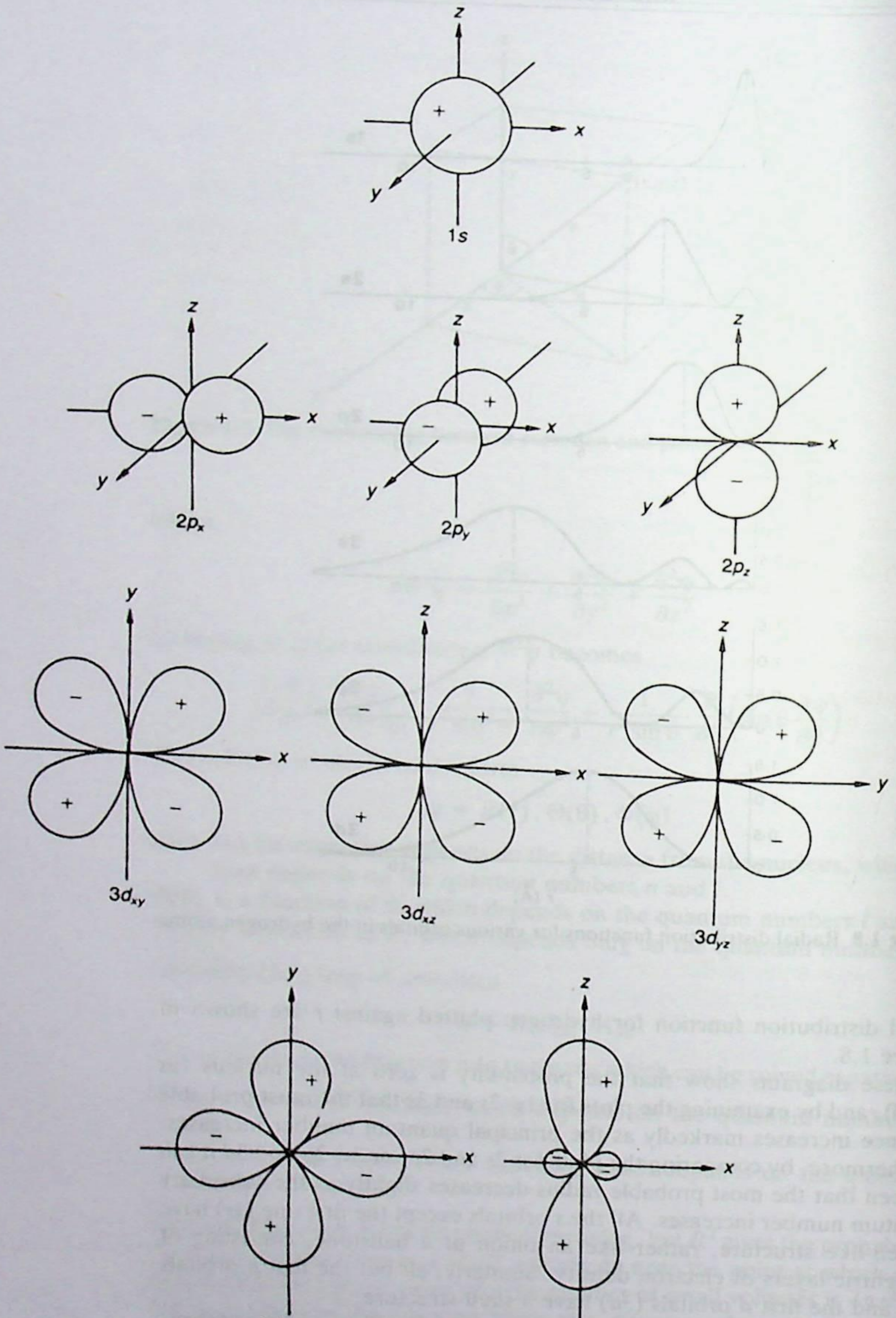


Figure 1.9 Boundary surface for the angular part of the wave function $A(\theta, \phi)$ for the 1*s*, 2*p* and 3*d* orbitals for a hydrogen atom shown as polar diagrams.

