1

Atoms, the constituents of matter

We now take it for granted that matter is made of atoms. Indeed, using modern imaging techniques, we can even 'see' individual atoms in matter, as we will describe in this chapter. But this fact is of enormous importance. Richard Feynman has said that if just one sentence of scientific knowledge were to survive to be passed to future generations, it would be that *all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*. And so, an understanding of matter begins with a study of atoms. In this chapter, we describe the main properties of atoms and their basic electronic structure; their mutual attraction and repulsion will be discussed in Chapter 2. We will see that atoms are extremely small and that any ordinary amount of matter contains an enormous number of atoms. And in this lies the apparently continuous nature of matter on an ordinary scale.

1.1 The mass of an atom

An atom has a well-defined mass and its mass can be determined with high accuracy. In practice, however, it is not the mass of a neutral atom that is measured, but the mass of the *ionized* atom. This is because the motion of a positively charged ion can be readily manipulated by electric or magnetic fields, which is done in a *mass spectrometer*. The atom is ionized by removing one of its electrons and, of course, the mass of the missing electron can be readily taken into account.

One type of mass spectrometer is the *time of flight mass spectrometer*. Its principle of operation is illustrated schematically in Figure 1.1. The atoms (or molecules) in a gas or vapour of the sample are ionized by a short pulse of energetic electrons or photons. The action of the electrons or photons is to knock out one of the atomic electrons, producing a positive ion. The bunch of ions that is produced passes into an *acceleration region*. A potential difference, V_{acc}, is maintained across this region that accelerates the ions, and they leave the acceleration region with kinetic energy given by

$$\frac{1}{2}Mv^2 = V_{\mathrm{acc}}e, \tag{1.1}$$

Physics of Matter, First Edition. George C. King.

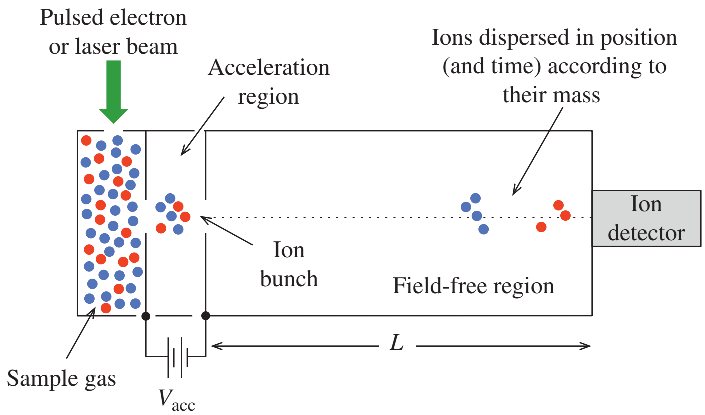

Figure 1.1 Schematic diagram of a time of flight mass spectrometer, illustrating its principle of operation. The atoms (or molecules) in a gas or vapour of the sample are ionized by a short pulse of energetic electrons or photons. The bunch of positive ions that is produced passes into the acceleration region where they are accelerated to a final kinetic energy $V_{acc}e$. The ions then travel through a field-free region, with individual ions travelling at constant velocity. The lighter ions in the bunch travel at a higher velocity than the heavier ones and strike the detector before the heavier ions. Hence, the ions are dispersed in time (and position) according to their mass; the variation in mass has been translated into a variation in arrival time at the detector.

where M and v are the mass and velocity of the ion, respectively, and e is the electronic charge. The ions then travel through a *field-free region* of length L. Because this region is field-free, i.e. there is no potential difference across it, the individual ions travel at constant velocity in this region. The ions then strike an ion detector at the far end of the region. The lighter ions in the bunch travel at a higher velocity and strike the detector before the heavier ions. Hence, the ions are dispersed in time (and position) according to their mass; their variation in mass has been converted into a variation in arrival time at the detector. The time t that the ions take to transverse the field-free region is recorded. Since $v = L/t$, we have

$$t = L\left(\frac{M}{2V_{acc}e}\right)^{1/2}, \tag{1.2}$$

and

$$M = \frac{2V_{acc}e}{L^2}t^2. \tag{1.3}$$

A mass spectrum is obtained by plotting the yield of detected ions versus t^2. Such a mass spectrum is shown schematically in Figure 1.2 for the example of a sample of chlorine gas. This element has two main isotopes ^{35}Cl and ^{37}Cl, where the superscript is the *mass number* of the isotope. The element has *isotopic abundances* in the ratio 3 : 1 and two peaks are observed in the mass spectrum. Indeed, the existence of isotopes was first discovered in a mass spectrometer by J.J. Thompson. If there are different gases in a sample, this will give rise to different peaks in the mass spectrum. In this way, the composition of the sample gas can be determined.

Mass spectrometers are used extensively in research and industry and for a variety of purposes. For example, a time of flight mass spectrometer was one of the instruments on board the *Rosetta* spacecraft,

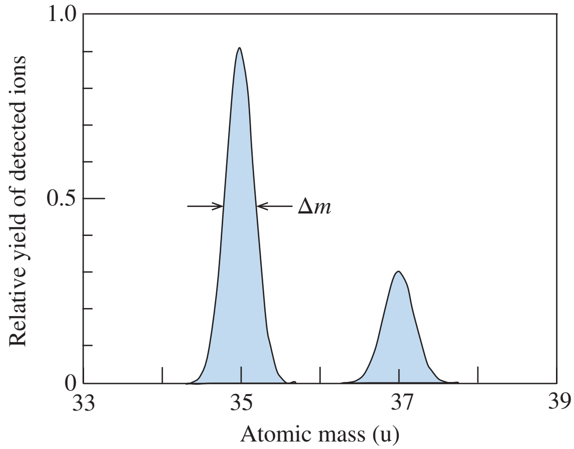

Figure 1.2 A mass spectrum of chlorine gas. Chlorine has two main isotopes ^{35}Cl and ^{37}Cl with isotopic abundances in the ratio 3 : 1 and two peaks are observed in the spectrum. Δm is the width of each peak in the spectrum, measured at half peak height, and is a measure of the ability of the mass spectrometer to resolve individual mass peaks.

which landed on comet Churyumov-Gerasimenko in 2014. The primary role of the spectrometer was to identify species present in the coma of the comet, which is the nebulous envelope of atoms and ions that surrounds the comet. This coma varies with distance of the comet from the sun and also the comets' rotation. A photograph of the time of flight spectrometer is shown in Figure 1.3. The relatively low weight of a time of flight spectrometer is an important advantage for rocket flights. A different type of spectrometer, which allows atomic masses to be determined with very high precision, is the *magnetic mass spectrometer*. In this type, the ions are passed between the poles of a large magnet. The magnet field disperses ions according to their mass; analogous to the way a glass prism disperses light according to wavelength. Using this

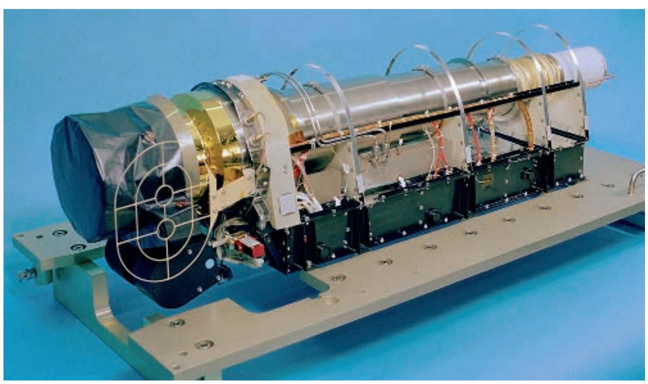

Figure 1.3 A photograph of the time of flight mass spectrometer that was aboard the Rosetta spacecraft that landed on comet Churyumov–Gerasimenko. The primary role of the spectrometer was to identify species present in the coma of the comet. The relatively low weight of a time of flight mass spectrometer is an important advantage for space flights. Source: ESA/Rosetta/ROSINA/UBern/BIRA/LATMOS/LMM/IRAP/MPS/SwRI/TUB/UMich/European Space Agency.

magnetic type of spectrometer, atomic masses can be measured with a precision of 1 part in 10^7 or 10^8. It is valuable to have this high precision when, for example, it is required to predict the amount of energy that would be produced in a particular nuclear reaction. If we know the total mass of the interacting nuclei before the reaction and the total mass of the reaction products, the mass difference Δm can be converted into the released energy via Einstein's equation of mass-energy equivalence $E = \Delta mc^2$.

1.1.1 Atomic masses

Precise measurements give the mass of a ^{12}C atom to be 1.992647×10^{-26} kg. A more natural and convenient unit is the *atomic mass unit* (u). This unit is defined so that the mass of a ^{12}C atom is taken to be exactly 12 u. In terms of the kilogram:

$$1\,\text{u} = 1.660539 \times 10^{-27}\,\text{kg}.$$

Other atomic masses are measured on this relative scale. For example, the atomic mass of ^{20}Ne, the most abundant isotope of neon, is 19.992436 u. We can also have the *relative atomic mass* A_r of an atom, which is given by

$$A_\text{r} = \frac{\text{Mass of the atom}}{\text{Mass of a }^{12}\text{C atom}} \times 12. \tag{1.4}$$

Clearly, being a ratio, A_r is a number and has no units. So, for example, the relative atomic mass of ^{20}Ne is 19.99, rounded to two significant figures.

Most elements in their natural state consist of several or more isotopes. In that case, we take a weighted mean of the atomic masses of the individual isotopes according to their natural abundance. This is called the *mean atomic mass*. Carbon has two stable isotopes: ^{12}C and ^{13}C with atomic masses of 12 u and 13.003355 u, respectively, and relative natural abundances of 98.89% and 1.11%, respectively. Hence, the mean atomic mass of carbon is

$$\left(\frac{98.89}{100} \times 12\right)\text{u} + \left(\frac{1.11}{100} \times 13.003355\right)\text{u} = 12.011\,\text{u}.$$

Worked example

In a particular time of flight mass spectrometer, the length L of the field-free region is 50 cm, the acceleration voltage V_acc is 100 V, and the pulse width Δt of the electron beam that is used to ionize the atoms is 0.1 μs. Would this mass spectrometer be able to resolve the two main isotopes of chlorine, ^{35}Cl and ^{37}Cl?

Solution

The finite width of the electron pulse results in an uncertainty Δt in the arrival time of the ions at the detector, and, in turn, this leads to an uncertainty Δm in the measured mass of the isotopes. From Equation (1.3), we have

$$M = \frac{2V_\text{acc}e}{L^2}t^2.$$

$$\frac{\Delta M}{\Delta t} \approx \frac{\mathrm{d}M}{\mathrm{d}t} = \frac{2V_{\mathrm{acc}}e}{L^2}2t = \frac{M}{t^2}2t.$$

Hence,

$$\frac{\Delta M}{M} \approx 2\frac{\Delta t}{t}.$$

The factor of 2 occurs because $m \propto t^2$. The ratio $M/\Delta M$ is called the *mass resolution* of the spectrometer.

$$t = L\left(\frac{M}{2V_{\mathrm{acc}}e}\right)^{1/2} = 50\times 10^{-2}\left(\frac{36\times 1.66\times 10^{-27}}{2\times 100\times 1.6\times 10^{-19}}\right)^{1/2} = 21.6\ \mu\mathrm{s},$$

where we have taken $M = (35+37)/2 = 36$. Hence,

$$\Delta M \approx 2M\frac{\Delta t}{t} = 2\times 36\times \frac{0.1}{21.6} = 0.33\ \mathrm{u}.$$

ΔM is much smaller than the mass difference (2 u) between the two isotopes, which could therefore be easily resolved by the spectrometer.

Avogadro's number and the mole

The number of atoms in 12 g (0.012 kg) of ^{12}C is

$$\frac{0.012\ \mathrm{kg}}{1.992647\times 10^{-26}\ \mathrm{kg}} = 6.022\times 10^{23}.$$

This is an important number, which is called *Avogadro's number*, and is given the symbol N_A. Again, it is convenient to have units that result in numerical values that are not too large. For the measure of an amount of substance, an appropriate unit is the *mole* (mol). It is defined as the amount of substance that contains as many elementary entities as there are atoms in 12 g (0.012 kg) of ^{12}C. Entities include atoms, molecules, and ions. Hence, 1 mol of helium contains 6.022×10^{23}atoms of helium atoms, 1 mol of oxygen gas contains 6.022×10^{23} molecules of O_2, and 1 mol of copper contains 6.022×10^{23} atoms of copper.

Suppose that we measure out a mass, *in grams*, of an element numerically equal to its relative atomic mass A_r. The number of atoms in this amount of the element is

$$\frac{A_r\times 10^{-3}\ \mathrm{kg}}{\text{Mass of atom (kg)}}, \tag{1.5}$$

which on substituting for A_r from Equation (1.4) is

$$\frac{12\times 10^{-3}\ \mathrm{kg}}{\text{Mass of a }^{12}\text{C atom (kg)}} = N_A. \tag{1.6}$$

We see that a mass A_r g of an element, having relative atomic mass A_r, contains Avogadro's number of atoms. And the amount of substance that this number corresponds to is 1 mol. For example, 1.2 kg of lead ($A_r = 207.3$) contains

$$\frac{1.2}{207.3 \times 10^{-3}} \times 6.022 \times 10^{23} = 3.5 \times 10^{24} \text{ atoms or } 5.8 \text{ mol.}$$

1.2 The size of an atom

Atoms do not have a sharp edge, as we will discuss in Section 1.3. Nevertheless, from a practical point of view, atoms do possess what amounts to a definite 'size'. We can see this from the fact that solids are essentially incompressible, which means that we cannot push atoms into each other. A number of ingenious methods were initially used to measure the sizes of atoms and molecules. In one method, a drop of a liquid that did not mix with water was placed onto a smooth body of water. The liquid spread out over the water and by measuring the area of the dispersed liquid, and knowing the volume of the initial drop of liquid, an upper limit to the diameter of the molecules in the liquid could be deduced. Now, using X-ray crystallography, we can determine the spacing between lattice planes in a crystal (see Section 8.4). Since crystals resist being compressed, we can take this separation as a measure of the size of the atoms.

