10

Atomic structure and atomic spectra

We now use the principles of quantum mechanics introduced in the preceding two chapters to describe the internal structures of atoms. We see what experimental information is available from a study of the spectrum of atomic hydrogen. Then we set up the Schrödinger equation for an electron in an atom and separate it into angular and radial parts. The wavefunctions obtained are the 'atomic orbitals' of hydrogenic atoms. Next, we use these hydrogenic atomic orbitals to describe the structures of many-electron atoms. In conjunction with the Pauli exclusion principle, we account for the periodicity of atomic properties. The spectra of many-electron atoms are more complicated than those of hydrogen, but the same principles apply. We see in the closing sections of the chapter how such spectra are described by using term symbols, and the origin of the finer details of their appearance.

In this chapter we see how to use quantum mechanics to describe the **electronic structure** of an atom, the arrangement of electrons around a nucleus. The concepts we meet are of central importance for understanding the structures and reactions of atoms and molecules, and hence have extensive chemical applications. We need to distinguish between two types of atoms. A **hydrogenic atom** is a one-electron atom or ion of general atomic number Z; examples of hydrogenic atoms are H, He^+, Li^{2+}, O^{7+}, and even U^{91+}. A **many-electron atom** (or *polyelectronic atom*) is an atom or ion with more than one electron; examples include all neutral atoms other than H. So even He, with only two electrons, is a many-electron atom. Hydrogenic atoms are important because their Schrödinger equations can be solved exactly. They also provide a set of concepts that are used to describe the structures of many-electron atoms and, as we shall see in the next chapter, the structures of molecules too.

The structure and spectra of hydrogenic atoms

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules are dissociated and the energetically excited H atoms that are produced emit light of discrete frequencies, producing a spectrum of a series of 'lines' (Fig. 10.1). The Swedish spectroscopist Johannes Rydberg noted (in 1890) that all of them are described by the expression

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad R_H = 109\ 677\ cm^{-1} \qquad (10.1)$$

with $n_1 = 1$ (the *Lyman series*), 2 (the *Balmer series*), and 3 (the *Paschen series*), and that in each case $n_2 = n_1 + 1, n_1 + 2, \ldots$. The constant R_H is now called the **Rydberg constant** for the hydrogen atom.
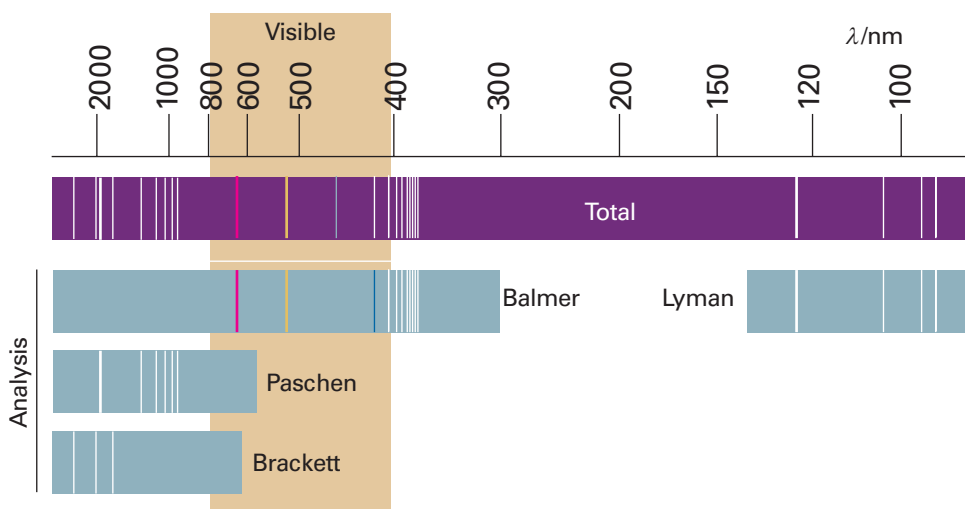
Fig. 10.1 The spectrum of atomic hydrogen. Both the observed spectrum and its resolution into overlapping series are shown. Note that the Balmer series lies in the visible region.

Self-test 10.1 Calculate the shortest wavelength line in the Paschen series.

[821 nm]

The form of eqn 10.1 strongly suggests that the wavenumber of each spectral line can be written as the difference of two **terms**, each of the form

$$T_n = \frac{R_H}{n^2} \tag{10.2}$$

The **Ritz combination principle** states that *the wavenumber of any spectral line is the difference between two terms*. We say that two terms T_1 and T_2 'combine' to produce a spectral line of wavenumber

$$\tilde{v} = T_1 - T_2 \tag{10.3}$$

Thus, if each spectroscopic term represents an energy hcT, the difference in energy when the atom undergoes a transition between two terms is $\Delta E = hcT_1 - hcT_2$ and, according to the Bohr frequency conditions (Section 8.1d), the frequency of the radiation emitted is given by $v = cT_1 - cT_2$. This expression rearranges into the Ritz formula when expressed in terms of wavenumbers (on division by c). The Ritz combination principle applies to all types of atoms and molecules, but only for hydrogenic atoms do the terms have the simple form (constant)/n^2.

Because spectroscopic observations show that electromagnetic radiation is absorbed and emitted by atoms only at certain wavenumbers, it follows that only certain energy states of atoms are permitted. Our tasks in the first part of this chapter are to determine the origin of this energy quantization, to find the permitted energy levels, and to account for the value of R_H.

10.1 The structure of hydrogenic atoms

The Coulomb potential energy of an electron in a hydrogenic atom of atomic number Z (and nuclear charge Ze) is

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{10.4}$$

where r is the distance of the electron from the nucleus and ε_0 is the vacuum permittivity. The hamiltonian for the electron and a nucleus of mass m_N is therefore

$$\hat{H} = \hat{E}_{K,electron} + \hat{E}_{K,nucleus} + \hat{V}$$

$$= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{10.5}$$

The subscripts on ∇^2 indicate differentiation with respect to the electron or nuclear coordinates.

(a) The separation of variables

Physical intuition suggests that the full Schrödinger equation ought to separate into two equations, one for the motion of the atom as a whole through space and the other for the motion of the electron relative to the nucleus. We show in *Further information 10.1* how this separation is achieved, and that the Schrödinger equation for the internal motion of the electron relative to the nucleus is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi \qquad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N} \tag{10.6}$$

where differentiation is now with respect to the coordinates of the electron relative to the nucleus. The quantity μ is called the **reduced mass**. The reduced mass is very similar to the electron mass because m_N, the mass of the nucleus, is much larger than the mass of an electron, so $1/\mu \approx 1/m_e$. In all except the most precise work, the reduced mass can be replaced by m_e.

Because the potential energy is centrosymmetric (independent of angle), we can suspect that the equation is separable into radial and angular components. Therefore, we write

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{10.7}$$

and examine whether the Schrödinger equation can be separated into two equations, one for R and the other for Y. As shown in *Further information 10.1*, the equation does separate, and the equations we have to solve are

$$\Lambda^2 Y = -l(l+1)Y \tag{10.8}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + V_{eff}u = Eu \qquad u = rR \tag{10.9}$$

where

$$V_{eff} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{10.10}$$

Equation 10.8 is the same as the Schrödinger equation for a particle free to move round a central point, and we considered it in Section 9.7. The solutions are the spherical harmonics (Table 9.3), and are specified by the quantum numbers l and m_l. We consider them in more detail shortly. Equation 10.9 is called the **radial wave equation**. The radial wave equation is the description of the motion of a particle of mass μ in a one-dimensional region $0 \leq r < \infty$ where the potential energy is V_{eff}.

(b) The radial solutions

We can anticipate some features of the shapes of the radial wavefunctions by analysing the form of V_{eff}. The first term in eqn 10.10 is the Coulomb potential energy of the

electron in the field of the nucleus. The second term stems from what in classical physics would be called the centrifugal force that arises from the angular momentum of the electron around the nucleus. When $l = 0$, the electron has no angular momentum, and the effective potential energy is purely Coulombic and attractive at all radii (Fig. 10.2). When $l \neq 0$, the centrifugal term gives a positive (repulsive) contribution to the effective potential energy. When the electron is close to the nucleus ($r \approx 0$), this repulsive term, which is proportional to $1/r^2$, dominates the attractive Coulombic component, which is proportional to $1/r$, and the net effect is an effective repulsion of the electron from the nucleus. The two effective potential energies, the one for $l = 0$ and the one for $l \neq 0$, are qualitatively very different close to the nucleus. However, they are similar at large distances because the centrifugal contribution tends to zero more rapidly (as $1/r^2$) than the Coulombic contribution (as $1/r$). Therefore, we can expect the solutions with $l = 0$ and $l \neq 0$ to be quite different near the nucleus but similar far away from it. We show in the *Justification* below that close to the nucleus the radial wavefunction is proportional to r^l, and the higher the orbital angular momentum, the less likely the electron is to be found (Fig. 10.3). We also show that far from the nucleus all wavefunctions approach zero exponentially.

Fig. 10.2 The effective potential energy of an electron in the hydrogen atom. When the electron has zero orbital angular momentum, the effective potential energy is the Coulombic potential energy. When the electron has nonzero orbital angular momentum, the centrifugal effect gives rise to a positive contribution that is very large close to the nucleus. We can expect the $l = 0$ and $l \neq 0$ wavefunctions to be very different near the nucleus.

Exploration Plot the effective potential energy against r for several nonzero values of the orbital angular momentum l. How does the location of the minimum in the effective potential energy vary with l?

....

Justification 10.1 *The shape of the radial wavefunction*

When r is very small (close to the nucleus), $u \approx 0$, so the right-hand side of eqn 10.9 is zero; we can also ignore all but the largest terms (those depending on $1/r^2$) in eqn 10.9 and write

$$-\frac{d^2u}{dr^2} + \frac{l(l+1)}{r^2}u \approx 0$$

The solution of this equation (for $r \approx 0$) is

$$u \approx Ar^{l+1} + \frac{B}{r^l}$$

Because $R = u/r$, and R cannot be infinite at $r = 0$, we must set $B = 0$, and hence obtain $R \approx Ar^l$.

Far from the nucleus, when r is very large, we can ignore all terms in $1/r$ and eqn 10.9 becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} \simeq Eu$$

where $\simeq$ means 'asymptotically equal to'. Because

$$\frac{d^2u}{dr^2} = \frac{d^2(rR)}{dr^2} = r\frac{d^2R}{dr^2} + 2\frac{dR}{dr} \simeq r\frac{d^2R}{dr^2}$$
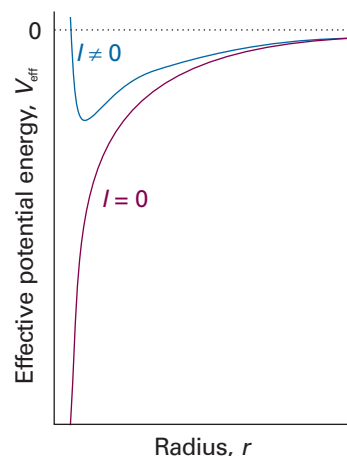
this equation has the form

$$-\frac{\hbar^2}{2\mu}\frac{d^2R}{dr^2} \simeq ER$$

The acceptable (finite) solution of this equation (for r large) is

$$R \simeq e^{-(2\mu|E|/\hbar^2)r}$$

and the wavefunction decays exponentially towards zero as r increases.

....
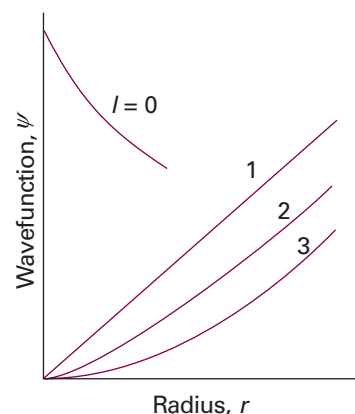
We shall not go through the technical steps of solving the radial equation for the full range of radii, and see how the form r^l close to the nucleus blends into the exponentially

Fig. 10.3 Close to the nucleus, orbitals with $l = 1$ are proportional to r, orbitals with $l = 2$ are proportional to r^2, and orbitals with $l = 3$ are proportional to r^3. Electrons are progressively excluded from the neighbourhood of the nucleus as l increases. An orbital with $l = 0$ has a finite, nonzero value at the nucleus.

decaying form at great distances (see *Further reading*). It is sufficient to know that the two limits can be matched only for integral values of a quantum number n, and that the allowed energies corresponding to the allowed solutions are

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2} \tag{10.11}$$

with $n = 1, 2, \ldots$ Likewise, the radial wavefunctions depend on the values of both n and l (but not on m_l), and all of them have the form

$$R(r) = (\text{polynomial in } r) \times (\text{decaying exponential in } r) \tag{10.12}$$

These functions are most simply written in terms of the dimensionless quantity ρ (rho), where

$$\rho = \frac{2Zr}{na_0} \qquad a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} \tag{10.13}$$

The **Bohr radius**, a_0, has the value 52.9 pm; it is so called because the same quantity appeared in Bohr's early model of the hydrogen atom as the radius of the electron orbit of lowest energy. Specifically, the radial wavefunctions for an electron with quantum numbers n and l are the (real) functions

$$R_{n,l}(r) = N_{n,l}\rho^l L_{n+1}^{2l+1}(\rho)e^{-\rho/2} \tag{10.14}$$

where L is a polynomial in ρ called an *associated Laguerre polynomial*: it links the $r \approx 0$ solutions on its left (corresponding to $R \propto \rho^l$) to the exponentially decaying function on its right. The notation might look fearsome, but the polynomials have quite simple forms, such as 1, ρ, and $2 - \rho$ (they can be picked out in Table 10.1). Specifically, we can interpret the components of this expression as follows:

1   The exponential factor ensures that the wavefunction approaches zero far from the nucleus.

Table 10.1 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
$1s$	1	0	$2\left(\dfrac{Z}{a}\right)^{3/2} e^{-\rho/2}$
$2s$	2	0	$\dfrac{1}{8^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2}(2-\rho)e^{-\rho/2}$
$2p$	2	1	$\dfrac{1}{24^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}$
$3s$	3	0	$\dfrac{1}{243^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2}(6-6\rho+\rho^2)e^{-\rho/2}$
$3p$	3	1	$\dfrac{1}{486^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2}(4-\rho)\rho e^{-\rho/2}$
$3d$	3	2	$\dfrac{1}{2430^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2}\rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$ with $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$. For an infinitely heavy nucleus (or one that may be assumed to be so), $\mu = m_e$ and $a = a_0$, the Bohr radius. The full wavefunction is obtained by multiplying R by the appropriate Y given in Table 9.3.
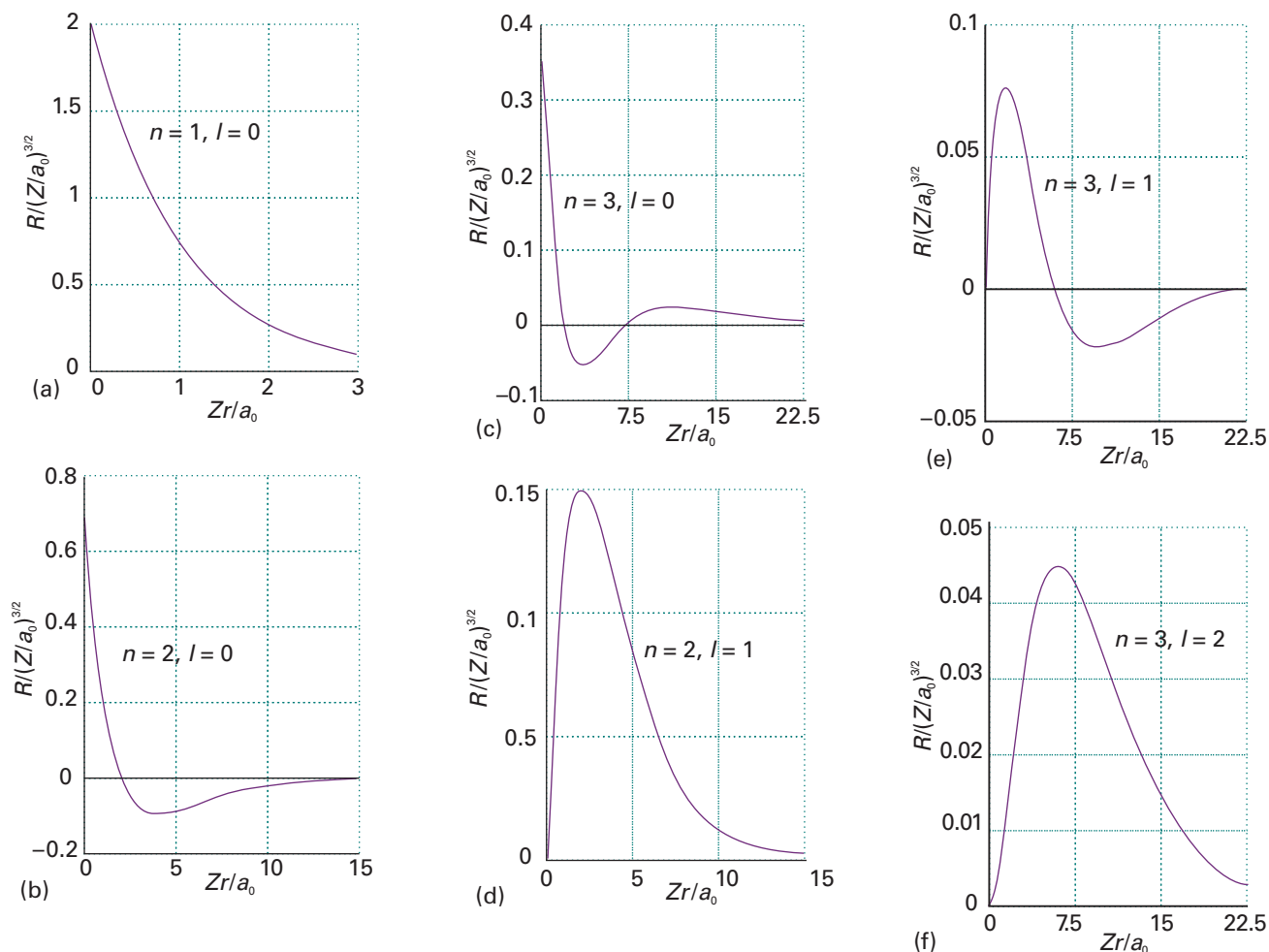
Fig. 10.4 The radial wavefunctions of the first few states of hydrogenic atoms of atomic number Z. Note that the orbitals with $l = 0$ have a nonzero and finite value at the nucleus. The horizontal scales are different in each case: orbitals with high principal quantum numbers are relatively distant from the nucleus.

Exploration Use mathematical software to find the locations of the radial nodes in hydrogenic wavefunctions with n up to 3.

2 The factor ρ^l ensures that (provided $l > 0$) the wavefunction vanishes at the nucleus.

3 The associated Laguerre polynomial is a function that oscillates from positive to negative values and accounts for the presence of radial nodes.

Expressions for some radial wavefunctions are given in Table 10.1 and illustrated in Fig. 10.4.

Comment 10.1
The zero at $r = 0$ is not a radial node because the radial wavefunction does not pass through zero at that point (because r cannot be negative). Nodes at the nucleus are all angular nodes.

Illustration 10.1 *Calculating a probability density*

To calculate the probability density at the nucleus for an electron with $n = 1$, $l = 0$, and $m_l = 0$, we evaluate ψ at $r = 0$:

$$\psi_{1,0,0}(0,\theta,\phi) = R_{1,0}(0)Y_{0,0}(\theta,\phi) = 2\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{1}{4\pi}\right)^{1/2}$$

The probability density is therefore

$$\psi_{1,0,0}(0,\theta,\phi)^2 = \frac{Z^3}{\pi a_0^3}$$

which evaluates to 2.15×10^{-6} pm^{-3} when $Z = 1$.

