Class: B. Tech (Unit II)

I have taken all course materials for Unit II from Book Concept of Modern Physics by Arthur Besier, Shobhit Mahajan & S. Rai Choudhury (McGraw Hill Education).

Students can download this book form given web address;

Web Address : **https://b-ok.cc/book/2700591/864ac0**

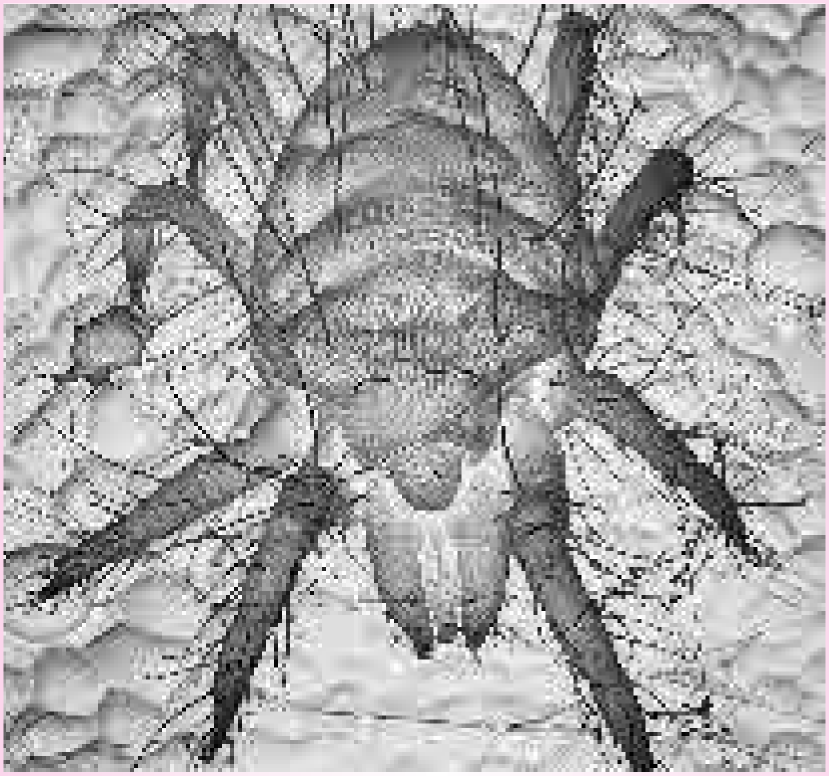
All topics of unit II (Quantum Mechanics) have been taken from **Chapter 3 & Chapter 5** from above said book (**https://b-ok.cc/book/2700591/864ac0**). I am sending pdf file of Chapter 3 & Chapter 5.

UNIT-1I: Quantum Mechanics (8 Hours)

Origin of the quantum Mechanics, Interpretation of Wave function, Normalization, Schrodinger time-independent & time-dependent equations, basic postulates of the quantum Mechanics, Probability Current Density, Expectation values, Operators, Hermitian operators, Communication relation between Position & Momentum operators; Applications of Schrödinger equation in Particle in a box, Single step barrier**,** Harmonic Oscillator, Problems.

CHAPTER 3

Wave Properties of Particles



In a scanning electron microscope, an electron beam that scans a specimen causes secondary electrons to be ejected in numbers that vary with the angle of the surface. A suitable data display suggests the three-dimensional form of the specimen. The high resolution of this image of a red spider mite on a leaf is a consequence of the wave nature of moving electrons.

Looking back, it may seem odd that two decades passed between the 1905 discovery of the particle properties of waves and the 1924 speculation that particles might show wave behavior. It is one thing, however, to suggest a revolutionary concept to explain otherwise mysterious data and quite another to suggest an equally revolutionary concept without a strong experimental mandate. The latter is just what Louis de Broglie did in 1924 when he proposed that moving objects have wave as well as particle characteristics. So different was the scientific climate at the time from that around the turn of the century that de Broglie's ideas soon received respectful attention, whereas the earlier quantum theory of light of Planck and Einstein had been largely ignored despite its striking empirical support. The existence of de Broglie waves was experimentally demonstrated by 1927, and the duality principle they represent provided the starting point for Schrödinger's successful development of quantum mechanics in the previous year.

3.1 DE BROGLIE WAVES

A moving body behaves in certain ways as though it has a wave nature

A photon of light of frequency ν has the momentum

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

since $\lambda\nu = c$. The wavelength of a photon is therefore specified by its momentum according to the relation

Photon wavelength

$$\lambda = \frac{h}{p} \tag{3.1}$$

De Broglie suggested that Eq. (3.1) is a completely general one that applies to material particles as well as to photons. The momentum of a particle of mass m and velocity v is $p = \gamma m v$, and its **de Broglie wavelength** is accordingly

De Broglie wavelength

$$\lambda = \frac{h}{\gamma m v} \tag{3.2}$$

Louis de Broglie (1892–1987), although coming from a French family long identified with diplomacy and the military and initially a student of history, eventually followed his older brother Maurice in a career in physics. His doctoral thesis in 1924 contained the proposal that moving bodies have wave properties that complement their particle properties: these "seemingly incompatible conceptions can each represent an aspect of the truth. . . . They may serve in turn to represent the facts without ever entering into direct conflict." Part of de Broglie's inspiration came from Bohr's theory of the hydrogen atom, in which the electron is supposed to follow only certain orbits around the nucleus. "This fact suggested to me the idea that electrons . . . could not be considered simply as particles but that periodicity must be assigned to them also." Two years later Erwin Schrödinger used the concept of de Broglie waves to develop a general theory that he and others applied to explain a wide variety of atomic phenomena. The existence of de Broglie waves was confirmed in diffraction experiments with electron beams in 1927, and in 1929 de Broglie received the Nobel Prize.

The greater the particle's momentum, the shorter its wavelength. In Eq. (3.2) γ is the relativistic factor

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$$

As in the case of em waves, the wave and particle aspects of moving bodies can never be observed at the same time. We therefore cannot ask which is the "correct" description. All that can be said is that in certain situations a moving body resembles a wave and in others it resembles a particle. Which set of properties is most conspicuous depends on how its de Broglie wavelength compares with its dimensions and the dimensions of whatever it interacts with.

Example 3.1

Find the de Broglie wavelengths of (*a*) a 46-g golf ball with a velocity of 30 m/s, and (*b*) an electron with a velocity of 10^7 m/s.

Solution

(*a*) Since $v \ll c$, we can let $\gamma = 1$. Hence

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(0.046\ \text{kg})(30\ \text{m/s})} = 4.8 \times 10^{-34}\ \text{m}$$

The wavelength of the golf ball is so small compared with its dimensions that we would not expect to find any wave aspects in its behavior.

(*b*) Again $v \ll c$, so with $m = 9.1 \times 10^{-31}$ kg, we have

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(9.1 \times 10^{-31}\ \text{kg})(10^7\ \text{m/s})} = 7.3 \times 10^{-11}\ \text{m}$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is 5.3×10^{-11} m. It is therefore not surprising that the wave character of moving electrons is the key to understanding atomic structure and behavior.

Example 3.2

Find the kinetic energy of a proton whose de Broglie wavelength is 1.000 fm = 1.000×10^{-15} m, which is roughly the proton diameter.

Solution

A relativistic calculation is needed unless pc for the proton is much smaller than the proton rest energy of $E_0 = 0.938$ GeV. To find out, we use Eq. (3.2) to determine pc:

$$pc = (\gamma m v)c = \frac{hc}{\lambda} = \frac{(4.136 \times 10^{-15}\ \text{eV}\cdot\text{s})(2.998 \times 10^8\ \text{m/s})}{1.000 \times 10^{-15}\ \text{m}} = 1.240 \times 10^9\ \text{eV}$$
$$= 1.2410\ \text{GeV}$$

Since $pc > E_0$ a relativistic calculation is required. From Eq. (1.24) the total energy of the proton is

$$E = \sqrt{E_0^2 + p^2c^2} = \sqrt{(0.938\ \text{GeV})^2 + (1.2340\ \text{GeV})^2} = 1.555\ \text{GeV}$$

The corresponding kinetic energy is

$$\text{KE} = E - E_0 = (1.555 - 0.938)\ \text{GeV} = 0.617\ \text{GeV} = 617\ \text{MeV}$$

De Broglie had no direct experimental evidence to support his conjecture. However, he was able to show that it accounted in a natural way for the energy quantization—the restriction to certain specific energy values—that Bohr had had to postulate in his 1913 model of the hydrogen atom. (This model is discussed in Chap. 4.) Within a few years Eq. (3.2) was verified by experiments involving the diffraction of electrons by crystals. Before we consider one of these experiments, let us look into the question of what kind of wave phenomenon is involved in the matter waves of de Broglie.

3.2 WAVES OF WHAT?

Waves of probability

In water waves, the quantity that varies periodically is the height of the water surface. In sound waves, it is pressure. In light waves, electric and magnetic fields vary. What is it that varies in the case of matter waves?

The quantity whose variations make up matter waves is called the **wave function**, symbol Ψ (the Greek letter psi). The value of the wave function associated with a moving body at the particular point x, y, z in space at the time t is related to the likelihood of finding the body there at the time.

