otic particles bound to a helium nucleus (and no electrons). [Hint. It is not necessary to specify the values of total spin associated with the levels.]

(3.5) The integrals in helium

(a) Show that the integral in eqn 3.24 gives the value stated in eqn 3.7.

(b) Estimate the ground-state energy of helium using the variational principle. (The details of this technique are not given in this book; see the section on further reading.)

(3.6) Calculation of integrals for the 1s2p configuration

(a) Draw a scale diagram of \( R_{1s}^2(r) \), \( R_{2s}^2(r) \) and \( R_{2p}^2(r) \). (See Table 2.2.)

(b) Calculate the direct integral in eqn 3.31 and show that it gives

\[
J_{1s\pi} = -\frac{e^2}{4\pi\varepsilon_0} \frac{13}{2a_0} \times 5^6.
\]

Give the numerical value in eV (cf. that given in the text).

(3.7) Expansion of \( 1/r_{12} \)

For \( r_1 < r_2 \) the binomial expansion of

\[
\frac{1}{r_{12}} \approx \left( r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12} \right)^{-1/2}
\]

is

\[
\frac{1}{r_{12}} = \frac{1}{r_2} \left\{ 1 - \frac{r_1}{r_2} \cos\theta_{12} + \left( \frac{r_1}{r_2} \right)^2 \right\}^{-1/2}
\]

\[
\approx \frac{1}{r_2} \left\{ 1 + \frac{r_1}{r_2} \cos\theta_{12} + \ldots \right\}.
\]

(3.36)

(When \( r_1 > r_2 \) we must interchange \( r_1 \) and \( r_2 \) to obtain convergence.) The cosine of the angle between \( r_1 \) and \( r_2 \) is

\[
\cos\theta_{12} = \hat{r}_1 \cdot \hat{r}_2
\]

\[
= \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2).
\]

(a) Show that the first two terms in the binomial expansion agree with the terms with \( k = 0 \) and \( l \) in eqn 3.30.

(b) The repulsion between a 1s- and an \( nl \)-electron is independent of \( m \). Explain why, physically or mathematically.

(c) Show that eqn 3.32 leads to eqn 3.34 for \( l = 1 \).

(d) For a 1s\nl configuration, the quantity \( K(r_1, r_2) \) in eqn 3.34 is proportional to \( r_1^l/r_2^{l+1} \) when \( r_1 < r_2 \). Explain this in terms of mathematical properties of the \( Y_{l,m} \) functions.
4.1 Shell structure and the periodic table

For multi-electron atoms we cannot solve the Hamiltonian analytically, but by making appropriate approximations we can explain their structure in a physically meaningful way. To do this, we start by considering the elementary ideas of atomic structure underlying the periodic table of the elements. In the ground states of atoms the electrons have the configuration that minimises the energy of the whole system. The electrons do not all fall down into the lowest orbital with \( n = 1 \) (the K-shell) because the Pauli exclusion principle restricts the number of electrons in a given (sub-)shell—two electrons cannot have the same set of quantum numbers. This leads to the ‘building-up’ principle: electrons fill up higher and higher shells as the atomic number \( Z \) increases across the periodic table.¹ Full shells are found at atomic numbers \( Z = 2, 10, \ldots \) corresponding to helium and the other inert gases. These inert gases, in a column on the right-hand side of the periodic table (see inside front cover), were originally grouped together because of their similar chemical properties, i.e. the difficulty in removing an electron from closed shells means that they do not readily undergo chemical reactions.² However, inert gas atoms can be excited to higher-lying configurations by bombardment with electrons in a gas discharge, and such processes are very important in atomic and laser physics, as in the helium-neon laser.

The ground states of the alkalis have the following electronic configurations:³

\[
\begin{align*}
\text{lithium} & : \text{Li} & 1s^2 2s^1 \\
\text{sodium} & : \text{Na} & 1s^2 2s^2 2p^6 3s^1 \\
\text{potassium} & : \text{K} & 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 \\
\text{rubidium} & : \text{Rb} & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1 \\
\text{cesium} & : \text{Cs} & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1 \\
\end{align*}
\]

The alert reader will notice that the sub-shells of the heavier alkalis are not filled in the same order as the hydrogenic energy levels, e.g. electrons occupy the 4s level in potassium before the 3d level (for reasons that emerge later in this chapter). Thus, strictly speaking, we should say that the inert gases have full sub-shells, e.g. argon has the electronic configuration
configuration $1s^22s^22p^63s^23p^6$ with the 3d sub-shell unoccupied.\footnote{This book takes a shell to be all energy levels of the same principal quantum number $n$, but the meaning of shell and sub-shell may be different elsewhere. We use sub-shell to denote all energy levels with specific values of $n$ and $l$ (in a shell with a given value of $n$). We used these definitions in Chapter 1; the inner atomic electrons involved in X-ray transitions follow the hydrogenic ordering.}

Each alkali metal comes next to an inert gas in the periodic table and much of the chemistry of the alkalis can be explained by the simple picture of their atoms as having a single unpaired electron outside a core of closed electronic sub-shells surrounding the nucleus. The unpaired valence electron determines the chemical bonding properties; since it takes less energy to remove this outer electron than to pull an electron out of a closed sub-shell (see Table 4.1), thus the alkalis can form singly-charged positive ions and are chemically reactive.\footnote{For a plot of the ionization energies of all the elements see Grant and Phillips (2001, Chapter 11, Fig. 18). This figure is accessible at http://www.oup.co.uk/best.textbooks/physics/ephys/illustrations/} However, we need more than this simple picture to explain the details of the spectra of the alkalis and in the following we shall consider the wavefunctions.

### Table 4.1 Ionization energies of the inert gases and alkalis.

<table>
<thead>
<tr>
<th>Element</th>
<th>$Z$</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2</td>
<td>24.6</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>5.4</td>
</tr>
<tr>
<td>Ne</td>
<td>10</td>
<td>21.6</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>5.1</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>15.8</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>4.3</td>
</tr>
<tr>
<td>Kr</td>
<td>36</td>
<td>14.0</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>4.2</td>
</tr>
<tr>
<td>Xe</td>
<td>54</td>
<td>12.1</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>3.9</td>
</tr>
</tbody>
</table>

4.2 The quantum defect

The energy of an electron in the potential proportional to $1/r$ depends only on its principal quantum number $n$, e.g. in hydrogen the 3s, 3p and 3d configurations all have the same gross energy. These three levels are not degenerate in sodium, or any atom with more than one electron, and this section explains why. Figure 4.1 shows the probability density of 3s-, 3p- and 3d-electrons in sodium. The wavefunctions in sodium have a similar shape (number of nodes) to those in hydrogen. The 3d wavefunction has a single lobe outside the core so that it experiences almost the same potential as in a hydrogen atom; therefore this electron, and other d configurations in sodium with $n > 3$, have binding energies similar to those in hydrogen, as shown in Fig. 4.2. In contrast, the wavefunctions for the s-electrons have a significant value at small $r$—they penetrate inside the core and ‘see’ more of the nuclear charge. Thus the screening of the nuclear charge by the other electrons in the atom is less effective for ns configurations than for nd, and s-electrons have lower energy than d-electrons with the same principal quantum number. (The np-electrons lie between these two.)\footnote{This dependence of the energy on the quantum number $l$ can also be explained in terms of the elliptical orbits of Bohr–Sommerfeld quantum theory rather than Schrödinger’s wavefunctions; however, we shall use only the ‘proper’ wavefunction description since the detailed correspondence between the elliptical classical trajectories and the radial wavefunctions can lead to confusion.} The following modified form of
Fig. 4.1 The probability density of the electrons in a sodium atom as a function of \( r \). The electrons in the \( n = 1 \) and \( n = 2 \) shells make up the core, and the probability density of the unpaired outer electron is shown for the \( n = 3 \) shell with \( l = 1, 2 \) and 3. The probability is proportional to \( |P(r)|^2 = r^2 |R(r)|^2 \); the \( r^2 \) factor accounts for the increase in volume of the spherical shell between \( r \) and \( r + dr \) (i.e. \( 4\pi r^2 dr \)) as the radial distance increases. The decreasing penetration of the core as \( l \) increases can be seen clearly—the 3d-electron lies mostly outside the core with a wavefunction and binding energy very similar to those for the 3d configuration in hydrogen. These wavefunctions could be calculated by the simple numerical method described in Exercise 4.10, making the ‘frozen core’ approximation, i.e. that the distribution of the electrons in the core is not affected by the outer electron—this gives sufficient accuracy to illustrate the qualitative features. (The iterative method described in Section 4.4 could be used to obtain more accurate numerical wavefunctions.)