Self-test 10.2 Evaluate the probability density at the nucleus of the electron for an electron with $n = 2$, $l = 0$, $m_l = 0$. $[(Z/a_0)^3/8\pi]$

10.2 **Atomic orbitals and their energies**

An **atomic orbital** is a one-electron wavefunction for an electron in an atom. Each hydrogenic atomic orbital is defined by three quantum numbers, designated n, l, and m_l. When an electron is described by one of these wavefunctions, we say that it 'occupies' that orbital. We could go on to say that the electron is in the state $|n,l,m_l\rangle$. For instance, an electron described by the wavefunction $\psi_{1,0,0}$ and in the state $|1,0,0\rangle$ is said to occupy the orbital with $n = 1$, $l = 0$, and $m_l = 0$.

The quantum number n is called the **principal quantum number**; it can take the values $n = 1, 2, 3, \ldots$ and determines the energy of the electron:

An electron in an orbital with quantum number n has an energy given by eqn 10.11.

The two other quantum numbers, l and m_l, come from the angular solutions, and specify the angular momentum of the electron around the nucleus:

An electron in an orbital with quantum number l has an angular momentum of magnitude $\{l(l+1)\}^{1/2}\hbar$, with $l = 0, 1, 2, \ldots, n-1$.

An electron in an orbital with quantum number m_l has a z-component of angular momentum $m_l\hbar$, with $m_l = 0, \pm1, \pm2, \ldots, \pm l$.

Note how the value of the principal quantum number, n, controls the maximum value of l and l controls the range of values of m_l.

To define the state of an electron in a hydrogenic atom fully we need to specify not only the orbital it occupies but also its spin state. We saw in Section 9.8 that an electron possesses an intrinsic angular momentum that is described by the two quantum numbers s and m_s (the analogues of l and m_l). The value of s is fixed at $\frac{1}{2}$ for an electron, so we do not need to consider it further at this stage. However, m_s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$, and to specify the electron's state in a hydrogenic atom we need to specify which of these values describes it. It follows that, to specify the state of an electron in a hydrogenic atom, we need to give the values of four quantum numbers, namely n, l, m_l, and m_s.

(a) **The energy levels**

The energy levels predicted by eqn 10.11 are depicted in Fig. 10.5. The energies, and also the separation of neighbouring levels, are proportional to Z^2, so the levels are four times as wide apart (and the ground state four times deeper in energy) in He$^+$ ($Z = 2$) than in H ($Z = 1$). All the energies given by eqn 10.11 are negative. They refer to the **bound states** of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy). There are also solutions of the Schrödinger equation with positive energies. These solutions correspond to **unbound states** of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon. The energies of the unbound electron are not quantized and form the continuum states of the atom.
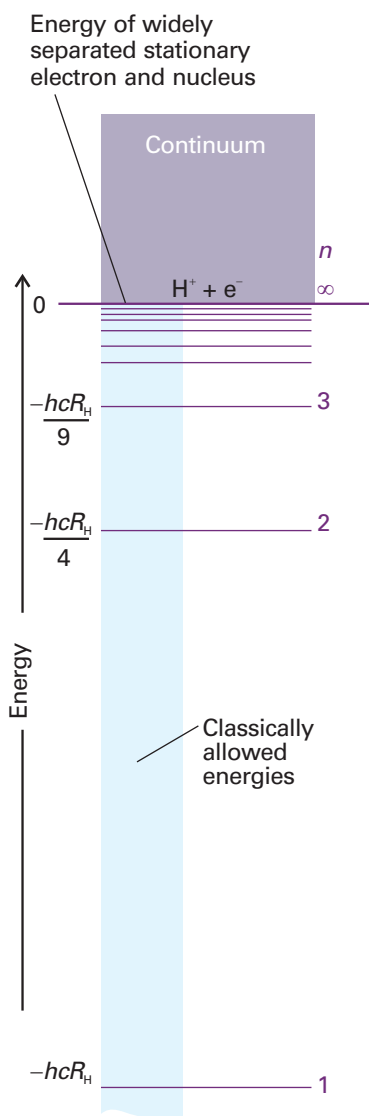
Fig. 10.5 The energy levels of a hydrogen atom. The values are relative to an infinitely separated, stationary electron and a proton.

Equation 10.11 is consistent with the spectroscopic result summarized by eqn 10.1, and we can identify the Rydberg constant for hydrogen ($Z = 1$) as

$$hcR_H = \frac{\mu_H e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \qquad [10.15]$$

where μ_H is the reduced mass for hydrogen. The **Rydberg constant** itself, R, is defined by the same expression except for the replacement of μ_H by the mass of an electron, m_e, corresponding to a nucleus of infinite mass:

$$R_H = \frac{\mu_H}{m_e} R \qquad R = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \qquad [10.16]$$

Insertion of the values of the fundamental constants into the expression for R_H gives almost exact agreement with the experimental value. The only discrepancies arise from the neglect of relativistic corrections (in simple terms, the increase of mass with speed), which the non-relativistic Schrödinger equation ignores.

(b) Ionization energies

The **ionization energy**, I, of an element is the minimum energy required to remove an electron from the ground state, the state of lowest energy, of one of its atoms. Because the ground state of hydrogen is the state with $n = 1$, with energy $E_1 = -hcR_H$ and the atom is ionized when the electron has been excited to the level corresponding to $n = \infty$ (see Fig. 10.5), the energy that must be supplied is

$$I = hcR_H \qquad (10.17)$$

The value of I is 2.179 aJ (a, for atto, is the prefix that denotes 10^{-18}), which corresponds to 13.60 eV.

Example 10.1 *Measuring an ionization energy spectroscopically*

The emission spectrum of atomic hydrogen shows lines at 82 259, 97 492, 102 824, 105 292, 106 632, and 107 440 cm^{-1}, which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the value of the Rydberg constant.

Method The spectroscopic determination of ionization energies depends on the determination of the series limit, the wavenumber at which the series terminates and becomes a continuum. If the upper state lies at an energy $-hcR_H/n^2$, then, when the atom makes a transition to E_{lower}, a photon of wavenumber
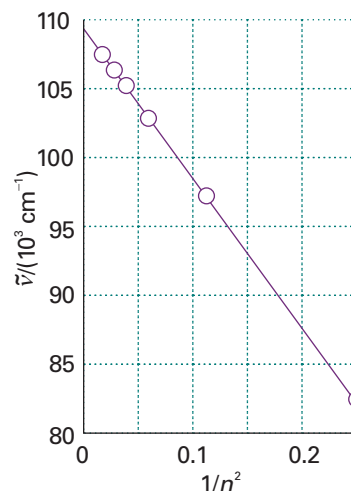
$$\tilde{\nu} = -\frac{R_H}{n^2} - \frac{E_{lower}}{hc}$$

is emitted. However, because $I = -E_{lower}$, it follows that

$$\tilde{\nu} = \frac{I}{hc} - \frac{R_H}{n^2}$$

A plot of the wavenumbers against $1/n^2$ should give a straight line of slope $-R_H$ and intercept I/hc. Use a computer to make a least-squares fit of the data to get a result that reflects the precision of the data.

Answer The wavenumbers are plotted against $1/n^2$ in Fig. 10.6. The (least-squares) intercept lies at 109 679 cm^{-1}, so the ionization energy is 2.1788 aJ (1312.1 kJ mol^{-1}).

Comment 10.2

The particle in a finite well, discussed in Section 9.3, is a primitive but useful model that gives insight into the bound and unbound states of the electron in a hydrogenic atom. Figure 9.15 shows that the energies of a particle (for example, an electron in a hydrogenic atom) are quantized when its total energy, E, is lower than its potential energy, V (the Coulomb interaction energy between the electron and the nucleus). When $E > V$, the particle can escape from the well (the atom is ionized) and its energies are no longer quantized, forming a continuum.

Fig. 10.6 The plot of the data in Example 10.1 used to determine the ionization energy of an atom (in this case, of H).

Exploration The initial value of n was not specified in Example 10.1. Show that the correct value can be determined by making several choices and selecting the one that leads to a straight line.

The slope is, in this instance, numerically the same, so $R_H = 109\ 679\ cm^{-1}$. A similar extrapolation procedure can be used for many-electron atoms (see Section 10.5).

Self-test 10.3 The emission spectrum of atomic deuterium shows lines at 15 238, 20 571, 23 039, and 24 380 cm^{-1}, which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the ionization energy of the ground state, (c) the mass of the deuteron (by expressing the Rydberg constant in terms of the reduced mass of the electron and the deuteron, and solving for the mass of the deuteron).

[(a) 328.1 kJ mol^{-1}, (b) 1312.4 kJ mol^{-1}, (c) 2.8×10^{-27} kg, a result very sensitive to R_D]

(c) Shells and subshells

All the orbitals of a given value of n are said to form a single **shell** of the atom. In a hydrogenic atom, all orbitals of given n, and therefore belonging to the same shell, have the same energy. It is common to refer to successive shells by letters:

$$n = \quad 1 \quad 2 \quad 3 \quad 4\dots$$
$$\quad\quad K \quad L \quad M \quad N\dots$$

Thus, all the orbitals of the shell with $n = 2$ form the L shell of the atom, and so on.

The orbitals with the same value of n but different values of l are said to form a **subshell** of a given shell. These subshells are generally referred to by letters:

$$l = \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6\dots$$
$$\quad\quad s \quad p \quad d \quad f \quad g \quad h \quad i\dots$$

The letters then run alphabetically (j is not used). Figure 10.7 is a version of Fig. 10.5 which shows the subshells explicitly. Because l can range from 0 to $n - 1$, giving n values in all, it follows that there are n subshells of a shell with principal quantum number n. Thus, when $n = 1$, there is only one subshell, the one with $l = 0$. When $n = 2$, there are two subshells, the $2s$ subshell (with $l = 0$) and the $2p$ subshell (with $l = 1$).

When $n = 1$ there is only one subshell, that with $l = 0$, and that subshell contains only one orbital, with $m_l = 0$ (the only value of m_l permitted). When $n = 2$, there are four orbitals, one in the s subshell with $l = 0$ and $m_l = 0$, and three in the $l = 1$ subshell with $m_l = +1, 0, -1$. When $n = 3$ there are nine orbitals (one with $l = 0$, three with $l = 1$, and five with $l = 2$). The organization of orbitals in the shells is summarized in Fig. 10.8. In general, the number of orbitals in a shell of principal quantum number n is n^2, so in a hydrogenic atom each energy level is n^2-fold degenerate.

(d) Atomic orbitals

The orbital occupied in the ground state is the one with $n = 1$ (and therefore with $l = 0$ and $m_l = 0$, the only possible values of these quantum numbers when $n = 1$). From Table 10.1 we can write (for $Z = 1$):

$$\psi = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \tag{10.18}$$

This wavefunction is independent of angle and has the same value at all points of constant radius; that is, the $1s$ orbital is *spherically symmetrical*. The wavefunction decays exponentially from a maximum value of $1/(\pi a_0^3)^{1/2}$ at the nucleus (at $r = 0$). It follows that the most probable point at which the electron will be found is at the nucleus itself.
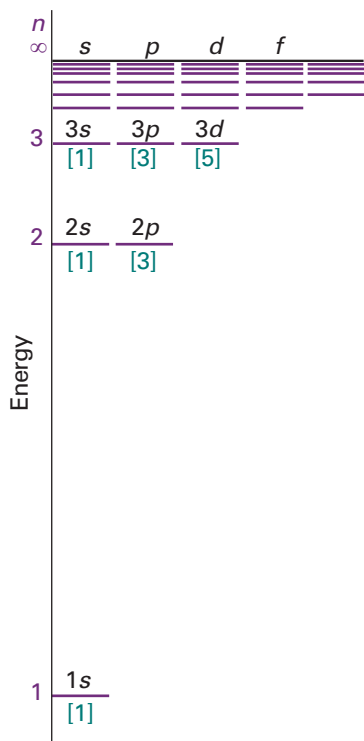
Fig. 10.7 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy.
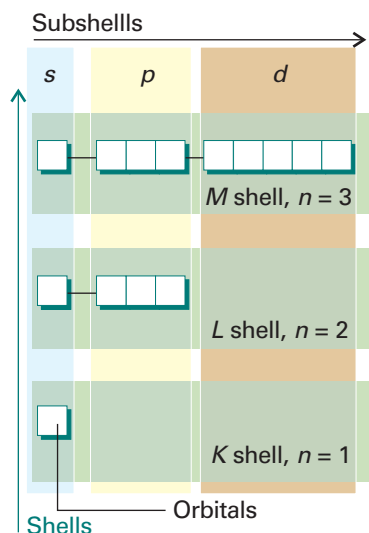
Fig. 10.8 The organization of orbitals (white squares) into subshells (characterized by l) and shells (characterized by n).
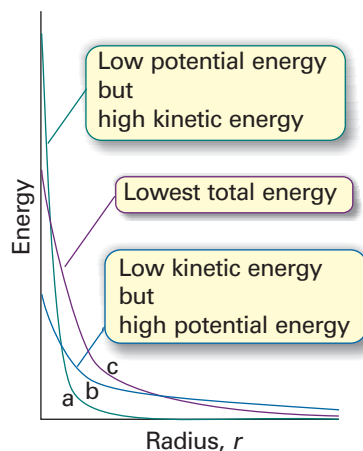
Fig. 10.9 The balance of kinetic and potential energies that accounts for the structure of the ground state of hydrogen (and similar atoms). (a) The sharply curved but localized orbital has high mean kinetic energy, but low mean potential energy; (b) the mean kinetic energy is low, but the potential energy is not very favourable; (c) the compromise of moderate kinetic energy and moderately favourable potential energy.
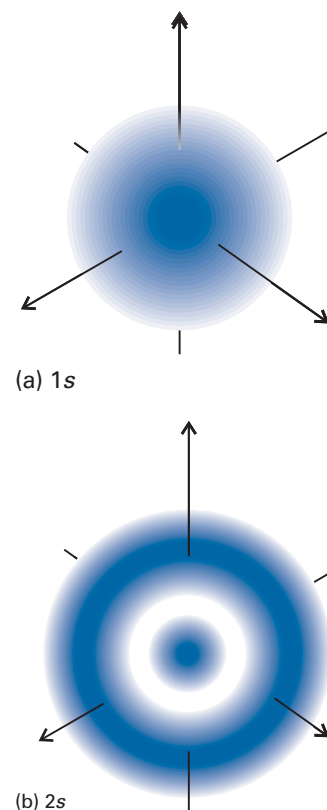

(a) 1s

(b) 2s

Fig. 10.10 Representations of the 1s and 2s hydrogenic atomic orbitals in terms of their electron densities (as represented by the density of shading)

We can understand the general form of the ground-state wavefunction by considering the contributions of the potential and kinetic energies to the total energy of the atom. The closer the electron is to the nucleus on average, the lower its average potential energy. This dependence suggests that the lowest potential energy should be obtained with a sharply peaked wavefunction that has a large amplitude at the nucleus and is zero everywhere else (Fig. 10.9). However, this shape implies a high kinetic energy, because such a wavefunction has a very high average curvature. The electron would have very low kinetic energy if its wavefunction had only a very low average curvature. However, such a wavefunction spreads to great distances from the nucleus and the average potential energy of the electron will be correspondingly high. The actual ground-state wavefunction is a compromise between these two extremes: the wavefunction spreads away from the nucleus (so the expectation value of the potential energy is not as low as in the first example, but nor is it very high) and has a reasonably low average curvature (so the expectation of the kinetic energy is not very low, but nor is it as high as in the first example).

The energies of ns orbitals increase (become less negative; the electron becomes less tightly bound) as n increases because the average distance of the electron from the nucleus increases. By the virial theorem with $b = -1$ (eqn 9.35), $\langle E_K \rangle = -\frac{1}{2}\langle V \rangle$ so, even though the average kinetic energy decreases as n increases, the total energy is equal to $\frac{1}{2}\langle V \rangle$, which becomes less negative as n increases.

One way of depicting the probability density of the electron is to represent $|\psi|^2$ by the density of shading (Fig. 10.10). A simpler procedure is to show only the **boundary surface**, the surface that captures a high proportion (typically about 90 per cent) of the electron probability. For the 1s orbital, the boundary surface is a sphere centred on the nucleus (Fig. 10.11).
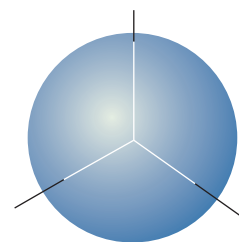
Fig. 10.11 The boundary surface of an s orbital, within which there is a 90 per cent probability of finding the electron.
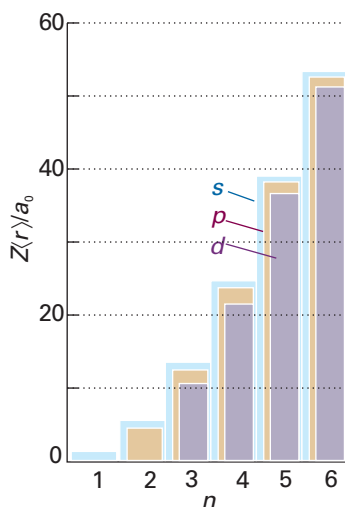
Fig. 10.12 The variation of the mean radius of a hydrogenic atom with the principal and orbital angular momentum quantum numbers. Note that the mean radius lies in the order $d < p < s$ for a given value of n.

The general expression for the mean radius of an orbital with quantum numbers l and n is

$$r_{n,l} = n^2 \left\{ 1 + \tfrac{1}{2}\left(1 - \frac{l(l+1)}{n^2} \right) \right\} \frac{a_0}{Z} \tag{10.19}$$

The variation with n and l is shown in Fig. 10.12. Note that, for a given principal quantum number, the mean radius decreases as l increases, so the average distance of an electron from the nucleus is less when it is in a $2p$ orbital, for instance, than when it is in a $2s$ orbital.

Example 10.2 *Calculating the mean radius of an orbital*

Use hydrogenic orbitals to calculate the mean radius of a $1s$ orbital.

Method The mean radius is the expectation value

$$\langle r \rangle = \int \psi^* r \psi \, d\tau = \int r |\psi|^2 \, d\tau$$

We therefore need to evaluate the integral using the wavefunctions given in Table 10.1 and $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$. The angular parts of the wavefunction are normalized in the sense that

$$\int_0^\pi \int_0^{2\pi} |Y_{l,m_l}|^2 \sin\theta d\theta \, d\phi = 1$$

The integral over r required is given in Example 8.7.

Answer With the wavefunction written in the form $\psi = RY$, the integration is

$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r R_{n,l}^2 |Y_{l,m_l}|^2 r^2 \, dr \sin\theta \, d\theta \, d\phi = \int_0^\infty r^3 R_{n,l}^2 \, dr$$

For a $1s$ orbital,

$$R_{1,0} = 2 \left(\frac{Z}{a_0^3} \right)^{1/2} e^{-Zr/a_0}$$

Hence

$$\langle r \rangle = \frac{4Z}{a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} \, dr = \frac{3a_0}{2Z}$$

Self-test 10.4 Evaluate the mean radius (a) of a $3s$ orbital by integration, and (b) of a $3p$ orbital by using the general formula, eqn 10.19.   [(a) $27a_0/2Z$; (b) $25a_0/2Z$]

All s-orbitals are spherically symmetric, but differ in the number of radial nodes. For example, the $1s$, $2s$, and $3s$ orbitals have 0, 1, and 2 radial nodes, respectively. In general, an ns orbital has $n - 1$ radial nodes.

