

Fig. 1.13 Graph of the wave function ψ_{1s} for the hydrogen 1s orbital, together with plots of ψ^2 and the radial distribution function.

$\psi^2 \equiv \text{electron density}$

name, the 1s orbital (since $n = 1$, $l = 0$, and $m_l = 0$, the only possibility for the first shell). The wave equation for the 1s orbital, ψ_{1s} , [pronounced (p)sī 1s] is given by an exponential function, Eqn 1.13, in which the only variable is r , the distance from the nucleus. The value a_0 is the Bohr radius (52.9 pm). The number e is approximately 2.71828 and is a number that, in its own way, is as significant as π . It is not to be confused with another e , the charge on an electron. For many purposes in chemistry, the equations look simpler using the Bohr radius, a_0 , as the *unit of length*, rather than picometres or Ångströms. Using a_0 as unit of length reduces Eqn 1.13 to Eqn 1.14.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \quad (1.13)$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r} \quad (1.14)$$

The *maximum* value for ψ_{1s} occurs at the nucleus ($r = 0$, see Fig. 1.13). The value for ψ_{1s} depends *only* on the distance away from the nucleus and *not* on direction. The symmetry of the ψ_{1s} wave function is *spherical*. The value of ψ_{1s} is positive for all values of r and non-zero out to $r = \text{infinity}$.

It is now appropriate to relate the electron density discussed earlier to the wave function. It is largely useless to relate values of the wave function itself to any physical property. This is because there is no direct physical significance! However the value of ψ^2 *does* have a physical significance, since ψ^2 corresponds to *electron density*. The value of ψ^2 is the probability of finding an electron at that point or *electron density* at that point. A plot of ψ^2 for the 1s orbital is superimposed upon that of ψ in Fig. 1.13.

The electron density is greatest in the vicinity of the nucleus. This is *not* the same as saying the electron is most likely to be found at the nucleus. After all, there is only one point at $r = 0$, while there are many at, say, the surface of the sphere with $r = 100$ pm. Loosely speaking, the number of points associated with a particular value of r goes up with the surface area of the sphere, that is with $4\pi r^2$. To get a more useful picture, the *radial distribution function*, a description of how much electron density is found at a given value of r is required.

The radial distribution function shows that the electron is more likely to be found at the Bohr radius than at any other radius. Although the electron density ψ^2 is greatest at the nucleus, the chances of finding it there are small since there is so little volume at the nucleus. To understand the radial distribution function better it is appropriate to consider some apparently unrelated concepts. Consider a box filled with a gas of some density. The total weight of gas in the box is given by volume \times density (Fig. 1.14).

The volume is given by the lid surface area multiplied by the depth, or thickness, of the box. If the gas density is constant, the calculation is trivial. The situation for electron density is analogous, but more difficult to calculate since the electron density is *not* constant and the shape of the orbital is spherical, at least in the case of hydrogen in the ground state. Mathematically, the way to proceed is through an *integration* of electron

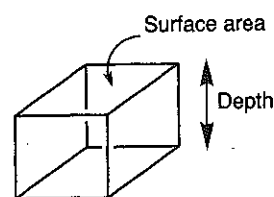


Fig. 1.14 The volume of a box.

density over the volume of the orbital. It is appropriate here just to visualize the integration process. This is conveniently done with recourse to an onion. Mentally, one can unravel a spherical orbital into shells (not to be confused with shells of orbitals!) in just the same way that an idealized onion can be unravelled into shells. The interesting property of each unravelled spherical 'orbital onion shell' is that if the ring is reasonably thin, then the electron density throughout that 'orbital onion ring' is approximately constant. Therefore if the volume of the 'orbital onion shell' is known, the total amount of electron density within that shell can be calculated using Eqn 1.15. The volume of a *thin* spherical onion shell is also given by the relationship surface area \times thickness. The surface area of a sphere is $4\pi r^2$. Since the electron density is ψ^2 , and the surface area is $4\pi r^2$, then the total electron density at radius r is given by Eqn 1.16, assuming *thin* shells each of equal thickness.

$$\text{Total in 'orbital onion shell'} = \text{surface area} \times \text{thickness} \times e^- \text{ density} \quad (1.15)$$

$$\text{total} = 4\pi r^2 \psi^2 \times \text{thickness of shell} \quad (1.16)$$

In this case the answer is known. For a hydrogen 1s orbital with one electron in it, the sum of the electron density in all the 'orbital onion shells' adds up to one electron. The quantity $4\pi r^2 \psi^2$ is proportional to the total amount of electron density at any given value of r . A plot of this function is included in Fig. 1.13. Mathematically, in the integration process, an exactly analogous process is followed, but in which the thickness of the shell is modified so that it becomes vanishingly thin. The radial distribution plot shows that the electron is to be found over a *range* of distances, but that it is *most likely* to be found at the Bohr radius, a_0 . Since it is not possible to state precisely where the electron is at any given time, it is better to talk in terms of the *probability* of finding the electron at some given distance.