Bohr’s formula works amazingly well for the energy levels of the alkalis:

\[
E(n, l) = -\frac{\hbar c}{2} \frac{R_\infty}{(n - \delta_l)^2}.
\]  

A quantity \( \delta_l \), called the quantum defect, is subtracted from the principal quantum number to give an effective principal quantum number \( n^* = n - \delta_l \). The values of the quantum defects for each \( l \) can be estimated by inspecting the energy levels shown in Fig. 4.2. The d-electrons have a very small quantum defect, \( \delta_d \approx 0 \), since their energies are nearly hydrogenic. We can see that the 3p configuration in sodium has comparable energy to the \( n = 2 \) shell in hydrogen, and similarly for 4p and \( n = 3 \), etc.; thus \( \delta_p \approx 1 \). It is also clear that the quantum defect for s-electrons is greater than that for p-electrons. A more detailed analysis shows that all the energy levels of sodium can be parametrised by the above formula and only three quantum defects:

---

7This differs from the modification used for X-ray transitions in Chapter 1—hardly surprising since the physical situation is completely different for the inner and outer electrons.
\[ \delta_n = 1.35, \quad \delta_p = 0.86, \quad \delta_d = 0.01, \quad \delta_f \approx 0.00 \quad \text{for} \quad l > 2. \]

There is a small variation with \( n \) (see Exercise 4.3). Having examined the variation in the quantum defects with orbital angular momentum quantum number for a given element, now let us compare the quantum defects in different alkalis. The data in Table 4.1 show that the alkalis have similar ionization energies despite the variation in atomic number. Thus the effective principal quantum numbers \( n^* = (13.6\text{eV/IE})^{1/2} \)
Table 4.2 The effective principal quantum numbers and quantum defects for the ground configuration of the alkaline earths. Note that the quantum defects do depend slightly on \( n \) (see Exercise 4.3), so the value given in this table for the 3s-electron in sodium differs slightly from the value given in the text (\( \delta_s = 1.35 \)) that applies for \( n > 5 \).

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
<th>( n^* )</th>
<th>( \delta_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2s</td>
<td>1.59</td>
<td>0.41</td>
</tr>
<tr>
<td>Na</td>
<td>3s</td>
<td>1.63</td>
<td>1.37</td>
</tr>
<tr>
<td>K</td>
<td>4s</td>
<td>1.77</td>
<td>2.23</td>
</tr>
<tr>
<td>Rb</td>
<td>5s</td>
<td>1.81</td>
<td>3.19</td>
</tr>
<tr>
<td>Cs</td>
<td>6s</td>
<td>1.87</td>
<td>4.13</td>
</tr>
</tbody>
</table>

(from eqn 4.1) are remarkably similar for all the ground configurations of the alkaline earths, as shown in Table 4.2.

In potassium the lowering of the energy for the s-electrons leads to the 4s sub-shell filling before 3d. By caesium (spelt cesium in the US) the 6s configuration has lower energy than 4f (\( \delta_f \approx 0 \) for Cs). The exercises give other examples, and quantum defects are tabulated in Kuhn (1969) and Woodgate (1980), amongst others.

### 4.3 The central-field approximation

The previous section showed that the modification of Bohr's formula by the quantum defects gives reasonably accurate values for the energies of the levels in alkalis. We described an alkali metal atom as a single electron orbiting around a core with a net charge of +1e, i.e. the nucleus surrounded by \( N - 1 \) electrons. This is a top-down approach where we consider just the energy required to remove the valence electron from the rest of the atom; this binding energy is equivalent to the ionization energy of the atom. In this section we start from the bottom up and consider the energy of all the electrons. The Hamiltonian for \( N \) electrons in the Coulomb potential of a charge +Ze is

\[
H = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{j>i}^{N} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right\}. \tag{4.2}
\]

The first two terms are the kinetic energy and potential energy for each electron in the Coulomb field of a nucleus of charge \( Z \). The term with \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) in the denominator is the electrostatic repulsion between the two electrons at \( \mathbf{r}_i \) and \( \mathbf{r}_j \). The sum is taken over all electrons with \( j > i \) to avoid double counting.\(^8\) This electrostatic repulsion is too large to be treated as a perturbation; indeed, at large distances the repulsion cancels out most of the attraction to the nucleus. To proceed further we make the physically reasonable assumption that a large part of the repulsion between the electrons can be treated as a central potential.

\(^8\)For example, lithium has three interactions between the three electrons, inversely proportional to \( r_{12}, r_{13} \), and \( r_{23} \); summing over all \( j \) for each value of \( i \) would give six terms.
This follows because the closed sub-shells within the core have a spherical charge distribution, and therefore the interactions between the different shells and between shells and the valence electron are also spherically symmetric. In this central-field approximation the total potential energy depends only on the radial coordinate:

$$ V_{CF} (r) = -\frac{Ze^2/4\pi\varepsilon_0}{r} + S(r). \tag{4.3} $$

In this approximation the Hamiltonian becomes

$$ H_{CF} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{CF} (r_i) \right\}. \tag{4.4} $$

For this form of potential, the Schrödinger equation for \( N \) electrons, \( H\psi = E_{\text{atom}} \psi \), can be separated into \( N \) one-electron equations, i.e. writing the total wavefunction as a product of single-electron wavefunctions, namely

$$ \psi_{\text{atom}} = \psi_1 \psi_2 \psi_3 \cdots \psi_N, \tag{4.5} $$

leads to \( N \) equations of the form

$$ \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 + V_{CF} (r_1) \right\} \psi_1 = E_1 \psi_1, \tag{4.6} $$

and similar for electrons \( i = 2 \) to \( N \). This assumes that all the electrons see the same potential, which is not as obvious as it may appear. This symmetric wavefunction is useful to start with (cf. the treatment of helium before including the effects of exchange symmetry); however, we know that the overall wavefunction for electrons, including spin, should be antisymmetric with respect to an interchange of the particle labels. (Proper antisymmetric wavefunctions are used in the Hartree–Fock method mentioned later in this chapter.) The total energy of the system is \( E_{\text{atom}} = E_1 + E_2 + \ldots + E_N \). The Schrödinger equations for each electron (eqn 4.6) can be separated into parts to give wavefunctions of the form \( \psi_1 = R(r_1)Y_{l_1,m_1}\psi_{\text{spin}} (1) \). Angular momentum is conserved in a central field and the angular equation gives the standard orbital angular momentum wavefunctions, as in hydrogen. In the radial equation, however, we have \( V_{CF} (r) \) rather than a potential proportional to \( 1/r \) and so the equation for \( P(r) = rR(r) \) is

$$ \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{CF} (r) + \frac{\hbar^2 l (l + 1)}{2mr^2} \right\} P(r) = EP(r). \tag{4.7} $$

To solve this equation we need to know the form of \( V_{CF} (r) \) and compute the wavefunctions numerically. However, we can learn a lot about the behaviour of the system by thinking about the form of the solutions, without actually getting bogged down in the technicalities of solving the equations. At small distances the electrons experience the full nuclear charge so that the central electric field is

$$ E(r) \rightarrow \frac{Ze}{4\pi\varepsilon_0 r^2 \hat{r}}. \tag{4.8} $$
Fig. 4.3 The change-over from the short- to the long-range is not calculated but is drawn to be a reasonable guess, using the following criteria. The typical radius of the 1s wavefunction around the nucleus of charge \( +Ze = +11e \) is about \( a_0/11 \), and so \( Z_{\text{eff}} \) will start to drop at this distance. We know that \( Z_{\text{eff}} \sim 1 \) at the distance at which the 3d wavefunction has appreciable probability since that eigenstate has nearly the same energy as in hydrogen. The form of the function \( Z_{\text{eff}}(r) \) can be found quantitatively by the Thomas–Fermi method described in Woodgate (1980).

