

PART 1

Structures and microstructures

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The electron structure of atoms

- What is a wavefunction?
- What is an atomic term?
- How are the energy levels of atoms labelled?

An atom of any element is made up of a small massive *nucleus*, in which almost all of the mass resides, surrounded by an *electron cloud*. Each element is differentiated from all others by the amount of positive charge on the nucleus, called the *proton number* or *atomic number*, Z . The proton number is an integer specifying the number of protons in the nucleus, each of which carries one unit of positive charge. In a neutral atom, the nuclear charge is exactly balanced by Z electrons in the outer electron cloud, each of which carries one unit of negative charge. Variants of atoms that have slightly more or fewer electrons than are required for charge neutrality are called *ions*; those which have lost electrons have an overall positive charge and those that have gained electrons have an overall negative charge. Positively charged ions are sometimes called *cations* and negatively charged ions are sometimes called *anions*.

The electrons associated with the chemical elements in a material (whether in the form of a gas, liquid or solid) control the chemical and physical properties of the atoms. The energies and regions of space occupied by electrons in an atom may be calculated using *quantum theory*.

1.1 The hydrogen atom

1.1.1 The quantum mechanical description

A hydrogen atom is the simplest of atoms. It consists of a nucleus consisting of a single proton carrying one unit of positive charge, together with a single bound electron carrying one unit of negative charge. *Hydrogenic* or *hydrogen-like* atoms or ions are very similar, in that they can be analysed in terms of a single electron bound to a nucleus with an apparent charge different from unity. Information about the electron can be obtained by solving the *Schrödinger equation*, in which the electron is represented as a wave. The permitted solutions to this equation, called *wavefunctions*, describe the energy and probability of location of the electron in any region around the nucleus. Each of the solutions contains three integer terms called *quantum numbers*. They are n , the *principal quantum number*, l , the *orbital angular momentum quantum number*, and m_l , the *magnetic quantum number*. The names of the last two quantum numbers pre-date modern

quantum chemistry. They are best regarded as labels rather than representing classical concepts such as the angular momentum of a solid body. The quantum numbers define the *state* of a system.

1.1.2 The energy of the electron

The principal quantum number, n , defines the energy of the electron. It can take integer values 1, 2, 3 . . . to infinity. The energy of the electron is lowest for $n=1$ and this represents the most stable or *ground state* of the hydrogen atom. The next lowest energy is given by $n=2$, then by $n=3$, and so on. The energy of each state is given by the simple formula:

$$E = \frac{-A}{n^2} \quad (1.1)$$

where A is a constant equal to $2.179 \times 10^{-18} \text{ J}$ (13.6 eV),¹ and E is the energy of the level with principal quantum number n . The negative sign in the equation indicates that the energy of the electron is chosen as zero when n is infinite, that is to say, when the electron is no longer bound to the nucleus.

There is only one wavefunction for the lowest energy, $n=1$, state. The states of higher energy each have n^2 different wavefunctions, all of which have the same energy, that is, there are four different wavefunctions corresponding to $n=2$, nine different wavefunctions for $n=3$, and so on. These wavefunctions are differentiated from each other by different values of the quantum numbers l and m_l , as explained below. Wavefunctions with the same energy are said to be *degenerate*.

It is often convenient to represent the energy associated with each value of the principal quantum number, n , as a series of steps or *energy levels* (Figure 1.1). It is important to be aware of the fact that the electron can only take the exact energy values given by equation (1.1). When an electron gains energy, it jumps from an energy level with a lower value of n to a level with a higher value of n . When

an electron loses energy, it drops from an energy level with a higher value of n to an energy level with a lower value. The discrete packets of energy given out or taken up in this way are *photons* of electromagnetic radiation (Chapter 14). The energy of a photon needed to excite an electron from energy E_1 , corresponding to an energy level n_1 , to energy E_2 , corresponding to an energy level n_2 , is given by:

$$\begin{aligned} E &= E_1 - E_2 = -2.179 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ J} \\ &= -13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ eV} \end{aligned} \quad (1.2)$$

The energy of the photon emitted when the electron falls back from E_2 to E_1 is the same. The frequency, ν (or the equivalent wavelength, λ), of the photons that are either emitted or absorbed during these energy changes is given by the equation:

$$E = h\nu = \frac{hc}{\lambda} \quad (1.3)$$

where h is the Planck constant. (Note that this equation applies to the transition between any two

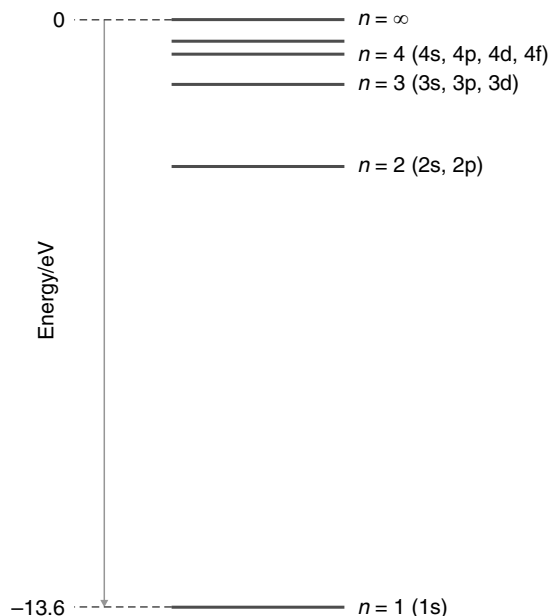


Figure 1.1 The energy levels available to an electron in a hydrogen atom.

¹ The unit of energy, *electron volt*, eV, is frequently used for atomic processes. $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

energy levels on any atom, not just between energy levels on hydrogen or a hydrogenic atom.) The energy needed to free the electron completely from the proton, which is called the *ionisation energy* of the hydrogen atom, is given by putting $n_1 = 1$ and $n_2 = \infty$ in equation (1.2). The ionisation energy is 13.6 eV (2.179×10^{-18} J).

In the case of a single electron attracted to a nucleus of charge $+Ze$, the energy levels are given by:

$$E = \frac{-AZ^2}{n^2} \quad (1.4)$$

This shows that the energy levels are much lower than in hydrogen, and that the ionisation energy of such atoms is considerably higher.

1.1.3 Electron orbitals

The principal quantum number is not sufficient to determine the location of the electron in a hydrogen atom. In addition, the two other interdependent quantum numbers, l and m_l , are needed.

