2.23 (a) By varying the parameter a in the trial function

$$\phi_0(x) = (a^2 - x^2)^2, \qquad |x| < a$$
$$= 0 \qquad\qquad |x| \geqslant a$$

obtain an upper bound for the ground state energy of a linear harmonic oscillator having the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2$$

(b) Show that the function $\phi_1(x) = x\phi_0(x)$ is a suitable trial function for the first excited state and obtain a variational estimate of the energy of this level.

2.24 Prove the result given in equation (2.402).

2.25 Let $E_{n,l}$ denote the discrete energy levels of a particle of mass m in a central potential $V(r)$, corresponding to a given orbital angular momentum quantum number l, and let $E_{n,l}^{\min}$ be their minimum value. Prove that $E_{n,l}^{\min} < E_{n,l+1}^{\min}$
(**Hint**: Write the Hamiltonian of the particle as

$$H = H_r + \frac{\mathbf{L}^2}{2mr^2}, \qquad H_r = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(r)$$

and note that H_r is a purely radial operator.)

2.26 Derive the equations (2.425) for $S_0(x)$, $S_1(x)$ and $S_2(x)$.

2.27 Derive the expression (2.432) for $S_2(x)$.

2.28 Solve the equations (2.425a) and (2.425b) in the case $E < V$ to obtain the WKB solutions (2.440).

3 One-electron atoms

In this chapter we begin our quantum mechanical study of atomic structure by considering the simplest atom, namely the hydrogen atom, which consists of a proton and an electron. Apart from small corrections, which we shall discuss in Chapter 5, the hydrogen atom may be considered as a non-relativistic system of two particles interacting by means of an attractive Coulomb potential. Other similar one-electron systems, called hydrogenic atoms, include the isotopes of hydrogen (deuterium, tritium) and the hydrogenic ions (He^+, Li^{++}, etc.) which we have already encountered in our study of the Bohr model. These hydrogenic systems will also be discussed in the present chapter.

Our starting point is the Schrödinger equation for one-electron atoms. After separating the centre of mass motion, we solve the eigenvalue equation for the relative motion in spherical polar coordinates, and obtain the energy levels and wave functions of the discrete spectrum. We then consider the expectation values of various operators, and prove the virial theorem. This is followed by a study of the bound state wave functions of one-electron atoms in parabolic coordinates. We conclude this chapter with a brief discussion of 'special' hydrogenic systems such as positronium, muonium, antihydrogen, muonic and hadronic atoms, and Rydberg atoms.

3.1 The Schrödinger equation for one-electron atoms

Let us consider a hydrogenic atom containing an atomic nucleus of charge Ze and an electron of charge $-e$ interacting by means of the Coulomb potential

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{3.1}$$

where r is the distance between the two particles. We denote by m the mass of the electron and M the mass of the nucleus. Since the interaction potential (3.1) only depends on the relative coordinate of the two particles, we may use the results of Section 2.7 to separate the motion of the centre of mass. Remembering that $\mathbf{P}$ is the total momentum associated with the motion of the centre of mass and $\mathbf{p}$ the relative momentum, the total energy of the atom can be split into two parts. The first one is the kinetic energy $P^2/[2(M+m)]$ corresponding to the motion of

the centre of mass, and the second one is the (internal) energy of the relative motion, governed by the Hamiltonian

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{3.2}$$

where

$$\mu = \frac{mM}{m+M} \tag{3.3}$$

is the reduced mass of the two particles. Thus, working in the centre of mass system (where $P = 0$) and in the position representation, we must solve the one-body time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3.4}$$

Instead of using the position representation, as we shall do below, it is also possible to solve the Schrödinger equation for one-electron atoms in momentum space. This is carried out in Appendix 5, where the hydrogenic wave functions in momentum space are obtained.

Solution in spherical polar coordinates

Because the interaction potential (3.1) is central, the wave equation (3.4) may be separated in spherical polar coordinates (see Section 2.6). Thus we write a particular solution of this equation as

$$\psi_{E,l,m}(r, \theta, \phi) = R_{E,l}(r)Y_{lm}(\theta, \phi) \tag{3.5}$$

where $Y_{lm}(\theta, \phi)$ is a spherical harmonic corresponding to the orbital angular momentum quantum number l and to the magnetic quantum number m (with $m = -l, -l+1, \ldots, +l$). The function $R_{E,l}(r)$ satisfies the radial Schrödinger equation

$$\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{l(l+1)}{r^2}\right] - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right\}R_{E,l}(r) = ER_{E,l}(r) \tag{3.6}$$

which we have obtained by substituting into (2.235) the expression (3.1) of the Coulomb potential, and making the change $m \to \mu$. As we remarked in Section 2.6, we can simplify (3.6) by introducing the new unknown function

$$u_{E,l}(r) = rR_{E,l}(r) \tag{3.7}$$

Thus, using (2.239) we find that $u_{E,l}(r)$ satisfies the equation

$$\frac{\mathrm{d}^2u_{E,l}}{\mathrm{d}r^2} + \frac{2\mu}{\hbar^2}[E - V_{\mathrm{eff}}(r)]u_{E,l}(r) = 0 \tag{3.8}$$

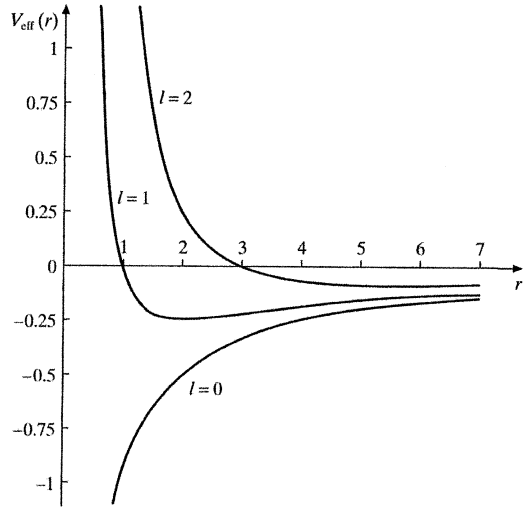

Figure 3.1 The effecitive potential $V_{\mathrm{eff}}(r)$ given by (3.9) for the case $Z = 1$ and for the values $l = 0, 1, 2$. The unit of length is $a_\mu = (m/\mu)a_0$ where a_0 is the Bohr radius (1.86). The unit of energy is $e^2/(4\pi\varepsilon_0 a_\mu)$.

where

$$V_{\mathrm{eff}}(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{3.9}$$

is the effective potential. Figure 3.1 shows $V_{\mathrm{eff}}(r)$ for the case $Z = 1$ and for the values $l = 0, 1, 2$.

The problem of solving the Schrödinger equation (3.4) therefore reduces to that of solving the radial one-dimensional equation (3.8) corresponding to a particle of mass μ moving in an effective potential V_{eff} made up of the Coulomb potential (3.1) plus the 'centrifugal barrier' potential $l(l+1)\hbar^2/(2\mu r^2)$. It is clear that since $V_{\mathrm{eff}}(r)$ tends to zero for large r, the solution $u_{E,l}(r)$ for $E > 0$ will have an oscillatory behaviour at infinity and will be an acceptable eigenfunction for any positive value of E. We therefore have a continuum spectrum for $E > 0$. The corresponding unbound states play an important role in the analysis of the scattering of electrons by ions; we shall return to such collision phenomena in Chapters 12 and 13. For the moment, however, we will only be concerned with the bound states of hydrogenic atoms, corresponding to the case $E < 0$.

Let us return to the radial equation (3.8). We shall look for solutions which vanish at $r = 0$, that is

$$u_{E,l}(0) = 0 \tag{3.10}$$

so that the radial function $R_{E,l}(r)$ – and hence the full wave function $\psi_{E,l,m}(\mathbf{r})$ given by (3.5) – remains finite at the origin [1]. It is convenient to introduce the dimensionless quantities

$$\rho = \left(-\frac{8\mu E}{\hbar^2}\right)^{1/2} r \tag{3.11}$$

and

$$\lambda = \frac{Ze^2}{4\pi\varepsilon_0\hbar}\left(-\frac{\mu}{2E}\right)^{1/2} = Z\alpha\left(-\frac{\mu c^2}{2E}\right)^{1/2} \tag{3.12}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c) \simeq 1/137$ is the fine structure constant and we recall that $E < 0$. In terms of the new quantities ρ and λ, the equation (3.8) now reads

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right] u_{E,l}(\rho) = 0 \tag{3.13}$$

As in the case of the harmonic oscillator (see Section 2.4) we first analyse the asymptotic behaviour of $u_{E,l}(\rho)$. To this end, we remark that when $\rho \to \infty$ the terms in $1/\rho$ and $1/\rho^2$ become negligible with respect to the constant term (–1/4), so that (3.13) reduces to the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{1}{4}\right] u_{E,l}(\rho) = 0 \tag{3.14}$$

whose solutions are $\exp(\pm\rho/2)$. Therefore, using the fact that the function $u_{E,l}(r)$ must be bounded everywhere, including infinity, we keep only the exponentially decreasing function and we have

$$u_{E,l}(\rho) \underset{\rho\to\infty}{\sim} \mathrm{e}^{-\rho/2} \tag{3.15}$$

This result suggests that we should search for a solution of the radial equation (3.13) having the form

$$u_{E,l}(\rho) = \mathrm{e}^{-\rho/2} f(\rho) \tag{3.16}$$

where we have written $f(\rho) \equiv f_{E,l}(\rho)$ to simplify the notation. Substituting (3.16) in (3.13), we obtain for $f(\rho)$ the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \frac{\mathrm{d}}{\mathrm{d}\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right] f(\rho) = 0 \tag{3.17}$$

[1] The finiteness of the wave function $\psi_{E,l,m}(\mathbf{r})$ is not really a necessary requirement. In fact, mildly singular wave functions are encountered in some cases, for example in the Dirac relativistic theory of one-electron atoms. The correct boundary condition is obtained by requiring that all the possible physical states are described by a complete, orthogonal set of wave functions. However, for a large class of potentials including the Coulomb potential (3.1), this condition may be shown to lead to the simpler requirement (3.10).

We now write a power series expansion for $f(\rho)$ in the form

$$f(\rho) = \rho^{l+1} g(\rho) \tag{3.18}$$

where

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k, \qquad c_0 \neq 0 \tag{3.19}$$

and we have used the fact (see Section 2.6) that $u_{E,l}(\rho)$ – and therefore $f(\rho)$ – behaves like ρ^{l+1} for all central potentials $V(r)$ which are less singular than r^{-2} at the origin. Upon substitution of (3.18) into (3.17) we find that the function $g(\rho)$ satisfies the differential equation

$$\left[\rho\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + (2l+2-\rho)\frac{\mathrm{d}}{\mathrm{d}\rho} + (\lambda - l - 1)\right] g(\rho) = 0 \tag{3.20}$$

Moreover, using the expansion (3.19) to solve the equation (3.20), we find that

$$\sum_{k=0}^{\infty} [k(k-1)c_k\rho^{k-1} + (2l+2-\rho)kc_k\rho^{k-1} + (\lambda - l - 1)c_k\rho^k] = 0 \tag{3.21}$$

or

$$\sum_{k=0}^{\infty} \{[k(k+1) + (2l+2)(k+1)]c_{k+1} + (\lambda - l - 1 - k)c_k\}\rho^k = 0 \tag{3.22}$$

so that the coefficients c_k must satisfy the recursion relation

$$c_{k+1} = \frac{k + l + 1 - \lambda}{(k+1)(k+2l+2)} c_k \tag{3.23}$$

If the series (3.19) does not terminate, we see from (3.23) that for large k

$$\frac{c_{k+1}}{c_k} \sim \frac{1}{k} \tag{3.24}$$

a ratio which is the same as that of the series for $\rho^p \exp(\rho)$, where p has a finite value. Thus in this case we deduce from (3.16) and (3.18) that the function $u_{E,l}(r)$ has an asymptotic behaviour of the type

$$u_{E,l}(\rho) \underset{\rho\to\infty}{\sim} \rho^{l+1+p}\, \mathrm{e}^{\rho/2} \tag{3.25}$$

which is clearly unacceptable.

