1

The electron structure of atoms

- What is a wavefunction and what information does it provide?
- Why does the periodic table summarise both the chemical and the physical properties of the elements?
- What is a term scheme?

1.1 Atoms

All matter is composed of aggregates of atoms. With the exception of radiochemistry and radioactivity (Chapter 16) atoms are neither created nor destroyed during physical or chemical changes. It has been determined that 90 chemically different atoms, the chemical elements, are naturally present on the Earth, and others have been prepared by radioactive transmutations. Chemical elements are frequently represented by symbols, which are abbreviations of the name of the element.

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. The nucleus is positively charged and in a neutral atom this charge is exactly balanced by an equivalent number of electrons, each of which carries one unit of negative charge. For our purposes, all nuclei can be imagined to consist of tightly bound subatomic particles called neutrons and protons, which are together called nucleons. Neutrons carry no charge and protons carry a charge of one unit of positive charge. Each element is differentiated from all others by the number of protons in the nucleus, called the proton number or atomic number, Z. In a neutral atom, the number of protons in the nucleus is exactly balanced by the Z electrons in the outer electron cloud. The number of neutrons in an atomic nucleus can vary slightly. The total number nucleons (protons plus neutrons) defines the mass number, A, of an atom. Variants of atoms that have the same atomic number but different mass numbers are called isotopes of the element. For example, the element hydrogen has three isotopes, with mass numbers 1, called hydrogen; 2 (one proton and one neutron), called deuterium; and 3 (one proton and two neutrons), called tritium. An important isotope of carbon is radioactive carbon-14, that has 14 nucleons in its nucleus, 6 protons and 8 neutrons.

The atomic mass of importance in chemical reactions is not the mass number but the average mass of a normally existing sample of the element. This will consist of various proportions of the isotopes that occur in nature. The mass of atoms is of the order of 10^{-24} g. For the purposes of calculating the mass changes that take place in chemical reactions, it is most common to use the

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mass, in grams, of one mole (6.022×10^{23}) of atoms or of the compound, called the molar mass. [A brief overview of chemical equations and the application of the mole are given in Section S1.1]. If it is necessary to work with the actual mass of an atom, as is necessary in radiochemical transformations (see Chapter 16), it is useful to work in atomic mass units, u. The atomic mass of an element in atomic mass units is numerically equal to the molar mass in grams. Frequently, when dealing with solids it is important to know the relative amounts of the atom types present as weights, the weight percent (wt%), or as atoms, the atom percent (at%). Details of these quantities and are given in Section S1.1.

The electrons associated with the chemical elements in a material (whether in the form of a gas, liquid or solid) control the important chemical and physical properties. These include chemical bonding, chemical reactivity, electrical properties, magnetic properties and optical properties. To understand this diversity, it is necessary to understand how the electrons are arranged and the energies that they have. The energies and regions of space occupied by electrons in an atom may be calculated by means of quantum theory.

Because the number of electrons is equal to the number of protons in the nucleus in a neutral atom, the chemical properties of an element are closely related to the atomic number of the element. An arrangement of the elements in the order of increasing atomic number, the periodic table, reflects these chemical and physical properties (Figure 1.1). The table is drawn so that the elements lie along a number of rows, called periods, and fall into a number of columns, called groups. The groups that contain the most elements (1, 2 and 13–18) are called main groups, and the elements in them are called main group elements. In older designs of the periodic table, these were given Roman numerals, I–VIII. The shorter groups (3–11) contain the

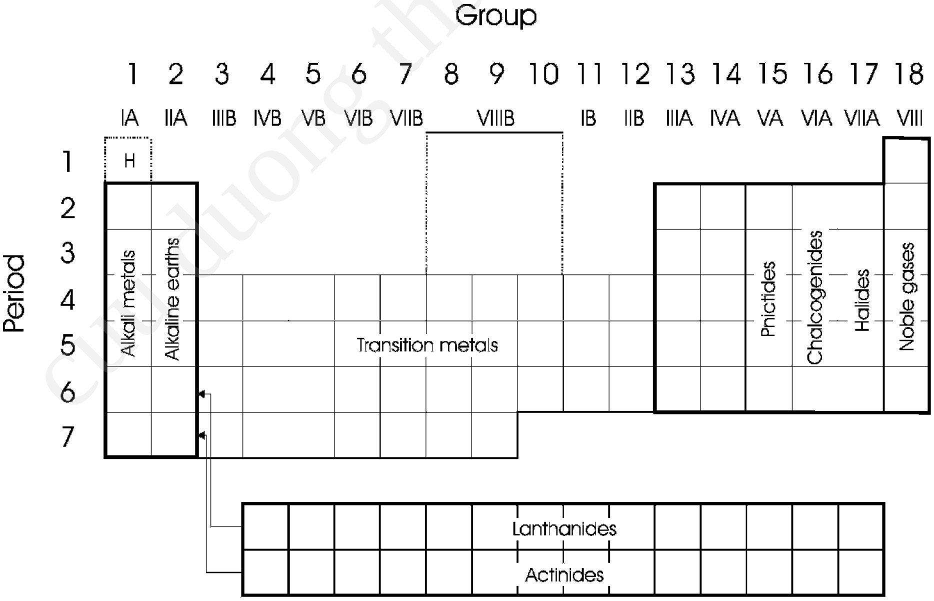


Figure 1.1 The periodic table of the elements. The table is made up of a series of columns, called groups, and rows, called periods. Each group and period is numbered. Elements in the same group have similar chemical and physical properties. The lanthanides and actinides fit into the table between groups 2 and 3, but are shown separately for compactness

transition metals. Group 12 is also conventionally associated with the transition metals. The blocks below the main table contain the inner transition metals. They are drawn in this way to save space. The upper row of this supplementary block contains elements called the lanthanides. They are inserted after barium, Ba, in Period 6 of the table. The lower block contains elements called the actinides. These are inserted after radium, Ra, in Period 7 of the table. The lightest atom, hydrogen, H, has unique properties and does not fit well in any group. It is most often included at the top of Group 1.

The chemical and physical properties of all elements in a single group are similar. However, the elements become more metallic in nature as the period number increases. The chemical and physical properties of the elements tend to vary smoothly across a period. Elements in Group 1 are most metallic in character, and elements in Group 18 are the least metallic. The properties of the elements lying within the transition metal blocks are similar. This family similarity is even more pronounced in the lanthanides and actinides.

The members of some groups have particular names that are often used. The elements in Group 1 are called the alkali metals; those in Group 2 are called the alkaline earth metals. The elements in Group 15 are called the pnictogens, and the compounds are called pnictides. The elements in Group 16 are called chalcogens and form compounds called chalcogenides. The elements in Group 17 are called the halogens, and the compounds that they form are called halides. The elements in Group 18 are very unreactive gases, called the noble gases.

