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$$p = \frac{h}{\lambda} \quad \text{and} \quad \epsilon = \frac{hc}{\lambda}, \tag{1.1}$$

where λ is the wavelength of the electromagnetic radiation. In comparison with macroscopic standards, the momentum and energy of a photon are tiny. For example, the momentum and energy of a visible photon with wavelength $\lambda = 663\,\text{nm}$ are

$$p = 10^{-27}\,\text{J s} \quad \text{and} \quad \epsilon = 3 \times 10^{-19}\,\text{J}.$$

We note that an electronvolt, $1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$, is a useful unit for the energy of a photon: visible photons have energies of the order of an eV and X-ray photons have energies of the order of 10 keV.

The evidence for the existence of photons emerged during the early years of the twentieth century. In 1923 the evidence became compelling when A. H. Compton showed that the wavelength of an X-ray increases when it is scattered by an atomic electron. This effect, which is now called *the Compton effect*, can be understood by assuming that the scattering process is a photon–electron collision in which energy and momentum are conserved. As illustrated in Fig. 1.1, the incident photon transfers momentum to a stationary electron so that the scattered photon has a lower momentum and hence a longer wavelength. In fact, when the photon is scattered through an angle θ by a stationary electron of mass m_e, the increase in wavelength is given by

$$\Delta\lambda = \frac{h}{m_e c}(1 - \cos\theta). \tag{1.2}$$

We note that the magnitude of this increase in wavelength is set by

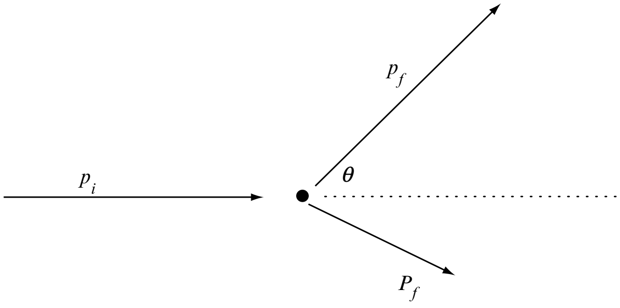

Fig. 1.1 A photon–electron collision in which a photon is scattered by a stationary electron through an angle θ. Because the electron recoils with momentum P_f, the magnitude of the photon momentum decreases from p_i to p_f and the photon wavelength increases.

by crystal lattices. Indeed, the first experiments to demonstrate the wave properties of electrons were crystal diffraction experiments by C. J. Davisson and L. H. Germer and by G. P. Thomson in 1927. Davisson's experiment involved electrons with energy around 54 eV and wavelength 0.17 nm which were diffracted by the regular array of atoms on the surface of a crystal of nickel. In Thomson's experiment, electrons with energy around 40 keV and wavelength 0.006 nm were passed through a polycrystalline target and diffracted by randomly orientated microcrystals. These experiments showed beyond doubt that electrons can behave like waves with a wavelength given by the de Broglie relation Eq. (1.3).

Since 1927, many experiments have shown that protons, neutrons, atoms and molecules also have wave-like properties. However, the conceptual implications of these properties are best explored by reconsidering the two-slit interference experiment illustrated in Fig. 1.2. We recall that a photon passing through two slits gives rise to wave-like disturbances which interfere constructively and destructively when the photon is detected on a screen positioned behind the slits. Particles of matter behave in a similar way. A particle of matter, like a photon, gives rise to wave-like disturbances which interfere constructively and destructively when the particle is detected on a screen. As more and more particles pass through the slits, an interference pattern builds up on the observation screen. This remarkable behaviour is illustrated in Fig. 1.3.

Interference patterns formed by a variety of particles passing through two slits have been observed experimentally. For example, two-slit interference patterns formed by electrons have been observed by A. Tonomura, J. Endo, T. Matsuda, T. Kawasaki and H. Exawa (*American Journal of Physics*, vol. 57, p. 117 (1989)). They also demonstrated that a pattern still emerges even when the source is so weak that only one electron is in transit at any one time, confirming that each electron seems to pass through both slits in a wave-like way before detection at a random point on the observation screen. Two-slit interference experiments have been carried out using neutrons by R. Gähler and A. Zeilinger (*American Journal of Physics*, vol. 59, p. 316 (1991)), and using atoms by O. Carnal and J. Mlynek (*Physical Review Letters*, vol. 66, p. 2689 (1991)). Even molecules as complicated as C_{60} molecules have been observed to exhibit similar interference effects as seen by M. Arndt *et al.* (*Nature*, vol. 401, p. 680 (1999)).

These experiments demonstrate that particles of matter, like photons, are not classical particles with well-defined trajectories. Instead, when presented with two possible trajectories, one for each slit, they seem to pass along both trajectories in a wave-like way, arrive at a random point on the screen and build up an interference pattern. In all cases the pattern consists of fringes with a spacing of $\lambda D/d$, where d is the slit separation, D is the screen distance and λ is the de Broglie wavelength given by Eq. (1.3).

Physicists have continued to use the ambiguous word *particle* to describe these remarkable microscopic objects. We shall live with this ambiguity, but we shall occasionally use the term *quantum particle* to remind the reader that the object under consideration has particle and wave-like properties. We have used this term in Fig. 1.3 because this figure provides a compelling illustration of particle and wave-like properties. Finally, we emphasize the role of Planck's constant in linking the particle and wave-like properties of a quantum particle. If Planck's constant were zero, all de Broglie wavelengths would be zero and particles of matter would only exhibit classical, particle-like properties.

1.3 ATOMS

It is well known that atoms can exist in states with discrete or quantized energy. For example, the energy levels for the hydrogen atom, consisting of an electron and a proton, are shown in Fig. 1.4. Later in this book we shall show that bound states of an electron and a proton have quantized energies given by

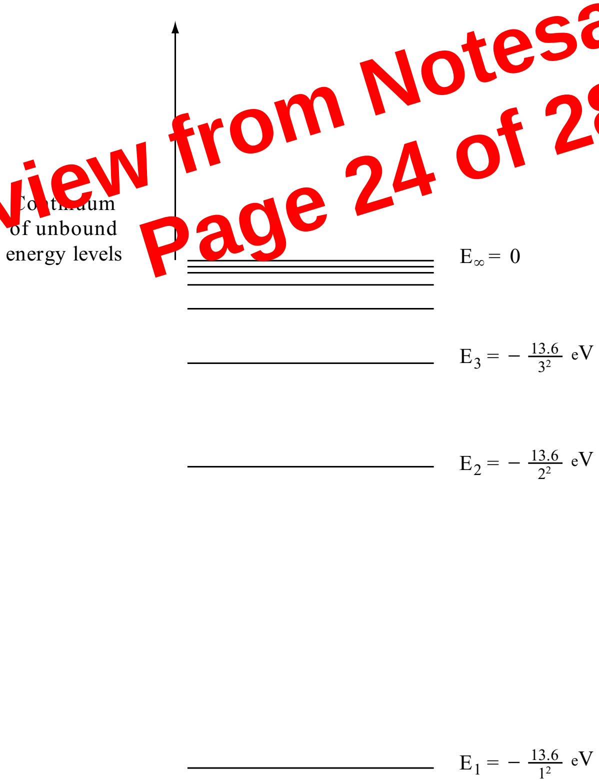

Fig. 1.4 A simplified energy level diagram for the hydrogen atom. To a good approximation the bound states have quantized energies given by $E_n = -13.6/n^2$ eV where n, the principal quantum number, can equal $1, 2, 3, \ldots$. When the excitation energy is above 13.6 eV, the atom is ionized and its energy can, in principle, take on any value in the continuum between $E = 0$ and $E = \infty$.

But quantized energy levels are not the most amazing property of atoms. Atoms are surprisingly resilient: in most situations they are unaffected when they collide with neighbouring atoms, but if they are excited by such encounters they quickly return to their original pristine condition. In addition, atoms of the same chemical element are identical: somehow the atomic number Z, the number of electrons in the atom, fixes a specific identity which is common to all atoms with this number of electrons. Finally, there is a wide variation in chemical properties, but there is a surprisingly small variation in size; for example, an atom of mercury with 80 electrons is only three times bigger than a hydrogen atom with one electron.

These remarkable properties show that atoms are not mini solar systems in which particle-like electrons trace well-defined, classical orbits around a nucleus. Such an atom would be unstable because the orbiting electrons would radiate electromagnetic energy and fall into the nucleus. Even in the absence of electromagnetic radiation, the pattern of orbits in such an atom would change whenever the atom collided with another atom. Thus, this classical picture cannot explain why atoms are stable, why atoms of the same chemical element are always identical or why atoms have a surprisingly small variation in size.

In fact, atoms can only be understood by focussing on the wave-like properties of atomic electrons. To some extent atoms behave like musical instruments. When a violin string vibrates with definite frequency, it forms a standing wave pattern of specific shape. When wave-like electrons, with definite energy, are confined inside an atom, they form a wave pattern of specific shape. An atom is resilient because, when left alone, it assumes the shape of the electron wave pattern of lowest energy, and when the atom is in this state of lowest energy there is no tendency for the electrons to radiate energy and fall into the nucleus. However, atomic electrons can be excited and assume the shapes of wave patterns of higher quantized energy.

One of the most surprising characteristics of electron waves in an atom is that they are *entangled* so that it is not possible to tell which electron is which. As a result, the possible electron wave patterns are limited to those that are compatible with a principle called the *Pauli exclusion principle*. These patterns, for an atom with an atomic number Z, uniquely determine the chemical properties of all atoms with this atomic number.

All these ideas will be considered in more detail in subsequent chapters, but at this stage we can show that the wave nature of atomic electrons provides a natural explanation for the typical size of atoms. Because the de Broglie wavelength of an electron depends upon the magnitude of Planck's constant h and the electron mass m_e, the size of an atom consisting of wave-like electrons also depends upon h and m_e. We also expect a dependence on the strength of the force which binds an electron to a nucleus; this is proportional to $e^2/4\pi\epsilon_0$, where e is the magnitude of the charge on an electron and on a proton. Thus, the order of magnitude of the size of atoms is expected to be a function of

However, because of the particle-like properties of light, the process of observation involves innumerable photon–particle collisions, with the scattered photons entering the lens of the microscope. To enter the lens, a scattered photon with wavelength λ and momentum h/λ must have a sideways momentum between

$$-\frac{h}{\lambda}\sin\alpha \quad \text{and} \quad +\frac{h}{\lambda}\sin\alpha.$$

Thus the sideways momentum of the scattered photon is uncertain to the degree

$$\Delta p \approx \frac{h}{\lambda}\sin\alpha. \tag{1.13}$$

The sideways momentum of the observed particle has a similar uncertainty, because momentum is conserved when the photon scatters.

We note that we can reduce the uncertainty in the momentum of the observed particle by increasing the wavelength of the radiation illuminating the particle, but this would result in a poorer spatial resolution of the microscope and an increase in the uncertainty in the position of the particle. Indeed, by combining Eq. (1.12) and Eq. (1.13), we find that the uncertainties in the position and in the momentum of the observed particle are approximately related by

$$\Delta x\,\Delta p \approx h. \tag{1.14}$$

This result is called the Heisenberg uncertainty principle. It asserts that greater accuracy in position is possible only at the expense of greater uncertainty in momentum, and vice versa. The precise statement of the principle is that the fundamental uncertainties in the simultaneous knowledge of the position and momentum of a particle obey the inequality

$$\Delta x\,\Delta p \geq \frac{\hbar}{2}, \qquad \text{where } \hbar = \frac{h}{2\pi}. \tag{1.15}$$

We shall derive this inequality in Section 7.4 of Chapter 7.

The Heisenberg uncertainty principle suggests that a precise determination of position, one with $\Delta x = 0$, is possible at the expense of total uncertainty in momentum. In fact, an analysis of the microscope experiment, which takes into account the Compton effect, shows that a completely precise determination of position is impossible. According to the Compton effect, Eq. (1.2), the wavelength of a scattered photon is increased by

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\theta),$$

where m is the mass of the observed particle and θ is an angle of scatter which will take the photon into the microscope lens. This implies that, even if we illuminate the particle with radiation of zero wavelength to get the best possible spatial resolution, the radiation entering the microscope lens has a wavelength of the order of h/mc. It follows that the resolution given by Eq. (1.12) is at best

$$\Delta x \approx \frac{\lambda}{\sin\alpha} \sim \frac{h}{mc\sin\alpha}, \tag{1.16}$$

which means that the minimum uncertainty in the position of an observed particle of mass m is of the order of h/mc.