The series (3.19) must therefore terminate, or in other words $g(\rho)$ must be a polynomial in ρ. Let us assume that the highest power of ρ in $g(\rho)$ is ρ^{n_r}, where the *radial quantum number* $n_r = 0, 1, 2, \ldots$ is a positive integer or zero. Then the coefficient $c_{n_r+1} = 0$, and from the recursion relation (3.23) we deduce that

$$\lambda = n_r + l + 1 \tag{3.26}$$

Let us introduce the *principal quantum number*

$$n = n_r + l + 1 \tag{3.27}$$

which is a positive integer ($n = 1, 2, \ldots$) since n_r and l can take on positive integer or zero values. Thus, from (3.26) and (3.27), we see that the eigenvalues of (3.13) are given by

$$\lambda = n, \qquad n = 1, 2, \ldots \tag{3.28}$$

3.2 Energy levels

Replacing in (3.12) the parameter λ by its value (3.28) we obtain the energy eigenvalues

$$\begin{aligned} E_n &= -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{\hbar^2} \\ &= -\frac{e^2}{(4\pi\varepsilon_0)a_0}\frac{\mu}{m}\frac{Z^2}{2n^2} \\ &= -\frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{2n^2} \end{aligned} \tag{3.29}$$

where $a_0 = 4\pi\varepsilon_0\hbar^2/(me^2)$ is the Bohr radius (1.86) and $a_\mu = 4\pi\varepsilon_0\hbar^2/(\mu e^2) = a_0 m/\mu$ is the modified Bohr radius (1.101). We may also write

$$E_n = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2} \tag{3.30}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c)$ is the fine structure constant. The first form (3.29) which does not contain the velocity of light c clearly shows that the energy levels E_n have been obtained by solving a non-relativistic equation. The second form (3.30), in which the energies E_n are expressed in terms of the rest mass energy μc^2, will be useful at a later stage when we shall discuss the relativistic corrections to the energy levels of one-electron atoms (see Chapter 5). Using atomic units (a.u.) defined in Appendix 14, we also have

$$E_n = -\frac{Z^2}{2n^2}\left(\frac{\mu}{m}\right) \tag{3.31}$$

where we have written explicitly the electron mass m (which is equal to unity in a.u.).

The energy values E_n, which we have obtained here by solving the Schrödinger equation for one-electron atoms, agree exactly with those found in Section 1.7 from the Bohr model. The agreement of this energy spectrum with the main features of the experimental spectrum was pointed out when we analysed the Bohr results. This agreement, however, is not perfect and we shall discuss in Chapter 5 various corrections (such as the fine structure arising from relativistic effects and the electron spin, the Lamb shift and the hyperfine structure due to nuclear

effects) which must be taken into account in order to explain the details of the experimental spectrum.

We note from (3.31) that since n may take on all integral values from 1 to $+\infty$, the energy spectrum corresponding to the Coulomb potential (3.1) contains an infinite number of discrete energy levels extending from $-(Z^2/2)(\mu/m)$ to zero. This is due to the fact that the magnitude of the Coulomb potential falls off slowly at large r. On the contrary, short-range potentials such as the square well have a finite (sometimes zero) number of bound states.

Another striking feature of the result (3.31) is that the energy eigenvalues depend only on the principal quantum number n, and are therefore degenerate with respect to l and m. Indeed, for each value of n the orbital quantum number l may take on the values $0, 1, \ldots, n-1$ and for each value of l the $(2l+1)$ possible values of the magnetic quantum number m are $-l, -l+1, \ldots, +l$. The total degeneracy of the energy level E_n is therefore given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2 \tag{3.32}$$

As we have already pointed out in Section 2.6, the degeneracy with respect to m is present for any central potential $V(r)$. On the other hand, the degeneracy with respect to l is characteristic of the Coulomb potential. This 'accidental' degeneracy can be traced to the existence of an additional constant of the motion, as we shall see in Section 3.5. The degeneracy with respect to l is removed if the dependence of the potential on r is modified. For example, we shall see in Chapters 8 and 9 that many properties of the alkali atoms can be understood in terms of the motion of a single 'valence' electron in a potential which is central, but which deviates from the $1/r$ Coulomb behaviour because of the presence of the 'inner' electrons. As a result, the energy of this valence electron does depend on l and the degeneracy with respect to l is removed, leading to n distinct levels E_{nl} for a given principal quantum number n. Finally, if an external magnetic field is applied to the atom, we shall see in Chapter 6 that the $(2l+1)$ degeneracy with respect to the magnetic quantum number m is removed.

Figure 3.2 shows an energy-level diagram for the hydrogen atom; it is similar to that displayed in Fig. 1.16 except that the degenerate energy levels with the same n but different l are shown separately. Following the usual spectroscopic notation, these levels are labelled by two symbols. The first one gives the value of the principal quantum number n and the second one indicates the orbital quantum number l according to the correspondence discussed in Section 2.5, namely

Value of l	0	1	2	3	4	5
	↕	↕	↕	↕	↕	↕
Code letter	s	p	d	f	g	h

Looking at the hydrogen atom spectrum (Fig. 3.2), we see that the ground state is a 1s state, the first excited state is fourfold degenerate and contains a 2s state and three 2p states (with $m = -1, 0, +1$), etc.

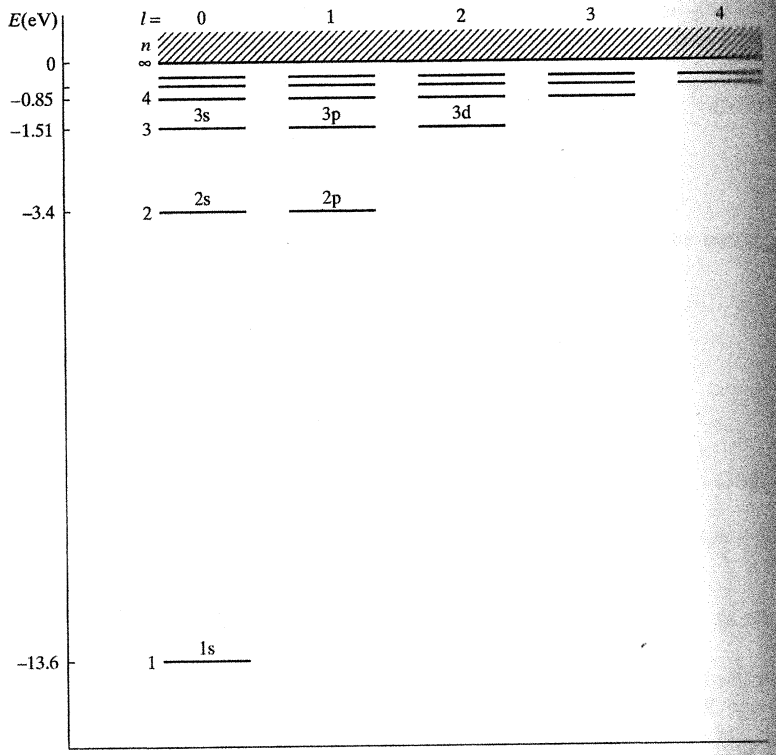

Figure 3.2 Energy-level diagram for atomic hydrogen.

Having obtained the energy levels of one-electron atoms within the framework of the Schrödinger non-relativistic theory, we may now ask about the spectral lines corresponding to transitions from one level to another. This problem will be discussed in detail in the next chapter, where we shall study the interaction of one-electron atoms with electromagnetic radiation. In particular, we shall calculate the transition rates for the most common transitions, the so-called electric dipole transitions, and we shall prove that these transitions obey the selection rules

$$\Delta l = l - l' = \pm 1 \qquad \Delta m = m - m' = 0, \pm 1 \tag{3.33}$$

while $\Delta n = n - n'$ is arbitrary. Here the symbols n, l, m refer to the quantum numbers of the upper state and n', l', m' to those of the lower state of the transition. Since the bound state energies E_n depend only on n, and because transitions can occur between states with any two values of n, it is clear that the Bohr frequency

rule (1.70) can still be applied to obtain the frequencies of the spectral lines corresponding to transitions between the energy levels. Thus, for a transition between two energy levels a and b, with energies $E_a < E_b$, we have

$$\nu_{ab} = Z^2 R(M)\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \tag{3.34}$$

where $R(M)$ is given by (1.102) and where $n_a = 1, 2, 3, \ldots$, $n_b = 2, 3, 4, \ldots$ with $n_b > n_a$.

3.3 The eigenfunctions of the bound states

Until now we have seen that the energy levels predicted by the Schrödinger theory for one-electron atoms agree with those already obtained in Section 1.7 using the Bohr model. However, the Schrödinger theory has much more predictive power than the old quantum theory since it also yields the *eigenfunctions* which enable one to calculate probability densities, expectation values of operators, transition rates, etc.

The radial eigenfunctions of the bound states

In order to obtain these eigenfunctions explicitly, let us return to (3.20). This equation can be identified with the *Kummer–Laplace differential equation*

$$z\frac{d^2w}{dz^2} + (c - z)\frac{dw}{dz} - aw = 0 \tag{3.35}$$

with $z = \rho$, $w = g$, $a = l + 1 - \lambda$ and $c = 2l + 2$. Within a multiplicative constant, the solution of (3.35), regular at the origin, is the *confluent hypergeometric function*

$$\begin{aligned} {}_1F_1(a, c, z) &= 1 + \frac{az}{c\ 1!} + \frac{a(a+1)z^2}{c(c+1)\ 2!} + \ldots \\ &= \sum_{k=0}^{\infty} \frac{(a)_k}{(c)_k}\frac{z^k}{k!} \end{aligned} \tag{3.36a}$$

where

$$\alpha_k = \alpha(\alpha + 1)\ldots(\alpha + k - 1), \qquad (\alpha)_0 = 1 \tag{3.36b}$$

In general, for large positive values of its argument the confluent hypergeometric series (3.36a) behaves asymptotically as

$${}_1F_1(a, c, z) \to \frac{\Gamma(c)}{\Gamma(a)} e^z z^{a-c} \tag{3.37}$$

where Γ is Euler's gamma function. Thus, in the present case the series (3.36a) for ${}_1F_1(l + 1 - \lambda, 2l + 2, \rho)$ is in general proportional to $\rho^{l-1-\lambda}\exp(\rho)$ for large ρ,

leading to a function $u_{El}(\rho)$ having the unacceptable asymptotic behaviour $u_{El}(\rho) \sim \rho^{-\lambda} \exp(\rho/2)$ (see (3.16) and (3.18)). The only way to obtain physically acceptable solutions of (3.20) is to require that the hypergeometric series for ${}_1F_1(l+1-\lambda, 2l+2, \rho)$ terminates, which implies that $l+1-\lambda = -n_r$ ($n_r = 0, 1, 2, \ldots$), and hence $\lambda = n_r + l + 1 = n$. The confluent hypergeometric function ${}_1F_1(l+1-\lambda, 2l+2, \rho) \equiv {}_1F_1(-n_r, 2l+2, \rho)$ then reduces to a *polynomial* of degree n_r, namely

$$
\begin{aligned}
&{}_1F_1(l+1-n, 2l+2, \rho) \\
&= \sum_{k=0}^{n-l-1} \frac{(k+l-n)(k-1+l-n)\ldots(1+l-n)}{(k+2l+1)(k-1+2l+1)\ldots(1+2l+1)} \frac{\rho^k}{k!}
\end{aligned}
\tag{3.38}
$$

in accordance with our foregoing discussion. We may readily verify the correctness of this result by using the recursion relation (3.23) which we derived above for the coefficients c_k of the function $g(\rho)$. Thus, setting $c_0 = 1$ and using the fact that $\lambda = n$, we find from (3.23) that

$$
c_k = \frac{(k+l-n)(k-1+l-n)\ldots(1+l-n)}{(k+2l+1)(k-1+2l+1)\ldots(1+2l+1)} \frac{1}{k!}
\tag{3.39}
$$

in agreement with (3.38). We also remark from (3.11) and (3.29) that

$$
\rho = \frac{2Z}{na_\mu} r = \frac{2Z}{na_0} \frac{\mu}{m} r
\tag{3.40}
$$

where we recall that $a_\mu = a_0 m/\mu$ is the modified Bohr radius. In atomic units (a.u.) such that $a_0 = 1$ and $m = 1$, we have

$$
\rho = \frac{2Z}{n} \mu r
\tag{3.41}
$$

The physically admissible solutions $g(\rho)$ of (3.20), corresponding to $\lambda = n$, may also be expressed in terms of *associated Laguerre polynomials*. To see how this comes about, we first define the *Laguerre polynomials* $L_q(\rho)$ by the relation

$$
L_q(\rho) = e^\rho \frac{d^q}{d\rho^q}(\rho^q e^{-\rho})
\tag{3.42}
$$

and we note that these Laguerre polynomials may also be obtained from the generating function

$$
\begin{aligned}
U(\rho, s) &= \frac{\exp[-\rho s/(1-s)]}{1-s} \\
&= \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q, \qquad |s| < 1
\end{aligned}
\tag{3.43}
$$

Differentiation of this generating function with respect to s yields the recurrence formula

$$
L_{q+1}(\rho) + (\rho - 1 - 2q)L_q(\rho) + q^2 L_{q-1}(\rho) = 0
\tag{3.44}
$$

Similarly, upon differentiation of $U(\rho, s)$ with respect to ρ, we find that

$$
\frac{d}{d\rho} L_q(\rho) - q \frac{d}{d\rho} L_{q-1}(\rho) + q L_{q-1}(\rho) = 0
\tag{3.45}
$$

Using (3.44) and (3.45), it is readily shown that the lowest order differential equation involving only $L_q(\rho)$ is

$$
\left[\rho \frac{d^2}{d\rho^2} + (1-\rho)\frac{d}{d\rho} + q\right] L_q(\rho) = 0
\tag{3.46}
$$

Next, we define the *associated Laguerre polynomials* $L_q^p(\rho)$ by the relation

$$
L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho)
\tag{3.47}
$$

Differentiating (3.46) p times, we find that $L_q^p(\rho)$ satisfies the differential equation

$$
\left[\rho \frac{d^2}{d\rho^2} + (p+1-\rho)\frac{d}{d\rho} + (q-p)\right] L_q^p(\rho) = 0
\tag{3.48}
$$

Setting $\lambda = n$ in (3.20) and comparing with (3.48), we see that the physically acceptable solution $g(\rho)$ of (3.20) is given (up to a multiplicative constant) by the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$. Note that this polynomial is of order $(n+l)-(2l+1) = n-l-1 = n_r$, in accordance with the discussion following (3.25).