Self-test 10.5 (a) Use the fact that a $2s$ orbital has radial nodes where the polynomial factor (Table 10.1) is equal to zero, and locate the radial node at $2a_0/Z$ (see Fig. 10.4). (b) Similarly, locate the two nodes of a $3s$ orbital.
    [(a) $2a_0/Z$; (b) $1.90a_0/Z$ and $7.10a_0/Z$]

(e) Radial distribution functions

The wavefunction tells us, through the value of $|\psi|^2$, the probability of finding an electron in any region. We can imagine a probe with a volume $d\tau$ and sensitive to electrons, and which we can move around near the nucleus of a hydrogen atom. Because the probability density in the ground state of the atom is $|\psi|^2 \propto e^{-2Zr/a_0}$, the reading from the detector decreases exponentially as the probe is moved out along any radius but is constant if the probe is moved on a circle of constant radius (Fig. 10.13).

Now consider the probability of finding the electron *anywhere* between the two walls of a spherical shell of thickness dr at a radius r. The sensitive volume of the probe is now the volume of the shell (Fig. 10.14), which is $4\pi r^2 dr$ (the product of its surface area, $4\pi r^2$, and its thickness, dr). The probability that the electron will be found between the inner and outer surfaces of this shell is the probability density at the radius r multiplied by the volume of the probe, or $|\psi|^2 \times 4\pi r^2 dr$. This expression has the form $P(r)dr$, where

$$P(r) = 4\pi r^2 \psi^2 \tag{10.20}$$

The more general expression, which also applies to orbitals that are not spherically symmetrical, is

$$P(r) = r^2 R(r)^2 \tag{10.21}$$

where $R(r)$ is the radial wavefunction for the orbital in question.

Fig. 10.13 A constant-volume electron-sensitive detector (the small cube) gives its greatest reading at the nucleus, and a smaller reading elsewhere. The same reading is obtained anywhere on a circle of given radius: the *s* orbital is spherically symmetrical.

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Justification 10.2 *The general form of the radial distribution function*

The probability of finding an electron in a volume element $d\tau$ when its wavefunction is $\psi = RY$ is $|RY|^2 d\tau$ with $d\tau = r^2 dr \sin\theta \, d\theta d\phi$. The total probability of finding the electron at any angle at a constant radius is the integral of this probability over the surface of a sphere of radius r, and is written $P(r)dr$; so

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

$$= r^2 R(r)^2 dr \overbrace{\int_0^\pi \int_0^{2\pi} |Y(\theta,\phi)|^2 \sin\theta d\theta d\phi}^{1} = r^2 R(r)^2 dr$$
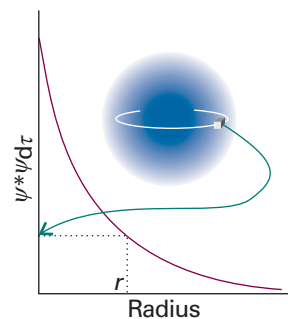
The last equality follows from the fact that the spherical harmonics are normalized to 1 (see Example 10.2). It follows that $P(r) = r^2 R(r)^2$, as stated in the text.

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The **radial distribution function**, $P(r)$, is a probability density in the sense that, when it is multiplied by dr, it gives the probability of finding the electron anywhere between the two walls of a spherical shell of thickness dr at the radius r. For a 1*s* orbital,

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0} \tag{10.22}$$

Let's interpret this expression:

1 Because $r^2 = 0$ at the nucleus, at the nucleus $P(0) = 0$.

2 As $r \to \infty$, $P(r) \to 0$ on account of the exponential term.

3 The increase in r^2 and the decrease in the exponential factor means that P passes through a maximum at an intermediate radius (see Fig. 10.14).

Fig. 10.14 The radial distribution function P gives the probability that the electron will be found anywhere in a shell of radius r. For a 1*s* electron in hydrogen, P is a maximum when r is equal to the Bohr radius a_0. The value of P is equivalent to the reading that a detector shaped like a spherical shell would give as its radius is varied.

The maximum of $P(r)$, which can be found by differentiation, marks the most probable radius at which the electron will be found, and for a 1s orbital in hydrogen occurs at $r = a_0$, the Bohr radius. When we carry through the same calculation for the radial distribution function of the 2s orbital in hydrogen, we find that the most probable radius is $5.2a_0 = 275$ pm. This larger value reflects the expansion of the atom as its energy increases.

Example 10.3 *Calculating the most probable radius*

Calculate the most probable radius, $r^\star$, at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z, and tabulate the values for the one-electron species from H to Ne^{9+}.

Method We find the radius at which the radial distribution function of the hydrogenic 1s orbital has a maximum value by solving $dP/dr = 0$. If there are several maxima, then we choose the one corresponding to the greatest amplitude (the outermost one).

Answer The radial distribution function is given in eqn 10.22. It follows that

$$\frac{dP}{dr} = \frac{4Z^3}{a_0^3}\left(2r - \frac{2Zr^2}{a_0}\right)e^{-2Zr/a_0}$$

This function is zero where the term in parentheses is zero, which is at

$$r^\star = \frac{a_0}{Z}$$

Then, with $a_0 = 52.9$ pm, the radial node lies at

	H	He^+	Li^{2+}	Be^{3+}	B^{4+}	C^{5+}	N^{6+}	O^{7+}	F^{8+}	Ne^{9+}
$r^\star$/pm	52.9	26.5	17.6	13.2	10.6	8.82	7.56	6.61	5.88	5.29

Notice how the 1s orbital is drawn towards the nucleus as the nuclear charge increases. At uranium the most probable radius is only 0.58 pm, almost 100 times closer than for hydrogen. (On a scale where $r^\star = 10$ cm for H, $r^\star = 1$ mm for U.) The electron then experiences strong accelerations and relativistic effects are important.

Self-test 10.6 Find the most probable distance of a 2s electron from the nucleus in a hydrogenic atom. $[(3 + 5^{1/2})a_0/Z]$

(f) *p* Orbitals

The three 2p orbitals are distinguished by the three different values that m_l can take when $l = 1$. Because the quantum number m_l tells us the orbital angular momentum around an axis, these different values of m_l denote orbitals in which the electron has different orbital angular momenta around an arbitrary z-axis but the same magnitude of that momentum (because l is the same for all three). The orbital with $m_l = 0$, for instance, has zero angular momentum around the z-axis. Its angular variation is proportional to $\cos\theta$, so the probability density, which is proportional to $\cos^2\theta$, has its maximum value on either side of the nucleus along the z-axis (at $\theta = 0$ and 180°). The wavefunction of a 2p-orbital with $m_l = 0$ is
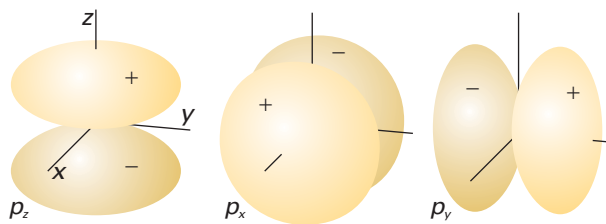
Fig. 10.15 The boundary surfaces of p orbitals. A nodal plane passes through the nucleus and separates the two lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction.

Exploration Use mathematical software to plot the boundary surfaces of the real parts of the spherical harmonics $Y_{1,m_l}(\theta,\phi)$. The resulting plots are not strictly the p orbital boundary surfaces, but sufficiently close to be reasonable representations of the shapes of hydrogenic orbitals.

$$\psi_{p_0} = R_{2,1}(r)Y_{1,0}(\theta,\phi) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta e^{-Zr/2a_0}$$

$$= r\cos\theta f(r)$$

where $f(r)$ is a function only of r. Because in spherical polar coordinates $z = r\cos\theta$, this wavefunction may also be written

$$\psi_{p_z} = zf(r) \tag{10.23}$$

All p orbitals with $m_l = 0$ have wavefunctions of this form regardless of the value of n. This way of writing the orbital is the origin of the name 'p_z orbital': its boundary surface is shown in Fig. 10.15. The wavefunction is zero everywhere in the xy-plane, where $z = 0$, so the xy-plane is a **nodal plane** of the orbital: the wavefunction changes sign on going from one side of the plane to the other.

The wavefunctions of $2p$ orbitals with $m_l = \pm 1$ have the following form:

$$\psi_{p_{\pm 1}} = R_{2,1}(r)Y_{1,\pm 1}(\theta,\phi) = \mp\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} re^{-Zr/2a_0}\sin\theta e^{\pm i\phi}$$

$$= \mp\frac{1}{2^{1/2}}r\sin\theta e^{\pm i\phi}f(r)$$

We saw in Chapter 8 that a moving particle can be described by a complex wavefunction. In the present case, the functions correspond to non-zero angular momentum about the z-axis: $e^{+i\phi}$ corresponds to clockwise rotation when viewed from below, and $e^{-i\phi}$ corresponds to counter-clockwise rotation (from the same viewpoint). They have zero amplitude where $\theta = 0$ and 180° (along the z-axis) and maximum amplitude at 90°, which is in the xy-plane. To draw the functions it is usual to represent them as standing waves. To do so, we take the real linear combinations

$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi f(r) = xf(r)$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r\sin\theta\sin\phi f(r) = yf(r) \tag{10.24}$$

These linear combinations are indeed standing waves with no net orbital angular momentum around the z-axis, as they are superpositions of states with equal and opposite values of m_l. The p_x orbital has the same shape as a p_z orbital, but it is directed

along the x-axis (see Fig. 10.15); the p_y orbital is similarly directed along the y-axis. The wavefunction of any p orbital of a given shell can be written as a product of x, y, or z and the same radial function (which depends on the value of n).

....

Justification 10.3 *The linear combination of degenerate wavefunctions*

We justify here the step of taking linear combinations of degenerate orbitals when we want to indicate a particular point. The freedom to do so rests on the fact that, whenever two or more wavefunctions correspond to the same energy, any linear combination of them is an equally valid solution of the Schrödinger equation.

Suppose ψ_1 and ψ_2 are both solutions of the Schrödinger equation with energy E; then we know that

$$H\psi_1 = E\psi_1 \qquad H\psi_2 = E\psi_2$$

Now consider the linear combination

$$\psi = c_1\psi_1 + c_2\psi_2$$

where c_1 and c_2 are arbitrary coefficients. Then it follows that

$$H\psi = H(c_1\psi_1 + c_2\psi_2) = c_1 H\psi_1 + c_2 H\psi_2 = c_1 E\psi_1 + c_2 E\psi_2 = E\psi$$

Hence, the linear combination is also a solution corresponding to the same energy E.

....

(g) *d* Orbitals

When $n = 3$, l can be 0, 1, or 2. As a result, this shell consists of one 3s orbital, three 3p orbitals, and five 3d orbitals. The five d orbitals have $m_l = +2, +1, 0, -1, -2$ and correspond to five different angular momenta around the z-axis (but the same *magnitude* of angular momentum, because $l = 2$ in each case). As for the p orbitals, d orbitals with opposite values of m_l (and hence opposite senses of motion around the z-axis) may be combined in pairs to give real standing waves, and the boundary surfaces of the resulting shapes are shown in Fig. 10.16. The real combinations have the following forms:

$$d_{xy} = xyf(r) \qquad d_{yz} = yzf(r) \qquad d_{zx} = zxf(r)$$
$$d_{x^2-y^2} = \tfrac{1}{2}(x^2 - y^2)f(r) \qquad d_{z^2} = (\tfrac{1}{2}\sqrt{3})(3z^2 - r^2)f(r) \tag{10.25}$$

Fig. 10.16 The boundary surfaces of d orbitals. Two nodal planes in each orbital intersect at the nucleus and separate the lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction.

Exploration To gain insight into the shapes of the f orbitals, use mathematical software to plot the boundary surfaces of the spherical harmonics $Y_{3,m_l}(\theta,\phi)$.
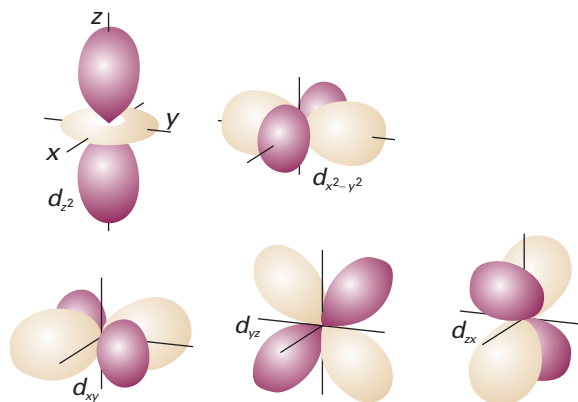
10.3 Spectroscopic transitions and selection rules

The energies of the hydrogenic atoms are given by eqn 10.11. When the electron undergoes a **transition**, a change of state, from an orbital with quantum numbers n_1, l_1, m_{l_1} to another (lower energy) orbital with quantum numbers n_2, l_2, m_{l_2}, it undergoes a change of energy ΔE and discards the excess energy as a photon of electromagnetic radiation with a frequency ν given by the Bohr frequency condition (eqn 8.10).

It is tempting to think that all possible transitions are permissible, and that a spectrum arises from the transition of an electron from any initial orbital to any other orbital. However, this is not so, because a photon has an intrinsic spin angular momentum corresponding to $s = 1$ (Section 9.8). The change in angular momentum of the electron must compensate for the angular momentum carried away by the photon. Thus, an electron in a d orbital ($l = 2$) cannot make a transition into an s orbital ($l = 0$) because the photon cannot carry away enough angular momentum. Similarly, an s electron cannot make a transition to another s orbital, because there would then be no change in the electron's angular momentum to make up for the angular momentum carried away by the photon. It follows that some spectroscopic transitions are **allowed**, meaning that they can occur, whereas others are **forbidden**, meaning that they cannot occur.

A **selection rule** is a statement about which transitions are allowed. They are derived (for atoms) by identifying the transitions that conserve angular momentum when a photon is emitted or absorbed. The selection rules for hydrogenic atoms are

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1 \tag{10.26}$$

The principal quantum number n can change by any amount consistent with the Δl for the transition, because it does not relate directly to the angular momentum.

....

Justification 10.4 *The identification of selection rules*

We saw in Section 9.10 that the rate of transition between two states is proportional to the square of the transition dipole moment, $\boldsymbol{\mu}_{\text{fi}}$, between the initial and final states, where (using the notation introduced in *Further information 9.1*)

$$\boldsymbol{\mu}_{\text{fi}} = \langle \text{f} | \boldsymbol{\mu} | \text{i} \rangle \tag{10.27}$$

and $\boldsymbol{\mu}$ is the electric dipole moment operator. For a one-electron atom $\boldsymbol{\mu}$ is multiplication by $-e\boldsymbol{r}$ with components $\mu_x = -ex$, $\mu_y = -ey$, and $\mu_z = -ez$. If the transition dipole moment is zero, the transition is forbidden; the transition is allowed if the transition moment is non-zero. Physically, the transition dipole moment is a measure of the dipolar 'kick' that the electron gives to or receives from the electromagnetic field.

To evaluate a transition dipole moment, we consider each component in turn. For example, for the z-component,

$$\mu_{z,\text{fi}} = -e\langle \text{f} | z | \text{i} \rangle = -e \int \psi_{\text{f}}^* z \psi_{\text{i}} \, d\tau \tag{10.28}$$

To evaluate the integral, we note from Table 9.3 that $z = (4\pi/3)^{1/2} r Y_{1,0}$, so

$$\int \psi_{\text{f}}^* z \psi_{\text{i}} d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} \overbrace{R_{n_{\text{f}},l_{\text{f}}} Y_{l_{\text{f}},m_{l,\text{f}}}^*}^{\psi_{\text{f}}} \overbrace{\left(\frac{4\pi}{3}\right)^{1/2} r Y_{1,0}}^{z} \overbrace{R_{n_{\text{i}},l_{\text{i}}} Y_{l_{\text{i}},m_{l,\text{i}}}}^{\psi_{\text{i}}} \overbrace{r^2 dr \sin\theta d\theta d\phi}^{d\tau}$$

This multiple integral is the product of three factors, an integral over r and two integrals over the angles, so the factors on the right can be grouped as follows:

$$\int \psi_{\text{f}}^* z \psi_{\text{i}} d\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty R_{n_{\text{f}},l_{\text{f}}} r R_{n_{\text{i}},l_{\text{i}}} r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l_{\text{f}},m_{l,\text{f}}}^* Y_{1,0} Y_{l_{\text{i}},m_{l,\text{i}}} \sin\theta d\theta d\phi$$
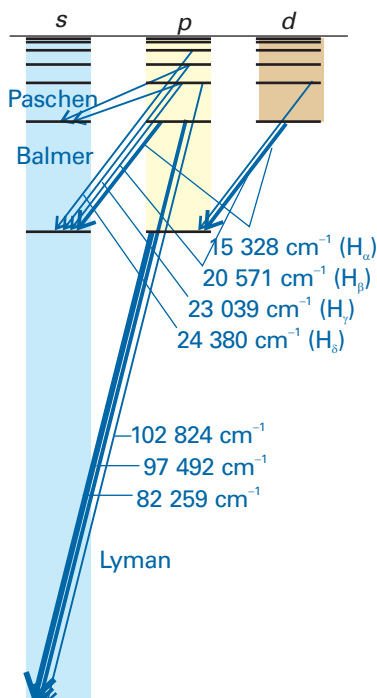
Fig. 10.17 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition.

It follows from the properties of the spherical harmonics (Comment 9.6) that the integral

$$\int_0^\pi \int_0^{2\pi} Y^\star_{l_f, m_{l_f}} Y_{1,m} Y_{l_i, m_{l_i}} \sin\theta \, d\theta d\phi$$

is zero unless $l_f = l_i \pm 1$ and $m_{l,f} = m_{l,i} + m$. Because $m = 0$ in the present case, the angular integral, and hence the z-component of the transition dipole moment, is zero unless $\Delta l = \pm 1$ and $\Delta m_l = 0$, which is a part of the set of selection rules. The same procedure, but considering the x- and y-components, results in the complete set of rules.

Illustration 10.2 *Applying selection rules*

To identify the orbitals to which a $4d$ electron may make radiative transitions, we first identify the value of l and then apply the selection rule for this quantum number. Because $l = 2$, the final orbital must have $l = 1$ or 3. Thus, an electron may make a transition from a $4d$ orbital to any np orbital (subject to $\Delta m_l = 0, \pm 1$) and to any nf orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any ns orbital or to another nd orbital is forbidden.

Self-test 10.7 To what orbitals may a $4s$ electron make electric-dipole allowed radiative transitions?   [to np orbitals only]

The selection rules and the atomic energy levels jointly account for the structure of a **Grotrian diagram** (Fig. 10.17), which summarizes the energies of the states and the transitions between them. The thicknesses of the transition lines in the diagram denote their relative intensities in the spectrum; we see how to determine transition intensities in Section 13.2.

The structures of many-electron atoms

The Schrödinger equation for a many-electron atom is highly complicated because all the electrons interact with one another. Even for a helium atom, with its two electrons, no analytical expression for the orbitals and energies can be given, and we are forced to make approximations. We shall adopt a simple approach based on what we already know about the structure of hydrogenic atoms. Later we shall see the kind of numerical computations that are currently used to obtain accurate wavefunctions and energies.