Max Born (1882–1970) grew up in Breslau, then a German city but today part of Poland, and received a doctorate in applied mathematics at Göttingen in 1907. Soon afterward he decided to concentrate on physics, and was back in Göttingen in 1909 as a lecturer. There he worked on various aspects of the theory of crystal lattices, his "central interest" to which he often returned in later years. In 1915, at Planck's recommendation, Born became professor of physics in Berlin where, among his other activities, he played piano to Einstein's violin. After army service in World War I and a period at Frankfurt University, Born was again in Göttingen, now as professor of physics. There a remarkable center of theoretical physics developed under his leadership: Heisenberg and Pauli were among his assistants and Fermi, Dirac, Wigner, and Goeppert were among those who worked with him, just to name future Nobel Prize winners. In those days, Born wrote, "There was complete freedom of teaching and learning in German universities, with no class examinations, and no control of students. The University just offered lectures and the student had to decide for himself which he wished to attend."

Born was a pioneer in going from "the bright realm of classical physics into the still dark and unexplored underworld of the new quantum mechanics;" he was the first to use the latter term. From Born came the basic concept that the wave function Ψ of a particle is related to the probability of finding it. He began with an idea of Einstein, who "sought to make the duality of particles (light quanta or photons) and waves comprehensible by interpreting the square of the optical wave amplitude as probability density for the occurrence of photons. This idea could at once be extended to the Ψ-function: $|\Psi|^2$ must represent the probability density for electrons (or other particles). To assert this was easy; but how was it to be proved? For this purpose atomic scattering processes suggested themselves." Born's development of the quantum theory of atomic scattering (collisions of atoms with various particles) not only verified his "new way of thinking about the phenomena of nature" but also founded an important branch of theoretical physics.

Born left Germany in 1933 at the start of the Nazi period, like so many other scientists. He became a British subject and was associated with Cambridge and then Edinburg universities until he retired in 1953. Finding the Scottish climate harsh and wishing to contribute to the democratization of postwar Germany, Born spent the rest of his life in Bad Pyrmont, a town near Göttingen. His textbooks on modern physics and on optics were standard works on these subjects for many years.

The wave function Ψ itself, however, has no direct physical significance. There is a simple reason why Ψ cannot by interpreted in terms of an experiment. The probability that something be in a certain place at a given time must lie between 0 (the object is definitely not there) and 1 (the object is definitely there). An intermediate probability, say 0.2, means that there is a 20% chance of finding the object. But the amplitude of a wave can be negative as well as positive, and a negative probability, say -0.2, is meaningless. Hence Ψ by itself cannot be an observable quantity.

This objection does not apply to $|\Psi|^2$, the square of the absolute value of the wave function, which is known as **probability density:**

> The probability of experimentally finding the body described by the wave function Ψ at the point x, y, z, at the time t is proportional to the value of $|\Psi|^2$ there at t.

A large value of $|\Psi|^2$ means the strong possibility of the body's presence, while a small value of $|\Psi|^2$ means the slight possibility of its presence. As long as $|\Psi|^2$ is not actually 0 somewhere, however, there is a definite chance, however small, of detecting it there. This interpretation was first made by Max Born in 1926.

There is a big difference between the probability of an event and the event itself. Although we can speak of the wave function Ψ that describes a particle as being spread out in space, this does not mean that the particle itself is thus spread out. When an experiment is performed to detect electrons, for instance, a whole electron is either found at a certain time and place or it is not; there is no such thing as a 20 percent of an electron. However, it is entirely possible for there to be a 20 percent chance that the electron be found at that time and place, and it is this likelihood that is specified by $|\Psi|^2$.

W. L. Bragg, the pioneer in x-ray diffraction, gave this loose but vivid interpretation: "The dividing line between the wave and particle nature of matter and radiation is the moment 'now.' As this moment steadily advances through time it coagulates a wavy future into a particle past. . . . Everything in the future is a wave, everything in the past is a particle." If "the moment 'now' " is understood to be the time a measurement is performed, this is a reasonable way to think about the situation. (The philosopher Søren Kierkegaard may have been anticipating this aspect of modern physics when he wrote, "Life can only be understood backwards, but it must be lived forwards.")

Alternatively, if an experiment involves a great many identical objects all described by the same wave function Ψ, the *actual density* (number per unit volume) of objects at x, y, z at the time t is proportional to the corresponding value of $|\Psi|^2$. It is instructive to compare the connection between Ψ and the density of particles it describes with the connection discussed in Sec. 2.4 between the electric field E of an electromagnetic wave and the density N of photons associated with the wave.

While the wavelength of the de Broglie waves associated with a moving body is given by the simple formula $\lambda = h/\gamma m v$, to find their amplitude Ψ as a function of position and time is often difficult. How to calculate Ψ is discussed in Chap. 5 and the ideas developed there are applied to the structure of the atom in Chap. 6. Until then we can assume that we know as much about Ψ as each situation requires.

3.3 DESCRIBING A WAVE

A general formula for waves

How fast do de Broglie waves travel? Since we associate a de Broglie wave with a moving body, we expect that this wave has the same velocity as that of the body. Let us see if this is true.

If we call the de Broglie wave velocity v_p, we can apply the usual formula

$$v_p = \nu\lambda$$

to find v_p. The wavelength λ is simply the de Broglie wavelength $\lambda = h/\gamma m v$. To find the frequency, we equate the quantum expression $E = h\nu$ with the relativistic formula for total energy $E = \gamma mc^2$ to obtain

$$h\nu = \gamma mc^2$$

$$\nu = \frac{\gamma mc^2}{h}$$

The de Broglie wave velocity is therefore

De Broglie phase velocity

$$v_p = \nu\lambda = \left(\frac{\gamma mc^2}{h}\right)\left(\frac{h}{\gamma m v}\right) = \frac{c^2}{v} \tag{3.3}$$

Because the particle velocity v must be less than the velocity of light c, the de Broglie waves always travel faster than light! In order to understand this unexpected result, we must look into the distinction between **phase velocity** and **group velocity.** (Phase velocity is what we have been calling wave velocity.)

Let us begin by reviewing how waves are described mathematically. For simplicity we consider a string stretched along the x axis whose vibrations are in the y direction, as in Fig. 3.1, and are simple harmonic in character. If we choose $t = 0$ when the displacement y of the string at $x = 0$ is a maximum, its displacement at any future time t at the same place is given by the formula

$$y = A \cos 2\pi\nu t \tag{3.4}$$

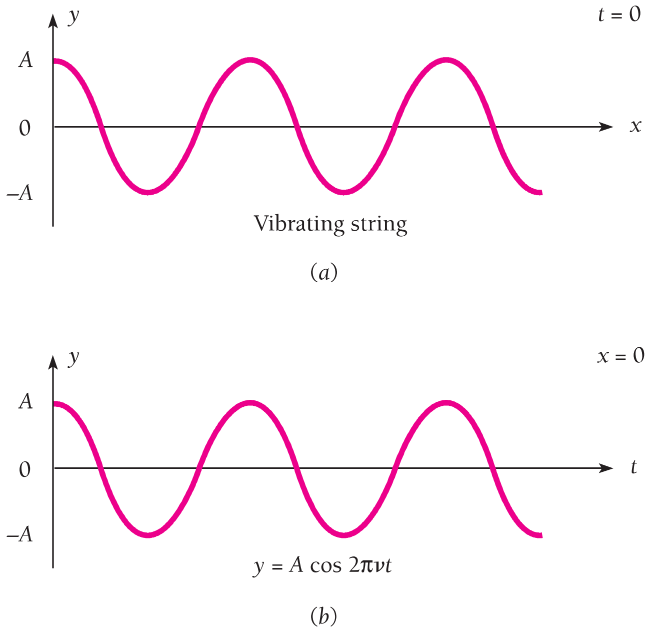


Figure 3.1 (*a*) The appearance of a wave in a stretched string at a certain time. (*b*) How the displacement of a point on the string varies with time.

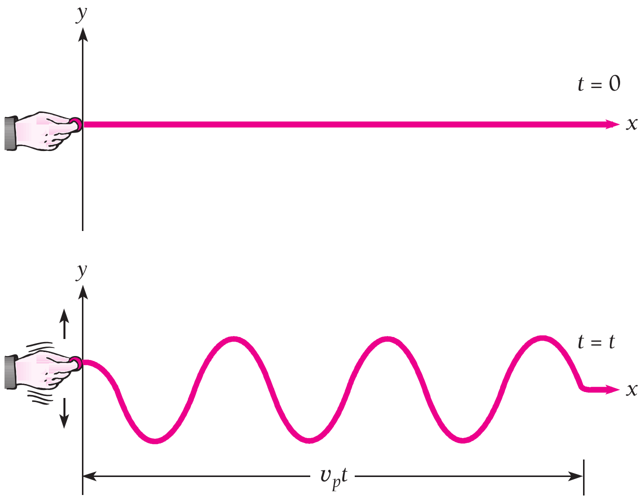


Figure 3.2 Wave propagation.

where A is the amplitude of the vibrations (that is, their maximum displacement on either side of the x axis) and ν their frequency.

Equation (3.4) tells us what the displacement of a single point on the string is as a function of time t. A complete description of wave motion in a stretched string, however, should tell us what y is at *any* point on the string at *any* time. What we want is a formula giving y as a function of both x and t.

To obtain such a formula, let us imagine that we shake the string at $x = 0$ when $t = 0$, so that a wave starts to travel down the string in the $+x$ direction (Fig. 3.2). This wave has some speed v_p that depends on the properties of the string. The wave travels the distance $x = v_p t$ in the time t, so the time interval between the formation of the wave at $x = 0$ and its arrival at the point x is x/v_p. Hence the displacement y of the string at x at any time t is exactly the same as the value of y at $x = 0$ *at the earlier time* $t - x/v_p$. By simply replacing t in Eq. (3.4) with $t - x/v_p$, then, we have the desired formula giving y in terms of both x and t:

Wave formula
$$y = A \cos 2\pi\nu\left(t - \frac{x}{v_p}\right) \tag{3.5}$$

As a check, we note that Eq. (3.5) reduces to Eq. (3.4) at $x = 0$.