The generating function for the associated Laguerre polynomials may be obtained by differentiating (3.43) p times with respect to ρ. That is,

$$
\begin{aligned}
U_p(\rho, s) &= \frac{(-s)^p \exp[-\rho s/(1-s)]}{(1-s)^{p+1}} \\
&= \sum_{q=p}^{\infty} \frac{L_q^p(\rho)}{q!} s^q, \qquad |s| < 1
\end{aligned}
\tag{3.49}
$$

An explicit expression for $L_{n+l}^{2l+1}(\rho)$ is given by

$$
L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!} \frac{\rho^k}{k!}
\tag{3.50}
$$

and is easily verified by substitution into (3.49), with $q = n+l$ and $p = 2l+1$.

Since the physically admissible solutions $g(\rho)$ of (3.20) are given within a multiplicative constant either by the confluent hypergeometric function ${}_1F_1(l+1-n, 2l+2, \rho)$ or by the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$, it is clear that these two functions differ only by a constant factor. This factor is readily found by comparing (3.38) and (3.50) at $\rho = 0$ and remembering that the confluent hypergeometric function is equal to unity at the origin (see (3.36)). Thus

$$
L_{n+l}^{2l+1}(\rho) = -\frac{[(n+l)!]^2}{(n-l-1)!(2l+1)!} {}_1F_1(l+1-n, 2l+2, \rho)
\tag{3.51}
$$

Using (3.7), (3.16), (3.18) and the foregoing results, we may now write the full hydrogenic radial functions as

$$R_{nl}(r) = N_{nl}e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{3.52a}$$

$$= \tilde{N}_{nl}e^{-\rho/2}\rho^l {}_1F_1(l+1-n, 2l+2, \rho) \tag{3.52b}$$

where N_{nl} and $\tilde{N}_{nl}$ are constants which will be determined below (apart from an arbitrary phase factor) by the normalisation condition. In (3.52) we have used the notation R_{nl} (which displays explicitly the quantum numbers n and l) instead of the symbol R_{El}, and we recall that $\rho = 2Zr/(na_\mu)$.

The hydrogenic wave functions of the discrete spectrum

Using (3.5), we see that the full eigenfunctions of the discrete spectrum for hydrogenic atoms may be written as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{3.53}$$

where the radial functions are given by (3.52) and the spherical harmonics provide the angular part of the wave functions. We require that the eigenfunctions (3.53) be normalised to unity, so that

$$\int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi |\psi_{nlm}(r, \theta, \phi)|^2 = 1 \tag{3.54}$$

Because the spherical harmonics are normalisd on the unit sphere (see (2.182)), the normalisation condition (3.54) implies that

$$\int_0^\infty |R_{nl}(r)|^2 r^2 \, dr = 1 \tag{3.55}$$

or

$$|N_{nl}|^2 \left(\frac{na_\mu}{2Z}\right)^3 \int_0^\infty e^{-\rho} \rho^{2l} [L_{n+l}^{2l+1}(\rho)]^2 \rho^2 \, d\rho = 1 \tag{3.56}$$

where we have used (3.52a). The integral over ρ can be evaluated by using the generating function (3.49) for the associated Laguerre polynomials (see Appendix 3). The result is

$$\int_0^\infty e^{-\rho} \rho^{2l} [L_{n+l}^{2l+1}(\rho)]^2 \rho^2 \, d\rho = \frac{2n[(n+l)!]^3}{(n-l-1)!} \tag{3.57}$$

so that the normalised radial functions for the bound states of hydrogenic atoms may be written as [2]

[2] In writing (3.58) we have used the fact that the radial eigenfunctions $R_{nl}(r)$ may be taken to be real without loss of generality.

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{3.58a}$$

or

$$R_{nl}(r) = \frac{1}{(2l+1)!}\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n+l)!}{2n(n-l-1)!}\right\}^{1/2}$$

$$\times e^{-\rho/2}\rho^l {}_1F_1(l+1-n, 2l+2, \rho) \tag{3.58b}$$

with

$$\rho = \frac{2Z}{na_\mu}r, \qquad a_\mu = \frac{(4\pi\varepsilon_0)\hbar^2}{\mu e^2} = a_0\frac{m}{\mu} \tag{3.58c}$$

where a constant multiplicative factor of modulus one is still arbitrary. In writing (3.58b) we have used equation (3.51) which relates the associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$ to the confluent hypergeometric function ${}_1F_1(l+1-n, 2l+2, \rho)$.

The first few radial eigenfunctions (3.58) are given explicitly by

$$\begin{aligned}
R_{10}(r) &= 2(Z/a_\mu)^{3/2} \exp(-Zr/a_\mu) \\
R_{20}(r) &= 2(Z/2a_\mu)^{3/2}(1 - Zr/2a_\mu) \exp(-Zr/2a_\mu) \\
R_{21}(r) &= \frac{1}{\sqrt{3}}(Z/2a_\mu)^{3/2}(Zr/a_\mu) \exp(-Zr/2a_\mu) \\
R_{30}(r) &= 2(Z/3a_\mu)^{3/2}(1 - 2Zr/3a_\mu + 2Z^2r^2/27a_\mu^2) \exp(-Zr/3a_\mu) \\
R_{31}(r) &= \frac{4\sqrt{2}}{9}(Z/3a_\mu)^{3/2}(1 - Zr/6a_\mu)(Zr/a_\mu) \exp(-Zr/3a_\mu) \\
R_{32}(r) &= \frac{4}{27\sqrt{10}}(Z/3a_\mu)^{3/2}(Zr/a_\mu)^2 \exp(-Zr/3a_\mu)
\end{aligned} \tag{3.59}$$

and are illustrated in Fig. 3.3 below. We recall that for an 'infinitely heavy' nucleus, a_μ reduces to the first Bohr radius a_0. We also note that in atomic units (a.u.) one has $a_0 = 1$ and $a_\mu = 1/\mu$.

Using the radial wave functions (3.58) together with the explicit expressions of the spherical harmonics given in Table 2.1, we display in Table 3.1 the complete normalised bound state hydrogenic eigenfunctions $\psi_{nlm}(r, \theta, \phi)$ for the first three shells (that is, the K, L and M shells corresponding respectively to the values $n = 1, 2$ and 3 of the principal quantum number). We have also indicated in Table 3.1 the spectroscopic notation, introduced in our discussion of the energy levels. We shall also refer to one-electron orbital wave functions such as the hydrogenic wave functions ψ_{nlm} as *orbitals*. In accordance with the spectroscopic notation, orbitals corresponding to $l = 0$ will be called s orbitals, those with $l = 1$ will be denoted as p orbitals, and so on.

Table 3.1 The complete normalised hydrogenic wave functions corresponding to the first three shells.

Shell	*Quantum numbers* n	l	m	*Spectroscopic notation*	*Wave function* $\psi_{nlm}(r, \theta, \phi)$
K	1	0	0	1s	$\frac{1}{\sqrt{\pi}}(Z/a_\mu)^{3/2}\exp(-Zr/a_\mu)$
L	2	0	0	2s	$\frac{1}{2\sqrt{2\pi}}(Z/a_\mu)^{3/2}(1-Zr/2a_\mu)\exp(-Zr/2a_\mu)$
	2	1	0	$2p_0$	$\frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\cos\theta$
	2	1	±1	$2p_{\pm1}$	$\mp\frac{1}{8\sqrt{\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\sin\theta\exp(\pm i\phi)$
M	3	0	0	3s	$\frac{1}{3\sqrt{3\pi}}(Z/a_\mu)^{3/2}(1-2Zr/3a_\mu+2Z^2r^2/27a_\mu^2)\exp(-Zr/3a_\mu)$
	3	1	0	$3p_0$	$\frac{2\sqrt{2}}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\cos\theta$
	3	1	±1	$3p_{\pm1}$	$\mp\frac{2}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\sin\theta\exp(\pm i\phi)$
	3	2	0	$3d_0$	$\frac{1}{81\sqrt{6\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)(3\cos^2\theta-1)$
	3	2	±1	$3d_{\pm1}$	$\mp\frac{1}{81\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin\theta\cos\theta\exp(\pm i\phi)$
	3	2	±2	$3d_{\pm2}$	$\frac{1}{162\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin^2\theta\exp(\pm 2i\phi)$

In some applications it is convenient to consider a different set of hydrogenic wave functions, in which the *real form* of the spherical harmonics is used for the angular part. As we saw in Section 2.5, the spherical harmonics in real form exhibit a directional dependence and behave like simple functions of Cartesian coordinates. Orbitals using the real form of the spherical harmonics for their angular part are therefore particularly convenient for discussion of some properties such as the directed valence characteristic of chemical bonds. We recall that the spherical harmonics in real form are not eigenfunctions of L_z (except, of course, for $m = 0$ where they coincide with the usual spherical harmonics). For a given n and l the hydrogenic wave functions obtained by using the real form of the spherical harmonics are distinguished by the symbols $x, y, z, 3z^2-r^2, xz, yz, xy$, etc. which have been introduced in Section 2.5. As an example, let us consider the three 2p wave functions (for which $n = 2$, $l = 1$ and $m = 0, \pm1$). Using the real forms of the spherical harmonics given in Table 2.2, together with the radial function $R_{21}(r)$ from (3.59), we see that the corresponding normalised hydrogenic wave functions are given by

$$\psi_{2p_x} = \psi_{2,1,\cos\phi} = \frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\sin\theta\cos\phi \tag{3.60a}$$

$$\psi_{2p_y} = \psi_{2,1,\sin\phi} = \frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\sin\theta\sin\phi \tag{3.60b}$$

$$\psi_{2p_z} = \psi_{2p_0} = \psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\cos\theta \tag{3.60c}$$

In what follows, unless otherwise stated, we shall always use the usual (complex) form of the spherical harmonics.

Discussion of the hydrogenic bound state wave functions. Probability density. Parity

Let us return to the hydrogenic wave functions (3.53). First of all, we note that

$$|\psi_{nlm}(r, \theta, \phi)|^2\,d\mathbf{r} = \psi^*_{nlm}(r, \theta, \phi)\psi_{nlm}(r, \theta, \phi)r^2\,dr\sin\theta\,d\theta\,d\phi \tag{3.61}$$

represents the probability of finding the electron in the volume element $d\mathbf{r}$ (given in spherical polar coordinates by $d\mathbf{r} = r^2\,dr\sin\theta\,d\theta\,d\phi$) when the system is in the stationary state specified by the quantum numbers (n, l, m). The quantity $|\psi_{nlm}|^2 = \psi^*_{nlm}\psi_{nlm}$ is the *probability density*. Using (3.53) and (2.184), we see that

$$\begin{aligned}|\psi_{nlm}(r, \theta, \phi)|^2 &= |R_{nl}(r)|^2|Y_{lm}(\theta, \phi)|^2\\ &= |R_{nl}(r)|^2(2\pi)^{-1}|\Theta_{lm}(\theta)|^2\end{aligned} \tag{3.62}$$

so that the probability density does not depend on the coordinate ϕ. In fact, we see from (3.62) that the behaviour of $|\psi_{nlm}|^2$ is completely specified by the product of the quantity $|R_{nl}(r)|^2$, which gives the *electron density* as a function of r *along a given direction*, and the *angular factor* $(2\pi)^{-1}|\Theta_{lm}(\theta)|^2$.