Although the periodic table was originally an empirical construction, an understanding of the electron structure of atoms has made the periodic table fundamentally understandable.

1.2 The hydrogen atom

1.2.1 The quantum mechanical description of a hydrogen atom

A hydrogen atom is the simplest of atoms. It comprises a nucleus consisting of a single proton together with a single bound electron. The 'planetary' model, in which the electron orbits the nucleus like a planet, was initially described by Bohr in 1913. Although this model gave satisfactory answers for the energy of the electron, it was unable to account for other details and was cumbersome when applied to other atoms. In part, the problem rests upon the fact that the classical quantities used in planetary motion, position and momentum (or velocity), cannot be specified with limitless precision for an electron. This is encapsulated in the Heisenberg uncertainty principle, which can be expressed as follows:

$$\Delta x\,\Delta p \geq \frac{h}{4\,\pi}$$

where Δx is the uncertainty in the position of the electron, Δp the uncertainty in the momentum and h is the Planck constant. When this is applied to an electron attached to an atomic nucleus, it means that the exact position cannot be specified when the energy is known, and classical methods cannot be used to treat the system.

The solution to the problem was achieved by regarding the electron as a wave rather than as a particle. The idea that all particles have a wave-like character was proposed by de Broglie. The relationship between the wavelength, λ, of the wave, called the de Broglie wavelength, is given by:

$$\lambda = \frac{h}{p}$$

where h is the Planck constant and p is the momentum of the particle. In the case of an electron, the resulting wave equation, the Schrödinger equation, describes the behaviour of the electron well. The Schrödinger equation is an equation that gives information about the probability of finding the electron in a localised region around the nucleus, thus avoiding the constraints imposed by the Uncertainty Principle. There are a large number of permitted solutions to this equation, called wavefunctions, ψ, which describe the energy and probability of the location of the electron in any region around the proton 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 predate modern quantum chemistry. They are best regarded as labels rather than representing classical concepts such as the angular momentum of a solid body. Quantum numbers define the state of a system. The solutions to the wave equation can be written in a number of mathematically equivalent ways, one set of which is given in Table 1.1 for the three lowest-energy s orbitals.

Table 1.1 Some s wavefunctions

Orbital	Wavefunction
1s	$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2s	$\psi = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\sigma)e^{-\sigma/2}$
3s	$\psi = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\sigma+2\sigma^2)e^{-\sigma/3}$

Note: Z is the atomic number of the nucleus; a_0 is the Bohr radius, 5.29×10^{-11} m; $\sigma = Zr/a_0$; and r is the radial position of the electron.

1.2.2 The energy of the electron

The principal quantum number, n, defines the energy of the electron. It can take integral values $1, 2, 3 \ldots$ 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:

$$E = \frac{-A}{n^2} \tag{1.1}$$

where A is a constant equal to 2.179×10^{-18} J (13.6 eV) and E is the energy of the level with principal quantum number n. [The unit of energy 'electron volt' (eV) is frequently used for atomic processes. $1\,\text{eV} = 1.602 \times 10^{-19}$ J.] 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 wave function 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 wave functions for $n = 3$ and so on. These wave functions 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. This representation is shown in Figure 1.2. It is important to be aware of the fact that the electron can only take the exact energy values given by Equation (1.1).

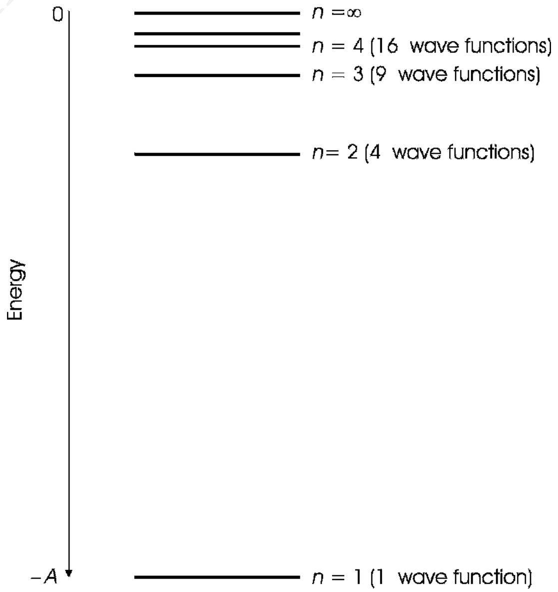


Figure 1.2 The energy levels available to an electron in a hydrogen atom. The energies are given by $-A/n^2$, and each level is n-fold degenerate. The lowest energy correspond to $n = 1$. The energy zero is taken at $n = \infty$, when the electron is removed from the atom

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 jumps 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 (see Chapter 14). The energy of a photon needed to excite an electron from an energy E_1, corresponding to an energy level n_1, to an energy E_2, corresponding to an energy level n_2, is given by:

$$E = E_1 - E_2 = -2.179 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\,\mathrm{J}$$
$$= -13.6\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\,\mathrm{eV} \qquad (1.2)$$

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 are given by the equation:

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

where h is the Planck constant and c is the speed of light. 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:

$$E = -AZ^2/n^2 \qquad (1.4)$$

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

1.2.3 The location of the electron

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 $0, 1, 2, \ldots, n-1$;
- m_l takes values of $0, \pm 1, \pm 2, \ldots, \pm l$.

Table 1.2 Quantum numbers and orbitals for the hydrogen atom

n	l	Orbital	m_l	Shell
1	0	1s	0	K
2	0	2s	0	L
	1	2p	$-1, 0, 1$	
3	0	3s	0	M
	1	3p	$-1, 0, 1$	
	2	3d	$-2, -1, 0, 1, 2$	
4	0	4s	0	N
	1	4p	$-1, 0, 1$	
	2	4d	$-2, -1, 0, 1, 2$	
	3	4f	$-3, -2, -1, 0, 1, 2, 3$	

Each set of quantum numbers defines the state of the system and is associated with a wavefunction. For a value of $n = 0$ there is only one wavefunction, corresponding to $n = 0$, $l = 0$ and $m_l = 0$. For $n = 2$, l can take values of 0 and 1, and m then can take values of 0, associated with $l = 0$, and -1, 0 and $+1$, associated with $l = 1$. The combinations possible are set out in Table 1.2.

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, ψ^2. With this information, it is possible to map out regions around the nucleus where the electron is most likely to be encountered. These regions 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. This terminology is summarised in Table 1.2.

The orbitals with the same 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, as set out in Table 1.2. For example, the L shell corresponds to the four orbitals associated with $n = 2$.

There is only one s orbital in any shell, 1s, 2s and so on. There are three different p orbitals in all shells from $n = 2$ upwards, corresponding to the m_l values of 1, 0 and -1. Collectively they are called 3p, 4p and so on. There are five *d* orbitals in the shells from $n = 3$ upwards, corresponding to the m_l values 2, 1, 0 -1, -2. Collectively they are called 3d, 4d, 5d and so on. There are seven different f orbitals in the shells from $n = 4$ upwards, corresponding to the m_l values 3, 2, 1, 0, -1, -2, -3. Collectively they are called 4f, 5f and so on.