Equation (3.5) may be rewritten

$$y = A \cos 2\pi\left(\nu t - \frac{\nu x}{v_p}\right)$$

Since the wave speed v_p is given by $v_p = \nu\lambda$ we have

Wave formula
$$y = A \cos 2\pi\left(\nu t - \frac{x}{\lambda}\right) \tag{3.6}$$

Equation (3.6) is often more convenient to use than Eq. (3.5).

Perhaps the most widely used description of a wave, however, is still another form of Eq. (3.5). The quantities **angular frequency** ω and **wave number** k are defined by the formulas

Angular frequency $$\omega = 2\pi\nu \tag{3.7}$$

Wave number $$k = \frac{2\pi}{\lambda} = \frac{\omega}{v_p} \tag{3.8}$$

The unit of ω is the radian per second and that of k is the radian per meter. Angular frequency gets its name from uniform circular motion, where a particle that moves around a circle ν times per second sweeps out $2\pi\nu$ rad/s. The wave number is equal to the number of radians corresponding to a wave train 1 m long, since there are 2π rad in one complete wave.

In terms of ω and k, Eq. (3.5) becomes

Wave formula $$y = A \cos (\omega t - kx) \tag{3.9}$$

In three dimensions k becomes a vector $\mathbf{k}$ normal to the wave fronts and x is replaced by the radius vector $\mathbf{r}$. The scalar product $\mathbf{k} \cdot \mathbf{r}$ is then used instead of kx in Eq. (3.9).

3.4 PHASE AND GROUP VELOCITIES

A group of waves need not have the same velocity as the waves themselves

The amplitude of the de Broglie waves that correspond to a moving body reflects the probability that it will be found at a particular place at a particular time. It is clear that de Broglie waves cannot be represented simply by a formula resembling Eq. (3.9), which describes an indefinite series of waves all with the same amplitude A. Instead, we expect the wave representation of a moving body to correspond to a **wave packet,** or **wave group,** like that shown in Fig. 3.3, whose waves have amplitudes upon which the likelihood of detecting the body depends.

A familiar example of how wave groups come into being is the case of **beats.** When two sound waves of the same amplitude but of slightly different frequencies are produced simultaneously, the sound we hear has a frequency equal to the average of the two original frequencies and its amplitude rises and falls periodically. The amplitude fluctuations occur as many times per second as the difference between the two original frequencies. If the original sounds have frequencies of, say, 440 and 442 Hz, we will hear a fluctuating sound of frequency 441 Hz with two loudness peaks, called beats, per second. The production of beats is illustrated in Fig. 3.4.

A way to mathematically describe a wave group, then, is in terms of a superposition of individual waves of different wavelengths whose interference with one another results in the variation in amplitude that defines the group shape. If the velocities of the waves are the same, the velocity with which the wave group travels is the common phase velocity. However, if the phase velocity varies with wavelength, the different individual waves do not proceed together. This situation is called **dispersion.** As a result the wave group has a velocity different from the phase velocities of the waves that make it up. This is the case with de Broglie waves.

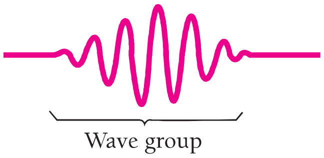


Figure 3.3 A wave group.

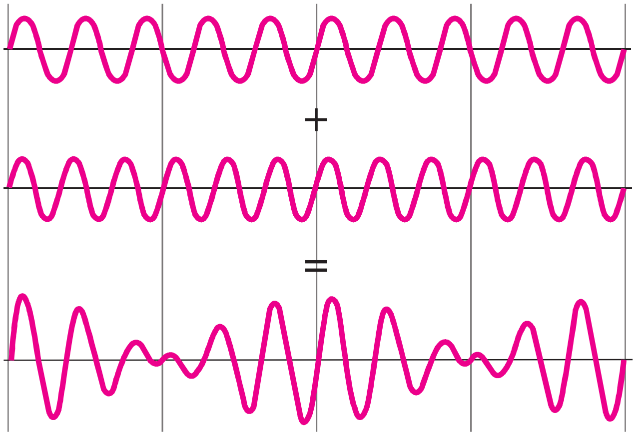


Figure 3.4 Beats are produced by the superposition of two waves with different frequencies.

It is not hard to find the velocity v_g with which a wave group travels. Let us suppose that the wave group arises from the combination of two waves that have the same amplitude A but differ by an amount $\Delta\omega$ in angular frequency and an amount Δk in wave number. We may represent the original waves by the formulas

$$y_1 = A \cos (\omega t - kx)$$

$$y_2 = A \cos [(\omega + \Delta\omega)t - (k + \Delta k)x]$$

The resultant displacement y at any time t and any position x is the sum of y_1 and y_2. With the help of the identity

$$\cos \alpha + \cos \beta = 2 \cos \tfrac{1}{2}(\alpha + \beta) \cos \tfrac{1}{2}(\alpha - \beta)$$

and the relation

$$\cos(-\theta) = \cos \theta$$

we find that

$$\begin{aligned} y &= y_1 + y_2 \\ &= 2A \cos \tfrac{1}{2}[(2\omega + \Delta\omega)t - (2k + \Delta k)x] \cos \tfrac{1}{2}(\Delta\omega\, t - \Delta k\, x) \end{aligned}$$

Since $\Delta\omega$ and Δk are small compared with ω and k respectively,

$$2\omega + \Delta\omega \approx 2\omega$$

$$2k + \Delta k \approx 2k$$

and so

Beats

$$y = 2A \cos (\omega t - kx) \cos \left(\frac{\Delta\omega}{2} t - \frac{\Delta k}{2} x\right) \tag{3.10}$$

Equation (3.10) represents a wave of angular frequency ω and wave number k that has superimposed upon it a modulation of angular frequency $\frac{1}{2}\Delta\omega$ and of wave number $\frac{1}{2}\Delta k$.

The effect of the modulation is to produce successive wave groups, as in Fig. 3.4. The phase velocity v_p is

Phase velocity

$$v_p = \frac{\omega}{k} \tag{3.11}$$

and the velocity v_g of the wave groups is

Group velocity

$$v_g = \frac{\Delta\omega}{\Delta k} \tag{3.12}$$

When ω and k have continuous spreads instead of the two values in the preceding discussion, the group velocity is instead given by

Group velocity

$$v_g = \frac{d\omega}{dk} \tag{3.13}$$

Depending on how phase velocity varies with wave number in a particular situation, the group velocity may be less or greater than the phase velocities of its member waves. If the phase velocity is the same for all wavelengths, as is true for light waves in empty space, the group and phase velocities are the same.

The angular frequency and wave number of the de Broglie waves associated with a body of mass m moving with the velocity v are

$$\omega = 2\pi\nu = \frac{2\pi\gamma mc^2}{h}$$

Angular frequency of de Broglie waves

$$= \frac{2\pi mc^2}{h\sqrt{1 - v^2/c^2}} \tag{3.14}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\gamma mv}{h}$$

Wave number of de Broglie waves

$$= \frac{2\pi mv}{h\sqrt{1 - v^2/c^2}} \tag{3.15}$$

Both ω and k are functions of the body's velocity v.

The group velocity v_g of the de Broglie waves associated with the body is

$$v_g = \frac{d\omega}{dk} = \frac{d\omega/dv}{dk/dv}$$

Now

$$\frac{d\omega}{dv} = \frac{2\pi mv}{h(1 - v^2/c^2)^{3/2}}$$

$$\frac{dk}{dv} = \frac{2\pi m}{h(1 - v^2/c^2)^{3/2}}$$

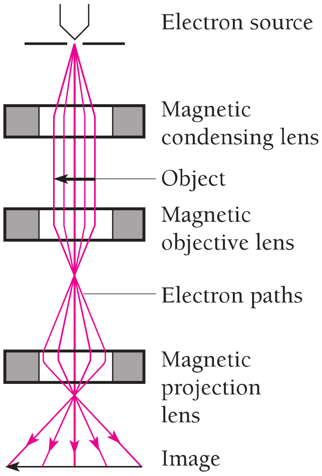


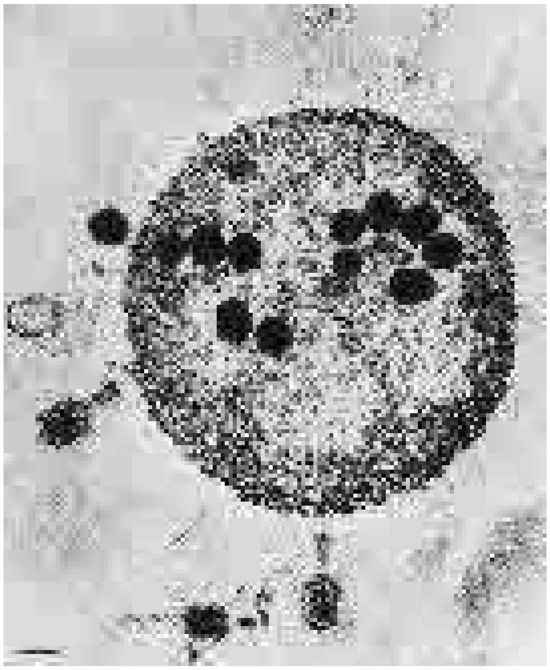
Figure 3.5 Because the wavelengths of the fast electrons in an electron microscope are shorter than those of the light waves in an optical microscope, the electron microscope can produce sharp images at higher magnifications. The electron beam in an electron microscope is focused by magnetic fields.