The spherical harmonics $Y_{lm}(\theta, \phi)$ and the angular factors $(2\pi)^{-1}|\Theta_{lm}(\theta)|^2$ have been studied in detail in Section 2.5. In particular, we refer the reader to polar plots shown in Fig. 2.6. We also recall that if the real form of the spherical harmonics is used (that is, if the sine and cosine functions of ϕ are used), then the probability density will depend on ϕ, the dependence being through the functions $\sin^2 m\phi$ and $\cos^2 m\phi$. Polar representations of the angular dependence of the probability density for s and p orbitals (in the real form) are given by Fig. 2.7.

We now turn our attention to the properties of the radial eigenfunctions $R_{nl}(r)$. We have already seen that the quantity $|R_{nl}(r)|^2$ represents the electron density as a function of r along a given direction. On the other hand, the *radial distribution function*

$$D_{nl}(r) = r^2|R_{nl}(r)|^2 \tag{3.63}$$

gives the probability per unit length that the electron is to be found at a distance r from the nucleus. Indeed, by integrating (3.61) over the polar angles θ and ϕ and using (3.53) we see that

$$D_{nl}(r)\,dr = r^2|R_{nl}(r)|^2\,dr\int_0^{\pi} d\theta\sin\theta\int_0^{2\pi} d\phi|Y_{lm}(\theta,\phi)|^2$$

$$= r^2|R_{nl}(r)|^2\,dr \tag{3.64}$$

represents the probability of finding the electron between the distances r and $r + dr$ from the nucleus, regardless of direction. The appearance of the factor of r^2 on the right side of (3.64) is because the volume enclosed between two spheres of radii r and $r + dr$ is proportional to that factor. The radial distribution functions $D_{nl}(r)$ corresponding to the first few radial eigenfunctions are plotted in Fig. 3.3.

Several interesting features emerge from the examination of the eigenfunctions $R_{nl}(r)$ and the radial distribution functions $D_{nl}(r)$.

1. Only for s states ($l = 0$) are the radial wave functions different from zero at $r = 0$. We also note that since $Y_{00} = (4\pi)^{-1/2}$ is independent of θ and ϕ, one has from (3.58)

$$|\psi_{n00}(0)|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi a_\mu^3 n^3} \tag{3.65}$$

a result which plays an important role in the theory of hyperfine structure (see Chapter 5). Moreover, each of the s-state radial eigenfunctions R_{n0} is such that $dR_{n0}/dr \neq 0$ at $r = 0$. This peculiar behaviour is due to the fact that the potential energy (3.1) is infinite at the origin.

2. For $l \neq 0$ the fact that R_{nl} is proportional to r^l for small r forces the wave function to remain small over distances from the nucleus which increase with l. This is because the effective potential (3.9) contains the centrifugal barrier term $l(l + 1)\hbar^2/(2\mu r^2)$ which prevents the electron from approaching the nucleus. Among the eigenfunctions which have the same n, the one with the lowest value of l has the largest amplitude in the vicinity of the nucleus.

3. The associated Laguerre polynomial $L_{n+l}^{2l+1}(\rho)$ is a polynomial of degree $n_r = n - l - 1$ having n_r radial nodes (zeros). Thus the radial distribution function $D_{nl}(r)$ will exhibit $n - l$ maxima. We note that there is only one maximum when, for a given n, the orbital quantum number l has its largest value $l = n - 1$. In this case $n_r = 0$, and we see from (3.50) and (3.58) that

$$R_{n,n-1}(r) \sim r^{n-1}\exp[-Zr/(na_\mu)] \tag{3.66}$$

Hence, $D_{n,n-1}(r) = r^2R_{n,n-1}^2(r)$ will have a maximum at a value of r obtained by solving the equation

$$\frac{dD_{n,n-1}}{dr} = \left(2nr^{2n-1} - \frac{2Z}{na_\mu}r^{2n}\right)\exp[-2Zr/(na_\mu)] = 0 \tag{3.67}$$

that is at

$$r = \frac{n^2a_\mu}{Z} \tag{3.68}$$

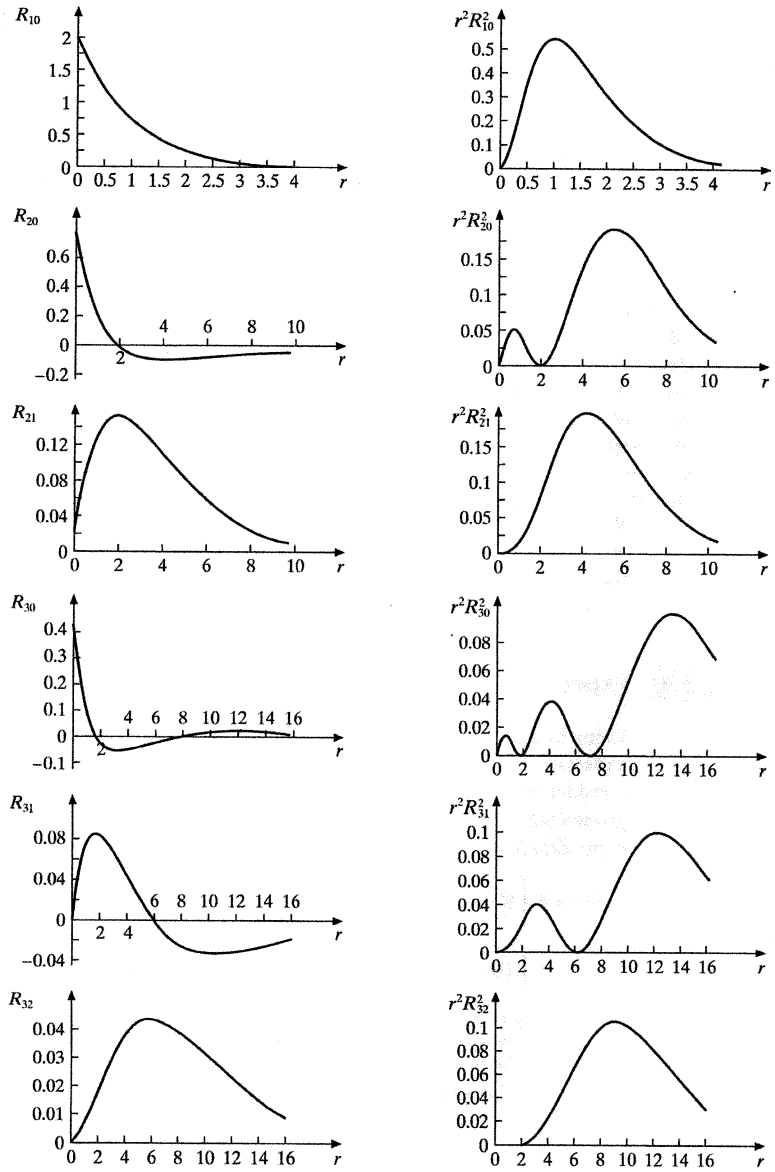

Figure 3.3 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen.

which is precisely the value (1.100) appearing in the Bohr model. However, in contrast to the Bohr model, the diffuseness of the electron cloud implies that the concept of size is less precise in the quantum mechanical theory, so that the value (3.68) should be interpreted as 'a most probable distance'. We see from (3.68) that this most probable distance is proportional to n^2 and inversely proportional to Z. More generally, the maximum value of $D_{nl}(r)$ recedes from the nucleus with increasing values of n (see Fig. 3.3) and becomes closer to the nucleus by a factor of Z^{-1} when Z increases.

To conclude our study of the hydrogenic bound state wave functions (3.53) we now discuss their *parity*. Since we have reduced the study of hydrogenic atoms to the problem of a particle of mass μ in a central field, we may use directly the results of Section 2.6. Thus the parity operation $\mathbf{r} \to -\mathbf{r}$ (that is, $(r, \theta, \phi) \to (r, \pi - \theta, \phi + \pi)$ in spherical polar coordinates) leaves the radial part $R_{nl}(r)$ of the hydrogenic wave function unaffected, while the angular part $Y_{lm}(\theta, \phi)$ has the parity of l, as shown by (2.252). As a result, under the parity operation $\mathcal{P}\mathbf{r} = -\mathbf{r}$ the hydrogenic wave functions (3.53) transform according to

$$\mathcal{P}[R_{nl}(r)Y_{lm}(\theta, \phi)] = R_{nl}(r)Y_{lm}(\pi - \theta, \phi + \pi) = R_{nl}(r)(-1)^l Y_{lm}(\theta, \phi) \tag{3.69}$$

We see that for l *even* the hydrogenic wave functions $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$ are unaffected by the parity operation: they are said to be of *even parity*. For l *odd* the wave functions ψ_{nlm} change sign under the parity operation and are said to be of *odd parity*.

3.4 Expectation values. The virial theorem

Using hydrogenic wave functions $\psi_{nlm}(\mathbf{r})$ normalised to unity, we can calculate the expectation (or average) values of various operators. As a simple example, let us consider the average value of the distance r when the hydrogenic atom is in the ground state, that is the quantity $\langle \psi_{100}|r|\psi_{100}\rangle \equiv \langle r\rangle_{100}$. We have $\psi_{100} = \pi^{-1/2}(Z/a_\mu)^{3/2}\exp(-Zr/a_\mu)$ and therefore

$$\begin{aligned}\langle r\rangle_{100} &= \int \psi^*_{100}(r) r \psi_{100}(r)\, \mathrm{d}\mathbf{r} \\ &= \int |\psi_{100}(r)|^2 r\, \mathrm{d}\mathbf{r} \\ &= \frac{Z^3}{\pi a_\mu^3}\int_0^\infty \mathrm{d}r\, r^3 \exp(-2Zr/a_\mu)\int_0^\pi \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\phi\end{aligned} \tag{3.70}$$

The angular integral has the value 4π and the radial integral is readily performed to give

$$\langle r\rangle_{100} = \frac{3a_\mu}{2Z} \tag{3.71}$$

For a general hydrogenic eigenstate $\psi_{nlm}(\mathbf{r})$ we may calculate in the same way

$$\begin{aligned}\langle r\rangle_{nlm} &= \int \psi^*_{nlm}(\mathbf{r}) r \psi_{nlm}(\mathbf{r})\, \mathrm{d}\mathbf{r} \\ &= \int_0^\infty |R_{nl}(r)|^2 r^3\, \mathrm{d}r\end{aligned} \tag{3.72}$$

Using the normalised radial eigenfunctions (3.58) it is found that

$$\langle r\rangle_{nlm} = a_\mu \frac{n^2}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\} \tag{3.73}$$

which is seen to agree with (3.71) when $n = 1$ and $l = 0$. We remark from (3.73) that $\langle r\rangle_{nlm}$, which we may interpret as the 'size' of the atom, is inversely proportional to Z and roughly proportional to n^2, in agreement with the discussion following (3.68). In fact, we see that for s states ($l = 0$) $\langle r\rangle_{nlm}$ is directly proportional to n^2; for states with $l \neq 0$ the deviations from this proportionality are small.

It is also interesting to evaluate the average values of r^k, where k is a positive or a negative integer, since the quantities $\langle r^k\rangle_{nlm}$ clearly exhibit the differences between the radial eigenfunctions. For example, one has

$$\langle r^2\rangle_{nlm} = a_\mu^2 \frac{n^4}{Z^2}\left\{1 + \frac{3}{2}\left[1 - \frac{l(l+1) - 1/3}{n^2}\right]\right\} \tag{3.74}$$

$$\begin{aligned}\langle r^3\rangle_{nlm} = a_\mu^3 \frac{n^6}{Z^3}\Bigg\{1 + \frac{27}{8}\Bigg[1 - \frac{1}{n^2}\left(\frac{35}{27} + \frac{10}{9}(l+2)(l-1)\right) \\ + \frac{1}{9n^4}(l+2)(l+1)l(l-1)\Bigg]\Bigg\}\end{aligned} \tag{3.75}$$

$$\left\langle \frac{1}{r}\right\rangle_{nlm} = \frac{Z}{a_\mu n^2} \tag{3.76}$$

$$\left\langle \frac{1}{r^2}\right\rangle_{nlm} = \frac{Z^2}{a_\mu^2 n^3 (l + 1/2)} \tag{3.77}$$

$$\left\langle \frac{1}{r^3}\right\rangle_{nlm} = \frac{Z^3}{a_\mu^3 n^3 l(l+1/2)(l+1)} \tag{3.78}$$

We note from (3.73)–(3.78) that $\langle r^k\rangle_{nlm} \sim (a_\mu/Z)^k$, a result which is easily explained since the Z dependence can be 'factored out' of the problem by defining a new reference length $\tilde{a}_\mu = a_\mu/Z$. We also remark that the expectation values of positive powers of r ($k > 0$) are mainly controlled by the principal quantum number n, while those corresponding to negative powers of r are strongly dependent on l

for $k < -1$. This is due to the fact that for positive powers ($k > 0$) the important contributions to the integral

$$\langle r^k \rangle_{nlm} = \int_0^\infty |R_{nl}(r)|^2 r^{k+2}\, dr \tag{3.79}$$

arise from large values of r, for which R_{nl} behaves essentially like r^{n-1} $\exp[-Zr/(na_\mu)]$. On the other hand, for negative powers such that $k < -1$ the main contributions to the integral (3.79) come from the region of small r, where R_{nl} is proportional to r^l.