finding an electron at a given direction θ, φ at any distance from the nucleus to infinity. The angular functions A are plotted as polar diagrams in Figure 1.9. It must be emphasized that *these polar diagrams do* **not** *represent the total wave function* ψ, but only the angular part of the wave function. (The total wave function is made up from contributions from both the radial and the angular functions.)

$$\psi = R(r) \,.\, A$$

Thus the probability of finding an electron simultaneously at a distance r and in a given direction θ, φ is $\psi^2_{r,\theta,\phi}$.

$$\psi^2_{r,\theta,\phi} = R^2(r) \,.\, A^2(\theta, \phi)$$

Polar diagrams, that is drawings of the the angular part of the wave function, are commonly used to illustrate the overlap of orbitals giving bonding between atoms. Polar diagrams are quite good for this purpose, as they show the signs + and − relating to the symmetry of the angular function. For bonding like signs must overlap. These shapes are slightly different from the shapes of the total wave function. There are several points about such diagrams:

1. It is difficult to picture an angular wave function as a mathematical equation. It is much easier to visualize a boundary surface, that is a solid shape, which for example contains 90% of the electron density. To emphasize that ψ is a continuous function, the boundary surfaces have been extended up to the nucleus in Figure 1.9. For p orbitals the electron density is zero at the nucleus, and some texts show a p orbital as two spheres which do not touch.
2. These drawings show the symmetry for the 1s, 2p, 3d orbitals. However, in the others, 2s, 3s, 4s . . . , 3p, 4p, 5p . . . , 4d, 5d . . . the sign (symmetry) changes inside the boundary surface of the orbital. This is readily seen as nodes in the graphs of the radial functions (Figure 1.8).

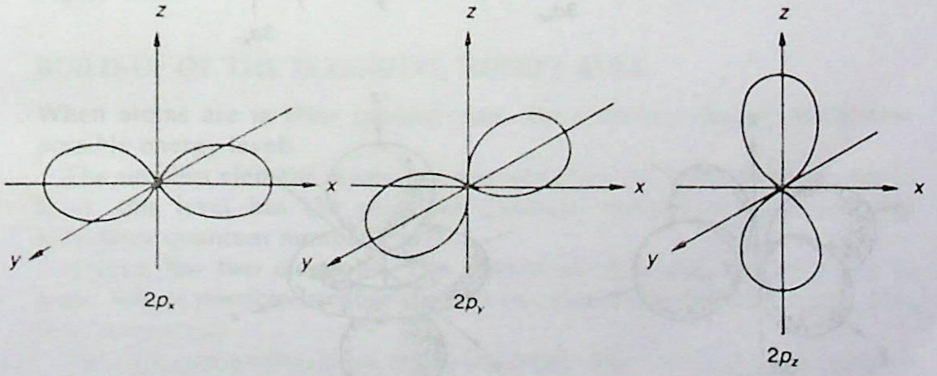


Figure 1.10 The angular part of the wave function squared $A^2(\theta, \phi)$ for the 2p orbitals for a hydrogen atom.

