2 \rightarrow n_f = 1$, $n_i = 3 \rightarrow n_f = 1$, and $n_i = 3 \rightarrow n_f = 2$.

Exercise 6.9

A hydrogen atom has the wave function $\Psi_{nlm}(\vec{r})$, where $n = 4,\ l = 3,\ m = 3$.

(a) What is the magnitude of the orbital angular momentum of the electron around the proton?

(b) What is the angle between the orbital angular momentum vector and the z-axis? Can this angle be reduced by changing n or m if l is held constant? What is the physical significance of this result?

(c) Sketch the shapes of the radial function and of the probability of finding the electron a distance r from the proton.

Exercise 6.10

An electron in a hydrogen atom is in the energy eigenstate

$$\psi_{2,1,-1}(r, \theta, \varphi) = Nre^{-r/2a_0}Y_{1,-1}(\theta, \varphi).$$

(a) Find the normalization constant, N.

(b) What is the probability per unit volume of finding the electron at $r = a_0$, $\theta = 45°$, $\varphi = 60°$?

(c) What is the probability per unit radial interval (dr) of finding the electron at $r = 2a_0$? (One must take an integral over θ and φ at $r = 2a_0$.)

(d) If the measurements of $\hat{L}^2$ and $\hat{L}_z$ were carried out, what will be the results?

Exercise 6.11

Consider a hydrogen atom which is in its ground state; the ground state wave function is given by

$$\Psi(r, \theta, \varphi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0},$$

where a_0 is the Bohr radius.

(a) Find the most probable distance between the electron and the proton when the hydrogen atom is in its ground state.

(b) Find the average distance between the electron and the proton.

Exercise 6.12

Consider a hydrogen atom whose state at time $t = 0$ is given by

$$\Psi(\vec{r}, 0) = \frac{1}{\sqrt{2}}\phi_{300}(\vec{r}) + \frac{1}{\sqrt{3}}\phi_{311}(\vec{r}) + \frac{1}{\sqrt{6}}\phi_{322}(\vec{r}).$$

(a) What is the time-dependent wave function?

(b) If a measurement of the energy were carried out, what values could be found and with what probabilities?

(c) Repeat part (b) for $\hat{L}^2$ and $\hat{L}_z$. That is, if a measurement of $\hat{L}^2$ and $\hat{L}_z$ were carried out, what values could be found and with what probabilities?

Exercise 6.13

The wave function of an electron in a hydrogen atom is given by

$$\psi_{21m_l m_s}(r, \theta, \varphi) = R_{21}(r)\left[\frac{1}{\sqrt{3}} Y_{10}(\theta, \varphi)\left|\frac{1}{2}, \frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}} Y_{11}(\theta, \varphi)\left|\frac{1}{2}, -\frac{1}{2}\right\rangle\right],$$

where $\left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$ are the spin state vectors.

(a) Is this wave function an eigenfunction of $\hat{J}_z$, the z-component of the electron's total angular momentum? If yes, find the eigenvalue. (*Hint:* For this, you need to calculate $\hat{J}_z \psi_{21m_l m_s}$.)

(b) If you measure the z-component of the electron's spin angular momentum, what values will you obtain? What are the corresponding probabilities?

(c) If you measure $\hat{\vec{J}}^2$, what values will you obtain? What are the corresponding probabilities?

Exercise 6.14

Consider a hydrogen atom whose state at time $t = 0$ is given by

$$\Psi(\vec{r}, 0) = A\phi_{200}(\vec{r}) + \frac{1}{\sqrt{5}}\phi_{311}(\vec{r}) + \frac{1}{\sqrt{3}}\phi_{422}(\vec{r}),$$

where A is a normalization constant.

(a) Find A so that the state is normalized.

(b) Find the state of this atom at any later time t.

(c) If a measurement of the energy were carried out, what values would be found and with what probabilities?

(d) Find the mean energy of the atom.

Exercise 6.15
Calculate the width of the probability density distribution for r for the hydrogen atom in its ground state: $\Delta r = \sqrt{\langle r^2 \rangle_{10} - \langle r \rangle_{10}^2}$.

Exercise 6.16
Consider a hydrogen atom whose wave function is given at time $t = 0$ by

$$\psi(\vec{r}, 0) = \frac{A}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0} + \frac{1}{\sqrt{2\pi}} \left(\frac{z - \sqrt{2}x}{r} \right) R_{21}(r),$$

where A is a real constant, a_0 is the Bohr radius, and $R_{21}(r)$ is the radial wave function: $R_{21}(r) = 1/\sqrt{6}(1/a_0)^{3/2}(r/2a_0)e^{-r/2a_0}$.