1.10 Other hydrogen s orbitals

The orbital described above is the 1s orbital and this orbital contains the electron when the hydrogen atom is in the ground state. As for the 1s orbital, the other *s* solutions, 2s, 3s, 4s, etc., are all spherically symmetrical. These solutions represent orbitals that are generally empty, but in principle it is possible for them to become occupied if the ground state electron is *promoted* from the 1s orbital to, say, the 2s orbital. If the hydrogen atom's electron is in any other orbital than the 1s, it is said to be in an *excited state*. An electron in each of the hydrogen 1s, 2s, and 3s orbitals is represented in Fig. 1.15 by dot-diagrams. The scale is the same and the number of dots is the same in each case, allowing a comparison of relative size and of electron densities. A number of important features emerge. The most obvious point is that the orbitals increase in size with increasing principal quantum number. This corresponds to increasing orbit size in the Bohr model of the atom.

The next point concerns *radial nodes*. The 2s orbital (Fig. 1.15) shows a ring around the nucleus at which the electron density drops to zero. In fact, in

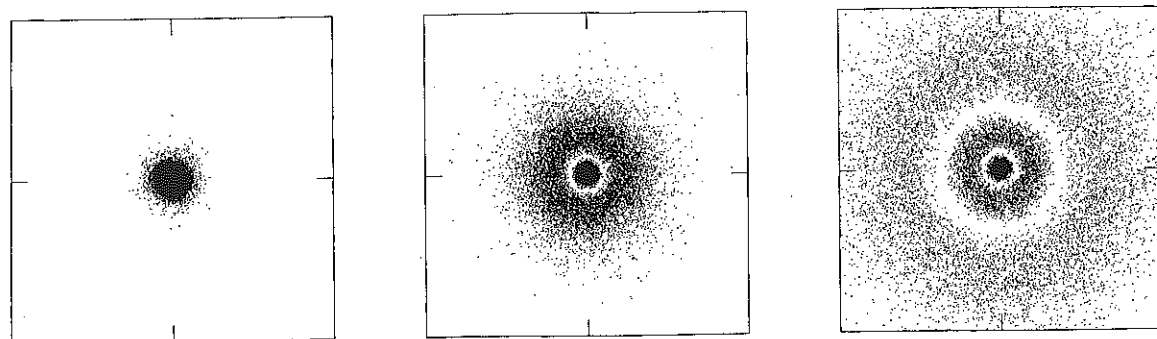


Fig. 1.15 Electron density dot diagrams (15 000 dots) representing the 1s (left), 2s (centre), and 3s (right) orbitals in the hydrogen atom. Each square is 2000 pm wide with the nucleus at the centre of each square.

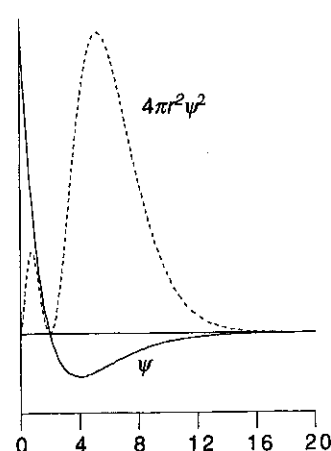


Fig. 1.16 Plot of ψ , and $4\pi r^2 \psi^2$ for the hydrogen 2s orbital.

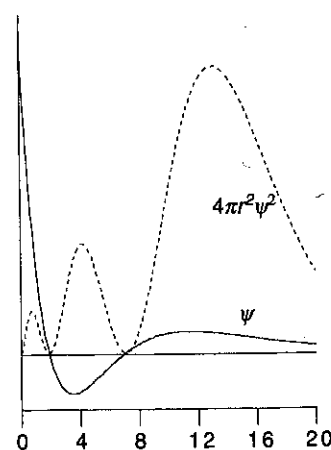


Fig. 1.17 Plot of ψ and $4\pi r^2 \psi^2$ for the hydrogen 3s orbital.

a three dimensional representation, there is a *spherical* surface at which the electron density drops to *exactly* zero. This feature is referred to as a *node*. The 3s orbital has *two* such spherical nodes. In general, the number of radial nodes shown by an s orbital with principal quantum number n is $n-1$.