10.4 The orbital approximation

The wavefunction of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it $\psi(r_1, r_2, \dots)$, where r_i is the vector from the nucleus to electron i. However, in the **orbital approximation** we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its 'own' orbital, and write

$$\psi(r_1, r_2, \dots) = \psi(r_1)\psi(r_2) \dots \tag{10.29}$$

We can think of the individual orbitals as resembling the hydrogenic orbitals, but corresponding to nuclear charges modified by the presence of all the other electrons in the atom. This description is only approximate, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

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Justification 10.5 *The orbital approximation*

The orbital approximation would be exact if there were no interactions between electrons. To demonstrate the validity of this remark, we need to consider a system in which the hamiltonian for the energy is the sum of two contributions, one for electron 1 and the other for electron 2:

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

In an actual atom (such as helium atom), there is an additional term corresponding to the interaction of the two electrons, but we are ignoring that term. We shall now show that if $\psi(r_1)$ is an eigenfunction of $\hat{H}_1$ with energy E_1, and $\psi(r_2)$ is an eigenfunction of $\hat{H}_2$ with energy E_2, then the product $\psi(r_1,r_2) = \psi(r_1)\psi(r_2)$ is an eigenfunction of the combined hamiltonian $\hat{H}$. To do so we write

$$\hat{H}\psi(r_1,r_2) = (\hat{H}_1 + \hat{H}_2)\psi(r_1)\psi(r_2) = \hat{H}_1\psi(r_1)\psi(r_2) + \psi(r_1)\hat{H}_2\psi(r_2)$$
$$= E_1\psi(r_1)\psi(r_2) + \psi(r_1)E_2\psi(r_2) = (E_1 + E_2)\psi(r_1)\psi(r_2)$$
$$= E\psi(r_1,r_2)$$

where $E = E_1 + E_2$. This is the result we need to prove. However, if the electrons interact (as they do in fact), then the proof fails.

....

(a) The helium atom

The orbital approximation allows us to express the electronic structure of an atom by reporting its **configuration**, the list of occupied orbitals (usually, but not necessarily, in its ground state). Thus, as the ground state of a hydrogenic atom consists of the single electron in a $1s$ orbital, we report its configuration as $1s^1$.

The He atom has two electrons. We can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a $1s$ hydrogenic orbital, but because $Z = 2$ that orbital is more compact than in H itself. The second electron joins the first in the $1s$ orbital, so the electron configuration of the ground state of He is $1s^2$.

(b) The Pauli principle

Lithium, with $Z = 3$, has three electrons. The first two occupy a $1s$ orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the $1s$ orbital because that configuration is forbidden by the **Pauli exclusion principle**:

No more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired.

Electrons with paired spins, denoted ↑↓, have zero net spin angular momentum because the spin of one electron is cancelled by the spin of the other. Specifically, one electron has $m_s = +\frac{1}{2}$, the other has $m_s = -\frac{1}{2}$ and they are orientated on their respective cones so that the resultant spin is zero (Fig. 10.18). The exclusion principle is the key to the structure of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by Wolfgang Pauli in 1924 when he was trying to account for the

$m_s = +\frac{1}{2}$

$m_s = -\frac{1}{2}$
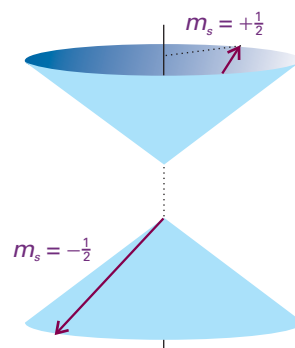
Fig. 10.18 Electrons with paired spins have zero resultant spin angular momentum. They can be represented by two vectors that lie at an indeterminate position on the cones shown here, but wherever one lies on its cone, the other points in the opposite direction; their resultant is zero.

absence of some lines in the spectrum of helium. Later he was able to derive a very general form of the principle from theoretical considerations.

The Pauli exclusion principle in fact applies to any pair of identical fermions (particles with half integral spin). Thus it applies to protons, neutrons, and ^{13}C nuclei (all of which have spin $\frac{1}{2}$) and to ^{35}Cl nuclei (which have spin $\frac{3}{2}$). It does not apply to identical bosons (particles with integral spin), which include photons (spin 1), ^{12}C nuclei (spin 0). Any number of identical bosons may occupy the same state (that is, be described by the same wavefunction).

The Pauli exclusion principle is a special case of a general statement called the **Pauli principle**:

> When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

By 'total wavefunction' is meant the entire wavefunction, including the spin of the particles. To see that the Pauli principle implies the Pauli exclusion principle, we consider the wavefunction for two electrons $\psi(1,2)$. The Pauli principle implies that it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function:

$$\psi(2,1) = -\psi(1,2) \tag{10.30}$$

Suppose the two electrons in an atom occupy an orbital ψ, then in the orbital approximation the overall wavefunction is $\psi(1)\psi(2)$. To apply the Pauli principle, we must deal with the total wavefunction, the wavefunction including spin. There are several possibilities for two spins: both α, denoted $\alpha(1)\alpha(2)$, both β, denoted $\beta(1)\beta(2)$, and one α the other β, denoted either $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$. Because we cannot tell which electron is α and which is β, in the last case it is appropriate to express the spin states as the (normalized) linear combinations

$$\sigma_+(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$
$$\sigma_-(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{10.31}$$

Comment 10.3

A stronger justification for taking linear combinations in eqn 10.31 is that they correspond to eigenfunctions of the total spin operators S^2 and S_z, with $M_S = 0$ and, respectively, $S = 1$ and 0. See Section 10.7.

because these combinations allow one spin to be α and the other β with equal probability. The total wavefunction of the system is therefore the product of the orbital part and one of the four spin states:

$$\psi(1)\psi(2)\alpha(1)\alpha(2) \quad \psi(1)\psi(2)\beta(1)\beta(2) \quad \psi(1)\psi(2)\sigma_+(1,2) \quad \psi(1)\psi(2)\sigma_-(1,2)$$

The Pauli principle says that for a wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of the product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = (1/2^{1/2})\{\alpha(2)\beta(1) + \beta(2)\alpha(1)\} = \sigma_+(1,2)$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$:

$$\sigma_-(2,1) = (1/2^{1/2})\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\}$$
$$= -(1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} = -\sigma_-(1,2)$$

This combination does change sign (it is 'antisymmetric'). The product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has paired α and β spins. This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the electrons are different, and both electrons may then have (but need not have) the same spin state. Nevertheless, even then the overall wavefunction must still be antisymmetric overall, and must still satisfy the Pauli principle itself.

A final point in this connection is that the acceptable product wavefunction $\psi(1)\psi(2)\sigma_-(1,2)$ can be expressed as a determinant:

$$\frac{1}{2^{1/2}}\begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix} = \frac{1}{2^{1/2}}\{\psi(1)\alpha(1)\psi(2)\beta(2) - \psi(2)\alpha(2)\psi(1)\beta(1)\}$$

$$= \psi(1)\psi(2)\sigma_-(1,2)$$

Any acceptable wavefunction for a closed-shell species can be expressed as a **Slater determinant**, as such determinants are known. In general, for N electrons in orbitals $\psi_a, \psi_b, \ldots$

$$\psi(1,2,\ldots,N) = \frac{1}{(N!)^{1/2}}\begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \ldots & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & \ldots & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_b(2)\alpha(2) & \psi_b(3)\alpha(3) & \ldots & \psi_b(N)\alpha(N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \ldots & \psi_z(N)\beta(N) \end{vmatrix}$$

[10.32]

Writing a many-electron wavefunction in this way ensures that it is antisymmetric under the interchange of any pair of electrons, as is explored in Problem 10.23.

Now we can return to lithium. In Li ($Z = 3$), the third electron cannot enter the $1s$ orbital because that orbital is already full: we say the K shell is *complete* and that the two electrons form a **closed shell**. Because a similar closed shell is characteristic of the He atom, we denote it [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is one with $n = 2$ and hence belonging to the L shell. However, we now have to decide whether the next available orbital is the $2s$ orbital or a $2p$ orbital, and therefore whether the lowest energy configuration of the atom is $[He]2s^1$ or $[He]2p^1$.

(c) Penetration and shielding

Unlike in hydrogenic atoms, the $2s$ and $2p$ orbitals (and, in general, all subshells of a given shell) are not degenerate in many-electron atoms. As will be familiar from introductory chemistry, an electron in a many-electron atom experiences a Coulombic repulsion from all the other electrons present. If it is at a distance r from the nucleus, it experiences an average repulsion that can be represented by a point negative charge located at the nucleus and equal in magnitude to the total charge of the electrons within a sphere of radius r (Fig. 10.19). The effect of this point negative charge, when averaged over all the locations of the electron, is to reduce the full charge of the nucleus from Ze to $Z_{eff}e$, the **effective nuclear charge**. In everyday parlance, Z_{eff} itself is commonly referred to as the 'effective nuclear charge'. We say that the electron experiences a **shielded** nuclear charge, and the difference between Z and Z_{eff} is called the **shielding constant**, σ:

$$Z_{eff} = Z - \sigma \qquad [10.33]$$

The electrons do not actually 'block' the full Coulombic attraction of the nucleus: the shielding constant is simply a way of expressing the net outcome of the nuclear
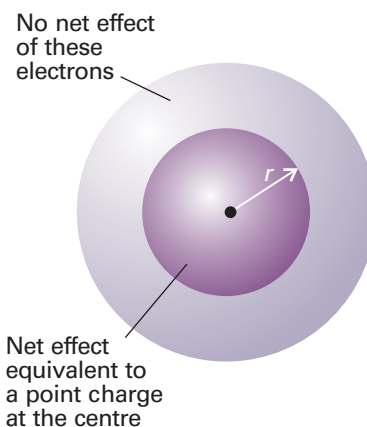
Fig. 10.19 An electron at a distance r from the nucleus experiences a Coulombic repulsion from all the electrons within a sphere of radius r and which is equivalent to a point negative charge located on the nucleus. The negative charge reduces the effective nuclear charge of the nucleus from Ze to $Z_{eff}e$.
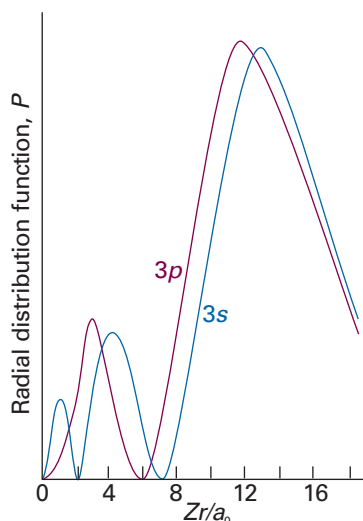
Fig. 10.20 An electron in an *s* orbital (here a 3*s* orbital) is more likely to be found close to the nucleus than an electron in a *p* orbital of the same shell (note the closeness of the innermost peak of the 3*s* orbital to the nucleus at $r = 0$). Hence an *s* electron experiences less shielding and is more tightly bound than a *p* electron.

Exploration Calculate and plot the graphs given above for $n = 4$.

Synoptic table 10.2* Effective nuclear charge, $Z_{eff} = Z - \sigma$

Element	Z	Orbital	Z_{eff}
He	2	1*s*	1.6875
C	6	1*s*	5.6727
		2*s*	3.2166
		2*p*	3.1358

* More values are given in the *Data section*.

attraction and the electronic repulsions in terms of a single equivalent charge at the centre of the atom.

The shielding constant is different for *s* and *p* electrons because they have different radial distributions (Fig. 10.20). An *s* electron has a greater **penetration** through inner shells than a *p* electron, in the sense that it is more likely to be found close to the nucleus than a *p* electron of the same shell (the wavefunction of a *p* orbital, remember, is zero at the nucleus). Because only electrons inside the sphere defined by the location of the electron (in effect, the core electrons) contribute to shielding, an *s* electron experiences less shielding than a *p* electron. Consequently, by the combined effects of penetration and shielding, an *s* electron is more tightly bound than a *p* electron of the same shell. Similarly, a *d* electron penetrates less than a *p* electron of the same shell (recall that the wavefunction of a *d* orbital varies as r^2 close to the nucleus, whereas a *p* orbital varies as r), and therefore experiences more shielding.

Shielding constants for different types of electrons in atoms have been calculated from their wavefunctions obtained by numerical solution of the Schrödinger equation for the atom (Table 10.2). We see that, in general, valence-shell *s* electrons do experience higher effective nuclear charges than *p* electrons, although there are some discrepancies. We return to this point shortly.

The consequence of penetration and shielding is that the energies of subshells of a shell in a many-electron atom in general lie in the order

$$s < p < d < f$$

The individual orbitals of a given subshell remain degenerate because they all have the same radial characteristics and so experience the same effective nuclear charge.

We can now complete the Li story. Because the shell with $n = 2$ consists of two non-degenerate subshells, with the 2*s* orbital lower in energy than the three 2*p* orbitals, the third electron occupies the 2*s* orbital. This occupation results in the ground-state configuration $1s^2 2s^1$, with the central nucleus surrounded by a complete helium-like shell of two 1*s* electrons, and around that a more diffuse 2*s* electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** because they are largely responsible for the chemical bonds that the atom forms. Thus, the valence electron in Li is a 2*s* electron and its other two electrons belong to its core.

(d) The building-up principle

The extension of this argument is called the **building-up principle**, or the *Aufbau principle*, from the German word for building up, which will be familiar from introductory courses. In brief, we imagine the bare nucleus of atomic number Z, and then feed into the orbitals Z electrons in succession. The order of occupation is

$$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d \quad 4p \quad 5s \quad 4d \quad 5p \quad 6s$$

and each orbital may accommodate up to two electrons. As an example, consider the carbon atom, for which $Z = 6$ and there are six electrons to accommodate. Two electrons enter and fill the 1*s* orbital, two enter and fill the 2*s* orbital, leaving two electrons to occupy the orbitals of the 2*p* subshell. Hence the ground-state configuration of C is $1s^2 2s^2 2p^2$, or more succinctly $[He]2s^2 2p^2$, with $[He]$ the helium-like $1s^2$ core. However, we can be more precise: we can expect the last two electrons to occupy different 2*p* orbitals because they will then be further apart on average and repel each other less than if they were in the same orbital. Thus, one electron can be thought of as occupying the $2p_x$ orbital and the other the $2p_y$ orbital (the *x*, *y*, *z* designation is arbitrary, and it would be equally valid to use the complex forms of these orbitals), and the lowest energy configuration of the atom is $[He]2s^2 2p_x^1 2p_y^1$. The same rule

applies whenever degenerate orbitals of a subshell are available for occupation. Thus, another rule of the building-up principle is:

Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

For instance, nitrogen ($Z = 7$) has the configuration [He]$2s^2 2p_x^1 2p_y^1 2p_z^1$, and only when we get to oxygen ($Z = 8$) is a $2p$ orbital doubly occupied, giving [He]$2s^2 2p_x^2 2p_y^1 2p_z^1$. When electrons occupy orbitals singly we invoke **Hund's maximum multiplicity rule**:

An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.

The explanation of Hund's rule is subtle, but it reflects the quantum mechanical property of **spin correlation**, that electrons with parallel spins behave as if they have a tendency to stay well apart, and hence repel each other less. In essence, the effect of spin correlation is to allow the atom to shrink slightly, so the electron–nucleus interaction is improved when the spins are parallel. We can now conclude that, in the ground state of the carbon atom, the two $2p$ electrons have the same spin, that all three $2p$ electrons in the N atoms have the same spin, and that the two $2p$ electrons in different orbitals in the O atom have the same spin (the two in the $2p_x$ orbital are necessarily paired).

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Justification 10.6 *Spin correlation*

Suppose electron 1 is described by a wavefunction $\psi_a(r_1)$ and electron 2 is described by a wavefunction $\psi_b(r_2)$; then, in the orbital approximation, the joint wavefunction of the electrons is the product $\psi = \psi_a(r_1)\psi_b(r_2)$. However, this wavefunction is not acceptable, because it suggests that we know which electron is in which orbital, whereas we cannot keep track of electrons. According to quantum mechanics, the correct description is either of the two following wavefunctions:

$$\psi_\pm = (1/2^{1/2})\{\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)\}$$

According to the Pauli principle, because ψ_+ is symmetrical under particle interchange, it must be multiplied by an antisymmetric spin function (the one denoted σ_-). That combination corresponds to a spin-paired state. Conversely, ψ_- is antisymmetric, so it must be multiplied by one of the three symmetric spin states. These three symmetric states correspond to electrons with parallel spins (see Section 10.7 for an explanation).

Now consider the values of the two combinations when one electron approaches another, and $r_1 = r_2$. We see that ψ_- vanishes, which means that there is zero probability of finding the two electrons at the same point in space when they have parallel spins. The other combination does not vanish when the two electrons are at the same point in space. Because the two electrons have different relative spatial distributions depending on whether their spins are parallel or not, it follows that their Coulombic interaction is different, and hence that the two states have different energies.

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Neon, with $Z = 10$, has the configuration [He]$2s^2 2p^6$, which completes the L shell. This closed-shell configuration is denoted [Ne], and acts as a core for subsequent elements. The next electron must enter the $3s$ orbital and begin a new shell, so an Na atom, with $Z = 11$, has the configuration [Ne]$3s^1$. Like lithium with the configuration [He]$2s^1$, sodium has a single s electron outside a complete core. This analysis has brought us to the origin of chemical periodicity. The L shell is completed by eight electrons, so the element with $Z = 3$ (Li) should have similar properties to the element with $Z = 11$ (Na). Likewise, Be ($Z = 4$) should be similar to $Z = 12$ (Mg), and so on, up to the noble gases He ($Z = 2$), Ne ($Z = 10$), and Ar ($Z = 18$).
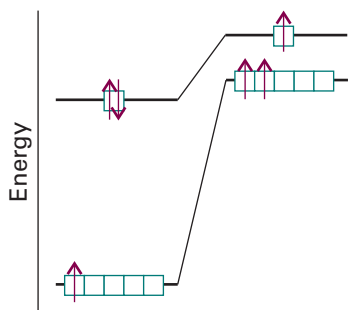
Fig. 10.21 Strong electron–electron repulsions in the $3d$ orbitals are minimized in the ground state of Sc if the atom has the configuration $[Ar]3d^14s^2$ (shown on the left) instead of $[Ar]3d^24s^1$ (shown on the right). The total energy of the atom is lower when it has the $[Ar]3d^14s^2$ configuration despite the cost of populating the high energy $4s$ orbital.

Comment 10.4

The web site for this text contains links to databases of atomic properties.

Ten electrons can be accommodated in the five $3d$ orbitals, which accounts for the electron configurations of scandium to zinc. Calculations of the type discussed in Section 10.5 show that for these atoms the energies of the $3d$ orbitals are always lower than the energy of the $4s$ orbital. However, spectroscopic results show that Sc has the configuration $[Ar]3d^14s^2$, instead of $[Ar]3d^3$ or $[Ar]3d^24s^1$. To understand this observation, we have to consider the nature of electron–electron repulsions in $3d$ and $4s$ orbitals. The most probable distance of a $3d$ electron from the nucleus is less than that for a $4s$ electron, so two $3d$ electrons repel each other more strongly than two $4s$ electrons. As a result, Sc has the configuration $[Ar]3d^14s^2$ rather than the two alternatives, for then the strong electron–electron repulsions in the $3d$ orbitals are minimized. The total energy of the atom is least despite the cost of allowing electrons to populate the high energy $4s$ orbital (Fig. 10.21). The effect just described is generally true for scandium through zinc, so their electron configurations are of the form $[Ar]3d^n4s^2$, where $n = 1$ for scandium and $n = 10$ for zinc. Two notable exceptions, which are observed experimentally, are Cr, with electron configuration $[Ar]3d^54s^1$, and Cu, with electron configuration $[Ar]3d^{10}4s^1$ (see *Further reading* for a discussion of the theoretical basis for these exceptions).