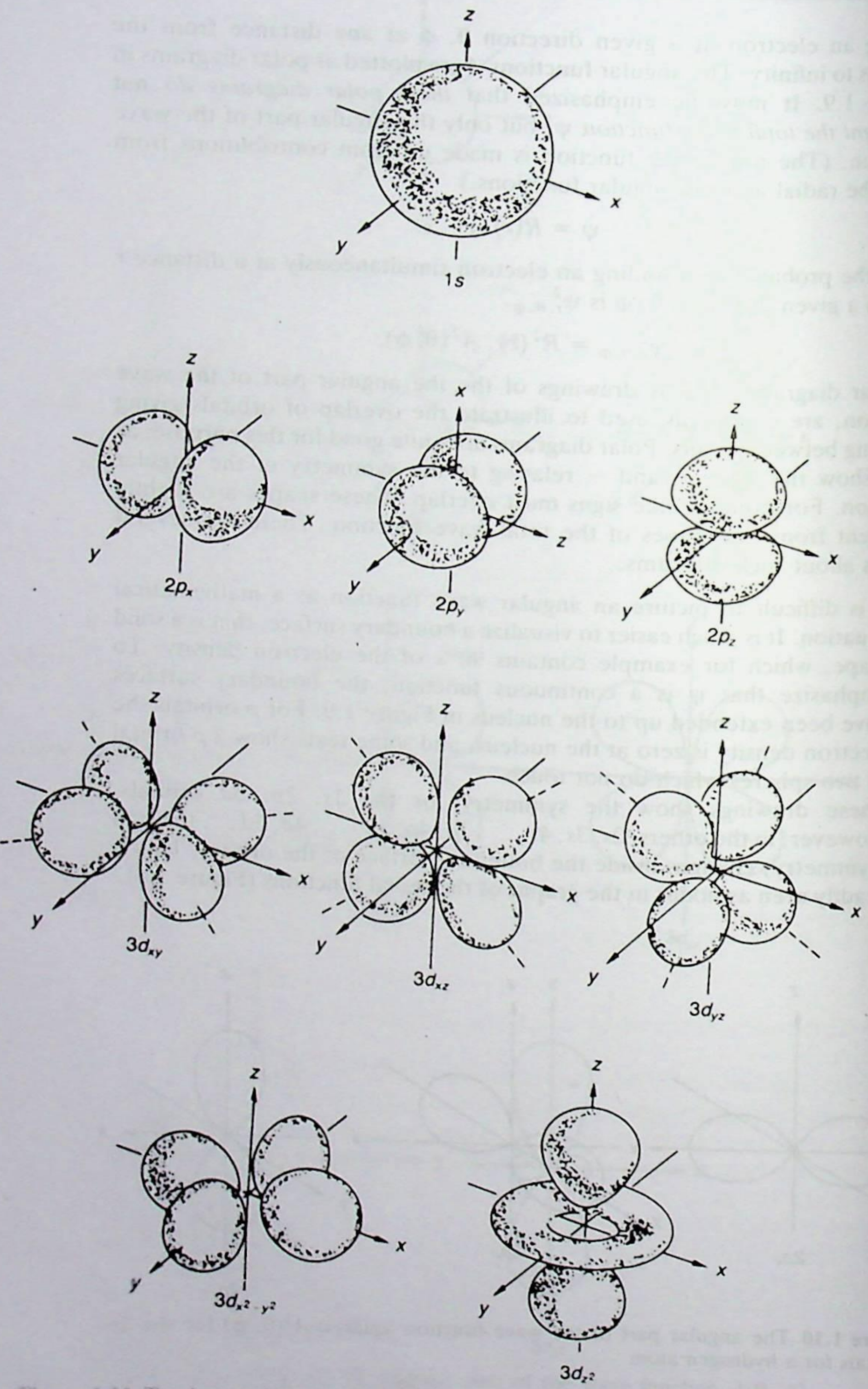


Figure 1.11 Total wave function (orbitals) for hydrogen.

3. The probability of finding an electron at a direction θ, ϕ is the wave function squared, A^2, or more precisely $\psi_\Theta^2\psi_\Phi^2$. The diagrams in Figure 1.9 are of the angular part of the wave function A, not A^2. Squaring does not change the shape of an *s* orbital, but it elongates the lobes of *p* orbitals (Figure 1.10). Some books use elongated *p* orbitals, but strictly these should **not** have signs, as squaring removes any sign from the symmetry. Despite this, many authors draw shapes approximating to the probabilities, i.e. squared wave functions, and put the signs of the wave function on the lobes, and refer to both the shapes and the wave functions as orbitals.
4. A full representation of the probability of finding an electron requires the total wave function squared and includes both the radial and angular probabilities squared. It really needs a three-dimensional model to display this probability, and show the shapes of the orbitals. It is difficult to do this adequately on a two-dimensional piece of paper, but a representation is shown in Figure 1.11. The orbitals are not drawn to scale. Note that the *p* orbitals are not simply two spheres, but are ellipsoids of revolution. Thus the $2p_x$ orbital is spherically symmetrical about the *x* axis, but is not spherical in the other direction. Similarly the p_y orbital is spherically symmetrical about the *y* axis, and both the p_z and the $3d_{z^2}$ are spherically symmetrical about the *z* axis.