Our analysis of Heisenberg's microscope experiment has illustrated the role of Planck's constant in a measurement: The minimum uncertainties in the position and momentum of an observed particle are related by $\Delta x\Delta p \approx h$, and the minimum uncertainty in position is not zero but of the order of h/mc. However, readers are warned that Heisenberg's microscope experiment can be misleading. In particular, readers should resist the temptation to believe that a particle can really have a definite position and momentum, which, because of the clumsy nature of the observation, cannot be measured. In fact, there is no evidence for the existence of particles with definite position and momentum. This concept is an unobservable idealization or a figment of the imagination of classical physicists. Indeed, the Heisenberg uncertainty principle can be considered as a danger signal which tells us how far we can go in using the classical concepts of position and momentum without getting into trouble with reality.

Measurement and wave–particle duality

In practice, the particle-like properties of a quantum particle are observed when it is detected, whereas its wave-like properties are inferred from the random nature of the observed particle-like properties. For example, in a two-slit experiment, particle-like properties are observed when the position of a quantum particle is measured on the screen, but the wave-like passage of the quantum particle through both the slits is not observed. It is inferred from a pattern of arrival at the screen which could only arise from the interference of two wave-like disturbances from the two slits.

However, the inferred properties of a quantum particle depend on the experiment and on the measurements that can take place in this experiment. We shall illustrate this subjective characteristic of a quantum particle by considering a modification of the two-slit experiment in which the screen can either be held fixed or be allowed to move as shown in Fig. 1.7.

When the pin in Fig. 1.7 is inserted, detectors on a fixed screen precisely measure the position of each arriving particle and an interference pattern builds with fringes separated by a distance of $\lambda D/d$.

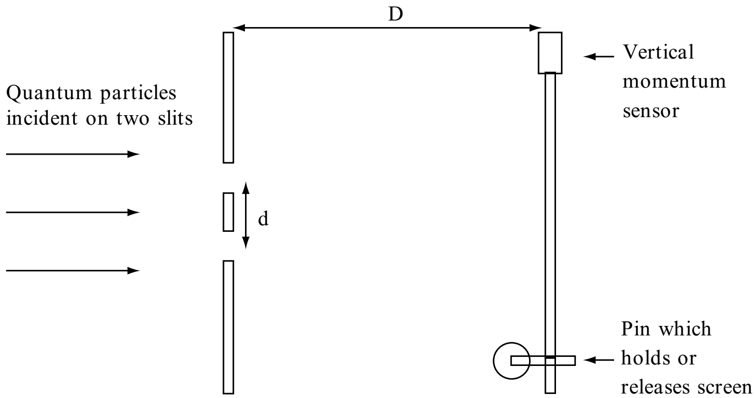

Fig. 1.7 A modified two-slit experiment in which the screen may move vertically and become a part of a detection system which identifies the slit through which each particle passes.

When the pin is withdrawn, the screen becomes a mobile detection system which is sensitive to the momentum $p = h/\lambda$ of the particles hitting the screen. It recoils when a particle arrives and, by measuring this recoil accurately, we can measure the vertical momentum of the particle detected at the screen and hence identify the slit from which the particle came. For example, near the centre of the screen, a particle from the upper slit has a downward momentum of $pd/2D$ and a particle from the lower slit has an upward momentum of $pd/2D$. In general, the difference in vertical momenta of particles from the two slits is approximately $\Delta p \approx pd/D$. Thus, if the momentum of the recoiling screen is measured with an accuracy of

$$\Delta p \approx \frac{pd}{D}, \tag{1.17}$$

we can identify the slit from which each particle emerges. When this is the case, a wave-like passage through both slits is not possible and an interference pattern should not build up. This statement can be verified by considering the uncertainties involved in the measurement of the momentum of the screen.

The screen is governed by the Heisenberg uncertainty principle and an accurate measurement of its momentum is only possible at the expense of an uncertainty in its position. In particular, if the uncertainty in the vertical momentum of the screen is $\Delta p \approx pd/D$, so that we can just identify the slit through which each particle passes, then the minimum uncertainty in the vertical position of the screen is

$$\Delta x \approx \frac{h}{\Delta p} \approx \frac{hD}{pd}. \tag{1.18}$$

$$\frac{\mathrm{d}\omega}{\mathrm{d}k} = \frac{\hbar k}{m}. \tag{2.12}$$

This equation may be integrated to give the following dispersion relation for the de Broglie waves describing a freely moving quantum particle of mass m:

$$\omega = \frac{\hbar k^2}{2m}. \tag{2.13}$$

In obtaining this relation we have set the constant of integration to zero because this constant gives rise to no observable consequences in non-relativistic quantum mechanics.

Our task is to find a wave equation which has sinusoidal solutions which obey this dispersion relation. The simplest such wave equation is called the Schrödinger equation. For a free particle moving in one dimension it has the form

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}. \tag{2.14}$$

It is easy to verify that the complex exponential

$$\Psi(x,t) = A\,\mathrm{e}^{i(kx-\omega t)} \tag{2.15}$$

is a solution of this equation provided ω and k obey the dispersion relation Eq. (2.13). If we substitute into Eq. (2.14), the left-hand side yields

$$i\hbar\frac{\partial\Psi}{\partial t} = i\hbar(-i\omega)A\,\mathrm{e}^{i(kx-\omega t)} = \hbar\omega A\,\mathrm{e}^{i(kx-\omega t)},$$

and the right-hand side yields

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{\hbar^2 k^2}{2m}A\,\mathrm{e}^{i(kx-\omega t)},$$

and we have a solution provided $\hbar\omega = \hbar^2k^2/2m$.

Because the sinusoidal solution, Eq. (2.15), describes a wave moving in the x direction with wave number k and angular velocity ω, we shall assume that it represents a free particle moving in the x direction with a sharply defined momentum $p = \hbar k$ and energy $E = p^2/2m = \hbar\omega$. There are, of course, many other solutions of the Schrödinger equation which represent other states of motion of the particle.

We emphasize that in order to accommodate the dispersion relation for de Broglie waves, Eq. (2.13), we have arrived at a wave equation, the free-particle

We can now rewrite Eq. (3.27) as

$$\langle p\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\left(\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} p\tilde{\Psi}(p,t)\,\mathrm{e}^{+ipx/\hbar}\,\mathrm{d}p\right)\mathrm{d}x.$$

If the order of integration is interchanged, we obtain

$$\langle p\rangle = \int_{-\infty}^{+\infty}\left(\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} \Psi^*(x,t)\,\mathrm{e}^{+ipx/\hbar}\,\mathrm{d}x\right)p\tilde{\Psi}(p,t)\,\mathrm{d}p.$$

We now use Eq. (3.20) to show that the integral in the brackets is equal to $\tilde{\Psi}^*(p,t)$ and obtain

$$\langle p\rangle = \int_{-\infty}^{+\infty} \tilde{\Psi}^*(p,t)p\tilde{\Psi}(p,t)\,\mathrm{d}p$$

which is identical to Eq. (3.26).

Operators

We shall now introduce an idea which will become increasingly important as we develop the basic elements of quantum mechanics. This is the idea that observables in quantum mechanics can be described by operators. At this stage we shall consider the role of operators in the calculation of position and momentum expectation values using Eq. (3.25) and Eq. (3.27). The recipe for the calculation is as follows:

- First prepare a sandwich with Ψ^* and Ψ.
- To find $\langle x\rangle$ insert x into the sandwich, and to find $\langle p\rangle$ insert $-i\hbar\,\partial/\partial x$ into the sandwich.
- Then integrate over x.

In this recipe, the position observable is represented by x and the momentum observable is represented by $-i\hbar\,\partial/\partial x$. However, both x and $-i\hbar\,\partial/\partial x$ can be considered as operators which act on the wave function; the real number x merely multiplies $\Psi(x,t)$ by a factor x, and the differential expression $-i\hbar\,\partial/\partial x$ differentiates $\Psi(x,t)$ and multiplies it by $-i\hbar$. To emphasize the role of operators in quantum physics we rewrite Eq. (3.25) and Eq. (3.27) as

$$\langle x\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\ \hat{x}\ \Psi(x,t)\,\mathrm{d}x \quad\text{and}\quad \langle p\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\ \hat{p}\ \Psi(x,t)\,\mathrm{d}x. \tag{3.29}$$

4.4 A PARTICLE IN A BOX II

One of the key features of quantum physics is that the possible energies of a confined particle are quantized. Indeed, the familiar quantized energy levels of atomic, nuclear and particle physics are manifestations of confinement. We shall illustrate the connection between confinement and quantized energy levels by considering a particle confined to a box.

A one-dimensional box

We begin by considering a particle moving in one dimension with potential energy

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < a \\ \infty & \text{elsewhere,} \end{cases} \tag{4.30}$$

This infinite square-well potential confines the particle to a one-dimensional box of size a, as shown in Fig. 4.2. In classical physics, the particle either lies at the bottom of the well with zero energy or it bounces back and forth between the barriers at $x = 0$ and $x = a$ with any energy up to infinity. In quantum physics, more varied states exist. Each is described by a wave function $\Psi(x, t)$ which obeys the one-dimensional Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi. \tag{4.31}$$

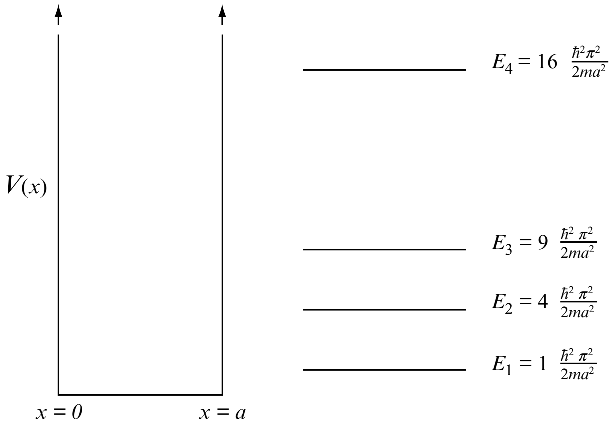

Fig. 4.2 Low-lying energy levels of a particle of mass m confined by an infinite square-well potential $V(x)$ with width a.

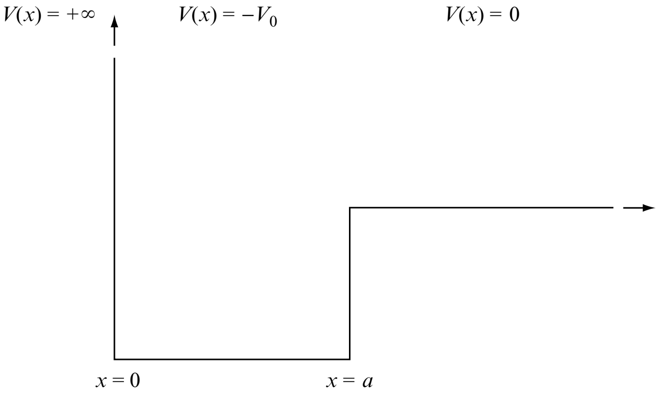

Fig. 5.1 The potential energy field given by Eq. (5.1) in which there are unbound states with a continuous range of energies and, if the well is deep enough, bound states with discrete energies.

The behaviour of a classical particle in this potential should be familiar. The energy of the particle, E, is given by the sum of its kinetic and potential energies,

$$E = \frac{p^2}{2m} + V(x).$$

When the energy is negative and somewhere between $E = -V_0$ and $E = 0$, the particle is bound or trapped in the well of depth V_0; it bounces back and forth between $x = 0$ and $x = a$ with kinetic energy $E + V_0$. But when the energy is positive, the particle is unbound. For example, it could approach the well from $x = +\infty$ with kinetic energy E, increase its kinetic energy to $E + V_0$ when it reaches $x = a$, hit the infinitely-high potential wall at $x = 0$ and then bounce back to $x = +\infty$.