We can estimate the size of an atom in the following way. We imagine the atoms in a solid to be packed together as illustrated by Figure 1.4. If the atomic radius is R, each atom will occupy a volume $\approx(2R)^3$. We recall that a mass A_r of an element contains Avagadro's number of atoms. And this mass has a volume $V = A_r/\rho$, where ρ is the density of the element. Hence, we have

$$V = \frac{A_r}{\rho} \approx N_A (2R)^3, \tag{1.7}$$

giving

$$R \approx \frac{1}{2}\left(\frac{A_r}{\rho N_A}\right)^{1/3}. \tag{1.8}$$

Table 1.1 lists the estimated radius of a number of elements across the periodic table that have been obtained using Equation (1.8). Also shown, in the last column of the table, are more accurate values of

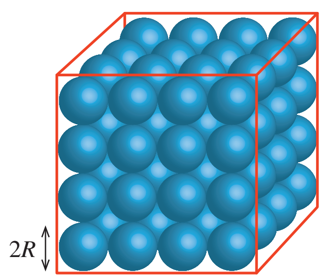

Figure 1.4 We can estimate the size of an atom by imagining the atoms in a solid to be packed together as in this figure. If the atomic radius is R, each atom will occupy a space of volume $\approx(2R)^3$.

Table 1.1 Estimated atomic radii obtained from Equation (1.8) for a number of elements across the periodic table. Also shown, in the final column, are accurate values of the radii obtained by sophisticated theoretical calculations. Note the small variation in atomic size with respect to atomic mass.

Element	ρ (g/cm^3)	A_r	Estimated atomic radius (nm)	Accurate atomic radius (nm)
Beryllium	1.85	9.01	0.10	0.11
Aluminium	2.70	26.98	0.13	0.12
Iron	7.87	55.85	0.16	0.16
Molybdenum	10.20	95.94	0.13	0.19
Barium	3.50	137.33	0.20	0.25
Platinum	21.50	195.08	0.13	0.18
Uranium	19.10	238.03	0.14	0.18

the atomic radii that have been obtained by sophisticated theoretical calculations. Despite the simplicity of our model, the two sets of values for the atomic radii are in reasonably good agreement. What is most revealing about the table is that light and heavy atoms have much the same size. As we see from Table 1.1, atomic radii lie typically within the range 0.1–0.3 nm. The essential reasons for this are as follows. As the mass of the elements increases, so also does the charge Ze on the nucleus, where Z is the *atomic number*. The electrons that are close to the nucleus feel the strong attraction of the nucleus and are drawn close to it. These electrons provide electrostatic shielding for electrons that are further away from the nucleus. Indeed the electrons that are furthest from the nucleus are almost completely shielded from the electrostatic attraction of the nucleus. And so they feel an attraction that is not so different from an electron in the singly charged ($Z = 1$) hydrogen atom. The size of an atom is determined solely by the electrons surrounding the nucleus, which has a size of $\sim 10^{-15}$m, while nearly all the mass of the atom is concentrated in the nucleus.

1.2.1 Scanning probe microscopy

We use a microscope to see small objects. However, the ultimate resolution of an optical microscope is limited by diffraction of the light that we use to observe the object. The diffraction limit, i.e. just how small an object we can resolve, is roughly half the wavelength λ of the light. Visible light spans the wavelength range from about 400 to 750 nm, and in practice, the best we can do with traditional optical microscopy is to resolve objects about 200 nm across. This is almost three orders of magnitude larger than the diameter of an atom, and clearly it is not possible to resolve atoms or molecules with an optical microscope. However, our ability to 'see' atoms changed dramatically in 1982 with the invention of *scanning probe microscopy* by Gerd Binnig and Heinrich Rohrer, an invention for which they were awarded the Nobel Prize in Physics in 1986. The principle of a scanning probe microscope is illustrated schematically in Figure 1.5. The microscope has a quartz crystal to which is attached an *extremely* sharp tip. This tip is positioned less than about 1 nm above the surface of the sample to be imaged. Crystalline quartz has a property called *piezoelectricity*. This means that when a potential difference is applied across the ends of a quartz crystal, the dimensions of the crystal change. Hence, by applying an appropriate voltage across the quartz crystal in the microscope, the tip can be moved across the surface of the sample. Indeed the tip can be moved in steps of less than 0.01 nm. In a similar way, the height of the tip above the surface can be controlled. Scanning probe microscopy exploits interactions that may exist between the tip and the atoms at the surface of the sample; there are no lenses or mirrors. Such tip-surface interactions produce a signal that can be measured. The tip is scanned in successive rows across the surface and as it does, the signal varies depending on the topology of the surface.

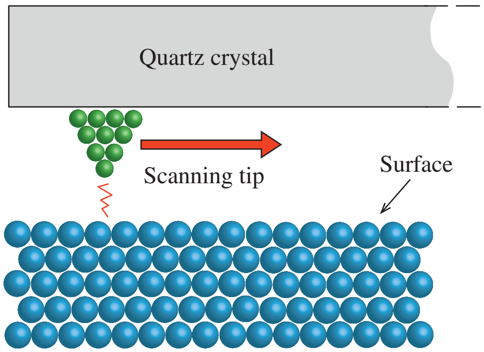

Figure 1.5 A schematic diagram to illustrate the principle of a scanning probe microscope. The microscope has a quartz crystal to which is attached an *extremely* sharp tip, which is positioned less than about 1 nm above the surface of the sample to be imaged. By applying a suitable voltage across the quartz crystal, which is piezoelectric, the tip can be moved in successive rows across the surface of the sample in steps of less than 0.01 nm. An interaction between the tip and the atoms at the surface of the sample produces a signal that can be measured. As the tip is scanned across the surface, the signal varies depending on the topology of the surface. The recorded signal is then processed to produce an image of the surface. Sub-atomic resolution is achieved because tip-surface interactions are very short range and because of the sharpness of the tip.

The recorded signal is then processed to produce an image of the surface. Sub-atomic resolution can be achieved, with details less than 0.1 nm being resolvable. This is because the tip-surface interactions have a very short range and because the tip can be made atomically sharp.

There are various scanning probe techniques that exploit the different possible interactions between the tip and the surface. *Scanning tunnelling microscopy* (STM) is based on the measurement of an electric current that flows between the tip and the surface. This current flow is due to *quantum mechanical tunnelling* of electrons across the narrow gap between the tip and surface. *Atomic force microscopy* (AFM) exploits various interatomic forces that the surface exerts on the tip. For example, this may be the van der Waals force that we will discuss in Section 2.3. The force can be detected as a deflection of the crystal to which the tip is attached or as a change in the vibrational frequency of the tip-crystal assembly.

The principle of one type of AFM, which exploits the change in the vibrational frequency of the tip-crystal assembly, is illustrated in Figure 1.6. This technique employs a quartz tuning fork, exactly like the kind that is found in a quartz watch. An atomically sharp tip is attached to one of the prongs of the tuning fork. The piezoelectric effect is exploited to drive the quartz tuning fork into oscillation by applying across it an AC voltage. Conversely, mechanical vibrations of the tuning fork produce an AC voltage signal, and this signal is used to determine the frequency of the vibrating tuning fork. The tuning fork is driven at its resonance frequency. The normal resonance frequency f_0 of such a quartz tuning fork is $2^{15} = 32.768$ kHz, but this is reduced somewhat by the addition of the sharp tip.

f_0 is the frequency of the tuning fork when it is far above a surface. When the tip is positioned just above a surface, the atoms on the surface exert a short-range force on the tip. This force causes the resonance frequency of the tuning fork to change to frequency f. The output frequency of the oscillator is adjusted to match the new resonance frequency f and the frequency difference $\Delta f = (f - f_0)$ is measured. The frequency difference Δf is recorded as the tip is scanned in rows across the surface. The recorded variation in Δf is then processed to produce an image of the surface.

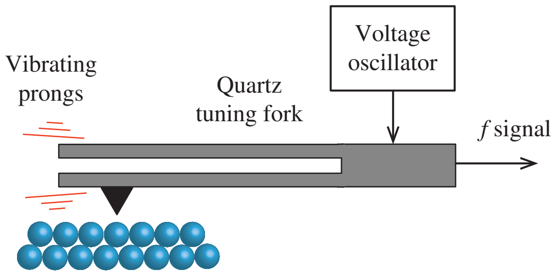

Figure 1.6 A schematic diagram to illustrate the principle of one type of atomic force microscope. An atomically sharp tip is attached to one of the prongs of a quartz tuning fork, exactly like the kind in a quartz watch. The piezoelectric effect is used to drive the quartz tuning fork into oscillation by the application of an AC voltage. The mechanical vibrations of the tuning fork produce an AC voltage signal, so that the vibrational frequency of the tuning fork can be measured. The tuning fork is driven at its resonance frequency. When the tip is positioned just above a surface, the atoms on the surface exert a short-range force on the tip, which causes the resonance frequency f_0 of the tuning fork to change to frequency f. The frequency difference $\Delta f = (f - f_0)$ is measured as the tip is scanned across successive rows of the surface. The recorded variation in Δf is processed to produce an image of the surface.

We can model the quartz tuning fork and its change in resonance frequency by the more familiar system of a mass m on the end of a spring of force constant k_0; see Figure 1.7a. The resonant frequency of vibration of the mass-spring system is

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k_0}{m}}. \tag{1.9}$$

If we add an additional spring of force constant k to the mass as in Figure 1.7b, the extra spring exerts an additional force on the mass and the resonant frequency changes to $f = (1/2\pi)\sqrt{(k_0 + k)/m}$. The frequency difference Δf is

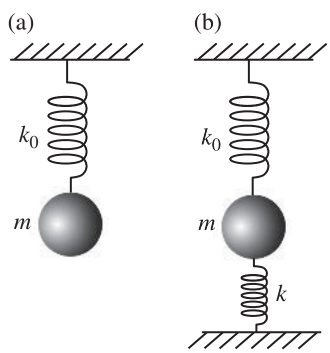

Figure 1.7 A model of the quartz tuning fork in an AFM instrument based on a mass-spring system. (a) This corresponds to the situation where the tip of the instrument is not close to the surface. The resonance frequency of the mass-spring system is $f_0 = (1/2\pi)\sqrt{k_0/m}$. (b) This corresponds to the situation where the tip of the instrument is very close to the surface. By attaching a second spring, the resonance frequency of the mass-spring system increases to $f = (1/2\pi)\sqrt{(k_0 + k)/m}$. To a good approximation $\Delta f = (f - f_0) = (f_0 - k_0)k$, when $k_0 \gg k$.

$$\Delta f = f - f_0 = \frac{1}{2\pi\, m^{1/2}} \left[(k_0 + k)^{1/2} - k_0^{1/2} \right]. \tag{1.10}$$

If $k_0 \gg k$, then to a good approximation

$$(k_0 + k)^{1/2} = k_0^{1/2} \left(1 + \frac{k}{2k_0} \right). \tag{1.11}$$

Substituting this result into Equation (1.10) and substituting for m from Equation (1.9), we obtain

$$\Delta f = \frac{f_0}{k_0} k. \tag{1.12}$$

The change in frequency Δf is a measure of the strength k of the additional force acting on the spring. Similarly, in the case of the quartz tuning fork, the difference Δf in its resonance frequency is a measure of the strength of the force acting on the tip due to the surface. Different parts of the surface will exert different amounts of force on the tip. Hence, the recorded variation in Δf can be processed to produce an image of the surface or indeed of a molecule attached to the surface.

The bottom half of Figure 1.8 shows an AFM image that was obtained of a pentacene molecule ($C_{22}H_{14}$), which was attached to an atomically flat surface. The image is essentially the measured variation of Δf for

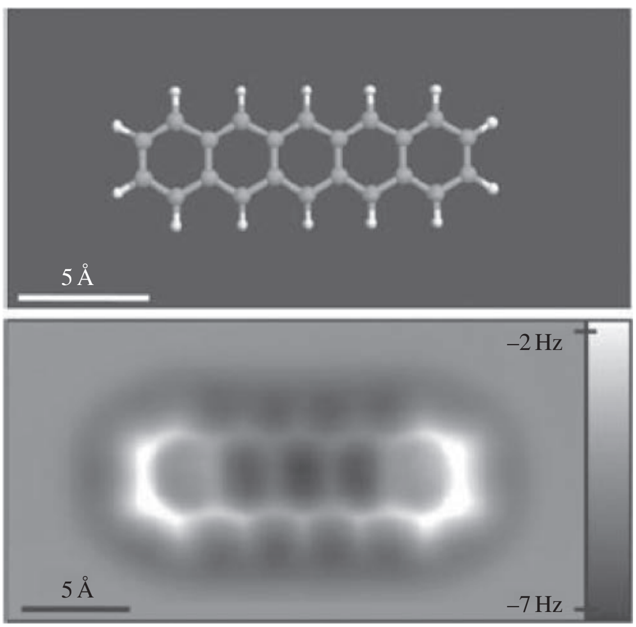

Figure 1.8 The bottom half of this figure shows an AFM image that was obtained of a pentacene molecule ($C_{22}H_{14}$). The image is essentially the measured variation of Δf for the tuning fork as the tip was scanned across the molecule. In this case, the end of the tip was terminated in a *single* atom of carbon monoxide that had been attached to the tip. The image clearly shows the structure of the pentacene molecule and its internal bonds. Indeed the AFM image closely resembles the ball and stick construction that is traditionally used to represent the molecule, which is shown in the top half of the figure. Source: Gross et al. (2009)/Reproduced from American Association for the Advancement of Science – AAAS.

the tuning fork as the tip was scanned across the molecule. In this case, the end of the tip was terminated in a *single* atom of carbon monoxide that had been attached to the tip. The image clearly shows the structure of the pentacene molecule and its internal bonds. Indeed the AFM image closely resembles the ball and stick construction that is traditionally used to represent the molecule, which is shown in the top half of Figure 1.8. In an extension of AFM, the tip can be used to manipulate the position of single atoms on a surface and hence to produce artificial structures on the atomic scale, i.e. *nanostructures*.