Electron Microscopes

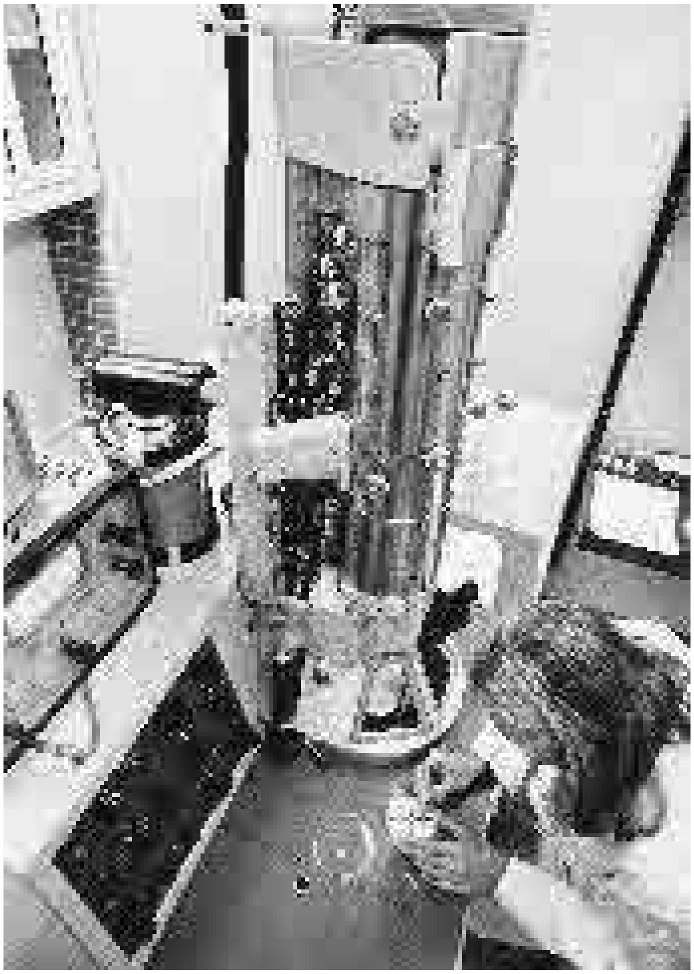
The wave nature of moving electrons is the basis of the electron microscope, the first of which was built in 1932. The resolving power of any optical instrument, which is limited by diffraction, is proportional to the wavelength of whatever is used to illuminate the specimen. In the case of a good microscope that uses visible light, the maximum useful magnification is about 500×; higher magnifications give larger images but do not reveal any more detail. Fast electrons, however, have wavelengths very much shorter than those of visible light and are easily controlled by electric and magnetic fields because of their charge. X-rays also have short wavelengths, but it is not (yet?) possible to focus them adequately.

In an electron microscope, current-carrying coils produce magnetic fields that act as lenses to focus an electron beam on a specimen and then produce an enlarged image on a fluorescent screen or photographic plate (Fig. 3.5). To prevent the beam from being scattered and thereby blurring the image, a thin specimen is used and the entire system is evacuated.

The technology of magnetic "lenses" does not permit the full theoretical resolution of electron waves to be realized in practice. For instance, 100-keV electrons have wavelengths of 0.0037 nm, but the actual resolution they can provide in an electron microscope may be only about 0.1 nm. However, this is still a great improvement on the ~200-nm resolution of an optical microscope, and magnifications of over 1,000,000× have been achieved with electron microscopes.



Electron micrograph showing bacteriophage viruses in an *Escherichia coli* bacterium. The bacterium is approximately 1 μm across.



An electron microscope.

and so the group velocity turns out to be

De Broglie group velocity

$$v_g = v \tag{3.16}$$

The de Broglie wave group associated with a moving body travels with the same velocity as the body.

The phase velocity v_p of de Broglie waves is, as we found earlier,

De Broglie phase velocity

$$v_p = \frac{\omega}{k} = \frac{c^2}{v} \tag{3.3}$$

This exceeds both the velocity of the body v and the velocity of light c, since $v < c$. However, v_p has no physical significance because the motion of the wave group, not the motion of the individual waves that make up the group, corresponds to the motion of the body, and $v_g < c$ as it should be. The fact that $v_p > c$ for de Broglie waves therefore does not violate special relativity.

Example 3.3

An electron has a de Broglie wavelength of 2.00 pm = 2.00×10^{-12} m. Find its kinetic energy and the phase and group velocities of its de Broglie waves.

Solution

(*a*) The first step is to calculate pc for the electron, which is

$$pc = \frac{hc}{\lambda} = \frac{(4.136 \times 10^{-15}\ \text{eV} \cdot \text{s})(3.00 \times 10^{8}\ \text{m/s})}{2.00 \times 10^{-12}\ \text{m}} = 6.20 \times 10^{5}\ \text{eV}$$
$$= 620\ \text{keV}$$

The rest energy of the electron is $E_0 = 511$ keV, so

$$\text{KE} = E - E_0 = \sqrt{E_0^2 + (pc)^2} - E_0 = \sqrt{(511\ \text{keV})^2 + (620\ \text{keV})^2} - 511\ \text{keV}$$
$$= 803\ \text{keV} - 511\ \text{keV} = 292\ \text{keV}$$

(*b*) The electron velocity can be found from

$$E = \frac{E_0}{\sqrt{1 - v^2/c^2}}$$

to be

$$v = c\sqrt{1 - \frac{E_0^2}{E^2}} = c\sqrt{1 - \left(\frac{511\ \text{keV}}{803\ \text{keV}}\right)^2} = 0.771c$$

Hence the phase and group velocities are respectively

$$v_p = \frac{c^2}{v} = \frac{c^2}{0.771c} = 1.30c$$
$$v_g = v = 0.771c$$

3.5 PARTICLE DIFFRACTION

An experiment that confirms the existence of de Broglie waves

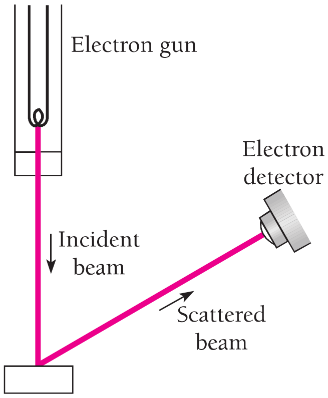


Figure 3.6 The Davisson-Germer experiment.

A wave effect with no analog in the behavior of Newtonian particles is diffraction. In 1927 Clinton Davisson and Lester Germer in the United States and G. P. Thomson in England independently confirmed de Broglie's hypothesis by demonstrating that electron beams are diffracted when they are scattered by the regular atomic arrays of crystals. (All three received Nobel Prizes for their work. J. J. Thomson, G. P.'s father, had earlier won a Nobel Prize for verifying the particle nature of the electron: the wave-particle duality seems to have been the family business.) We shall look at the experiment of Davisson and Germer because its interpretation is more direct.

Davisson and Germer were studying the scattering of electrons from a solid using an apparatus like that sketched in Fig. 3.6. The energy of the electrons in the primary beam, the angle at which they reach the target, and the position of the detector could all be varied. Classical physics predicts that the scattered electrons will emerge in all directions with only a moderate dependence of their intensity on scattering angle and even less on the energy of the primary electrons. Using a block of nickel as the target, Davisson and Germer verified these predictions.

In the midst of their work an accident occurred that allowed air to enter their apparatus and oxidize the metal surface. To reduce the oxide to pure nickel, the target was baked in a hot oven. After this treatment, the target was returned to the apparatus and the measurements resumed.

Now the results were very different. Instead of a continuous variation of scattered electron intensity with angle, distinct maxima and minima were observed whose positions depended upon the electron energy! Typical polar graphs of electron intensity after the accident are shown in Fig. 3.7. The method of plotting is such that the intensity at any angle is proportional to the distance of the curve at that angle from the point of scattering. If the intensity were the same at all scattering angles, the curves would be circles centered on the point of scattering.

Two questions come to mind immediately: What is the reason for this new effect? Why did it not appear until after the nickel target was baked?

De Broglie's hypothesis suggested that electron waves were being diffracted by the target, much as x-rays are diffracted by planes of atoms in a crystal. This idea received

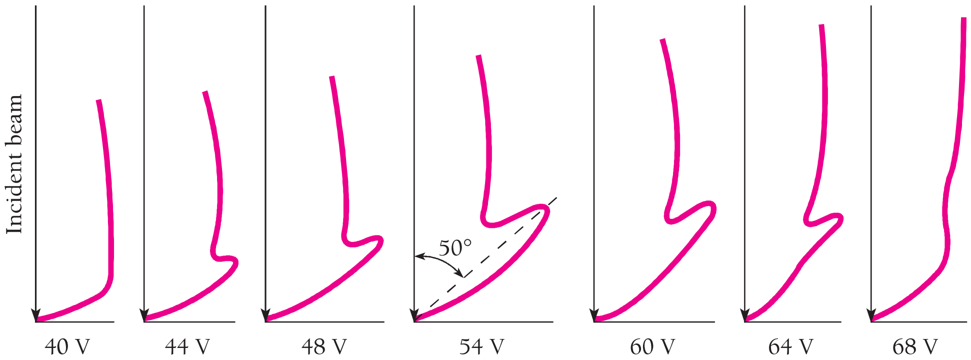


Figure 3.7 Results of the Davisson-Germer experiment, showing how the number of scattered electrons varied with the angle between the incoming beam and the crystal surface. The Bragg planes of atoms in the crystal were not parallel to the crystal surface, so the angles of incidence and scattering relative to one family of these planes were both 65° (see Fig. 3.8).

support when it was realized that heating a block of nickel at high temperature causes the many small individual crystals of which it is normally composed to form into a single large crystal, all of whose atoms are arranged in a regular lattice.