The behaviour of a quantum particle in this potential is described by a wave function $\Psi(x,\ t)$ which is a solution of the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi. \tag{5.2}$$

When the particle has definite energy E, the wave function has the form

$$\Psi(x,\ t) = \psi(x)\,\mathrm{e}^{-iEt/\hbar}, \tag{5.3}$$

where $\psi(x)$ is an eigenfunction satisfying the energy eigenvalue equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi. \tag{5.4}$$

Once we have solved this eigenvalue equation and found all the possible energy eigenvalues and eigenfunctions, we can represent any quantum state of the particle in the potential as a linear superposition of energy eigenfunctions.

To solve the eigenvalue equation, we note that the potential $V(x)$ given by Eq. (5.1) takes on constant values in three regions of x: $(-\infty < x < 0)$, $(0 < x < a)$ and $(a < x < +\infty)$. We shall find solutions of Eq. (5.4) in these three regions and then join the solutions together at $x = 0$ and at $x = a$ to obtain physically acceptable eigenfunctions. Because the potential $V(x)$ changes abruptly at $x = 0$ and $x = a$, we can only require the eigenfunctions $\psi(x)$ to be as smooth as possible. In particular, we shall require $\psi(x)$ to be continuous at $x = 0$ and $x = a$ in order to avoid unacceptable abrupt changes in the position probability density. The differential equation (5.4) with potential (5.1) then implies that the first derivative of $\psi(x)$ is continuous at $x = a$ and discontinuous at $x = 0$.[1]

We are interested in two types of eigenfunctions. The eigenfunctions for bound states and the eigenfunctions for unbound states.

Bound states

If a bound state exists, it has a negative energy somewhere between $E = -V_0$ and $E = 0$. We shall set $E = -\epsilon$, where ϵ is the binding energy, and seek solutions of Eq. (5.4).

In the region $(-\infty < x < 0)$, the potential energy is infinite and the only finite solution of Eq. (5.4) is $\psi(x) = 0$, signifying that the particle is never found in the negative x region.

In the region $(0 < x < a)$, the potential energy is $V(x) = -V_0$ and Eq. (5.4) has the form

$$\frac{d^2\psi}{dx^2} = -k_0^2\psi, \quad \text{where} \quad E = \frac{\hbar^2 k_0^2}{2m} - V_0. \tag{5.5}$$

The general solution of this second-order differential equation has the form

$$\psi(x) = C\sin(k_0 x + \gamma),$$

where C and γ are arbitrary constants. To ensure continuity of $\psi(x)$ at $x = 0$, we shall set the constant γ to zero to give

$$\psi(x) = C\sin k_0 x. \tag{5.6}$$

---

[1] The infinite change in the potential at $x = 0$ forces a discontinuity in $d\psi/dx$ at $x = 0$. A more rigorous approach would be to consider a potential energy with a finite value V_1 in the region $x \leq 0$, require the continuity of $\psi(x)$ and $d\psi/dx$ at $x = 0$ and then take the limit $V_1 \to \infty$.

In the region $(a < x < +\infty)$, the potential energy is zero and Eq. (5.4) has the form

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi, \quad \text{where} \quad E = -\frac{\hbar^2\alpha^2}{2m}. \tag{5.7}$$

The general solution is

$$\psi(x) = A\,e^{-\alpha x} + A'\,e^{+\alpha x},$$

where A and A' are arbitrary constants. To ensure that the eigenfunction is finite at infinity, we set A' to zero to give a solution which falls off exponentially with x:

$$\psi(x) = A\,e^{-\alpha x}. \tag{5.8}$$

Our next task is to join the solution given by Eq. (5.6), which is valid in the region $(0 < x < a)$, onto the solution given by Eq. (5.8), which is valid in the region $(a < x < +\infty)$. As mentioned earlier, we shall require the eigenfunction and its first derivative to be continuous at $x = a$. Continuity of $\psi(x)$ gives

$$C\sin k_0 a = A\,e^{-\alpha a} \tag{5.9}$$

and continuity of $d\psi/dx$ gives

$$k_0 C\cos k_0 a = -\alpha A\,e^{-\alpha a}. \tag{5.10}$$

If we divide Eq. (5.10) by Eq. (5.9), we obtain

$$k_0 \cot k_0 a = -\alpha. \tag{5.11}$$

Equation (5.11) sets the condition for a smooth join at $x = a$ of the functions $C\sin k_0 x$ and $A\,e^{-\alpha x}$. It is a non-trivial condition which is only satisfied when the parameters k_0 and α take on special values. And once we have found these special values, we will be able to find the binding energies of the bound states from $\epsilon = \hbar^2\alpha^2/2m$.

To find these binding energies, we note that α and k_0 are not independent parameters. They are defined by

$$E = -\frac{\hbar^2\alpha^2}{2m} \quad \text{and} \quad E = \frac{\hbar^2 k_0^2}{2m} - V_0,$$

which imply that

$$\alpha^2 + k_0^2 = w^2, \quad \text{where } w \text{ is given by} \quad V_0 = \frac{\hbar^2 w^2}{2m}. \tag{5.12}$$

Thus, we have two simultaneous equations for α and k_0, Eq. (5.11) and Eq. (5.12). These equations may be solved graphically by finding the points of intersection of the curves

$$\alpha = -k_0 \cot k_0 a \quad \text{and} \quad \alpha^2 + k_0^2 = w^2,$$

as illustrated in Fig. 5.2.

Inspection of Fig. 5.2 shows the number of points of intersection, and hence the number of bound states, increase as the well becomes deeper. In particular, there are no bound states for a shallow well with

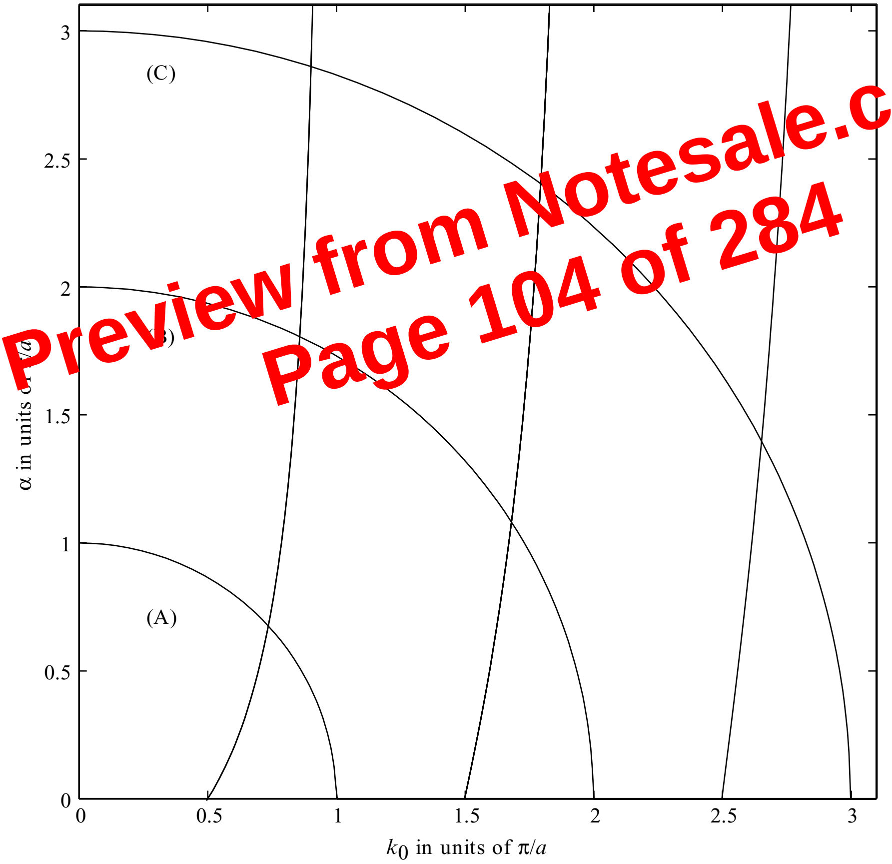

Fig. 5.2 Graphical solution of the simultaneous equations $\alpha = -k_0 \cot k_0 a$ and $\alpha^2 + k_0^2 = w^2$. The units of k_0 and α are π/a. Three values for the well-depth parameter, $w = \pi/a$, $w = 2\pi/a$ and $w = 3\pi/a$, are labelled by (A), (B) and (C), respectively. For (A) there is one point of intersection and one bound state, for (B) there are two points of intersection and two bound states and for (C) there are three points of intersection and three bound states.

$$w < \frac{\pi}{2a}.$$

There is one bound state when

$$\frac{\pi}{2a} < w < \frac{3\pi}{2a},$$

and two bound states when

$$\frac{3\pi}{2a} < w < \frac{5\pi}{2a},$$

and so on.

To illustrate the nature of the bound states, we shall consider a potential with well-depth parameter $w = 2\pi/a$ which corresponds to a well with depth

$$V_0 = \frac{2\hbar^2\pi^2}{ma^2}.$$

In this case two bound states exist, a ground state and a first excited state with binding energies

$$\epsilon_1 = 3.26\,\frac{\hbar^2\pi^2}{2ma^2} \quad\text{and}\quad \epsilon_2 = 1.17\,\frac{\hbar^2\pi^2}{2ma^2}.$$

The corresponding eigenfunctions are shown in Fig. 5.3. These eigenfunctions show that a bound quantum particle can be found outside the classical region of confinement ($0 < x < a$). Specifically, for $x > 0$, bound-state eigenfunctions have non-zero values given by

$$\psi(x) = A\,\mathrm{e}^{-\alpha x}.$$

Hence the position probability densities for a bound particle fall off exponentially as x penetrates into the classically forbidden region. Because the parameter α is related to the binding energy ϵ via $\epsilon = \hbar^2\alpha^2/2m$, the degree of quantum penetration into the classically forbidden region is more pronounced when the binding energy is low. The phenomenon of quantum penetration will be considered further in Section 5.2.

Unbound states

We shall now consider a particle with positive energy E that approaches the well, shown in Fig. 5.1, from the right and is then reflected at $x = 0$. It is useful to write the energy of the particle as

By substituting this value for β into Eq. (5.42) we can illustrate the incredible sensitivity of the electron tunnelling probability. For example, there is a measurable 2 % change in the probability when the gap between the surfaces changes by a mere 0.001 nm!

The extreme sensitivity of electron tunnelling is exploited in a device called the *scanning tunnelling microscope*. In this device a sharp metal probe is positioned near to a surface under investigation. The separation is made small enough to induce the tunnelling of electrons between the probe and the surface, and a potential difference between the probe and the surface is also established so that there is a net current of electrons in one direction. As the probe is moved or scanned across the surface, surface features of atomic dimensions will give rise to measurable changes in the current of tunnelling electrons. In this way the scanning tunnelling microscope can produce a map of the locations of individual atoms on the surface.

Tunnelling protons

The centre of the sun consists of an ionized gas of electrons, protons and light atomic nuclei at a temperature T of about 10^7 K. The protons and other light nuclei collide frequently, occasionally get close and occasionally fuse to release energy which is ultimately radiated from the solar surface as sunshine.

To understand the issues involved in the generation of solar thermonuclear energy, we shall focus on two protons approaching each other near the centre of the sun. They move in the ionized gas with thermal kinetic energies of the order of

$$E \approx kT \approx 1\,\text{keV}.$$

The mutual potential energy of the two protons depends on their separation. As illustrated in Fig. 5.5, the potential energy at large separation r is dominated by the repulsive Coulomb potential

$$V(r) = \frac{e^2}{4\pi\epsilon_0 r}.$$

But at small separations, when r becomes comparable with the range of nuclear forces given by $r_N \approx 2 \times 10^{-15}$ m, the potential energy becomes attractive. The net effect is a Coulomb barrier which rises to a height of about 1 MeV at a separation of about 2×10^{-15} m or 2 fm.