- l takes values of 0, 1, 2 . . . ($n - 1$)
- m_l takes values of 0, ± 1 , ± 2 . . . $\pm l$

Each set of quantum numbers defines the *state* of the system and is associated with a wavefunction. For a value of $n = 1$, there is only one wavefunction, corresponding to $n = 1$, $l = 0$ and $m_l = 0$. For $n = 2$, l can take values of 0 and 1, and m_l can then take values of 0, associated with $l = 0$, and -1 , 0 and $+1$, associated with $l = 1$. For $n = 3$, l can take values of 0, 1 and 2, and m_l then can take values of 0, associated with $l = 0$, -1 , 0 and $+1$, associated with $l = 1$, and -2 , -1 , 0, $+1$, $+2$, associated with $l = 2$. These states are referred to as *orbitals* and for historical reasons they are given letter symbols. Orbitals with $l = 0$ are called *s orbitals*, those with $l = 1$ are called *p orbitals*, those with $l = 2$ are called *d orbitals*, and those with $l = 3$ are called *f orbitals* (Table 1.1).

The set of orbitals derived from a single value of the principal quantum number form a *shell*. The lowest energy shell is called the K shell, and corresponds to $n = 1$. The other shells are labelled alphabetically

Table 1.1 Quantum numbers and orbitals for the hydrogen atom

n	l	m_l	Orbital	Shell
1	0	0	1s	K
2	0	0	2s	L
	1	$-1, 0 +1$	2p (3 orbitals)	
3	0	0	3s	M
	1	$-1, 0 +1$	3p (3 orbitals)	
	2	$-2, -1, 0 +1, +2$	3d (5 orbitals)	
4	0	0	4s	N
	1	$-1, 0 +1$	4p (3 orbitals)	
	2	$-2, -1, 0 +1, +2$	4d (5 orbitals)	
	3	$-3, -2, -1, 0, +1, +2, +3$	4f (7 orbitals)	

(Table 1.1). For example, the L shell corresponds to the four orbitals associated with $n = 2$.

There is only one s orbital in any shell, labelled 1s, 2s and so on. There are three p orbitals in all shells from $n = 2$ upwards, collectively called 3p, 4p and so on. There are five d orbitals in the shells from $n = 3$ upwards, collectively called 3d, 4d, 5d and so on. There are seven f orbitals in the shells from $n = 4$ upwards, collectively called 4f, 5f and so on.

1.1.4 Orbital shapes

The *probability* of encountering the electron in a certain small volume of space surrounding a point with coordinates x , y and z is proportional to the square of the wavefunction at that point. With this information, it is possible to map out regions around the nucleus where the electron density is greatest.

The probability of encountering an electron in an s orbital does not depend upon direction but does vary with distance from the nucleus (Figure 1.2a,b,c). This probability peaks at a radial distance of 0.05292 nm for a 1s orbital – equal to the distance calculated by Bohr as the minimum allowed radius of an orbiting ‘planetary’ electron around a proton, and called the *Bohr radius*. As the electron is promoted to the 2s, 3s, 4s orbitals, the maximum probability peaks further and further from the nucleus. Thus a high-energy electron is most likely to be found far from the

nucleus. Generally, s orbitals are drawn as spherical *boundary surfaces* that enclose an arbitrary volume in which there is a high probability, say 95%, that the electron will be found (Figure 1.2d,e).

All other wavefunctions are specified by three quantum numbers and can be divided into two parts: a radial part, with similar probability shapes to those shown in Figure 1.2, multiplied by an angular part. The maximum probability of finding the electron depends upon both the radial and angular parts of the wavefunction, and the resulting boundary surfaces have complex shapes. For many purposes, however, it is sufficient to describe only the angular part of the wavefunction.

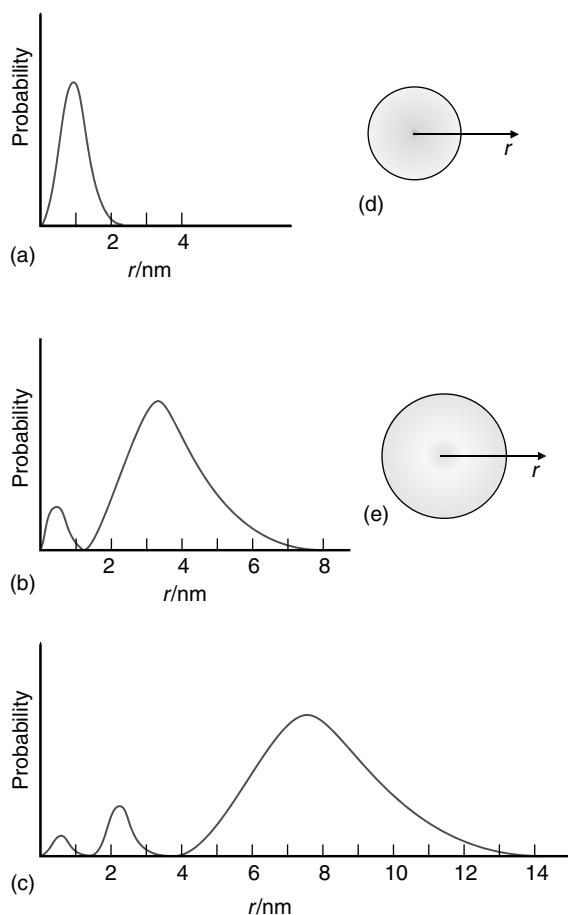


Figure 1.2 The probability of finding an electron at a distance r from the nucleus: (a) 1s; (b) 2s; (c) 3s. The boundary surfaces of the orbitals: (d) 1s; (e) 2s.

The boundary surfaces of the angular parts of the three p orbitals are approximately dumbbell-shaped, each consisting of two lobes. These lie along three mutually perpendicular directions, which it is natural to equate to x , y and z -axes (Figure 1.3). The corresponding orbitals are labelled np_x , np_y and np_z , for