Let us see whether we can verify that de Broglie waves are responsible for the findings of Davisson and Germer. In a particular case, a beam of 54-eV electrons was directed perpendicularly at the nickel target and a sharp maximum in the electron distribution occurred at an angle of 50° with the original beam. The angles of incidence and scattering relative to the family of Bragg planes shown in Fig. 3.8 are both 65°. The spacing of the planes in this family, which can be measured by x-ray diffraction, is 0.091 nm. The Bragg equation for maxima in the diffraction pattern is

$$n\lambda = 2d \sin \theta \tag{2.13}$$

Here $d = 0.091$ nm and $\theta = 65°$. For $n = 1$ the de Broglie wavelength λ of the diffracted electrons is

$$\lambda = 2d \sin \theta = (2)(0.091 \text{ nm})(\sin 65°) = 0.165 \text{ nm}$$

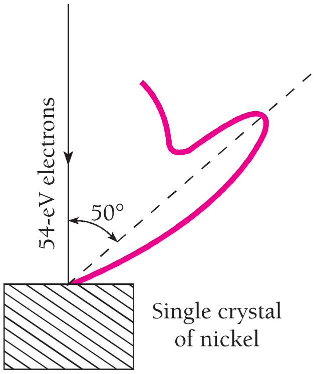


Figure 3.8 The diffraction of the de Broglie waves by the target is responsible for the results of Davisson and Germer.

Now we use de Broglie's formula $\lambda = h/\gamma m v$ to find the expected wavelength of the electrons. The electron kinetic energy of 54 eV is small compared with its rest energy mc^2 of 0.51 MeV, so we can let $\gamma = 1$. Since

$$\text{KE} = \tfrac{1}{2}mv^2$$

the electron momentum mv is

$$\begin{aligned} mv &= \sqrt{2m\text{KE}} \\ &= \sqrt{(2)(9.1 \times 10^{-31} \text{ kg})(54 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} \\ &= 4.0 \times 10^{-24} \text{ kg} \cdot \text{m/s} \end{aligned}$$

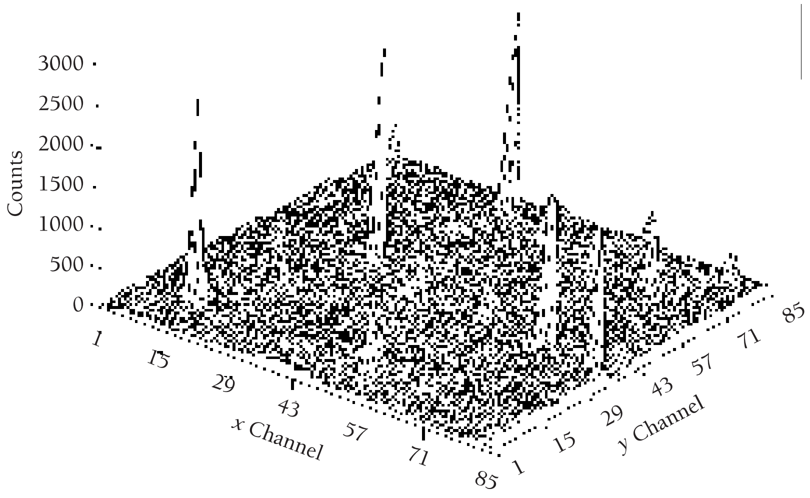
The electron wavelength is therefore

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{4.0 \times 10^{-24} \text{ kg} \cdot \text{m/s}} = 1.66 \times 10^{-10} \text{ m} = 0.166 \text{ nm}$$

which agrees well with the observed wavelength of 0.165 nm. The Davisson-Germer experiment thus directly verifies de Broglie's hypothesis of the wave nature of moving bodies.

Analyzing the Davisson-Germer experiment is actually less straightforward than indicated above because the energy of an electron increases when it enters a crystal by an amount equal to the work function of the surface. Hence the electron speeds in the experiment were greater inside the crystal and the de Broglie wavelengths there shorter than the values outside. Another complication arises from interference between waves diffracted by different families of Bragg planes, which restricts the occurrence of maxima to certain combinations of electron energy and angle of incidence rather than merely to any combination that obeys the Bragg equation.

Electrons are not the only bodies whose wave behavior can be demonstrated. The diffraction of neutrons and of whole atoms when scattered by suitable crystals has been observed, and in fact neutron diffraction, like x-ray and electron diffraction, has been used for investigating crystal structures.



Neutron diffraction by a quartz crystal. The peaks represent directions in which constructive interference occurred. (*Courtesy Frank J. Rotella and Arthur J. Schultz, Argonne National Laboratory*)

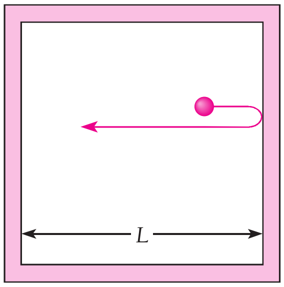


Figure 3.9 A particle confined to a box of width L. The particle is assumed to move back and forth along a straight line between the walls of the box.

3.6 PARTICLE IN A BOX

Why the energy of a trapped particle is quantized

The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely.

The simplest case is that of a particle that bounces back and forth between the walls of a box, as in Fig. 3.9. We shall assume that the walls of the box are infinitely hard, so the particle does not lose energy each time it strikes a wall, and that its velocity is sufficiently small so that we can ignore relativistic considerations. Simple as it is, this model situation requires fairly elaborate mathematics in order to be properly analyzed, as we shall learn in Chap. 5. However, even a relatively crude treatment can reveal the essential results.

From a wave point of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls. In both cases the wave variable (transverse displacement for the string, wave function Ψ for the moving particle) must be 0 at the walls, since the waves stop there. The possible de Broglie wavelengths of the particle in the box therefore are determined by the width L of the box, as in Fig. 3.10. The longest wavelength is specified by $\lambda = 2L$, the next by $\lambda = L$, then $\lambda = 2L/3$, and so forth. The general formula for the permitted wavelengths is

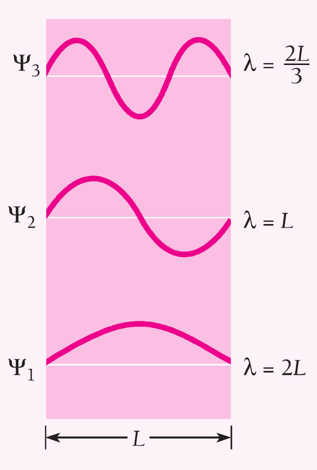


Figure 3.10 Wave functions of a particle trapped in a box L wide.

De Broglie wavelengths of trapped particle

$$\lambda_n = \frac{2L}{n} \qquad n = 1, 2, 3, \ldots \tag{3.17}$$

Because $mv = h/\lambda$, the restrictions on de Broglie wavelength λ imposed by the width of the box are equivalent to limits on the momentum of the particle and, in turn, to limits on its kinetic energy. The kinetic energy of a particle of momentum mv is

$$\mathrm{KE} = \tfrac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{h^2}{2m\lambda^2}$$

The permitted wavelengths are $\lambda_n = 2L/n$, and so, because the particle has no potential energy in this model, the only energies it can have are

Particle in a box $$E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots \tag{3.18}$$

Each permitted energy is called an **energy level,** and the integer n that specifies an energy level E_n is called its **quantum number.**

We can draw three general conclusions from Eq. (3.18). These conclusions apply to *any* particle confined to a certain region of space (even if the region does not have a well-defined boundary), for instance an atomic electron held captive by the attraction of the positively charged nucleus.

1 A trapped particle cannot have an arbitrary energy, as a free particle can. The fact of its confinement leads to restrictions on its wave function that allow the particle to have only certain specific energies and no others. Exactly what these energies are depends on the mass of the particle and on the details of how it is trapped.

2 A trapped particle cannot have zero energy. Since the de Broglie wavelength of the particle is $\lambda = h/mv$, a speed of $v = 0$ means an infinite wavelength. But there is no way to reconcile an infinite wavelength with a trapped particle, so such a particle must have at least some kinetic energy. The exclusion of $E = 0$ for a trapped particle, like the limitation of E to a set of discrete values, is a result with no counterpart in classical physics, where all non-negative energies, including zero, are allowed.

3 Because Planck's constant is so small—only 6.63×10^{-34} J · s—quantization of energy is conspicuous only when m and L are also small. This is why we are not aware of energy quantization in our own experience. Two examples will make this clear.

Example 3.4

An electron is in a box 0.10 nm across, which is the order of magnitude of atomic dimensions. Find its permitted energies.

Solution

Here $m = 9.1 \times 10^{-31}$ kg and $L = 0.10$ nm $= 1.0 \times 10^{-10}$ m, so that the permitted electron energies are

$$E_n = \frac{(n^2)(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{(8)(9.1 \times 10^{-31}\ \text{kg})(1.0 \times 10^{-10}\ \text{m})^2} = 6.0 \times 10^{-18} n^2\ \text{J}$$
$$= 38n^2\ \text{eV}$$

The minimum energy the electron can have is 38 eV, corresponding to $n = 1$. The sequence of energy levels continues with $E_2 = 152$ eV, $E_3 = 342$ eV, $E_4 = 608$ eV, and so on (Fig. 3.11). If such a box existed, the quantization of a trapped electron's energy would be a prominent feature of the system. (And indeed energy quantization is prominent in the case of an atomic electron.)