Worked example

Compare the number of water molecules in a teaspoon of water with the number of teaspoons of water in all the oceans of the world.

Solution

The molecular weight of water is 18 u and so 18 g of water contains Avagadro's number N_A of molecules. Taking the volume of a teaspoon to be 5 ml, it contains 5 g of water. The number of molecules in 5 g water

$$= 5 \times \frac{6.02 \times 10^{23}}{18} = 1.7 \times 10^{23}.$$

About 97% of Earth's water is found in its oceans. According to the United States Geological Survey, there are 1.3×10^{18} m^3 of water in the oceans. 1 m^3 = 10^6 ml.

Hence, the number of teaspoons of water in the oceans

$$= \frac{1.3 \times 10^{18} \times 10^6}{5} = 2.6 \times 10^{23}.$$

We see that the number of water molecules in a teaspoon of water is roughly the same as the number of teaspoons of water in all the oceans of the world.

1.3 Atomic structure

By the beginning of the twentieth century, the *emission spectra* of a variety of atoms had been measured. These were obtained by exciting the atoms in an electrical discharge and analysing the emitted radiation with either a prism or a diffraction grating in an *optical spectrometer*. The resulting emission spectra appear as a set of *discrete* spectral lines of different wavelengths (or colours) that are characteristic of the atom. Quite early on, it was realised that these spectra provide valuable information about the atoms that produce them. The scientist Anders Ångström measured the emission spectrum of atomic hydrogen and observed a *series* of four visible spectral lines. The spectrum of hydrogen is illustrated in Figure 1.9, showing the

Figure 1.9 The emission spectrum of hydrogen that lies in the visible region of the electromagnetic spectrum, showing the four lines of the Balmer series.

different colours of the lines: violet, blue, green, and red. Then in 1885, Johann Balmer, a school teacher, discovered that the wavelengths of the four hydrogen lines could be beautifully fitted by the simple formula

$$\lambda = 364.6\frac{n^2}{(n^2-4)}\ \text{nm}, \tag{1.13}$$

where $n = 3, 4,$ or 5. Clearly, any successful theory of atomic structure would need to provide an explanation for this formula. In 1911, Rutherford proposed his model of the atom in which all the positive charge of the atom and essentially all its mass are concentrated in a tiny region called the nucleus. And around this nucleus, the atomic electrons circulate. Rutherford based his model on the observation that alpha particles could be scattered through a large angle by traversing a single atom, which could only happen if the nucleus was extremely small ($\sim 10^{-15}$ m). The physicist Niels Bohr worked for a brief period in Rutherford's laboratory in Manchester. And in 1913, adopting Rutherford's model, he devised a theory of the hydrogen atom. Bohr's theory was spectacularly successful in accounting for the observed hydrogen spectrum and for this work, Bohr was awarded the 1922 Nobel Prize in Physics.

1.3.1 The Bohr model of the hydrogen atom

In the Bohr model of the hydrogen atom, a single electron moves in a circular orbit around the nucleus, a proton; in a somewhat analogous way in which a planet orbits the Sun. Bohr's model is based on classical physics and herein lie two particular difficulties. Since the electron is continuously changing direction in its circular orbit, it is continuously accelerating. According to classical physics, an accelerating charge emits electromagnetic radiation. Therefore the electron should continuously lose energy and spiral into the nucleus. Cleary, it does not; atoms are observed to be stable. The other difficulty is that classical theory allows for all possible orbits and all orbital radii. But, the spectral lines observed in emission spectra are discrete, i.e. the emitted photons have a well-defined wavelength and energy. This indicates that electrons occupy energy levels with fixed energies so that when an electron makes a transition between them, the photon that is emitted also has a well-defined energy. To circumvent these difficulties Bohr made a number of postulates; specific quantitative predictions that could be tested by experiment. His postulates are:

1. An electron in an atom moves in a circular orbit about the nucleus under the influence of the electrostatic attraction between the electron and the nucleus, obeying the laws of classical mechanics.

2. Instead of the infinity of orbits that would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is an integral multiple of a fundamental unit of angular momentum, denoted as $\hbar$, which is Planck's constant h divided by 2π. Note that this postulate introduces the concept of *quantization*. Hence, we have

$$L = n\hbar, \quad n = 1, 2, 3, \ldots. \tag{1.14}$$

3. Despite the fact that the electron is accelerating, it moves in an allowed orbit without radiating electromagnetic energy and its total energy E remains constant.

4. Electromagnetic radiation is emitted if an electron discontinuously makes a transition from an orbit of total energy E_i to an orbit of energy E_f. The frequency ν of the radiation is given by

$$\nu = \frac{(E_i - E_f)}{h} \tag{1.15}$$

Note that this equation is just the Planck–Einstein relation that the energy of a photon is equal to $h\nu$. We see that Bohr retained the classical description of the electrostatic interaction between the nucleus and the electron. But he did not retain the classical behaviour for the electron to continuously lose energy; with the conclusion that this behaviour does not apply to electrons in atoms.

In the Bohr model, the equation of motion of the electron about the nucleus is

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}, \tag{1.16}$$

where r is the radius of the orbit, v; m and e are the velocity, mass, and charge of the electron, respectively; Ze is the charge on the nucleus ($Z = 1$ for hydrogen); and ε_0 is the permittivity of free space. (Here we have made the approximation that the nucleus is infinitely more massive than the electron, which is reasonable since the ratio of the masses of the proton and the electron is 1836:1.) From Equation (1.14), the orbital angular momentum of the electron is

$$L = mvr = n\hbar. \tag{1.17}$$

Solving for v and substituting into Equation (1.16), we obtain

$$r_n = 4\pi\varepsilon_0 \frac{n^2\hbar^2}{mZe^2}. \tag{1.18}$$

We see that the quantization of angular momentum has restricted the possible circular orbits that the electron can occupy. The corresponding radii are proportional to n^2. The smallest orbit has $n = 1$ and taking this value of n, we have

$$r_1 = 4\pi\varepsilon_0 \frac{\hbar^2}{me^2} = a_0, \tag{1.19}$$

where a_0 is called the *Bohr radius*. Using the values of the fundamental constants in Equation (1.19), we find that the smallest radius has the value 0.053 nm, a value that is consistent with the characteristic size of an atom, see Table 1.1.

The electron has both kinetic energy K and potential energy V. From Equation (1.16), the kinetic energy of the electron is given by

$$K = \frac{1}{2}mv^2 = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}. \tag{1.20}$$

The potential energy of the electron is equal to the work done in taking the electron from infinity to distance r from the nucleus:

$$V = \frac{1}{4\pi\varepsilon_0}\int_{\infty}^{r}\frac{Ze^2}{r^2}\,\mathrm{d}r = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}. \tag{1.21}$$

The potential energy is negative as the electron is bound to the nucleus, i.e. work must be done to remove the electron from its orbit to infinity. The total energy E of the electron, kinetic plus potential, is then

$$E = K + V = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} = -\frac{1}{2}V. \tag{1.22}$$

Using Equations (1.21) and (1.22), we find that in the $n = 1$ orbit, the electron has a negative potential energy of $-27.2\,\text{eV}$ and the kinetic energy of $+13.6\,\text{eV}$; the kinetic energy is positive of course. Hence, its total energy is $-13.6\,\text{eV}$. Notice that the total energy E is equal to half the potential energy V, and that the kinetic energy K is numerically equal to half the potential energy. These relations hold for the motion of any classical (or quantum) system with a potential of the form $V \propto -(1/r)$, and are examples of the *virial theorem*. Substituting for r from Equation (1.19) into Equation (1.22), we obtain the energy E_n of the nth level:

$$E_n = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2}, \tag{1.23}$$

where n is the corresponding *quantum number* of the level. Evaluating Equation (1.23) with the known values of the fundamental constants and taking $Z = 1$, we obtain the possible energy levels of the hydrogen atom. These are shown in Figure 1.10, together with the corresponding values of n. The energies are given in electron volts (eV). This is a convenient unit of energy to use when dealing with atomic energy levels, and is defined as the energy an electron gains when it falls through a potential of 1 V. In terms of the joule,

$$1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}.$$

The $n = 1$ level corresponds to the *ground state* of hydrogen, which has the lowest energy, i.e. the most negative energy with a value of $-13.6\,\text{eV}$. If we wanted to completely remove the electron from the $n = 1$ level to infinity, we would have to supply 13.6 eV of energy. This is the *binding energy* of the electron. It follows that we can write the energy E_n of the nth level as $E_n = -13.6(1/n^2)\,\text{eV}$.

If the atom is excited by, for example, an electrical discharge, the electron is promoted to a higher lying level, with $n > 1$. After a short time, $\sim 10^{-8}$ seconds, the electron will return to a lower lying level. If the

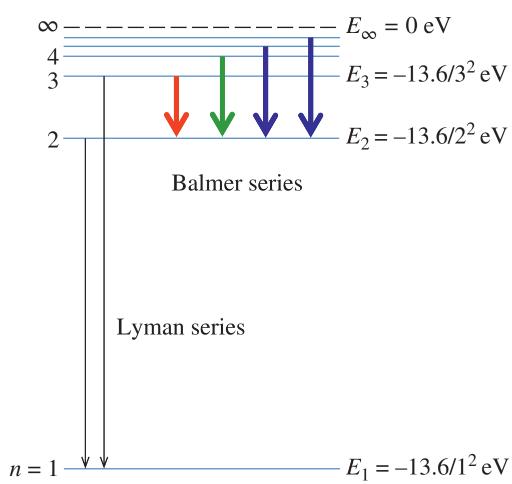

Figure 1.10 The allowed energy levels of the hydrogen atom according to the Bohr model. Also indicated are the values of the quantum number n and the corresponding binding energies for the levels, i.e. the amount of energy required to remove an electron from an orbit to infinity. The four visible emission lines of the Balmer series are also illustrated, as well as two members of the Lyman series.

electron makes a transition between energy levels with quantum number n_i and n_f, respectively, a photon is emitted with an energy given by

$$(E_i - E_f) = \frac{mZ^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right). \tag{1.24}$$

The wavelength of this photon is

$$\lambda = \frac{hc}{(E_i - E_f)}, \tag{1.25}$$

in accord with Bohr's fourth postulate. Then substituting for $(E_i - E_f)$ and rearranging Equation (1.25), we obtain

$$\lambda = \frac{4\pi\hbar^3 c(4\pi\varepsilon_0)^2}{mZ^2 e^4}\,\frac{n_f^2 n_i^2}{\left(n_i^2 - n_f^2\right)}. \tag{1.26}$$

Equations (1.25) and (1.26) are the essential predictions of the Bohr model.

When we take $n_f = 2$ and use the accepted values of the fundamental constants in Equation (1.26), we obtain

$$\begin{aligned}\lambda &= \frac{4\pi\left(1.056\times10^{-34}\right)^3\times\left(3\times10^8\right)\times\left(4\pi\times8.854\times10^{-12}\right)^2}{9.109\times10^{-31}\times\left(1.602\times10^{-19}\right)^4}\,\frac{4n_{\mathrm{i}}^2}{(n_i^2-4)}\\ &= 366.4\,\frac{n_i^2}{(n_i^2-4)}\ \text{nm}.\end{aligned}$$

We see that Bohr's model agrees exactly with the form of Balmers' formula, Equation (1.13), and moreover, the value of the constant (366.4) is in agreement with that obtained by Balmer, within the accuracy of the experimental measurements available to him. The interpretation of the Balmer formula then is that it represents the wavelengths for the transitions of an electron from a higher lying energy level with $n > 2$, to the $n = 2$ level. Figure 1.10 shows the electron transitions corresponding to the Balmer series, where the colours of the arrows indicate the colour of the emitted radiation.

Equation (1.26) also predicts the wavelengths of the photons emitted when an electron makes a transition to levels with other values of n_f. The series of wavelengths for $n_f = 5$ had in fact already been observed and is called the Pfund series. However, the series for $n_f = 1, 3$ and 4 had not. But when they were looked for, they were indeed observed and their wavelengths were fitted accurately by Equation (1.26). Making predictions is an important test of any theory and these predictions were a triumph for the Bohr model. These series in hydrogen are named after the investigators who first observed them and are respectively the Lyman series, with $n_f = 1$, the Paschen series, with $n_f = 3$, the Brackett series with $n_f = 4$, and the Pfund series with $n_f = 5$.

Bohr's model also explains the sharp spectral lines in the *absorption* spectrum of an atom. As the electron can only be in one of the allowed energy levels, the atom can only absorb discrete amounts of electromagnetic energy, i.e. photons of a particular wavelength. Bohr's model also works well for hydrogen-like atoms such as singly ionized helium, He^+ ($Z = 2$), and doubly ionized lithium, Li^{++} ($Z = 3$).

Despite its spectacular success in explaining the hydrogen spectrum, the Bohr model has significant shortcomings. There is no justification for the postulates of fixed stable orbits, the absence of energy loss of the circulating electrons, or for the quantization of angular momentum except for the fact that the model accurately agrees with experimental data obtained for the hydrogen spectrum. Furthermore, the Bohr model does not explain the spectra of atoms that are more complicated than hydrogen; even the spectrum of helium that has just two electrons. A correct description of the atomic structure had to wait for the arrival of *quantum mechanics*. But despite its shortcomings, the Bohr model gives a useful pictorial representation of the atom that is easy to visualise and, moreover, the mathematics involved are easy to understand. And indeed, the Bohr model is often useful as a first step in explaining a variety of phenomena in matter.

Worked example

In one type of *extrinsic semiconductor*, a tiny amount of phosphorous is added to a crystal of silicon. The phosphorous atoms occupy sites in the crystal lattice normally occupied by silicon atoms. Silicon has four electrons that are involved in bonding with other silicon atoms. But phosphorous has five available electrons, only four of which can bond to the silicon atoms. The remaining electron is then only weakly bound to the phosphorous atom and can easily be removed from it. We can view this situation as a single electron bound to a positively and singly charged phosphorous atom, analogous to the hydrogen atom. Use the Bohr model to determine the radius of the electron's orbit in a phosphorous atom and the amount of energy required to remove it from the atom. Note that when an electron moves in a crystal, it has an effective mass m_e due to the periodic nature of the electrical potential it experiences in the crystal lattice. The relative permittivity ε_r of silicon is 11.6 and the effective mass m_e is $0.26m$, where m is the mass of an electron.