Using the result (3.76) we may immediately obtain the average value of the potential energy $V(r) = -Ze^2/[(4\pi\varepsilon_0)r]$. The result is

$$\langle V \rangle_{nlm} = -\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle_{nlm} = -\frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{n^2} = 2E_n \tag{3.80}$$

where we have also used the equation (3.29) which gives the energy eigenvalues E_n. From (3.80) we can also deduce the average value of the kinetic energy operator $T = -(\hbar^2/2\mu)\nabla^2$. That is,

$$\langle T \rangle_{nlm} = E_n - \langle V \rangle_{nlm} = -E_n \tag{3.81}$$

so that

$$2\langle T \rangle = -\langle V \rangle \tag{3.82}$$

where we have dropped the subscripts. The result (3.82) is a particular case of the *virial theorem*, which we shall now prove.

The virial theorem

Let us denote by H the Hamiltonian of a physical system and by Ψ its state vector, solution of the time-dependent Schrödinger equation (2.46). We have proved in Section 2.2 that the time rate of change of the expectation value $\langle A \rangle \equiv \langle \Psi | A | \Psi \rangle$ of an operator which does not depend explicitly on the time t satisfies the equation (2.56), namely

$$i\hbar \frac{d}{dt}\langle \Psi | A | \Psi \rangle = \langle \Psi | [A, H] | \Psi \rangle \tag{3.83}$$

where $[A, H] = AH - HA$ is the commutator of the operators A and H.

Let us further assume that H is time-independent and denote respectively by E_n and ψ_n its eigenenergies and eigenfunctions. For a *stationary state* $\Psi_n = \psi_n \exp(-iE_n t/\hbar)$ and a time-independent operator A it is clear that the expectation value $\langle \Psi_n | A | \Psi_n \rangle = \langle \psi_n | A | \psi_n \rangle$ does not depend on t so that (3.83) reduces in this case to

$$\langle \psi_n | [A, H] | \psi_n \rangle = 0 \tag{3.84}$$

We now apply this result to the particular case of the non-relativistic motion of a particle of mass μ in a potential $V(\mathbf{r})$, the corresponding time-independent Hamiltonian being

$$H = \frac{p^2}{2\mu} + V = T + V \tag{3.85}$$

where $T = p^2/(2\mu) = -\hbar^2\nabla^2/(2\mu)$ is the kinetic energy operator. Moreover, we choose A to be the time-independent operator $\mathbf{r}\cdot\mathbf{p}$. We then have from (3.84)

$$\langle \psi_n | [(\mathbf{r}\cdot\mathbf{p}), H] | \psi_n \rangle \equiv \langle [(\mathbf{r}\cdot\mathbf{p}), H] \rangle = 0 \tag{3.86}$$

Using the algebraic properties (2.120) of the commutators, together with the fundamental commutation relations (2.119) and the fact that $\mathbf{p} = -i\hbar\nabla$, we find that

$$\begin{aligned}[(\mathbf{r}\cdot\mathbf{p}), H] &= \left[(xp_x + yp_y + zp_z), \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z)\right] \\ &= \frac{i\hbar}{\mu}(p_x^2 + p_y^2 + p_z^2) - i\hbar\left(x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z}\right) \\ &= 2i\hbar T - i\hbar(\mathbf{r}\cdot\nabla V)\end{aligned} \tag{3.87}$$

From (3.86) and (3.87) we therefore obtain the relation

$$2\langle T \rangle = \langle \mathbf{r}\cdot\nabla V \rangle \tag{3.88}$$

which is known as the virial theorem [3]. It is worth noting that this result may also be obtained by choosing the operator A to be $\mathbf{p}\cdot\mathbf{r}$ instead of $\mathbf{r}\cdot\mathbf{p}$. Indeed, the difference between $\mathbf{r}\cdot\mathbf{p}$ and $\mathbf{p}\cdot\mathbf{r}$ is a constant, and therefore commutes with H.

If the interaction potential is spherically symmetric and proportional to r^s, we deduce from (3.88) that

$$\begin{aligned}2\langle T \rangle &= \left\langle r\frac{\partial V}{\partial r} \right\rangle \\ &= s\langle V \rangle\end{aligned} \tag{3.89}$$

---

[3] We recall that in classical mechanics the *virial* of a particle is defined as the quantity $-(1/2)\mathbf{F}\cdot\mathbf{r}$, where $\mathbf{F}$ is the force acting on the particle and the bar denotes a *time average*. If the motion is periodic (or even if the motion is not periodic, but the coordinate and velocity of the particle remain finite) and $\bar{T}$ denotes the time average of the kinetic energy of the particle, one has (Goldstein, 1980)

$$\bar{T} = -\tfrac{1}{2}\overline{\mathbf{F}\cdot\mathbf{r}}$$

and this relation is known as the *virial theorem*. If the force is derivable from a potential V the virial theorem becomes

$$2\bar{T} = \overline{\mathbf{r}\cdot\nabla V}$$

which is the classical analogue of (3.88).

For example the case $s = 2$ corresponds to the isotropic three dimensional harmonic oscillator, for which $\langle T \rangle = \langle V \rangle$. On the other hand the case $s = -1$, corresponding to the hydrogenic atom, yields the relation $2\langle T \rangle = -\langle V \rangle$, in agreement with our result (3.82).

3.5 One-electron atoms in parabolic coordinates

We have seen in Section 2.6 that the time-independent Schrödinger equation describing the motion of a particle in *any central potential* can always be separated in spherical polar coordinates. This property has been employed above to obtain the energy levels and wave functions of the discrete spectrum of one-electron atoms. In this section, we shall use the fact that if the central potential is the *Coulomb potential* (3.1), then a separation of the Schrödinger equation (3.4) can also be carried out in *parabolic coordinates*. Such a separation turns out to be useful in the treatment of problems in which a particular direction of space is singled out, for example by the existence of an additional external electric field as in the Stark effect (see Section 6.1) or in Coulomb scattering (see Section 12.5).

The parabolic coordinates (ξ, η, ϕ) are related to the Cartesian coordinates (x, y, z) and the spherical polar coordinates (r, θ, ϕ) of the vector $\mathbf{r}$ by

$$\begin{aligned} x &= \sqrt{\xi\eta}\cos\phi \\ y &= \sqrt{\xi\eta}\sin\phi \\ z &= \tfrac{1}{2}(\xi - \eta) \\ r &= \tfrac{1}{2}(\xi + \eta) \\ \xi &= r + z = r(1 + \cos\theta) \\ \eta &= r - z = r(1 - \cos\theta) \\ \phi &= \tan^{-1}(y/x) \end{aligned} \tag{3.90}$$

with $0 \leqslant \xi \leqslant \infty$, $0 \leqslant \eta \leqslant \infty$, $0 \leqslant \phi \leqslant 2\pi$. The surfaces $\xi =$ constant and $\eta =$ constant are paraboloids of revolution about the Z axis with the origin as focus. In parabolic coordinates, the volume element is given by

$$\mathrm{d}\mathbf{r} = \tfrac{1}{4}(\xi + \eta)\,\mathrm{d}\xi\,\mathrm{d}\eta\,\mathrm{d}\phi \tag{3.91}$$

the expression for the operator ∇^2 is

$$\nabla^2 = \frac{4}{\xi + \eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2} \tag{3.92}$$

and the Coulomb potential (3.1) is given by

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} = -\frac{2Ze^2}{(4\pi\varepsilon_0)(\xi + \eta)} \tag{3.93}$$

Using (3.92) and (3.93), the Schrödinger equation (3.4) reads in parabolic coordinates

$$-\frac{\hbar^2}{2\mu}\left\{\frac{4}{\xi + \eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2}\right\}\Psi - \frac{2Ze^2}{(4\pi\varepsilon_0)(\xi + \eta)}\Psi = E\Psi \tag{3.94}$$

Let us look for eigenfunctions having the form

$$\psi(\xi, \eta, \phi) = f(\xi)g(\eta)\Phi(\phi) \tag{3.95}$$

Upon substitution of (3.95) into (3.94), and dividing through by ψ, we find that

$$\frac{4\xi\eta}{\xi + \eta}\left[\frac{1}{f}\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi\frac{\mathrm{d}f}{\mathrm{d}\xi}\right) + \frac{1}{g}\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\eta\frac{\mathrm{d}g}{\mathrm{d}\eta}\right)\right] + \frac{4\mu Ze^2\xi\eta}{\hbar^2(4\pi\varepsilon_0)(\xi + \eta)} + \frac{2\mu E\xi\eta}{\hbar^2} = -\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} \tag{3.96}$$

so that the ϕ part of the equation separates at once. Since the left-hand side of (3.96) depends only on ξ and η, and the right-hand side depends only on ϕ, both sides must be equal to a constant that we call m^2. The equation

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2 \tag{3.97}$$

is then readily solved. The physically acceptable normalised solutions are the same as (2.161),

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\phi} \tag{3.98}$$

where m is the *magnetic quantum number* such that $m = 0, \pm1, \pm2, \ldots$.

The remaining part of the equation (3.96) can be separated into its ξ and η parts as follows. Let us introduce the 'separation constants' ν_1 and ν_2 such that

$$\nu_1 + \nu_2 = \frac{\mu Ze^2}{\hbar^2(4\pi\varepsilon_0)} = \frac{Z}{a_\mu} \tag{3.99}$$

where we recall that $a_\mu = 4\pi\varepsilon_0\hbar^2/(\mu e^2)$. Multiplying the equation (3.96) by $(\xi + \eta)/(4\xi\eta)$ and using (3.98), we find that the equations for $f(\xi)$ and $g(\eta)$ are

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\xi\frac{\mathrm{d}f}{\mathrm{d}\xi}\right) + \left(\frac{\mu E\xi}{2\hbar^2} - \frac{m^2}{4\xi} + \nu_1\right)f = 0 \tag{3.100a}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\eta\frac{\mathrm{d}g}{\mathrm{d}\eta}\right) + \left(\frac{\mu E\eta}{2\hbar^2} - \frac{m^2}{4\eta} + \nu_2\right)g = 0 \tag{3.100b}$$

These two equations are of the same form, differing only in their constant terms.

Energy levels

Let us restrict our attention on the bound states ($E < 0$). The equations (3.100) may be solved by a method similar to that used to solve (3.6). Setting

$$\beta = \left(-\frac{2\mu E}{\hbar^2}\right)^{1/2}, \qquad \rho_1 = \beta\xi, \qquad \lambda_1 = \frac{\nu_1}{\beta} \tag{3.101}$$

we find that equation (3.100a) reduces to

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\rho_1^2} + \frac{1}{\rho_1}\frac{\mathrm{d}f}{\mathrm{d}\rho_1} + \left(-\frac{1}{4} + \frac{\lambda_1}{\rho_1} - \frac{m^2}{4\rho_1^2}\right) f = 0 \tag{3.102}$$

Similarly, starting from (3.100b) and setting

$$\rho_2 = \beta\eta, \qquad \lambda_2 = \frac{\nu_2}{\beta} \tag{3.103}$$

one obtains for g the equation

$$\frac{\mathrm{d}^2 g}{\mathrm{d}\rho_2^2} + \frac{1}{\rho_2}\frac{\mathrm{d}g}{\mathrm{d}\rho_2} + \left(-\frac{1}{4} + \frac{\lambda_2}{\rho_2} - \frac{m^2}{4\rho_2^2}\right) g = 0 \tag{3.104}$$

Following the method used in Section 3.1, one finds that the asymptotic behaviour of f is given by $\exp(-\rho_1/2)$, and that f behaves like $\rho_1^{|m|/2}$ for small values of ρ_1. We therefore look for a solution of the equation (3.102) having the form

$$f(\rho_1) = \mathrm{e}^{-\rho_1/2}\rho_1^{|m|/2} v(\rho_1) \tag{3.105}$$

and we obtain for $v(\rho_1)$ the equation

$$\left[\rho_1\frac{\mathrm{d}^2}{\mathrm{d}\rho_1^2} + (|m| + 1 - \rho_1)\frac{\mathrm{d}}{\mathrm{d}\rho_1} + \left(\lambda_1 - \frac{1}{2}(|m| + 1)\right)\right] v = 0 \tag{3.106}$$

This equation can be identified with the Kummer–Laplace differential equation (3.35). The physically acceptable solutions are given by

$$v = C\, L_{n_1+|m|}^{|m|}(\rho_1) = \tilde{C}_1 F_1(-n_1, |m| + 1, \rho_1) \tag{3.107}$$

where C and $\tilde{C}$ are constants, and the number

$$n_1 = \lambda_1 - \tfrac{1}{2}(|m| + 1) \tag{3.108}$$

is a positive integer or zero.