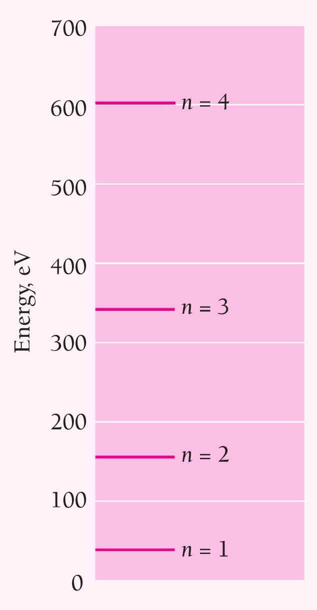


Figure 3.11 Energy levels of an electron confined to a box 0.1 nm wide.

Example 3.5

A 10-g marble is in a box 10 cm across. Find its permitted energies.

Solution

With $m = 10$ g $= 1.0 \times 10^{-2}$ kg and $L = 10$ cm $= 1.0 \times 10^{-1}$ m,

$$E_n = \frac{(n^2)(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{(8)(1.0 \times 10^{-2}\ \text{kg})(1.0 \times 10^{-1}\ \text{m})^2}$$
$$= 5.5 \times 10^{-64} n^2\ \text{J}$$

The minimum energy the marble can have is 5.5×10^{-64} J, corresponding to $n = 1$. A marble with this kinetic energy has a speed of only 3.3×10^{-31} m/s and therefore cannot be experimentally distinguished from a stationary marble. A reasonable speed a marble might have is, say, $\frac{1}{3}$ m/s—which corresponds to the energy level of quantum number $n = 10^{30}$! The permissible energy levels are so very close together, then, that there is no way to determine whether the marble can take on only those energies predicted by Eq. (3.18) or any energy whatever. Hence in the domain of everyday experience, quantum effects are imperceptible, which accounts for the success of Newtonian mechanics in this domain.

3.7 UNCERTAINTY PRINCIPLE 1

We cannot know the future because we cannot know the present

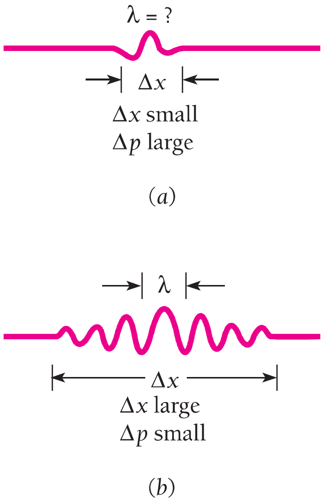


Figure 3.12 (*a*) A narrow de Broglie wave group. The position of the particle can be precisely determined, but the wavelength (and hence the particle's momentum) cannot be established because there are not enough waves to measure accurately. (*b*) A wide wave group. Now the wavelength can be precisely determined but not the position of the particle.

To regard a moving particle as a wave group implies that there are fundamental limits to the accuracy with which we can measure such "particle" properties as position and momentum.

To make clear what is involved, let us look at the wave group of Fig. 3.3. The particle that corresponds to this wave group may be located anywhere within the group at a given time. Of course, the probability density $|\Psi|^2$ is a maximum in the middle of the group, so it is most likely to be found there. Nevertheless, we may still find the particle anywhere that $|\Psi|^2$ is not actually 0.

The narrower its wave group, the more precisely a particle's position can be specified (Fig. 3.12*a*). However, the wavelength of the waves in a narrow packet is not well defined; there are not enough waves to measure λ accurately. This means that since $\lambda = h/\gamma m v$, the particle's momentum $\gamma m v$ is not a precise quantity. If we make a series of momentum measurements, we will find a broad range of values.

On the other hand, a wide wave group, such as that in Fig. 3.12*b*, has a clearly defined wavelength. The momentum that corresponds to this wavelength is therefore a precise quantity, and a series of measurements will give a narrow range of values. But where is the particle located? The width of the group is now too great for us to be able to say exactly where the particle is at a given time.

Thus we have the **uncertainty principle:**

> It is impossible to know both the exact position and exact momentum of an object at the same time.

This principle, which was discovered by Werner Heisenberg in 1927, is one of the most significant of physical laws.

A formal analysis supports the above conclusion and enables us to put it on a quantitative basis. The simplest example of the formation of wave groups is that given in Sec. 3.4, where two wave trains slightly different in angular frequency ω and wave number k were superposed to yield the series of groups shown in Fig. 3.4. A moving body corresponds to a single wave group, not a series of them, but a single wave group can also be thought of in terms of the superposition of trains of harmonic waves. However, an infinite number of wave trains with different frequencies, wave numbers, and amplitudes is required for an isolated group of arbitrary shape, as in Fig. 3.13.

At a certain time t, the wave group $\Psi(x)$ can be represented by the **Fourier integral**

$$\Psi(x) = \int_0^\infty g(k) \cos kx \, dk \tag{3.19}$$

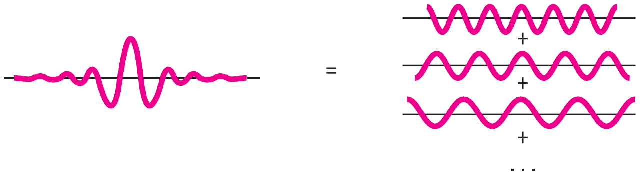


Figure 3.13 An isolated wave group is the result of superposing an infinite number of waves with different wavelengths. The narrower the wave group, the greater the range of wavelengths involved. A narrow de Broglie wave group thus means a well-defined position (Δx smaller) but a poorly defined wavelength and a large uncertainty Δp in the momentum of the particle the group represents. A wide wave group means a more precise momentum but a less precise position.

where the function $g(k)$ describes how the amplitudes of the waves that contribute to $\Psi(x)$ vary with wave number k. This function is called the **Fourier transform** of $\Psi(x)$, and it specifies the wave group just as completely as $\Psi(x)$ does. Figure 3.14 contains graphs of the Fourier transforms of a pulse and of a wave group. For comparison, the Fourier transform of an infinite train of harmonic waves is also included. There is only a single wave number in this case, of course.

Strictly speaking, the wave numbers needed to represent a wave group extend from $k = 0$ to $k = \infty$, but for a group whose length Δx is finite, the waves whose amplitudes $g(k)$ are appreciable have wave numbers that lie within a finite interval Δk. As Fig. 3.14 indicates, the narrower the group, the broader the range of wave numbers needed to describe it, and vice versa.

The relationship between the distance Δx and the wave-number spread Δk depends upon the shape of the wave group and upon how Δx and Δk are defined. The minimum value of the product $\Delta x\ \Delta k$ occurs when the envelope of the group has the familiar bell shape of a Gaussian function. In this case the Fourier transform happens to be a Gaussian function also. If Δx and Δk are taken as the standard deviations of the respective functions $\Psi(x)$ and $g(k)$, then this minimum value is $\Delta x\ \Delta k = \frac{1}{2}$. Because wave groups in general do not have Gaussian forms, it is more realistic to express the relationship between Δx and Δk as

$$\Delta x\ \Delta k \geq \tfrac{1}{2} \tag{3.20}$$

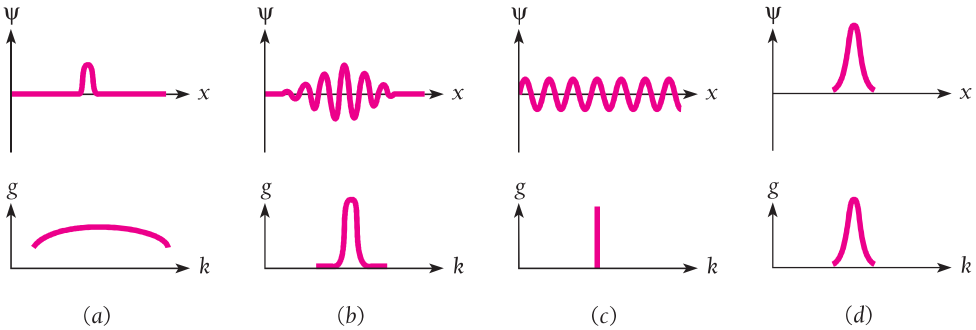


Figure 3.14 The wave functions and Fourier transforms for (a) a pulse, (b) a wave group, (c) a wave train, and (d) a Gaussian distribution. A brief disturbance needs a broader range of frequencies to describe it than a disturbance of greater duration. The Fourier transform of a Gaussian function is also a Gaussian function.

Gaussian Function

When a set of measurements is made of some quantity x in which the experimental errors are random, the result is often a **Gaussian distribution** whose form is the bell-shaped curve shown in Fig. 3.15. The **standard deviation** σ of the measurements is a measure of the spread of x values about the mean of x_0, where σ equals the square root of the average of the squared deviations from x_0. If N measurements were made,

Standard deviation

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_1 - x_0)^2}$$

The width of a Gaussian curve at half its maximum value is 2.35σ.

The ***Gaussian function*** $f(x)$ that describes the above curve is given by

Gaussian function

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-(x-x_0)^2/2\sigma^2}$$

where $f(x)$ is the probability that the value x be found in a particular measurement. Gaussian functions occur elsewhere in physics and mathematics as well. (Gabriel Lippmann had this to say about the Gaussian function: "Experimentalists think that it is a mathematical theorem while mathematicians believe it to be an experimental fact.")