At large distances the other \( N - 1 \) electrons screen most of the nuclear charge so that the field is equivalent to that of charge \( +1e \):

\[
E(r) \rightarrow \frac{e}{4\pi\varepsilon_0 r^2} \hat{r}.
\]  

(4.9)

These two limits can be incorporated in a central field of the form

\[
E_{\text{CF}}(r) \rightarrow \frac{Z_{\text{eff}}e}{4\pi\varepsilon_0 r^2} \hat{r}.
\]  

(4.10)

The effective atomic number \( Z_{\text{eff}}(r) \) has limiting values of \( Z_{\text{eff}}(0) = Z \) and \( Z_{\text{eff}}(r) \rightarrow 1 \) as \( r \rightarrow \infty \), as sketched in Fig. 4.3.\(^9\) The potential energy of an electron in the central field is obtained by integrating from infinity:

\[
V_{\text{CF}}(r) = e \int_\infty^r |E_{\text{CF}}(r')| \, dr'.
\]  

(4.11)

The form of this potential is shown in Fig. 4.4.

So far, in our discussion of the sodium atom in terms of the wave function of the valence electron in a central field we have neglected

\[\text{Fig. 4.4} \text{ The form of the potential energy of an electron in the central-field approximation (} e_0^2 = e^2/4\pi\varepsilon_0 \text{). This approximate sketch for a sodium atom shows that the potential energy crosses over from} V_{\text{CF}}(r) = -e_0^2/M/r \text{ at long range to} -11e_0^2/M/r + V_{\text{offset}}; \text{the constant} V_{\text{offset}} \text{ comes from the integration in eqn 4.11 (if} Z_{\text{eff}}(r) = 11 \text{ for all} r \text{ then} V_{\text{offset}} = 0 \text{ but this is not the case). For electrons with} l > 0 \text{ the effective potential should also include the term that arises from the angular momentum, as shown in Fig. 4.5.}\]
the fact that the central field itself depends on the configuration of the electrons in the atom. For a more accurate description we must take into account the effect of the outer electron on the other electrons, and hence on the central field. The energy of the whole atom is the sum of the energies of the individual electrons (in eqn 4.6), e.g. a sodium atom in the 3s configuration has energy \( E(1s^22s^22p^6\ 3s) = 2E_{1s} + 2E_{2s} + 6E_{2p} + E_{3s} = E_{\text{core}} + E_{3s} \). This is the energy of the neutral atom relative to the bare nucleus (Na\(^{11+}\)).\(^{10}\) It is more useful to measure the binding energy relative to the singly-charged ion (Na\(^{+}\)) with energy \( E(1s^22s^22p^6) = 2E'_{1s} + 2E'_{2s} + 6E'_{2p} = E'_{\text{core}} \). The dashes are significant—the ten electrons in the ion and the ten electrons in the core of the atom have slightly different binding energies because the central field is not the same in the two cases. The ionization energy is \( IE = E_{\text{atom}} - E_{\text{ion}} = (E_{\text{core}} - E'_{\text{core}}) + E_{3s} \). From the viewpoint of valence electrons, the difference in \( E_{\text{core}} \) between the neutral atom and the ion can be attributed to core polarization, i.e. a change in the distribution of charge in the core produced by the valence electron.\(^{11}\) To calculate the energy of multi-

Fig. 4.5 The total potential in the central-field approximation including the term that is proportional to \( l(l + 1)/r^2 \) drawn here for \( l = 2 \) and the same approximate electrostatic \( V_{CF}(r) \) as shown in Fig. 4.4. The angular momentum leads to a ‘centrifugal barrier’ that tends to keep the wavefunctions of electrons with \( l > 0 \) away from \( r = 0 \) where the central-field potential is deepest.

\(^{10}\)This is a crude approximation, especially for inner electrons.

\(^{11}\)This effect is small in the alkalis and it is reasonable to use the frozen core approximation that assumes \( E_{\text{core}} \approx E'_{\text{core}} \). This approximation becomes more accurate for a valence electron in higher levels where the influence on the core becomes smaller.
electron atoms properly we should consider the energy of the whole system rather than focusing attention on only the valence electron. For example, neon has the ground configuration $1s^22s^22p^6$ and the electric field changes significantly when an electron is excited out of the 2p subshell, e.g. into the $1s^22s^22p^53s$ configuration.

Quantum defects can be considered simply as empirical quantities that happen to give a good way of parametrising the energies of the alkalis but there is a physical reason for the form of eqn 4.1. In any potential that tends to $1/r$ at long range the levels of bound states bunch together as the energy increases—at the top of the well the classically allowed region gets larger and so the intervals between the eigenenergies and the stationary solutions get smaller. More quantitatively, in Exercise 1.12 it was shown, using the correspondence principle, that such a potential has energies $E \propto 1/k^2$, with $\Delta k = 1$ between energy levels, but $k$ is not itself necessarily an integer. For the special case of a potential proportional to $1/r$ for all distances, $k$ is an integer that we call the principal quantum number $n$ and the lowest energy level turns out to be $n = 1$. For a general potential in the central-field approximation we have seen that it is convenient to write $k$ in terms of the integer $n$ as $k = n - \delta$, where $\delta$ is a non-integer (quantum defect). To find the actual energy levels of an alkali and hence $\delta$ (for a given value of $l$) requires the numerical calculation of the wavefunctions, as outlined in the following section.

### 4.4 Numerical solution of the Schrödinger equation

Before describing particular methods of solution, let us look at the general features of the wavefunction for particles in potential wells. The radial equation for $P(r)$ has the form

$$\frac{d^2P}{dr^2} = -\frac{2m}{\hbar^2} \left( E - V(r) \right) P,$$

(4.12)

where the potential $V(r)$ includes the angular momentum term in eqn 4.7. Classically, the particle is confined to the region where $E - V(r) > 0$ since the kinetic energy must be positive. The positions where $E = V(r)$ are the classical turning points where the particle instantaneously comes to rest, cf. at the ends of the swing of a pendulum. The quantum wavefunctions are oscillatory in the classically allowed region, with the curvature and number of nodes both increasing as $E - V(r)$ increases, as shown in Fig. 4.6. The wavefunctions penetrate some way into the classically forbidden region where $E - V(r) < 0$; but in this region the solutions decay exponentially and the probability falls off rapidly.