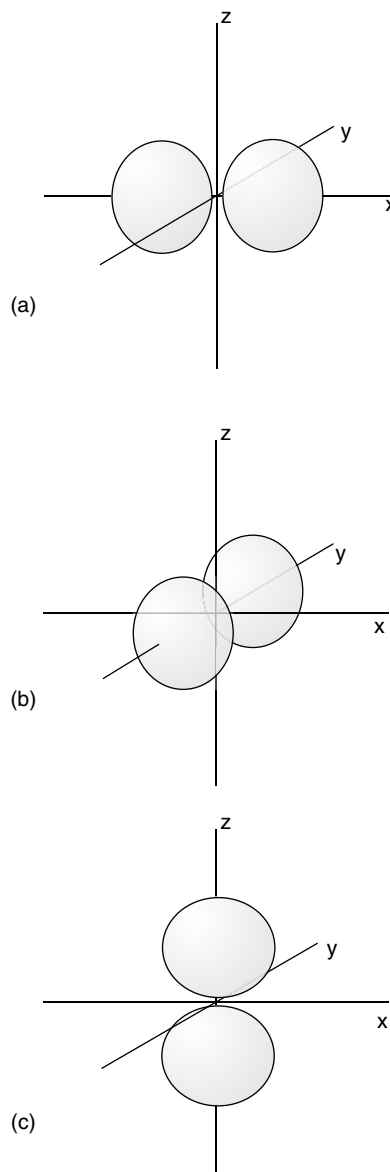


Figure 1.3 The boundary surfaces of the p orbitals: (a) p_x ; (b) p_y ; (c) p_z .

example, $2p_x$, $2p_y$ and $2p_z$. Note that the electron occupies both lobes of the p orbital. The probability of encountering a p electron on the perpendicular plane that separates the two halves of the dumbbell is zero, and this plane is called a *nodal plane*. The sign of the wavefunction is of importance when orbitals overlap to form bonds. The two lobes of each p orbital are labelled as $+$ and $-$, and the sign changes as a nodal plane is crossed. The radial probability of encountering an electron in a p orbital is zero at the nucleus, and increases with distance from the nucleus. The maximum probability is further from the nucleus for an electron in a $3p$ orbital than a $2p$ orbital, and so on, so that $3p$ orbitals have a greater extension in space than $2p$ orbitals.

The distribution of the electron in either the d or f orbitals is more complicated than those of the p orbitals. There are five d orbitals, and seven f orbitals. Three of the $3d$ set of wavefunctions have lobes lying between pairs of axes, d_{xy} between the x - and y -axes, d_{xz} between the x - and z -axes, and d_{yz} between the y - and z -axes. The other two orbitals have lobes along the axes, $d_{x^2-y^2}$ pointing along x and y , and d_{z^2} pointing along the z -axis (Figure 1.4). Except for the d_{z^2} orbital, two perpendicular planar nodes separate the lobes and intersect at the nucleus. In the d_{z^2} orbital, the nodes are conical surfaces.

1.2 Many-electron atoms

1.2.1 The orbital approximation

If we want to know the energy levels and electron distribution of an atom with a nuclear charge of $+Z$ surrounded by Z electrons, it is necessary to write out a more extended form of the Schrödinger equation that takes into account not only the attraction of the nucleus for each electron, but also the repulsive interactions between the electrons themselves. The resulting equation has proved impossible to solve analytically, but increasingly accurate numerical solutions have been available for many years.

The simplest level of approximation, called the *orbital approximation*, supposes that an electron moves in a potential due to the nucleus and the average field of all the other electrons present in the

atom. This means that the electron experiences an *effective nuclear charge*, Z_{eff} , which is considered to be located as a point charge at the nucleus of the atom. In this approximation the orbital shapes are the same as for hydrogen, but the energy levels of all of the orbitals drop sharply as Z_{eff} increases (Figure 1.5). When one reaches lithium, $Z=3$, the $1s$ orbital energy has already decreased so much that it forms a chemically unreactive shell. This is translated into the concept of an atom as consisting of unreactive *core electrons*, surrounded by a small number of outermost *valence electrons*, which are of chemical significance. Moreover, the change of energy as Z increases justifies the approximation that the valence electrons of all atoms are at similar energies.

Although *shapes* of the orbitals are not changed from the shapes found for hydrogen, the radial part of the wave function is altered, and the *extension* of the orbitals increases as the effective nuclear charge increases. This corresponds to the idea that heavy atoms are larger than light atoms. In addition, a different effective nuclear charge is experienced by electrons in differing orbitals. This has the effect of separating the energy of the ns , np , nd and nf orbitals that are identical in hydrogen. It is found that for any value of n , the s orbitals have lowest energy, the three p orbitals have equal and slightly higher energy, the five d orbitals have equal and slightly higher energy again, and the seven f orbitals have equal and slightly higher energy again (Figure 1.6). However, the energy differences between the higher energy orbitals are very small, and this simple ordering is not followed exactly for heavier atoms.

1.2.2 Electron spin and electron configuration

The results presented so far, derived from solutions to the simplest form of the Schrödinger equation, do not explain the observed properties of atoms exactly. In order to account for the discrepancy the electron is allocated a fourth quantum number called the *spin quantum number*, s . The spin quantum number has a value of $1/2$. The spin of an electron on an atom