The mathematical equations used to represent these orbitals can look somewhat daunting, but they are based upon exponential functions related to that of the 1s orbital already seen. Equations 1.17 and 1.18 give the formulae for these orbitals and, for clarity, the unit of length is a_0 as in Eqn 1.13.

$$\psi_{2s} = \frac{1}{4\sqrt{2}\pi} (2-r)e^{-r/2} \quad (1.17)$$

$$\psi_{3s} = \frac{1}{81\sqrt{3}\pi} (27-18r+2r^2)e^{-r/3} \quad (1.18)$$

It is a worthwhile exercise to plot the wave functions ψ_{2s} and ψ_{3s} . It should then soon be apparent that the radial nodes represent spherical surfaces at which the *sign* of the wave function switches from one sign to the other, that is positive to negative or negative to positive. For instance, the wave function for the 2s orbital (Fig. 1.16) changes from being positive to negative at one particular distance, $r = 2a_0$, from the nucleus. The 3s orbital wave function (Fig. 1.17) changes sign twice, from positive to negative and back to positive again, which is why there are two radial nodes. The electron density is *not* affected by the *sign* of the wave function. Recall that electron density is calculated from the wave function by squaring it. Squaring a real negative number *always* gives a positive number, that is the electron density is always positive, or perhaps zero if the wave function happens to be zero at that point. This seems sensible since common sense requires that there can never be negative electron density, or a negative probability. Zero or positive, yes, but never negative.

It is instructive to compare the radial distribution plots for the 1s, 2s, and 3s orbitals. These are plotted together in Fig 1.18 on the same scale so that a reasonable comparison can be made. The effective size of the s orbitals increases with increasing values of the principal quantum number. It should also be apparent that, for $n = 2$ and $n = 3$, although the electron density is greater in the regions closer to the nucleus, because of the greater volumes

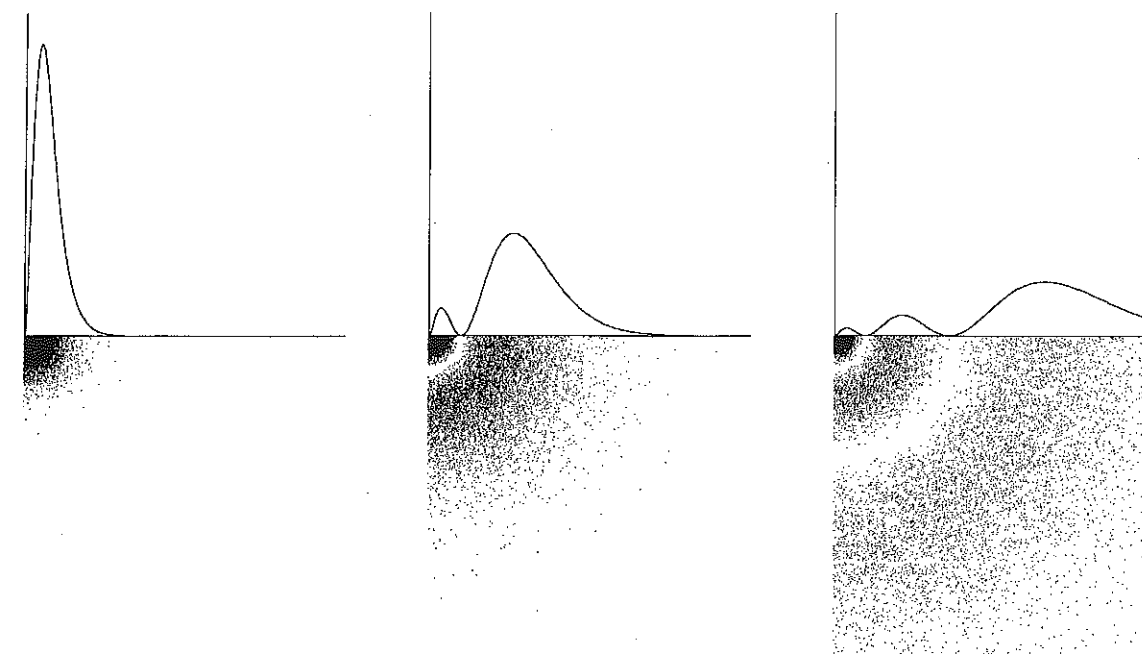


Fig. 1.18 The radial distribution functions for the 1s, 2s, and 3s orbitals related to quadrants of the electron density dot representations of electron density. The 3s orbital shows *two* spherical radial nodes, the 2s orbital shows *one*, and the 1s *none*.