At gallium, the building-up principle is used in the same way as in preceding periods. Now the $4s$ and $4p$ subshells constitute the valence shell, and the period terminates with krypton. Because 18 electrons have intervened since argon, this period is the first 'long period' of the periodic table. The existence of the d-block elements (the 'transition metals') reflects the stepwise occupation of the $3d$ orbitals, and the subtle shades of energy differences and effects of electron–electron repulsion along this series gives rise to the rich complexity of inorganic d-metal chemistry. A similar intrusion of the f orbitals in Periods 6 and 7 accounts for the existence of the f block of the periodic table (the lanthanoids and actinoids).

We derive the configurations of cations of elements in the s, p, and d blocks of the periodic table by removing electrons from the ground-state configuration of the neutral atom in a specific order. First, we remove valence p electrons, then valence s electrons, and then as many d electrons as are necessary to achieve the specified charge. For instance, because the configuration of V is $[Ar]3d^34s^2$, the V^{2+} cation has the configuration $[Ar]3d^3$. It is reasonable that we remove the more energetic $4s$ electrons in order to form the cation, but it is not obvious why the $[Ar]3d^3$ configuration is preferred in V^{2+} over the $[Ar]3d^14s^2$ configuration, which is found in the isoelectronic Sc atom. Calculations show that the energy difference between $[Ar]3d^3$ and $[Ar]3d^14s^2$ depends on Z_{eff}. As Z_{eff} increases, transfer of a $4s$ electron to a $3d$ orbital becomes more favourable because the electron–electron repulsions are compensated by attractive interactions between the nucleus and the electrons in the spatially compact $3d$ orbital. Indeed, calculations reveal that, for a sufficiently large Z_{eff}, $[Ar]3d^3$ is lower in energy than $[Ar]3d^14s^2$. This conclusion explains why V^{2+} has a $[Ar]3d^3$ configuration and also accounts for the observed $[Ar]4s^03d^n$ configurations of the M^{2+} cations of Sc through Zn.

The configurations of anions of the p-block elements are derived by continuing the building-up procedure and adding electrons to the neutral atom until the configuration of the next noble gas has been reached. Thus, the configuration of the O^{2-} ion is achieved by adding two electrons to $[He]2s^22p^4$, giving $[He]2s^22p^6$, the same as the configuration of neon.

(e) Ionization energies and electron affinities

The minimum energy necessary to remove an electron from a many-electron atom in the gas phase is the **first ionization energy**, I_1, of the element. The **second ionization energy**, I_2, is the minimum energy needed to remove a second electron (from the
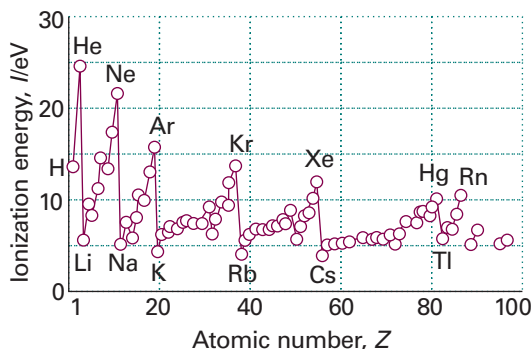
Fig. 10.22 The first ionization energies of the elements plotted against atomic number.

singly charged cation). The variation of the first ionization energy through the periodic table is shown in Fig. 10.22 and some numerical values are given in Table 10.3. In thermodynamic calculations we often need the **standard enthalpy of ionization**, $\Delta_{ion}H^{\ominus}$. As shown in the *Justification* below, the two are related by

$$\Delta_{ion}H^{\ominus}(T) = I + \tfrac{5}{2}RT \tag{10.34}$$

At 298 K, the difference between the ionization enthalpy and the corresponding ionization energy is 6.20 kJ mol^{-1}.

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Justification 10.7 *The ionization enthalpy and the ionization energy*

It follows from Kirchhoff's law (Section 2.9 and eqn 2.36) that the reaction enthalpy for

$$M(g) \rightarrow M^{+}(g) + e^{-}(g)$$
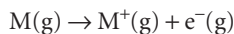
at a temperature T is related to the value at $T = 0$ by

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(0) + \int_0^T \Delta_r C_p^{\ominus} dT$$

The molar constant-pressure heat capacity of each species in the reaction is $\tfrac{5}{2}R$, so $\Delta_r C_p^{\ominus} = +\tfrac{5}{2}R$. The integral in this expression therefore evaluates to $+\tfrac{5}{2}RT$. The reaction enthalpy at $T = 0$ is the same as the (molar) ionization energy, I. Equation 10.33 then follows. The same expression applies to each successive ionization step, so the overall ionization enthalpy for the formation of M^{2+} is

$$\Delta_r H^{\ominus}(T) = I_1 + I_2 + 5RT$$

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The **electron affinity**, E_{ea}, is the energy released when an electron attaches to a gas-phase atom (Table 10.4). In a common, logical, but not universal convention (which we adopt), the electron affinity is positive if energy is released when the electron attaches to the atom (that is, $E_{ea} > 0$ implies that electron attachment is exothermic). It follows from a similar argument to that given in the *Justification* above that the **standard enthalpy of electron gain**, $\Delta_{eg}H^{\ominus}$, at a temperature T is related to the electron affinity by

$$\Delta_{eg}H^{\ominus}(T) = -E_{ea} - \tfrac{5}{2}RT \tag{10.35}$$

Note the change of sign. In typical thermodynamic cycles the $\tfrac{5}{2}RT$ that appears in eqn 10.35 cancels that in eqn 10.34, so ionization energies and electron affinities can be used directly. A final preliminary point is that the electron-gain enthalpy of a species X is the negative of the ionization enthalpy of its negative ion:

$$\Delta_{eg}H^{\ominus}(X) = -\Delta_{ion}H^{\ominus}(X^{-}) \tag{10.36}$$

Synoptic table 10.3* First and second ionization energies

Element	$I_1/$(kJ mol^{-1})	$I_2/$(kJ mol^{-1})
H	1312	
He	2372	5251
Mg	738	1451
Na	496	4562

* More values are given in the *Data section*.

Synoptic table 10.4* Electron affinities, $E_a/$(kJ mol^{-1})

Cl	349		
F	322		
H	73		
O	141	O^{-}	−844

* More values are given in the *Data section*.

As ionization energy is often easier to measure than electron affinity, this relation can be used to determine numerical values of the latter.

As will be familiar from introductory chemistry, ionization energies and electron affinities show periodicities. The former is more regular and we concentrate on it. Lithium has a low first ionization energy because its outermost electron is well shielded from the nucleus by the core ($Z_{eff} = 1.3$, compared with $Z = 3$). The ionization energy of beryllium ($Z = 4$) is greater but that of boron is lower because in the latter the outermost electron occupies a $2p$ orbital and is less strongly bound than if it had been a $2s$ electron. The ionization energy increases from boron to nitrogen on account of the increasing nuclear charge. However, the ionization energy of oxygen is less than would be expected by simple extrapolation. The explanation is that at oxygen a $2p$ orbital must become doubly occupied, and the electron–electron repulsions are increased above what would be expected by simple extrapolation along the row. In addition, the loss of a $2p$ electron results in a configuration with a half-filled subshell (like that of N), which is an arrangement of low energy, so the energy of $O^+ + e^-$ is lower than might be expected, and the ionization energy is correspondingly low too. (The kink is less pronounced in the next row, between phosphorus and sulfur because their orbitals are more diffuse.) The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the more highly charged nuclei for the outermost electrons.

The outermost electron in sodium is $3s$. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core. As a result, the ionization energy of sodium is substantially lower than that of neon. The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

Electron affinities are greatest close to fluorine, for the incoming electron enters a vacancy in a compact valence shell and can interact strongly with the nucleus. The attachment of an electron to an anion (as in the formation of O^{2-} from O^-) is invariably endothermic, so E_{ea} is negative. The incoming electron is repelled by the charge already present. Electron affinities are also small, and may be negative, when an electron enters an orbital that is far from the nucleus (as in the heavier alkali metal atoms) or is forced by the Pauli principle to occupy a new shell (as in the noble gas atoms).

10.5 **Self-consistent field orbitals**

The central difficulty of the Schrödinger equation is the presence of the electron–electron interaction terms. The potential energy of the electrons is

$$V = -\sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{10.37}$$

The prime on the second sum indicates that $i \neq j$, and the factor of one-half prevents double-counting of electron pair repulsions (1 with 2 is the same as 2 with 1). The first term is the total attractive interaction between the electrons and the nucleus. The second term is the total repulsive interaction between the electrons; r_{ij} is the distance between electrons i and j. It is hopeless to expect to find analytical solutions of a Schrödinger equation with such a complicated potential energy term, but computational techniques are available that give very detailed and reliable numerical solutions for the wavefunctions and energies. The techniques were originally introduced by D.R. Hartree (before computers were available) and then modified by V. Fock to take into account the Pauli principle correctly. In broad outline, the **Hartree–Fock self-consistent field** (HF-SCF) procedure is as follows.

Imagine that we have a rough idea of the structure of the atom. In the Ne atom, for instance, the orbital approximation suggests the configuration $1s^2 2s^2 2p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now consider one of the $2p$ electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. This equation has the form

$$H(1)\psi_{2p}(1) + V(\text{other electrons})\psi_{2p}(1)$$
$$- V(\text{exchange correction})\psi_{2p}(1) = E_{2p}\psi_{2p}(1) \tag{10.38}$$

A similar equation can be written for the $1s$ and $2s$ orbitals in the atom. The various terms are as follows:

1 The first term on the left is the contribution of the kinetic energy and the attraction of the electron to the nucleus, just as in a hydrogenic atom.

2 The second takes into account the potential energy of the electron of interest due to the electrons in the other occupied orbitals.

3 The third term takes into account the spin correlation effects discussed earlier.

Although the equation is for the $2p$ orbital in neon, it depends on the wavefunctions of all the other occupied orbitals in the atom.

There is no hope of solving eqn 10.38 analytically. However, it can be solved numerically if we guess an approximate form of the wavefunctions of all the orbitals except $2p$. The procedure is then repeated for the other orbitals in the atom, the $1s$ and $2s$ orbitals. This sequence of calculations gives the form of the $2p$, $2s$, and $1s$ orbitals, and in general they will differ from the set used initially to start the calculation. These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals is obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the current cycle. The solutions are then self-consistent and accepted as solutions of the problem.

Figure 10.23 shows plots of some of the HF-SCF radial distribution functions for sodium. They show the grouping of electron density into shells, as was anticipated by the early chemists, and the differences of penetration as discussed above. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity. They also considerably extend that discussion by providing detailed wavefunctions and precise energies.
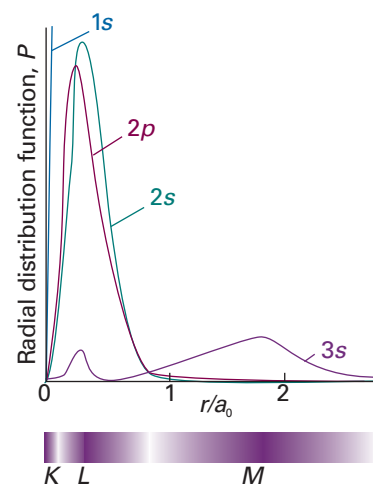
Fig. 10.23 The radial distribution functions for the orbitals of Na based on SCF calculations. Note the shell-like structure, with the $3s$ orbital outside the inner K and L shells.

The spectra of complex atoms

The spectra of atoms rapidly become very complicated as the number of electrons increases, but there are some important and moderately simple features that make atomic spectroscopy useful in the study of the composition of samples as large and as complex as stars (*Impact I10.1*). The general idea is straightforward: lines in the spectrum (in either emission or absorption) occur when the atom undergoes a transition with a change of energy $|\Delta E|$, and emits or absorbs a photon of frequency $\nu = |\Delta E|/h$ and $\tilde{\nu} = |\Delta E|/hc$. Hence, we can expect the spectrum to give information about the energies of electrons in atoms. However, the actual energy levels are not given solely by the energies of the orbitals, because the electrons interact with one another in various ways, and there are contributions to the energy in addition to those we have already considered.

Comment 10.5

The web site for this text contains links to databases of atomic spectra.

IMPACT ON ASTROPHYSICS
I10.1 Spectroscopy of stars

The bulk of stellar material consists of neutral and ionized forms of hydrogen and helium atoms, with helium being the product of 'hydrogen burning' by nuclear fusion. However, nuclear fusion also makes heavier elements. It is generally accepted that the outer layers of stars are composed of lighter elements, such as H, He, C, N, O, and Ne in both neutral and ionized forms. Heavier elements, including neutral and ionized forms of Si, Mg, Ca, S, and Ar, are found closer to the stellar core. The core itself contains the heaviest elements and ^{56}Fe is particularly abundant because it is a very stable nuclide. All these elements are in the gas phase on account of the very high temperatures in stellar interiors. For example, the temperature is estimated to be 3.6 MK half way to the centre of the Sun.

Astronomers use spectroscopic techniques to determine the chemical composition of stars because each element, and indeed each isotope of an element, has a characteristic spectral signature that is transmitted through space by the star's light. To understand the spectra of stars, we must first know why they shine. Nuclear reactions in the dense stellar interior generate radiation that travels to less dense outer layers. Absorption and re-emission of photons by the atoms and ions in the interior give rise to a quasi-continuum of radiation energy that is emitted into space by a thin layer of gas called the *photosphere*. To a good approximation, the distribution of energy emitted from a star's photosphere resembles the Planck distribution for a very hot black body (Section 8.1). For example, the energy distribution of our Sun's photosphere may be modelled by a Planck distribution with an effective temperature of 5.8 kK. Superimposed on the black-body radiation continuum are sharp absorption and emission lines from neutral atoms and ions present in the photosphere. Analysis of stellar radiation with a spectrometer mounted on to a telescope yields the chemical composition of the star's photosphere by comparison with known spectra of the elements. The data can also reveal the presence of small molecules, such as CN, C_2, TiO, and ZrO, in certain 'cold' stars, which are stars with relatively low effective temperatures.

The two outermost layers of a star are the *chromosphere*, a region just above the photosphere, and the *corona*, a region above the chromosphere that can be seen (with proper care) during eclipses. The photosphere, chromosphere, and corona comprise a star's 'atmosphere'. Our Sun's chromosphere is much less dense than its photosphere and its temperature is much higher, rising to about 10 kK. The reasons for this increase in temperature are not fully understood. The temperature of our Sun's corona is very high, rising up to 1.5 MK, so black-body emission is strong from the X-ray to the radio-frequency region of the spectrum. The spectrum of the Sun's corona is dominated by emission lines from electronically excited species, such as neutral atoms and a number of highly ionized species . The most intense emission lines in the visible range are from the Fe^{13+} ion at 530.3 nm, the Fe^{9+} ion at 637.4 nm, and the Ca^{4+} ion at 569.4 nm.

Because only light from the photosphere reaches our telescopes, the overall chemical composition of a star must be inferred from theoretical work on its interior and from spectral analysis of its atmosphere. Data on the Sun indicate that it is 92 per cent hydrogen and 7.8 per cent helium. The remaining 0.2 per cent is due to heavier elements, among which C, N, O, Ne, and Fe are the most abundant. More advanced analysis of spectra also permit the determination of other properties of stars, such as their relative speeds (Problem 10.27) and their effective temperatures (Problem 13.29).

10.6 Quantum defects and ionization limits

One application of atomic spectroscopy is to the determination of ionization energies. However, we cannot use the procedure illustrated in Example 10.1 indiscriminately

because the energy levels of a many-electron atom do not in general vary as $1/n^2$. If we confine attention to the outermost electrons, then we know that, as a result of penetration and shielding, they experience a nuclear charge of slightly more than $1e$ because in a neutral atom the other $Z - 1$ electrons cancel all but about one unit of nuclear charge. Typical values of Z_{eff} are a little more than 1, so we expect binding energies to be given by a term of the form $-hcR/n^2$, but lying slightly lower in energy than this formula predicts. We therefore introduce a **quantum defect**, δ, and write the energy as $-hcR/(n - \delta)^2$. The quantum defect is best regarded as a purely empirical quantity.

There are some excited states that are so diffuse that the $1/n^2$ variation is valid: these states are called **Rydberg states**. In such cases we can write

$$\tilde{v} = \frac{I}{hc} - \frac{R}{n^2} \qquad (10.39)$$

and a plot of wavenumber against $1/n^2$ can be used to obtain I by extrapolation; in practice, one would use a linear regression fit using a computer. If the lower state is not the ground state (a possibility if we wish to generalize the concept of ionization energy), the ionization energy of the ground state can be determined by adding the appropriate energy difference to the ionization energy obtained as described here.

10.7 Singlet and triplet states

Suppose we were interested in the energy levels of a He atom, with its two electrons. We know that the ground-state configuration is $1s^2$, and can anticipate that an excited configuration will be one in which one of the electrons has been promoted into a $2s$ orbital, giving the configuration $1s^1 2s^1$. The two electrons need not be paired because they occupy different orbitals. According to Hund's maximum multiplicity rule, the state of the atom with the spins parallel lies lower in energy than the state in which they are paired. Both states are permissible, and can contribute to the spectrum of the atom.
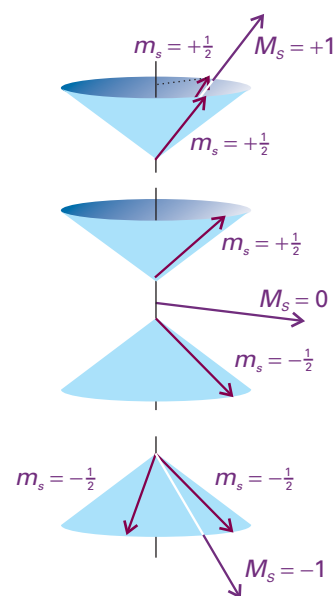
Parallel and antiparallel (paired) spins differ in their overall spin angular momentum. In the paired case, the two spin momenta cancel each other, and there is zero net spin (as was depicted in Fig. 10.18). The paired-spin arrangement is called a **singlet**. Its spin state is the one we denoted σ_- in the discussion of the Pauli principle:

$$\sigma_-(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \qquad (10.40a)$$

The angular momenta of two parallel spins add together to give a nonzero total spin, and the resulting state is called a **triplet**. As illustrated in Fig. 10.24, there are three ways of achieving a nonzero total spin, but only one way to achieve zero spin. The three spin states are the symmetric combinations introduced earlier:

$$\alpha(1)\alpha(2) \qquad \sigma_+(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \qquad \beta(1)\beta(2) \qquad (10.40b)$$

The fact that the parallel arrangement of spins in the $1s^1 2s^1$ configuration of the He atom lies lower in energy than the antiparallel arrangement can now be expressed by saying that the triplet state of the $1s^1 2s^1$ configuration of He lies lower in energy than the singlet state. This is a general conclusion that applies to other atoms (and molecules) and, *for states arising from the same configuration, the triplet state generally lies lower than the singlet state*. The origin of the energy difference lies in the effect of spin correlation on the Coulombic interactions between electrons, as we saw in the case of Hund's rule for ground-state configurations. Because the Coulombic interaction between electrons in an atom is strong, the difference in energies between singlet and triplet states of the same configuration can be large. The two states of $1s^1 2s^1$ He, for instance, differ by $6421 \ cm^{-1}$ (corresponding to 0.80 eV).