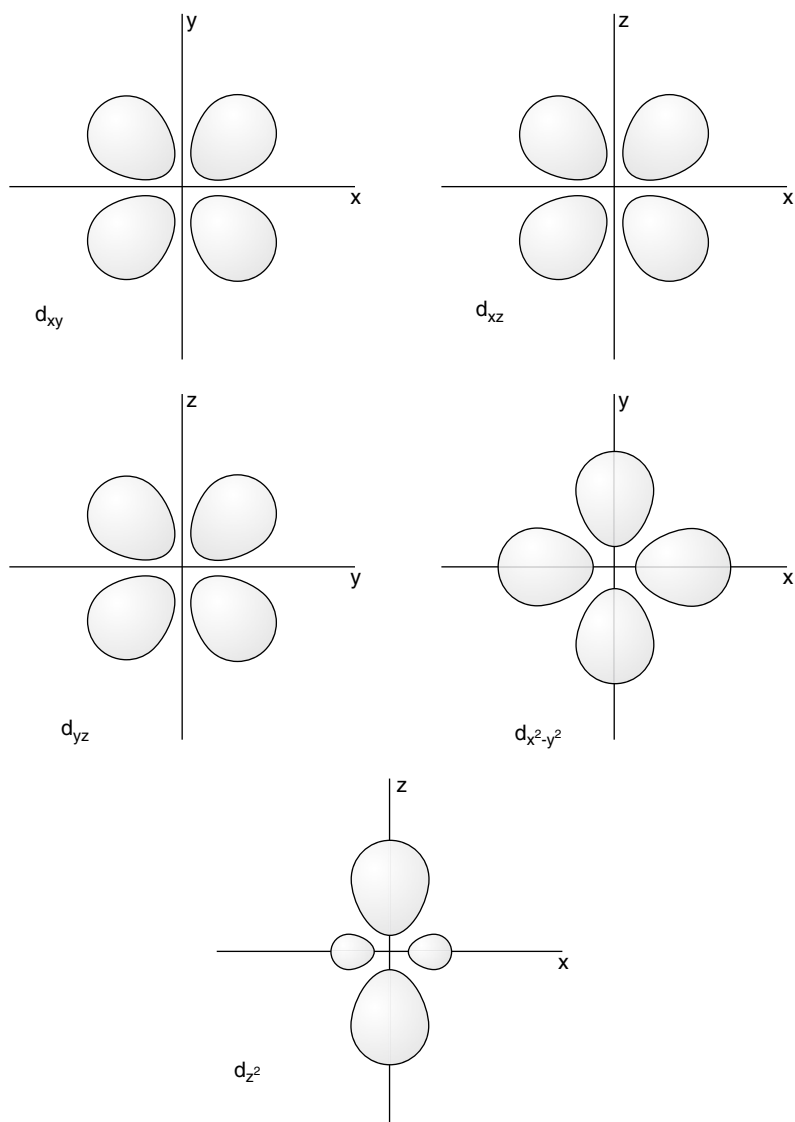


Figure 1.4 The boundary surfaces of the d orbitals: (a) d_{xy} ; (b) d_{xz} ; (c) d_{yz} ; (d) $d_{x^2-y^2}$; (e) d_{z^2} .

can adopt one of two different directions, represented by a quantum number, m_s , which takes values of $+\frac{1}{2}$ or $-\frac{1}{2}$. These two spin directions have considerable significance in chemistry and physics and are frequently represented by $\uparrow$, *spin up*, or α , and $\downarrow$, *spin down* or β . Although the spin quantum number was originally postulated to account for certain experimental observations, it arises naturally in

more sophisticated formulations of the Schrödinger equation that take into account the effects of relativity.

The *electron configuration* of an atom is the description of the number of electrons in each orbital, based upon the orbital model. This is usually given for the lowest energy possible, called the *ground state*. To obtain the electron configuration

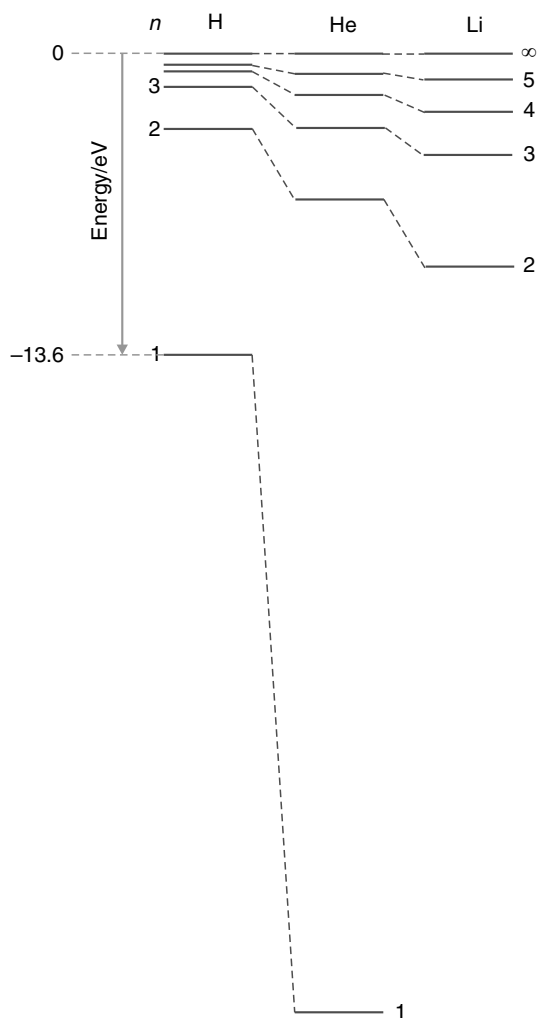


Figure 1.5 The decrease in energy of the orbitals of the first three elements in the periodic table, hydrogen, helium and lithium, as the charge on the nucleus increases.

of an atom, the electrons are fed into the orbitals, starting with the lowest energy orbital, $1s$, and then continuing to the higher energy orbitals so as to fill them systematically from the bottom up (Figure 1.6). This is called the *Aufbau* (or *building up*) *principle*. Before the configurations can be constructed, it is vital to know that each orbital can hold a maximum of two electrons, which must have opposite values of m_s , either $+\frac{1}{2}$ or $-\frac{1}{2}$. This fundamental feature of quantum mechanics is due to the *Pauli Exclusion Principle*: no more than two

electrons can occupy a single orbital, and if they do, the spins must be different, that is, *spin up* and *spin down*. Two electrons in a single orbital are said to be *spin paired*.

The electron configurations of the elements can now be described. Each orbital can hold a maximum of two electrons, so that s orbitals can hold two electrons, the three p orbitals can hold a total of six electrons, the five d orbitals can hold a total of ten electrons and the seven f orbitals a total of 14 electrons. When electrons are allocated to the p , d and f orbitals, the lowest energy situation is that in which the electrons go into an unoccupied orbital if possible. This situation is expressed in *Hund's first rule*: when electrons have a choice of several orbitals of equal energy, the lowest energy, or ground state, configuration corresponds to the occupation of separate orbitals with parallel spins rather than fewer orbitals with paired spins.

Hydrogen has only one electron, and it will go into the orbital of lowest energy, the $1s$ orbital. The electron configuration is written as $1s^1$. Helium has two electrons and both can be placed in the $1s$ orbital to give an electron configuration $1s^2$. There is only one orbital associated with the $n=1$ quantum number, hence the corresponding shell (K) is now filled. Further electrons must now be added to the L shell, corresponding to the $2s$ and $2p$ orbitals. Proceeding as before, the electron configuration of the next few elements are Li, $1s^2 2s^1$ or, in a compact notation [He] $2s^1$; Be, [He] $2s^2$; B, [He] $2s^2 2p^1$; C, [He] $2s^2 2p^2$ and so on. Note that it is normal practice to replace the configuration of filled inner shells corresponding to a noble gas by a contraction: [He] for helium, [Ne] for neon, [Ar] for argon, [Kr] for krypton, [Xe] for xenon and [Rn] for radon. Thus the electron configuration of Rb is written [Kr] $5s^1$, signifying a single electron outside of the K, L, M and N closed shells that make up the configuration of the noble gas krypton.