How can we find $P(r)$ in eqn 4.12 without knowing the potential $V(r)$? The answer is firstly to find the wavefunctions for a potential $V_{\text{CF}}(r)$ that is 'a reasonable guess', consistent with eqn 4.11 and the limits on the central electric field in the previous equations. Then, secondly, we
make the assumed potential correspond closely to the real potential, as described in the next section. Equation 4.12 is a second-order differential equation and we can numerically calculate \( P(r) \), the value of the function at \( r \), from two nearby values, e.g. \( u(r - \delta r) \) and \( u(r - 2\delta r) \).\(^{13}\) Thus, working from near \( r = 0 \), the method gives the numerical value of the function at all points going out as far as is necessary. The region of the calculation needs to extend beyond the classical turning point(s) by an amount that depends on the energy of the wavefunction being calculated. These general features are clearly seen in the plots produced in Exercise 4.10. Actually, that exercise describes a method of finding the radial wavefunction \( R(r) \) rather than \( P(r) = rR(r) \) but similar principles apply.\(^{14}\) If you carry out the exercise you will find that the behaviour at large \( r \) depends very sensitively on the energy \( E \)—the wavefunction diverges if \( E \) is not an eigenenergy of the potential—this gives a way of searching for those eigenenergies. If the wavefunction diverges upwards for \( E' \) and downwards for \( E'' \) then we know that an eigenenergy of the system \( E_k \) lies between these two values, \( E' < E_k < E'' \). Testing further values between these upper and lower bounds narrows the range and gives a more precise value of \( E_k \) (as in the Newton–Raphson method for finding roots). This so-called ‘shooting’ method is the least sophisticated method of computing wavefunctions and energies, but it is adequate for illustrating the principles of such calculations. Results are not given here since they can readily be calculated—the reader is strongly encouraged to implement the numerical method of solution, using a spreadsheet program, as described in Exercise 4.10. This shows how to find the wavefunctions for an electron in an arbitrary potential and verifies that the energy levels obey a quantum defect formula such as eqn 4.1 in any potential that is proportional to \( 1/r \) at long range (see Fig. 4.7).

---

\(^{13}\) The step size \( \delta r \) must be small compared to the distance over which the wavefunction varies; but the number of steps must not be so large that round-off errors begin to dominate.

\(^{14}\) In a numerical method there is no reason why we should not calculate the wavefunction directly; \( P(r) \) was introduced to make the equations neater in the analytical approach.
Fig. 4.7 Simple modifications of the potential energy that could be used for the numerical solution of the Schrödinger equation described in Exercise 4.10. For all these potentials \( V(r) = -e^2/4\pi\varepsilon_0 r \) for \( r \geq r_{\text{core}} \). (a) Inside the radial distance \( r_{\text{core}} \) the potential energy is \( V(r) = -Ze^2/4\pi\varepsilon_0 r + V_{\text{offset}} \), drawn here for \( Z = 3 \) and an offset chosen so that \( V(r) \) is continuous at \( r = r_{\text{core}} \). This corresponds to the situation where the charge of the core is an infinitely thin shell. The deep potential in the inner region means that the wavefunction has a high curvature, so small steps must be used in the numerical calculation (in this region). The hypothetical potentials in (b) and (c) are useful for testing the numerical method and for showing why the eigenenergies of any potential proportional to \( 1/r \) at long range obey a quantum defect formula (like eqn 4.1). The form of the solution depends sensitively on the energy in the outer region \( r \geq r_{\text{core}} \), but in the inner region where \( |E| \ll |V(r)| \) it does not, e.g. the number of nodes ('wiggles') in this region changes slowly with energy \( E \). Thus, broadly speaking, the problem reduces to finding the wavefunction in the outer region that matches boundary conditions, at \( r = r_{\text{core}} \), that are almost independent of the energy—the potential energy curve shown in (b) is an extreme example that gives useful insight into the behaviour of the wavefunction for more realistic central fields.

4.4.1 Self-consistent solutions

The numerical method described above, or a more sophisticated one, can be used to find the wavefunctions and energies for a given potential in the central-field approximation. Now we shall think about how to determine \( V_{\text{CF}} \) itself. The potential of the central field in eqn 4.2 includes the electrostatic repulsion of the electrons. To calculate this mutual repulsion we need to know where the electrons are, i.e. their wavefunctions, but to find the wavefunctions we need to know the potential. This argument is circular. However, going round and round this loop can be useful in the following sense. As stated above, the method starts by making a reasonable estimate of \( V_{\text{CF}} \) and then computing the electronic wavefunctions for this potential. These wavefunctions are then used to calculate a new average potential (using the central-field approximation) that is more realistic than the initial guess. This improved potential is then used to calculate more accurate wavefunctions, and so on. On suc-


cessive iterations, the changes in the potential and wavefunctions should get smaller and converge to a self-consistent solution, i.e. where the wavefunctions give a certain \( V_{CE}(r) \), and solving the radial equation for that central potential gives back the same wavefunctions (within the required precision).\(^\text{15}\) This self-consistent method was devised by Hartree. However, the wavefunctions of multi-electron atoms are not simply products of individual wavefunctions as in eqn 4.5. In our treatment of the excited configurations of helium we found that the two-electron wavefunctions had to be antisymmetric with respect to the permutation of the electron labels. This symmetry requirement for identical fermions was met by constructing symmetrised wavefunctions that were linear combinations of the simple product states (i.e. the spatial part of these functions is \( \psi_{\text{space}}^{A} \) and \( \psi_{\text{space}}^{S} \)). A convenient way to extend this symmetrisation to \( N \) particles is to write the wavefunction as a Slater determinant:

\[
\psi = \begin{vmatrix}
\psi_{a}(1) & \psi_{a}(2) & \cdots & \psi_{a}(N) \\
\psi_{b}(1) & \psi_{b}(2) & \cdots & \psi_{b}(N) \\
\psi_{c}(1) & \psi_{c}(2) & \cdots & \psi_{c}(N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{x}(1) & \psi_{x}(2) & \cdots & \psi_{x}(N)
\end{vmatrix}.
\]

Here \( a, b, c, \ldots, x \) are the possible sets of quantum numbers of the individual electrons,\(^\text{16}\) and 1, 2, \ldots, \( N \) are the electron labels. The change of sign of a determinant on the interchange of two columns makes the wavefunction antisymmetric. The Hartree–Fock method uses such symmetrised wavefunctions for self-consistent calculations and nowadays this is the standard way of computing wavefunctions, as described in Bransden and Joachain (2003). In practice, numerical methods need to be adapted to the particular problem being considered, e.g. numerical values of the radial wavefunctions that give accurate energies may not give a good value for a quantity such as the expectation value \( \langle 1/r^3 \rangle \) that is very sensitive to the behaviour at short range.

4.5 The spin–orbit interaction: a quantum mechanical approach

The spin–orbit interaction \( \beta s \cdot l \) (see eqn 2.49) splits the energy levels to give fine structure. For the single valence in an alkali we could treat this interaction in exactly the same way as for hydrogen in Chapter 2, i.e. use the vector model that treats the angular momenta as vectors obeying classical mechanics (supplemented with rules such as the restriction of the angular momentum to integer or half-integer values). However, in this chapter we shall use a quantum mechanical treatment and regard the vector model as a useful physical picture that illustrates the behaviour of the quantum mechanical operators. The previous discussion of fine structure in terms of the vector model had two steps that require further justification.

\(^{15}\)The number of iterations required, before the changes when going round the loop become very small, depends on how well the initial potential is chosen, but the final self-consistent solution should not depend on the initial choice. In general, it is better to let a computer do the work rather than expend a lot of effort improving the starting point.

\(^{16}\)Including both space and spin.
The wavefunction for an alkali metal atom in the central-field approximation is a product of a radial wavefunction (which does not have an analytical expression) and angular momentum eigenfunctions (as in hydrogen).

More explicitly, we have $|l m_1 s m_s\rangle \equiv Y_{l,m_1} \psi_{s,m_s}$, where $\psi_{s,m_s} = |m_s = +1/2\rangle$ or $|m_s = -1/2\rangle$.