The probability that a measurement lie inside a certain range of x values, say between x_1 and x_2, is given by the area of the $f(x)$ curve between these limits. This area is the integral

$$P_{x_1x_2} = \int_{x_1}^{x_2} f(x)\,dx$$

An interesting questions is what fraction of a series of measurements has values within a standard deviation of the mean value x_0. In this case $x_1 = x_0 - \sigma$ and $x_2 = x_0 + \sigma$, and

$$P_{x_0\pm\sigma} = \int_{x_0-\sigma}^{x_0+\sigma} f(x)\,dx = 0.683$$

Hence 68.3 percent of the measurements fall in this interval, which is shaded in Fig. 3.15. A similar calculation shows that 95.4 percent of the measurements fall within two standard deviations of the mean value.

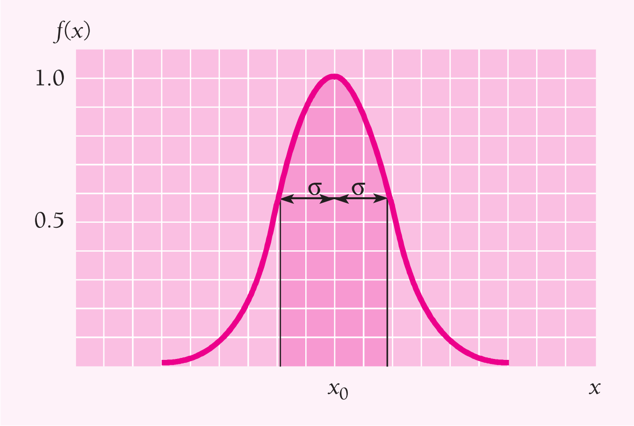


Figure 3.15 A Gaussian distribution. The probability of finding a value of x is given by the Gaussian function $f(x)$. The mean value of x is x_0, and the total width of the curve at half its maximum value is 2.35σ, where σ is the standard deviation of the distribution. The total probability of finding a value of x within a standard deviation of x_0 is equal to the shaded area and is 68.3 percent.

The de Broglie wavelength of a particle of momentum p is $\lambda = h/p$ and the corresponding wave number is

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$$

In terms of wave number the particle's momentum is therefore

$$p = \frac{hk}{2\pi}$$

Hence an uncertainty Δk in the wave number of the de Broglie waves associated with the particle results in an uncertainty Δp in the particle's momentum according to the formula

$$\Delta p = \frac{h\,\Delta k}{2\pi}$$

Since $\Delta x\,\Delta k \geq \frac{1}{2}$, $\Delta k \geq 1/(2\Delta x)$ and

Uncertainty principle

$$\Delta x\,\Delta p \geq \frac{h}{4\pi} \tag{3.21}$$

This equation states that the product of the uncertainty Δx in the position of an object at some instant and the uncertainty Δp in its momentum component in the x direction at the same instant is equal to or greater than $h/4\pi$.

If we arrange matters so that Δx is small, corresponding to a narrow wave group, then Δp will be large. If we reduce Δp in some way, a broad wave group is inevitable and Δx will be large.

Werner Heisenberg (1901–1976) was born in Duisberg, Germany, and studied theoretical physics at Munich, where he also became an enthusiastic skier and mountaineer. At Göttingen in 1924 as an assistant to Max Born, Heisenberg became uneasy about mechanical models of the atom: "Any picture of the atom that our imagination is able to invent is for that very reason defective," he later remarked. Instead he conceived an abstract approach using matrix algebra. In 1925, together with Born and Pascual Jordan, Heisenberg developed this approach into a consistent theory of quantum mechanics, but it was so difficult to understand and apply that it had very little impact on physics at the time. Schrödinger's wave formulation of quantum mechanics the following year was much more successful; Schrödinger and others soon showed that the wave and matrix versions of quantum mechanics were mathematically equivalent.

In 1927, working at Bohr's institute in Copenhagen, Heisenberg developed a suggestion by Wolfgang Pauli into the uncertainty principle. Heisenberg initially felt that this principle was a consequence of the disturbances inevitably produced by any measuring process. Bohr, on the other hand, thought that the basic cause of the uncertainties was the wave-particle duality, so that they were built into the natural world rather than solely the result of measurement. After much argument Heisenberg came around to Bohr's view. (Einstein, always skeptical about quantum mechanics, said after a lecture by Heisenberg on the uncertainty principle: "Marvelous, what ideas the young people have these days. But I don't believe a word of it.") Heisenberg received the Nobel Prize in 1932.

Heisenberg was one of the very few distinguished scientists to remain in Germany during the Nazi period. In World War II he led research there on atomic weapons, but little progress had been made by the war's end. Exactly why remains unclear, although there is no evidence that Heisenberg, as he later claimed, had moral qualms about creating such weapons and more or less deliberately dragged his feet. Heisenberg recognized early that "an explosive of unimaginable consequences" could be developed, and he and his group should have been able to have gotten farther than they did. In fact, alarmed by the news that Heisenberg was working on an atomic bomb, the U.S. government sent the former Boston Red Sox catcher Moe Berg to shoot Heisenberg during a lecture in neutral Switzerland in 1944. Berg, sitting in the second row, found himself uncertain from Heisenberg's remarks about how advanced the German program was, and kept his gun in his pocket.

These uncertainties are due not to inadequate apparatus but to the imprecise character in nature of the quantities involved. Any instrumental or statistical uncertainties that arise during a measurement only increase the product $\Delta x\,\Delta p$. Since we cannot know exactly both where a particle is right now and what its momentum is, we cannot say anything definite about where it will be in the future or how fast it will be moving then. *We cannot know the future for sure because we cannot know the present for sure.* But our ignorance is not total: we can still say that the particle is more likely to be in one place than another and that its momentum is more likely to have a certain value than another.

H-Bar

The quantity $h/2\pi$ appears often in modern physics because it turns out to be the basic unit of angular momentum. It is therefore customary to abbreviate $h/2\pi$ by the symbol $\hbar$ ("h-bar"):

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34}\ \text{J}\cdot\text{s}$$

In the remainder of this book $\hbar$ is used in place of $h/2\pi$. In terms of $\hbar$, the uncertainty principle becomes

Uncertainty principle

$$\Delta x\,\Delta p \geq \frac{\hbar}{2} \tag{3.22}$$

Example 3.6

A measurement establishes the position of a proton with an accuracy of $\pm 1.00 \times 10^{-11}$ m. Find the uncertainty in the proton's position 1.00 s later. Assume $v \ll c$.

Solution

Let us call the uncertainty in the proton's position Δx_0 at the time $t = 0$. The uncertainty in its momentum at this time is therefore, from Eq. (3.22),

$$\Delta p \geq \frac{\hbar}{2\Delta x_0}$$

Since $v \ll c$, the momentum uncertainty is $\Delta p = \Delta(mv) = m\,\Delta v$ and the uncertainty in the proton's velocity is

$$\Delta v = \frac{\Delta p}{m} \geq \frac{\hbar}{2m\,\Delta x_0}$$

The distance x the proton covers in the time t cannot be known more accurately than

$$\Delta x = t\,\Delta v \geq \frac{\hbar t}{2m\,\Delta x_0}$$

Hence Δx is inversely proportional to Δx_0: the *more* we know about the proton's position at $t = 0$, the *less* we know about its later position at $t > 0$. The value of Δx at $t = 1.00$ s is

$$\begin{aligned}\Delta x &\geq \frac{(1.054 \times 10^{-34}\ \text{J}\cdot\text{s})(1.00\ \text{s})}{(2)(1.672 \times 10^{-27}\ \text{kg})(1.00 \times 10^{-11}\ \text{m})} \\ &\geq 3.15 \times 10^{3}\ \text{m}\end{aligned}$$

This is 3.15 km—nearly 2 mi! What has happened is that the original wave group has spread out to a much wider one (Fig. 3.16). This occurred because the phase velocities of the component waves vary with wave number and a large range of wave numbers must have been present to produce the narrow original wave group. See Fig. 3.14.

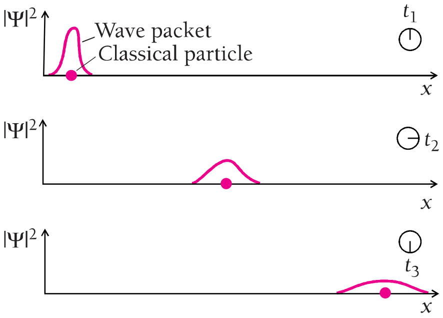


Figure 3.16 The wave packet that corresponds to a moving packet is a composite of many individual waves, as in Fig. 3.13. The phase velocities of the individual waves vary with their wave lengths. As a result, as the particle moves, the wave packet spreads out in space. The narrower the original wavepacket—that is, the more precisely we know its position at that time—the more it spreads out because it is made up of a greater span of waves with different phase velocities.

3.8 UNCERTAINTY PRINCIPLE II

A particle approach gives the same result

The uncertainty principle can be arrived at from the point of view of the particle properties of waves as well as from the point of view of the wave properties of particles.

We might want to measure the position and momentum of an object at a certain moment. To do so, we must touch it with something that will carry the required information back to us. That is, we must poke it with a stick, shine light on it, or perform some similar act. The measurement process itself thus requires that the object be interfered with in some way. If we consider such interferences in detail, we are led to the same uncertainty principle as before even without taking into account the wave nature of moving bodies.