involved further away, the greatest overall amount of electron density is found in the outermost region of the 2s and 3s orbitals.

1.11 Hydrogen p orbitals

The p orbitals ($l = 1$) are altogether different in appearance. One of each of the three 2p and 3p orbitals for the hydrogen atom are plotted in Fig. 1.19 on the same scale used in Fig 1.18. As the principal quantum number increases, the overall size of the orbital increases. However the most striking feature is that the orbitals *are not spherically symmetrical*, that is, they are *directional*. The shape of these orbitals may be generated from these two-dimensional cross-sections by rotating about the vertical axis (straight up and down the page).

Consider first the 2p orbital. The top of Fig. 1.19 represents the solution for which $m_l = 0$. Since this orbital has most of its electron density along the z-axis, it is called the $2p_z$ orbital. The 2p orbitals possess nodes. In each case there is a *nodal plane* dividing the two *lobes* of the orbital (the xy plane in the case of the $2p_z$ orbital). As for the s orbitals, increasing the principal quantum number is associated with extra nodal surfaces. In the case of the 3p orbital (Fig. 1.19, bottom) the second nodal surface is a sphere with radius $6a_0$.

When $n = 2$, the solutions to the wave functions are referred to as the $2p_1$, $2p_0$, and $2p_{-1}$ orbitals (the 1, 0, and -1 subscripts are the three possible

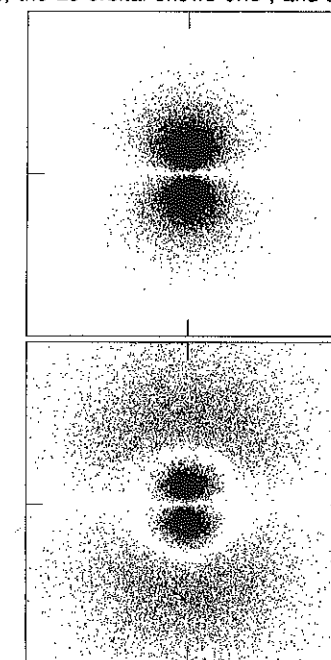


Fig. 1.19 Electron density dot diagrams (15 000 dots) of 2p (top) and 3p orbitals of the H atom. The squares are 2000 pm wide. The nucleus is at the centre of the squares.

values for m_l). For the purposes of this discussion, these three solutions are not totally convenient. The equations of the $2p$ orbitals for which $m_l = +1$ and -1 contain an *imaginary number*, i , the square root of -1 . However, mathematically it is perfectly justifiable to 'mix' these two solutions by taking *linear combinations*. The result of taking these linear combinations is two orbitals identical in appearance to the $2p_z$ orbital but which are directed along the x and y axes in the same way as the p_z orbital is directed along the z axis. These two new orbitals are referred to as the $2p_x$ and $2p_y$ orbitals, and their equations (Eqns 1.20 and 1.21) no longer contain i .

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{2p_1} + \psi_{2p_{-1}}) \quad (1.20)$$

$$\psi_{2p_y} = \frac{1}{\sqrt{2}}(\psi_{2p_1} - \psi_{2p_{-1}}) \quad (1.21)$$

The three $2p$ orbitals (Fig. 1.20) are identical in shape but differ in the directions in which they point. Therefore it is *not* correct to directly relate the m_l values 1, 0, and -1 to the coordinate axes x , y , and z . For the s orbitals, the wave functions and electron densities are at a *maximum* at the nucleus. For the $2p$ and $3p$ orbitals, the nucleus coincides with nodal surfaces and so the electron density is *zero* at the nucleus.