Proof of these commutation relations:

$$[s_x l_x + s_y l_y + s_z l_z, l_z] = s_z [l_z, l_z] + s_y [l_y, l_z] = -i s_x l_y + i s_y l_x \neq 0.$$

Similarly, $[s_x l_x + s_y l_y + s_z l_z, s_z] = -i s_y l_x + i s_x l_y \neq 0$. Note that $[s \cdot 1, l_z] = -[s \cdot 1, s_z]$ and hence $s \cdot 1$ commutes with $l_z + s_z$.

Fig. 4.8 The total angular momentum of the atom $j = l + s$ is a fixed quantity in the absence of an external torque. Thus an interaction between the spin and orbital angular momenta $\beta s \cdot 1$ causes these vectors to rotate (precess) around the direction of $j$ as shown.

As for helium in Section 3.2 and in the classical treatment of the normal Zeeman effect in Section 1.8.

These commutation relations for the operators correspond to the conservation of the total angular momentum, and its component along the $z$-axis. Only an external torque on the atom affects these quantities. The spin–orbit interaction is an internal interaction.

(a) The possible values of the total angular momentum obtained by the addition of the electron’s spin, $s = 1/2$, and its orbital angular momentum are $j = l + 1/2$ or $l - 1/2$. This is a consequence of the rules for the addition of angular momentum in quantum mechanics (vector addition but with the resultant quantised).

(b) The vectors have squared magnitudes given by $j^2 = j(j + 1)$, $l^2 = l(l + 1)$ and $s^2 = 3/4$, where $j$ and $l$ are the relevant angular momentum quantum numbers.

Step (b) arises from taking the expectation values of the quantum operators in the Hamiltonian for the spin–orbit interaction. This is not straightforward since the atomic wavefunctions $R(r) |l m_1 s m_s\rangle$ are not eigenstates of this operator$^{17}$—this means that we must face the complications of degenerate perturbation theory. This situation arises frequently in atomic physics and merits a careful discussion.

We wish to determine the effect of an interaction of the form $s \cdot 1$ on the angular eigenfunctions $|l m_1 s m_s\rangle$. These are eigenstates of the operators $l^2$, $s^2$ and $s_z$ labelled by the respective eigenvalues.$^{18}$ There are $2(2l+1)$ degenerate eigenstates for each value of $l$ because the energy does not depend on the orientation of the atom in space, or the direction of its spin, i.e. energy is independent of $m_1$ and $m_s$. The states $|l m_1 s m_s\rangle$ are not eigenstates of $s \cdot 1$ because this operator does not commute with $l_z$ and $s_z$: $[s \cdot 1, l_z] \neq 0$ and $[s \cdot 1, s_z] \neq 0$.$^{19}$ Quantum operators only have simultaneous eigenfunctions if they commute. Since $|l m_1 s m_s\rangle$ is an eigenstate of $l_z$ it cannot simultaneously be an eigenstate of $s \cdot 1$, and similarly for $s_z$. However, $s \cdot 1$ does commute with $l^2$ and $s^2$: $[s \cdot 1, l^2] = 0$ and $[s \cdot 1, s^2] = 0$ (which are easy to prove since $s_x, s_y, s_z, l_x, l_y$ and $l_z$ all commute with $s^2$ and $l^2$). So $l$ and $s$ are good quantum numbers in fine structure. Good quantum numbers correspond to constants of motion in classical mechanics—the magnitudes of $l$ and $s$ are constant but the orientations of these vectors change because of their mutual interaction, as shown in Fig. 4.8. If we try to evaluate the expectation value using wavefunctions that are not eigenstates of the operator then things get complicated. We would find that the wavefunctions are mixed by the perturbation, i.e. in the matrix formalism of quantum mechanics the matrix representing the spin–orbit interaction in this basis has off-diagonal elements. The matrix could be diagonalised by following the standard procedure for finding the eigenvalues and eigenvectors,$^{20}$ but a p-electron gives six degenerate states so the direct approach would require the diagonalisation of a $6 \times 6$ matrix. It is much better to find the eigenfunctions at the outset and work in the appropriate eigenbasis. The ‘lock-before-you-lead’ approach requires some preliminary reasoning.

We define the operator for the total angular momentum as $j = l + s$. The operator $j^2$ commutes with the interaction, as does its component $j_z$: $[s \cdot 1, j^2] = 0$ and $[s \cdot 1, j_z] = 0$. Thus $j$ and $m_j$ are good quantum numbers.$^{21}$ Hence suitable eigenstates for calculating the expectation value of $s \cdot 1$ are $|l s j m_j\rangle$. Mathematically these new eigenfunctions can be expressed as combinations of the old basis set:
\[ |lsjm_j\rangle = \sum_{m_l,m_s} C(lsjm_j; m_l,m_s) |l m_l s m_s\rangle. \]

An eigenfunction labelled by \( l, s, j \) and \( m_j \) is a linear combination of eigenfunctions with the same values of \( l \) and \( s \) but various values \( m_l \) and \( m_s \). The coefficients \( C \) are the Clebsch–Gordan coefficients for their values for many possible combinations of angular momenta tabulated in more advanced books. Particular values of Clebsch–Gordan coefficients are not needed for the problems in this book but it is important to know that, in principle, one set of functions can be expressed in terms of another complete set—with the same number of eigenfunctions in each basis.

Finally, we use the identity \(^{22}\) \( j^2 = l^2 + s^2 + 2s \cdot l \) to express the expectation value of the spin–orbit interaction as
\[
\langle lsjm_j | s \cdot l | lsjm_j \rangle = \frac{1}{2} \langle lsjm_j | j^2 - l^2 - s^2 | lsjm_j \rangle
= \frac{1}{2} \{ j(j + 1) - l(l + 1) - s(s + 1) \}.
\]

The states \( |lsjm_j\rangle \) are eigenstates of the operators \( j^2 \), \( l^2 \) and \( s^2 \). The importance of the proper quantum treatment may not yet be apparent since all we appear to have gained over the vector model is being able to write the wavefunctions symbolically as \( |lsjm_j\rangle \). We will, however, need the proper quantum treatment when we consider further interactions that perturb these wavefunctions.

### 4.6 Fine structure in the alkalis

The fine structure in the alkalis is well approximated by an empirical modification of eqn 2.56 called the Landé formula:

\[
\Delta E_{FS} = \frac{Z_i^2 Z_o^2}{(n^*)^3 l(l + 1)} \alpha^3 \hbar c R_{\infty}. \tag{4.13}
\]

In the denominator the effective principal quantum number cubed \((n^*)^3\) (defined in Section 4.2) replaces \( n^2 \). The effective atomic number \( Z_{\text{eff}} \), which was defined in the discussion of the central-field approximation, tends to the inner atomic number \( Z_i \approx Z \) as \( r \to 0 \) (where the electron 'sees' most of the nuclear charge); outside the core the field corresponds to an outer atomic number \( Z_o \approx 1 \) (for neutral atoms). The Landé formula can be justified by seeing how the central-field approximation modifies the calculation of the fine structure in hydrogen (Section 2.3.2). The spin–orbit interaction depends on the electric field that the electron moves through; in an alkali metal atom this field is proportional to \( Z_{\text{eff}}(r)r/r^3 \) rather than \( r/r^3 \) as in hydrogen.\(^{23}\) Thus the expectation value of the spin–orbit interaction depends on

\[
\left< \frac{Z_{\text{eff}}(r)}{r^2} \right> \equiv \left< \frac{1}{r} \frac{\partial V_{\text{CF}}(r)}{\partial r} \right>.
\]

\(^{22}\) This applies both for vector operators, where \( j^2 = j_x^2 + j_y^2 + j_z^2 \), and for classical vectors where this is simply \( j^2 = |j|^2 \).

