Quantum Mechanics

Third edition

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3.3 SEPARATION IN SPHERICAL POLAR COORDINATES

Although there are applications of quantum mechanics in which Cartesian coordinates can be usefully employed, many interesting physical systems, particularly atoms and nuclei, are much more nearly spherical than they are rectangular. Spherically symmetric systems where the potential $V(r)$ is independent of the direction of **r**, are usually best treated using spherical polar coordinates (r, θ, ϕ). These are related to the Cartesian coordinates (x, y, z) by the expressions

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \tag{3.22}$$

and the geometrical relationship between the two systems is shown in Fig. 3.2. The Schrödinger equation (3.7) can be written in spherical polar coordinates as

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}\right]+V(r)u=Eu \tag{3.23}$$

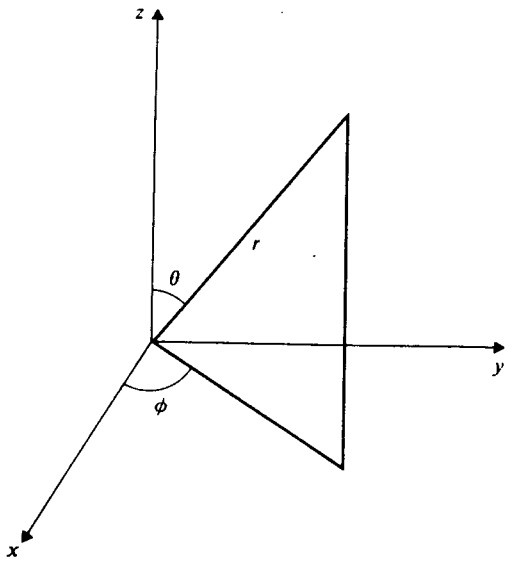

Figure 3.2 The geometrical relationship between the spherical polar coordinates r, θ, ϕ and the Cartesian axes x, y, z.

where the standard expression (derived in many mathematics textbooks) is used to express $\nabla^2 u$ in spherical polar coordinates, and we have represented the particle mass by μ rather than m because the latter symbol will be used later to represent a quantum number.

We now proceed to separate the variables and do so in two stages. We first put $u(r, \theta, \phi) = R(r)Y(\theta, \phi)$, substitute into (3.23), divide through by u and multiply through by r^2 to get

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + r^2V - r^2E\right] + \left[-\frac{\hbar^2}{2\mu}\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) - \frac{\hbar^2}{2\mu}\frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0 \qquad (3.24)$$

The contents of the first square bracket are independent of θ and ϕ and those of the second are independent of r so they must be separately equal to constants, and the sum of the two constants must be equal to zero. We call these constants $-\lambda$ and λ, and so obtain

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(V + \frac{\lambda}{r^2}\right)R = ER \qquad (3.25)$$

and

$$-\frac{\hbar^2}{2\mu}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) - \frac{\hbar^2}{2\mu}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \lambda Y \qquad (3.26)$$

Equation (3.26) does not contain the potential V. This means that if we can solve (3.26) for $Y(\theta, \phi)$, the solutions will represent the angular parts of the wave functions for *any* spherically symmetric potential $V(r)$ and we then 'only' have to solve the radial equation (3.25) to get the complete wave function in a particular case. We shall now show how the general solutions to (3.26) are obtained and return to the solution of the radial equation for particular potentials later.

Continuing the separation process, we put $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, substitute into (3.18), divide through by Y, and multiply through by $\sin^2\theta$ to get

$$\left[-\frac{\hbar^2}{2\mu}\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \lambda\sin^2\theta\right] + \left[-\frac{\hbar^2}{2\mu}\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}\right] = 0 \qquad (3.27)$$

The contents of the first square bracket are independent of ϕ while those of the second are independent of θ, so they must each be equal to a constant and the sum of the two constants must be equal to zero. We call these constants $-\nu$ and ν, and get

$$-\frac{\hbar^2}{2\mu}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \lambda\sin^2\theta\Theta + \nu\Theta = 0 \qquad (3.28)$$

and

$$-\frac{\hbar^2}{2\mu}\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \nu \qquad (3.29)$$

The solution to (3.29) is straightforward, giving

$$\Phi = A\exp[\pm i(2\mu\nu/\hbar^2)^{1/2}\phi] \qquad (3.30)$$

where A is a constant. We can now apply the condition that the wave function, and hence Φ, must be single valued† so that

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

Thus

$$\exp[\pm i(2\mu\nu/\hbar^2)^{1/2}2\pi] = 1$$

and so

$$(2\mu\nu/\hbar^2)^{1/2} = m \qquad (3.31)$$

where m is an integer which can be positive or negative or zero. Substituting back into (3.30), we get

$$\Phi = (2\pi)^{-1/2}\exp(im\phi) \qquad (3.32)$$

where the factor $(2\pi)^{-1/2}$ is included as a first step to normalizing the wave

†See footnote to p. 21.

function; it ensures that

$$\int_0^{2\pi} |\Phi|^2 \, d\phi = 1 \tag{3.33}$$

We have now completed the solution of one of the three differential equations and obtained one quantum condition (3.31).