$m_s = +\frac{1}{2}$ $M_S = +1$

$m_s = +\frac{1}{2}$

$m_s = +\frac{1}{2}$

$M_S = 0$

$m_s = -\frac{1}{2}$

$m_s = -\frac{1}{2}$ $m_s = -\frac{1}{2}$

$M_S = -1$

Fig. 10.24 When two electrons have parallel spins, they have a nonzero total spin angular momentum. There are three ways of achieving this resultant, which are shown by these vector representations. Note that, although we cannot know the orientation of the spin vectors on the cones, the angle between the vectors is the same in all three cases, for all three arrangements have the same total spin angular momentum (that is, the resultant of the two vectors has the same length in each case, but points in different directions). Compare this diagram with Fig. 10.18, which shows the antiparallel case. Note that, whereas two paired spins are precisely antiparallel, two 'parallel' spins are not strictly parallel.
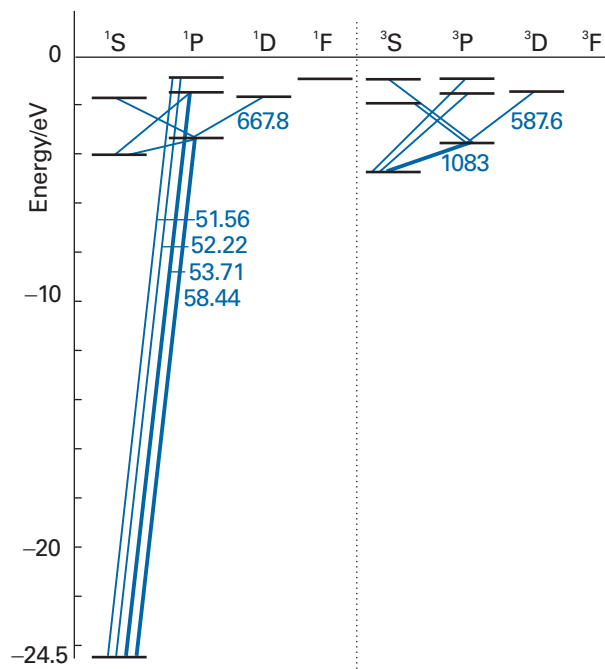
Fig. 10.25 Part of the Grotrian diagram for a helium atom. Note that there are no transitions between the singlet and triplet levels.

The spectrum of atomic helium is more complicated than that of atomic hydrogen, but there are two simplifying features. One is that the only excited configurations it is necessary to consider are of the form $1s^1nl^1$: that is, only one electron is excited. Excitation of two electrons requires an energy greater than the ionization energy of the atom, so the He^+ ion is formed instead of the doubly excited atom. Second, no radiative transitions take place between singlet and triplet states because the relative orientation of the two electron spins cannot change during a transition. Thus, there is a spectrum arising from transitions between singlet states (including the ground state) and between triplet states, but not between the two. Spectroscopically, helium behaves like two distinct species, and the early spectroscopists actually thought of helium as consisting of 'parahelium' and 'orthohelium'. The Grotrian diagram for helium in Fig. 10.25 shows the two sets of transitions.

Comment 10.6

We have already remarked that the electron's spin is a purely quantum mechanical phenomenon that has no classical counterpart. However a classical model can give us partial insight into the origin of an electron's magnetic moment. Namely, the magnetic field generated by a spinning electron, regarded classically as a moving charge, induces a magnetic moment. This model is merely a visualization aid and cannot be used to explain the magnitude of the magnetic moment of the electron or the origin of spin magnetic moments in electrically neutral particles, such as the neutron.

10.8 **Spin–orbit coupling**

An electron has a magnetic moment that arises from its spin (Fig. 10.26). Similarly, an electron with orbital angular momentum (that is, an electron in an orbital with $l > 0$) is in effect a circulating current, and possesses a magnetic moment that arises from its orbital momentum. The interaction of the spin magnetic moment with the magnetic field arising from the orbital angular momentum is called **spin–orbit coupling**. The strength of the coupling, and its effect on the energy levels of the atom, depend on the relative orientations of the spin and orbital magnetic moments, and therefore on the relative orientations of the two angular momenta (Fig. 10.27).

(a) The total angular momentum

One way of expressing the dependence of the spin–orbit interaction on the relative orientation of the spin and orbital momenta is to say that it depends on the total angular momentum of the electron, the vector sum of its spin and orbital momenta. Thus, when the spin and orbital angular momenta are nearly parallel, the total angular
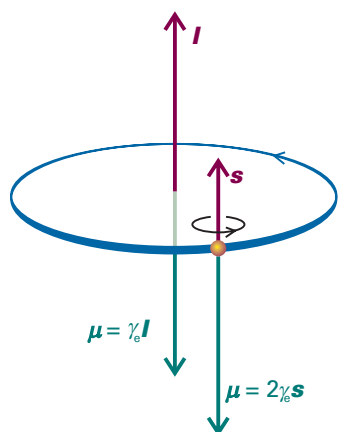
Fig. 10.26 Angular momentum gives rise to a magnetic moment (μ). For an electron, the magnetic moment is antiparallel to the orbital angular momentum, but proportional to it. For spin angular momentum, there is a factor 2, which increases the magnetic moment to twice its expected value (see Section 10.10).
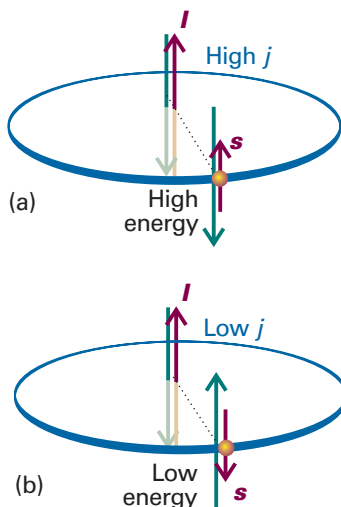
Fig. 10.27 Spin–orbit coupling is a magnetic interaction between spin and orbital magnetic moments. When the angular momenta are parallel, as in (a), the magnetic moments are aligned unfavourably; when they are opposed, as in (b), the interaction is favourable. This magnetic coupling is the cause of the splitting of a configuration into levels.

momentum is high; when the two angular momenta are opposed, the total angular momentum is low.

The total angular momentum of an electron is described by the quantum numbers j and m_j, with $j = l + \frac{1}{2}$ (when the two angular momenta are in the same direction) or $j = l - \frac{1}{2}$ (when they are opposed, Fig. 10.28). The different values of j that can arise for a given value of l label **levels** of a term. For $l = 0$, the only permitted value is $j = \frac{1}{2}$ (the total angular momentum is the same as the spin angular momentum because there is no other source of angular momentum in the atom). When $l = 1$, j may be either $\frac{3}{2}$ (the spin and orbital angular momenta are in the same sense) or $\frac{1}{2}$ (the spin and angular momenta are in opposite senses).

**Example 10.4** *Identifying the levels of a configuration*

Identify the levels that may arise from the configurations (a) d^1, (b) s^1.

Method In each case, identify the value of l and then the possible values of j. For these one-electron systems, the total angular momentum is the sum and difference of the orbital and spin momenta.

Answer (a) For a d electron, $l = 2$ and there are two levels in the configuration, one with $j = 2 + \frac{1}{2} = \frac{5}{2}$ and the other with $j = 2 - \frac{1}{2} = \frac{3}{2}$. (b) For an s electron $l = 0$, so only one level is possible, and $j = \frac{1}{2}$.

Self-test 10.8 Identify the levels of the configurations (a) p^1 and (b) f^1.

[(a) $\frac{3}{2}, \frac{1}{2}$; (b) $\frac{7}{2}, \frac{5}{2}$]
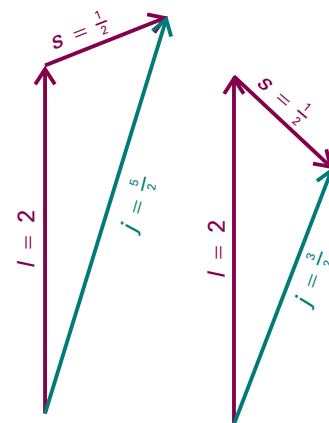
Fig. 10.28 The coupling of the spin and orbital angular momenta of a d electron ($l = 2$) gives two possible values of j depending on the relative orientations of the spin and orbital angular momenta of the electron.

The dependence of the spin–orbit interaction on the value of j is expressed in terms of the **spin–orbit coupling constant**, A (which is typically expressed as a wavenumber). A quantum mechanical calculation leads to the result that the energies of the levels with quantum numbers s, l, and j are given by

$$E_{l,s,j} = \tfrac{1}{2}hcA\{j(j+1) - l(l+1) - s(s+1)\} \tag{10.41}$$

Comment 10.7

The scalar product (or dot product) $\boldsymbol{u}\cdot\boldsymbol{v}$ of two vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ with magnitudes u and v is $\boldsymbol{u}\cdot\boldsymbol{v} = uv\cos\theta$, where θ is the angle between the two vectors.

Justification 10.8 *The energy of spin–orbit interaction*

The energy of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\boldsymbol{B}$ is equal to their scalar product $-\boldsymbol{\mu}\cdot\boldsymbol{B}$. If the magnetic field arises from the orbital angular momentum of the electron, it is proportional to $\boldsymbol{l}$; if the magnetic moment $\boldsymbol{\mu}$ is that of the electron spin, then it is proportional to $\boldsymbol{s}$. It then follows that the energy of interaction is proportional to the scalar product $\boldsymbol{s}\cdot\boldsymbol{l}$:

Energy of interaction $= -\boldsymbol{\mu}\cdot\boldsymbol{B} \propto \boldsymbol{s}\cdot\boldsymbol{l}$

We take this expression to be the first-order perturbation contribution to the hamiltonian. Next, we note that the total angular momentum is the vector sum of the spin and orbital momenta: $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$. The magnitude of the vector $\boldsymbol{j}$ is calculated by evaluating

$$\boldsymbol{j}\cdot\boldsymbol{j} = (\boldsymbol{l}+\boldsymbol{s})\cdot(\boldsymbol{l}+\boldsymbol{s}) = \boldsymbol{l}\cdot\boldsymbol{l} + \boldsymbol{s}\cdot\boldsymbol{s} + 2\boldsymbol{s}\cdot\boldsymbol{l}$$

That is,

$$\boldsymbol{s}\cdot\boldsymbol{l} = \tfrac{1}{2}\{j^2 - l^2 - s^2\}$$

where we have used the fact that the scalar product of two vectors $\boldsymbol{u}$ and v is $\boldsymbol{u}\cdot v = uv\cos\theta$, from which it follows that $\boldsymbol{u}\cdot\boldsymbol{u} = u^2$.

The preceding equation is a classical result. To make the transition to quantum mechanics, we treat all the quantities as operators, and write

$$\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{l}} = \tfrac{1}{2}\{\hat{\jmath}^2 - \hat{l}^2 - \hat{s}^2\} \tag{10.42}$$

At this point, we calculate the first-order correction to the energy by evaluating the expectation value:

$$\langle j,l,s|\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{l}}|j,l,s\rangle = \tfrac{1}{2}\langle j,l,s|\hat{\jmath}^2 - \hat{l}^2 - \boldsymbol{s}^2|j,l,s\rangle = \tfrac{1}{2}\{j(j+1) - l(l+1) - s(s+1)\}\hbar^2 \tag{10.43}$$

Then, by inserting this expression into the formula for the energy of interaction ($E \propto \boldsymbol{s}\cdot\boldsymbol{l}$), and writing the constant of proportionality as $hcA/\hbar^2$, we obtain eqn 10.42. The calculation of A is much more complicated: see *Further reading*.
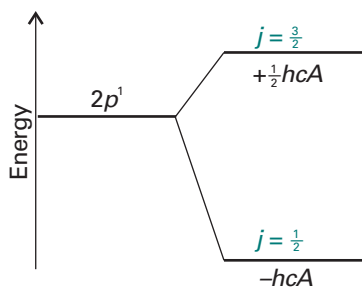
Fig. 10.29 The levels of a ^2P term arising from spin–orbit coupling. Note that the low-j level lies below the high-j level in energy.

Illustration 10.3 *Calculating the energies of levels*

The unpaired electron in the ground state of an alkali metal atom has $l = 0$, so $j = \tfrac{1}{2}$. Because the orbital angular momentum is zero in this state, the spin–orbit coupling energy is zero (as is confirmed by setting $j = s$ and $l = 0$ in eqn 10.41). When the electron is excited to an orbital with $l = 1$, it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. In this configuration the electron can have $j = \tfrac{3}{2}$ or $j = \tfrac{1}{2}$, and the energies of these levels are

$$E_{3/2} = \tfrac{1}{2}hcA\{\tfrac{3}{2}\times\tfrac{5}{2} - 1\times 2 - \tfrac{1}{2}\times\tfrac{3}{2}\} = \tfrac{1}{2}hcA$$
$$E_{1/2} = \tfrac{1}{2}hcA\{\tfrac{1}{2}\times\tfrac{3}{2} - 1\times 2 - \tfrac{1}{2}\times\tfrac{3}{2}\} = -hcA$$

The corresponding energies are shown in Fig. 10.29. Note that the baricentre (the 'centre of gravity') of the levels is unchanged, because there are four states of energy $\tfrac{1}{2}hcA$ and two of energy $-hcA$.

The strength of the spin–orbit coupling depends on the nuclear charge. To understand why this is so, imagine riding on the orbiting electron and seeing a charged nucleus apparently orbiting around us (like the Sun rising and setting). As a result, we find ourselves at the centre of a ring of current. The greater the nuclear charge, the greater this current, and therefore the stronger the magnetic field we detect. Because the spin magnetic moment of the electron interacts with this orbital magnetic field, it follows that the greater the nuclear charge, the stronger the spin–orbit interaction. The coupling increases sharply with atomic number (as Z^4). Whereas it is only small in H (giving rise to shifts of energy levels of no more than about 0.4 cm^{-1}), in heavy atoms like Pb it is very large (giving shifts of the order of thousands of reciprocal centimetres).

(b) Fine structure

Two spectral lines are observed when the p electron of an electronically excited alkali metal atom undergoes a transition and falls into a lower s orbital. One line is due to a transition starting in a $j = \frac{3}{2}$ level and the other line is due to a transition starting in the $j = \frac{1}{2}$ level of the same configuration. The two lines are an example of the **fine structure** of a spectrum, the structure in a spectrum due to spin–orbit coupling. Fine structure can be clearly seen in the emission spectrum from sodium vapour excited by an electric discharge (for example, in one kind of street lighting). The yellow line at 589 nm (close to 17 000 cm^{-1}) is actually a doublet composed of one line at 589.76 nm (16 956.2 cm^{-1}) and another at 589.16 nm (16 973.4 cm^{-1}); the components of this doublet are the 'D lines' of the spectrum (Fig. 10.30). Therefore, in Na, the spin–orbit coupling affects the energies by about 17 cm^{-1}.
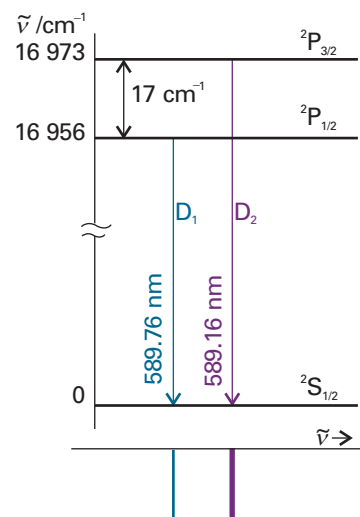
Fig. 10.30 The energy-level diagram for the formation of the sodium D lines. The splitting of the spectral lines (by 17 cm^{-1}) reflects the splitting of the levels of the ^{2}P term.

Example 10.5 *Analysing a spectrum for the spin–orbit coupling constant*

The origin of the D lines in the spectrum of atomic sodium is shown in Fig. 10.30. Calculate the spin–orbit coupling constant for the upper configuration of the Na atom.

Method We see from Fig. 10.30 that the splitting of the lines is equal to the energy separation of the $j = \frac{3}{2}$ and $\frac{1}{2}$ levels of the excited configuration. This separation can be expressed in terms of A by using eqn 10.40. Therefore, set the observed splitting equal to the energy separation calculated from eqn 10.40 and solve the equation for A.

Answer The two levels are split by

$$\Delta \tilde{v} = A \, \tfrac{1}{2} \{ \tfrac{3}{2}(\tfrac{3}{2} + 1) - \tfrac{1}{2}(\tfrac{1}{2} + 1) \} = \tfrac{3}{2} A$$

The experimental value is 17.2 cm^{-1}; therefore

$$A = \tfrac{2}{3} \times (17.2 \text{ cm}^{-1}) = 11.5 \text{ cm}^{-1}$$

The same calculation repeated for the other alkali metal atoms gives Li: 0.23 cm^{-1}, K: 38.5 cm^{-1}, Rb: 158 cm^{-1}, Cs: 370 cm^{-1}. Note the increase of A with atomic number (but more slowly than Z^4 for these many-electron atoms).

Self-test 10.9 The configuration . . . $4p^6 5d^1$ of rubidium has two levels at 25 700.56 cm^{-1} and 25 703.52 cm^{-1} above the ground state. What is the spin–orbit coupling constant in this excited state?   [1.18 cm^{-1}]
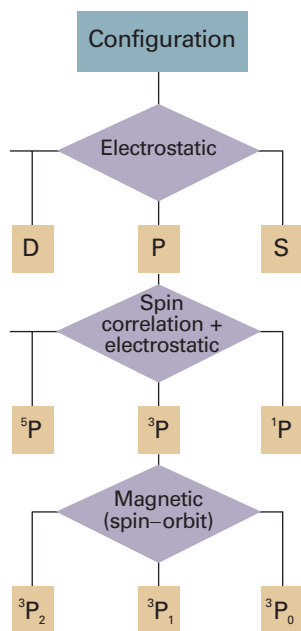
Fig. 10.31 A summary of the types of interaction that are responsible for the various kinds of splitting of energy levels in atoms. For light atoms, magnetic interactions are small, but in heavy atoms they may dominate the electrostatic (charge–charge) interactions.
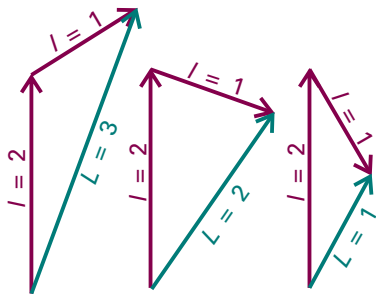
Fig. 10.32 The total angular orbital momenta of a p electron and a d electron correspond to $L = 3$, 2, and 1 and reflect the different relative orientations of the two momenta.

10.9 Term symbols and selection rules

We have used expressions such as 'the $j = \frac{3}{2}$ level of a configuration'. A **term symbol**, which is a symbol looking like $^2P_{3/2}$ or $^3D_2$, conveys this information much more succinctly. The convention of using lowercase letters to label orbitals and uppercase letters to label overall states applies throughout spectroscopy, not just to atoms.

A term symbol gives three pieces of information:

1 The letter (P or D in the examples) indicates the total orbital angular momentum quantum number, L.

2 The left superscript in the term symbol (the 2 in $^2P_{3/2}$) gives the multiplicity of the term.

3 The right subscript on the term symbol (the $\frac{3}{2}$ in $^2P_{3/2}$) is the value of the total angular momentum quantum number, J.

We shall now say what each of these statements means; the contributions to the energies which we are about to discuss are summarized in Fig. 10.31.

(a) The total orbital angular momentum

When several electrons are present, it is necessary to judge how their individual orbital angular momenta add together or oppose each other. The **total orbital angular momentum quantum number**, L, tells us the magnitude of the angular momentum through $\{L(L+1)\}^{1/2}\hbar$. It has $2L+1$ orientations distinguished by the quantum number M_L, which can take the values $L, L-1, \ldots, -L$. Similar remarks apply to the **total spin quantum number**, S, and the quantum number M_S, and the **total angular momentum quantum number**, J, and the quantum number M_J.