1.2.3 The periodic table

The periodic table (Figure 1.7 and front endpaper), originally an empirical arrangement of the elements in terms of chemical properties, is understandable in

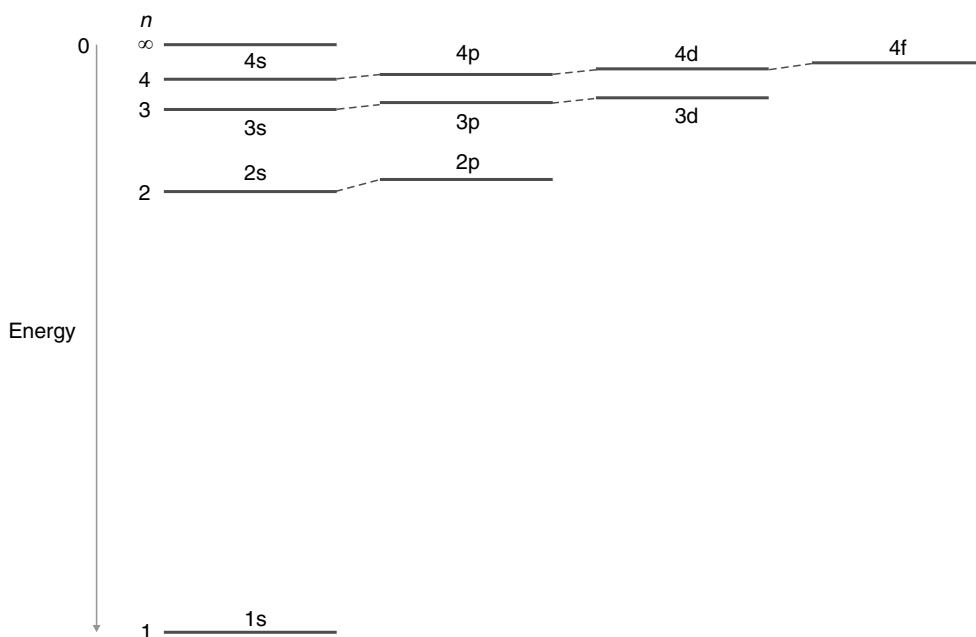


Figure 1.6 The schematic energy levels for a light, many-electron atom.

terms of the electron configurations just discussed. The chemical and many physical properties of the elements are simply controlled by the outer (valence) electrons. The valence electron

configuration varies in a systematic and repetitive way as the various shells are filled. This leads naturally to the periodicity displayed in the periodic table. For example, the filled shells are very stable

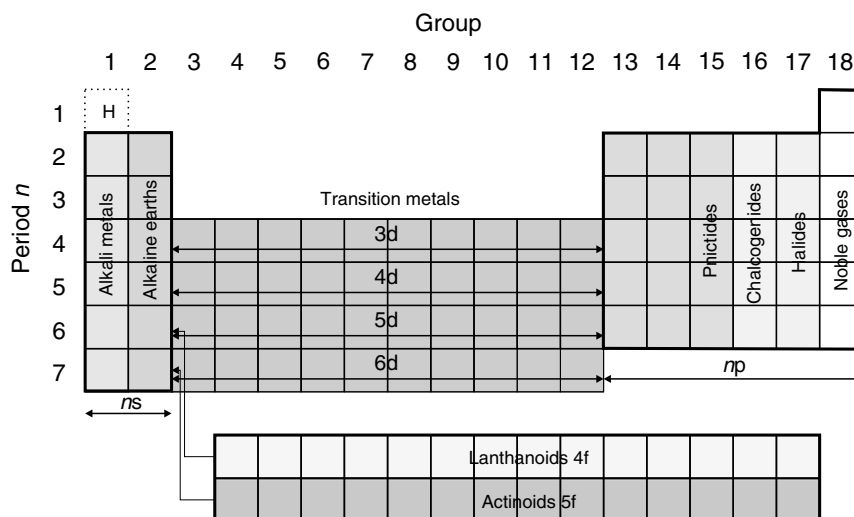


Figure 1.7 The relationship between electronic configuration and the periodic table arrangement.

configurations and only take part in chemical reactions under extreme conditions. The atoms with this configuration, the *noble gases*, are placed in group 18 of the periodic table. A new noble gas appears each time a shell is filled. Following any noble gas is an element with one electron in the outermost s orbital, lithium, sodium, potassium, and so on. These are the *alkali metals*, found in Group 1, and once again, a new alkali metal is found after each filled shell. Similarly, the *alkaline earth* elements, typified by magnesium, calcium and strontium, listed in Group 2 of the periodic table, all have two valence electrons, both in the outermost s orbital. Thus, the periodic table simply expresses the Aufbau principle in a chart format.

The outermost electrons take part in chemical bonding. The main group elements are those with electrons in outer s and p orbitals giving rise to strong chemical bonds (Chapter 2). The valence electron configuration of all the elements in any group is identical, indicating that the chemical and physical properties of these elements will be very similar. The d and f orbitals are shielded by s and p orbitals from strong interactions with surrounding atoms and do not take part in strong chemical bonding. Those elements with partly filled d orbitals are called *transition metals*, typified by iron and nickel, while those with partly filled f orbitals are called the *lanthanoids* (4f) or *actinoids* (5f). The electrons in these orbitals are responsible for many of the interesting electronic, magnetic and optical properties of solids.

1.3 Atomic energy levels

1.3.1 Spectra and energy levels

Spectra are a record of transitions between electron energy levels. Each spectral line can be related to the switch from one energy level to another. The frequency ν (or the equivalent wavelength, λ) of the spectral line is related to the energy separation of the two energy levels, ΔE , by equation (1.3):

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

where h is Planck's constant.

The electron configurations described above, which essentially apply to a single electron moving under the combined electrostatic field of the nucleus and all of the other electrons, are not able to account for the observed transitions. A more complex model of the atom is required to derive the possible energy levels appropriate to any electron configuration. There are a number of ways of deriving these *many-electron* quantum numbers and the associated *many-electron states* of the atom.

The approach most frequently encountered, called *Russell-Saunders coupling*, makes the approximation that the electrostatic repulsion between electrons is the most important energy term. To obtain revised configurations, all of the individual s values of the electrons are summed to yield a total spin angular momentum quantum number S . (Note that one-electron quantum numbers are written in lower case, while many-electron quantum numbers are written in upper case.) Similarly, all of the individual l values for the electrons present are summed to give a total orbital angular momentum quantum number L . The values of S and L can also be summed to give a total angular momentum quantum number J .

An alternative approach to Russell-Saunders coupling is to assume that the interaction between the orbital angular momentum and the spin angular momentum is the most important. This interaction is called *spin-orbit coupling*. In this case, the s and l quantum numbers for an individual electron are added to give a total angular momentum number j for a single electron. These values of j are then added to give the total angular momentum quantum number J , for the whole atom. The technique of adding j values to obtain energy levels is called *j-j coupling*.