1.2.4 Orbital shapes

The probability of encountering an electron in an s orbital does not depend upon direction. A surface of constant probability of encountering the electron is spherical. 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, as in Figures 1.3d and 1.3e. However, the probability of encountering an s electron does vary with distance from the nucleus, as shown in Figures 1.3a–1.3c for the 1s, 2s and 3s orbitals. The positions of the peaks in Figure 1.3 represent regions in which the probability of encountering the electron is greatest. These peaks can be equated with the shells described in Table 1.2. As can be seen from Figure 1.3, the maximum probability of finding an electron is further from the nucleus for an electron in a 3s orbital than it is for an electron in a 2s orbital. Thus, electrons with higher energies are most likely to be found further from the nucleus.

Because the other wavefunctions depend upon three quantum numbers it is more difficult to draw them in two-dimensions. These wavefunctions can be divided into two parts, a radial part, with similar probability shapes to those shown in Figure 1.3, multiplied by an angular part. The maximum probability of finding the electron depends on both the radial and angular part of the wavefunction. The resulting boundary surfaces have complex shapes.

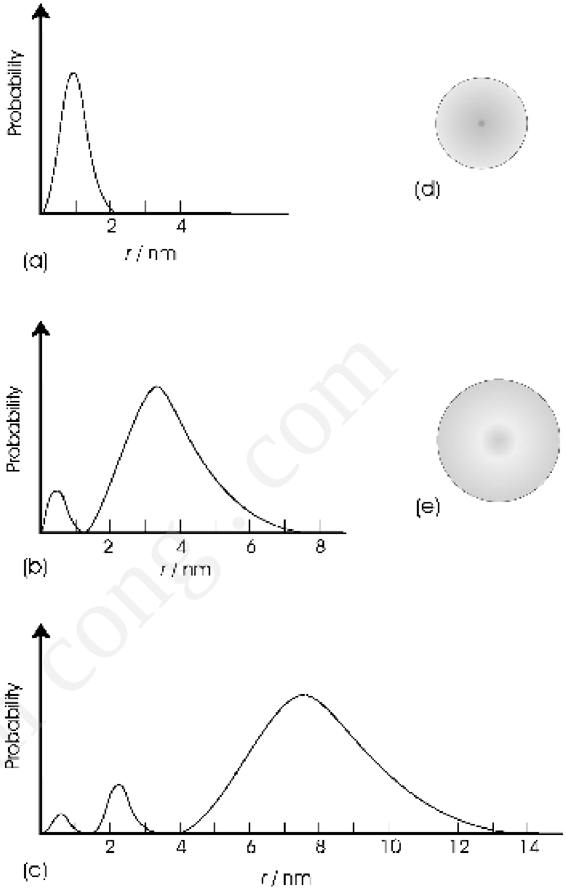


Figure 1.3 The probability of finding (a) a 1s, (b) a 2s and (c) a 3s electron at a distance *r* from the nucleus; the boundary surfaces of (d) the 1s and (e) the 2s orbitals

For many purposes, however, it is sufficient to describe the boundary surfaces of the angular part of the wavefunctions.

The boundary surfaces of the angular parts of each of the three p orbitals are approximately dumbbell shaped and lie along three mutually perpendicular directions, which it is natural to equate to *x*, *y* and *z* axes, as sketched in Figures 1.4a–1.4c. The corresponding orbitals are labelled $n\,p_x$, $n\,p_y$ and $n\,p_z$, for example $2\,p_x$, $2\,p_y$ and $2\,p_z$. Note that if a p orbital contains only one electron, it occupies both lobes. Similarly, when two electrons are accommodated in a p orbital they also occupy both lobes. The probability of encountering a p

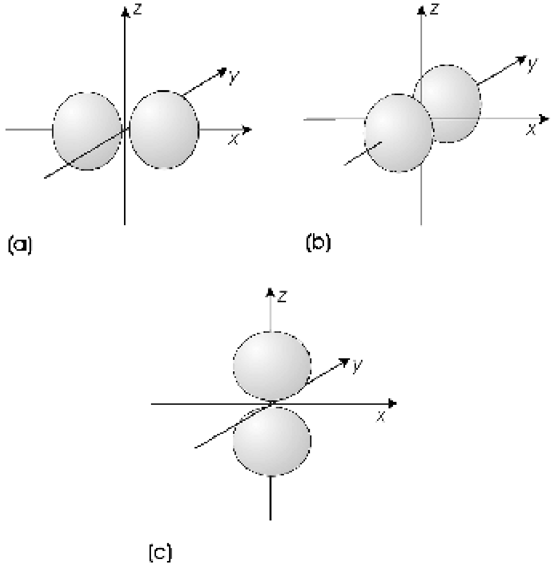


Figure 1.4 The boundary surfaces of the p orbitals: (a) p_x, (b) p_y and (c) p_z. The sign of the wave function is opposite in each lobe of the orbital

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 for an electron in a 2p orbital, and so on, so that 3p orbitals have a greater extension in space than do 2p orbitals.

The electron distribution of an 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. The shapes of the angular part of the 3d set of wavefunctions is drawn in Figure 1.5. Three of these have lobes lying between pairs of axes: d_{xy}, between the x and y axes (Figure 1.5a); d_{xz}, between

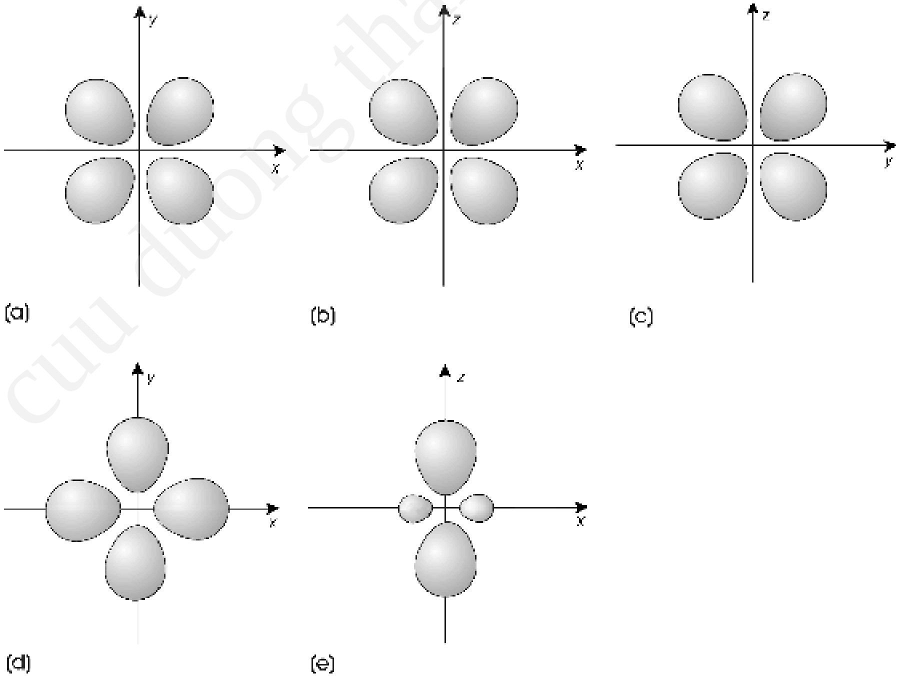


Figure 1.5 The boundary surfaces of the d orbitals: (a) d_{xy}, (b) d_{xz}, (c) d_{yz}, with lobes lying between the axes, and (d) $d_{x^2-y^2}$ and (e) d_{z^2}, with lobes lying along the axes