Returning to the equation for Θ (3.28), we can substitute from (3.31) and rearrange to get

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + (\lambda' \sin^2\theta - m^2)\Theta = 0 \tag{3.34}$$

where $\lambda' = 2\mu\lambda/\hbar^2$. The solution of this equation is made simpler if we make the substitution $v = \cos\theta$ and write $P(v) \equiv \Theta(\theta)$, leading to

$$\frac{d}{d\theta} = -\sin\theta \frac{d}{dv} = -(1 - v^2)^{1/2} \frac{d}{dv}$$

Equation (3.34) then becomes

$$\frac{d}{dv}\left[(1 + v^2)\frac{dP}{dv}\right] + \left[\lambda' - \frac{m^2}{1 - v^2}\right]P = 0 \tag{3.35}$$

We first consider the simpler special case where m is equal to zero; Eq. (3.35) is then

$$\frac{d}{dv}\left[(1 - v^2)\frac{dP}{dv}\right] + \lambda' P = 0 \tag{3.36}$$

The method of series solution which was previously employed in the case of the one-dimensional simple harmonic oscillator (Sec. 2.6) can now be applied and we put

$$P = \sum_{p=0}^{\infty} a_p v^p \tag{3.37}$$

Hence

$$\begin{aligned}\frac{d}{dv}\left[(1 - v^2)\frac{dP}{dv}\right] &= \frac{d}{dv}\sum_{p=0}^{\infty}\left[a_p p v^{p-1} - a_p p v^{p+1}\right] \\ &= \sum_{p=0}^{\infty} a_p p(p-1)v^{p-2} - \sum_{p=0}^{\infty} a_p p(p+1)v^p \\ &= \sum_{p=0}^{\infty}\left[a_{p+2}(p+2)(p+1) - a_p p(p+1)\right]v^p \end{aligned} \tag{3.38}$$

We can now substitute from (3.38) into (3.36):

$$\sum_{p=0}^{\infty}\left\{a_{p+2}(p+2)(p+1) - a_p[p(p+1) - \lambda']\right\}v^p = 0$$

This can be true only if the coefficient of each power of v is zero, so we obtain the recurrence relation

$$\begin{aligned}\frac{a_{p+2}}{a_p} &= \frac{p(p+1) - \lambda'}{(p+1)(p+2)} \\ &\to 1 \qquad \text{as } p \to \infty\end{aligned} \tag{3.39}$$

Thus, for large p the series (3.37) is identical to the Taylor expansion of the function $(1 - v)^{-1}$ which diverges to infinity at the points $v = \pm 1$. Such a divergence in the wave function is not consistent with physical boundary conditions so the series must terminate at some finite value of p, say $p = l$, and we therefore obtain the second quantum condition

$$\lambda' = l(l+1) \tag{3.40}$$

where l is an integer which is greater than or equal to zero, along with the requirement that $a_0 = 0$ if l is odd and $a_1 = 0$ if l is even. Thus P ($\equiv P_l$) is a polynomial of degree l which contains either only odd powers or only even powers of v. These polynomials are known as the Legendre polynomials and their properties are described in many mathematics textbooks. Explicit forms, corresponding to particular values of l, are easily obtained from (3.40) and (3.39); for example

$$\left.\begin{aligned} P_0(v) &= 1 \\ P_1(v) &= v \\ P_2(v) &= \tfrac{1}{2}(3v^2 - 1) \\ P_3(v) &= \tfrac{1}{2}(5v^3 - 3v) \end{aligned}\right\} \tag{3.41}$$

where the values of the constants a_0 and a_1 have been chosen in accordance with established convention.