In a similar way, the solution of equation (3.104) shows that the number

$$n_2 = \lambda_2 - \tfrac{1}{2}(|m| + 1) \tag{3.109}$$

must be a positive integer or zero. From (3.108) and (3.109), it follows that

$$\lambda_1 + \lambda_2 = n_1 + n_2 + |m| + 1 = n \tag{3.110}$$

where n is a positive integer ($n = 1, 2, \ldots$). By combining (3.99), (3.101), (3.103) and (3.110), we find that

$$\beta = \frac{\nu_1 + \nu_2}{n} = \frac{Z}{n a_\mu} \tag{3.111}$$

so that the energy eigenvalues are given by

$$E_n = -\frac{\hbar^2\beta^2}{2\mu} = -\frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{2n^2} \tag{3.112}$$

in agreement with (3.29).

The energy levels E_n are degenerate, since they depend only on the principal quantum number n, and we see from (3.110) that there are various ways in which the two *parabolic quantum numbers* n_1 and n_2 and the magnetic quantum number m can be combined to obtain n. Indeed, for a given n, the number $|m|$ can take on the n distinct values $|m| = 0, 1, \ldots, n-1$. If $m = 0$, there are n ways of choosing the pair (n_1, n_2). If $|m| > 0$, there are $n - |m|$ ways of choosing the pair (n_1, n_2), and two ways of choosing m ($m = \pm|m|$). The total degeneracy of the energy level E_n is therefore

$$n + 2\sum_{|m|=1}^{n-1}(n - |m|) = n + 2\left[n(n-1) - \frac{n(n-1)}{2}\right] = n^2 \tag{3.113}$$

in agreement with our previous result (3.32).

Eigenfunctions of the bound states

It follows from the above discussion that the hydrogenic eigenfunctions of the discrete spectrum can be labelled in parabolic coordinates by the three quantum numbers n_1, n_2 and m, and are given by

$$\psi_{n_1 n_2 m}(\xi, \eta, \phi) = f_{n_1|m|}(\rho_1) g_{n_2|m|}(\rho_2)\frac{\mathrm{e}^{\mathrm{i}m\phi}}{\sqrt{2\pi}} \tag{3.114}$$

where $\rho_1 = \beta\xi$, $\rho_2 = \beta\eta$ and $\beta = Z/(na_\mu)$. From (3.105) and (3.107), we have

$$f_{n_1|m|}(\rho_1) = C\mathrm{e}^{-\rho_1/2}\rho_1^{|m|/2} L_{n_1+|m|}^{|m|}(\rho_1) \tag{3.115a}$$

$$= \tilde{C}\mathrm{e}^{-\rho_1/2}\rho_1^{|m|/2}\, {}_1F_1(-n_1, |m| + 1, \rho_1) \tag{3.115b}$$

Equations similar to (3.115) may be written down for $g_{n_2|m|}(\rho_2)$, with n_2 replacing n_1 and ρ_2 replacing ρ_1. The constants C and $\tilde{C}$ can be determined (apart from an arbitrary multiplicative factor of modulus one) by requiring that the eigenfunctions $\psi_{n_1 n_2 m}$ be normalised to unity. That is,

$$\int |\psi_{n_1 n_2 m}|^2\, \mathrm{d}\mathbf{r} = \frac{1}{4}\int_0^\infty \mathrm{d}\xi \int_0^\infty \mathrm{d}\eta \int_0^{2\pi} \mathrm{d}\phi\, |\psi_{n_1 n_2 m}(\xi, \eta, \phi)|^2 (\xi + \eta) = 1 \tag{3.116}$$

where we have used the expression (3.91) of the volume element in parabolic coordinates. It is then found that

$$f_{n_1|m|}(\rho_1) = \frac{2^{1/4}}{n}\left(\frac{Z}{a_\mu}\right)^{3/4}\left\{\frac{n_1!}{[(n_1+|m|)!]^3}\right\}^{1/2} e^{-\rho_1/2}\rho_1^{|m|/2}L_{n_1+|m|}^{|m|}(\rho_1) \tag{3.117a}$$

and

$$g_{n_2|m|}(\rho_2) = \frac{2^{1/4}}{n}\left(\frac{Z}{a_\mu}\right)^{3/4}\left\{\frac{n_2!}{[(n_2+|m|)!]^3}\right\}^{1/2} e^{-\rho_2/2}\rho_2^{|m|/2}L_{n_2+|m|}^{|m|}(\rho_2) \tag{3.117b}$$

Thus, the normalised eigenfunctions of the bound states of one-electron atoms are given in parabolic coordinates by

$$\psi_{n_1n_2m}(\xi,\eta,\phi) = \frac{\sqrt{2}}{n^2}\left(\frac{Z}{a_\mu}\right)^{3/2}\left\{\frac{n_1!n_2!}{[(n_1+|m|)!(n_2+|m|)!]^3}\right\}^{1/2} \times e^{-(\rho_1+\rho_2)/2}(\rho_1\rho_2)^{|m|/2}L_{n_1+|m|}^{|m|}(\rho_1)L_{n_2+|m|}^{|m|}(\rho_2)\frac{e^{im\phi}}{\sqrt{2\pi}} \tag{3.118a}$$

with

$$\rho_1 = \beta\xi,\ \rho_2 = \beta\eta,\ \beta = \frac{Z}{na_\mu},\ n = n_1 + n_2 + |m| + 1 \tag{3.118b}$$

These eigenfunctions, in contrast to the eigenfunctions $\psi_{nlm}(r,\theta,\phi)$ in spherical polar coordinates, are asymmetrical with respect to the plane $z = 0$. For $n_1 > n_2$, the probability of finding the electron with $z > 0$ is larger than that of finding it with $z < 0$; the opposite happens when $n_1 < n_2$.

For a given energy level E_n, that is for a fixed value of the principal quantum number n, and for a fixed value of the magnetic quantum number m (with $n > |m|$), the parabolic quantum numbers n_1 and n_2 can be chosen in $n - |m|$ different ways so that $n_1 + n_2 = n - |m| - 1$. Similarly, in the treatment using spherical polar coordinates, for fixed values of n and m the orbital angular momentum quantum number l can be chosen in $n - |m|$ different ways such that $|m| \leq l \leq n - 1$. Hence, for fixed n and m, the $n - |m|$ products of functions $f_{n_1|m|}(\beta\xi)g_{n_2|m|}(\beta\eta)$ are linear combinations of the $n - |m|$ products of radial functions $R_{nl}(r)$ and angular functions $\Theta_{lm}(\theta)$. It follows that for fixed values of n and m, any eigenfunction $\psi_{n_1n_2m}(\xi,\eta,\phi)$ in parabolic coordinates is a linear combination of eigenfunctions $\psi_{nlm}(r,\theta,\phi)$ in spherical polar coordinates. For the non-degenerate ground state with $n = 1$ ($n_1 = n_2 = m = 0$), we have

$$\psi_{000}(\xi,\eta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}\exp\left[-\frac{Z}{2a_\mu}(\xi+\eta)\right] = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2}\exp(-Zr/a_\mu) \tag{3.119}$$

which is identical to the ground state wave function ψ_{100} in spherical polar coordinates.

We now examine briefly the cause of the separability of the Schrödinger equation (3.4) for one-electron atoms in parabolic coordinates. In classical mechanics, it can be shown that the *constants of the motion* for the two-body Coulomb problem are the energy E, the orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and the (classical) *Runge–Lenz vector* [4]

$$\mathbf{A}_c = \frac{4\pi\varepsilon_0}{\mu Ze^2}(\mathbf{L}\times\mathbf{p}) + \frac{\mathbf{r}}{r} \tag{3.120}$$

which is such that $\mathbf{A}_c \cdot \mathbf{L} = 0$ and is a symmetry axis for the trajectory.

In quantum mechanics, the analogue of the classical Runge–Lenz vector (3.120) is the *Runge–Lenz operator*

$$\mathbf{A} = \frac{4\pi\varepsilon_0}{2\mu Ze^2}[\mathbf{L}\times\mathbf{p} - \mathbf{p}\times\mathbf{L}] + \frac{\mathbf{r}}{r} \tag{3.121}$$

where $\mathbf{p} = -i\hbar\nabla$ and the term in brackets has been symmetrized so that the operator $\mathbf{A}$ is Hermitian. It can be proved (Problem 3.8) that

$$[H, \mathbf{A}] = 0 \tag{3.122}$$

where H is the hydrogenic Hamiltonian (3.2). In addition, it can be shown (Problem 3.8) that $\mathbf{A}\cdot\mathbf{L} = \mathbf{L}\cdot\mathbf{A} = 0$ and that the three operators A_x, A_y and A_z do not mutually commute. Each of these three operators commutes with the corresponding component of $\mathbf{L}$ (for example A_z commutes with L_z) but not with $\mathbf{L}^2$. The fact that there exists a new constant of the motion (A_z) which does not commute with another conserved quantity ($\mathbf{L}^2$) leads to an additional degeneracy of the energy levels, which in the present case is the 'accidental' Coulomb degeneracy mentioned in Section 3.2. From our study of central forces in Section 2.6 and the foregoing discussion, we note that one can construct *two independent complete sets of commuting observables* for the two-body Coulomb problem. The first set consists of the operators H, $\mathbf{L}^2$, L_z and leads to the separability of the Schrödinger equation in spherical polar coordinates for all central potentials. The second set is made of the operators H, L_z, A_z, and leads to the separability of the Schrödinger equation for the two-body Coulomb problem in parabolic coordinates.

3.6 Special hydrogenic systems: positronium; muonium; antihydrogen; muonic and hadronic atoms; Rydberg atoms

Let us recall some of the key results we have obtained for hydrogenic systems. The energy eigenvalues are given by (3.29) and the frequencies of the transitions by (3.34). In particular, the ionisation potential $I_P = |E_{n=1}|$ is just

[4] See Goldstein (1980).

$$I_P = \frac{e^2}{(4\pi\varepsilon_0)a_\mu}\frac{Z^2}{2} \tag{3.123}$$

and the 'extension' a of the wave function describing the relative motion of the system is roughly given in the ground state (see (3.68)) by

$$a = \frac{a_\mu}{Z} = \frac{(4\pi\varepsilon_0)\hbar^2}{Z\mu e^2} \tag{3.124}$$

where $\mu = mM/(m+M)$ is the reduced mass.

The hydrogenic systems we have considered so far correspond to an atomic nucleus of mass M and charge Ze and an electron of mass m and charge $-e$ interacting by means of the Coulomb potential (3.1). The 'normal' hydrogen atom, containing a proton and an electron is the prototype of these hydrogenic systems. The hydrogenic ions He^+ ($Z=2$), Li^{++} ($Z=3$), Be^{3+} ($Z=4$), etc. are also examples of such systems. As we have already noted in Chapter 1, and as we can see again from the above formulae, the value of a for these ions is reduced with respect to that of the hydrogen atom by a factor of Z and their ionisation potential is increased by a factor of Z^2 (neglecting small reduced mass effects).

The (neutral) isotopes of atomic hydrogen, deuterium and tritium, also provide examples of hydrogenic systems. Here the proton is replaced by a nucleus having the same charge $+e$, namely a deuteron (containing one proton and one neutron) in the case of deuterium or a triton (containing one proton and two neutrons) in the case of tritium. Since $M_d \simeq 2M_p$ and $M_t \simeq 3M_p$, where M_p is the mass of the proton, M_d the mass of the deuteron and M_t the mass of the triton, we see that the reduced mass μ is slightly different for hydrogen, deuterium and tritium, the relative differences being of the order of 10^{-3}. Thus the quantities I_P and a are nearly identical for the three atoms, the small differences in the value of μ giving rise to *isotopic shifts* of the spectral lines (of the order of 10^{-3}) which we have already discussed in Chapter 1.