the x and z axes (Figure 1.5b); and d_{yz}, between the y and z axes (Figure 1.5c). The other two orbitals have lobes along the axes: $d_{x^2-y^2}$ pointing along the x and y axes (Figure 1.5d) and d_{z^2} pointing along the z axis (Figure 1.5e). 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.

1.3 Many-electron atoms

1.3.1 The orbital approximation

If we want to know the energy levels 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 each electron moves in a potential due to the nucleus and the average field of all the other electrons present in the atom. That is, as the atomic number increases by one unit, from Z to $(Z+1)$, an electron is added to the atom and feels the potential of the nucleus diluted by the electron cloud of the original Z electrons. 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. Compared with hydrogen, the energy levels of all of the orbitals drop sharply as Z_{eff} increases (Figure 1.6). Even when one reaches lithium ($Z = 3$) the 1s orbital energy has 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.

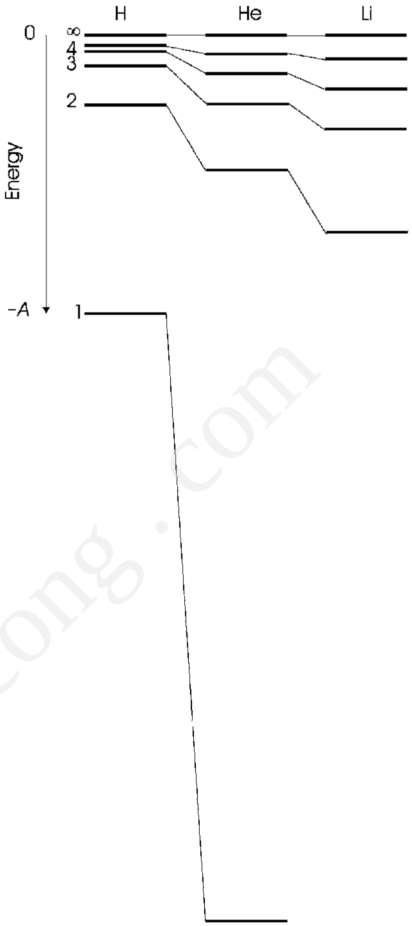


Figure 1.6 The schematic decrease in energy of the orbitals of the first three elements in the periodic table – hydrogen, helium and lithium – as the charge on the nucleus increases

In fact, the effective nuclear charge is different for electrons in different orbitals. This has the effect of separating the energy of the ns, np, nd and nf orbitals (where n represents the principal quantum number, say 4), which are identical in hydrogen. It is found that for any value of n, the s orbitals have the lowest energy and 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 1.7). However, the energy differences between the higher energy orbitals are very small, and this simple ordering is not followed exactly for heavier atoms (see Section S1.2.2).

In the orbital approximation, the electrons move in the potential of a central point nucleus. This potential does not change the overall form of the angular part of the wavefunction and hence the shapes of the orbitals are not changed from the shapes found for hydrogen. However, the radial part of the wavefunction 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.

1.3.2 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 $\frac{1}{2}$. Like the orbital angular momentum quantum number, the spin of an electron in an atom can adopt one of two different directions, represented by a quantum number, m_s, which take 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 arrows: $\uparrow$ for spin up, or α, and $\downarrow$ for 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 of an atom, the electrons are fed into the orbitals, starting with the lowest-energy orbital, 1s, and then proceeding to the higher-energy orbitals so as fill them up systematically from the 'bottom' up (Figure 1.7). 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 a result of 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.

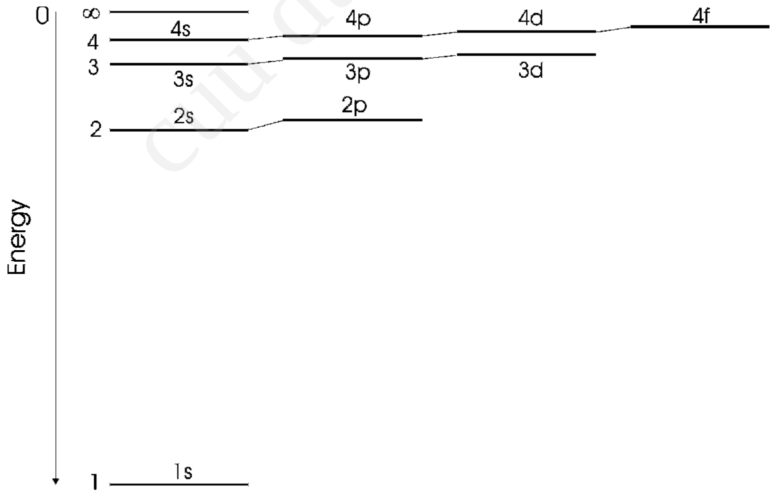


Figure 1.7 Schematic of the energy levels for a light many-electron atom

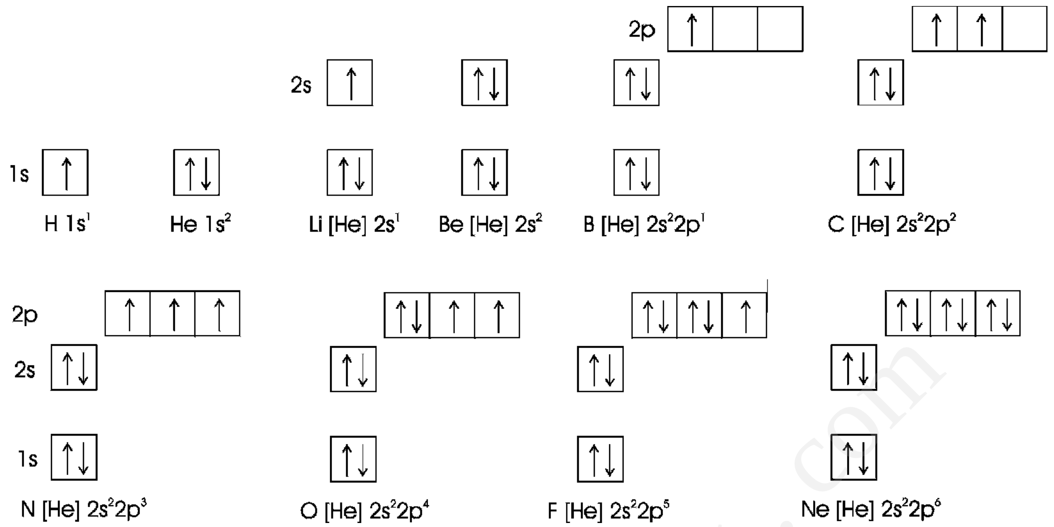


Figure 1.8 The building up of the electron configurations of the first 10 atoms in the periodic table

The electron configurations of the first few elements, derived in this way, are built up schematically in Figure 1.8.