The solution of (3.35) in the general case of non-zero values of m is more complicated and the reader is referred to a mathematics textbook for the details. We note that (3.35) is independent of the sign of m, so we expect the solutions to be characterized by l and $|m|$ and we write them as $P_l^{|m|}(v)$. It can be shown† that

$$P_l^{|m|}(v) = (1 - v^2)^{|m|/2}\frac{d^{|m|}P_l}{dv^{|m|}} \tag{3.42}$$

†The mathematically inclined reader can verify this result by substituting it into (3.35) and using Leibniz's expression for the nth derivative of a product to show that the result is equivalent to $(1 - v^2)^{|m|/2}$ times the $|m|$th derivative of the left-hand side of Eq. (3.36).

We can use (3.42) to obtain a condition restricting the allowed values of m. P_l is a polynomial of degree l so its $|m|$th derivative, and hence $P_l^{|m|}$, will be zero if $|m|$ is greater than l. But if $P_l^{|m|}$ is zero, the whole wave function must be zero over all space, and this is physically unrealistic. We therefore have the condition

$$-l \leqslant m \leqslant l \tag{3.43}$$

We have now solved the differential equations in θ and ϕ so we can combine the solutions to obtain expressions for the angular part of the wave function, which we now write as $Y_{lm}(\theta, \phi)$, the suffixes l and m emphasizing the importance of these quantum numbers in characterizing the functions.

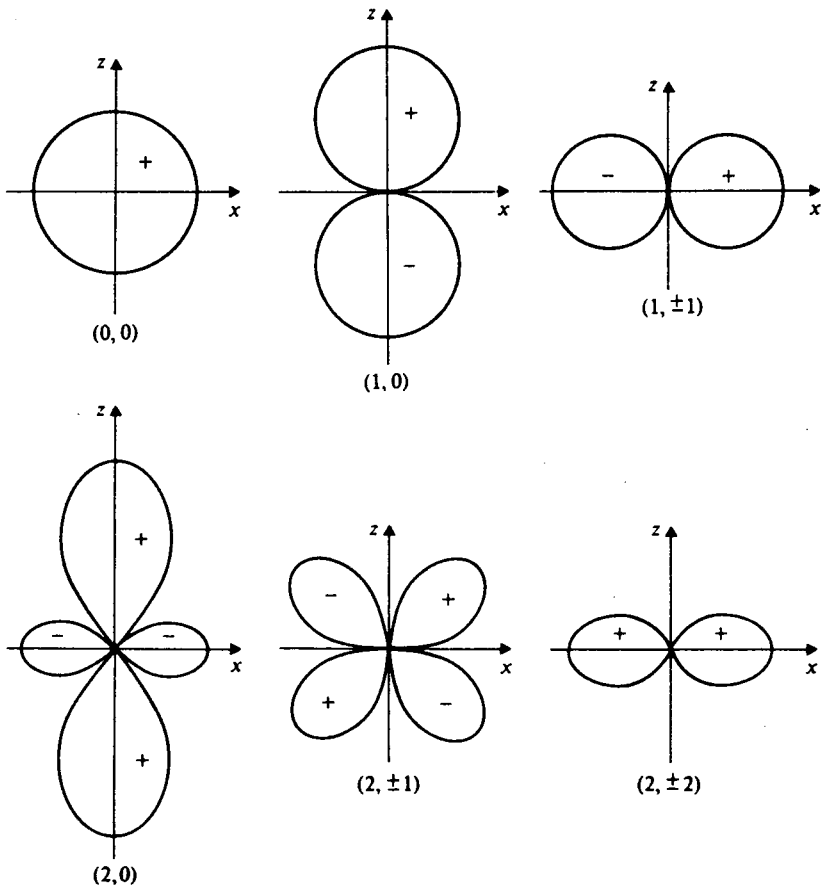

Figure 3.3 Polar plots of the sections at $y = 0$ through the spherical harmonics with quantum numbers (l, m). The distance from the origin of a point on a curve is proportional to the magnitude of the function in that direction. The sign of the function in each region of space is also indicated.

We have

$$Y_{lm}(\theta, \phi) = (-1)^m \left[\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta)\, e^{im\phi} \qquad m \geqslant 0 \tag{3.44}$$

and $$Y_{l=m}(\theta, \phi) = (-1)^m Y_{lm}(\theta, \phi)$$

where it can be shown that the factor in square brackets ensures normalization of the function when it is integrated over all solid angles; that is,

$$\int_0^{2\pi} \int_0^{\pi} |Y_{lm}(\theta, \phi)|^2 \sin\phi \, d\theta \, d\phi = 1 \tag{3.45}$$