PAULI EXCLUSION PRINCIPLE

Three quantum numbers *n*, *l* and *m* are needed to define an orbital. Each orbital may hold up to two electrons, provided they have opposite spins. An extra quantum number is required to define the spin of an electron in an orbital. Thus four quantum numbers are needed to define the energy of an electron in an atom. The Pauli exclusion principle states that no two electrons in one atom can have all four quantum numbers the same. By permutating the quantum numbers, the maximum number of electrons which can be contained in each main energy level can be calculated (see Figure 1.12).

BUILD-UP OF THE ELEMENTS, HUND'S RULE

When atoms are in their ground state, the electrons occupy the lowest possible energy levels.

The simplest element, hydrogen, has one electron, which occupies the 1*s* level; this level has the principal quantum number $n = 1$, and the subsidiary quantum number $l = 0$.

Helium has two electrons. The second electron also occupies the 1*s* level. This is possible because the two electrons have opposite spins. This level is now full.

The next atom lithium has three electrons. The third electron occupies the next lowest level. This is the 2*s* level, which has the principal quantum number $n = 2$ and subsidiary quantum number $l = 0$.

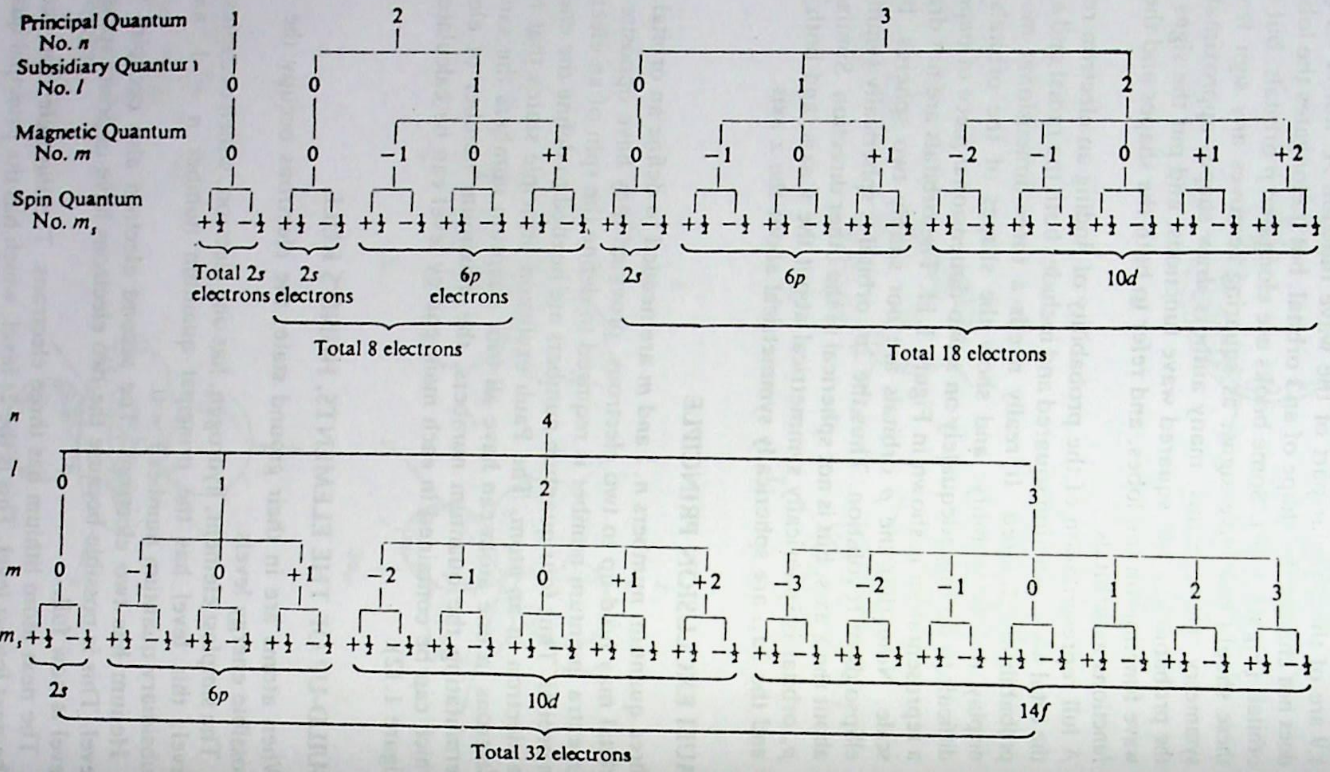


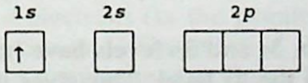
Figure 1.12 Quantum numbers, the permissible number of electrons and the shape of the periodic table

The fourth electron in beryllium also occupies the 2*s* level. Boron must have its fifth electron in the 2*p* level as the 2*s* level is full. The sixth electron in carbon is also in the 2*p* level. Hund's rule states that the number of unpaired electrons in a given energy level is a maximum. Thus in the ground state the two *p* electrons in carbon are unpaired. They occupy separate *p* orbitals and have parallel spins. Similarly in nitrogen the three *p* electrons are unpaired and have parallel spins.

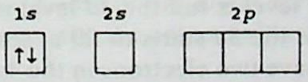