- H: hydrogen has only one electron, and it will go into the orbital of lowest energy, the 1s orbital. The four quantum numbers specifying this state are $n = 1$, $l = 0$, $m_l = 0$ and $m_s = +\frac{1}{2}$. The electron configuration is written as $1s^1$.

- He: helium has two electrons. The first will be allocated to the 1s orbital, as in hydrogen. The lowest energy will prevail if the second is be allocated to the same orbital. This can be done provided m_s has a value of $-\frac{1}{2}$ and the electrons are spin paired. The electron configuration is written $1s^2$. There is only one orbital associated with the $n = 1$ quantum number, hence the shell corresponding to $n = 1$, the K shell is now filled, and holds just 2 electrons.

- Li: lithium has three electrons. Two of these can be placed in the 1s orbital, which is then filled. The next lowest energy corresponds to the 2s orbital, and the third electron is allocated to this. It will have quantum numbers $n = 2$, $l = 0$, $m_l = 0$ and $m_s = +\frac{1}{2}$, and the electron configuration is written $1s^2\ 2s^1$. This configuration is often written in a more compact form as [He] $2s^1$. The part of the configuration written [He] refers to the core electrons, which generally do not take part in chemical reactions. The electron outside the core is the chemically reactive valence electron.

- Be: beryllium has four electrons. The first three are allocated as for lithium. The fourth can be allocated to the 2s orbital, with quantum numbers $n = 2$, $l = 0$, $m_l = 0$ and $m_s = -\frac{1}{2}$, giving an electron configuration $1s^2\ 2s^2$, or [He] $2s^2$. Note that the L shell is not filled, because there are three p orbitals still available to the $n = 2$ quantum number.

- B: boron has five electrons. The first four of them will be distributed as in beryllium. The fifth must enter a 2p orbital, with $n = 2$, $l = 1$, $m_l = 0$ or ± 1. The electron can be assigned the four quantum numbers $n = 2$, $l = 1$, $m_l = +1$ and $m_s = \frac{1}{2}$, and the configuration $1s^2\ 2s^2\ 2p^1$, or [He] $2s^2\ 2p^1$.

- C: carbon has six electrons. The first five are allocated as for boron. The sixth electron also enters a p orbital. There is a choice here. The electron can go into the already half-occupied orbital or into one of the empty orbitals. The lowest-energy situation is that in which the electron goes into an unoccupied orbital. 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 one orbital with paired spins. Thus, as the first p electron has a spin of $+\frac{1}{2}$, the second electron also has a spin of $+\frac{1}{2}$. This gives an electron distribution $1s^2\ 2s^2\ 2p^2$, or [He] $2s^2\ 2p^2$.

- N: nitrogen has one more electron, and following the rules laid down it is allocated to the remaining empty p orbital, with quantum numbers $n = 2$, $l = 1$, $m_l = -1$ and $s = +\frac{1}{2}$, giving a configuration $1s^2\ 2s^2\ 2p^3$, or [He] $2s^2\ 2p^3$.

- O: oxygen has eight electrons. The first seven are placed as in nitrogen. The eighth electron must be added to one of the half-filled p orbitals. The quantum numbers for the new electron will be $n = 2$, $l = 1$, $m_l = 1$ and $s = -\frac{1}{2}$, giving a distribution of $1s^2\ 2s^2\ 2p^4$, or [He] $2s^2\ 2p^4$.

- F: fluorine possesses one more electron than oxygen, and so we expect its state to be $n = 2$, $l = 1$, $m_l = 0$ and $s = -\frac{1}{2}$, that is, $1s^2\ 2s^2\ 2p^5$, or [He] $2s^2\ 2p^5$.

- Ne: neon has six electrons, filling the 2p orbitals. The state occupied by the last electron is represented by $n = 2$, $l = 1$, $m_l = -1$ and $s = -\frac{1}{2}$, and the distribution by $1s^2\ 2s^2\ 2p^6$, or [He] $2s^2\ 2p^6$. This is often written as [Ne]. The L shell is now filled. It has been shown that all filled shells have only radial symmetry and are especially stable.

To summarise, the building up procedure we have used is called the Aufbau principle. Each electron occupies one electron state, represented by four quantum numbers, one of which represents the spin of the electron. Each orbital can contain two electrons with opposite spins. In a set of orbitals of equal energy, electrons tend to keep apart and so make the total electron spin a maximum.

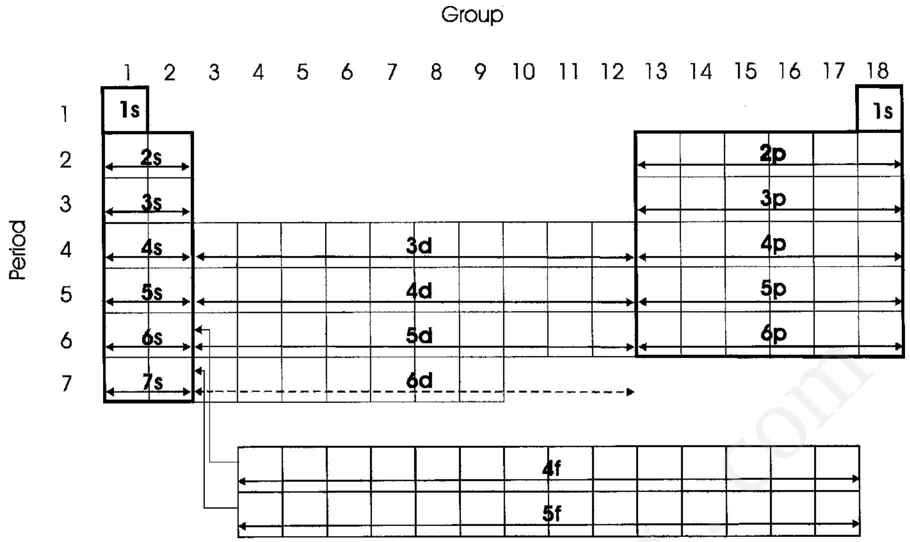
The electron configurations of the rest of the elements are derived in the same way. The M shell $(n = 3)$, with a maximum capacity of 18 electrons, consists of one 3s orbital, three 3p orbitals and five 3d orbitals. The N shell $(n = 4)$ can hold 32 electrons in one 4s, three 4p, five 4d and seven 4f orbitals. The maximum number of electrons in each shell is $2n$, where n is the principal quantum number.