The phase factors $(-1)^m$ in (3.44) are arbitrary, but chosen in accordance with established convention. The functions Y_{lm} are known as *spherical harmonics* and the reader is once again referred to an appropriate mathematics textbook for a discussion of their properties and a derivation of the form of the normalizing constant. Explicit expressions for the spherical harmonics with l less than or equal to 2 are given below and illustrated in Fig. 3.3 by polar diagrams.

$$\left.\begin{aligned}
Y_{00} &= \frac{1}{(4\pi)^{1/2}} \\
Y_{10} &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\
Y_{1\pm1} &= \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi} \\
Y_{20} &= \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\
Y_{2\pm1} &= \mp\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta\, e^{\pm i\phi} \\
Y_{2\pm2} &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm 2i\phi}
\end{aligned}\right\} \tag{3.46}$$

A notable feature of Fig. 3.3 is that the wave functions have a particular orientation in space even though the potential is spherically symmetric and the direction of the z axis (sometimes known as the axis of quantization) is therefore arbitrary. This apparent paradox is resolved in the same way as in the similar case of a particle in a square box discussed above. We first note that m does not enter Eq. (3.25) which determines the energy levels of the system, so there are always $2l + 1$ degenerate states that differ only in their values of m. If we measure the energy of such a system, we shall not be able to tell which of these wave functions is appropriate and we must therefore average their squared moduli in order to calculate the position

probability distribution. The apparently angularly dependent part of this quantity will therefore be given by

$$(2l+1)^{-1}\sum_{m=-l}^{l}|Y_{lm}(\theta,\phi)|^2$$

It is one of the standard properties of the spherical harmonics that the above quantity is spherically symmetric (as can be readily verified in the cases where $l = 0$, 1 and 2 by substituting the expressions given in Eq. (3.46)) so we once again see that the predictions of quantum mechanics concerning physically measurable quantities are consistent with what would be expected from the symmetry of the problem.

The physical significance of the quantum numbers l and m will be discussed in detail later (Chapter 5). For the moment we note that these cannot be directly connected with the quantization of the energy of the system as the latter quantity appears only in the radial equation which we have yet to solve. It will turn out that l and m are associated with the quantization of the angular momentum of a particle in a central field: the square of the angular momentum has the value $l(l+1)\hbar^2$ and the z component of angular momentum has the value $m\hbar$.

The Radial Equation

We now turn our attention to the radial equation (3.25) which determines the energy levels of the system. Substituting the expression for λ obtained from the angular solution (3.40) we get

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

This can be simplified by making the substitution $\chi(r) = rR(r)$ which gives

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{dr^2}+\left[V(r)+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]\chi=E\chi \qquad (3.47)$$

Apart from the second term within the square brackets, Eq. (3.47) is identical in form to the one-dimensional Schrödinger equation. However, an additional boundary condition applies in this case: χ must equal zero at $r = 0$ otherwise $R = r^{-1}\chi$ would be infinite at that point.†

As well as being mathematically convenient, the function $\chi(r)$ has a physical interpretation in that $|\chi|^2\,dr$ is the probability of finding the electron

†The observant reader will have noticed that if $R \sim r$ then $\int_0^r |\mathbf{R}|^2\,\mathbf{r}^2 d\mathbf{r}$ will be finite and therefore the boundary condition set out in Chapter 2 is not breached. It can be shown that the condition $\chi=0$ at $r=0$ follows from the requirement that the solutions of the Schrödinger equation expressed in spherical polar coordinates must also be solutions when the equation is written in Cartesians. Further details on this point can be found in P. A. M. Dirac *The Principles of Quantum Mechanics* (Oxford 1974) Chapter 6.

at a distance between r and $r + dr$ from the origin averaged over all directions. This follows from the fact that this probability is obtained by integrating $|\psi(r,\theta,\phi)|^2$ over a spherical shell of radius r and thickness dr. That is, it is given by

$$|R^2(r)|r^2\,dr\int_0^{2\pi}\int_0^{\pi}|Y(\theta,\phi)^2|\sin\theta\,d\theta\,d\phi$$
$$=|\chi^2(r)|$$

using (3.45).

To progress further with the solution of the radial equation, the form of the potential $V(r)$ must be known, and in the next section we shall consider the particular example of the hydrogenic atom.