Solution

From Equation (1.19), the radius of the $n = 1$ orbit of the hydrogen atom is

$$r_H = 4\pi\varepsilon_0 \frac{\hbar^2}{me^2} = a_0.$$

Taking $n = 1$ again for the orbit of the electron in the case of the phosphorous atom, we have

$$r_P = 4\pi\varepsilon_r\varepsilon_0 \frac{\hbar^2}{m_e e^2} = 4\pi(11.6)\varepsilon_0 \frac{\hbar^2}{(0.26)me^2} = \frac{11.6}{0.26} \times a_0 = 2.4\,\text{nm}.$$

From Equation (1.23), we find that the energy of the $n = 1$ level of the hydrogen atom is

$$E_H = -\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = -13.6\,\text{eV}.$$

This means that the electron is bound by 13.6 eV, and this is the amount of energy that is required to remove it from the atom. For the case of a phosphorous atom,

$$E_P = -\frac{(0.26)me^4}{(4\pi\varepsilon_0)^2(11.6)^2 2\hbar^2} = -\frac{0.26}{(11.6)^2} \times 13.6 = -0.026\,\text{eV}.$$

Thus, the energy required to remove the electron from the phosphorous atom is 0.026 eV. This is about the same as the *thermal energy* a particle has at room temperature. This means that the spare electron in nearly all the phosphorous atoms is liberated and is able to move freely through the silicon crystal. This increases the electrical conductivity of the crystal enormously.

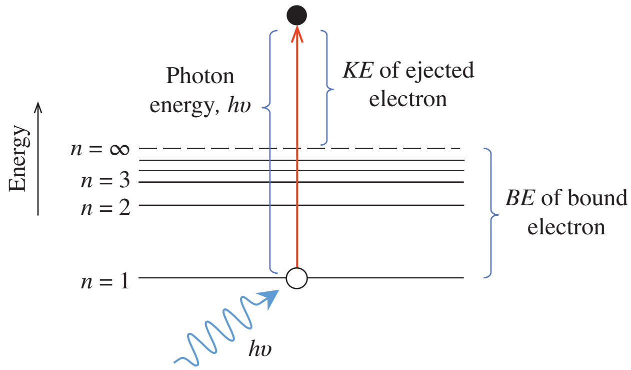

Figure 1.11 An energy level diagram for the situation where an energetic photon ejects the electron from the $n = 1$ orbit of hydrogen. The kinetic energy KE of the ejected electron is equal to the photon energy $h\nu$ minus the binding energy BE of the bound electron.

We have seen that we need to supply 13.6 eV of energy to completely remove the electron from a hydrogen atom. If we excite the atom with a photon that has energy greater than this, the ejected electron will have a non-zero kinetic energy and it will move away from the ionized atom. If we know the energy $h\nu$ of the incident photon and we measure the kinetic energy KE of the ejected electron, we can determine the energy required to remove the electron, i.e. its binding energy BE. The equation to describe this is just

$$BE = h\nu - KE. \tag{1.27}$$

An energy level diagram for this *ionization process* is illustrated in Figure 1.11. Of course, we know the binding energy for atomic hydrogen but we can use this principle to determine unknown binding energies in other atoms. And, in turn, this allows us to map out the energy levels of the atoms. This is the basis of *photoelectron spectroscopy* that is widely used to obtain this kind of information in gases, solids, and even liquids.

1.3.2 The Schrödinger equation

Following Bohr's model of the atom, key advances were made in the development of a quantum theory of the atom. It had already been observed that light has a particle-like nature. This was evident, for example, in the photoelectric effect. It was then natural to ask whether particles might have a wave-like nature. In 1924, Luis de Broglie put forward this idea in his doctoral dissertation, even though there was no experimental evidence to support it. de Broglie postulated that the wavelength λ associated with a particle is

$$\lambda = \frac{h}{p}, \tag{1.28}$$

where p is the momentum of the particle and h is Planck's constant. It was not long before experimental evidence arrived to support de Broglie's hypothesis. In 1927, the C. J. Davisson and L. H. Germer observed that a beam of electrons was diffracted by a crystal of nickel, just as X-rays are diffracted by a crystal. And shortly afterwards, G.P. Thompson performed diffraction experiments that also demonstrated the wave-like properties of electrons.

We can apply the hypothesis of de Broglie to Bohr's theory of the hydrogen atom. From Bohr's postulate for the quantization of angular momentum,

$$L = mvr = pr = n\hbar,$$

and substituting for p from the de Broglie relationship, Equation (1.28), we readily obtain

$$n\lambda = 2\pi r. \tag{1.29}$$

Thus, the allowed orbits are those for which the circumference of the orbit contains exactly an integral number of de Broglie wavelengths. We imagine an electron moving along its orbit at constant speed accompanied by its de Broglie wave. If the de Broglie wave satisfies the condition $n\lambda = 2\pi r$, constructive interference can occur and a standing wave will be produced. (In an analogous way, a standing wave is set up on a taut string that is fixed at both its ends if the waves on the string satisfy the condition $n\lambda/2 = L$, where L is the length of the string.) The standing wave for the case of the $n = 4$ orbit of hydrogen is illustrated in Figure 1.12. On the other hand, if the de Broglie wavelength does not satisfy this condition, destructive interference will result and a standing wave will not be formed; with the conclusion that an electron only exists in the orbit if Equation (1.29) is satisfied. We see that the quantum conditions of Bohr's theory can be interpreted on the basis of a *wave picture*.

Using a wave picture to describe a particle in a physical situation is the approach of *quantum mechanics*. And it is the key to understanding the behaviour of matter on the atomic, molecular, and nuclear scales. The wave equation to express this wave picture was developed by Erwin Schrödinger in 1926 and is the famous *Schrödinger equation*. It is the fundamental equation of quantum mechanics just as Newton's laws are fundamental to classical mechanics. And just like Newton's laws of motion, the Schrödinger equation cannot be derived. Its validity, like Newton's laws of motion, lies in its agreement with the experiment.

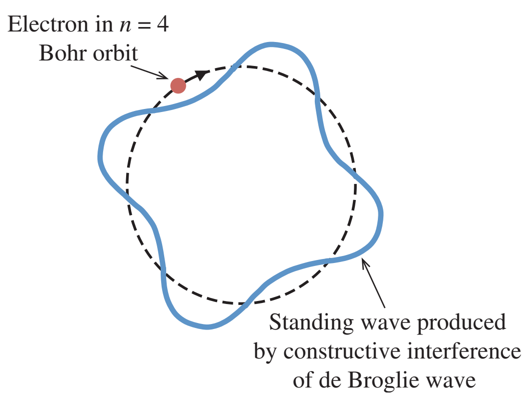

Figure 1.12 A picture that relates the Bohr orbit of an electron to a wave representation showing the formation of a standing wave. We imagine an electron moving along its orbit at constant speed accompanied by its de Broglie wave. If the de Broglie wave satisfies the condition $n\lambda = 2\pi r$, constructive interference can occur and a standing wave will be produced. This is illustrated for the case of the $n = 4$ orbit.

The Schrödinger equation

Schrödinger's equation, in Cartesian coordinates, is

$$\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right]+(E-V)\psi=0 \tag{1.30}$$

where E is the total energy of the particle, V is its potential energy and $\psi \equiv \psi(x, y, z)$ is the *wave function* that represents the wave nature of the particle. (Strictly speaking, Equation (1.30) is the *time-independent* Schrödinger equation, which can be used when the forces acting on the particle do not change with time t. This is the case for electrons in their bound states in an atom.) A physical interpretation of the wave function ψ was first stated as a postulate by Max Born in 1926. According to this postulate, the wave function ψ is a *complex* function of spatial coordinates and the *square of the magnitude* of ψ is a measure of the probability of the particle being at a particular place. More specifically, $|\psi|^2\,\mathrm{d}V$ *gives the probability of the particle being in the elemental volume* $\mathrm{d}V$. In a more compact notation, the Schrödinger equation can be written as

$$\frac{\hbar^2}{2m}\nabla^2\psi+(E-V)\psi=0, \tag{1.31}$$

where ∇^2 is the *Laplacian operator*:

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}. \tag{1.32}$$

Schrödinger used his equation to solve the atomic structure of the hydrogen atom, obtaining the wave functions of the bound states of the electron and the associated energies. He found that the allowed energies are quantised just as Bohr had found. Indeed, Schrödinger's equation gives *exactly* the same expression for the allowed energy levels in the hydrogen atom as the Bohr model. But Schrödinger did not have to postulate quantization. Instead, as we shall see, the *boundary conditions* imposed on Schrödinger's equation naturally led to energy quantization.

We make again an analogy with the familiar situation of standing waves on a taut string. The one-dimensional wave equation for such waves is

$$\frac{\partial^2 y}{\partial t^2}=v^2\frac{\partial^2 y}{\partial x^2} \tag{1.33}$$

where y is the transverse displacement of the wave at position x along the length of the string and v is the wave velocity. The string is stretched between two fixed points, which we take to be at $x=0$ and $x=L$. Since Equation (1.33) is a linear differential equation with constant coefficients, we can separate the variables so that the solution can be written

$$y(x,t)=X(x)\,T(t), \tag{1.34}$$

where $X(x)$ is a function of x alone and $T(t)$ is a function of t alone. From Equations (1.33) and (1.34), we obtain

$$\frac{\partial^2 y}{\partial x^2}=T(t)\frac{\partial^2 X}{\partial x^2}, \tag{1.35}$$

$$\frac{\partial^2 y}{\partial t^2} = X(x)\frac{\partial^2 T}{\partial t^2}, \tag{1.36}$$

and, hence,

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = \frac{1}{v^2 T}\frac{\partial^2 T}{\partial t^2}. \tag{1.37}$$

The left-hand side of this equation depends only on x and the right-hand side depends only on t. This can only be the case if both sides are equal to the same constant, which we will call $-\omega^2/v^2$. Hence, we obtain

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = \frac{1}{v^2 T}\frac{\partial^2 T}{\partial t^2} = -\frac{\omega^2}{v^2}. \tag{1.38}$$

We now have two ordinary differential equations

$$\frac{\mathrm{d}^2 T}{\mathrm{d}t^2} = -\omega^2 T; \tag{1.39}$$

$$\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} = -\frac{\omega^2}{v^2}X. \tag{1.40}$$

Equation (1.39) has the same form as that of simple harmonic motion (SHM) and has the general solution $T = A\cos(\omega t + \phi)$. ϕ is a phase angle that we can choose to be equal to zero for the sake of convenience. Equation (1.40) has the general solution $X = B\cos(\omega/v)x + C\sin(\omega/v)x$, where B and C are constants. From Equation (1.34), we therefore have

$$y(x, t) = \left(B\cos\frac{\omega}{v}x + C\sin\frac{\omega}{v}x\right)A\cos\omega t. \tag{1.41}$$

We now impose the boundary conditions $y = 0$ at $x = 0$ and at $x = L$ for all $t > 0$. The first condition gives $B = 0$. The second condition gives $C\sin([\omega/v]L) = 0$, which is satisfied if

$$\frac{\omega}{v}L = n\pi, \quad n = 1, 2, 3, \ldots. \tag{1.42}$$

(Since we are not interested in the trivial solution $y(x, t) \equiv 0$, we exclude the value $n = 0$). Hence, n must take one of the discrete values given by Equation (1.42), and so we write it as

$$\omega_n = \frac{n\pi v}{L}, \tag{1.43}$$

where for each n we have an associated ω_n. We have the familiar result that the standing waves on a taut string can only have certain frequencies of vibration; an example of a physical system where integral numbers occur naturally. In an analogous way, we will see that the Schrödinger equation *plus* the boundary conditions we impose on it leads naturally to quantized energy levels of the hydrogen atom.

A particle in an infinite potential well

We illustrate the application of the Schrödinger equation with the example of a particle trapped in a one-dimensional potential well.

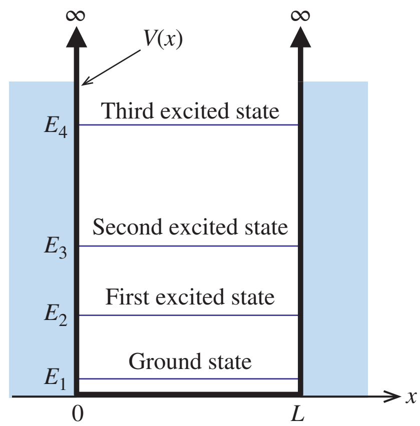

Figure 1.13 An infinite potential well. The walls of the well are at $x = 0$ and $x = L$. They are rigid and impenetrable so that a particle that is trapped in the well can never be outside the walls. This means that the potential energy $V(x)$ must be infinite beyond the walls of the well. Inside the well, $V(x) = 0$. The first four allowed energy levels, for $n = 1, 2, 3$ and 4, are superimposed on the potential well and scale as n^2. The particle has the lowest energy when it is in the energy level with $n = 1$, which is called the ground state for the particle. This energy is finite and is called *zero-point energy.*

The potential well is illustrated in Figure 1.13. The walls of the well are at $x = 0$ and $x = L$. They are rigid and impenetrable so that the particle can never be outside the walls. This means that the potential energy $V(x)$ must be infinite beyond the walls of the well. Inside the well we take $V(x)$ to be zero. Thus we have

$$\begin{aligned} V(x) &= \infty, \quad x < 0, x > L \\ &= 0, \quad 0 \leq x \leq L. \end{aligned} \tag{1.44}$$

The one-dimensional Schrödinger equation, see Equation (1.30), is

$$\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + (E - V)\psi = 0. \tag{1.45}$$

As the particle can never penetrate the walls, its wave function must be zero beyond the walls. Hence,

$$\psi = 0 \text{ for } x = \ \leq 0 \text{ and for } x = \ \geq L.$$

Inside the well, the potential energy $V(x) = 0$, and hence

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}E\psi, \quad 0 > x < L.$$

This equation has the general solution

$$\psi = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right).$$

The boundary condition $\psi = 0$ at $x = 0$ gives $B = 0$. Hence,

$$\psi = A \sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right). \tag{1.46}$$

The boundary condition $\psi = 0$ at $x = L$ gives $0 = A \sin\sqrt{(2mE)/\hbar^2}L$. The solution $A = 0$ is not acceptable as that would give $\psi = 0$ for all x, which would mean that there was no particle in the well. Hence, we must have

$$\sin\sqrt{\frac{2mE}{\hbar^2}}L = 0, \text{ or } \sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L}.$$

Substituting this result in Equation (1.46) gives

$$\psi_n = A_n \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots. \tag{1.47}$$

We have a family of solutions, each corresponding to a value of the integer n. Note that we exclude the $n = 0$ value since this would also give $\psi = 0$ for all x.