To show the positions of the electrons in an atom, the symbols 1*s*, 2*s*, 2*p*, etc. are used to denote the main energy level and sub-level. A superscript indicates the number of electrons in each set of orbitals. Thus for hydrogen, the 1*s* orbital contains one electron, and this is shown as $1s^1$. For helium the 1*s* orbital contains two electrons, denoted $1s^2$. The electronic structures of the first few atoms in the periodic table may be written:

H	$1s^1$
He	$1s^2$
Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$

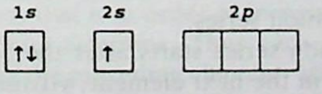
An alternative way of showing the electronic structure of an atom is to draw boxes for orbitals, and arrows for the electrons.



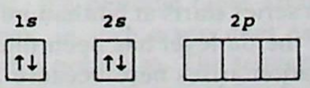
Electronic structure of H atom in the ground state



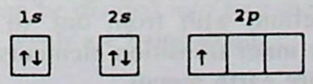
Electronic structure of He atom in the ground state



Electronic structure of Li atom in the ground state



Electronic structure of Be atom in the ground state



Electronic structure of B atom in the ground state

	1s	2s	2p	3s	3p
Electronic structure of C atom in the ground state	↑↓	↑↓	↑ ↑		
Electronic structure of N atom in the ground state	↑↓	↑↓	↑ ↑ ↑		
Electronic structure of O atom in the ground state	↑↓	↑↓	↑↓ ↑ ↑		
Electronic structure of F atom in the ground state	↑↓	↑↓	↑↓ ↑↓ ↑		
Electronic structure of Ne atom in the ground state	↑↓	↑↓	↑↓ ↑↓ ↑↓		
Electronic structure of Na atom in the ground state	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	

The process continues in a similar way.

SEQUENCE OF ENERGY LEVELS

It is important to know the sequence in which the energy levels are filled. Figure 1.13 is a useful aid. From this it can be seen that the order of filling of energy levels is: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, etc.

After the 1*s*, 2*s*, 2*p*, 3*s* and 3*p* levels have been filled at argon, the next two electrons go into the 4*s* level. This gives the elements potassium and calcium. Once the 4*s* level is full the 3*d* level is the next lowest in energy, not the 3*p* level. Thus the 3*d* starts to fill at scandium. The elements from scandium to copper have two electrons in the 4*s* level and an incomplete 3*d* level, and all behave in a similar manner chemically. Such a series of atoms is known as a transition series.