3.4 THE HYDROGENIC ATOM

We are now ready to apply quantum theory to the real physical situation of an electron moving under the influence of a positively charged nucleus. If this nucleus consists of a single proton, the system is a hydrogen atom, but the theory is also applicable to the more general case of an atom with atomic number Z (and hence nuclear charge Ze) with all but one of its electrons removed (for example, He^+, Li^{++}, etc.); in general such a system is described as a *hydrogenic atom*. The potential energy of interaction between the electron and the nucleus is $-Ze^2/4\pi\varepsilon_0 r$, so Eq. (3.47) becomes† in this case

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi}{dr^2}+\left[-\frac{Ze^2}{4\pi\varepsilon_0 r}+\frac{l(l+1)\hbar^2}{2\mu r^2}\right]\chi=E\chi \qquad (3.48)$$

The solution of Eq. (3.48) will again involve considerable manipulation which is simplified by making a suitable substitution. We define a new variable ρ so that

$$\rho=(-8\mu E/\hbar^2)^{1/2}r \qquad (3.49)$$

(note that E is negative for bound states as the potential is zero when r is

†We have assumed above that the electron is moving in the field of a fixed nucleus, but this will not be exactly true as the nucleus is also moving in the field of the electron. As is shown in Chapter 10, this nuclear motion can be allowed for in exactly the same way as in classical mechanics by taking r to be the distance between the nucleus and the electron, and μ to be the reduced mass of the nucleus (mass m_N) and the electron (mass m_e). That is,

$$\mu = m_N m_e/(m_N+m_e)$$

Because the mass of the electron is much smaller than that of the nucleus, μ is very nearly equal to m_e and the effect of nuclear motion is small, although large enough to have a significant effect on the comparison between the theoretical and experimental values of the Rydberg constant discussed below.

infinite) and hence

$$\frac{d^2\chi}{dr^2} = -\frac{8\mu E}{\hbar^2}\frac{d^2\chi}{d\rho^2} \tag{3.50}$$

Equation (3.48) now becomes

$$\frac{d^2\chi}{d\rho^2} - l(l+1)\frac{\chi}{\rho^2} + \left(\frac{\beta}{\rho} - \frac{1}{4}\right)\chi = 0 \tag{3.51}$$

where the constant β is defined as

$$\beta = \left(-\frac{\mu}{2E}\right)^{1/2}\frac{Ze^2}{4\pi\varepsilon_0\hbar} \tag{3.52}$$

We first consider the solution to (3.51) in the case of very large ρ when the equation becomes

$$\frac{d^2\chi}{d\rho^2} - \tfrac{1}{4}\chi = 0 \tag{3.53}$$

leading to

$$\chi \sim \exp(-\rho/2) \tag{3.54}$$

(where we have rejected a possible solution with positive exponent because it diverges to infinity at large ρ). This suggests that we try

$$\chi = F(\rho)\exp(-\rho/2) \tag{3.55}$$

as a solution to (3.51). On substitution we get

$$\frac{d^2F}{d\rho^2} - \frac{dF}{d\rho} - \frac{l(l+1)}{\rho^2}F + \frac{\beta}{\rho}F = 0 \tag{3.56}$$

We now look for a series solution to (3.56) and put

$$F = \sum_{p=1}^{\infty} a_p\rho^p \tag{3.57}$$

The lower limit of this summation is $p = 1$ rather than $p = 0$, otherwise F and, therefore, χ would not be zero at $\rho = 0$. Thus

$$\frac{dF}{d\rho} = \sum_{p=1}^{\infty} pa_p\rho^{p-1} \tag{3.58}$$

and

$$\frac{d^2F}{d\rho^2} = \sum_{p=1}^{\infty} p(p-1)a_p\rho^{p-2}$$

$$= \sum_{p=1}^{\infty} (p+1)pa_{p+1}\rho^{p-1} \tag{3.59}$$

Also

$$F/\rho^2 = \sum_{p=1}^{\infty} a_p\rho^{p-2}$$

$$= a_1\rho^{-1} + \sum_{p=1}^{\infty} a_{p+1}\rho^{p-1} \tag{3.60}$$

Substituting from Eqs (3.57) to (3.60) into (3.56) we get

$$-l(l+1)a_1\rho^{-1} + \sum_{p=1}^{\infty}[(p+1)pa_{p+1} - pa_p - l(l+1)a_{p+1} + \beta a_p]\rho^{p-1} \tag{3.61}$$