The value of L (a non-negative integer) is obtained by coupling the individual orbital angular momenta by using the **Clebsch–Gordan series**:

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2| \tag{10.44}$$

The modulus signs are attached to $l_1 - l_2$ because L is non-negative. The maximum value, $L = l_1 + l_2$, is obtained when the two orbital angular momenta are in the same direction; the lowest value, $|l_1 - l_2|$, is obtained when they are in opposite directions. The intermediate values represent possible intermediate relative orientations of the two momenta (Fig. 10.32). For two p electrons (for which $l_1 = l_2 = 1$), $L = 2$, 1, 0. The code for converting the value of L into a letter is the same as for the $s, p, d, f, \ldots$ designation of orbitals, but uses uppercase Roman letters:

L: 0   1   2   3   4   5   6 . . .

       S   P   D   F   G   H   I . . .

Thus, a p^2 configuration can give rise to D, P, and S terms. The terms differ in energy on account of the different spatial distribution of the electrons and the consequent differences in repulsion between them.

A closed shell has zero orbital angular momentum because all the individual orbital angular momenta sum to zero. Therefore, when working out term symbols, we need consider only the electrons of the unfilled shell. In the case of a single electron outside a closed shell, the value of L is the same as the value of l; so the configuration $[Ne]3s^1$ has only an S term.

Example 10.6 *Deriving the total orbital angular momentum of a configuration*

Find the terms that can arise from the configurations (a) d^2, (b) p^3.

Method Use the Clebsch–Gordan series and begin by finding the minimum value of L (so that we know where the series terminates). When there are more than two electrons to couple together, use two series in succession: first couple two electrons, and then couple the third to each combined state, and so on.

Answer (a) The minimum value is $|l_1 - l_2| = |2 - 2| = 0$. Therefore,

$$L = 2 + 2, 2 + 2 - 1, \ldots, 0 = 4, 3, 2, 1, 0$$

corresponding to G, F, D, P, S terms, respectively. (b) Coupling two electrons gives a minimum value of $|1 - 1| = 0$. Therefore,

$$L' = 1 + 1, 1 + 1 - 1, \ldots, 0 = 2, 1, 0$$

Now couple l_3 with $L' = 2$, to give $L = 3, 2, 1$; with $L' = 1$, to give $L = 2, 1, 0$; and with $L' = 0$, to give $L = 1$. The overall result is

$$L = 3, 2, 2, 1, 1, 1, 0$$

giving one F, two D, three P, and one S term.

Self-test 10.10 Repeat the question for the configurations (a) $f^1 d^1$ and (b) d^3.
[(a) H, G, F, D, P; (b) I, 2H, 3G, 4F, 5D, 3P, S]

(b) The multiplicity

When there are several electrons to be taken into account, we must assess their total spin angular momentum quantum number, S (a non-negative integer or half integer). Once again, we use the Clebsch–Gordan series in the form

$$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2| \tag{10.45}$$

to decide on the value of S, noting that each electron has $s = \frac{1}{2}$, which gives $S = 1, 0$ for two electrons (Fig. 10.33). If there are three electrons, the total spin angular momentum is obtained by coupling the third spin to each of the values of S for the first two spins, which results in $S = \frac{3}{2}$, and $S = \frac{1}{2}$.

The **multiplicity** of a term is the value of $2S + 1$. When $S = 0$ (as for a closed shell, like $1s^2$) the electrons are all paired and there is no net spin: this arrangement gives a singlet term, ^1S. A single electron has $S = s = \frac{1}{2}$, so a configuration such as $[Ne]3s^1$ can give rise to a doublet term, ^2S. Likewise, the configuration $[Ne]3p^1$ is a doublet, ^2P. When there are two unpaired electrons $S = 1$, so $2S + 1 = 3$, giving a triplet term, such as ^3D. We discussed the relative energies of singlets and triplets in Section 10.7 and saw that their energies differ on account of the different effects of spin correlation.

(c) The total angular momentum

As we have seen, the quantum number j tells us the relative orientation of the spin and orbital angular momenta of a single electron. The **total angular momentum quantum number**, J (a non-negative integer or half integer), does the same for several electrons. If there is a single electron outside a closed shell, $J = j$, with j either $l + \frac{1}{2}$ or $|l - \frac{1}{2}|$. The $[Ne]3s^1$ configuration has $j = \frac{1}{2}$ (because $l = 0$ and $s = \frac{1}{2}$), so the $2s$ term has a single level, which we denote $^2S_{1/2}$. The $[Ne]3p^1$ configuration has $l = 1$; therefore

Comment 10.8
Throughout our discussion of atomic spectroscopy, distinguish italic *S*, the total spin quantum number, from Roman S, the term label.
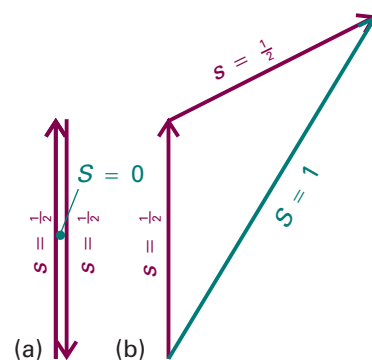
Fig. 10.33 For two electrons (each of which has $s = \frac{1}{2}$), only two total spin states are permitted ($S = 0, 1$). The state with $S = 0$ can have only one value of M_S ($M_S = 0$) and is a singlet; the state with $S = 1$ can have any of three values of M_S ($+1, 0, -1$) and is a triplet. The vector representation of the singlet and triplet states are shown in Figs. 10.18 and 10.24, respectively.

$j = \frac{3}{2}$ and $\frac{1}{2}$; the ^2P term therefore has two levels, $^2P_{3/2}$ and $^2P_{1/2}$. These levels lie at different energies on account of the magnetic spin–orbit interaction.

If there are several electrons outside a closed shell we have to consider the coupling of all the spins and all the orbital angular momenta. This complicated problem can be simplified when the spin–orbit coupling is weak (for atoms of low atomic number), for then we can use the **Russell–Saunders coupling** scheme. This scheme is based on the view that, if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating cooperatively. We therefore imagine that all the orbital angular momenta of the electrons couple to give a total L, and that all the spins are similarly coupled to give a total S. Only at this stage do we imagine the two kinds of momenta coupling through the spin–orbit interaction to give a total J. The permitted values of J are given by the Clebsch–Gordan series

$$J = L + S, L + S - 1, \ldots, |L - S| \tag{10.46}$$

For example, in the case of the ^3D term of the configuration $[Ne]2p^13p^1$, the permitted values of J are 3, 2, 1 (because ^3D has $L = 2$ and $S = 1$), so the term has three levels, $^3D_3$, $^3D_2$, and $^3D_1$.

When $L \geq S$, the multiplicity is equal to the number of levels. For example, a ^2P term has the two levels $^2P_{3/2}$ and $^2P_{1/2}$, and ^3D has the three levels $^3D_3$, $^3D_2$, and $^3D_1$. However, this is not the case when $L < S$: the term ^2S, for example, has only the one level $^2S_{1/2}$.

Example 10.7 *Deriving term symbols*

Write the term symbols arising from the ground-state configurations of (a) Na and (b) F, and (c) the excited configuration $1s^22s^22p^13p^1$ of C.

Method Begin by writing the configurations, but ignore inner closed shells. Then couple the orbital momenta to find L and the spins to find S. Next, couple L and S to find J. Finally, express the term as $^{2S+1}\{L\}_J$, where $\{L\}$ is the appropriate letter. For F, for which the valence configuration is $2p^5$, treat the single gap in the closed-shell $2p^6$ configuration as a single particle.

Answer (a) For Na, the configuration is $[Ne]3s^1$, and we consider the single $3s$ electron. Because $L = l = 0$ and $S = s = \frac{1}{2}$, it is possible for $J = j = s = \frac{1}{2}$ only. Hence the term symbol is $^2S_{1/2}$. (b) For F, the configuration is $[He]2s^22p^5$, which we can treat as $[Ne]2p^{-1}$ (where the notation $2p^{-1}$ signifies the absence of a $2p$ electron). Hence $L = 1$, and $S = s = \frac{1}{2}$. Two values of $J = j$ are allowed: $J = \frac{3}{2}, \frac{1}{2}$. Hence, the term symbols for the two levels are $^2P_{3/2}, ^2P_{1/2}$. (c) We are treating an excited configuration of carbon because, in the ground configuration, $2p^2$, the Pauli principle forbids some terms, and deciding which survive (^1D, ^3P, ^1S, in fact) is quite complicated. That is, there is a distinction between 'equivalent electrons', which are electrons that occupy the same orbitals, and 'inequivalent electrons', which are electrons that occupy different orbitals. For information about how to deal with equivalent electrons, see *Further reading*. The excited configuration of C under consideration is effectively $2p^13p^1$. This is a two-electron problem, and $l_1 = l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$. It follows that $L = 2, 1, 0$ and $S = 1, 0$. The terms are therefore ^3D and ^1D, ^3P and ^1P, and ^3S and ^1S. For ^3D, $L = 2$ and $S = 1$; hence $J = 3, 2, 1$ and the levels are $^3D_3$, $^3D_2$, and $^3D_1$. For ^1D, $L = 2$ and $S = 0$, so the single level is $^1D_2$. The triplet of levels of ^3P is $^3P_2$, $^3P_1$, and $^3P_0$, and the singlet is $^1P_1$. For the ^3S term there is only one level, $^3S_1$ (because $J = 1$ only), and the singlet term is $^1S_0$.

Self-test 10.11 Write down the terms arising from the configurations (a) $2s^1 2p^1$, (b) $2p^1 3d^1$.

[(a) $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$;
(b) $^3F_4$, $^3F_3$, $^3F_2$, $^1F_3$, $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, $^3P_1$, $^3P_0$, $^1P_1$]

Russell–Saunders coupling fails when the spin–orbit coupling is large (in heavy atoms). In that case, the individual spin and orbital momenta of the electrons are coupled into individual j values; then these momenta are combined into a grand total, J. This scheme is called **jj-coupling**. For example, in a p^2 configuration, the individual values of j are $\frac{3}{2}$ and $\frac{1}{2}$ for each electron. If the spin and the orbital angular momentum of each electron are coupled together strongly, it is best to consider each electron as a particle with angular momentum $j = \frac{3}{2}$ or $\frac{1}{2}$. These individual total momenta then couple as follows:

$j_1 = \frac{3}{2}$ and $j_2 = \frac{3}{2}$ $J = 3, 2, 1, 0$
$j_1 = \frac{3}{2}$ and $j_2 = \frac{1}{2}$ $J = 2, 1$
$j_1 = \frac{1}{2}$ and $j_2 = \frac{3}{2}$ $J = 2, 1$
$j_1 = \frac{1}{2}$ and $j_2 = \frac{1}{2}$ $J = 1, 0$

For heavy atoms, in which jj-coupling is appropriate, it is best to discuss their energies using these quantum numbers.

Although jj-coupling should be used for assessing the energies of heavy atoms, the term symbols derived from Russell–Saunders coupling can still be used as labels. To see why this procedure is valid, we need to examine how the energies of the atomic states change as the spin–orbit coupling increases in strength. Such a **correlation diagram** is shown in Fig. 10.34. It shows that there is a correspondence between the low spin–orbit coupling (Russell–Saunders coupling) and high spin–orbit coupling (jj-coupling) schemes, so the labels derived by using the Russell–Saunders scheme can be used to label the states of the jj-coupling scheme.

(d) Selection rules

Any state of the atom, and any spectral transition, can be specified by using term symbols. For example, the transitions giving rise to the yellow sodium doublet (which were shown in Fig. 10.30) are

$3p^1 \, ^2P_{3/2} \rightarrow 3s^1 \, ^2S_{1/2}$ $3p^1 \, ^2P_{1/2} \rightarrow 3s^1 \, ^2S_{1/2}$

By convention, the upper term precedes the lower. The corresponding absorptions are therefore denoted

$^2P_{3/2} \leftarrow \, ^2S_{1/2}$ $^2P_{1/2} \leftarrow \, ^2S_{1/2}$

(The configurations have been omitted.)

We have seen that selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon has a spin of 1. They can therefore be expressed in terms of the term symbols, because the latter carry information about angular momentum. A detailed analysis leads to the following rules:

$\Delta S = 0$ $\Delta L = 0, \pm 1$ $\Delta l = \pm 1$ $\Delta J = 0, \pm 1$, but $J = 0 \leftarrow\!\!\!|\!\!\!\rightarrow J = 0$ (10.47)

where the symbol $\leftarrow\!\!\!|\!\!\!\rightarrow$ denotes a forbidden transition. The rule about ΔS (no change of overall spin) stems from the fact that the light does not affect the spin directly. The rules about ΔL and Δl express the fact that the orbital angular momentum of an
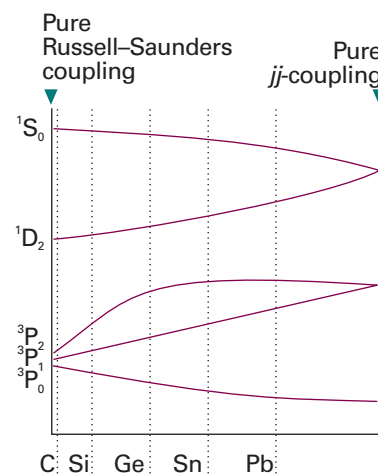
Fig. 10.34 The correlation diagram for some of the states of a two-electron system. All atoms lie between the two extremes, but the heavier the atom, the closer it lies to the pure jj-coupling case.

individual electron must change (so $\Delta l = \pm 1$), but whether or not this results in an overall change of orbital momentum depends on the coupling.

The selection rules given above apply when Russell–Saunders coupling is valid (in light atoms). If we insist on labelling the terms of heavy atoms with symbols like ^{3}D, then we shall find that the selection rules progressively fail as the atomic number increases because the quantum numbers S and L become ill defined as jj-coupling becomes more appropriate. As explained above, Russell–Saunders term symbols are only a convenient way of labelling the terms of heavy atoms: they do not bear any direct relation to the actual angular momenta of the electrons in a heavy atom. For this reason, transitions between singlet and triplet states (for which $\Delta S = \pm 1$), while forbidden in light atoms, are allowed in heavy atoms.

Checklist of key ideas

☐ 1. A hydrogenic atom is a one-electron atom or ion of general atomic number Z. A many-electron (polyelectronic) atom is an atom or ion with more than one electron.

☐ 2. The Lyman, Balmer, and Paschen series in the spectrum of atomic hydrogen arise, respectively, from the transitions $n \rightarrow 1$, $n \rightarrow 2$, and $n \rightarrow 3$.

☐ 3. The wavenumbers of all the spectral lines of a hydrogen atom can be expressed as $\tilde{v} = R_H(1/n_1^2 - 1/n_2^2)$, where R_H is the Rydberg constant for hydrogen.

☐ 4. The Ritz combination principle states that the wavenumber of any spectral line is the difference between two spectroscopic energy levels, or terms: $\tilde{v} = T_1 - T_2$.

☐ 5. The wavefunction of the hydrogen atom is the product of a radial wavefunction and a radial wavefunction: $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$.

☐ 6. An atomic orbital is a one-electron wavefunction for an electron in an atom.

☐ 7. The energies of an electron in a hydrogen atom are given by $E_n = -Z^2\mu e^4/32\pi^2\varepsilon_0^2\hbar^2 n^2$, where n is the principal quantum number, $n = 1, 2, \ldots$.

☐ 8. All the orbitals of a given value of n belong to a given shell; orbitals with the same value of n but different values of l belong to different subshells.

☐ 9. The radial distribution function is a probability density that, when it is multiplied by dr, gives the probability of finding the electron anywhere in a shell of thickness dr at the radius r; $P(r) = r^2 R(r)^2$.

☐ 10. A selection rule is a statement about which spectroscopic transitions are allowed; a Grotrian diagram is a diagram summarizing the energies of the states and atom and the transitions between them.

☐ 11. In the orbital approximation it is supposed that each electron occupies its 'own' orbital, $\psi(r_1, r_2, \ldots) = \psi(r_1)\psi(r_2)\ldots$.

☐ 12. The Pauli exclusion principle states that no more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spins must be paired.

☐ 13. The Pauli principle states that, when the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

☐ 14. The effective nuclear charge Z_{eff} is the net charge experienced by an electron allowing for electron–electron repulsions.

☐ 15. Shielding is the effective reduction in charge of a nucleus by surrounding electrons; the shielding constant σ is given by $Z_{eff} = Z - \sigma$.

☐ 16. Penetration is the ability of an electron to be found inside inner shells and close to the nucleus.

☐ 17. The building-up (*Aufbau*) principle is the procedure for filling atomic orbitals that leads to the ground-state configuration of an atom.

☐ 18. Hund's maximum multiplicity rule states that an atom in its ground state adopts a configuration with the greatest number of unpaired electrons.

☐ 19. The first ionization energy I_1 is the minimum energy necessary to remove an electron from a many-electron atom in the gas phase; the second ionization energy I_2 is the minimum energy necessary to remove an electron from an ionized many-electron atom in the gas phase.

☐ 20. The electron affinity E_{ea} is the energy released when an electron attaches to a gas-phase atom.

☐ 21. A singlet term has $S = 0$; a triplet term has $S = 1$.

☐ 22. Spin–orbit coupling is the interaction of the spin magnetic moment with the magnetic field arising from the orbital angular momentum.

☐ 23. Fine structure is the structure in a spectrum due to spin–orbit coupling.

☐ 24. A term symbol is a symbolic specification of the state of an atom, $^{2S+1}\{L\}_J$.

☐ 25. The allowed values of a combined angular momenta are obtained by using the Clebsch–Gordan series: $J = j_1 + j_2$, $j_1 + j_2 - 1, \ldots |j_1 - j_2|$.

26. The multiplicity of a term is the value of $2S+1$; provided $L \geq S$, the multiplicity is the number of levels of the term.

28. A level is a group of states with a common value of J.

29. Russell–Saunders coupling is a coupling scheme based on the view that, if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating cooperatively.

30. jj-Coupling is a coupling scheme based on the view that the individual spin and orbital momenta of the electrons are coupled into individual j values and these momenta are combined into a grand total, J.

31. The selection rules for spectroscopic transitions in polyelectronic atoms are: $\Delta S = 0$, $\Delta L = 0, \pm 1$, $\Delta l = \pm 1$, $\Delta J = 0, \pm 1$, but $J = 0 \leftarrow\!\!|\!\!\rightarrow J = 0$.

Further reading

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Further information

Further information 10.1 *The separation of motion*

The separation of internal and external motion

Consider a one-dimensional system in which the potential energy depends only on the separation of the two particles. The total energy is

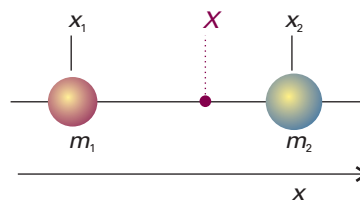$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V$$

where $p_1 = m_1\dot{x}_1$ and $p_2 = m_2\dot{x}_2$, the dot signifying differentiation with respect to time. The centre of mass (Fig. 10.35) is located at

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}x_2 \qquad m = m_1 + m_2$$

and the separation of the particles is $x = x_1 - x_2$. It follows that

$$x_1 = X + \frac{m_2}{m}x \qquad x_2 = X - \frac{m_1}{m}x$$

The linear momenta of the particles can be expressed in terms of the rates of change of x and X:

Fig. 10.35 The coordinates used for discussing the separation of the relative motion of two particles from the motion of the centre of mass.

$$p_1 = m_1\dot{x}_1 = m_1\dot{X} + \frac{m_1 m_2}{m}\dot{x} \qquad p_2 = m_2\dot{x}_2 = m_2\dot{X} - \frac{m_1 m_2}{m}\dot{x}$$

Then it follows that

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \tfrac{1}{2}m\dot{X}^2 + \tfrac{1}{2}\mu\dot{x}^2$$

where μ is given in eqn 10.6. By writing $P = m\dot{X}$ for the linear momentum of the system as a whole and defining p as $\mu\dot{x}$, we find

$$E = \frac{P^2}{2m} + \frac{p^2}{2\mu} + V$$

The corresponding hamiltonian (generalized to three dimensions) is therefore

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2_{\text{c.m.}} - \frac{\hbar^2}{2\mu}\nabla^2 + V$$

where the first term differentiates with respect to the centre of mass coordinates and the second with respect to the relative coordinates.