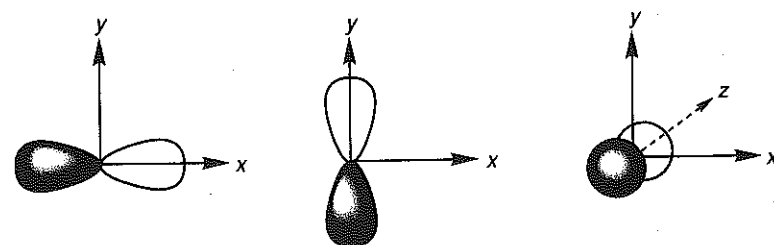


Fig. 1.20 Schematic representations of the $2p_x$, $2p_y$, and $2p_z$ orbitals.



Fig. 1.21 The shading indicates the sign of the wave function of a $2p$ orbital.

1.12 Wave function shading and signs

The schematic representation of a p orbital shown in Fig. 1.21 contains two pieces of information. The shape of the diagram corresponds to ψ^2 , the probability density. The shading indicates the relative sign of the wave function, that is, whether it is positive or negative. The relative signs of the wave function are often explicitly indicated by adding '+' or '-' signs. *These signs have nothing to do with electric charge.* They refer only to whether the value of the wave function is positive or negative. Whether the sign of the wave function is positive or negative is not of particular importance for atoms but is very important when addressing how atoms bond together to give molecules.

1.13 Hydrogen d orbitals

There are *five* independent d orbital solutions for each principal quantum number > 2 . These correspond to values of m_l of -2 , -1 , 0 , 1 , and 2 . Four of the equations, those for which m_l is not zero, contain i , the imaginary square

root of -1 and it is convenient to make linear combinations to produce functions related to the coordinate axes x , y , and z .

Four of the resulting wave functions, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, and $3d_{x^2-y^2}$ are similar in appearance (Figs. 1.23 and 1.24), differing only in their relative orientations. The four lobes of electron density in the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals are orientated between the coordinate axes. The $3d_{x^2-y^2}$ orbital is the same size and shape, but orientated so that the lobes are directed along the x and y axes.

The $3d_{z^2}$ orbital (Figs 1.23 and 1.24) is a different shape. One half of the total electron density is located in two major lobes directed along the z axis. The other half of the electron density is located in a ring- or doughnut-shaped region centred around the xy plane. The orbital possesses *cylindrical symmetry* in that a three-dimensional representation is generated by rotating the dot diagram about the z axis. Mathematically, the $3d_{z^2}$ orbital function corresponds to a linear combination of $3d_{z^2-y^2}$ and $3d_{z^2-x^2}$ functions and an equivalent name for the $3d_{z^2}$ orbital is the $3d_{2z^2-x^2-y^2}$ orbital.

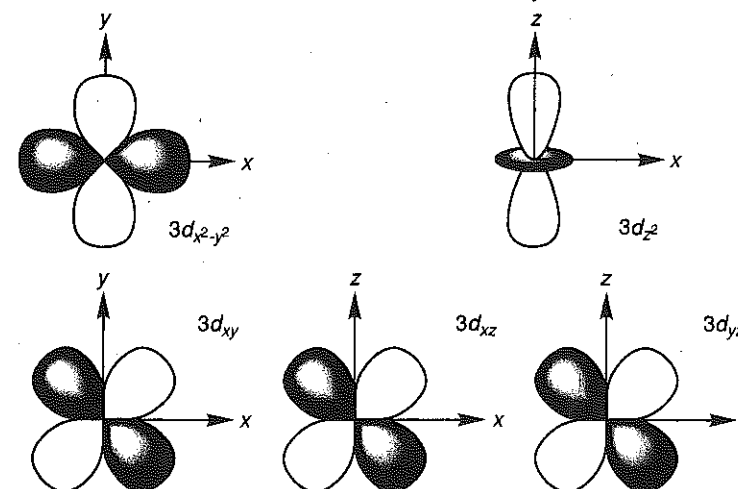


Fig. 1.23 The five d orbitals. Note the changes in axis labelling for each orbital.

1.14 Occupancy of orbitals

Any orbital can accommodate just *two* electrons. It can also hold zero or one electron, but *never* three or more. While the preceding pages indicate that it is not always appropriate to regard the electron as a little hard ball, certain properties of electrons are best treated as if the electrons spin about an axis passing through a diameter of the electron, rather like the earth spins about an axis every 24 hours. Therefore when there are two electrons in an orbital, one is said to *rotate* or *spin* in one direction and the second in the other. This is unfortunate terminology perhaps but, again, in common usage. The *spin quantum number* differentiates between the two directions of spin. The spin quantum number takes the values $+1/2$ or $-1/2$. This spin is not to be confused with the notion of electrons rotating about, or orbiting, the nucleus.