\(^{23}\) This modification is equivalent to using \( V_{\text{CF}} \) in place of the hydrogenic potential proportional to \( 1/r \).
rather than \(1/r^3\) as in hydrogen (eqn 2.51). This results in fine structure for the alkalis, given by the Landé formula, that scales as \(Z^2\)—this lies between the dependence on \(Z^4\) for hydrogenic ions (no screening) and the other extreme of no dependence on atomic number for complete screening. The effective principal quantum number \(n^*\) is remarkably similar across the alkalis, as noted in Section 4.2.

As a particular numerical example of the scaling, consider the fine structure of sodium (\(Z = 11\)) and of caesium (\(Z = 55\)). The 3p configuration of sodium has a fine-structure splitting of 1700 m\(^{-1}\), so for a \(Z^2\)-dependence the fine structure of the 6p configuration of caesium should be (using \(n^*\) from Table 4.2)

\[
1.7 \times 10^3 \times \left( \frac{55}{11} \right)^2 \times \left( \frac{2.1}{2.4} \right)^3 = 28.5 \times 10^3 \text{ m}^{-1}.
\]

This estimate gives only half the actual value of \(55.4 \times 10^3\) m\(^{-1}\), but the prediction is much better than if we had used a \(Z^4\) scaling. (A logarithmic plot of the energies of the gross and fine structure against atomic number is given in Fig. 5.7. This shows that the actual trend of the fine structure lies close to the \(Z^2\)-dependence predicted.)

The fine structure causes the familiar yellow line in sodium to be a doublet comprised of the two wavelengths \(\lambda = 589.0\) nm and 589.6 nm. This, and other doublets in the emission spectrum of sodium, can be resolved by a standard spectrograph. In caesium the transitions between the lowest energy configurations (6s–6p) give spectral lines at \(\lambda = 852\) nm and 894 nm—this ‘fine structure’ is not very fine.

### 4.6.1 Relative intensities of fine-structure transitions

The transitions between the fine-structure levels of the alkalis obey the same selection rules as in hydrogen since the angular momentum functions are the same in both cases. It takes a considerable amount of calculation to find absolute values of the transition rates\(^{24}\) but we can find the relative intensities of the transitions between different fine-structure levels from a simple physical argument. As an example we shall look at p to s transitions in sodium, as shown in Fig. 4.9. The \(3P_{1/2} - 3S_{1/2}\) transition has half the intensity of the \(3P_{3/2} - 3S_{1/2}\) transition.\(^{25}\) This 1:2 intensity ratio arises because the strength of each component is proportional to the statistical weight of the levels (\(2j + 1\)). This gives 2:4 for \(j = 1/2\) and 3/2. To explain this we first consider the situation without fine structure. For the 3p configuration the wavefunctions have the form \(R_{3p}(r) |lm_ism_i\rangle\) and the decay rate of these states (to 3s) is independent of the values of \(m_l\) and \(m_s\).\(^{26}\) Linear combinations of the states \(R(r) |lm_ism_i\rangle\) with different values of \(m_l\) and \(m_s\) (but the same values of \(n, l, \) and \(s\), and hence the same lifetime) make up the eigenstates of the fine structure, \(|isjm_j\rangle\). Therefore an alkali atom has the same lifetime for both values of \(j\).\(^{27}\)

---

24 The rates of the allowed transitions depend on integrals involving the radial wavefunctions (carried out numerically for the alkalis) and the integrals over the angular part of the wavefunction given in Section 2.2.1, where we derived the selection rules.

25 This shortened form of the full LS-coupling scheme notation gives all the necessary information for a single electron, cf. 3p \(^2P_{3/2} - ^2S_{1/2}\).

26 This must be true for the physical reason that the decay rate is the same whatever the spatial orientation of the atom, and similarly for the spin states. All the different angular states have the same radial integral, i.e. that between the 3p and 3s radial wavefunctions.

27 This normal situation for fine structure may be modified slightly in a case like caesium where the large separation of the components means that the \(\omega^3\) factor in the lifetime (eqn 1.24) leads to differences, even though the matrix elements are similar.
Each state has the same excitation rate, as in a gas discharge lamp. For example, then all the states will have equal populations and the intensity of a given component of the line is proportional to the number contributing \( m_j \) states. Similarly, the fine structure of transitions from \( s \) to \( p \) configurations, e.g. \( 5S_{1/2} \rightarrow 3P_{3/2} \) and \( 5S_{1/2} \rightarrow 3P_{1/2} \), have an intensity ratio of 2:1—in this case the lower frequency component has twice the intensity of the higher component, i.e. the opposite of the \( p \rightarrow s \) transition shown in Fig. 4.9 (and such information can be used to identify the lines in an observed spectrum). More generally, there is a sum rule for intensities: the sum of the intensities to, or from, a given level is proportional to its degeneracy; this can be used when both upper and lower configurations have fine structure (see Exercise 4.8).

The discussion of the fine structure has shown that spin leads to a splitting of energy levels of a given \( n \), of which \( l \) levels have different \( m_j \). These fine-structure levels are degenerate with respect to \( m_j \), but an external magnetic field removes this degeneracy. The calculation of the effect of an external magnetic field in Chapter 1 was a classical treatment that led to the normal Zeeman effect. This does not accurately describe what happens for atoms with one valence electron because the contribution of the spin magnetic moment leads to an anomalous Zeeman effect. The splitting of the fine-structure level into \( 2j + 1 \) states (or Zeeman sub-levels) in an applied field is shown in Fig. 4.10. It is straightforward to calculate the Zeeman energy for an atom with a single valence electron, as shown in quantum texts, but to avoid repetition the standard treatment is not given here; in the next chapter we shall derive a general formula for the Zeeman effect on atoms with any number of valence electrons that covers the single-electron case (see Exercise 5.13). We also look at the Zeeman effect on hyperfine structure in Chapter 6.

**Fig. 4.10** In an applied magnetic field of magnitude \( B \) the four states of different \( m_j \) of the \( ^2P_{3/2} \) level have energies of \( E_{\text{Zeeman}} = g_j \mu_B B m_j \)—the factor \( g_j \) arises from the projection of the contributions to the magnetic moment from \( l \) and \( s \) onto \( \mathbf{j} \) (see Exercise 5.13).

**Further reading**

This chapter has concentrated on the alkalis and mentioned the neighbouring inert gases; a more general discussion of the periodic table is given in *Physical Chemistry* by Atkins (1994).

The self-consistent calculations of atomic wavefunctions are discussed in Hartree (1957), Slater (1960), Cowan (1981), in addition to the textbook by Bransden and Joachain (2003).

The numerical solution of the Schrödinger equation for the bound states of a central field in Exercise 4.10 is discussed in French and Taylor (1978), Eisberg and Resnick (1985) and Rioux (1991). Such numerical methods can also be applied to particles with positive energies in the potential to model scattering in quantum mechanics, as described in Greenhow (1990). The numerical method described in this book has deliberately been kept simple to allow quick implementation, but the Numerov method is more precise for this type of problem.
Exercises

(4.1) **Configuration of the electrons in francium**
Write down the full electronic configuration of francium (atomic number $Z = 87$). This element comes below caesium in the periodic table.

(4.2) **Finding the series limit for sodium**
Eight ultraviolet absorption lines in sodium have wavenumbers of

\[
38\,541, \quad 40\,383, \quad 39\,299, \quad 40\,566, \\
39\,795, \quad 40\,706, \quad 40\,137, \quad 40\,814, 
\]
in units of cm$^{-1}$. Devise an extrapolation procedure to find the ionization limit of sodium with a precision justified by the data. Convert the result into electron volts. (You may find a spreadsheet program useful for manipulating the numbers.) What is the effective principal quantum number $n^*$ of the valence electron in the ground configuration?