Thus, when protons approach each other near the centre of the sun, they do so with energies of the order of keV and they encounter a Coulomb barrier measured in MeV. According to classical physics, there is a well-defined distance of closest approach r_C, which is given by

$$\psi(\mathbf{r}) = \frac{u(r)}{r}, \tag{5.46}$$

where $u(r)$, as shown in problem 2 at the end of the chapter, obeys

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + V(r)u = E. \tag{5.47}$$

We shall not attempt to solve this equation. Instead, we shall use the results we obtained for a one-dimensional barrier to write down a plausible form of the eigenfunction and then estimate the probability of tunnelling through a Coulomb barrier.

We begin by considering a three-dimensional barrier with constant height V_B and width $r_C - r_N$. In this case, the function $u(r)$ decays exponentially in the classically forbidden region as r gets smaller and it is given by

$$u(r) \propto \mathrm{e}^{\beta r},$$

where β is given by

$$E = -\frac{\hbar^2\beta^2}{2\mu} + V_B.$$

The probability that the protons tunnel from $r = r_C$ to $r = r_N$ is approximately equal to the ratio of $|u(r_N)|^2$ to $|u(r_C)|^2$, and it is given by

$$T \approx |\ \exp[-\beta(r_C - r_N)]\ |^2. \tag{5.48}$$

We now consider the Coulomb barrier shown in Fig. 5.5. In this case, the eigenfunction in the classically forbidden region ($r_N < r < r_C$) is again approximately given by

$$u(r) \propto \mathrm{e}^{\beta r},$$

but β now depends on r because it is given by

$$E = -\frac{\hbar^2\beta^2}{2\mu} + \frac{e^2}{4\pi\epsilon_0 r}.$$

The probability that the two protons tunnel from $r = r_C$ to $r = r_N$ is now approximately given by a generalization of Eq. (5.48)

$$T \approx \left| \exp\left[- \int_{r_N}^{r_C} \beta \, \mathrm{d}r \right] \right|^2. \tag{5.49}$$

If we assume that $r_C >> r_N$ and evaluate the integral in Eq. (5.49) by substituting $r = r_C \cos^2 \theta$, we find that

$$T \approx \exp\left[- \left(\frac{E_G}{E} \right)^{1/2} \right] \tag{5.50}$$

where E is the relative energy of the protons and E_G is defined by

$$E_G = \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 2\pi^2 \mu c^2. \tag{5.51}$$

The energy E_G is called *the Gamow energy* and its value is 493 keV.

We can now estimate the probability that two protons tunnel through the Coulomb barrier which normally keeps them well apart when they collide near the centre of the sun. By substituting a typical thermal energy of $E = 1$ keV into Eq. (5.50), we obtain

$$T \approx \exp[-22] \approx 3 \times 10^{-10}.$$

Thus, with a probability of about one in 3 billion, protons colliding near the centre of the sun tunnel through the Coulomb barrier. And when they do so they have a chance of fusing and releasing thermonuclear energy.

In practice, stars evolve slowly by adjusting their temperature so that the average thermal energy of nuclei is well below the Coulomb barrier. Fusion then proceeds at a rate proportional to the tunnelling probability. Because this probability is very low, fusion proceeds at a slow pace and the nuclear fuel lasts for an astronomically long time scale.

PROBLEMS 5

1. Consider a particle of mass m in the one-dimensional potential energy field

$$V(x) = \begin{cases} 0 & \text{if } -\infty < x < -a \\ -V_0 & \text{if } -a < x < +a \\ 0 & \text{if } +a < x < +\infty. \end{cases}$$

Because the potential is symmetric about $x = 0$, there are two types of energy eigenfunctions. There are symmetric eigenfunctions which obey

We note that when $n = 0$, i.e. when the particle is in the ground state of the oscillator, the product of Δx and Δp is as small as it can be.

- Because the position and momentum of the particle are uncertain, the potential energy and the kinetic energy are uncertain. The expectation values of these uncertain observables are

$$\frac{1}{2}m\omega^2\langle x^2\rangle = \frac{1}{2}E_n \quad \text{and} \quad \frac{\langle p^2\rangle}{2m} = \frac{1}{2}E_n.$$

  Not surprisingly, the sum of the expectation values of the uncertain potential and kinetic energies is equal to E_n, the sharply defined total energy of the state.

Finally, it is useful to consider in general terms why the quantum ground state of the harmonic oscillator is so different from the classical ground state in which the particle lies at rest at the bottom of the well with zero kinetic energy and zero potential energy. When a quantum particle is precisely localized at the centre of the well, it has a highly uncertain momentum and, hence, a high kinetic energy. Similarly, when its momentum is precisely zero, it has a highly uncertain position and it may be found in regions of high potential energy. It follows that the sum of the kinetic and potential energies of a quantum particle in a harmonic oscillator potential has a minimum value when its position and momentum are uncertain, but not too uncertain. This minimum is called the *zero point energy of the harmonic oscillator*. A lower bound for this energy is derived using these ideas in problem 1 at the end of this chapter.

Non-stationary states

The general wave function of a particle in a harmonic oscillator potential has the form

$$\Psi(x,t) = \sum_{n=0,1,2\ldots} c_n\psi_n(x)\,\mathrm{e}^{-iE_nt/\hbar}. \tag{6.15}$$

This wave function represents a state of uncertain energy because when the energy is measured many outcomes are possible: $E_0 = \frac{1}{2}\hbar\omega$, $E_1 = \frac{3}{2}\hbar\omega$, ... with probabilities $|c_0|^2, |c_1|^2, \ldots$.

This wave function also represents a non-stationary state, a state with time-dependent observable properties. For example, the position probability amplitude $|\Psi(x,t)|^2$ has time-dependent terms which arise from the interference of terms involving different energy eigenfunctions, $\psi_n(x)$. In particular, the inter-

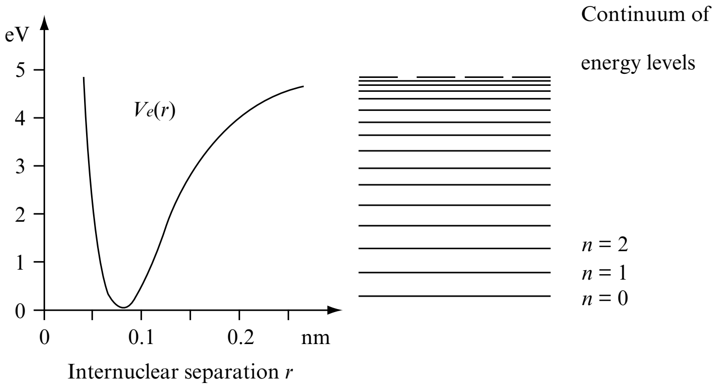

Fig. 6.4 The effective internuclear potential $V_e(r)$ and the vibrational energy levels of the hydrogen molecule. The potential energy near the minimum is approximately quadratic and acts like a harmonic oscillator potential, and the lowest vibrational levels are approximately equally spaced and given by the $E_n = (n + \frac{1}{2})\hbar\omega$. The vibrational levels become more closely spaced as the degree of excitation increases and the dissociation of the molecule gives rise to a continuum of energy levels.

If classical physics were applicable, the nuclei would have energy

$$E_{\text{classical}} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{1}{2}kx^2.$$

where m_1 and m_2 are the masses of the nuclei and p_1 and p_2 are the magnitudes of their momenta. In the centre-of-mass frame, we can set $p_1 = p_2 = p$ and, by introducing the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2},$$

we obtain

$$E_{\text{classical}} = \frac{p^2}{2\mu} + \frac{1}{2}kx^2.$$

This energy is the same as the energy of a single particle of mass μ on a spring with elastic constant k. Accordingly, we expect the vibrating nuclei in a diatomic molecule to act like a harmonic oscillator with classical frequency $\omega = \sqrt{k/\mu}$, where μ is the reduced mass of the nuclei and k is an elastic constant characterizing the strength of the molecular bond between the nuclei.

The quantum mechanical behaviour of this oscillator is described by a wave function $\Psi(x, t)$ which satisfies the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}k^2x^2\right]\Psi. \tag{6.18}$$

This equation is almost identical to Eq. (6.8), which formed the starting point for our discussion of the quantum oscillator. Indeed, if we replace the mass m by the reduced mass μ, we can apply all our results to a diatomic molecule. Most importantly, we can use Eq. (6.12) to write down an expression for the vibrational energy levels of a diatomic molecule with reduced mass μ and elastic constant k:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad \text{where} \quad \omega = \sqrt{\frac{k}{\mu}}. \tag{6.19}$$

The quantum number n can take on the values $0, 1, 2, \ldots$, but, when n is large, the harmonic oscillator model for molecular vibrations breaks down. This occurs when the vibrational energy becomes comparable with the dissociation energy of the molecule, as shown for the hydrogen molecule in Fig. 6.4.

A transition from one vibrational level of the molecule to another is often accompanied by the emission or absorption of electromagnetic radiation, usually in the infrared part of the spectrum. This is particularly so for diatomic molecules with two different nuclei, i.e. heteronuclear diatomic molecules. For such molecules, the electrons form an electric dipole which can strongly absorb or emit electromagnetic radiation. In fact, this mechanism leads to transitions between adjacent vibrational levels and the emission or absorption of photons with energy[4]

$$E = \hbar\sqrt{\frac{k}{\mu}}.$$

These photons give rise to a prominent spectral line with wavelength

$$\lambda = \frac{hc}{E} = 2\pi c\sqrt{\frac{\mu}{k}}. \tag{6.20}$$

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[4] The probability for transition from ψ_m to ψ_n induced by electric dipole radiation is proportional to $|x_{m,\,n}|^2$ where

$$x_{m,\,n} = \int_{-\infty}^{+\infty} \psi_m^*(x)x\psi_n(x)\,\mathrm{d}x.$$

By using the properties of the harmonic oscillator eigenfunctions, one can show that $x_{m,\,n} = 0$ if $|m - n| \neq 1$. (See problem 11 at the end of this chapter.)

As an example, we consider the carbon monoxide molecule. The reduced mass of the nuclei is $\mu = 6.85\,\mathrm{amu}$, and, when transitions between adjacent vibrational levels occur, infrared radiation with wavelength $\lambda = 4.6\,\mu\mathrm{m}$ is emitted or absorbed. If we substitute these values for μ and λ into Eq. (6.20), we find that the elastic constant, characterizing the strength of the bond in the carbon monoxide molecule, is $k = 1908\,\mathrm{N m^{-1}}$.

In reality, the situation is more complex. First of all, transitions between adjacent vibrational levels have slightly different wavelengths, because the vibrational energy levels are only approximately equally spaced; as illustrated in Fig. 6.4, a harmonic oscillator potential does not exactly describe the interaction between the nuclei in a diatomic molecule. Second, the molecule may rotate and each vibrational level is really a band of closely spaced levels with different rotational energies; accordingly, there is a band of spectral lines associated with each vibrational transition.

6.5 THREE-DIMENSIONAL OSCILLATORS

We shall conclude this chapter by considering a particle of mass m in the three-dimensional harmonic oscillator potential

$$V(r) = \tfrac{1}{2}kr^2 = \tfrac{1}{2}k(x^2 + y^2 + z^2). \tag{6.21}$$

A classical particle at a distance r from the origin would experience a central force towards the origin of magnitude kr. When displaced from the origin and released, it executes simple harmonic motion with angular frequency $\omega = \sqrt{k/m}$, but more complicated motion occurs when the particle is displaced and also given a transverse velocity.