Broadly speaking, Russell-Saunders coupling works well for lighter atoms and *j-j* coupling for heavier atoms. Other coupling schemes have also been worked out which find use for medium and heavy atoms.

1.3.2 Terms and term symbols

In the Russell-Saunders coupling scheme, the total spin angular momentum quantum number, $S(2)$, for two electrons is obtained by combining the

individual quantum numbers s_1 and s_1 in the following way:

$$S(2) = (s_1 + s_2), (s_1 + s_2 - 1), \dots |s_1 - s_2|$$

where $|s_1 - s_2|$ is the modulus (absolute value, taken as positive) of $s_1 - s_2$. As s_1 and s_2 are equal to $1/2$, then $S(2) = 1$ or 0 .

In order to obtain the value of S for three electrons, $S(3)$, the value for two electrons, $S(2)$, is combined with the spin quantum number ($s_3 = 1/2$) of the third electron, in the same way:

$$S(3) = (S(2) + 1/2), (S(2) + 1/2 - 1), \dots \\ |S(2) - 1/2|$$

Both of the values for $S(2)$, 1 and 0, are permitted, so we obtain:

- $S(3) = 1 + 1/2, 1 + 1/2 - 1 = 3/2, 1/2$
- $S(3) = 0 + 1/2 = 1/2$

Thus $S(3)$ can take values of $3/2$ or $1/2$.

The same procedure, called the *Clebsch-Gordon rule*, is used to obtain the S values for four electrons, by combining s_4 with $S(3)$, and so on. It will be found that for an even number of electrons, S values are integers, and for an odd number of electrons, S values are half-integers. As all electrons in filled shells are spin-paired, it is only necessary to count the spins in the outer unfilled orbitals to obtain values of S for the atom as a whole.

The total angular momentum quantum number, L , is obtained in a similar fashion. For two electrons with individual angular momentum quantum numbers l_1 and l_2 , the total angular momentum quantum number, $L(2)$ is:

$$L(2) = (l_1 + l_2), (l_1 + l_2 - 1), \dots |l_1 - l_2|$$

In the case of three electrons, the Clebsch-Gordon rule is applied thus:

$$L(3) = (L(2) + l_3), (L(2) + l_3 - 1), \dots |L(2) - l_3|$$

using every value of $L(2)$ obtained previously. As before, all closed shells have zero angular

momentum, so in deciding L , only outer electrons in unfilled shells need to be counted.

The value of S is not used directly, but is replaced by the *spin multiplicity*, $2S + 1$. Similarly, the total angular momentum quantum number, L , is replaced by a letter symbol similar to that used for the single electron quantum number l . The correspondence is:

L	0	1	2	3	4	5	6
Letter	S	P	D	F	G	H	I

After $L = 3$, F, the sequence of letters is alphabetic, omitting J. Be aware that the symbol S has two interpretations, as the value of L (S Roman) and as the value of total spin (S italic).

The compatible combinations of S and L are written in the form ^{2S+1}L , called a *term symbol*. It represents a set of energy levels, called a *term* in spectroscopic parlance. States with a multiplicity of 1 are called *singlet* states, states with a multiplicity of 2 are called *doublet* states, with multiplicity of three, *triplets*, with multiplicity 4, *quartets*, and so on. Hence, 1S is called singlet S, and 3P is called triplet P.

For example, the terms arising from the two p electrons on carbon, C, with $l_1 = l_2 = 1$, are obtained in the following way:

$$S = 1/2 + 1/2, 1/2 - 1/2 = 1, 0.$$

$$2S + 1 = 3 \text{ or } 1.$$

$$L = (1 + 1), (1 + 1 - 1), |1 - 1| = 2, 1, 0 (D, P, S)$$

The total number of possible terms for the two p electrons is given by combining these values:

$$^3D, ^3P, ^3S, ^1D, ^1P, ^1S$$

Note that not all of these possibilities are allowed for any particular configuration, because the Pauli Exclusion Principle limits the number of electrons in each orbital to two with opposed spins. When this is taken into account (the method is straightforward but time-consuming and is not described here) the allowed terms are:

$$^3P, ^1D, ^1S$$

In general the *energies* of the terms are difficult to obtain and must be calculated using quantum mechanical procedures. Fortunately the lowest energy (ground state) term is easily found, using Hund's *second rule*: (a) *The term with the lowest energy has the highest multiplicity*; (b) *For terms with the same value of multiplicity, the term with the highest value of L is lowest in energy*.

There is a simple method for determining the ground state of any atom or ion. The procedure is:

1. Draw a set of boxes corresponding to the number of orbitals available. For a p electron, this is three (Figure 1.8).
2. Label each box with the value of m_l , highest on the left and lowest on the right.
3. Fill the boxes with unpaired electrons, from left to right. When each box contains one electron, start again at the left.
4. Sum the m_s values of each electron, $+\frac{1}{2}$ or $-\frac{1}{2}$, to give the maximum value of S .
5. Sum the m_l values of each electron to give a maximum value of L .
6. Write the ground term ^{2S+1}L .

Using this technique (Figure 1.8), the ground term of both the $2p^2$ and $2p^4$ configurations is 3P .

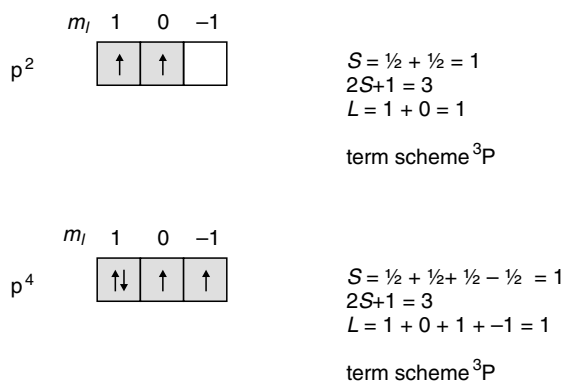


Figure 1.8 The derivation of ground state term symbols for p^2 and p^4 electron configurations.

1.3.3 Levels

The term symbol does not account for the true energy level complexity found in atoms. For example, the spectrum of an atom in a magnetic field has more lines present than the same atom in the absence of the magnetic field, a feature called the *Zeeman effect*. A similar, but different, change, called the *Stark effect*, arises in the presence of a strong electric field.