Positronium, muonium

In addition to deuterium and tritium, there also exist other 'less conventional' isotopes of hydrogen, in which the role of the nucleus is played by another particle. For example, *positronium* (e^+e^-) is a bound hydrogenic system made of a positron e^+ (the antiparticle of the electron, having the same mass as the electron, but the opposite charge) and an electron e^-. *Muonium* (μ^+e^-) is another non-conventional isotope of hydrogen, in which the proton has been replaced by a positive muon μ^+, a particle which is very similar to the positron e^+, except that it has a mass $M_{\mu^+} \simeq 207m$ and that it is unstable, with a lifetime of about 2.2×10^{-6} s. Both positronium and muonium may thus be considered as light isotopes of hydrogen. Positronium was first observed in 1951 by M. Deutsch *et al.* and muonium in 1960 by V.W. Hughes *et al.* Table 3.2 gives the values of the reduced mass μ, the 'radius' a and the ionisation potential I_P for positronium and muonium, compared with those of the hydrogen atom.

Positronium and muonium have attracted a great deal of interest because they only contain *leptons* (that is, particles which are not affected by the strong

Table 3.2 The reduced mass μ, ground state 'radius' a and ionisation potential I_P of some 'unconventional' hydrogenic systems, compared with the corresponding quantities for the hydrogen atom (pe^-). Atomic units are used. The masses of the particles considered are $M_p = M_{\bar{p}} \simeq 1836$, $M_{\mu^-} = M_{\mu^+} \simeq 207$, $M_{\pi^-} \simeq 273$, $M_{K^-} \simeq 966$, $M_{\Sigma^-} \simeq 2343$, the unit of mass being the electron mass m.

System	*Reduced mass μ*	*'Radius' a*	*Ionisation potential I_P*
(pe^-), $(\bar{p}e^+)$	$\frac{1836}{1837} \simeq 1$	$\simeq a_0 = 1$	$\simeq \frac{e^2}{(4\pi\varepsilon_0)2a_0} = 0.5$
(e^+e^-)	0.5	2	0.25
(μ^+e^-)	$\frac{207}{208} \simeq 1$	$\simeq a_0 = 1$	$\simeq 0.5$
$(p\mu^-)$	$\simeq 186$	$\simeq 5.4 \times 10^{-3}$	$\simeq 93$
$(p\pi^-)$	$\simeq 238$	$\simeq 4.2 \times 10^{-3}$	$\simeq 119$
(pK^-)	$\simeq 633$	$\simeq 1.6 \times 10^{-3}$	$\simeq 317$
$(p\bar{p})$	$\simeq 918$	$\simeq 1.1 \times 10^{-3}$	$\simeq 459$
$(p\Sigma^-)$	$\simeq 1029$	$\simeq 9.7 \times 10^{-4}$	$\simeq 515$

interactions) and hence are particularly suitable systems to verify the predictions of quantum electrodynamics (QED). We remark that both positronium and muonium are *unstable*. Indeed, muonium has a lifetime of 2.2×10^{-6} s (which is the lifetime of the muon μ^+ itself) while in positronium the electron and the positron may annihilate, their total energy including their rest mass energy being completely converted into electromagnetic radiation (photons).

Antihydrogen

In 1996, G. Baur *et al.* reported the first observation of atoms of *antihydrogen* ($\bar{p}e^+$), a bound state system made of an antiproton $\bar{p}$ and a positron e^+, in an experiment performed at CERN (the European laboratory for particle physics in Geneva) using a 'flight' method. The basic idea is that an antiproton $\bar{p}$ passing through the Coulomb field of a nucleus with charge Ze will create an electron–positron pair. Occasionally, the antiproton will capture a positron from the produced pair and form a fast-moving antihydrogen atom. In the experiment of Baur *et al.*, a jet of xenon atoms ($Z = 54$) was fired across the antiproton beam from CERN's Low Energy Antiproton Ring (LEAR). Nine atoms of antihydrogen were detected, which lasted about 40 nanoseconds (1 ns = 10^{-9} s) before the positrons were annihilated by collisions with electrons in the detector. That time was too short and the number of antihydrogen atoms formed was too few to make high-precision comparisons between hydrogen and antihydrogen, its antimatter counterpart. The new challenge is to trap antihydrogen atoms, and to use high-resolution laser spectroscopy (see Section 15.2) to compare the spectral lines of antihydrogen with those of hydrogen. Such studies would provide a stringent test

of the charge–parity–time ($\mathcal{CPT}$) theorem [5] and might reveal conceivable small differences between the gravitational forces acting on matter and antimatter.

Muonic atoms

In 1947, J.A. Wheeler suggested that negatively charged particles other than the electron could form a bound system with a nucleus. These negative particles can be *leptons* such as the negative muon μ^- (which is a kind of 'heavy electron' having the same mass and lifetime as the positive muon μ^+, but a negative charge $-e$) or *hadrons* (particles which can have strong interactions). The unusual 'atoms' formed in this way are sometimes called 'exotic atoms'. We shall return shortly to hadronic atoms and examine for the moment the muonic atoms which are formed when a negative muon μ^- is captured by the Coulomb attraction of a nucleus of charge Ze as the muon is slowing down in bulk matter.

As a first example, let us consider the simplest muonic atom ($p\mu^-$) which contains a proton p and a muon μ^-. Since the muon has a mass which is about 207 times that of the electron, the reduced mass of the muon with respect to the proton is approximately 186 times the electron mass. As a result, the 'radius' a of the muonic atom ($p\mu^-$) is 186 times smaller than that of the hydrogen atom, the ionisation potential I_P of ($p\mu^-$) being 186 times larger than the corresponding quantity for atomic hydrogen (see Table 3.2). The frequencies of the spectral lines corresponding to transitions between the energy levels of ($p\mu^-$) may thus be obtained from those of the hydrogen atom by multiplying the latter by a factor of 186. For transitions between the lowest energy levels of ($p\mu^-$) the spectral lines are therefore lying in the X-ray region.

Let us now assume that the negative muon μ^- is captured by the Coulomb field of a nucleus $\mathcal{N}$ of charge Ze. Assuming that we are dealing with a heavy nucleus, so that we may neglect the reduced mass effect, we see that equation (3.124) would then yield for the bound system ($\mathcal{N}\mu^-$) the value $a \simeq a_0/(207Z)$, while (3.123) would give an ionisation potential I_P larger than that of hydrogen by a factor of $207Z^2$. Thus for the case of muonic lead (corresponding to a nucleus with $Z = 82$) we would have $I_P \simeq 19$ MeV (1 MeV = 10^6 eV) and $a \simeq 3 \times 10^{-15}$ m = 3 fermi (1 fermi or femtometer = 10^{-15} m). In fact this value of a is smaller than the radius R of the lead nucleus, which is given by $R \simeq 6.7$ fermi, so that the expressions (3.123)–(3.124) cannot be used any more! Indeed, they have been derived on the assumption that the two particles of the hydrogenic system interact by means of the Coulomb potential (3.1) for *all values* of the relative distance r, that is both particles are considered to be *point-like*. This assumption is an excellent one for 'usual' (electronic) atoms or ions such as hydrogen, deuterium, tritium, He^+, Li^{2+}, etc., where the finite extension of the nucleus gives rise to very small effects such

[5] The $\mathcal{CPT}$ theorem says that if (mathematically) a particle is replaced by its antiparticle (charge conjugation operation $\mathcal{C}$), its position in space is reflected (parity operation $\mathcal{P}$) and the direction of time is reversed (time reversal operation $\mathcal{T}$), then the equations governing the mass and interactions of the particle are unchanged.

as the *volume effect*, which will be shown in Chapter 5 to yield tiny shifts of the energies associated with low-lying s states. However, for muonic atoms with large values of Z (such as muonic lead) the volume effect may lead to important shifts of the low-lying levels (in particular of the 1s and 2s states). Nevertheless the main *qualitative* features predicted by (3.123)–(3.124) are correct: the ionisation potential I_P is of the order of several MeV, the spectral lines corresponding to transitions between the lowest energy levels lie at the limit of the X-ray and γ-ray regions, and in the 1s state the muon spends a significant fraction of its time within the nucleus. The fact that the muon acts as a probe of the nucleus and that the energy spectrum of muonic atoms is therefore sensitive to the internal structure of the nucleus constitutes one of the major interests of the study of muonic atoms.

We conclude this brief discussion of muonic atoms by three remarks. First, muonic atoms are unstable, since the negative muon μ^- has a finite lifetime $\tau \simeq 2.2 \times 10^{-6}$ s (which is the same as that of its antiparticle, the positive muon μ^+). Secondly, muonic atoms usually keep an electron cloud, but the influence of the electrons on the hydrogenic system (nucleus + muon μ^-) is almost always negligible, since the muon μ^- remains on the average much closer to the nucleus than the electrons. Thirdly, the muon is often captured into an excited state of the (nucleus + muon) system. It will then 'cascade' down to the ground state, either by emitting radiation in the form of X-rays or by means of radiationless transitions known as *Auger transitions* (see Chapter 9), in which electrons from the cloud are ejected.

Hadronic atoms

In contrast with the leptons (such as the electron e^-, the positron e^+ and the muons μ^- and μ^+) which participate only in the electromagnetic and weak interactions, the hadrons participate in the *strong* (nuclear-type) interactions in addition to the electromagnetic and weak interactions. There are two kinds of hadrons, the *baryons* (such as the proton p, the neutron n, the antiproton $\bar{p}$, the antineutron $\bar{n}$, the hyperons $\Sigma, \Xi, \ldots$) which have half-odd integer spin ($\frac{1}{2}, \frac{3}{2}, \ldots$) and are therefore fermions, and the *mesons* (such as the π-mesons, the K-mesons, etc.) which have zero or integer spin ($0, 1, \ldots$) and hence are bosons. Among the hadrons those having a negative charge can form with a nucleus $\mathcal{N}$ a 'hydrogenic-type' system which is referred to as a *hadronic atom*. In particular, the system ($\mathcal{N}\pi^-$) is called a *pionic atom*, ($\mathcal{N}K^-$) is known as a *kaonic atom* while ($\mathcal{N}\bar{p}$) is called an *antiprotonic atom*. Hydrogenic-type systems containing a nucleus and a negative hyperon – for example, ($\mathcal{N}\Sigma^-$) – are known as *hyperonic atoms*. All these hadronic atoms are unstable, but their lifetime is long enough so that some of their spectral lines have actually been observed.

Since hadrons interact strongly with nuclei, it is clear that the theory of hydrogenic systems which we have developed in this chapter – and which only takes into account the Coulomb interaction (3.1) – cannot be directly applied to hadronic atoms. Thus the values of a and I_P listed in Table 3.2 only give a rough estimate of the 'radius' and of the ionisation potentials of the hadronic atoms ($p\pi^-$), (pK^-), ($p\bar{p}$)

and ($p\Sigma^-$). However, because the strong interactions have a short range, *excited states* of hadronic atoms and in particular those with $l \neq 0$ for which the wave function is very small in the vicinity of the origin can essentially be studied by using the theory of this chapter. The energies of these excited states are thus given by

$$E_n \simeq -\frac{1}{n^2} I_P \tag{3.125}$$

and their 'radii' by

$$a_n \simeq n^2 a \tag{3.126}$$

where I_P and a are given respectively by (3.123) and (3.124).

Rydberg atoms

A highly excited atom (or ion) has an electron with a large principal quantum number n. The electron (or the atom) is said to be in a 'high Rydberg state' and the highly excited atom is also referred to more simply as a 'Rydberg atom'.

Several characteristic quantities of the hydrogen atom are compared in Table 3.3 for $n = 1$, arbitrary n and $n = 100$. It is clear from the examination of this table that highly excited hydrogen atoms with $n \simeq 100$ exhibit some remarkable properties. For example, *their size is enormous* on the atomic scale. Indeed, with electron orbital radii of the order of 10^{-7} m, such atoms are as big as simple bacteria! Also, their geometrical cross-section being proportional to n^4 is therefore 10^8 larger when $n = 100$ than in the ground state $n = 1$. On the other hand, the electron in a high Rydberg state is *very weakly bound*, its binding energy being smaller than the binding energy of the ground state by a factor n^2. For example, the energy required to ionise a hydrogen atom with $n = 100$ is only 1.36×10^{-3} eV. We also remark that the energy separation ΔE between adjacent levels is given for large n by

$$\Delta E = E_{n+1} - E_n = I_P^H \left(\frac{1}{n^2} - \frac{1}{(n+1)^2} \right) \simeq 2I_P^H/n^3 \tag{3.127}$$

Table 3.3 Comparison of some characteristic quantities of the hydrogen atom for different values of the principal quantum number n.