The behaviour of a quantum particle is governed by a Hamiltonian operator $\hat{H}$ which is the sum of three one-dimensional Hamiltonians:

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z \tag{6.22}$$

where

$$\begin{aligned}
\hat{H}_x &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2,\\
\hat{H}_y &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}m\omega^2 y^2,\\
\hat{H}_z &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + \frac{1}{2}m\omega^2 z^2.
\end{aligned}$$

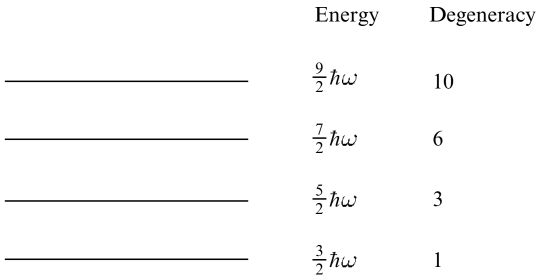


Fig. 6.5 The four lowest energy levels of a particle in a three-dimensional harmonic oscillator potential. The degeneracy of each level is denoted on the right-hand side.

$$E_{1,0,0} = \frac{5}{2}\hbar\omega \quad \text{and} \quad \psi_{1,0,0}(x,y,z) = \left(\frac{1}{a\sqrt{\pi}}\right)^{3/2} 2^{1/2}\left(\frac{x}{a}\right) \mathrm{e}^{-(x^2+y^2+z^2)/2a^2}.$$

$$E_{0,1,0} = \frac{5}{2}\hbar\omega \quad \text{and} \quad \psi_{0,1,0}(x,y,z) = \left(\frac{1}{a\sqrt{\pi}}\right)^{3/2} 2^{1/2}\left(\frac{y}{a}\right) \mathrm{e}^{-(x^2+y^2+z^2)/2a^2}.$$

$$E_{0,0,1} = \frac{5}{2}\hbar\omega \quad \text{and} \quad \psi_{0,0,1}(x,y,z) = \left(\frac{1}{a\sqrt{\pi}}\right)^{3/2} 2^{1/2}\left(\frac{z}{a}\right) \mathrm{e}^{-(x^2+y^2+z^2)/2a^2}.$$

In a similar way we can find six states with energy $7\hbar\omega/2$, ten states with energy $9\hbar\omega/2$, and so on.

The energy levels of the three-dimensional harmonic oscillator are shown in Fig. 6.5. This diagram also indicates the degeneracy of each level, the degeneracy of an energy level being the number of independent eigenfunctions associated with the level. This degeneracy arises because the Hamiltonian for the three-dimensional oscillator has rotational and other symmetries.

6.6 THE OSCILLATOR EIGENVALUE PROBLEM

For the benefit of mathematically inclined readers we shall now discuss the problem of finding the energy eigenfunctions and eigenvalues of a one-dimensional harmonic oscillator. The method used is interesting and introduces mathematical methods which are very useful in advanced quantum mechanics. *This section may be omitted without significant loss of continuity.*

In order to simplify the task of finding the eigenvalues and eigenfunctions, we shall clean up the eigenvalue equation (6.10) and give it a gentle massage. We note that this equation contains three dimensional constants: Planck's constant $\hbar$, the classical angular frequency ω, and the mass of the confined particle m. With these constants we can construct an energy $\hbar\omega$ and a length $\sqrt{\hbar/m\omega}$. Hence, it is natural to measure the energy E in units of $\hbar\omega$

The ground state

Two possible eigenvalues and eigenfunctions are immediately apparent from an inspection of the alternative expressions for the eigenvalue equation given by Eq. (6.30) and Eq. (6.31).

First, Eq. (6.30) is clearly satisfied if

$$\epsilon = -\frac{1}{2} \quad \text{and} \quad \left[q - \frac{\mathrm{d}}{\mathrm{d}q} \right] \psi(q) = 0.$$

This first-order differential equation for $\psi(q)$ has the solution

$$\psi(q) = A\,\mathrm{e}^{+q^2/2}$$

where A is a constant. But this solution must be discarded because it does not satisfy the boundary conditions, $\psi(q) \to 0$ as $q \to \pm\infty$, which are needed for a normalizable wave function.

Second, Eq. (6.31) is clearly satisfied if

$$\epsilon = +\frac{1}{2} \quad \text{and} \quad \left[q + \frac{\mathrm{d}}{\mathrm{d}q} \right] \psi(q) = 0.$$

In this case the differential equation for $\psi(q)$ has the solution

$$\psi(q) = A\,\mathrm{e}^{-q^2/2},$$

which is an acceptable eigenfunction because $\psi(q) \to 0$ as $q \to \pm\infty$. Later we shall show that this is the eigenfunction of the ground state. Accordingly, we shall use the quantum number $n = 0$ as a label and take the ground state eigenvalue and eigenfunction to be

$$\epsilon_0 = +\tfrac{1}{2} \quad \text{and} \quad u_0(q) = A_0\,\mathrm{e}^{-q^2/2}, \tag{6.32}$$

where A_0 is a normalization constant.

If we use Eq. (6.28) to express the dimensionless variables ϵ and q in terms of the dimensional variables E and x, we find that the ground state of a harmonic oscillator with angular frequency ω has energy

$$E_0 = \tfrac{1}{2}\hbar\omega \tag{6.33}$$

and that its eigenfuction, as a function of x, is given by

7

Observables and operators

Operators have to be used in quantum mechanics to describe observable quantities because measurements may have uncertain outcomes. In Chapter 3 we used the operators

$$\hat{\mathbf{r}} = \mathbf{r} \quad \text{and} \quad \hat{\mathbf{p}} = -i\hbar\nabla$$

to calculate the expectation values and the uncertainties in the position and momentum of a particle. In Chapter 4 we used the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

to explore the energy properties of a particle. And in the next chapter we shall consider in detail a fourth operator, the operator describing the orbital angular momentum of a particle,

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}.$$

In this chapter we shall consider some physical properties of observables in quantum mechanics and link these properties to the mathematical properties of the operators which describe observables. In so doing, concepts that were implicit in the use of operators in earlier chapters will be clarified and developed. This chapter will deal with concepts that are more abstract and mathematical than those encountered elsewhere in this book. *It may be omitted without significant loss of continuity*.

In fact, we have three commuting operators,

$$[\hat{x}, \hat{y}] = [\hat{x}, \hat{p}_z] = [\hat{y}, \hat{p}_z] = 0,$$

and simultaneous eigenfunctions of the form

$$\psi_{x'y'p'_z}(x, y, z) = \delta(x - x')\delta(y - y')\frac{1}{\sqrt{2\pi\hbar}}\,\mathrm{e}^{-ip'_z z}.$$

Moreover, any wave function $\Psi(x, y, z, t)$ can be expressed as linear superposition of these eigenfunctions as follows:

$$\Psi(x, y, z, t) = \int_{-\infty}^{+\infty} \mathrm{d}x' \int_{-\infty}^{+\infty} \mathrm{d}y' \int_{-\infty}^{+\infty} \mathrm{d}p'_z \; c(x', y', p'_z, t)\psi_{x'y'p'_z}(x, y, z).$$

In this expression $c(x', y', p'_z, t)$ is a probability amplitude for three compatible observables. In fact, the probability of finding the particle at time t localized between x' and $x' + \mathrm{d}x'$ and between y' and $y' + \mathrm{d}y'$, and with momentum in the z direction between p'_z and $p'_z + \mathrm{d}p'_z$, is $|c(x', y', p'_z, t)|^2 \, \mathrm{d}x' \, \mathrm{d}y' \, \mathrm{d}p'_z$.

This example has illustrated the general procedure of defining a quantum state of a particle moving in three dimensions by specifying a set of three compatible observables. This procedure will be used in Chapter 9 when we construct stationary states of the hydrogen atom by specifying the energy, the magnitude of the orbital angular momentum and the z component of the orbital angular momentum.

7.5 CONSTANTS OF MOTION

Observables that are compatible with the energy observable have a particular physical significance. They are *constants of the motion*. To explain the significance of this statement we consider the expectation value for an observable A for a particle with wave function Ψ,

$$\langle A(t) \rangle = \int \Psi^* \hat{A} \, \Psi \, \mathrm{d}^3\mathbf{r}. \tag{7.20}$$

In general, the expectation value $\langle A(t) \rangle$ will vary with time as the wave function $\Psi(\mathbf{r}, t)$ ebbs and flows in accord with the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi. \tag{7.21}$$

For example, the W boson is a spin-one particle with $s = 1$ and $m_s = +1, 0, -1$ and the electron is a spin-half particle with $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. Thus, spin angular momentum can be integer, like orbital angular momentum, but it can also be half-integer.

Orbital and spin angular momenta may be combined to give a total angular momentum with magnitude and z component given by

$$J = \sqrt{j(j+1)}\hbar \quad \text{and} \quad J_z = m_j\hbar, \tag{8.4}$$

where, in general, the quantum numbers j and m_j may take on integer and half-integer values given by

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots\ldots. \quad \text{and} \quad m_j = \begin{cases} +j \\ +(j-1) \\ \vdots \\ -(j-1) \\ -j. \end{cases} \tag{8.5}$$

The actual values of the quantum number j depend on the orbital and spin angular momenta being combined. It can be shown that, when an orbital angular momentum with quantum number l is combined with a spin with quantum number s, several total angular momenta may arise with quantum numbers

$$j = l + s, l + s - 1, \ldots |l - s|. \tag{8.6}$$

For example, we can have $j = \frac{3}{2}$ and $\frac{1}{2}$ when $l = 1$ and $s = \frac{1}{2}$, and we can have $j = 2, 1$ and 0 when $l = 1$ and $s = 1$. We note that, in general, two angular momenta with quantum numbers j_1 and j_2 may be combined to give an angular momentum with quantum number j which can take on the values

$$j = j_1 + j_2,\ j_1 + j_2 - 1,\ \ldots\ , |j_1 - j_2|.$$

Earlier we referred to an angular momentum defined by two quantum numbers as a fuzzy vector. The fuzziness arises because, when one of its Cartesian components is sharply defined, the other two components are uncertain but quantized when measured. In view of the uncertainties we have already encountered in position, momentum and energy, uncertain angular momentum should not be a surprise. Indeed, the uncertainty in orbital angular momentum can be directly traced to the uncertainties in the position and momentum of a particle, as indicated in problem 3 at the end of Chapter 7. But it is surprising that angular momentum in any given direction can only equal an integer or

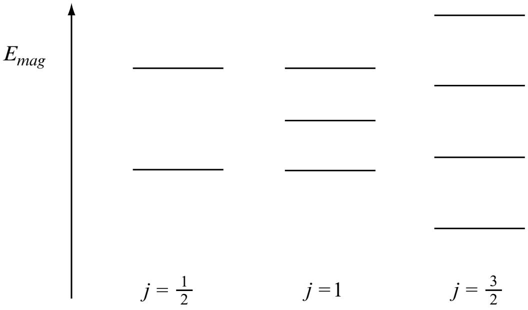


Fig. 8.2 The energy levels in a magnetic field of an atom in states with angular momentum quantum numbers $j = \frac{1}{2}$, 1 and $\frac{3}{2}$. The spacing between levels is given by $g\mu_B B$ where B is the strength of the magnetic field, μ_B is the Bohr magneton and g is a Landé g-factor, a constant which depends on the spin and orbital angular momentum quantum numbers of the atomic state.