The electron configurations of the elements in the first two periods are listed in Section S1.2.1. The configuration of the ground state depends upon the energy of the orbitals and the interaction of the electrons. These effects are very delicately balanced in the heavier atoms, so that a strict Aufbau arrangement does not always hold good. For example, chromium (Cr) has an electron configuration of [Ar] $3d^5\ 4s^1$, in contrast to that of its neighbours – vanadium (V) with [Ar] $3d^3\ 4s^2$, and manganese (Mn) with [Ar] $3d^5\ 4s^2$ – both of which have the 4s shell filled. This indicates that the half-filled d orbital has a special stability that can influence the configuration.

1.3.3 The periodic table

The periodic table, described in Section 1.1, was an empirical construction. However, it is fundamentally understandable in terms of the electron configurations just discussed. The chemical and many physical properties of the elements are simply controlled by the valence electrons. The valence electron configuration varies in a systematic and repetitive way as the various shells are filled. This leads naturally to both the periodicity and the repetitive features displayed in the periodic table (Figure 1.9).

Figure 1.9(a) shows the relationship between the outer orbitals that are partly filled and the position of the element in the periodic table. The filled shells are very stable configurations and take part in chemical reactions only under extreme conditions. The atoms with this configuration, the noble gases,



(a)

	Group 1/I	Group 2/II	Group 13/III	Group 14/IV	Group 15/V	Group 16/VI	Group 17/VII	Group 18/VIII
Period 2	lithium Li 3 2p — 2s ↑ core 2	beryllium Be 4 2p — 2s ↑↓ core 2	boron B 5 2p ↑ 2s ↑↓ core 2	carbon C 6 2p ↑↑ 2s ↑↓ core 2	nitrogen N 7 2p ↑↑↑ 2s ↑↓ core 2	oxygen O 8 2p ↑↓↑↑ 2s ↑↓ core 2	fluorine F 9 2p ↑↓↑↓↑ 2s ↑↓ core 2	neon Ne 10 2p ↑↓↑↓↑↓ 2s ↑↓ core 2
Period 3	sodium Na 11 3p — 3s ↑ core 10	magnesium Mg 12 3p — 3s ↑↓ core 10	aluminium Al 13 3p ↑ 3s ↑↓ core 10	silicon Si 14 3p ↑↑ 3s ↑↓ core 10	phosphorus P 15 3p ↑↑↑ 3s ↑↓ core 10	sulphur S 16 3p ↑↓↑↑ 3s ↑↓ core 10	chlorine Cl 17 3p ↑↓↑↓↑ 3s ↑↓ core 10	argon Ar 18 3p ↑↓↑↓↑↓ 3s ↑↓ core 10
Period 4	potassium K 19 4p — 4s ↑ core 18	calcium Ca 20 4p — 4s ↑↓ core 18	gallium Ga 31 4p ↑ 4s ↑↓ core 28	germanium Ge 32 4p ↑↑ 4s ↑↓ core 28	arsenic As 33 4p ↑↑↑ 4s ↑↓ core 28	selenium Se 34 4p ↑↓↑↑ 4s ↑↓ core 28	bromine Br 35 4p ↑↓↑↓↑ 4s ↑↓ core 28	krypton Kr 36 4p ↑↓↑↓↑↓ 4s ↑↓ core 28
Period 5	rubidium Rb 37 5p — 5s ↑ core 36	strontium Sr 38 5p — 5s ↑↓ core 36	indium In 49 5p ↑ 5s ↑↓ core 46	tin Sn 50 5p ↑↑ 5s ↑↓ core 46	antimony Sb 51 5p ↑↑↑ 5s ↑↓ core 46	tellurium Te 52 5p ↑↓↑↑ 5s ↑↓ core 46	iodine I 53 5p ↑↓↑↓↑ 5s ↑↓ core 46	xenon Xe 54 5p ↑↓↑↓↑↓ 5s ↑↓ core 46
Period 6	caesium Cs 55 6p — 6s ↑ core 54	barium Ba 56 6p — 6s ↑↓ core 54	thallium Tl 81 6p ↑ 6s ↑↓ core 78	lead Pb 82 6p ↑↑ 6s ↑↓ core 78	bismuth Bi 83 6p ↑↑↑ 6s ↑↓ core 78	polonium Po 84 6p ↑↓↑↑ 6s ↑↓ core 78	astatine At 85 6p ↑↓↑↓↑ 6s ↑↓ core 78	radon Rn 86 6p ↑↓↑↓↑↓ 6s ↑↓ core 78

(b)

Figure 1.9 (a) The relationship between the electron configuration of atoms and the periodic table arrangement, and (b) part of the periodic table, giving the valence (outer-electron) structure of the main group elements 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. These are the alkali metals, and once again, a ‘new’ alkali metal is found after each filled shell. The alkali metals are in Group 1 of the periodic table. Similarly, the alkaline earth elements, 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.

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 (Figure 1.9b). 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. The electrons in these orbitals are responsible for many of the interesting electronic, magnetic and optical properties of solids. Because of their importance, the electron configurations of the 3d transition metals and the lanthanides are set out in Sections S1.2.2 and S1.2.3.

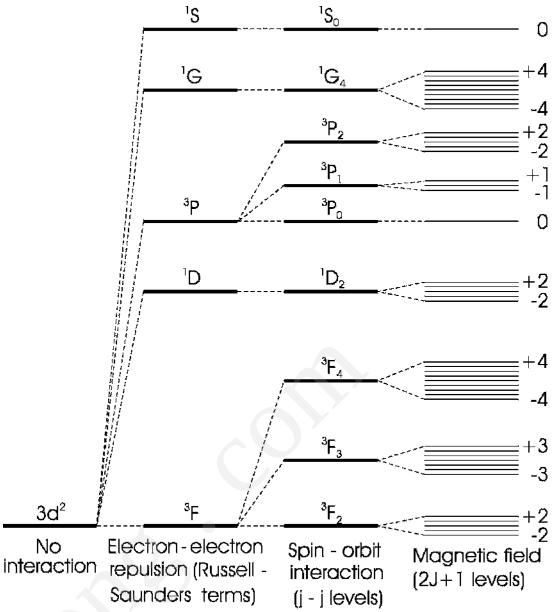


Figure 1.10 The evolution of the energy levels of an atom with a $3d^2$ electron configuration, taking into account increasing electron–electron and other interactions, the energy scales are schematic

1.4 Atomic energy levels

1.4.1 Electron energy levels

Spectra are a record of transitions between electron energy levels. Each spectral line can be related to the transition from one energy level to another. It is found that an ion in a magnetic field has a more complex spectrum, with more lines present, than has the same ion in the absence of the magnetic field. The presence of additional lines in the spectrum of an atom or ion when in a magnetic field is called the Zeeman effect. A similar, but different, complexity, called the Stark effect, arises in the presence of a strong electric field. The electron configurations described are not able to account for all of the observed transitions, and to derive the possible energy levels appropriate to any electron configuration a more complex model of the atom is required. These steps are outlined below and are summarised in Figure 1.10.