The condition $\sqrt{(2mE)/\hbar^2} = n\pi/L$ gives the allowed energies that the particle can have, which we write as

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2, \quad n = 1, 2, 3, \ldots. \tag{1.48}$$

The energies are quantized and this quantization arises because of the boundary conditions, Equation (1.44). The allowed levels for $n = 1$, 2, 3 and 4 are superimposed on the potential well in Figure 1.13. They scale as n^2. The particle has the lowest energy when it is in the energy level with $n = 1$, which is the ground state of the particle. This energy is finite; it is not zero. This is a consequence of the *Heisenberg uncertainty principle*, which we will discuss later. A particle bound in a potential well must always have a finite amount of energy, which is called the *zero-point energy*.

We determine the value of the constant A_n in Equation (1.47) by requiring the wave functions to be normalised. This is the mathematical statement that the particle must be *somewhere* between the two walls of the potential well. Hence,

$$\int_0^L |\psi_n|^2 \mathrm{d}x = A_n^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x = 1. \tag{1.49}$$

Evaluating the integral gives $A_n = \sqrt{2/L}$, for any value of n. Hence, the normalized wave functions are

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \ldots. \tag{1.50}$$

The wave functions for the $n = 1$, 2 and 3 states are shown in the top half of Figure 1.14. The close similarity between the wave functions and standing waves on a taut string is apparent.

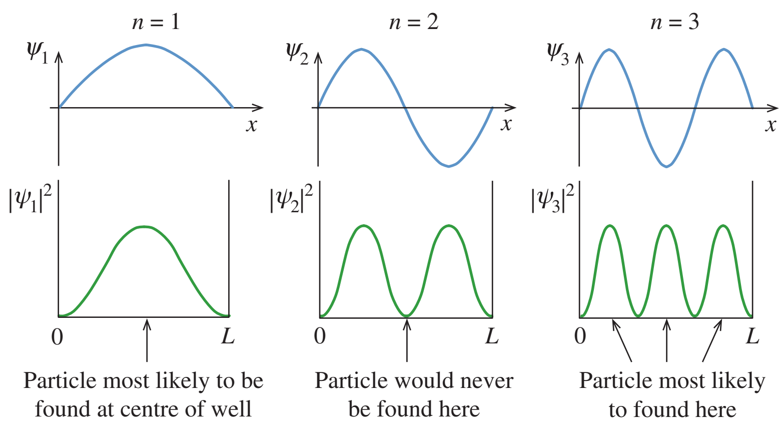

Figure 1.14 The top half of the figure shows the wave functions ψ_n for the $n = 1$, 2 and 3 states of a particle in an infinite potential well. The close similarity between the wave functions and standing waves on a taut string is evident. The bottom half of the figure shows the probability densities $|\psi_n|^2$ for the $n = 1$, 2 and 3 states. There are places where the particle is likely to be found and places where it is never to be found.

The connection between the wave function $\psi(x)$ and the behaviour of the associated particle is expressed in terms of the *probability density* $P(x)$, where

$$P(x) = |\psi(x)|^2. \tag{1.51}$$

The quantity $P(x)$ specifies the probability per unit length of the x-axis of finding the particle near the coordinate x. In other words, *if a measurement is made to locate a particle associated with the wave function* $\psi(x)$, *then the probability that the particle will be found between* x *and* $x + dx$ *is equal to* $P(x)\mathrm{d}x = |\psi(x)|^2\mathrm{d}x$. (This result is just the one-dimensional statement for the more general statement given previously that $|\psi|^2\mathrm{d}V$ gives the probability of the particle being in the elemental volume $\mathrm{d}V$.) It follows that the probability of the particle being in the range between x_1 and x_2 is

$$\int_{x_1}^{x_2} P(x)\mathrm{d}x = \int_{x_1}^{x_2} |\psi(x)|^2\mathrm{d}x. \tag{1.52}$$

In the present case, we have

$$\int_{x_1}^{x_2} |\psi_n|^2\mathrm{d}x = \frac{2}{L}\int_{x_1}^{x_2} \sin^2\left(\frac{\pi x}{L}\right)\mathrm{d}x.$$

The functions $|\psi_n|^2$ for $n = 1$, 2, and 3 are shown in the bottom half of Figure 1.14. We see that there are places where the particle is likely to be found and places where it is never to be found.

The function $P(x)$ is an example of a *probability distribution function*. We will encounter a number of other examples of probability distributions in our study of the physics of matter.

Worked example

A particle of mass m is confined in a one-dimensional infinite potential well of width L, where

$$\begin{aligned} V(x) &= \infty, \quad x < 0, x > L \\ &= 0, \quad 0 \leq x \leq L. \end{aligned}$$

For the ground state, ($n = 1$) of the particle, determine the following probabilities: (a) the probability that the particle will be between $x = 0$ and $x = L/2$, (b) the probability that the particle will be between $x = 0$ and $x = L/4$, (c) the probability that the particle will be in an interval of width $0.01L$ at $x = 0.5L$, and (d) if $L = 0.2$ nm, and the mass of the particle is equal to the electronic mass, what is the ground state energy of the particle?

Solution

For the ground state with $n = 1$, we have $|\psi_1|^2 = (2/L)\sin^2(\pi x/L)$.

(a) From the symmetry of the function $|\psi_1|^2$, we can say straight away that the probability that the particle will be between $x = 0$ and $x = L/2$ is 0.5.

(b) The probability that the particle will be between $x = 0$ and $x = L/4$ is equal to

$$\frac{2}{L}\int_0^{L/4} \sin^2\left(\frac{\pi x}{L}\right) \mathrm{d}x.$$

We evaluate the integral using the standard integral

$$\int \sin^2(ax) = \frac{x}{2} - \frac{\sin(2ax)}{4a},$$

and find that it is equal to 0.091, i.e. the probability of the particle being within the first quarter of the well is 9.1%. See Figure 1.15.

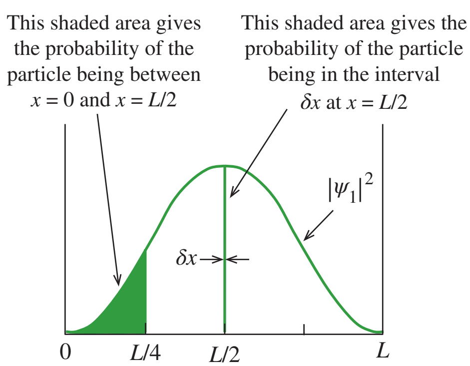

Figure 1.15 The probability density $|\psi_1|^2$ for the ground ($n = 1$) state of a particle in an infinite potential well. The area under the curve for a given range of x gives the probability of finding the particle within that range.

(c) The interval, $0.01L$, which we shall call δx, is much smaller than the length L of the well. Hence we can approximate the area under the curve to be $\psi_1^2\delta x$, where ψ_1^2 is evaluated at the interval; in this case at $x = 0.5L$. Hence, the probability is

$$\frac{2}{L}\sin^2\left(\frac{\pi \times 0.5}{L}\right) \times 0.01L = 0.02 = 2\%.$$

(d) $$E_1 = \frac{\pi^2\hbar^2}{2mL^2} = \frac{\pi^2 \times \left(1.055 \times 10^{-34}\right)^2}{2 \times 9.11 \times 10^{-31} \times \left(0.2 \times 10^{-9}\right)^2} = 1.51 \times 10^{-18}\text{J} = 9.42\,\text{eV}.$$

This energy is similar to that of the electron in the ground state of hydrogen.

1.3.3 The Schrödinger equation and the hydrogen atom

The potential energy for the hydrogen atom is

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r},$$

with $Z = 1$. This form of this potential is illustrated in Figure 1.16. It is plotted twice as a function of r, with increasing r on both sides of the origin ($r = 0$), to emphasise the spherical nature of the potential well in which the electron finds itself. The blue horizontal lines represent the allowed energy levels in this potential well. As the potential depends only on radial distance r, it is more convenient to use the spherical coordinates, r, θ, and ϕ instead of the rectangular coordinates x, y and z. They are related by

$$\begin{aligned} z &= r\cos\theta \\ x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \end{aligned} \tag{1.53}$$

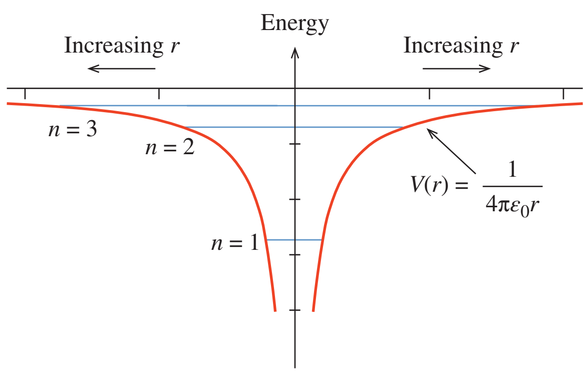

Figure 1.16 The form of the $1/r$ Coulomb potential. It is plotted twice as a function of r, with increasing r on both sides of the origin ($r = 0$), to emphasise the spherical nature of this potential. The blue horizontal lines represent the allowed energy levels in this potential well.

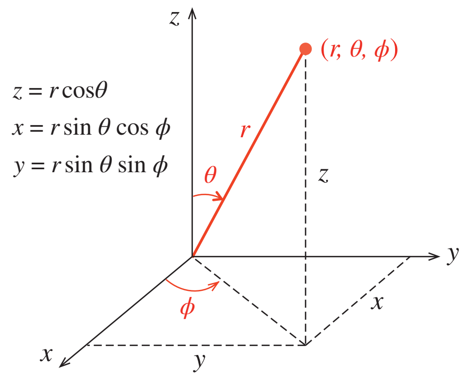

Figure 1.17 This figure shows the relationship between the rectangular and spherical coordinate systems.

as shown in Figure 1.17. The transformation of Schrödinger's from rectangular coordinates to spherical coordinates is straightforward but involves a good deal of algebraic manipulation. The resulting form of the equation is

$$-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)-\frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+V(r)\psi=E\psi \tag{1.54}$$

This equation looks formidable but there are standard methods to solve such equations, either analytically or by using *numerical methods*. In the case of the hydrogen atom, Schrödinger's equation can be solved exactly.

The first step in solving Equation (1.54) is to separate the variables by writing the wave function as a product of functions of every single variable; just as we did for standing waves on a taut string:

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi), \tag{1.55}$$

where $R(r)$ depends only on radial distance r, $\Theta(\theta)$ depends only on angle θ and $\Phi(\phi)$ depends only on angle ϕ. When this form of ψ is substituted into Equation (1.54) the equation can be transformed into three separate ordinary differential equations; one for $R(r)$, one for $\Theta(\theta)$ and one for $\Phi(\phi)$:

$$\frac{d^2\Phi}{d\phi^2}=-m_l^2\Phi \tag{1.56}$$

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_l^2\Theta}{\sin^2\theta}=l(l+1)\,\Theta \tag{1.57}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m_l}{\hbar^2}(E-V)R=l(l+1)\frac{R}{r^2}, \tag{1.58}$$

where m_l and l are constants. The solution of Equation (1.56) is

$$\Phi(\phi)=A\exp(im_l\phi), \tag{1.59}$$

where A is a constant and $i=\sqrt{-1}$, as can be readily be shown by substituting this solution into Equation (1.56). One of the conditions on the wave function $\psi(r,\theta,\phi)$ is that it must be *single valued*, i.e. the probability of finding the particle at any point (r, θ, ϕ) must have only one value. For example, the value of $\psi(r, \theta, \phi)$ must be the same at angles ϕ and $(\phi + 2\pi)$, see Figure 1.17. It then follows that $\Phi(\phi) = \Phi(\phi + 2\pi)$, or

$$\Phi(\phi) = A\exp(im_l\phi) = A\exp(im_l[\phi + 2\pi]). \tag{1.60}$$

This can only be true when m_l is 0 or a positive or negative integer, $\pm1, \pm2, \pm3, \ldots$. For these values of m_l in the differential equation for variable θ, Equation (1.57), this equation has only acceptable solutions for certain values of $l(l+1)$, for which

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \ldots.$$

And, for these values of $l(l+1)$ in Equation (1.58), this equation is found to have acceptable values only for certain values of the total energy E. Hence, the imposition of the boundary conditions gives the result that the *energy E is quantized*. Further analysis of Equation (1.58) gives the following expression for the allowed energies:

$$E_n = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2}, \tag{1.61}$$

where $n = l+1, l+2, l+3, \ldots$. Strikingly, Equation (1.61) is exactly the same result as given by the Bohr model for the allowed energies of the hydrogen atom, Equation (1.23).

n is called the *principal quantum number*, l is called the *orbital quantum number* and m_l is called the *magnetic quantum number* and their allowed values are more conveniently expressed as

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ l &= 0, 1, 2, \ldots (n-1) \\ m_l &= -l, (-l+1), \ldots (l+1), l. \end{aligned} \tag{1.62}$$

For any given value of n there are n values of l and for each value of l there are $2l+1$ values of m_l. The principal quantum number n is associated with the dependence of the wave function ψ_{nlm} on radial distance r. Since the potential energy $V(r)$ depends only on r and not on θ or ϕ, the energy of an allowed energy level in hydrogen depends only on n; see Equation (1.61). The quantum number l gives the angular momentum L of the electron according to

$$L = \sqrt{l(l+1)}\hbar. \tag{1.63}$$

That the energy of the electron does not depend on l is a peculiarity of the inverse-square force and holds only for an inverse $(1/r)$ potential. Notice that the quantum mechanical result for the angular momentum is different from the Bohr result $L = n\hbar$.