The coefficient of each power of ρ must vanish so we have

$$a_1 = 0 \qquad \text{unless } l = 0$$

and

$$\frac{a_{p+1}}{a_p} = \frac{p-\beta}{p(p+1) - l(l+1)} \tag{3.62}$$

$$\to p^{-1} \qquad \text{as } p \to \infty \tag{3.63}$$

We first note that the denominator on the right-hand side of (3.62) is zero if $p = l$. This implies that a_{l+1} (and, by implication, all other a_p where p is greater than l) must be infinite unless a_l is zero. But if a_l equals zero then it also follows from (3.62) that a_{l-1}, a_{l-2} etc must also equal zero. We conclude, therefore, that all a_p with p less than or equal to l must be zero if the solution is to represent a physically realistic wave function. We also see that (3.63) is identical to the recurrence relation for the terms in the series expansion of $\exp(\rho)$ and so χ, which equals $F\exp(-\rho/2)$, will diverge like $\exp(\rho/2)$ as ρ tends to infinity. However, just as in the case of solutions to the harmonic oscillator and Legendre polynomial equations, this divergence can be prevented by ensuring that the series terminates after a finite number of terms. For this to occur at the term $p = n$ we must have

$$\beta = n > l \tag{3.64}$$

and hence, using (3.52)

$$E \equiv E_n = -\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2 n^2} \tag{3.65}$$

We have thus derived expressions for the discrete energy levels of the hydrogenic atom in terms of the reduced mass of the electron and nucleus, the nuclear charge, and the fundamental constants e, $\hbar$, and ε_0. It should be noted that the energy levels (3.65) are not only independent of m, as would be expected from the earlier discussion, but are also independent of l. This

additional degeneracy is a particular feature of the Coulomb potential and is not a general property of a spherically symmetric system.

It is now an acid test of the theory developed so far that we compare the above energy levels with those experimentally measured from observations of atomic spectra. We saw in Chapter 1 that the line spectra of hydrogen could be accounted for if the hydrogen atom were assumed to have a set of energy levels given by

$$E_n = -2\pi\hbar c R_0/n^2 \tag{3.66}$$

where n is a positive integer and R_0 is a constant whose currently accepted best value is $1.096\,775\,9\,(1) \times 10^7\ \mathrm{m}^{-1}$, the bracketed number indicating the experimental error in the last place. Comparison of (3.65) and (3.66) shows at once that these have the same form so that there is at least qualitative agreement between theory and experiment. Quantitative comparison is made using the measured values of the fundamental constants

$$\mu = 9.104\,575\,(89) \times 10^{-31}\ \mathrm{kg}$$
$$\varepsilon_o = 8.854\,187\,82\,(7) \times 10^{-12}\ \mathrm{F\,m^{-1}}$$
$$\hbar = 1.054\,588\,7\,(57) \times 10^{-34}\ \mathrm{J\,s}$$
$$e = 1.602\,189\,2\,(46) \times 10^{-19}\ \mathrm{C}$$
$$c = 2.997\,924\,6\,(1) \times 10^{8}\ \mathrm{m\,s^{-1}}$$

to obtain an estimate of R_0 from Eq. (3.65) as $1.096\,775\,7\,(95) \times 10^7\ \mathrm{m}^{-1}$. Thus the agreement between theory and experiment is well within the range of the extremely small experimental errors. Similar agreement is obtained for other hydrogenic atoms when the appropriate values of the nuclear charge and the reduced mass are substituted into Eq. (3.65). These results therefore represent an important test of quantum mechanical theory which it has passed with flying colours.† Our belief in quantum mechanics does not of course rest on this result alone, and indeed an identical expression to (3.65) was derived by Niels Bohr using an earlier theory which was subsequently shown to be incorrect when applied to other more complex systems. However, although we shall compare the results of calculation and experiment on a number of other occasions when we shall always find agreement within the limits of experimental error, there are very few examples of physical quantities whose values can be both measured experimentally to such high precision and also calculated exactly by solving the appropriate quantum-mechanical equations.

†Of course the quantum theory of atomic spectra is now so well established that formulae such as (3.65) are themselves used in determining the best values of the fundamental constants, but the fact that a wide variety of experimental data can be successfully and consistently used in this way is itself a confirmation of the theory.