1.4.2 The vector model

In this model, classical ideas are grafted onto the quantum mechanics of the atom. The quantum number *l* is associated with the angular momentum of the electron around the nucleus. It is represented by an angular momentum vector, ***l***. Similarly, the spin quantum number of the electron, *s*, is associated with a spin angular momentum vector, ***s***. (Vectors in the following text are specified in bold type and quantum numbers in normal type.) In the vector model of the atom, the two angular momentum vectors are added together to get a total angular momentum for the atom as a whole. This is then related to the electron energy levels of the atom.

There are two ways of tackling this task. The first of these makes the approximation that the electrostatic repulsion between electrons is the most important energy term. In this approximation, called Russell–Saunders coupling, all of the individual ***s*** vectors of the electrons are summed vectorially to yield a total spin angular momentum vector ***S***. Similarly, all of the individual ***l*** vectors for the electrons present are summed vectorially to give a total orbital angular momentum vector, ***L***. The vectors ***S*** and ***L*** can also be summed vectorially to give a total angular momentum vector ***J***. Note that the convention is to use lower-case letters for a single electron and upper-case for many electrons.

The 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*** vectors for an individual electron are added vectorially to give a total angular momentum vector ***j*** for a single electron. These values of ***j*** are then added vectorially to give the total angular momentum vector ***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. In reality, the energy levels derived from each scheme represent approximations to those found by experiment, which may be regarded as intermediate between the two.

1.4.3 Terms and term schemes

For almost all purposes, the Russell–Saunders coupling scheme is adequate for the specification of the energy levels of an isolated many-electron atom. In general, it is not necessary to work directly with the vectors ***S***, ***L*** and ***J***. Instead, many electron quantum numbers (not vectors), S, L and J, are used to label the energy levels in a simple way. The method of derivation is set out in Section S1.3.1. 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 set out in Table 1.3. After $L = 3$ (F) the sequence of letter is alphabetic, omitting J. Be aware that the symbol S has two interpretations, as the symbol when $L = 0$ (upright S) and as the value of total spin (italic S).

Table 1.3 The correspondence of L values and letter symbols

L	Symbol
0	S
1	P
2	D
3	F
4	G
5	H

The combinations are written in the following form:

$$^{2S+1}L$$

This is 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, states with a multiplicity of three are called triplets, states with a multiplicity of 4 are called quartets and so on. Hence, ^{1}S is called singlet S, and ^{3}P is called triplet P.

The energies of the terms are difficult to obtain simply, and they must be calculated by using quantum mechanical procedures. However, the lowest-energy term, the ground-state term, is easily found by using the method described in Section S1.3.2.

The term symbol does not account for the true complexity found in most atoms. This arises 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:

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

where $|L-S|$ is the modulus (absolute value, taken to be positive whether the expression within the vertical lines is negative or positive) of L and S. Thus the term ^{3}P has J values given by:

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

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 energy level, a doublet two, a triplet three and so on. Thus, the ground-state term ^{3}P is composed of three levels, $^3P_0$, $^3P_1$ and $^3P_2$. The separation of these energy levels is controlled by the magnitude of the interaction between L and S. Hund's third rule (see Section S1.3.2 for the first and second rules) allows the values of J to be sorted in order of energy. The level with the lowest energy is that with the lowest J value if the valence shell is up to half full and that with the highest J value if the valence shell is more than half full.

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 $g_J \mu_B B$, where g_J is the Landé g-value, given by

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

μ_B is a fundamental physical constant, the Bohr magneton, and B is the magnetic induction (more information on this is found in Chapter 12, on magnetic properties)

The way in which these levels of complexity modify the energy levels of a 3d^2 transition metal atom or ion is drawn schematically in Figure 1.10. At the far left-hand side of the figure, the electron configuration is shown. This is useful chemically, but is unable to account for the spectra of the atom. Russell–Saunders coupling is a good approximation to use for the 3d transition metals, and the terms that arise from this are given to the right-hand side of the configuration in Figure 1.10. In Russell–Saunders coupling the electron–electron repulsion is considered to dominate the interactions. The terms are spilt 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. In this case $2J+1$ levels arise. 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 for 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.

Answers to introductory questions

What is a wavefunction and what information does it provide?

A wavefunction, ψ, is a solution to the Schrödinger equation. For atoms, wavefunctions describe the energy and probability of location of the electrons in any region around the proton nucleus. The simplest wavefunctions are found for the hydrogen atom. 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. These simplest wavefunctions do not include the electron spin quantum number, m_s, which is introduced in more complete descriptions of atoms. Quantum numbers define the state of a system. More complex wavefunctions arise when many-electron atoms or molecules are considered.

Why does the periodic table summarise both the chemical and the physical properties of the elements?

The periodic table was originally formulated empirically. However, it is fundamentally understandable in terms of electron configurations. The chemical and many physical properties of the elements are dominated by the valence electrons. The valence electron configuration varies in a systematic and repetitive way as the various shells are filled. This filling corresponds to the groups of the periodic table.

The filled shells are very stable configurations and take part in chemical reactions only 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. These are the alkali metals and, once again, a ‘new’ alkali metal is occurs after each filled shell. The alkali metals are found in Group 1 of the periodic table. Similarly, the alkaline earth elements, listed in Group 2 of the periodic table, all have two valence electrons, both in the outermost s orbital. The transition metals have partly filled d orbitals, and the lanthanides partly filled f orbitals. Thus, the periodic table simply expresses the Aufbau principle in a chart, which itself accounts for the periodic variation of properties.

What is a term scheme?

A term scheme is a representation of an energy level in an isolated many-electron atom, derived via the Russell–Saunders coupling scheme. In general, a term scheme is written as a collection of many-electron quantum numbers S and L. 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 term scheme is written ^{2S+1}L. States with a multiplicity of 1 are called singlet states, states with a multiplicity of 2 are called doublet states, those with a multiplicity of three are called triplets, those with a multiplicity 4 are called quartets and so on. Hence, ^{1}S is called singlet S, and ^{3}P is called triplet P.