The quantum number m_l, which is associated with angle ϕ, is related to the angular momentum of the electron along a certain direction in space. For an isolated atom, all directions are equivalent. But when we place an atom in say an external magnetic field, we do introduce a particular direction, which is conventionally called the z-direction. Then the z-component of the angular momentum of the electron is given by

$$L_z = m_l\hbar. \tag{1.64}$$

In the absence of an external magnetic field, the energy does not depend on m_l.

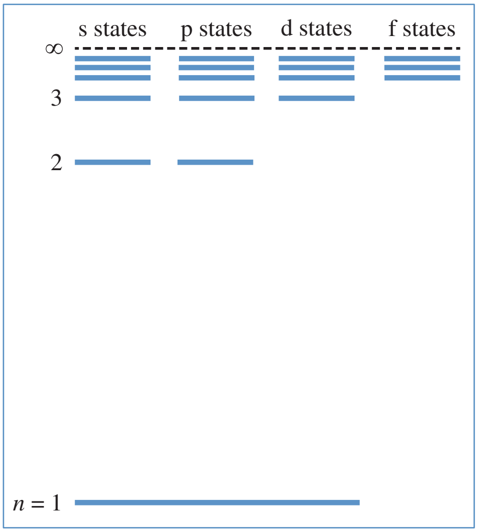

Figure 1.18 The energy levels of the hydrogen atom given by the Schrödinger equation. This figure is similar to Figure 1.10 from the Bohr model, but now, electronic states with the same value of n but different values of l are shown.

It is conventional to refer to the wave function ψ_{nlm} of an electron in an atom as an *orbital*, and an electron that is described by a particular wave function is said to occupy that orbital. The orbital gives all the information about the spatial position of the electron. It replaces the Bohr description of an electron moving in an orbit.

The energy levels for the hydrogen atom, as given by the solution of Schrödinger's equation, are shown in Figure 1.18. This figure is similar to Figure 1.10 from the Bohr model, but now, electronic states with the same value of n but different values of l are shown. By tradition, the various values of the orbital quantum number l are usually labelled with letters, according to the following scheme:

$l = 0$:	s states
$l = 1$:	p states
$l = 2$:	d states
$l = 3$:	f states
$l = 4$:	g states

The historical origin of this labelling system dates back to the early days of atomic physics when spectral lines were labelled as s for *sharp*, p for *principal*, d for *diffuse* and f for *fundamental*.

The ground state of the hydrogen atom

For the ground state of hydrogen, $n = 1$ and hence the angular momentum quantum number l must be equal to 0. Consequently, the electron is in the 1s orbital. Note, that as $l = 0$, the electron has zero angular momentum. This is a quantum effect and is clearly in contrast to the Bohr model in which an electron in the $n = 1$ orbit has angular momentum $L = \hbar$. The magnetic quantum number m_l is also equal to zero.

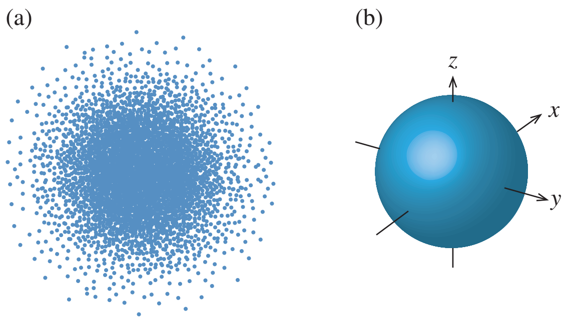

Figure 1.19 (a) A pictorial representation of the probability density for the ground state of hydrogen. The density of dots represents the probability density; the higher the dot density, the more likely the electron is to be found at that place. This gives a reasonably good impression of the charge distribution in the hydrogen ground state. (b) The boundary surface of the hydrogen ground state. There is a 90% probability that the electron will be within the volume enclosed by the surface; and a 10% probability that the electron will be outside that volume.

The solution of Schrödinger's equation for the hydrogen atom gives the following normalized wave function for its ground state:

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right), \tag{1.65}$$

where $a_0 = 4\pi\varepsilon_0(\hbar^2/me^2) = 0.53$ nm, which we recognise as the Bohr radius. Inspection of Equation (1.65) shows that the wave function depends only on radius r and has no dependence on θ or ϕ, i.e. the wave function has the same amplitude at all points of the same radial distance from the nucleus, regardless of direction; the wave function is said to be *spherically symmetric*.

We recall that the physical significance of the wave function is that $|\psi|^2 \mathrm{d}V$ gives the probability of the particle being within the elemental volume dV; the quantity $|\psi|^2$ is the probability density. As the electron is obviously charged, its probability density then gives the charge distribution in an atom, which is central to the chemical reactivity of the atom, i.e. the way atoms interact with each other to form matter. Figure 1.19a is a pictorial representation of the probability density for the ground state of hydrogen. In this figure, the density of dots represents the probability density; the higher the density of the dots, the more likely the electron is to be found at that place. An alternative way to represent $|\psi|^2$ is as a closed surface called a *boundary surface*, such that there is a 90% probability that the electron will be within the volume enclosed by the surface. For the hydrogen ground state,

$$|\psi_{100}|^2 = \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right), \tag{1.66}$$

and the boundary surface for this state is shown in Figure 1.19b. Since $|\psi|^2$ is a function of r alone, the boundary surface also has a spherical shape.

We are often more interested in knowing the probability that an electron will be found at a given radial distance from the nucleus, regardless of its angular position. In that case, the elemental volume dV is the volume of the thin spherical shell between r and $r + \mathrm{d}r$, which is equal to $4\pi r^2 \mathrm{d}r$. Thus the probability of the electron being between r and $r + \mathrm{d}r$ is

$$P(r)\mathrm{d}r = 4\pi|\psi|^2 r^2 \mathrm{d}r. \tag{1.67}$$

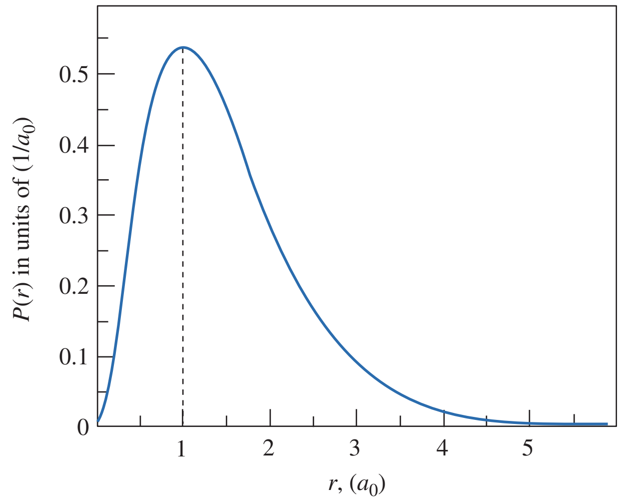

Figure 1.20 The radial probability density $P(r)$ as a function of radial distance r for the ground state of hydrogen. Note that $P(r)$ is plotted in units of $(1/a_0)$. We see that the radial position of an electron given by the Schrödinger equation is markedly different to the prediction of the Bohr model. In the Bohr model, the radius of an orbit corresponding to allowed energy is well defined. In quantum mechanics, we do not have a well-defined radius but a probability of finding the electron at a particular value of r.

$P(r) = 4\pi|\psi|^2 r^2$ is called the *radial probability density*. Substituting the ground state wave function into Equation (1.67) gives

$$P(r)\mathrm{d}r = 4\pi \frac{1}{\pi a_0^3} \exp\left(\frac{-2r}{a_0}\right) r^2 \mathrm{d}r. \tag{1.68}$$

Figure 1.20 shows $P(r)$ plotted as a function of r. We see that the radial position of an electron given by the Schrödinger equation is markedly different to the prediction of the Bohr model. In that model, the electron moves in an orbit with a well defined radius as given by Equation (1.18). In quantum mechanics, we do not have a well-defined radius but a *probability* of finding the electron at a particular value of r. Since the probability of the electron being between r and $r + \mathrm{d}r$ is $P(r)\mathrm{d}r$, it follows that the most probable radius for the electron is that which gives the maximum value of $P(r)$. This is found by differentiating $P(r)$ with respect to r and equating the result to zero. From Equation (1.68) we have

$$\frac{\mathrm{d}}{\mathrm{d}r} P(r) = \frac{4}{a_0^3}\left[2r\exp\left(\frac{-2r}{a_0}\right) + r^2 \exp\left(\frac{-2r}{a_0}\right)\left(-\frac{2}{a_0}\right)\right].$$

Putting $\frac{\mathrm{d}}{\mathrm{d}r} P(r) = 0$, cancelling the non-zero exponential term and simplifying, we obtain $r = a_0$. We find that the most probable radius occurs at $r = a_0$. Strikingly, this is the radius of the electron orbit that is predicted by the Bohr model.

Worked example

Determine the radius of the boundary surface for the ground state of hydrogen.

Solution

There is a 90% probability that the electron will be within the volume enclosed by a boundary surface, which for the hydrogen ground state has a spherical shape; see Figure 1.19. If the radius of the boundary surface is r_b, then the probability of the electron being within a sphere of radius r_b is

$$\int_0^{r_b} P(r)\mathrm{d}r = 4\pi\int_0^{r_b} |\psi|^2 r^2 \mathrm{d}r = 4\pi \frac{1}{\pi a_0^3}\int_0^{r_b} \exp\left(\frac{-2r}{a_0}\right) r^2 \mathrm{d}r,$$

where we have substituted for the ground state wave function. The integral can be solved by the integration of parts. Putting in the limits, the result is

$$4\pi \frac{1}{\pi a_0^3}\int_0^{r_b} \exp\left(\frac{-2r}{a_0}\right) r^2 \mathrm{d}r = \frac{4}{a_0^3}\left[\left(-\frac{a_0 r_b^2}{2} - \frac{a_0^2 r_b}{2} - \frac{a_0^3}{4}\right)\exp\left(\frac{-2r_b}{a_0}\right) + \frac{a_0^3}{4}\right].$$

This must be equal to 0.9, corresponding to a 90% probability. Expressing r in units of the Bohr radius a_0, we then obtain

$$4\left[\left(-\frac{r_b^2}{2} - \frac{r_b}{2} - \frac{1}{4}\right)\exp(-2r_b) + \frac{1}{4}\right] = 0.9.$$

Letting the function on the left-hand side of the equation be $y(r_b)$, we plot in Figure 1.21, $y(r_b)$ against r_b, in units of a_0. We see that the value of r_b that gives a value of 0.9 for $y(r_b)$ is $2.7a_0$, and hence this is the value of the corresponding radius for the boundary surface of the hydrogen ground state.

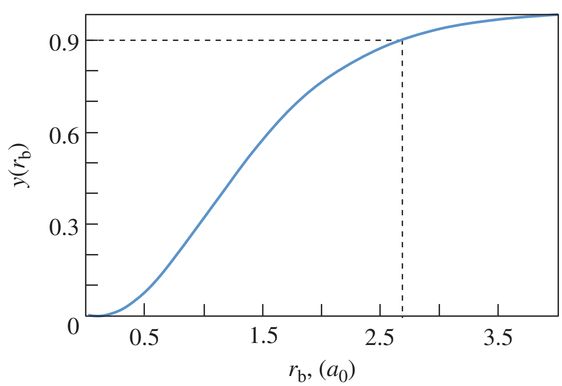

Figure 1.21 A plot of the function $y(r_b)$ against radial distance r_b, measured in units of the Bohr radius a_0.

Heisenberg's uncertainty principle

The fact that the radial position of the electron in a hydrogen atom does not have a well-defined orbit but is governed by a probability distribution is an illustration of Heisenberg's uncertainty principle. This principle is a statement about our knowledge of the properties of a particle. If we want to know where a particle is located, we measure its position, say x. That measurement will not be absolutely perfect but will have some uncertainty Δx. Similarly, if we want to know how fast a particle is going, we need to measure its velocity v_x or equivalently its momentum p_x. This measurement will also have some uncertainty Δp_x. Classical physics places no limits on how small the uncertainties Δx and Δp_x can be. It says that a particle at any instant of time has an exact position and an exact momentum and we can measure both x and p_x with arbitrary precision. The Heisenberg's uncertainty principle makes the bold statement that no matter how well we make the measurement, we cannot measure both x and p simultaneously with arbitrarily good precision. Any measurement we make is limited by the condition

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}. \tag{1.69}$$

This is a statement of Heisenberg's uncertainty principle. The principle arises because of the wave-like nature of particles. In the case of the ground state of hydrogen, the electron is spread out in space and there is not a precise value of its radial position, see Figure 1.20. Similarly, the de Broglie relationship between momentum and wavelength implies that we cannot know the momentum of a particle more accurately than we know its wavelength.

The position-momentum uncertainty relationship, Equation (1.69), provides a powerful way of estimating the ground-state energy of a particle in a given potential $V(r)$. It is especially useful in cases where the form of the potential makes an exact analytical solution of the Schrödinger equation, difficult or impossible. The basis of the calculation is the assumption that the uncertainty Δp in the momentum of the particle is of the same order as the momentum p itself. As an example, consider a particle of mass m in a one-dimensional, infinite potential well of width L. For the value of Δx, we take the value of L itself. Using Equation (1.69), we find that the value of Δp is $\approx \hbar/L$. On the assumption that p is of the same order as Δp, we have

$$p \approx \frac{\hbar}{L}.$$

Taking the potential V to be zero at the bottom of the potential well, the energy E of the particle is equal to its kinetic energy $p^2/2m$. Hence, we have

$$E = \frac{p^2}{2m} \approx \frac{\hbar^2}{2mL^2}.$$

This approximate result is in reasonable agreement with the exact result from Equation (1.48):

$$E = \frac{\pi^2 \hbar^2}{2mL^2}.$$

If we apply the approximate result to the case of an electron confined to an atom with a typical dimension of 0.1 nm, we find

$$E \approx \frac{\hbar^2}{2mL^2} \approx \frac{\left(1 \times 10^{-34}\right)^2}{2 \times 9 \times 10^{-31} \times \left(1 \times 10^{-10}\right)^2} \approx 6 \times 10^{-19}\ \mathrm{J} \approx 4\ \mathrm{eV}.$$

This is roughly the kinetic energy of an electron in the ground state of an atom.