The Hydrogenic Atom Wave Functions

We now complete our consideration of the hydrogenic atom by discussing the form of the wave functions associated with the different energy levels. We saw above that the radial part of the wave function is consistent with the boundary conditions only if the series (3.57) for F starts at the term $p = l + 1$ and terminates at $p = n$. We thus have

$$F_n(\rho) = \sum_{p=l+1}^{n} a_p \rho^p \tag{3.67}$$

where the coefficients a_p can be expressed in terms of a_{l+1} using the recurrence relation (3.62) with $\beta = n$. The polynomials so obtained are known as the *associated Laguerre functions*. We can then use (3.55) and the definition of ρ in terms of r to obtain $\chi(r)$ and hence $R(r)$. This can be combined with the appropriate spherical harmonic to produce an expression for the complete time-independent part of the wave function, $u(r, \theta, \phi)$, which will be normalized, provided the spherical harmonic has been normalized in accordance with (3.45) and the constant a_{l+1} has been chosen so that

$$\int_0^\infty |R|^2 r^2\, dr = 1 \tag{3.68}$$

Formally, then, we have

$$u_{nlm} = R_{nl}(r)\, Y_{lm}(\theta, \phi) \tag{3.69}$$

where the suffixes indicate the dependence of the various functions on the quantum numbers n, l, and m. The wave functions corresponding to the five states of lowest energy as determined in this way are

$$\left.\begin{aligned}
u_{100} &= (Z^3/\pi a_0^3)^{1/2} \exp(-Zr/a_0) \\
u_{200} &= (Z^3/8\pi a_0^3)^{1/2} (1 - Zr/2a_0) \exp(-Zr/2a_0) \\
u_{210} &= (Z^3/32\pi a_0^3)^{1/2} (Zr/a_0) \cos\theta \exp(-Zr/2a_0) \\
u_{21\pm1} &= \mp (Z^3/\pi a_0^3)^{1/2} (Zr/8a_0) \sin\theta \exp(\pm i\phi) \exp(-Zr/2a_0)
\end{aligned}\right\} \tag{3.70}$$

where the constant a_0 is defined as

$$\begin{aligned} a_0 &= 4\pi\varepsilon_o\hbar^2/\mu e^2 \\ &= 0.529\,177 \times 10^{-10}\ \mathrm{m} \end{aligned} \tag{3.71}$$

and is known as the *Bohr radius*.

The value of the azimuthal quantum number l is often denoted by a particular letter code: states with $l = 0$, 1, 2, and 3 are labelled s, p, d, and f respectively. This letter is sometimes prefixed by a number equal to the quantum number n; thus for example, the first state in (3.70) is known as the $1s$ state, the second is $2s$, and the others are $2p$ states.