(4.3) **Quantum defects of sodium**
The binding energies of the 3s, 4s, 5s and 6s configurations in sodium are 5.14 eV, 1.92 eV, 1.01 eV and 0.63 eV, respectively. Calculate the quantum defects for these configurations and comment on what you find.

Estimate the binding energy of the 8s configuration and make a comparison with the $n = 8$ shell in hydrogen.

(4.4) **Quantum defect**
Estimate the wavelength of laser radiation that excites the 5s $^2S_{1/2} - 7s \ ^5S_{1/2}$ transition in rubidium by simultaneous absorption of two photons with the same frequency ($IE($Rb$) = 4.17$ eV). (Two-photon spectroscopy is described in Section 8.4 but specific details are not required here.)

(4.5) **Application of quantum defects to helium and helium-like ions**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Binding energy (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s2s</td>
<td>35,250</td>
</tr>
<tr>
<td>1s2p</td>
<td>28,206</td>
</tr>
<tr>
<td>1s3s</td>
<td>14,266</td>
</tr>
<tr>
<td>1s3p</td>
<td>12,430</td>
</tr>
<tr>
<td>1s3d</td>
<td>12,214</td>
</tr>
</tbody>
</table>

(a) Calculate the wavelength of the 1s3d–1s2p line in helium and compare it with the Balmer-$\alpha$ line in hydrogen.

(b) Calculate the quantum defects for the configurations of helium in the table. Estimate the binding energies of the 1s4f configurations.

(c) The levels belonging to the 1s$^2$4f configuration of the Li$^+$ ion all lie at an energy of 72.24 eV above the ion’s ground state. Estimate the second ionization energy of this ion. Answer: 75.64 eV.

(4.6) **Quantum defects and fine structure of potassium**
An atomic vapour of potassium absorbs light at the wavelengths (in nm): 769.9, 766.5, 404.7, 404.4, 344.7 and 344.6. These correspond to the transitions from the ground configuration 4s. Explain these observations as fully as you can and estimate the mean wavelength of the next doublet in the series, and its splitting. (Potassium has $IE = 4.34$ eV.)

(4.7) **The $Z$-scaling of fine structure**
Calculate the fine-structure splitting of the 3p configuration of the hydrogen-like ion Na$^{+10}$ (in eV). Explain why it is larger than the fine structure of the same configuration in the neutral sodium (0.11 eV) and hydrogen (1.1 × 10$^{-5}$ eV).

(4.8) **Relative intensities of fine-structure components**

(a) An emission line in the spectrum of an alkali has three fine-structure components corresponding to the transitions $^2D_{3/2} - ^2P_{3/2}$, $^2D_{3/2} - ^2P_{3/2}$ and $^2D_{3/2} - ^2P_{1/2}$. These components have intensities $a$, $b$ and $c$, respectively, that are in the ratio 1:9:5. Show that these satisfy the rule that the sum of the intensities of the transitions to, or from, a given level is proportional to its statistical weight $(2J + 1)$.

(b) Sketch an energy-level diagram of the fine-structure levels of the two terms $n'f$ $^2F$ and $n'd$ $^2D$ (for $n' > n$). Mark the three allowed electric dipole transitions and find their relative intensities.

\[28\] For a discussion of how to determine the quantum defect for a series of lines by an iterative method see Softley (1994).
(4.9) **Spherical symmetry of a full sub-shell**

The sum $\sum_{m=1}^{l} |Y_{l,m}|^2$ is spherically symmetric. Show this for the specific case of $l = 1$ and comment on the relevance of the general expression, that is true for all values of $l$, to the central-field approximation.

(4.10) **Numerical solution of the Schrödinger equation**

This exercise goes through a method of finding the wavefunctions and their energies for a potential (in the central-field approximation). This shows how numerical calculations are carried out in a simple case that can be implemented easily on a computer with readily available spreadsheet programs. Of course, the properties of hydrogen-like atoms are well known and so the first stage really serves as a way of testing the numerical method (and checking that the formulae have been typed correctly). It is straightforward to extend the numerical method to deal with other cases, e.g. the potentials in the central-field approximation illustrated in Fig. 4.7.

(a) **Derivation of the equations**

Show from eqn 2.4, and other equations in Chapter 2, that

$$\frac{d^2 R}{dx^2} + \frac{2}{x} \frac{dR}{dx} + \left(\overline{E} - \overline{V}(x)\right) R(x) = 0,$$

(4.14)

where the position and energy have been turned into dimensionless variables: $x = r/a_0$ and $\overline{E}$ is the energy in units of $e^2/8\pi\varepsilon_0a_0 = 13.6$ eV (equal to half the atomic unit of energy used in some of the references). In these units the effective potential is

$$\overline{V}(x) = \frac{l(l+1)}{x^2} - \frac{2}{x},$$

(4.15)

where $l$ is the orbital angular momentum quantum number.

The derivatives of a function $f(x)$ can be approximated by

$$\frac{df}{dx} = \frac{f(x + \delta/2) + f(x - \delta/2)}{\delta},$$

$$\frac{d^2 f}{dx^2} = \frac{f(x + \delta) + f(x - \delta) - 2f(x)}{\delta^2},$$

where $\delta$ is a small step size.

Show that the second derivative follows by applying the procedure used to obtain the first derivative twice. Show also that substitution into eqn 4.14 gives the following expression for the value of the function at $x + \delta$ in terms of its value at the two previous points:

$$R(x + \delta) = \left\{ 2R(x) + \left(\overline{V}(x) - \overline{E}\right) R(x) \delta^2 - \left(1 - \frac{\delta}{x}\right) R(x - \delta) \right\} \left(\frac{1 + \frac{\delta}{x}}{1 + \frac{\delta}{x}}\right).$$

(4.16)

If we start the calculation near the origin then

$$R(2\delta) = \frac{1}{2} \left\{ 2 + \left(\overline{V}(\delta) - \overline{E}\right) \delta^2 \right\} R(\delta),$$

$$R(3\delta) = \frac{1}{3} \left\{ 2R(2\delta) + \left(\overline{V}(2\delta) - \overline{E}\right) R(2\delta) \delta^2 + R(\delta) \right\},$$

etc. Note that in the first equation the value of $R(x)$ at $x = 2\delta$ depends only on $R(\delta)$—it can easily be seen why by inspection of eqn 4.16 for the case of $x = \delta$ (for this value of $x$ the coefficient of $R(0)$ is zero). Thus the calculation starts at $x = \delta$ and works outwards from there.

At all other positions ($x > \delta$) the value of the function depends on its values at the two preceding points. From these recursion relations we can calculate the function at all subsequent points.

The calculated functions will not be normalised and the starting conditions can be multiplied by an arbitrary constant without affecting the eigenenergies, as will become clear from looking at the results. In the following $R(\delta) = 1$ is the suggested choice but any starting value works.

(b) **Implementation of the numerical method using a spreadsheet program**

Follow these instructions.

1. Type the given text labels into cells A1, B1, C1, D2, E2 and F2 and the three numbers into cells D1, E1 and F1 so that it has the following form:
Column A will contain the x-coordinates, the potential will be in column B and the function in column C. Cells D1, E1 and F1 contain the step size, energy and orbital angular momentum quantum number \( (l = 1) \), respectively.

2. Put 0 into A2 and the formula \( = A2+DS1 \) into A3. Copy cell A3 to the block A4:A1002. (Or start with a smaller number of steps and adjust D1 accordingly.)

3. The potential diverges at \( x = 0 \) so type inf. into B2 (or leave it blank, remembering not to refer to it).
Put the formula
\[
\frac{-2/A3+SF1*(SF1+1)/(A3*A3)}
\]
into cell B3 (as in eqn 4.15). Copy B3 into the block B4:B1002.