These result from the interaction between the spin and the orbital momentum (spin-orbit coupling) that is ignored in Russell-Saunders coupling. A new quantum number, J , is needed. It is given by:

$$J = (L + S), (L + S - 1), \dots |L - S|$$

where $|L - S|$ is the modulus (absolute value, taken as positive) of L minus S . Thus the term 3P has J values given by:

$$J = (1 + 1), (1 + 1 - 1), \dots |1 - 1| = 2, 1, 0$$

The new quantum number is incorporated as a subscript to the term, now written $^{2S+1}L_J$, and this is no longer called a term symbol, but a *level*. Each value of J represents a different energy level. It is found that a singlet term always gives one level, a doublet, two, a triplet three, and so on. Thus, ground state term 3P is composed of three levels: 3P_0 , 3P_1 and 3P_2 . The magnitude of the energy difference between these levels depends upon the strength of the interaction between L and S .

In a magnetic field, each of the $^{2S+1}L_J$ levels splits into $(2J + 1)$ separated energy levels. The spacing between the levels is given by $g_J \mu_B \mathbf{B}$, where g_J is the Landé g-value:

$$g_J = 1 + \frac{(J(J + 1) - L(L + 1) + S(S + 1))}{2J(J + 1)}$$

μ_B is a fundamental physical constant, the Bohr magneton, and $\mathbf{B}$ is the magnetic induction. (For more information, see section 12.1.3.) Hund's *third rule* allows the values of J to be sorted in order of energy: *The level with the lowest energy is that with lowest J value if the valence shell is up to half full,*

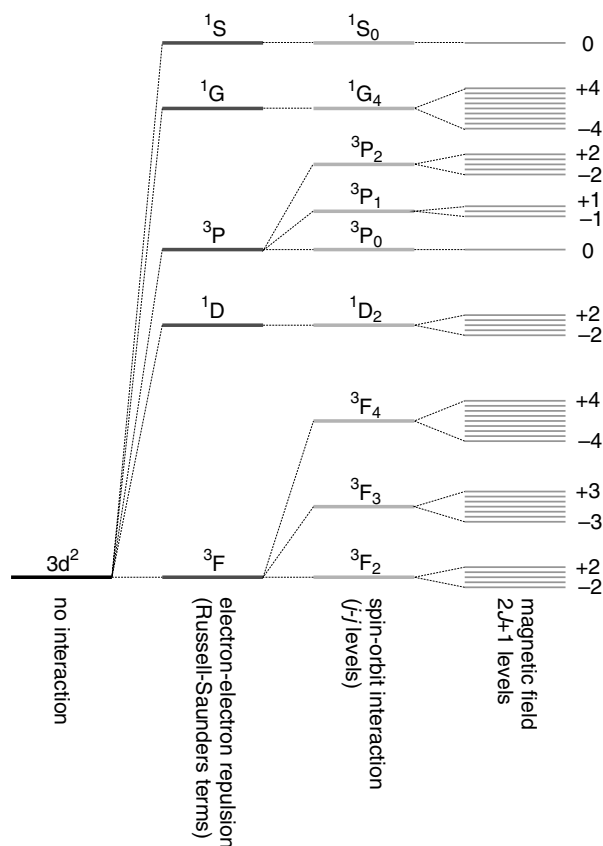


Figure 1.9 The evolution of the energy levels of an atom with a $3d^2$ electron configuration, taking into account increasing interactions. The energy scales are schematic.

and that with the highest J value if the valence shell is more than half full.

These increasing degrees of complexity are illustrated for a $3d^2$ transition metal atom in Figure 1.9. At the far left of the figure, the electron configuration is shown. This is useful chemically, but is unable to account for the spectra of the atom. The Russell-Saunders terms that arise from this arrangement are given to the right of the configuration. In Russell-Saunders coupling the electron–electron repulsion is considered to dominate the interactions. The terms are split further if spin–orbit coupling ($j-j$ coupling), is introduced. The number of levels that arise is the same as the multiplicity of the term, $2S + 1$. Finally, the levels are split further in a magnetic field to give $2J + 1$ levels. The magnitude of the splitting is proportional to the magnetic field,

and the separation of each of the new energy levels is the same.

Note that in a heavy atom it might be preferable to go from the electron configuration to levels derived by $j-j$ coupling, and then add on a smaller effect due to electron–electron repulsion (Russell-Saunders coupling) before finally including the magnetic field splitting. In real atoms, the energy levels determined experimentally are often best described by an intermediate model between the two extremes of Russell-Saunders and $j-j$ coupling.

1.3.4 Electronic energy level calculations

The allowed energies of the electrons in an atom are found by solving the Schrödinger equation. The

solution of this equation is possible for hydrogen, but is impossible even for the next atom, helium, with two electrons attached to a single nucleus. The reason for this is that each electron is attracted to the nucleus and repelled by the other electron. Thus the electrons do not move independently of one another, but their motion is *correlated*. This correlation term, which must be included in the calculation, is the central problem.

There are a number of ways of approximately calculating the electron energy levels. One will be described here, the *Hartree-Fock* procedure, because it provides a simple picture of atomic structure, and leads naturally to estimates of the electronic energies of molecules and non-molecular solids (Chapter 2). Take helium as the simplest example. In this case the wavefunction describing the two-electron atom, $\psi(\mathbf{r}_1, \mathbf{r}_2)$, which is a function of the position of the electrons, $\mathbf{r}_1$ and $\mathbf{r}_2$, is the product of (say), two hydrogenic 1s orbitals:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi 1s(\mathbf{r}_1)\alpha \phi 1s(\mathbf{r}_2)\beta - \phi 1s(\mathbf{r}_1)\beta \phi 1s(\mathbf{r}_2)\alpha$$

where $\phi 1s(\mathbf{r}_1)\alpha$ means that electron 1 is in the 1s orbital with spin α , and $\phi 1s(\mathbf{r}_2)\beta$ means that electron 2 is in the 1s orbital with spin β , and so on. (Note that any orbital functions can be chosen, not just hydrogenic orbitals, if they make computation easier.) Now electrons are indistinguishable and they have a spin, $\uparrow$ or $\downarrow$. Moreover, two electrons with the same spin cannot occupy the same orbital. To take this into account, the wavefunction of the system must change sign when any two electrons are exchanged, called *exchange symmetry*. This restriction on swapping electron positions lowers the energy by an amount called the *exchange energy*.