Further reading

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

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

D.A. McQuarrie, P.A. Rock, 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:

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

The quantum mechanics of atoms is described lucidly in:

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

An invaluable dictionary of quantum mechanical language and expressions is:

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

Problems and exercises

Quick quiz

1 What is the name of the element whose symbol is Pb?
   (a) Tin
   (b) Phosphorus
   (c) Lead

2 What is the name of the element whose symbol is Hg?
   (a) Mercury
   (b) Silver
   (c) Holmium

3 What is the name of the element whose symbol is Ag?
   (a) Argon

(b) Silver

(c) Mercury

4 What is the chemical symbol for gold?
(a) Au
(b) G
(c) Sb

5 What is the chemical symbol for potassium?
(a) P
(b) Po
(c) K

6 An isotope is:
(a) The nucleus of the atom
(b) A subatomic particle
(c) An atom with a specified number of protons and neutrons

7 The periodic table contains how many periods?
(a) 18
(b) 7
(c) 14

8 Iodine is an example of:
(a) A halogen
(b) A chalcogen
(c) An alkaline earth metal

9 Magnesium is an example of:
(a) A transition metal
(b) An alkaline earth metal
(c) An alkali metal

10 Nickel is an example of:
(a) A transition metal
(b) A lanthanide
(c) An actinide

11 A wavefunction is:
(a) A description of an electron
(b) An atomic energy level
(c) A solution to the Schrödinger equation

12 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

13 The Pauli principle leads to the conclusion that:
(a) The position and momentum 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

14 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

15 The outer electron configuration of the noble gases is:
(a) $n\mathrm{s}^2\, n\mathrm{p}^6$
(b) $n\mathrm{s}^2\, n\mathrm{p}^6 (n+1)\mathrm{s}^1$
(c) $n\mathrm{s}^2\, n\mathrm{p}^5$

16 The valence electron configuration of the alkali metals is:
(a) $n\mathrm{s}^2$
(b) $n\mathrm{p}^1$
(c) $n\mathrm{s}^1$

17 The valence electron configuration of carbon is:
(a) $1\mathrm{s}^2 2\mathrm{p}^2$
(b) $2\mathrm{s}^2 2\mathrm{p}^2$
(c) $2\mathrm{s}^2 2\mathrm{p}^4$

18 The valence electron configuration of calcium, strontium and barium is:
(a) $n\mathrm{s}^2\, n\mathrm{p}^2$
(b) $n\mathrm{s}^2$
(c) $(n-1)\mathrm{d}^1\, n\mathrm{s}^2$

19 What atom has filled K, L, M and N shells?
(a) Argon
(b) Krypton
(c) Xenon

20 How many electrons can occupy orbitals with $n = 3$, $l = 2$?
(a) 6 electrons
(b) 10 electrons
(c) 14 electrons

21 How many permitted l values are there for $n = 4$?
(a) One
(b) Two
(c) Three

22 How many electrons can occupy the 4f orbitals?
(a) 14
(b) 10
(c) 7

23 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

24 A term symbol is:
(a) A label for an atomic energy level
(b) A label for an orbital
(c) A description of a configuration

25 The many-electron quantum number symbol D represents:
(a) $L = 1$
(b) $L = 2$
(c) $L = 3$

26 An atom has a term ^1S. What is the value of the spin quantum number, S?
(a) ½
(b) 0
(c) 1

27 An atom has a term ^1S. What is the value of the orbital quantum number, L?
(a) 2
(b) 1
(c) 0

Calculations and questions

1.1 The velocity of an electron crossing a detector is determined to an accuracy of $\pm 10\,\mathrm{m\,s^{-1}}$. What is the uncertainty in its position?

1.2 A particle in an atomic nucleus is confined to a volume with a diameter of approximately $1.2 \times 10^{-15}\,A^{1/3}\,\mathrm{m}$, where A is the mass number of the atomic species. What is the uncertainty in the velocity of a proton trapped within a sodium nucleus with a mass number of 23?

1.3 The wavelength of an electron in an electron microscope is 0.0122 nm. What is the electron velocity?

1.4 The velocity of a proton scattered by an energetic cosmic ray is $2 \times 10^3\,\mathrm{m\,s^{-1}}$. What is the wavelength of the proton?

1.5 What velocity must a proton attain in a proton microscope to have the same wavelength as green light in an optical microscope (350 nm)?

1.6 The velocity of an argon (Ar) atom at the surface of the Earth is $397\,\mathrm{m\,s^{-1}}$. What is its wavelength?

1.7 The velocity of a krypton (Kr) atom at the Earth's surface is $274\,\mathrm{m\,s^{-1}}$. What is its wavelength?

1.8 What energy is required to liberate an electron in the $n = 3$ orbital of a hydrogen atom?

1.9 What is the energy change when an electron moves from the $n = 2$ orbit to the $n = 6$ orbit in a hydrogen atom?

1.10 Calculate the energy of the lowest orbital (the ground state) of the single-electron hydrogen-like atoms with $Z = 2$ (He^+) and $Z = 3$ (Li^{2+}).

1.11 What are the frequencies (ν) and wavelengths (λ) 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?

1.12 What are the frequencies (ν) and wavelengths (λ) 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?

1.13 What are the frequencies (ν) and wavelengths (λ) 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?

1.14 What are the frequencies (ν) and wavelengths (λ) 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?

1.15 Sodium lights emit light of a yellow colour, with photons of wavelength 589 nm. What is the energy of these photons?

1.16 Mercury lights emit photons with a wavelength of 435.8 nm. What is the energy of the photons?

1.17 What are the possible quantum numbers for an electron in a 2p orbital?

1.18 Starting from the configuration of the nearest lower noble gas, what are the electron configurations of C, P, Fe, Sr and W?

1.19 Titanium has the term symbol ^3F. What are the possible values of J? What is the ground-state level?

1.20 Phosphorus has the term symbol ^4S. What are the possible values of J? What is the ground-state level?

1.21 Scandium has a term symbol ^2D. What are the possible values of J? What is the ground-state level?

1.22 Boron has a term symbol ^2P. What are the possible values of J? What is the ground-state level?

1.23 What is the splitting g_J, for sulphur, with a ground state $^3P_2$?

1.24 What is the splitting g_J, for iron, with a ground state $^5D_4$?

1.25 Sketch the 1s, 2s and 3s orbitals, roughly to scale, from the wavefunctions given in Table 1.1. [Note: answer is not provided at the end of this book.]

1.26 Older forms of the periodic table have Group 1 divided into IA, containing the alkali metals, Li, Na, K, Rb and Cs, and IB, containing the metals Cu, Ag and Au; Group 2 was divided into IIA, containing Be, Mg, Ca, Sr and Ba, and IIB, containing Zn, Cd and Hg; and Group 3 was divided in to IIIA, containing Sc, Y and the lanthanides, and IIIB, containing B, Al, Ga and In. Why should this be? [Note: answer not provided at the end of this book.]

1.27 Draw a diagram equivalent to Figure 1.10 for a chlorine atom, with a ground state $^2P_{3/2}$. [Note: answer is not provided at the end of this book.]