The radial parts of the wave functions (3.70) are plotted as functions of

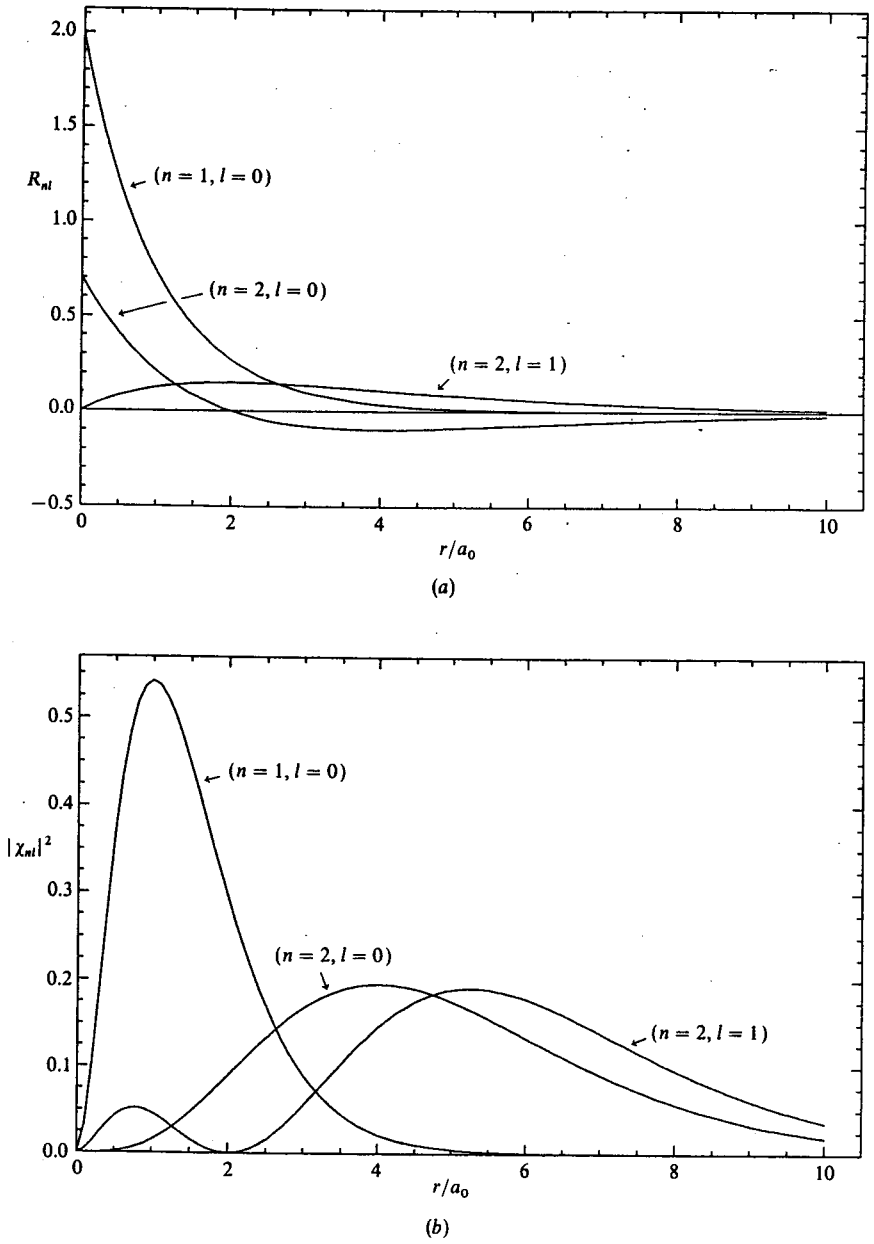

Figure 3.4 The radial parts, $R_{n,l}$, of the wave functions corresponding to some of the energy states of the hydrogen atom are shown in (a). The corresponding radial probability distributions, $|\chi_{n,l}|^2 = r^2|R_{n,l}|^2$, are displayed in ($b$).

r in Fig. 3.4 for the case of the hydrogen atom where $Z = 1$. We see that the constant a_0 characterizes the width of the wave function of the lowest energy state and that this width increases for states of higher energy. We can combine (3.71) and (3.65) to express the energy levels in terms of a_0:

$$E_n = -\frac{Z^2e^2}{2(4\pi\varepsilon_0)a_0n^2} \tag{3.72}$$

As the potential energy is given by $V = -Ze^2/4\pi\varepsilon_0 r$, an electron with the above total energy could only have positive kinetic energy for values of r less than $2n^2a_0/Z$. These limits are indicated in Fig. 3.4 and we see that the exponential tails of the wave functions penetrate the classically forbidden region in a manner very similar to that discussed in the one-dimensional cases in Chapter 2.

Figure 3.4 also shows $|\chi^2(r)| = r^2|R^2(r)|$ for each state as a function of r. As we pointed out earlier, this expression equals the probability that the electron be found at a distance between r and $r + dr$ from the origin (in any direction). We see that this probability reaches a maximum at $r = a_0$ in the case of the ground state wave function. We particularly note that in all cases $|\chi^2|$ equals zero at the origin, even though the square of the wave function is actually a maximum at that point. The reader should think carefully about this apparent contradiction and how it can be resolved by understanding the different nature of the two probability distributions represented by $|\psi^2|$ and $|\chi^2|$.

PROBLEMS

3.1 Calculate the energy levels and obtain expressions for the associated wave functions in the case of a particle moving in two dimensions in a rectangular, infinite-walled box of sides a and b. Discuss the degeneracy of the system and the symmetry of the position probability distribution when $a = b$.

3.2 What is the symmetry of the position probability distribution and how is it related to the degeneracy in the case of a particle confined to a three-dimensional box with cubic symmetry (that is, with $a = b = c$)?

3.3 A particle moves in two dimensions in a circularly symmetric potential. Show that the time-independent Schrödinger equation can be separated in plane polar coordinates and that the angular part of the wave function has the form $(2\pi)^{1/2}\exp(im\phi)$ where m is an integer. What is the symmetry of the position probability distribution in this case?

3.4 Consider a circularly symmetric two-dimensional system similar to that described in Prob. 3.3 where the potential is zero for all values of r less than a and infinite otherwise. Show that the radial part $R(r)$ of the wave function must satisfy the equation

$$\frac{d^2R}{d\rho^2} + \frac{1}{\rho}\frac{dR}{d\rho} + \left(1 - \frac{m^2}{\rho^2}\right)R = 0$$

where $\rho = (2\mu E)^{1/2}r$. In the case where $m = 0$ show that $R = \sum_{k=0}^{\infty} A_k\rho^k$ where $A_k = 0$ if k is odd and $A_{k+2} = -A_k/(k+2)^2$. Given that the first zero of this function is at $\rho = 2.405$, obtain an expression for the energy of the ground state of the system.