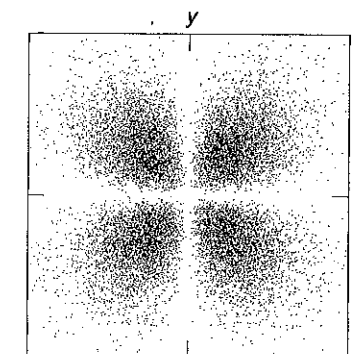


Fig. 1.22 Dot diagram (2000 pm square, 15 000 dots) for the hydrogen $3d_{xy}$ orbital. The yz and xz planes are nodal surfaces. The nucleus is at the centre of the square.

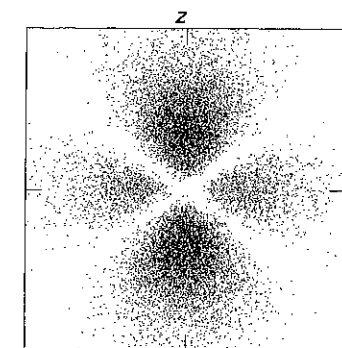


Fig 1.24 Dot diagram (2000 pm square, 15 000 dots) for the hydrogen $3d_{z^2}$ orbital. The apices of two nodal cones intersect at the nucleus, which is at the centre of the square.

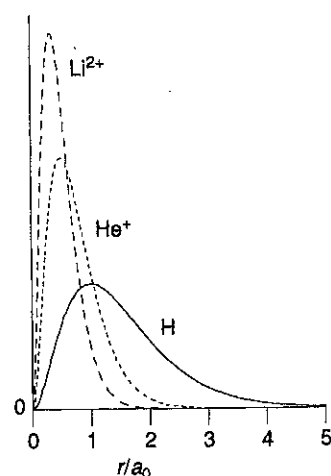


Fig. 1.25 Radial distribution functions for the H, He⁺, and Li²⁺ 1s orbitals.

1.15 Wave equation for other one-electron atoms

Hydrogen is the only neutral one-electron atom. All other one-electron atoms are positively charged and normally referred to as ions (or more specifically cations). The wave equations for one-electron ions such as He⁺ or Li²⁺ are closely related to those of hydrogen. The most important additional factor is the charge on the nucleus. In hydrogen, the nucleus has a charge of +1 from the single proton. In helium, the nucleus has a charge of +2, while in lithium the charge is +3. The effect of the extra positive nuclear charge on the electron is easy to imagine. It will be drawn inwards as a result of the extra attraction. This is expressed in the wave function (Eqn 1.22) for the 1s orbital for any one-electron atom which now contains a number Z which is the size of the nuclear charge.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr} \quad (1.22)$$

The hydrogen 1s wave function is also described by this equation and for hydrogen $Z = 1$. For helium $Z = 2$, for lithium, $Z = 3$, and so on. Figure 1.25 shows plots of ψ^2 and $4\pi r^2 \psi^2$ for H, He⁺, and Li²⁺ and the contraction arising from the increased nuclear charge is very apparent.

1.16 Building-up principle for many electron atoms

The Schrödinger equation can be solved for atoms other than hydrogen, but not exactly for any system containing more than one electron. This is due to complications arising from electron-electron repulsions. Although the hydrogen wave function solutions are technically only suitable for one-electron atoms, fortunately the hydrogen orbital wave functions are adaptable for many-electron atoms. The justification for adapting the one-electron functions for many-electron systems is that the results are good.

The electronic configuration of an element is a listing of the occupancy of the various atomic orbitals. The process by which the electronic configuration is derived for ever-increasing numbers of electrons is the *building-up principle* also called the *Aufbau principle*.

Ground state hydrogen has the electron in an orbital for which $n = 1$, $l = 0$, and $m_l = 0$. That is, the electron is in a 1s orbital. This is denoted 1s¹. The reason the single electron normally resides in the 1s orbital is that the energy of an electron within the 1s orbital is at the lowest possible energy. Electrons in any other orbital are at a higher energy.

What about helium? The 1s orbital can hold two electrons. The 1s orbital is still the lowest energy orbital, therefore the second electron also resides in the 1s orbital. It is more favourable to place the second electron in the 1s orbital and take an electron-electron repulsion penalty than to place the second electron in some higher energy orbital such as the 2s orbital. Note that the energy of an electron in the helium 1s orbitals is not the same as the energy of an electron in a hydrogen 1s orbital because of the greater nuclear charge.