The first excited state of the hydrogen atom

The principal quantum number n is 2 for the first excited state of hydrogen. Hence, l can be either 0 or 1. With $l = 0$ and $m_l = 0$, the state is designated as the 2s state. The solution of Schrödinger's equation gives the following normalized wave function for the 2s state:

$$\psi_{200} = C_{200}\left(2 - \frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right),$$

where C_{200} is the normalization constant, and we have taken the hydrogen nuclear charge $Z = 1$. As for the ground state of hydrogen, this wave function is spherically symmetric, with no dependence on θ or ϕ. Consequently, the probability density $|\psi_{200}|^2$ is also spherically symmetric. Its boundary surface looks just like that of the hydrogen ground state (see Figure 1.19b), but it is correspondingly larger.

The radial probability density $P(r)$ for the 2s state is shown in Figure 1.22. We see that $P(r)$ has two maxima. The largest maximum occurs close to $r = 5a_0$, and there is also a maximum at a much smaller radial distance; indicating that the electron spends a substantial amount of time close to the nucleus. The radial probability density is zero at $r = 2a_0$, as can also be deduced from the form of the wave function ψ_{200}. Hence, the electron is not to be found at this position.

For $n = 2$, $l = 1$, designated as 2p states, m_l can be $+1$, 0 or -1. The corresponding wave functions are

$$\psi_{210} = C_{210}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\cos\theta$$

and

$$\psi_{21\pm1} = C_{21\pm1}\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right)\sin\theta\exp(\pm i\phi).$$

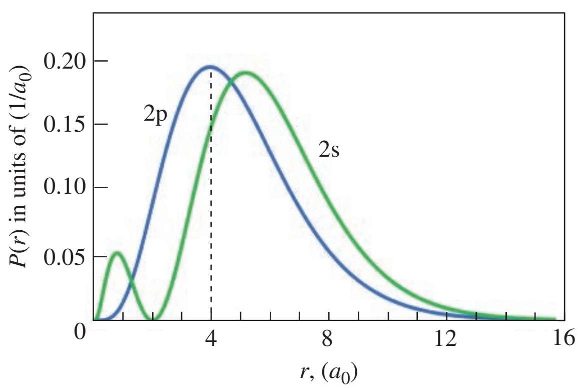

Figure 1.22 The radial probability densities $P(r)$ for the 2s and 2p states in hydrogen. There are two maxima in the 2s probability density. The largest maximum occurs close to $r = 5a_0$. However, there is also a maximum at a much smaller radial distance indicating that the electron spends a substantial amount of time close to the nucleus. The radial probability density is zero at $r = 2a_0$, and hence the electron is not found at this position. Note that the radial probability densities are different for the 2s and 2p states as $P(r)$ depends on quantum number l. However, $P(r)$ does not depend on angles θ and ϕ and so $P(r)$ is the same for all the three possible 2p wave functions; $l = 0, \pm 1$. Strikingly, the most probable radius for the 2p state has the same value as the prediction of the Bohr theory for the $n = 2$ orbit.

These wave functions *do* contain an angular dependence in addition to a radial dependence. The wave function ψ_{210} depends on θ and the $|\psi|^2_{21\pm1}$ wave functions depend on both θ and ϕ.

The radial probability density $P(r)$ is the same for all three possible 2p wave functions, with $l=0, \pm 1$, as radial probability density depends only on radius r and not on the angular part of the wave equation. $P(r)$ for the 2p states is shown in Figure 1.22. Interestingly, the most probable radius for a 2p state has the same value as the Bohr radius for the $n=2$ orbit. This is a general characteristic of the hydrogen atom; the most probable radius for the highest value of l for a given value of n is the same as the prediction of the Bohr model for that value of n.

The angular dependences of the 2p wave functions do, however, affect their probability densities $|\psi|^2$, which are

$$|\psi_{210}|^2 = C_{210}^2 \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right)\cos^2\theta$$

and

$$|\psi|^2_{21\pm1} = C_{21\pm1}^2 \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right)\sin^2\theta.$$

The probability densities have a radial part that is multiplied by an angular part. The probability density $|\psi_{210}|^2$ has a $\cos^2\theta$ term and the $|\psi|^2_{21\pm1}$ probability density has a $\sin^2\theta$ term. (The $\exp(\pm i\phi)$ term cancels out when the wave functions are squared.)

In Figure 1.23 we show the form of $\cos^2\theta$ and $\sin^2\theta$ in polar coordinates. These angular terms modulate the radial parts of the probability densities and we obtain the resultant probability densities for the 2p wave functions that are illustrated pictorially in Figure 1.24. Figure 1.24a illustrates the probability density for the 2p, $l=0$ state and Figure 1.24b illustrates the probability density for the 2p, $l=\pm 1$ states. Note that since these probability densities do not depend on angle ϕ, they have rotational symmetry about the z-axis, i.e. the size and shape of the probability density do not change if it is rotated about the z-axis. Hence, in a three-dimensional view, the 2p, $l=\pm 1$ probability density looks like a fuzzy doughnut. In particular,

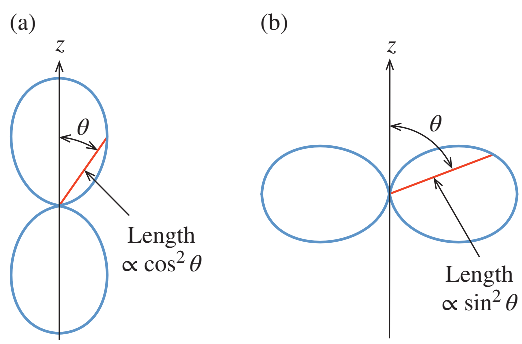

Figure 1.23 The form of (a) $\cos^2\theta$ and (b) $\sin^2\theta$ in polar coordinates.

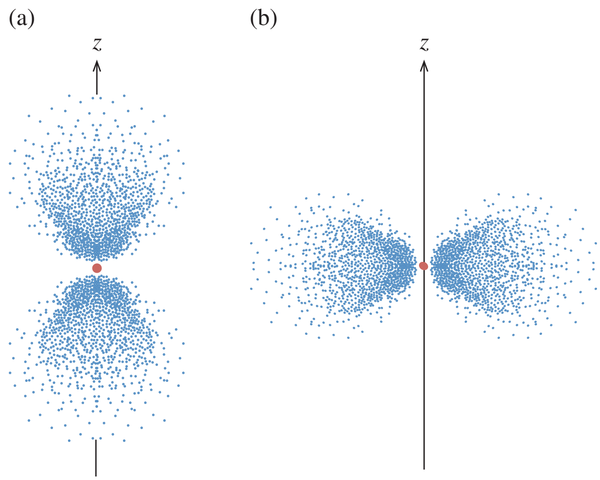

Figure 1.24 A pictorial representation of the probability density ψ^2 for (a) the 2p, $l = 0$ state and (b) the 2p, $l = \pm 1$ states in hydrogen. These probability densities do not depend on angle ϕ, and so have rotational symmetry about the z-axis. Hence, in a three-dimensional view, the 2p, $l = \pm 1$ probability density looks like a fuzzy doughnut. The figure illustrates the directionality of the probability densities and hence the electronic charge densities. This directionality can be of great importance when atoms combine to form molecules.

Figure 1.24 illustrates the directionality of the probability densities and hence the electronic charge densities. This directionality can be of great importance when atoms combine to form molecules.

Wave functions and probability densities may seem to be mathematical constructions. However, an international team of researchers have used a *quantum microscope* to directly observe the probability density for an excited state in the hydrogen atom.[1] In this elegant experiment, hydrogen atoms are ionized in a two-step process by laser radiation. The hydrogen atoms are in a static electric field. This field projects the ejected photoelectrons towards a two-dimensional electron detector, via an electrostatic lens. The detected photoelectrons produce a pattern on the detector that gives an image of the probability density. An example of the images obtained by the researchers is shown in Figure 1.25. It corresponds to the probability density for an excited state of hydrogen with $n = 30$, where the electron is far from the nucleus. In this experiment, the physical reality of a probability density is truly being observed.

Electron spin

To complete our description of an electronic state of hydrogen, we need to introduce the concept of *electron spin*. Spin is an intrinsic angular momentum that every electron possesses. Although it is tempting to think of an electron spinning about its axis like a top, that classical picture is not correct just as the Bohr model of classical orbits is not correct. Instead, it is best to think of the spin as a measurable intrinsic property of the electron, just like the electron charge or mass. The quantum number associated with electron spin is given the symbol s. Like orbital angular momentum, the spin angular momentum of an electron is quantized, but s

[1] A. S. Stodolna, A. Rouzée, F. Lépine, S. Cohen, F. Robicheaux, A. Gijsbertsen, J. H. Jungmann, C. Bordas, and M. J. J. Vrakking, Physical Review Letters, Vol. 110, 213001 (2013).

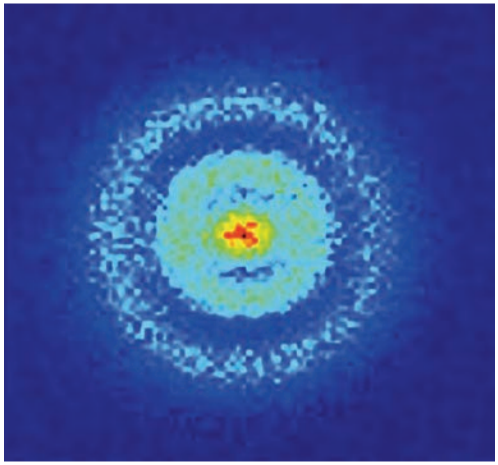

Figure 1.25 A direct visualization of the probability density for an excited state of hydrogen with $n = 30$, obtained using a quantum microscope. Source: A. S. Stodolna et al. (2013) / with permission of American Physical Society.

has the single positive value of ½. The z-component of spin is described by the magnetic quantum number m_s that can take just two values: $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, which is reminiscent of the expression $L_z = m_l\hbar$ for the z-component of orbital angular momentum. To completely specify the quantum state of an electron, we thus need four quantum numbers: n, l, m_l and m_s. For example, in the ground state of hydrogen, $n = 1$, $l = 0$, $m_l = 0$ and m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

The existence of electron spin was first postulated in 1925 by two graduate students George Uhlenbeck and Samuel Goudsmit. They were trying to understand why certain spectral lines in the optical spectra of hydrogen and alkali metals are composed of closely spaced *pairs* of lines. The familiar yellow light of sodium, for example, is a *doublet* with wavelengths 588.995 nm and 589.592 nm, respectively. The quantum basis of electron spin was established later, in 1929, by P. A. M. Dirac who developed a relativistic theory of quantum mechanics. Dirac's theory showed that the electron *must* have an intrinsic angular momentum $s = \frac{1}{2}$. Experimental evidence for electron spin also came from the *Stern Gerlach experiment*. In this experiment, a beam of silver atoms is passed through an inhomogeneous magnetic field. It is observed that the beam splits into two separate beams. The conclusion of the experiment is that the beam of silver atoms is displaced one way or the other according to the two spin states of the electron.

1.3.4 Multi-electron atoms

As we proceed through the periodic table, hydrogen ($Z = 1$), helium ($Z = 2$), lithium ($Z = 3$), etc., the charge on the nucleus increases by one unit from one element to the next, as does the number of atomic electrons. Each of the Z electrons will interact not only with the nucleus but also with every other electron. This introduces a great deal of complexity and, consequently, it is not possible to solve exactly the Schrödinger equation for a multi-electron atom; even for the helium atom, which has just two electrons. We can make a comparison here with planetary motion about the Sun. The mass of each planet is tiny compared to the mass of the Sun; the mass of the Sun is ten thousand times bigger than the mass of the largest planet, Jupiter. Consequently, the Sun's gravitational pull on a particular planet is very much greater than the gravitational pull of the other planets. Hence, when computing the orbit of a particular planet we can ignore the gravitational attraction of all the other planets, except for the most detailed calculations. In the case of a multi-electron atom, however, the mutual Coulomb repulsion of the electrons cannot be ignored; even though it will, in general, be smaller that the Coulomb attraction between an electron and the nucleus of charge $+Ze$. Fortunately, there are powerful *approximation methods* that do allow us to determine the wave functions and energy levels of electrons in a multi-electron atom to a high degree of accuracy. One approximation is called the *central field approximation.* In this approximation, each electron moves *independently* in a *net spherical potential* $V_{\text{net}}(r)$, which is due to the Coulomb attraction of the nucleus and the *average* effect of the Coulomb repulsion of all the other electrons. Hence, when solving the Schrödinger equation for a multi-electron atom, the potential energy $-e^2/4\pi\varepsilon_0 r$, that we use for the hydrogen atom, is replaced by the net potential $V_{\text{net}}(r)$. Solving the Schrödinger equation then gives the possible wave functions of an electron in that net potential. A crucially important advantage of the central field approximation is that we are now dealing with *single-electron* wave functions; the 'motion' of an individual electron is decoupled from the individual 'motion' of the other $Z-1$ electrons, in analogy to the case of planetary motion above.