To solve the equation, electron 1 is supposed to experience an *effective* potential due to the nucleus and the charge density contributed by electron 2. The function $\phi(\mathbf{r}_2)$ is chosen and the effective potential is calculated. The Schrödinger equation written using the effective potentials is the *Hartree-Fock equation* for He. This approximate Schrödinger equation is used to calculate $\phi(\mathbf{r}_1)$ and the energy ϵ_1 . In general the new $\phi(\mathbf{r}_1)$ will be different than the original choice because

that was a hydrogenic function that ignored the potential due to the other electron. The process is now repeated for the orbital of electron 2 using the revised orbital of electron 1. This is continued until the revised input does not lead to any further change in the output orbitals, at which point the orbitals are *self-consistent*. The orbitals and energies are called *Hartree-Fock self-consistent field* (HF-SCF) orbitals and energies.

The main shortcoming of the method is that electronic correlation has been completely ignored and the results lack an important energy term. When energies are known experimentally from, for example, spectra, the correlation energy can be derived by subtracting the Hartree-Fock energy:

$$\text{Correlation energy} = E_{\text{exp}} - E_{\text{HF}}$$

Further reading

Elementary chemical concepts and an introduction to the periodic table are clearly explained in the early chapters of:

Atkins, P. and Jones, L. (1997) *Chemistry*, 3rd edn. W.H. Freeman, New York.

McQuarrie, D.A. and Rock, P.A. (1991) *General Chemistry*, 3rd edn. W.H. Freeman, New York.

The outer electron structure of atoms is described in the same books, and in greater detail in:

Atkins, P., de Paula, J. and Friedman, R. (2009) Chapter 4, *Quanta, Matter, and Change*. Oxford University Press, Oxford.

Shriver, D.F., Atkins, P.W. and Langford, C.H. (1994) Chapter 1, *Inorganic Chemistry*, 2nd edn. Oxford University Press, Oxford.

The quantum mechanics of atoms is described lucidly by:

McQuarrie, D.A. (1983) *Quantum Chemistry*. University Science Books, Mill Valley, CA.

An invaluable dictionary of quantum mechanical language and expressions is:

Atkins, P.W. (1991) *Quanta*, 2nd edn. Oxford University Press, Oxford.

Problems and exercises

Quick quiz

- 1 A wavefunction is
 - (a) A description of an electron.
 - (b) An atomic energy level.
 - (c) A solution to the Schrödinger equation
- 2 An orbital is
 - (a) A bond between an electron and a nucleus.
 - (b) A region where the probability of finding an electron is high.
 - (c) An electron orbit around an atomic nucleus.
- 3 The Pauli Exclusion principle leads to the conclusion that
 - (a) The position of an electron cannot be specified with limitless precision.
 - (b) Only two electrons of opposite spin can occupy a single orbital
 - (c) No two electrons can occupy the same orbital.
- 4 The configuration of an atom is
 - (a) The number of electrons around the nucleus.
 - (b) The electron orbitals around the nucleus.
 - (c) The arrangement of electrons in the various orbitals.
- 5 The outer electron configuration of the noble gases is
 - (a) ns^2np^6 .
 - (b) $ns^2np^6(n+1)s^1$.
 - (c) ns^2np^5 .
- 6 The valence electron configuration of the alkali metals is
 - (a) ns^2 .
 - (b) np^1 .
 - (c) ns^1 .
- 7 The valence electron configuration of carbon is
 - (a) $1s^22p^2$.
 - (b) $2s^22p^2$.
 - (c) $2s^22p^4$.
- 8 The valence electron configuration of calcium, strontium and barium is
 - (a) ns^2np^2 .
 - (b) ns^2 .
 - (c) $(n-1)d^1ns^2$.
- 9 What atom has filled K, L, M and N shells?
 - (a) Argon.
 - (b) Krypton.
 - (c) Xenon.
- 10 How many electrons can occupy orbitals with $n=3, l=2$?
 - (a) 6 electrons.
 - (b) 10 electrons.
 - (c) 14 electrons.
- 11 How many permitted l values are there for $n=4$?
 - (a) One.
 - (b) Two.
 - (c) Three.
- 12 How many electrons can occupy the 4f orbitals?
 - (a) 14.
 - (b) 10.
 - (c) 7.
- 13 Russell-Saunders coupling is
 - (a) A procedure to obtain the energy of many-electron atoms.
 - (b) A description of atomic energy levels.
 - (c) A procedure to obtain many-electron quantum numbers.
- 14 A term symbol is
 - (a) A label for an atomic energy level.
 - (b) A label for an orbital.
 - (c) A description of a configuration.
- 15 The many-electron quantum number symbol D represents
 - (a) $L=1$.
 - (b) $L=2$.
 - (c) $L=3$.

- 16 An atom has a term 1S . What is the value of the spin quantum number, S ?
- $\frac{1}{2}$.
 - 0.
 - 1.
- 17 An atom has a term 1S . What is the value of the orbital quantum number, L ?
- 2.
 - 1.
 - 0.

Calculations and questions

- What energy is required to liberate an electron in the $n = 3$ orbital of a hydrogen atom?
- What is the energy change when an electron moves from the $n = 2$ orbital to the $n = 6$ orbital in a hydrogen atom?
- Calculate the energy of the lowest orbital (the ground state) of the single-electron hydrogen-like atoms with $Z = 2$, (He^+) and 3, (Li^{2+}).
- What are the frequencies and wavelengths of the photons emitted from a hydrogen atom when an electron makes a transition from $n = 4$ to the lower levels $n = 1, 2$ and 3?
- What are the frequencies and wavelengths of the photons emitted from a hydrogen atom when an electron makes a transition from $n = 5$ to the lower levels $n = 1, 2$ and 3?
- What are the frequencies and wavelengths of photons emitted when an electron on a Li^{2+} ion makes a transition from $n = 3$ to the lower levels $n = 1$ and 2?
- What are the frequencies and wavelengths of photons emitted when an electron on a He^+ ion makes a transition from $n = 4$ to the lower levels $n = 1, 2$ and 3?
- Sodium lights emit yellow colour, with photons of wavelength 589 nm. What is the energy of these photons?
- Mercury lights emit photons with a wavelength 435.8 nm. What is the energy of the photons?
- What are the possible quantum numbers for an electron in a 2p orbital?
- Titanium has the term symbol 3F . What are the possible values of J ? What is the ground state level?
- Phosphorus has the term symbol 4S . What are the possible values of J ? What is the ground state level?
- Scandium has a term symbol 2D . What are the possible values of J ? What is the ground state level?
- Boron has a term symbol 2P . What are the possible values of J ? What is the ground state level?
- What is the splitting g_J , for sulphur, with ground state 3P_2 ?
- What is the splitting g_J , for iron, with a ground state 5D_4 ?
- Draw a diagram equivalent to Figure 1.9, for the ground state of a chlorine atom, with a ground state $^2P_{3/2}$.