The main features of a Stern–Gerlach experiment are illustrated in Fig. 8.3. A beam of atoms is passed through a magnetic field produced by specially shaped poles of an electromagnet. The direction of the magnetic field is largely in one direction, the z direction say, but its strength, $B(x, y, z)$, increases markedly as z increases. In this field each atom acquires an energy

$$E_{mag}(x, y, z) = -\mu_z B(x, y, z)$$

which depends upon the z component of its magnetic moment μ_z and on the location in the field. Because this magnetic energy varies strongly with z, the atom is deflected by a force in the z direction which is given by

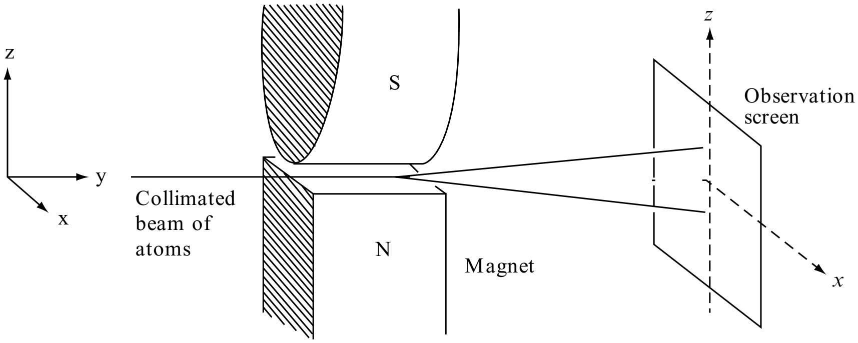


Fig. 8.3 The Stern–Gerlach experiment in which atoms pass through a non-uniform magnetic field which separates out atoms according to the value of the magnetic moment in the direction of maximum non-uniformity of the field.

simpler angular shapes. These basis wave functions are usually taken to be wave functions with specific orbital angular momentum properties. Accordingly, we shall consider some wave functions with simple angular dependence and deduce the orbital angular momentum properties of the particle they describe. The properties of the following wave functions will be explored: The spherically symmetric wave function given by

$$\psi_{(0,0)} = R(r), \tag{8.18}$$

where $R(r)$ is any well-behaved function of $r = \sqrt{x^2 + y^2 + z^2}$, and the wave functions

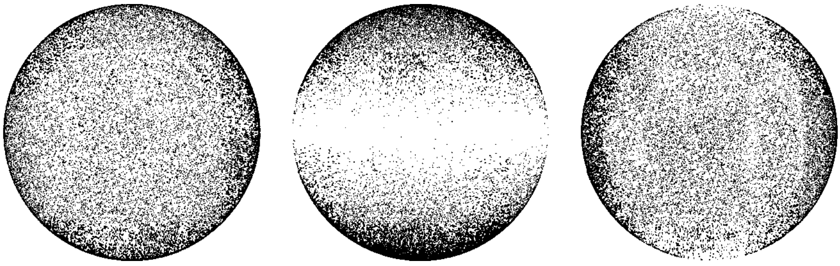
$$\psi_{(1,0)} = R(r)\frac{z}{r}, \quad \psi_{(1,+1)} = R(r)\frac{(x+iy)}{r}, \quad \psi_{(1,-1)} = R(r)\frac{(x-iy)}{r}. \tag{8.19}$$

The rationale for the labels (0,0), (1,0) and (1, ± 1) will become clear after we have determined the angular momentum properties of the states described by these wave functions.

The position probability densities for these wave functions,

$$|\psi_{(0,0)}|^2 = |R(r)|^2, \quad |\psi_{(1,0)}|^2 = |R(r)|^2\frac{z^2}{r^2} \quad \text{and} \quad |\psi_{(1,\pm1)}|^2 = |R(r)|^2\frac{(x^2+y^2)}{r^2},$$

are illustrated in Fig. 8.4. We note that a particle described by the wave function $\psi_{(0,0)}$ is equally likely to be found at any point on the surface of a sphere of radius r, whereas particular regions of the surface are more likely locations for a particle described by the wave functions $\psi_{(1,0)}$ and $\psi_{(1,\pm1)}$. For the wave function $\psi_{(1,0)}$ the North and South poles are more probable



(0, 0) (1, 0) (1,±1)

Fig. 8.4 The position probability densities on the surface of a sphere for a particle with wave functions $\psi_{(0,0)}, \psi_{(1,0)}$ and $\psi_{(1,\pm1)}$ given by Eqs. (8.18) and (8.19). For future reference, these wave functions have orbital angular quantum numbers (l, m_l) equal to (0, 0), (1, 0) and (1, ± 1). (This figure was produced with the permission of Thomas D. York.)

$L^2 = 2\hbar^2$ and $L_z = 0$. Therefore, it describes a particle with a precise magnitude $L = \sqrt{2}\hbar$ and precise z component $L_z = 0$, but its orbital angular momentum in the x and y directions are uncertain.

Clearly, we can construct other wave functions with similar properties. For example, if we replace z in the expression for $\psi_{(1,0)}$ by x or by y, we obtain the wave functions

$$\psi'_{(1,0)} = R(r)\frac{x}{r} \quad \text{and} \quad \psi''_{(1,0)} = R(r)\frac{y}{r}. \tag{8.22}$$

Both these wave functions describe a particle with an orbital angular momentum of magnitude $L = \sqrt{2}\hbar$; but for $\psi'_{(1,0)}$ the x component is zero and the y and z components are uncertain, and for $\psi''_{(1,0)}$ the y component is zero and the z and x components are uncertain.

We shall finally consider the wave functions

$$\psi_{(1,+1)} = R(r)\frac{(x+iy)}{r} \quad \text{and} \quad \psi_{(1,-1)} = R(r)\frac{(x-iy)}{r},$$

both of which describe a quantum particle which is more likely to be found near the Equator and never at the North or South poles as shown in Fig. 8.4. By evaluating the action of the angular momentum operators on the functions $x \pm iy$ it is easy to show that these wave functions are not eigenfunctions of $\hat{L}_x$ or of $\hat{L}_y$, but that they are both simultaneous eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$. In fact,

$$\hat{L}_z\psi_{(1,+1)} = +\hbar\psi_{(1,+1)} \quad \text{and} \quad \hat{L}^2\psi_{(1,+1)} = 2\hbar^2\psi_{(1,+1)}$$

and

$$\hat{L}_z\psi_{(1,-1)} = -\hbar\psi_{(1,-1)} \quad \text{and} \quad \hat{L}^2\psi_{(1,-1)} = 2\hbar^2\psi_{(1,-1)}.$$

Thus, the wave function $\psi_{(1,+1)}$ describes a particle with $L_z = +\hbar$ and $L = \sqrt{2}\hbar$, and the wave function $\psi_{(1,-1)}$ describes a particle with $L_z = -\hbar$ and $L = \sqrt{2}\hbar$; in both cases, the x and y components of the orbital angular momentum are uncertain.

By exploring the properties of these simple wave functions, we have illustrated three general properties of orbital angular momentum in quantum physics:

- Orbital angular momentum in quantum physics is quantized and the natural unit for angular momentum is

$$\hbar = 1.055 \times 10^{-34}\ \text{J s}.$$

- The orbital angular momentum of a quantum particle is at best a fuzzy vector. We have only been able to specify precisely the magnitude and just one of the components of orbital angular momentum. This is because the components of angular momentum are non-compatible observables as discussed generally in Chapter 7.

- A quantum particle with specific orbital angular momentum properties has a wave function with a specific angular shape. If the orbital angular momentum is zero the wave function is spherically symmetric, and if the orbital angular momentum is non-zero the wave function has angular dependence.

Spherical harmonics

So far we have considered wave functions to be functions of the Cartesian coordinates x, y and z. In practice, it is more useful to consider wave functions to be functions of the spherical polar coordinates r, θ and ϕ illustrated Fig. 8.5. This figure shows that the Cartesian and spherical coordinates of the point P are related by

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad \text{and} \qquad z = r\cos\theta.$$

When a quantum state is represented by a wave function $\Psi(r,\theta,\phi)$, the dependence on θ and ϕ specifies an angular shape that determines the orbital angular momentum properties of the state. In fact, all possible orbital angular momentum properties can be described using simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$. These eigenfunctions are called *spherical harmonics*. They are denoted $Y_{l,m_l}(\theta,\phi)$ and they satisfy the eigenvalue equations:

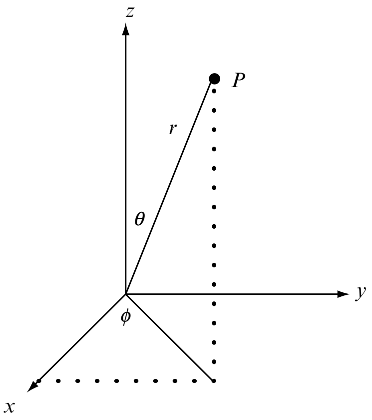


Fig. 8.5 The spherical polar coordinates $(r,\ \theta,\ \phi)$ of the point P.

any internal field. What is the spacing between these closely spaced levels in eV?

4. Two particles of mass m are attached to the ends of a massless rod of length a. The system is free to rotate in three dimensions about its centre of mass.

   (a) Write down an expression for the classical kinetic energy of rotation of the system, and show that the quantum rotational energy levels are given by

   $$E_l = \frac{l(l+1)\hbar^2}{ma^2} \quad \text{with} \quad l = 0, 1, 2, \ldots.$$

   (b) What is the degeneracy of the lth energy level?

   (c) The H_2 molecule consists of two protons separated by a distance of 0.075 nm. Find the energy needed to excite the first excited rotational state of the molecule.

5. (a) By considering the relation between Cartesian and spherical polar co-ordinates,

   $$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad \text{and} \quad z = r\cos\theta,$$

   and the chain rule

   $$\frac{\partial\psi}{\partial\phi} = \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial\phi} + \frac{\partial\psi}{\partial y}\frac{\partial y}{\partial\phi} + \frac{\partial\psi}{\partial z}\frac{\partial z}{\partial\phi},$$

   show that the operator for the z component of the orbital angular momentum of a particle,

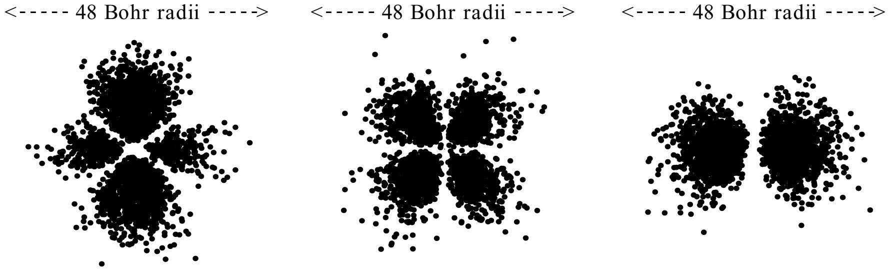
   $$\widehat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right),$$

   can be rewritten as

   $$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

   (b) Verify that

   $$Z_{m_l}(\phi) = \frac{e^{im_l\phi}}{\sqrt{2\pi}}$$



3d state with m=0 3d state with m=+1 or −1 3d state with m=+2 or −2

Fig. 9.7 The size and shape of the 3d states of the hydrogen atom with a z component of orbital angular momentum equal to $m\hbar$.

9.4 RADIATIVE TRANSITIONS

When a hydrogen atom interacts with an electromagnetic field, quantum states with quantum numbers n, l and m_l are, in general, no longer stationary states with definite energy, and radiative transitions between these states may take place in which electromagnetic energy is either absorbed or emitted.

The most probable radiative transitions are called *electric dipole transitions*. They are caused by an interaction of the electric field component **E** of the electromagnetic field with the operator describing the electric dipole moment of the electron–nucleus system. The electric dipole operator is $\mathbf{d} = -e\mathbf{r}$, where $\mathbf{r}$ is the vector position operator for the electron in the atom, and the interaction is given by

$$\hat{H}_I = -\mathbf{d} \cdot \mathbf{E}. \tag{9.26}$$

In the presence of this interaction, the probability for a transition between states with quantum numbers n_i, l_i, m_{l_i} and n_f, l_f, m_{l_f} is proportional to

$$\left| \int \psi^*_{n_f,\, l_f,\, m_{l_f}}(\mathbf{r})\; \hat{H}_I\; \psi_{n_i,\, l_i,\, m_{l_i}}(\mathbf{r})\; \mathrm{d}^3\mathbf{r} \right|^2. \tag{9.27}$$

We can easily prove that electric dipole transitions always involve a change in parity by showing that the integral in Eq. (9.27) is zero if the initial and final states have the same parity. We show this by considering the effect of changing the integration variable from $\mathbf{r}$ to $-\mathbf{r}$. The interaction $\hat{H}_I = -\mathbf{d} \cdot \mathbf{E}$ changes sign, but the sign of the eigenfunction, $\psi_{n_i,\, l_i,\, m_{l_i}}(\mathbf{r})$ or $\psi_{n_f,\, l_f,\, m_{l_f}}(\mathbf{r})$, is unchanged if the eigenfunction has even parity and it is changed if the eigenfunction has odd parity, as shown by Eqs. (9.13) and (9.14). Thus, when both eigenfunctions have the same parity, the integrand in Eq. (9.27) changes sign when the integration variable $\mathbf{r}$ is changed to $-\mathbf{r}$ and this implies that the integral must be zero.