In order to find the approximate form of the net potential $V_{\text{net}}(r)$, we start with the following considerations. When an electron is far from the nucleus, it is *screened* from the nucleus by the other $(Z-1)$ electrons. Effectively it sees a charge $+e$. We therefore expect, as r tends to infinity, a potential energy of the form

$$V_{\text{net}}(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \quad r \to \infty.$$

But when r is small and the electron is close to the nucleus the electron sees a bare, unscreened nucleus and we expect a potential energy of the form

$$V_{\text{net}}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}, \quad r \to 0.$$

A simple model for $V_{\text{net}}(r)$ that reproduces this behaviour is

$$V_{\text{net}}(r) = -\frac{e^2}{4\pi\varepsilon_0 r}\left[(Z-1)e^{-r/a} + 1\right],$$

where a is the *screening radius* for a particular atom and is the order of the Bohr radius a_0. Then to find the possible wave functions of an electron, we solve the Schrödinger equation, Equation (1.54) using the net potential $V_{\text{net}}(r)$:

$$-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V_{\text{net}}(r)\psi = E\psi. \qquad (1.70)$$

As noted above, this differs from the Schrödinger equation for hydrogen only in that we have replaced the $-e^2/4\pi\varepsilon_0 r$ potential energy for the hydrogen atom with the net potential $V_{\text{net}}(r)$. Hence, the Schrödinger equation can be readily solved, although because of the more complicated form of the potential, the equation must be solved numerically.

The resulting probability distributions for the Z individual electrons give the distribution of electronic charge. We can then use Gauss' law of electrostatics to calculate the electric field $E(r)$ that this distribution produces. And from this, we can calculate an improved estimate of the net potential $V_{\text{net}}(r)$ that an electron experiences. In general, this refined or improved form of the potential will differ from the initial estimate of $V_{\text{net}}(r)$. If it is appreciably different, the above procedure is repeated using the improved form of $V_{\text{net}}(r)$ in the Schrödinger equation. This iterative procedure may be repeated over a number of cycles until the $V_{\text{net}}(r)$ obtained at the end of a cycle is essentially the same as that used at the beginning of the cycle. That is, there is *self consistency* between the form of $V_{\text{net}}(r)$ that is put into the Schrödinger equation and the form of it that is obtained from its solution.

We are dealing with single-electron wave functions in the central field approximation. This means that the wave functions for the electrons in a multi-electron atom can be labelled by the same quantum numbers used to label the wave functions of the hydrogen atom. These are the principal quantum number n, the orbital angular quantum number l, the magnetic quantum number m, and the electron spin quantum number m_s. Hence the wave functions are labelled 1s, 2s, 2p, 3s, 3p, 3d, etc., just as they are for hydrogen. The Z electrons fill the allowed energy levels in the sequence 1s, 2s, 2p, 3s, 3p, 3d, etc., in accord with the *Pauli exclusion principle* that we describe in the next section.

A major difference between the hydrogen atom and a multi-electron atom is that the energy of an electron in a multi-electron atom depends on both n and l. This arises because the form of the potential does not now have a $1/r$ dependence; $V_{\text{net}}(r)$ is more complicated than that. Whereas, for example, the 2s and 2p states of hydrogen have the same energy, their energies are different in a multi-electron atom.

This is illustrated in Figure 1.26, which shows the energy levels of the lithium atom ($Z = 3$). Also shown in the figure are the higher energy levels of hydrogen. While it takes 13.6 eV to ionize hydrogen, it takes just 5.4 eV to ionize lithium. Notice that the higher l levels in lithium, for a particular value of n, have higher

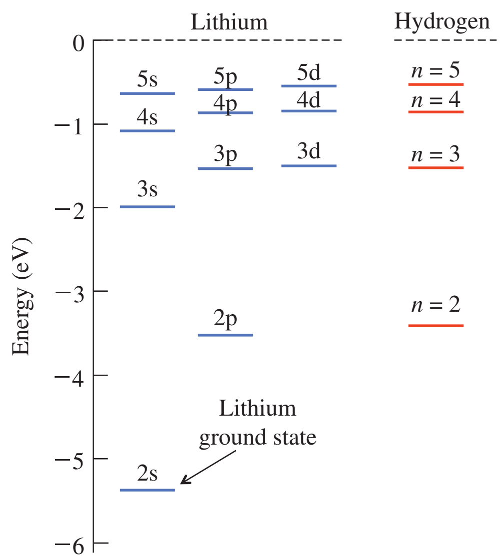

Figure 1.26 The energy levels of the lithium atom. Also shown in the figure are the higher energy levels of the hydrogen atom. Notice that the higher l levels in lithium, for a particular value of n have higher energy than the lower l levels. The electron configuration for the ground state of lithium ($Z = 3$) is $1s^2 2s$; the atom has two electrons in the 1s state and a third electron in the 2s state. The first excitation of lithium is obtained by raising the third electron to the 2p state.

energy than the lower l levels. The reason is that electrons in higher l states spend less time close to the nucleus and are therefore less tightly bound. Hence, it takes less energy to remove them from the atom and so their energy levels are closer to the ionization limit. Despite these differences, however, there is a good deal of similarity between the arrangement of the energy levels in lithium and hydrogen. This similarity supports the single-electron approach for the lithium atom.

The periodic table and the Pauli exclusion principle

Atoms of different atomic number Z have different physical and chemical properties. Strikingly, these properties vary with Z in a periodic way. For example, the alkali metals lithium, sodium, and potassium ($Z = 3$, 11, and 19, respectively) have similar chemical properties, while the halogens fluorine, chlorine, and bromine ($Z = 9$, 17, and 35, respectively) again exhibit similar properties to each other. Quantum mechanics explains why the properties of the elements vary in this periodic fashion. Two basic concepts are involved. First, each electron occupies a single-electron state with definite energy and second, the energy levels are filled with electrons according to the Pauli exclusion principle. This principle was formulated in 1925 by the physicist, Wolfgang Pauli. He developed it to explain the optical spectrum of helium. The Pauli exclusion principle states that *no two electrons can be in the same quantum state*, i.e. *that no two electrons can have exactly the same set of quantum numbers n, l, m_l, and m_s*. We emphasise that the properties of atoms and therefore of all matter depend crucially on this fundamental principle. Using the Pauli exclusion principle we list in Table 1.2 the possible sets of quantum numbers for electron states in an atom for the principal quantum number $n = 1$, 2, and 3. Electrons with the same value of n are described as being in the same *shell* as, roughly speaking, they all have similar values of radius. The 'number of states' column gives the maximum number of electrons that can be found in these states. For example, the maximum the number of electron states for $n = 3$ is 18. We thus obtain the following order in which the electrons fill the orbitals: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, etc. where the superscripts indicate the number of electrons in a particular orbital. Table 1.3 shows how this works for the first 11 elements in the periodic table. The fourth column gives the *electron configuration* of the atomic ground states. We can see for example, that the ground state of lithium has two electrons in the 1s state and the third electron in the 2s state; see also Figure 1.26. The first excitation of lithium is obtained by raising the third electron to the 2p state. The table also lists the ionization potentials of the elements.

The physical and chemical properties of elements can be largely explained by their electron configurations. A striking example of this is provided by the variation in ionization potentials for the elements; the amount of energy required to remove the least-bound electron. Figure 1.27 shows this variation for elements up to $Z = 95$. The rare gas atoms helium, neon, argon, krypton, xenon, and radon have *closed shell*

Table 1.2 The possible sets of quantum numbers for electron states in an atom for principal quantum number $n = 1$, 2, and 3.

n	l	m_l	m_s	Spectroscopic notation	Number of states	Total number of states
1	0	0	±½	1s	2	2
2	0	0	±½	2s	2	8
2	1	−1, 0, +1	±½	2p	6	
3	0	0	±½	3s	2	18
3	1	−1, 0, +1	±½	3p	6	
3	2	−2, −1, 0, +1, +2	±½	3d	10	

Table 1.3 The electron configurations and ionization potentials for the first eleven elements in the periodic table.

Element	Symbol	Z	Electronic configuration	Ionization potential (eV)
Hydrogen	H	1	1s	13.6
Helium	He	2	$1s^2$	24.6
Lithium	Li	3	$1s^22s$	5.4
Beryllium	Be	4	$1s^22s^2$	9.3
Boron	B	5	$1s^22s^22p$	8.3
Carbon	C	6	$1s^22s^22p^2$	11.3
Nitrogen	N	7	$1s^22s^22p^3$	14.5
Oxygen	O	8	$1s^22s^22p^4$	13.6
Flourine	F	9	$1s^22s^22p^5$	17.4
Neon	Ne	10	$1s^22s^22p^6$	21.6
Sodium	Na	11	$1s^22s^22p^63s$	5.1

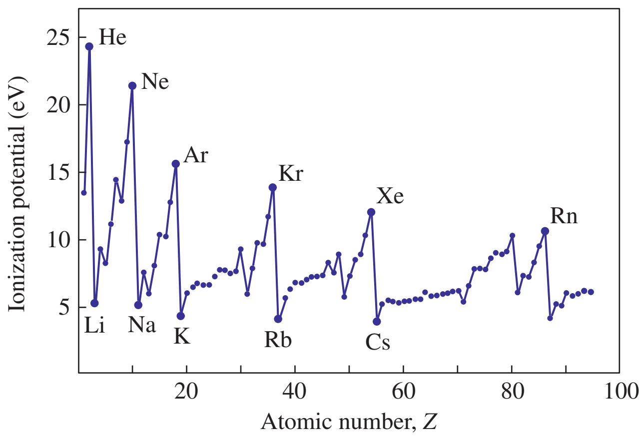

Figure 1.27 The variation of ionization potential with an atomic number for atoms up to $Z = 95$.

configurations. These are particularly stable structures and it takes a large amount of energy to excite one of its electrons. For example, neon has the closed-shell, electron configuration $1s^22s^22p^6$, and it takes 21.6 eV to remove a 2p electron from the atom.

This makes the rare gas atoms chemically inert, with little tendency to gain or lose an electron. On the other hand, the alkali metals lithium, sodium, potassium, rubidium, and caesium have just one electron in their outermost shell. This electron is far from the nucleus and is shielded by the inner electrons so that it effectively sees a charge of $+e$. Consequently, it is only loosely bound to the atom and the ionization potential is low. For example, it takes just 5.1 eV to remove the 3s electron from a sodium atom. Consequently, the alkali metals are extremely reactive. Note that because of the high stability of closed shell configurations most properties of atoms arise from those electrons that are outside the stable closed shells. These are called *valence* electrons.

Problems 1

1.1 (a) When a teaspoon of oil (a few cm^3) was placed on the surface of a calm lake, it was found that the oil covered an area of about $2000\ m^2$. Use this information to estimate the size of the oil molecules. (b) Suppose a car tyre lasts 30,000 km and that a layer of rubber 1 molecule thick is deposited on the road as the car moves along the road, estimate the size of the rubber molecules.

1.2 What is the time of flight for a Xe^{++} doubly-charged ion in a time of flight spectrometer with an acceleration voltage of 60 V and a 0.75 m flight tube. The atomic weight of xenon is 131 u.

1.3 Water can be converted into hydrogen and oxygen gases according to the reaction $H_2O \rightarrow H_2 + O$ by electrolysis. How many moles of these gases are produced from 5 l of water?

1.4 The density of potassium is $860\ kg/m^3$. Estimate the diameter of a potassium atom. The atomic weight of potassium is 39 u.

1.5 One mole of any gas occupies 22.4 l at 0 °C and atmospheric pressure. Determine the mass of $1\ m^3$ of air at 0 °C. Assume a molecular weight of 30 u.

1.6 Obtain a value for the mass of the Earth's atmosphere. The radius of the Earth is 6380 km. Take atmospheric pressure to be 1.0×10^5 Pa.

1.7 Atoms with very high values of quantum number n can be produced. They are called *high Rydberg states* and are well described by the Bohr model. Calculate the radius of a hydrogen atom with $n = 150$. What is the separation in energy between the $n = 150$ and $n = 151$ states?

1.8 Calculate (a) the energy in eV required to ionize a hydrogen atom from its first excited state and (b) the energy required to fully ionize a Li^{++} doubly-charged ion.

1.9 It takes 24.6 eV to remove one electron from helium. What is the total amount of energy required to remove both the electrons from a helium atom? What is the doubly-charged ion of helium He^{++} usually called?

1.10 The mass of the muon particle is 207 times that of the electron, but can be treated to be similar in all other respects. Muonic hydrogen consists of a bound state of a proton and a negative muon. Calculate (a) the Bohr radius for muonic hydrogen, (b) the binding energy of the muon in muonic hydrogen and (c) the energy of the 1s to 2p transition.

1.11 Positronium is a short-lived atomic state consisting of an electron bound electrostatically to a positron. Calculate the ionisation energy of positronium and the wavelength of the light given off when positronium de-excites from $n = 2$ to $n = 1$. Note that in the case of hydrogen, we could assume that the mass of the nucleus was infinitely more massive than the electron. In the case of positronium, this is not so and the mass of the electron m must be replaced with the reduced mass of the positronium system, which is $m/2$, where m is the mass of an electron.

1.12 An electron microscope produces an electron beam in which the electrons are accelerated through a voltage of 2.5 keV. Estimate the theoretical spatial resolution of the microscope, i.e. the size of the smallest particle it can distinguish.

1.13 Use the uncertainty principle to estimate the energy of a proton in a nucleus. Take the diameter of the nucleus to be 2×10^{-15} m.

1.14 An estimate of the lowest energy of a particle in a potential well is obtained from the relationship $\Delta p \Delta x \sim \hbar$, where Δp and Δx are, respectively, the uncertainties in the momentum and position of the particle. (a) A particle of mass m moves in a vee-shaped potential of the form

$$V(x) = -bx \quad (x \le 0)$$
$$V(x) = +bx \quad (x \ge 0).$$

Use the above relationship to show that the energy of the lowest state is $(\hbar^2 b^2/m)^{1/3}$, within a numerical factor of order unity. Show that this result is correct dimensionally. (b) A particle undergoing SHM moves in a potential $V(x)$ that has the form $V(x) = \frac{1}{2}kx^2$, where k is the 'spring constant' and x is the displacement from equilibrium. If the mass of the particle is m, show that the energy of the lowest state of the particle is $\hbar\omega$ within a numerical factor of order unity, where ω is the angular frequency of the vibrational motion.