4. This is the crucial stage that calculates the function. Type the number 1 into cell C3. (We leave C2 blank since, as explained above, the value of the function at \( x = 0 \) does not affect the solution given by the recursion relation in eqn 4.16.) Now move to cell C4 and enter the following formula for the recursion relation:
\[
(2*C3+(B3-SE1)*C3+SD1*SD1 - (1-SD1/A3)*C2 )/ (1+SD1/A3). 
\]
Copy this into the block C5:C1002. Create an xy-plot of the wavefunction (with data points connected by smooth lines and no markers); the x series is A2:A1002 and the y series is C2:C1002. Insert this graph on the sheet.

5. Now play around with the parameters and observe the effect on the wavefunction for a particular energy.

(i) Show that the initial value of the function does not affect its shape, or the eigenenergy, by putting 0.1 (or any number) into cell C3.

(ii) Change the energy, e.g. put -0.251 into cell E1, then -0.249, and observe the change in behaviour at large \( x \). (The divergence is exponential, so even a small energy discrepancy gives a large effect.) Try the different energies again with bigger and smaller step sizes in D1. It is important to search for the eigenenergy using an appropriate range of \( x \). The eigenenergy lies between the two values of the trial energy that give opposite divergence, i.e. upwards and downwards on the graph.

(iii) Change F1 to 0 and find a solution for \( l = 0 \).

6. Produce a set of graphs labelled clearly with the trial energy that illustrate the principles of the numerical solution, for the two functions with \( n = 2 \) and two other cases. Compare the eigenenergies with the Bohr formula.
Calculate the effective principal quantum number for each of the solutions, e.g. by putting \( =SQRT(-1/E1) \) in G1 (and the label \( n* \) in G2).
(The search for eigenenergies can be automated by exploiting the spreadsheet's ability to optimise parameters subject to constraints (e.g. the 'Goal Seek' command, or similar). Ask the program to make the last value of the function (in cell C1002) have the value of zero by adjusting the energy (cell E1). This procedure can be recorded as a macro that searches for the eigenenergies with a single button click.)

7. Implement one, or more, of the following suggestions for improving the basic method described above.

(i) Find the eigenenergies for a potential that tends to the Coulomb potential \(-2/x\) in dimensionless units\) at long range, like those shown in Fig. 4.7, and show that the quantum defects for that potential depend on \( l \) but only weakly on \( n \).

(ii) For the potential shown in Fig. 4.7(c) compare the wavefunction in the inner and outer regions for several different energies. Give a qualitative explanation of the observed behaviour.

(iii) Calculate the function \( P(r) = rR(r) \) by putting A3*C3 in cell D3 and copying this to the rest of the columns.
Make a plot of $P(r)$, $R(r)$ and $V(r)$ for at least two different values of $n$ and $l$. Adjust the value in C3, as in stage 5(i), to scale the functions to convenient values for plotting on the same axes as the potential.

(iv) Attempt a semi-quantitative calculation of the quantum defects in the lithium atom, e.g. model $V_{\text{CF}}(r)$ as in Fig. 4.7(a) for some reasonable choice of $r_{\text{core}}$.\footnote{This simple model corresponds to all the inner electron charge being concentrated on a spherical shell. Making the transition from the inner to outer regions smoother does not make much difference to the qualitative behaviour, as you can check with the program.}

(v) Numerically calculate the sum of $r^2 R^2(r) \delta$ for all the values of the function and divide through by its square root to normalise the wavefunction. With normalised functions (stored in a column of the spreadsheet) you can calculate the electric dipole matrix elements (and their ratios), e.g. $|\langle 3p | r | 2s \rangle|^2 / |\langle 3p | r | 1s \rangle|^2 = 36$, as in Exercise 7.6 (not forgetting the $\omega^3$ factor from eqn 7.23).

(vi) Assess the accuracy of this numerical method by calculating some eigenenergies using different step sizes. (More sophisticated methods of numerical integration provided in mathematical software packages can be compared to the simple method, if desired, but the emphasis here is on the atomic physics rather than the computation. Note that methods that calculate higher derivatives of the function cannot cope with discontinuities in the potential.)
The $LS$-coupling scheme

In this chapter we shall look at atoms with two valence electrons, e.g. alkaline earth metals such as Mg and Ca. The structures of these elements have many similarities with helium, and we shall also use the central-field approximation that was introduced for the alkalis in the previous chapter. We start with the Hamiltonian for $N$ electrons in eqn 4.2 and insert the expression for the central potential $V_{\text{CF}}(r)$ (eqn 4.3) to give

$$H = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{CF}}(r_i) + \sum_{j>i}^{N} \frac{e^2/4\pi\varepsilon_0}{r_{ij}} - S(r_i) \right].$$

This Hamiltonian can be written as $H = H_{\text{CF}} + H_{\text{re}}$, where the central-field Hamiltonian $H_{\text{CF}}$ is that defined in eqn 4.4 and

$$H_{\text{re}} = \sum_{i=1}^{N} \left( \sum_{j>i}^{N} \frac{e^2/4\pi\varepsilon_0}{r_{ij}} - S(r_i) \right)$$

(5.1)

is the residual electrostatic interaction. This represents that part of the repulsion not taken into account by the central field. One might think that the field left over is somehow non-central. This is not necessarily true. For configurations such as $1s^2$ in He, or $3s^4$ in Mg, both electrons have spherically-symmetric distributions but a central field cannot completely account for the repulsion between them—a potential $V_{\text{CF}}(r)$ does not include the effect of the correlation of the electrons' positions that leads to the exchange integral.\(^1\) The residual electrostatic interaction perturbs the electronic configurations $n_1l_1n_2l_2$ that are the eigenstates of the central field. These angular momentum eigenstates for the two electrons are products of their orbital and spin functions $|l_1m_{l_1}s_{l_1}m_{s_1}\rangle |l_2m_{l_2}s_{l_2}m_{s_2}\rangle$, and their energy does not depend on the atom's orientation so that all the different $m_l$ states are degenerate, e.g. the configuration $3p^4p$ has $(2l_1 + 1)(2l_2 + 1) = 9$ degenerate combinations of $Y_{l_1,m_{l_1}}Y_{l_2,m_{l_2}}$. Each of these spatial states has four spin functions associated with it, but we do not need to consider thirty-six degenerate states since the problem separates into spatial and spin parts, as in helium. Nevertheless, the direct approach would require diagonalising matrices of larger dimensions than the simple $2 \times 2$ matrix whose determinant was given in eqn 3.17. Therefore, instead of that brute-force approach, we use the 'look-before-you-leap' method that starts by finding the eigenstates of the perturbation $H_{\text{re}}$. In that representation, $H_{\text{re}}$ is a diagonal matrix with the eigenvalues as its diagonal elements.

\(^1\)Choosing $S(r)$ to account for all the repulsion between the spherically-symmetric core and the electrons outside the closed shells, and also within the core, leaves the repulsion between the two valence electrons, i.e. $H_{\text{re}} \approx e^2/4\pi\varepsilon_0r_{12}$. This approximation highlights the similarity with helium (although the expectation value is evaluated with different wavefunctions). Although it simplifies the equations nicely, this is not the best approximation for accurate calculations—$S(r)$ can be chosen to include most of the direct integral (cf. Section 3.3.2). For alkali metal atoms, which we studied in the last chapter, the repulsion between electrons gives a spherically-symmetric potential, so that $H_{\text{re}} = 0$.

\(^2\)For two $p$-electrons we cannot ignore $m_l$ as we did in the treatment of $1s\text{nl}$ configurations in helium. Configurations with one, or more, $s$-electrons can be treated in the way already described for helium but with the radial wavefunctions calculated numerically.