Quantity	$n = 1$	*Arbitrary* n	$n = 100$
Radius a_n of Bohr orbit (in m)	$a_0 \simeq 5.3 \times 10^{-11}$	$\simeq n^2 a_0$	5.3×10^{-7}
Geometric cross-section πa_n^2 (in m^2)	$\pi a_0^2 \simeq 8.8 \times 10^{-21}$	$\simeq n^4 \pi a_0^2$	8.8×10^{-13}
Binding energy $\lvert E_n \rvert$ (in eV)	$I_P^H \simeq 13.6$	I_P^H/n^2	1.36×10^{-3}
Energy separation ΔE between adjacent levels (in eV)		$\simeq 2I_P^H/n^3$ (n large)	2.7×10^{-5}
Root-mean-square velocity of electron v_n (in m s^{-1})	$v_0 \simeq c\alpha \simeq 2.2 \times 10^6$	$\simeq v_0/n$	2.2×10^4
Period T_n (in s)	$T_0 = 1.5 \times 10^{-16}$	$\simeq n^3 T_0$	1.5×10^{-10}

where $I_P^H \simeq 13.6$ eV is the ionisation potential of the hydrogen atom. Thus for $n = 100$ this energy separation is given by $\Delta E \simeq 2.7 \times 10^{-5}$ eV ($= 0.22$ cm^{-1} in units of reciprocal centimetres), so that the selective excitation of atoms in highly excited states requires experimental techniques with extremely high resolution. A highly excited hydrogen atom left to itself has a relatively long lifetime, increasing roughly as n^3 for a fixed angular momentum quantum number l. However, even thermal collisions can transfer enough energy to the atom to ionise it, although it is possible that a neutral system passing through the (very large) Rydberg atom will leave it undisturbed.

Many of the studies concerning Rydberg atoms also deal with excited states of atoms other than hydrogen. However, for a large enough n, a Rydberg atom of any kind may be considered as an 'ionic core' plus a single highly excited electron. If this electron has enough angular momentum, so that it does not significantly penetrate the core, it will essentially move in a Coulomb field corresponding to an effective charge $Z_{\text{eff}} = 1$ (in atomic units). Such Rydberg atoms are therefore very similar to highly excited (Rydberg) hydrogen atoms.

Rydberg atoms have been studied intensively [6], since they are important in such diverse areas as astrophysics, plasma physics and quantum optics, as well as in tests of quantum electrodynamics and in studies of the classical limit of quantum mechanics. For instance, when making radiative transitions from an initial (high n) energy level to a neighbouring one of lower energy, Rydberg atoms in interstellar space emit radio waves which can be detected by radio telescopes (see Chapter 16). In astrophysical and laboratory plasmas, the recombination of low-energy electrons and ions accompanied with the emission of radiation (radiative recombination) results in Rydberg atoms.

The development of widely tunable and monochromatic dye lasers [7] around 1970 made it possible to excite atoms to single, well-defined Rydberg states, and to study the properties of these Rydberg states in great detail [8]. Of particular interest is the behaviour of Rydberg atoms in the presence of external electric and magnetic fields, which we shall study in Chapter 6.

The fact that transitions between neighbouring levels of Rydberg atoms occur at long wavelengths (corresponding to radio-frequency or microwave radiation) makes it possible to construct resonant cavities large enough to study the coupling of Rydberg states to radiation during a relatively long time. If the cavity is tuned to a particular transition frequency, the properties of the atoms can be altered. For instance the rate of spontaneous emission of radiation can be changed. By studying these changes, it is possible to make fundamental tests of low-energy QED. More generally, the study of Rydberg atoms interacting with radiation in a cavity is the subject of *cavity quantum electrodynamics*. Of particular interest is the *one-atom maser* (or micromaser) demonstrated in 1985 by D. Meschede,

[6] For a detailed account, see Gallagher (1994).
[7] Dye lasers are discussed in Chapter 15.
[8] See Connerade (1998).

H. Walther and G. Müller, which will be discussed in Chapter 16. With this device, the interaction of a single Rydberg atom with a single mode of an electromagnetic field in a cavity could be studied. At the other intensity extreme, J.E. Bayfield and P.M. Koch showed in 1974 that Rydberg atoms in microwave fields provide an excellent testing ground to study the properties of atoms in strong radiation fields.

From Bohr's correspondence principle, we expect that Rydberg atoms, which are in states with a large quantum number n, will behave quasi-classically, and hence are ideal systems for studying the quantum–classical interface. Of special interest is the transition from quantum systems to corresponding classical systems which exhibit 'chaotic' behaviour resulting in the exponential increase with time in sensitivity to the initial state of the system [9]. It follows that with the passage of time the state of such classical systems cannot be predicted from the initial values of the dynamical variables. In contrast, the evolution of a quantum system depends on the first derivative of the wave function with respect to time, so that it cannot display chaotic behaviour in the classical sense [9]. Nevertheless, there are characteristic signs in the distribution of energy levels of quantum systems with large quantum numbers which indicate that the corresponding classical system is chaotic. Rydberg atoms are an ideal test-bed for studying these connections.

Problems

3.1 Using the explicit expressions of the hydrogenic wave functions given in Table 3.1, calculate the expectation values $\langle r\rangle$, $\langle r^2\rangle$, $\langle 1/r\rangle$, $\langle p\rangle$ and $\langle p^2\rangle$ for the following states: (i) 1s, (ii) 2s, (iii) 2p. Verify that the virial theorem (3.82) is satisfied.

3.2 Any region of space in which the kinetic energy T of a particle would become negative is forbidden for classical motion. For a hydrogen atom in the ground state, of total energy $E_{1s} = -\frac{1}{2}$ a.u.

(a) Find the classically forbidden region.
(b) Using the ground state wave function $\psi_{1s}(r)$, calculate the probability of finding the electron in this region.

3.3 Consider a hydrogen atom of which the wave function at $t = 0$ is the following superposition of energy eigenfunctions $\psi_{nlm}(\mathbf{r})$

$$\Psi(\mathbf{r}, t=0) = \frac{1}{\sqrt{14}}[2\psi_{100}(r) - 3\psi_{200}(r) + \psi_{322}(\mathbf{r})]$$

(a) Is this wave function an eigenfunction of the parity operator?
(b) What is the probability of finding the system in the ground state (100)? In the state (200)? In the state (322)? In another eigenstate?
(c) What is the expectation value of the energy? Of the operator $\mathbf{L}^2$? Of the operator L_z?

[9] See Blümel and Reinhardt (1997).

3.4 Consider a tritium atom, containing a nucleus, ^{3}H (the triton) and an electron. The triton nucleus, which consists of one proton ($Z = 1$) and two neutrons, is unstable, since by beta emission it decays to ^{3}He, which contains two protons ($Z = 2$) and one neutron. This decay process occurs very rapidly with respect to characteristic atomic times, and will be assumed here to take place instantaneously. As a result, there is a sudden doubling of the Coulomb attraction between the atomic electron and the nucleus when the tritium nucleus ^{3}H decays by beta emission into ^{3}He. Assuming that the tritium atom is in the ground state when the decay takes place, and neglecting recoil effects ($M = \infty$), find the probability that immediately after the decay the He^+ ion can be found:

(a) In its ground state 1s.
(b) In any state other than the ground state. (Total probability for excitation or ionisation.)
(c) In the 2s state.
(d) In a state with $l \neq 0$.

3.5 The electron and the proton of an hydrogen atom interact not only through the electrostatic potential (3.1), but also by means of the gravitational interaction. Using perturbation theory (Section 2.8), obtain the relative energy shift $\Delta E/E_{1s}$, where ΔE is the energy change due to the gravitational force and E_{1s} is the ground state energy of hydrogen, as given by (3.29) with $Z = 1$ and $n = 1$. (**Note**: The gravitational constant is $G = 6.673 \times 10^{-11}$ N m^2 kg^{-2}.)

3.6 Using the definition (2.21), obtain the momentum space wave functions of the hydrogen atom for the 1s, 2s and 2p states. Compare your results with those of Appendix 5.
(**Hints**: Use the expansion (2.261) of a plane wave in spherical harmonics, and the known integral

$$\int_0^\infty e^{-ax} j_l(bx) x^{l+1}\, dx = \frac{(2b)^l l!}{(a^2 + b^2)^{l+1}}$$

Note that integrals involving higher powers of x can be obtained by differentiating this result with respect to the parameter a.)

3.7 Consider a one-electron atom bound state labelled by the parabolic quantum numbers $n_1 = 1$, $n_2 = 0$ and the magnetic quantum number $m = 0$. Show that the corresponding eigenfunction in parabolic coordinates, $\psi_{100}(\xi, \eta, \phi)$, can be written as the following linear combination of eigenfunctions $\psi_{nlm}(r, \theta, \phi)$ in spherical polar coordinates:

$$\psi_{100}(\xi, \eta, \phi) = -\frac{1}{\sqrt{2}}\psi_{200}(r, \theta, \phi) + \frac{1}{\sqrt{2}}\psi_{210}(r, \theta, \phi)$$

3.8 The Runge–Lenz operator **A** is defined by the relation (3.121). Prove that

(a)

$$[H, \mathbf{A}] = 0$$

where H is the hydrogenic Hamiltonian (3.2).

(b)

$$\mathbf{L}\cdot\mathbf{A} = 0$$

(c)

$$[A_x, A_y] = i\hbar\left(-\frac{2(4\pi\varepsilon_0)^2}{\mu Z^2 e^4}H\right)L_z$$

$$[A_y, A_z] = i\hbar\left(-\frac{2(4\pi\varepsilon_0)^2}{\mu Z^2 e^4}H\right)L_x$$

$$[A_z, A_x] = i\hbar\left(-\frac{2(4\pi\varepsilon_0)^2}{\mu Z^2 e^4}H\right)L_y$$

3.9 Consider the Hamiltonian

$$H = H_0 + H'$$

where

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{(4\pi\varepsilon_0)r}$$

is the hydrogenic Hamiltonian, and

$$H' = -\frac{\varepsilon}{r^2}$$

is a small perturbation. Show that this perturbation removes the 'accidental' Coulomb degeneracy with respect to l, the energy eigenvalues E_{nl} depending now on both quantum numbers n and l.

4 Interaction of one-electron atoms with electromagnetic radiation

In this chapter, we shall discuss the interaction of hydrogenic atoms with electromagnetic radiation. We shall first show how spectral lines arise, and at a later stage we shall study the photoelectric effect and the scattering of radiation by atomic systems. In considering the interaction of an atom with radiation, there are three basic processes to analyse. First, just as a classical oscillating charge will radiate spontaneously, an atom can make a spontaneous transition from an excited state to a state of lower energy, emitting a photon which is the quantum of the electromagnetic field. This process is called *spontaneous emission*. Secondly, an atom can *absorb* a photon from an external radiation field, making a transition from a state of lower to a state of higher energy. Finally, an atom can also emit a photon under the influence of an external radiation field. This process is called *stimulated emission*; it is distinct from spontaneous emission because it requires (like absorption) the presence of an external radiation field. Stimulated emission has important applications in the LASER (an acronym for Light Amplification by Stimulated Emission of Radiation) and the MASER (Microwave Amplification by Stimulated Emission of Radiation), which produce intense beams of coherent radiation, and which will be discussed in Chapter 15.

In a rigorous treatment, we would have to start by studying quantum electrodynamics, in which the electromagnetic field is expressed in terms of its quanta – the photons. Each photon corresponding to a field of frequency ν carries an amount of energy $h\nu$. Even in comparatively weak fields the photon density can be very high (see Problem 4.1). Under these circumstances the number of photons can be treated as a continuous variable and the field can be described classically by using Maxwell's equations. We shall proceed by using a *semi-classical* theory in which the radiation field is treated classically, but the atomic system is described by using quantum mechanics. The approximation will also be made that the influence of the atom on the external field can be neglected. Clearly these assumptions do not hold in the case of spontaneous emission, because only one photon is concerned – and one is not a large number! The proper treatment of spontaneous emission is well understood, but is beyond the scope of this book. Nevertheless, we shall be able to find the transition rate for spontaneous emission indirectly using a statistical argument due to Einstein.