A second transition series starts after the 5*s* orbital has been filled, at strontium, because in the next element, yttrium, the 4*d* level begins to fill up. A third transition series starts at lanthanum where the electrons start to fill the 5*d* level after the 6*d* level has been filled with two electrons.

A further complication arises here because after lanthanum, which has one electron in the 5*d* level, the 4*f* level begins to fill, giving the elements from cerium to lutetium with from one to 14*f* electrons. These are sometimes called the inner transition elements, but are usually known as the lanthanides or rare earth metals.

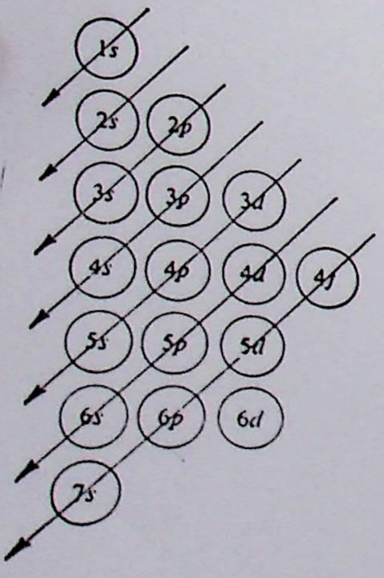


Figure 1.13 Sequence of filling energy levels.

ARRANGEMENT OF THE ELEMENTS IN GROUPS IN THE PERIODIC TABLE

The chemical properties of an element are largely governed by the number of electrons in the outer shell, and their arrangement. If the elements are arranged in groups which have the same outer electronic arrangement, then elements within a group should show similarities in chemical and physical properties. One great advantage of this is that initially it is only necessary to learn the properties of each group rather than the properties of each individual element.

Elements with one *s* electron in their outer shell are called Group 1 (the alkali metals) and elements with two *s* electrons in their outer shell are called Group 2 (the alkaline earth metals). These two groups are known as the *s*-block elements, because their properties result from the presence of *s* electrons.

Elements with three electrons in their outer shell (two *s* electrons and one *p* electron) are called Group 13, and similarly Group 14 elements have four outer electrons, Group 15 elements have five outer electrons, Group 16 elements have six outer electrons and Group 17 elements have seven outer electrons. Group 18 elements have a full outer shell of electrons. Groups 13, 14, 15, 16, 17 and 18 all have *p* orbitals filled and because their properties are dependent on the presence of *p* electrons, they are called jointly the *p*-block elements.

In a similar way, elements where *d* orbitals are being filled are called the *d*-block, or transition, elements. In these, *d* electrons are being added to the penultimate shell. For example, the element scandium Sc is the first transition element, and follows immediately after the element calcium Ca, which is in Group 2. The outer shell of calcium contains two *s* electrons. Scandium also has two *s* electrons, but also has one *d* electron (albeit in the pentultimate shell); hence the scandium group is called Group 3. Similarly, titanium Ti (the second transition element) has two *s* electrons, and also two *d* electrons (in the penultimate shell); hence the titanium group is called Group 4. Up to ten *d* electrons can be added; hence the transition metals are arranged in Group 3 to Group 12 inclusive.

Finally, elements where *f* orbitals are filling are called the *f*-block, and here the *f* electrons are entering the antepenultimate (or second from the outside) shell.

In the periodic table (Table 1.4), the elements are arranged in order of increasing atomic number, that is in order of increased nuclear charge, or increased number of orbital electrons. Thus each element contains one more orbital electron than the preceding element. Instead of listing the 103 elements as one long list, the periodic table arranges them into several horizontal rows or periods, in such a way that each row begins with an alkali metal and ends with a noble gas. The sequence in which the various energy levels are filled determines the number of elements in each period, and the periodic table can be divided into four main regions according to whether the *s*, *p*, *d* or *f* levels are being filled.