(a) Write down $\psi(\vec{r}, 0)$ in terms of $\sum_{nlm} \phi_{nlm}(\vec{r})$ where $\phi_{nlm}(\vec{r})$ is the hydrogen wave function $\phi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi)$.

(b) Find A so that $\psi(\vec{r},\ 0)$ is normalized. (Recall that $\int \phi^*_{n'l'm'}(\vec{r}) \phi_{nlm}(\vec{r}) d^3 r = \delta_{n',n} \delta_{l',l} \delta_{m',m}$.)

(c) Write down the wave function $\psi(\vec{r}, t)$ at any later time t.

(d) Is $\psi(\vec{r}, 0)$ an eigenfunction of $\hat{\vec{L}}^2$ and $\vec{L}_2$? If yes, what are the eigenvalues?

(e) If a measurement of the energy is made, what value could be found and with what probability?

(f) What is the probability that a measurement of $\hat{L}_z$ yields $1\hbar$?

(g) Find the mean value of r in the state $\psi(\vec{r}, 0)$.

Exercise 6.17
Consider a pendulum undergoing small harmonic oscillations (with angular frequency $\omega = \sqrt{g/l}$, where g is the acceleration due to gravity and l is the length of the pendulum). Show that the quantum energy levels and the corresponding degeneracies of the pendulum are given by $E_n = (n + 1)\hbar\omega$ and $g_n = n + 1$, respectively.

Exercise 6.18
Consider a proton that is trapped inside an infinite central potential well

$$V(r) = \begin{cases} -V_0, & 0 < r < a, \\ +\infty, & r \geq a, \end{cases}$$

where $V_0 = 5104.34$ MeV and $a = 10$ fm.

(a) Find the energy and the (normalized) radial wave function of this particle for the s states (i.e., $l = 0$).

(b) Find the number of bound states that have energies lower than zero; you may use the values $mc^2 = 938$ MeV and $\hbar c = 197$ MeV fm.

(c) Calculate the energies of the levels that lie just below and just above the zero-energy level; express your answer in MeV.

Exercise 6.19
Consider the function $\psi(\vec{r}) = -A\,(x + iy)\, e^{-r/2a_0}$, where a_0 is the Bohr radius and A is a real constant.

(a) Is $\psi(\vec{r})$ an eigenfunction to $\hat{\vec{L}}^2$ and $\hat{L}_z$? If yes, write $\psi(\vec{r})$ in terms of $R_{nl}(r) Y_{lm}(\theta, \varphi)$ and find the values of the quantum numbers n, m, l; $R_{nl}(r)$ are the radial wave functions of the hydrogen atom.

(b) Find the constant A so that $\psi(\vec{r})$ is normalized.

(c) Find the mean value of r and the most probable value of r in this state.

Exercise 6.20

The wave function of a hydrogen-like atom at time $t = 0$ is

$$\Psi(\vec{r}, 0) = \frac{1}{\sqrt{11}}\left[\sqrt{3}\psi_{2,1,-1}(\vec{r}) - \psi_{2,1,0}(\vec{r}) + \sqrt{5}\psi_{2,1,1}(\vec{r}) + \sqrt{2}\psi_{3,1,1}(\vec{r})\right],$$

where $\psi_{nlm}(\vec{r})$ is a normalized eigenfunction (i.e., $\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi)$).

(a) What is the time-dependent wave function?

(b) If a measurement of energy is made, what values could be found and with what probabilities?

(c) What is the probability for a measurement of $\hat{L}_z$ which yields $-1\hbar$?

Exercise 6.21

Using the fact that the radial momentum operator is given by $\hat{p}_r = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r$, calculate the commutator $[\hat{r},\ \hat{p}_r]$ between the position operator, $\hat{r}$, and the radial momentum operator.

Exercise 6.22

Calculate $\Delta r\,\Delta p_r$ with respect to the state

$$\psi_{2,1,0}(\vec{r}) = \frac{1}{\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{2a_0}e^{-r/2a_0}\,Y_{1,0}(\theta, \varphi),$$

and verify that $\Delta r\,\Delta p_r$ satisfies the Heisenberg uncertainty principle.