The values of n , l , and m_l are the same for the second helium electron, but the spin quantum number differs for the two electrons. One electron takes the

value $+\frac{1}{2}$ while the second takes the value $-\frac{1}{2}$. The spins are opposite in direction. The electronic configuration of helium is written as 1s². This is represented on an energy level diagram (Fig. 1.26) using half-arrows. An electron with one spin quantum number is said to be 'spin-up' while an electron with the other spin quantum number is said to be 'spin-down'.

The electronic configuration of helium conveniently illustrates the *Pauli exclusion principle* which simply states that no two electrons in any one atom are allowed the same set of four quantum numbers. Each electron in any given atom *must* have a unique address. In the case of helium for instance, the two 1s electrons cannot both be spin up (Fig. 1.27), since this would require the spin quantum numbers to be the same.

Now consider the third element, lithium (Fig. 1.28). Since the first shell is fully occupied by two electrons, the third *must* go into an orbital for which $n = 2$ (since the $n = 3$ orbitals are all higher in energy than all the $n = 2$ orbitals). At first sight it could go into either the 2s or one of the 2p orbitals since for a hydrogen-like atom we have already seen that these orbitals are degenerate. However for a many-electron atom the orbitals are *not* degenerate and the 2s orbital is lower in energy than the 2p. This means the 2s orbital is occupied first. The reason for this is a consequence of *orbital screening*, or *shielding*. The electronic configuration of lithium is 1s²2s¹.

1.17 Orbital shielding

Consider the third electron in a lithium atom. It is affected by the charge on the nucleus (+3). However it is also repelled by the charge on the inner two electrons. Figure 1.29 shows the radial distribution functions for the lithium 1s, 2s, and 2p orbitals. It is clear that the electrons in the 1s orbital are much closer to the nucleus than any electrons in the 2s or 2p orbital. The two inner electrons in the 1s orbital *screen* the third electron from the full effect of the nuclear +3 charge. The difference between the full nuclear charge, Z , and the screening effect of the inner two electrons is called the *effective nuclear charge*, or Z_{eff} . In general, for any many-electron atom, any particular electron will always be screened from the nucleus to some extent by the remaining electrons.

$$Z_{\text{eff}} = Z - \text{screening constant} \quad (1.22)$$

Figure 1.29 shows the radial density functions of the 2s and 2p orbitals superimposed on the same plot for the 1s orbital in the lithium atom. An electron in the 2s orbital is screened from the nucleus by a different amount than an electron in a 2p orbital. Examine the region closer to the nucleus, where r is small. There is a significant amount of electron density very close to the nucleus for the 2s orbital which is *effectively inside* the 1s orbital. In other words the 2s orbital intrudes *inside* the volume of space occupied by the 1s orbital. There is no such effect for the 2p orbital, although there is some penetration. The upshot this is that the 1s electrons shield an electron in the 2s orbital *less* effectively than they shield an electron in a 2p orbital. The effective nuclear charge, Z_{eff} experienced by an electron in a 2s orbital is *greater* than that experienced by an electron in a 2p orbital. The energy of an

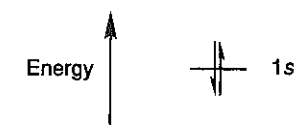


Fig. 1.26 An energy level plot for helium.

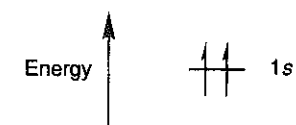


Fig. 1.27 This configuration for He is forbidden by the Pauli exclusion principle.



Fig. 1.28 An energy level diagram for ground state lithium (1s²2s¹).

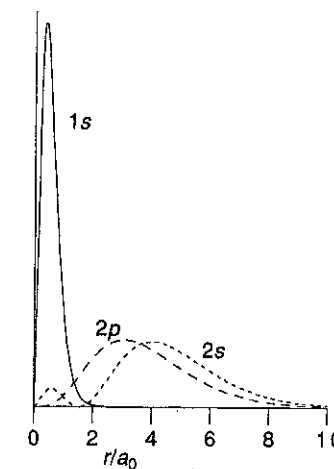


Fig 1.29 Radial distribution functions for lithium 1s, 2s, and a 2p orbital.