Now we write the overall wavefunction as the product $\psi_{\text{total}} = \psi_{\text{c.m.}}\psi$, where the first factor is a function of only the centre of mass coordinates and the second is a function of only the relative coordinates. The overall Schrödinger equation, $H\psi_{\text{total}} = E_{\text{total}}\psi_{\text{total}}$, then separates by the argument that we have used in Sections 9.2a and 9.7, with $E_{\text{total}} = E_{\text{c.m.}} + E$.

The separation of angular and radial motion

The laplacian in three dimensions is given in eqn 9.51a. It follows that the Schrödinger equation in eqn 10.6 is

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)RY + VRY = ERY$$

Because R depends only on r and Y depends only on the angular coordinates, this equation becomes

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2Y}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{R}{r^2}\Lambda^2Y\right) + VRY = ERY$$

If we multiply through by r^2/RY, we obtain

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + 2r\frac{\mathrm{d}R}{\mathrm{d}r}\right) + Vr^2 - \frac{\hbar^2}{2\mu Y}\Lambda^2Y = Er^2$$

At this point we employ the usual argument. The term in Y is the only one that depends on the angular variables, so it must be a constant. When we write this constant as $\hbar^2 l(l+1)/2\mu$, eqn 10.10 follows immediately.

Discussion questions

10.1 Describe the separation of variables procedure as it is applied to simplify the description of a hydrogenic atom free to move through space.

10.2 List and describe the significance of the quantum numbers needed to specify the internal state of a hydrogenic atom.

10.3 Specify and account for the selection rules for transitions in hydrogenic atoms.

10.4 Explain the significance of (a) a boundary surface and (b) the radial distribution function for hydrogenic orbitals.

10.5 Outline the electron configurations of many-electron atoms in terms of their location in the periodic table.

10.6 Describe and account for the variation of first ionization energies along Period 2 of the periodic table.

10.7 Describe the orbital approximation for the wavefunction of a many-electron atom. What are the limitations of the approximation?

10.8 Explain the origin of spin–orbit coupling and how it affects the appearance of a spectrum.

Exercises

10.1a When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of 1.59 Mm s^{-1}. Calculate the ionization energy of krypton.

10.1b When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of xenon, electrons are ejected with a speed of 1.79 Mm s^{-1}. Calculate the ionization energy of xenon.

10.2a By differentiation of the 2s radial wavefunction, show that it has two extrema in its amplitude, and locate them.

10.2b By differentiation of the 3s radial wavefunction, show that it has three extrema in its amplitude, and locate them.

10.3a Locate the radial nodes in the 3s orbital of an H atom.

10.3b Locate the radial nodes in the 4p orbital of an H atom where, in the notation of Table 10.1, the radial wavefunction is proportional to $20 - 10\rho + \rho^2$.

10.4a The wavefunction for the ground state of a hydrogen atom is Ne^{-r/a_0}. Determine the normalization constant N.

10.4b The wavefunction for the 2s orbital of a hydrogen atom is $N(2 - r/a_0)e^{-r/2a_0}$. Determine the normalization constant N.

10.5a Calculate the average kinetic and potential energies of an electron in the ground state of a hydrogen atom.

10.5b Calculate the average kinetic and potential energies of a 2s electron in a hydrogenic atom of atomic number Z.

10.6a Write down the expression for the radial distribution function of a 2s electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

10.6b Write down the expression for the radial distribution function of a 3s electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

10.7a Write down the expression for the radial distribution function of a 2p electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

10.7b Write down the expression for the radial distribution function of a $3p$ electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

10.8a What is the orbital angular momentum of an electron in the orbitals (a) $1s$, (b) $3s$, (c) $3d$? Give the numbers of angular and radial nodes in each case.

10.8b What is the orbital angular momentum of an electron in the orbitals (a) $4d$, (b) $2p$, (c) $3p$? Give the numbers of angular and radial nodes in each case.

10.9a Calculate the permitted values of j for (a) a d electron, (b) an f electron.

10.9b Calculate the permitted values of j for (a) a p electron, (b) an h electron.

10.10a An electron in two different states of an atom is known to have $j = \frac{3}{2}$ and $\frac{1}{2}$. What is its orbital angular momentum quantum number in each case?

10.10b What are the allowed total angular momentum quantum numbers of a composite system in which $j_1 = 5$ and $j_2 = 3$?

10.11a State the orbital degeneracy of the levels in a hydrogen atom that have energy (a) $-hcR_H$; (b) $-\frac{1}{9}hcR_H$; (c) $-\frac{1}{25}hcR_H$.

10.11b State the orbital degeneracy of the levels in a hydrogenic atom (Z in parentheses) that have energy (a) $-4hcR_{atom}$ (2); (b) $-\frac{1}{4}hcR_{atom}$ (4), and (c) $-hcR_{atom}$ (5).

10.12a What information does the term symbol $^1D_2$ provide about the angular momentum of an atom?

10.12b What information does the term symbol $^3F_4$ provide about the angular momentum of an atom?

10.13a At what radius does the probability of finding an electron at a point in the H atom fall to 50 per cent of its maximum value?

10.13b At what radius in the H atom does the radial distribution function of the ground state have (a) 50 per cent, (b) 75 per cent of its maximum value?

10.14a Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $2s \rightarrow 1s$, (b) $2p \rightarrow 1s$, (c) $3d \rightarrow 2p$?

10.14b Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $5d \rightarrow 2s$, (b) $5p \rightarrow 3s$, (c) $6p \rightarrow 4f$?

10.15a (a) Write the electronic configuration of the Ni^{2+} ion. (b) What are the possible values of the total spin quantum numbers S and M_S for this ion?

10.15b (a) Write the electronic configuration of the V^{2+} ion. (b) What are the possible values of the total spin quantum numbers S and M_S for this ion?

10.16a Suppose that an atom has (a) 2, (b) 3 electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

10.16b Suppose that an atom has (a) 4, (b) 5 electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

10.17a What atomic terms are possible for the electron configuration ns^1nd^1? Which term is likely to lie lowest in energy?

10.17b What atomic terms are possible for the electron configuration np^1nd^1? Which term is likely to lie lowest in energy?

10.18a What values of J may occur in the terms (a) ^1S, (b) ^2P, (c) ^3P? How many states (distinguished by the quantum number M_J) belong to each level?

10.18b What values of J may occur in the terms (a) ^3D, (b) ^4D, (c) ^2G? How many states (distinguished by the quantum number M_J) belong to each level?

10.19a Give the possible term symbols for (a) Li $[He]2s^1$, (b) Na $[Ne]3p^1$.

10.19b Give the possible term symbols for (a) Sc $[Ar]3d^14s^2$, (b) Br $[Ar]3d^{10}4s^24p^5$.

Problems*

Numerical problems

10.1 The *Humphreys series* is a group of lines in the spectrum of atomic hydrogen. It begins at 12 368 nm and has been traced to 3281.4 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?

10.2 A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?

10.3 The Li^{2+} ion is hydrogenic and has a Lyman series at 740 747 cm^{-1}, 877 924 cm^{-1}, 925 933 cm^{-1}, and beyond. Show that the energy levels are of the form $-hcR/n^2$ and find the value of R for this ion. Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and find the ionization energy of the ion.

10.4 A series of lines in the spectrum of neutral Li atoms rise from combinations of $1s^22p^1$ ^2P with $1s^2nd^1$ ^2D and occur at 610.36 nm, 460.29 nm, and 413.23 nm. The d orbitals are hydrogenic. It is known that the ^2P term lies at 670.78 nm above the ground state, which is $1s^22s^1$ ^2S. Calculate the ionization energy of the ground-state atom.

10.5‡ W.P. Wijesundera, S.H. Vosko, and F.A. Parpia (*Phys. Rev.* A **51**, 278 (1995)) attempted to determine the electron configuration of the ground state of lawrencium, element 103. The two contending configurations are $[Rn]5f^{14}7s^27p^1$ and $[Rn]5f^{14}6d7s^2$. Write down the term symbols for each of these configurations, and identify the lowest level within each configuration. Which level would be lowest according to a simple estimate of spin–orbit coupling?

10.6 The characteristic emission from K atoms when heated is purple and lies at 770 nm. On close inspection, the line is found to have two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Account for this observation, and deduce what information you can.

10.7 Calculate the mass of the deuteron given that the first line in the Lyman series of H lies at 82 259.098 cm^{-1} whereas that of D lies at 82 281.476 cm^{-1}. Calculate the ratio of the ionization energies of H and D.

10.8 Positronium consists of an electron and a positron (same mass, opposite charge) orbiting round their common centre of mass. The broad features of the spectrum are therefore expected to be hydrogen-like, the differences arising largely from the mass differences. Predict the wavenumbers of the first three lines of the Balmer series of positronium. What is the binding energy of the ground state of positronium?

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

10.9   The *Zeeman effect* is the modification of an atomic spectrum by the application of a strong magnetic field. It arises from the interaction between applied magnetic fields and the magnetic moments due to orbital and spin angular momenta (recall the evidence provided for electron spin by the Stern–Gerlach experiment, Section 9.8). To gain some appreciation for the so-called *normal Zeeman effect*, which is observed in transitions involving singlet states, consider a *p* electron, with $l = 1$ and $m_l = 0, \pm 1$. In the absence of a magnetic field, these three states are degenerate. When a field of magnitude B is present, the degeneracy is removed and it is observed that the state with $m_l = +1$ moves up in energy by $\mu_B B$, the state with $m_l = 0$ is unchanged, and the state with $m_l = -1$ moves down in energy by $\mu_B B$, where $\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24}$ J T^{-1} is the Bohr magneton (see Section 15.1). Therefore, a transition between a $^1S_0$ term and a $^1P_1$ term consists of three spectral lines in the presence of a magnetic field where, in the absence of the magnetic field, there is only one. (a) Calculate the splitting in reciprocal centimetres between the three spectral lines of a transition between a $^1S_0$ term and a $^1P_1$ term in the presence of a magnetic field of 2 T (where 1 T = 1 kg s^{-2} A^{-1}). (b) Compare the value you calculated in (a) with typical optical transition wavenumbers, such as those for the Balmer series of the H atom. Is the line splitting caused by the normal Zeeman effect relatively small or relatively large?

10.10   In 1976 it was mistakenly believed that the first of the 'superheavy' elements had been discovered in a sample of mica. Its atomic number was believed to be 126. What is the most probable distance of the innermost electrons from the nucleus of an atom of this element? (In such elements, relativistic effects are very important, but ignore them here.)

Theoretical problems

10.11   What is the most probable point (not radius) at which a 2*p* electron will be found in the hydrogen atom?

10.12   Show by explicit integration that (a) hydrogenic 1*s* and 2*s* orbitals, (b) $2p_x$ and $2p_y$ orbitals are mutually orthogonal.

10.13‡   Explicit expressions for hydrogenic orbitals are given in Tables 10.1 and 9.3. (a) Verify both that the $3p_x$ orbital is normalized (to 1) and that $3p_x$ and $3d_{xy}$ are mutually orthogonal. (b) Determine the positions of both the radial nodes and nodal planes of the 3*s*, $3p_x$, and $3d_{xy}$ orbitals. (c) Determine the mean radius of the 3*s* orbital. (d) Draw a graph of the radial distribution function for the three orbitals (of part (b)) and discuss the significance of the graphs for interpreting the properties of many-electron atoms. (e) Create both *xy*-plane polar plots and boundary surface plots for these orbitals. Construct the boundary plots so that the distance from the origin to the surface is the absolute value of the angular part of the wavefunction. Compare the *s*, *p*, and *d* boundary surface plots with that of an *f*-orbital; e.g. $\psi_f \propto x(5z^2 - r^2) \propto \sin \theta$ $(5 \cos^2 \theta - 1)\cos \phi$.

10.14   Determine whether the p_x and p_y orbitals are eigenfunctions of l_z. If not, does a linear combination exist that is an eigenfunction of l_z?

10.15   Show that l_z and l^2 both commute with the hamiltonian for a hydrogen atom. What is the significance of this result?

10.16   The 'size' of an atom is sometimes considered to be measured by the radius of a sphere that contains 90 per cent of the charge density of the electrons in the outermost occupied orbital. Calculate the 'size' of a hydrogen atom in its ground state according to this definition. Go on to explore how the 'size' varies as the definition is changed to other percentages, and plot your conclusion.

10.17   Some atomic properties depend on the average value of $1/r$ rather than the average value of r itself. Evaluate the expectation value of $1/r$ for (a) a hydrogen 1*s* orbital, (b) a hydrogenic 2*s* orbital, (c) a hydrogenic 2*p* orbital.

10.18   One of the most famous of the obsolete theories of the hydrogen atom was proposed by Bohr. It has been replaced by quantum mechanics but, by a remarkable coincidence (not the only one where the Coulomb potential is concerned), the energies it predicts agree exactly with those obtained from the Schrödinger equation. In the Bohr atom, an electron travels in a circle around the nucleus. The Coulombic force of attraction ($Ze^2/4\pi\varepsilon_0 r^2$) is balanced by the centrifugal effect of the orbital motion. Bohr proposed that the angular momentum is limited to integral values of $\hbar$. When the two forces are balanced, the atom remains in a stationary state until it makes a spectral transition. Calculate the energies of a hydrogenic atom using the Bohr model.

10.19   The Bohr model of the atom is specified in Problem 10.18. What features of it are untenable according to quantum mechanics? How does the Bohr ground state differ from the actual ground state? Is there an experimental distinction between the Bohr and quantum mechanical models of the ground state?

10.20   Atomic units of length and energy may be based on the properties of a particular atom. The usual choice is that of a hydrogen atom, with the unit of length being the Bohr radius, a_0, and the unit of energy being the (negative of the) energy of the 1*s* orbital. If the positronium atom (e$^+$,e$^-$) were used instead, with analogous definitions of units of length and energy, what would be the relation between these two sets of atomic units?

10.21   Some of the selection rules for hydrogenic atoms were derived in *Justification* 10.4. Complete the derivation by considering the *x*- and *y*-components of the electric dipole moment operator.

10.22‡   Stern–Gerlach splittings of atomic beams are small and require either large magnetic field gradients or long magnets for their observation. For a beam of atoms with zero orbital angular momentum, such as H or Ag, the deflection is given by $x = \pm(\mu_B L^2/4E_K)dB/dz$, where μ_B is the Bohr magneton (Problem 10.9), L is the length of the magnet, E_K is the average kinetic energy of the atoms in the beam, and dB/dz is the magnetic field gradient across the beam. (a) Use the Maxwell–Boltzmann velocity distribution to show that the average translational kinetic energy of the atoms emerging as a beam from a pinhole in an oven at temperature T is $2kT$. (b) Calculate the magnetic field gradient required to produce a splitting of 1.00 mm in a beam of Ag atoms from an oven at 1000 K with a magnet of length 50 cm.

10.23   The wavefunction of a many-electron closed-shell atom can expressed as a Slater determinant (Section 10.4b). A useful property of determinants is that interchanging any two rows or columns changes their sign and therefore, if any two rows or columns are identical, then the determinant vanishes. Use this property to show that (a) the wavefunction is antisymmetric under particle exchange, (b) no two electrons can occupy the same orbital with the same spin.

Applications: to astrophysics and biochemistry

10.24   Hydrogen is the most abundant element in all stars. However, neither absorption nor emission lines due to neutral hydrogen are found in the spectra of stars with effective temperatures higher than 25 000 K. Account for this observation.

10.25   The distribution of isotopes of an element may yield clues about the nuclear reactions that occur in the interior of a star. Show that it is possible to use spectroscopy to confirm the presence of both ^{4}He$^+$ and ^{3}He$^+$ in a star by calculating the wavenumbers of the $n = 3 \rightarrow n = 2$ and of the $n = 2 \rightarrow n = 1$ transitions for each isotope.

10.26‡   Highly excited atoms have electrons with large principal quantum numbers. Such *Rydberg atoms* have unique properties and are of interest to astrophysicists . For hydrogen atoms with large *n*, derive a relation for the separation of energy levels. Calculate this separation for $n = 100$; also calculate the average radius, the geometric cross-section, and the ionization energy. Could a thermal collision with another hydrogen atom ionize this Rydberg atom? What minimum velocity of the second atom is required? Could a normal-sized neutral H atom simply pass through the Rydberg atom leaving it undisturbed? What might the radial wavefunction for a 100*s* orbital be like?

10.27 The spectrum of a star is used to measure its *radial velocity* with respect to the Sun, the component of the star's velocity vector that is parallel to a vector connecting the star's centre to the centre of the Sun. The measurement relies on the *Doppler effect*, in which radiation is shifted in frequency when the source is moving towards or away from the observer. When a star emitting electromagnetic radiation of frequency v moves with a speed s relative to an observer, the observer detects radiation of frequency $v_{\text{receding}} = vf$ or $v_{\text{approaching}} = v/f$, where $f = \{(1 - s/c)/(1 + s/c)\}^{1/2}$ and c is the speed of light. It is easy to see that $v_{\text{receding}} < v$ and a receding star is characterized by a *red shift* of its spectrum with respect to the spectrum of an identical, but stationary source. Furthermore, $v_{\text{approaching}} > v$ and an approaching star is characterized by a *blue shift* of its spectrum with respect to the spectrum of an identical, but stationary source. In a typical experiment, v is the frequency of a spectral line of an element measured in a stationary Earth-bound laboratory from a calibration source, such as an arc lamp. Measurement of the same spectral line in a star gives v_{star} and the speed of recession or approach may be calculated from the value of v and the equations above. (a) Three Fe I lines of the star HDE 271 182, which belongs to the Large Magellanic Cloud, occur at 438.882 nm, 441.000 nm, and 442.020 nm. The same lines occur at 438.392 nm, 440.510 nm, and 441.510 nm in the spectrum of an Earth-bound iron arc. Determine whether HDE 271 182 is receding from or approaching the Earth and estimate the star's radial speed with respect to the Earth. (b) What additional information would you need to calculate the radial velocity of HDE 271 182 with respect to the Sun?

10.28 The *d*-metals iron, copper, and manganese form cations with different oxidation states. For this reason, they are found in many oxidoreductases and in several proteins of oxidative phosphorylation and photosynthesis (*Impact* I7.2 and I23.2). Explain why many *d*-metals form cations with different oxidation states.

10.29 Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and dementia, is also a member of the group but its chemical properties are dominated by the +3 oxidation state. Examine this issue by plotting the first, second, and third ionization energies for the Group 13 elements against atomic number. Explain the trends you observe. *Hints.* The third ionization energy, I_3, is the minimum energy needed to remove an electron from the doubly charged cation: $E^{2+}(g) \rightarrow E^{3+}(g) + e^-(g)$, $I_3 = E(E^{3+}) - E(E^{2+})$. For data, see the links to databases of atomic properties provided in the text's web site.