It can also be shown, by noting that the angular dependence of the eigenfunctions $\psi_{n_f,l_f,m_{l_f}}(\mathbf{r})$ and $\psi_{n_i,l_i,m_{l_i}}(\mathbf{r})$ are given by spherical harmonics, that the integral in Eq. (9.27), and hence the probability of transition, is zero unless the difference $\Delta l = l_f - l_i$ is $+1$ or -1. This means that all electric dipole transitions in the hydrogen atom also obey the *selection rule*

$$\Delta l = \pm 1. \tag{9.28}$$

The electric dipole transitions between low-lying states of the hydrogen atom are shown as dotted lines in Fig. 9.8, where spectroscopic notation, 1s, 2s, 2p, etc. has been used to label the levels corresponding to states with different values for the principal quantum number n and orbital angular momentum quantum number l; for example, 2s corresponds to $n = 2$ and $l = 0$ and 2p corresponds to $n = 2$ and $l = 1$.

The transitions shown in Fig. 9.8 may be *induced* or *spontaneous*. Induced transitions between states with energy E_{n_i} and E_{n_f} occur strongly when the atom interacts with an external electromagnetic field which oscillates with an angular frequency ω which satisfies the resonant condition

$$\hbar\omega = |E_{n_f} - E_{n_i}|$$

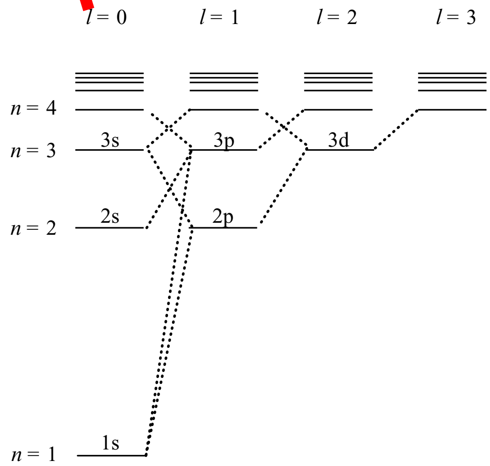


Fig. 9.8 Electric dipole radiative transitions between low-lying energy levels of the hydrogen atom with different values for the quantum numbers n and l. Spectroscopic notation, 1s, 2s, 2p, etc. has been used to label the energy levels; for example, 2s corresponds to $n = 2$ and $l = 0$ and 2p corresponds to $n = 2$ and $l = 1$. We note that the electric dipole transitions shown by the dotted lines obey the $\Delta l = \pm 1$ selection rule given in Eq. (9.28).

$$E(2p_{3/2}) = E_2 - \tfrac{1}{64}\,\alpha^4 m_e c^2.$$

We note that the difference in energies of the $2p_{3/2}$ and $2p_{1/2}$ states can be verified by observing a small difference in the wavelengths of the radiation emitted by the transitions $2p_{3/2} \rightarrow 1s_{1/2}$ and $2p_{1/2} \rightarrow 1s_{1/2}$. We also note that the $2s_{1/2}$ and $2p_{1/2}$ states are predicted to have the same energy, but that this degeneracy is removed by a small effect called the *Lamb shift* which arises from the quantum field properties of the electromagnetic field.

9.7 THE COULOMB EIGENVALUE PROBLEM

In this section we shall find the energy levels and eigenfunctions of an electron in a Coulomb potential by solving the eigenvalue problem defined by the differential equation (9.15) and the boundary conditions (9.16). *This section may be omitted without significant loss of continuity.*

As a first step we shall tidy up Eq. (9.15) by setting

$$r = q a_0 \quad \text{and} \quad E = -\gamma^2 E_R, \tag{9.36}$$

so that q is a dimensionless measure of distance and γ^2 is a dimensionless measure of the binding energy. If we use the definitions for a_0 and E_R, Eqs. (9.19) and (9.20), we find that the radial eigenfunction $u(q)$, when expressed as a function q, satisfies the differential equation

$$\frac{d^2u}{dq^2} + \left[\frac{2}{q} - \frac{l(l+1)}{q^2}\right]u = \gamma^2 u \tag{9.37}$$

and the boundary conditions

$$u(q) = 0 \quad \text{at} \quad q = 0 \quad \text{and} \quad \text{at} \quad q = \infty. \tag{9.38}$$

Our next step is to find the behaviour of $u(q)$ at large q and at small q. At large q the differential equation (9.37) becomes

$$\frac{d^2u}{dq^2} = \gamma^2 u.$$

The general solution is

$$u(q) = A\,e^{-\gamma q} + B\,e^{+\gamma q},$$

where A and B are constants, but to satisfy the boundary condition $u(q) \rightarrow 0$ as $q \rightarrow \infty$ we set $B = 0$ to give

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where $|c_{m_s}|^2$ is equal to the probability that the particle has a z component of spin equal to $m_s\hbar$. (See footnote 2 below.)

When the spatial and spin properties of a particle are independent of each other, the quantum state may be represented by a product

$$\Phi(\mathrm{p}) = \psi(\mathbf{r}_\mathrm{p})\chi(\mathrm{p}).$$

For example, the first term $\psi(\mathbf{r}_\mathrm{p})$ describing the spatial properties of the particle could be a hydrogen–like wave function with quantum numbers n, l, m_l and the second term $\chi(\mathrm{p})$ could be a spin state with quantum numbers $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. When this is the case, we have a single-particle quantum state of the form

$$\Phi_{n,l,m_l,m_s}(\mathrm{p}) = \psi_{n,l,m_l}(\mathbf{r}_\mathrm{p})\chi_{s,m_s}(\mathrm{p}).$$

We can now write down expressions for quantum states which describe the spatial and spin properties of two identical particles.

When both particles occupy the same single-particle state, say one with spatial and spin quantum numbers n, l, m_l, m_s, we can construct a symmetrical state for two identical particles of the form

$$\Phi^{(\mathrm{S})}(\mathrm{p}, \mathrm{q}) = \Phi_{n,l,m_l,m_s}(\mathrm{p})\Phi_{n,l,m_l,m_s}(\mathrm{q}). \tag{10.17}$$

But an antisymmetric two-particle state for two identical particles cannot be constructed when both particles occupy the same single-particle state. This implies that, when identical particles have antisymmetric exchange symmetry, two or more particles cannot occupy the same single-particle state.

When the particles are associated with two different single-particle states, it is possible to construct both symmetric and antisymmetric two-particle states. For example, we can have a symmetric state of the form

$$\begin{aligned}\Phi^{(\mathrm{S})}(\mathrm{p}, \mathrm{q}) = \frac{1}{\sqrt{2}}[&\Phi_{n,l,m_l,m_s}(\mathrm{p})\Phi_{n',l',m_l',m_s'}(\mathrm{q}) \\ &+ \Phi_{n,l,m_l,m_s}(\mathrm{q})\Phi_{n',l',m_l',m_s'}(\mathrm{p})]\end{aligned} \tag{10.18}$$

---

[2] In general, the probability amplitude c_{m_s} depends on time, but to keep the notation simple we shall ignore time dependence. The spin eigenvectors $\chi_{s,m_s}(\mathrm{p})$ are less abstract if they are represented by column matrices with $2s + 1$ components; for example, a particle with spin $s = \frac{1}{2}$ can be described using the matrices

$$\chi_{\frac{1}{2},+\frac{1}{2}}(\mathrm{p}) = \begin{pmatrix}1\\0\end{pmatrix}_\mathrm{p} \quad \text{and} \quad \chi_{\frac{1}{2},-\frac{1}{2}}(\mathrm{p}) = \begin{pmatrix}0\\1\end{pmatrix}_\mathrm{p},$$

where the subscript p is necessary because a matrix representing particle p must be distinguished from a matrix representing another particle. The mathematics of the representation of spin quantum states is covered in more advanced books, but this mathematics will not be needed here.

most one proton and by one neutron. Similarly, theoretical models of protons, neutrons and other hadrons are governed by the idea that quarks of a specific flavour and colour also act like systems of identical fermions with antisymmetric quantum states.

The boson way of being indistinguishable also leads to important physical phenomena. Because bosons are described by symmetric quantum states, many bosons may occupy the same single-particle state and when this happens quantum-mechanical behaviour on a macroscopic scale may arise.

The most important example of boson togetherness is the coherent light of a laser. This coherence arises because photons, bosons with spin one, have a high probability to have the same energy and momentum, in much the same way as two particles with a symmetric wave function have a high probability of being at the same location.

Boson togetherness is also responsible for the superfluidity of liquid helium at temperatures below 2.2 K. Liquid helium consists of a system of weakly interacting helium atoms which behave like bosons because they consist of a ^{4}He nucleus with spin zero and two electrons with a combined spin of zero. At low temperatures, a considerable fraction of the atoms in liquid helium 'condense' into the same lowest-energy state. They form a *Bose–Einstein condensate* in which the atoms have wave functions which are coherent with each other and move collectively without friction. Recently almost pure Bose–Einstein condensates have been produced by cooling atoms in magnetic traps; indeed the 2001 Nobel Prize in Physics was awarded to Eric Cornell, Wolfgang Ketterle and Carl Wieman for their work in producing the first pure Bose–Einstein condensate in 1995.

Surprisingly, boson-like togetherness also occurs in situations where fermion-like behaviour is expected. It occurs in the superconductivity of metals at low temperatures because pairs of electrons act like indistinguishable bosons. It also probably occurs when liquid helium-3 becomes a superfluid at very low temperatures. Helium-3 atoms, unlike the normal helium atoms, are fermions because the ^{3}He nucleus has spin half, but pairs of helium-3 atoms can act like a system of indistinguishable bosons and give rise to collective motion with no friction in liquid helium-3.

PROBLEMS 10

1. In Section 10.1 we explained why the wave function of two identical particles has a definite exchange symmetry. In this problem we show that this exchange symmetry remains unchanged as the wave function evolves.

Given that the time evolution of the wave function for two particles is governed by the Schrödinger equation,

$$i\hbar \frac{\partial \Psi(\mathbf{r}_\mathrm{p}, \mathbf{r}_\mathrm{q}, t)}{\partial t} = \hat{H}(\mathbf{r}_\mathrm{p}, \mathbf{r}_\mathrm{q})\Psi(\mathbf{r}_\mathrm{p}, \mathbf{r}_\mathrm{q}, t),$$

10, quantum states which describe a system of indistinguishable electrons must be antisymmetric whenever two electrons are exchanged. This can only be achieved if electrons are assigned to orbitals in accordance with the Pauli exclusion principle; i.e. not more than one electron may occupy an orbital with the same quantum numbers n, l, m_l, m_s. This means that at most two electrons can be assigned to 1s orbitals, one with quantum numbers $n = 1$, $l = 0$, $m_l = 0$, and $m_s = +\frac{1}{2}$, and one with quantum numbers $n = 1$, $l = 0$, $m_l = 0$, and $m_s = -\frac{1}{2}$. Similarly, not more than two electrons can be assigned to 2s orbitals, but up to six electrons can be assigned to 2p orbitals because there are six of these orbitals with quantum numbers $n = 2$, $l = 1$, $m_l = +1, 0, -1$, and $m_s = \pm\frac{1}{2}$. When the 1s, 2s and 2p orbitals are fully occupied, additional electrons may only be assigned to orbitals with principal quantum numbers n greater than 2. These orbitals have higher energy and also a limited capacity.

We can illustrate how to use this construction kit for atomic states by considering a carbon atom containing six electrons which may occupy energy levels similar to those shown on the right-hand-side of Fig. 11.2. The ground state is obtained by assigning six electrons to orbitals with the lowest possible energy; a maximum of two electrons can have the energy E_{1s}, a maximum of two can have the energy E_{2s} and the minimum energy for each of the two remaining electrons is E_{2p}. These assignments give an *electron configuration* denoted by $(1s)^2(2s)^2(2p)^2$ with energy

$$E = 2E_{1s} + 2E_{2s} + 2E_{2p}.$$

The first excited state of the carbon atom is obtained by assigning only one electron to a 2s orbital and three electrons to 2p orbitals. This gives rise to the electron configuration $(1s)^2(2s)(2p)^3$ with energy

$$E = 2E_{1s} + E_{2s} + 3E_{2p}.$$

If the energy levels shown in Fig. 11.2 for the screened potential $V_A(r)$ are used as a rough guide, the energy of the ground state is $-41.1E_R$ and the energy of the first excited state is $-40.6E_R$. Clearly, states of higher excitation may be obtained by assigning more electrons to 2p orbitals or by assigning electrons to 3s, 3p, 3d, ... orbitals.

In the preceding paragraph we have followed custom and given the wrong impression that particular electrons are in particular orbitals. This is not the case. Because all the electrons in the atom are indistinguishable, each electron is equally associated with each of the occupied orbitals. In fact, like the two-electron state given by Eq. (10.19), the multi-electron quantum state is antisymmetric when any two of the electrons are exchanged.

We have also wrongly given the impression that the central potential which represents the effect of the attraction of the nucleus and of the average effects of electron–electron repulsion, is easy to find. In fact, the central potential and the

$$E = \frac{\hbar^2}{2m_e R^2} - \frac{e^2}{4\pi\epsilon_0 R}. \tag{11.9}$$

For future reference, we will rewrite this energy as

$$E = \frac{A_1}{R^2} - \frac{B_1}{R}, \tag{11.10}$$

where A_1 and B_1 are the constants

$$A_1 = \frac{\hbar^2}{2m_e} \quad \text{and} \quad B_1 = \frac{e^2}{4\pi\epsilon_0}, \tag{11.11}$$

which determine the kinetic energy and the potential energy for a state of the hydrogen atom with spatial extent R. We note that for a state with large R, the energy is dominated by the potential energy $-B_1/R$, that for a state with small R, the energy is dominated by the kinetic energy of localization A_1/R^2, and that a balance between the attractive effect of the potential energy and the repulsive effect of the kinetic energy gives rise to a minimum energy when

$$\frac{\mathrm{d}E}{\mathrm{d}R} = -2\frac{A_1}{R^3} + \frac{B_1}{R^2} = 0,$$

i.e. when $R = 2A_1/B_1$. We conclude that this model predicts a ground state with an energy and size given by

$$E_1 = -\frac{B_1^2}{4A_1} \quad \text{and} \quad R_1 = \frac{2A_1}{B_1}. \tag{11.12}$$

When we substitute for A_1 and B_1 and use the expressions for the Bohr radius a_0 and Rydberg energy E_R, Eqs. (9.19) and (9.20), we find that Eq. (11.12) gives the correct energy and radius for the ground state of the hydrogen atom,

$$E_1 = -E_R \quad \text{and} \quad R_1 = a_0. \tag{11.13}$$

We shall now show that the model, with minor adjustments, can also describe the energy and size of the ground state of the helium atom. In this atom there are two electrons and a nucleus of charge $2e$. If both electrons are in the same single-particle state, the energy of a two-electron quantum state of size R is roughly given by

$$E = 2\frac{\hbar^2}{2m_e R^2} - 4\frac{e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 R_{ee}}, \tag{11.14}$$

son for the first 11 elements are shown in Fig 11.5. The solid circles give energies and radii for real atoms in which the Pauli principle has a governing role, and the open circles give the energies and radii for hypothetical atoms in which the Pauli principle plays no role.

We see that without the Pauli principle, the ionization energies steadily increase and the radii steadily decrease with atomic number Z. In particular, the periodicity of chemical properties of real atoms is replaced by a chemistry in which atoms steadily become less reactive than helium. A world without the Pauli exclusion principle would be very different. One thing is for certain: it would be a world with no chemists.

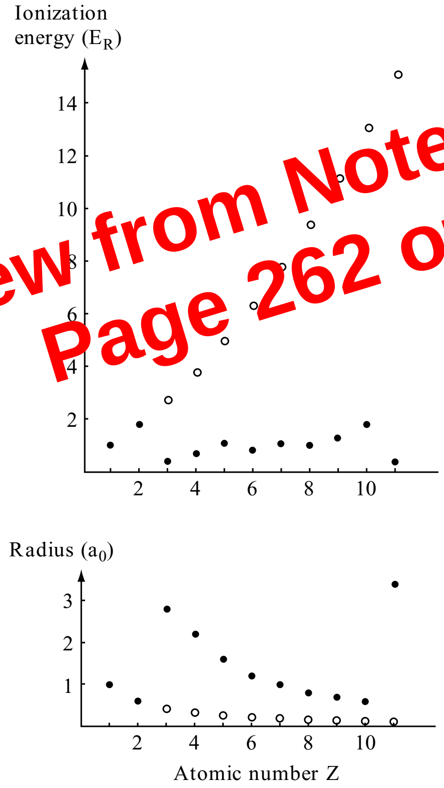

Fig. 11.5 The effect of the Pauli exclusion principle on the ionization energies and radii of the first 11 elements. The solid circles correspond to atoms in which the Pauli principle constrains the behaviour of the electrons and the hollow circles correspond to atoms in which the constraints of the Pauli principle are not imposed. The Pauli principle has no effect on the ground states of the first elements, hydrogen and helium. The Rydberg energy and the Bohr radius have been used as units for the ionization energies and radii.

is a fundamental length in a relativistic theory of the electron. Show that this length is $\alpha^2 a_0$ where a_0 is the Bohr radius and $\alpha = e^2/4\pi\epsilon_0\hbar c$. The constant α is called the fine structure constant and it is approximately equal to $1/137$.

5. The force between the electron and the proton, $e^2/4\pi\epsilon_0 r^2$, causes a centripetal acceleration equal to $m_e v^2/r$. The orbital angular momentum of the electron is $L = mvr$.

6. Make use of the fact that the magnitude of the momentum of a particle is at least as big as the uncertainty in its momentum and use the uncertainty principle Eq. (1.15).

7. Use the uncertainty principle to show that the uncertainty in the momentum of the quark, and hence the minimum value of its average momentum, is small compared with mc where m is the mass of the quark.

8. Evaluate the de Broglie wavelength of electrons with kinetic energy 200 eV and consider the condition for strong diffraction by a slit.

9. Show that the de Broglie wavelength of a 54 eV electron is $\lambda = 0.166$ nm. The condition for constructive interference of waves scattered by atoms on the surface is $D \sin\phi = n\lambda$. Show that this condition is satisfied when $D = 0.215$ nm, $\phi = 50$ degrees and $n = 1$.

10. Show that the wave due to a conduction electron in copper is strongly diffracted by the lattice of atoms. To do this show that the de Broglie wavelength of a 7 eV electron is 0.46 nm and that this is comparable with the distance between atoms in copper.

11. Show that the de Broglie wavelength of a neutron with thermal energy $\frac{3}{2}kT$ is comparable with the distance between atoms in a solid if $T = 300$ K.

12. Estimate the thermal energy of an oxygen molecule at $T = 273$ K and show that the de Broglie wavelength is much smaller than the typical distance between molecules in air.

CHAPTER 2

1. The phase and group velocities are given by

$$v_{phase} = \frac{\omega}{k} \quad \text{and} \quad v_{group} = \frac{d\omega}{dk}.$$

Verify that $v_{group} = \frac{3}{2} v_{phase}$.

2. Use

$$\int \cos k'(x - ct)\, dk' = \frac{\sin k'(x - ct)}{(x - ct)}$$

$$\langle V\rangle = \int_0^\infty N\,\mathrm{e}^{-\alpha r}\left(\frac{-e^2}{4\pi\epsilon_0 r}\right)N\,\mathrm{e}^{-\alpha r}4\pi r^2\ \mathrm{d}r$$

and

$$\langle T\rangle = \int_0^\infty N\,\mathrm{e}^{-\alpha r}\left(\frac{-\hbar^2}{2m_e r}\ \frac{\mathrm{d}^2}{\mathrm{d}r^2}rN\,\mathrm{e}^{-\alpha r}\right)4\pi r^2\ \mathrm{d}r.$$

(c) Find the minimum of $\langle E\rangle = \langle T\rangle + \langle V\rangle$ by setting $\mathrm{d}\langle E\rangle/\mathrm{d}a = 0$.

2. (a) The minimum of $V_e(r)$ is found using

$$\frac{\mathrm{d}V_e}{\mathrm{d}r} = \frac{L^2}{mr^3} - \frac{e^2}{4\pi\epsilon_0 r^2} = 0.$$

(b) The maximum and minimum distances r, which occur when $p_r = 0$, are given by

$$\frac{e^2}{8\pi\epsilon_0 a} = \frac{L^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

3. Use the integral given in problem 1 to evaluate

$$N^2\int_0^\infty r^{2l+2}\,\mathrm{e}^{-2r/(l+1)a_0}\ \mathrm{d}r.$$

(b) Find the maximum of $r^{2l+2}\,\mathrm{e}^{-2r/(l+1)a_0}$.

(c) Use the integral given in problem 1 to evaluate

$$\int_0^\infty u^*_{0,\,l}(r)ru_{0,\,l}(r)\ \mathrm{d}r \quad \text{and} \quad \int_0^\infty u^*_{0,\,l}(r)r^2u_{0,\,l}(r)\ \mathrm{d}r.$$

(e) For $l >> 1$, the orbital angular momentum L tends to $l\hbar$ and $r_{\text{most probable}}$ and $\langle r\rangle$ both tend to l^2a_0 or $L^2a_0/\hbar^2$.

4. (a) The eigenfunction is normalized if $N_1 = 1/\sqrt{\pi a_0^3}$.

(b) Show that

$$\int_0^\infty \psi_2^*(r)\psi_1(r)r^2\ \mathrm{d}r = 0$$

if $\lambda = -1/2a_0$.

8. Choose $\mathbf{k}$ to be along the z axis so that $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} = \mathrm{e}^{ikr\cos\theta}$ and write $\mathrm{d}^3\mathbf{r} = r^2\,\mathrm{d}r\,\mathrm{d}(\cos\theta)\,\mathrm{d}\phi$. Integrate from $\phi = 0$ to 2π, from $\cos\theta = -1$ to $+1$ and from $r = 0$ to ∞.

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PHYSICAL CONSTANTS AND CONVERSION FACTORS

Symbol	Description	Numerical Value
c	velocity of light in vacuum	299 792 458 m s^{-1}, exactly
μ_0	permeability of vacuum	$4\pi \times 10^{-7}$ N A^{-2}, exactly
ϵ_0	permittivity of vacuum where $c = 1/\sqrt{\epsilon_0\mu_0}$	8.854×10^{-12} C^2 N^{-1} m^{-2}
h	Planck constant	6.626×10^{-34} J s
$\hbar$	$h/2\pi$	1.055×10^{-34} J s
G	gravitational constant	6.674×10^{-11} m^3 kg^{-1} s^{-2}
e	elementary charge	1.602×10^{-19} C
eV	electronvolt	1.602×10^{-19} J
α	fine structure constant, $e^2/4\pi\epsilon_0\hbar c$	1/137.0
m_e	electron mass	9.109×10^{-31} kg
m_ec^2	electron rest-mass energy	0.511 MeV
μ_B	Bohr magneton, $e\hbar/2m_e$	9.274×10^{-24} J T^{-1}
E_R	Rydberg energy $\alpha^2 m_e c^2/2$	13.61 eV
a_0	Bohr radius $(1/\alpha)$ $(\hbar/m_ec)$	0.5292×10^{-10} m
Å	angstrom	10^{-10} m
m_p	proton mass	1.673×10^{-27}kg
m_pc^2	proton rest-mass energy	938.272 MeV
m_nc^2	neutron rest-mass energy	939.566 MeV
μ_N	nuclear magneton, $e\hbar/2m_p$	5.051×10^{-27} J T^{-1}
fm	femtometre or fermi	10^{-15} m
b	barn	10^{-28} m^2
u	atomic mass unit, $\frac{1}{12}m(^{12}\mathrm{C}$ atom)	1.661×10^{-27} kg
N_A	Avogadro constant, atoms in gram mol	6.022×10^{23} mol^{-1}
T_t	triple-point temperature	273.16 K
k	Boltzmann constant	1.381×10^{-23} J K^{-1}
R	molar gas constant, N_Ak	8.315 J mol^{-1} K^{-1}
σ	Stefan–Boltzmann constant, $(\pi^2/60)$ $(k^4/\hbar^3c^2)$	5.670×10^{-8} W m^{-2} K^{-4}