Suppose we look at an electron using light of wavelength λ, as in Fig. 3.17. Each photon of this light has the momentum h/λ. When one of these photons bounces off the electron (which must happen if we are to "see" the electron), the electron's

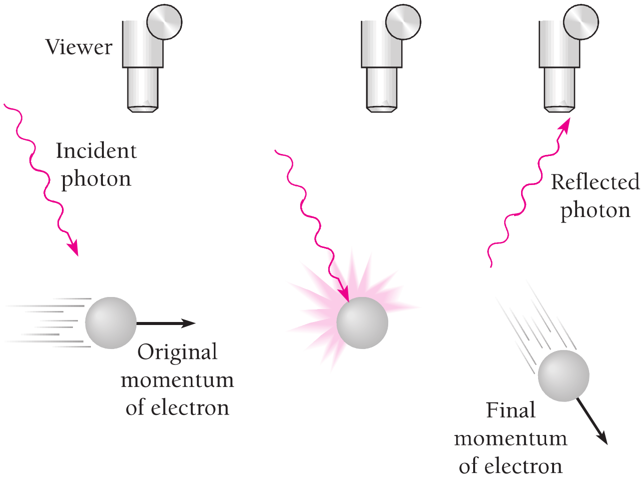


Figure 3.17 An electron cannot be observed without changing its momentum.

original momentum will be changed. The exact amount of the change Δp cannot be predicted, but it will be of the same order of magnitude as the photon momentum h/λ. Hence

$$\Delta p \approx \frac{h}{\lambda} \tag{3.23}$$

The longer the wavelength of the observing photon, the smaller the uncertainty in the electron's momentum.

Because light is a wave phenomenon as well as a particle phenomenon, we cannot expect to determine the electron's location with perfect accuracy regardless of the instrument used. A reasonable estimate of the minimum uncertainty in the measurement might be one photon wavelength, so that

$$\Delta x \geq \lambda \tag{3.24}$$

The shorter the wavelength, the smaller the uncertainty in location. However, if we use light of short wavelength to increase the accuracy of the position measurement, there will be a corresponding decrease in the accuracy of the momentum measurement because the higher photon momentum will disturb the electron's motion to a greater extent. Light of long wavelength will give a more accurate momentum but a less accurate position.

Combining Eqs. (3.23) and (3.24) gives

$$\Delta x\, \Delta p \geq h \tag{3.25}$$

This result is consistent with Eq. (3.22), $\Delta x\, \Delta p \geq \hbar/2$.

Arguments like the preceding one, although superficially attractive, must be approached with caution. The argument above implies that the electron can possess a definite position and momentum at any instant and that it is the measurement process that introduces the indeterminacy in $\Delta x\, \Delta p$. On the contrary, *this indeterminacy is inherent in the nature of a moving body*. The justification for the many "derivations" of this kind is first, they show it is impossible to imagine a way around the uncertainty principle; and second, they present a view of the principle that can be appreciated in a more familiar context than that of wave groups.

3.9 APPLYING THE UNCERTAINTY PRINCIPLE

A useful tool, not just a negative statement

Planck's constant h is so small that the limitations imposed by the uncertainty principle are significant only in the realm of the atom. On such a scale, however, this principle is of great help in understanding many phenomena. It is worth keeping in mind that the lower limit of $\hbar/2$ for $\Delta x\, \Delta p$ is rarely attained. More usually $\Delta x\, \Delta p \geq \hbar$, or even (as we just saw) $\Delta x\, \Delta p \geq h$.

Example 3.7

A typical atomic nucleus is about 5.0×10^{-15} m in radius. Use the uncertainty principle to place a lower limit on the energy an electron must have if it is to be part of a nucleus.

Solution

Letting $\Delta x = 5.0 \times 10^{-5}$ m we have

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{1.054 \times 10^{-34}\ \text{J} \cdot \text{s}}{(2)(5.0 \times 10^{-15}\ \text{m})} \geq 1.1 \times 10^{-20}\ \text{kg} \cdot \text{m/s}$$

If this is the uncertainty in a nuclear electron's momentum, the momentum p itself must be at least comparable in magnitude. An electron with such a momentum has a kinetic energy KE many times greater than its rest energy mc^2. From Eq. (1.24) we see that we can let KE $= pc$ here to a sufficient degree of accuracy. Therefore

$$\text{KE} = pc \geq (1.1 \times 10^{-20}\ \text{kg} \cdot \text{m/s})(3.0 \times 10^{8}\ \text{m/s}) \geq 3.3 \times 10^{-12}\ \text{J}$$

Since 1 eV $= 1.6 \times 10^{-19}$ J, the kinetic energy of an electron must exceed 20 MeV if it is to be inside a nucleus. Experiments show that the electrons emitted by certain unstable nuclei never have more than a small fraction of this energy, from which we conclude that nuclei cannot contain electrons. The electron an unstable nucleus may emit comes into being at the moment the nucleus decays (see Secs. 11.3 and 12.5).

Example 3.8

A hydrogen atom is 5.3×10^{-11} m in radius. Use the uncertainty principle to estimate the minimum energy an electron can have in this atom.

Solution

Here we find that with $\Delta x = 5.3 \times 10^{-11}$ m.

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq 9.9 \times 10^{-25}\ \text{kg} \cdot \text{m/s}$$

An electron whose momentum is of this order of magnitude behaves like a classical particle, and its kinetic energy is

$$\text{KE} = \frac{p^2}{2m} \geq \frac{(9.9 \times 10^{-25}\ \text{kg} \cdot \text{m/s})^2}{(2)(9.1 \times 10^{-31}\ \text{kg})} \geq 5.4 \times 10^{-19}\ \text{J}$$

which is 3.4 eV. The kinetic energy of an electron in the lowest energy level of a hydrogen atom is actually 13.6 eV.

Energy and Time

Another form of the uncertainty principle concerns energy and time. We might wish to measure the energy E emitted during the time interval Δt in an atomic process. If the energy is in the form of em waves, the limited time available restricts the accuracy with which we can determine the frequency ν of the waves. Let us assume that the minimum uncertainty in the number of waves we count in a wave group is one wave. Since the frequency of the waves under study is equal to the number of them we count divided by the time interval, the uncertainty $\Delta\nu$ in our frequency measurement is

$$\Delta\nu \geq \frac{1}{\Delta t}$$

The corresponding energy uncertainty is

$$\Delta E = h\,\Delta\nu$$

and so

$$\Delta E \geq \frac{h}{\Delta t} \qquad \text{or} \qquad \Delta E\,\Delta t \geq h$$

A more precise calculation based on the nature of wave groups changes this result to

Uncertainties in energy and time

$$\Delta E\,\Delta t \geq \frac{\hbar}{2} \tag{3.26}$$

Equation (3.26) states that the product of the uncertainty ΔE in an energy measurement and the uncertainty Δt in the time at which the measurement is made is equal to or greater than $\hbar/2$. This result can be derived in other ways as well and is a general one not limited to em waves.

Example 3.9

An "excited" atom gives up its excess energy by emitting a photon of characteristic frequency, as described in Chap. 4. The average period that elapses between the excitation of an atom and the time it radiates is 1.0×10^{-8} s. Find the inherent uncertainty in the frequency of the photon.

Solution

The photon energy is uncertain by the amount

$$\Delta E \geq \frac{\hbar}{2\Delta t} \geq \frac{1.054 \times 10^{-34}\ \text{J}\cdot\text{s}}{2(1.0 \times 10^{-8}\ \text{s})} \geq 5.3 \times 10^{-27}\ \text{J}$$

The corresponding uncertainty in the frequency of light is

$$\Delta\nu = \frac{\Delta E}{h} \geq 8 \times 10^{6}\ \text{Hz}$$

This is the irreducible limit to the accuracy with which we can determine the frequency of the radiation emitted by an atom. As a result, the radiation from a group of excited atoms does not appear with the precise frequency ν. For a photon whose frequency is, say, 5.0×10^{14} Hz, $\Delta\nu/\nu = 1.6 \times 10^{-8}$. In practice, other phenomena such as the doppler effect contribute more than this to the broadening of spectral lines.

EXERCISES

It is only the first step that takes the effort. —Marquise du Deffand

3.1 De Broglie Waves

1. A photon and a particle have the same wavelength. Can anything be said about how their linear momenta compare? About how the photon's energy compares with the particle's total energy? About how the photon's energy compares with the particle's kinetic energy?
2. Find the de Broglie wavelength of (*a*) an electron whose speed is 1.0×10^8 m/s, and (*b*) an electron whose speed is 2.0×10^8 m/s.
3. Find the de Broglie wavelength of a 1.0-mg grain of sand blown by the wind at a speed of 20 m/s.
4. Find the de Broglie wavelength of the 40-keV electrons used in a certain electron microscope.
5. By what percentage will a nonrelativistic calculation of the de Broglie wavelength of a 100-keV electron be in error?
6. Find the de Broglie wavelength of a 1.00-MeV proton. Is a relativistic calculation needed?
7. The atomic spacing in rock salt, NaCl, is 0.282 nm. Find the kinetic energy (in eV) of a neutron with a de Broglie wavelength of 0.282 nm. Is a relativistic calculation needed? Such neutrons can be used to study crystal structure.
8. Find the kinetic energy of an electron whose de Broglie wavelength is the same as that of a 100-keV x-ray.
9. Green light has a wavelength of about 550 nm. Through what potential difference must an electron be accelerated to have this wavelength?
10. Show that the de Broglie wavelength of a particle of mass m and kinetic energy KE is given by

$$\lambda = \frac{hc}{\sqrt{\mathrm{KE}(\mathrm{KE} + 2mc^2)}}$$

11. Show that if the total energy of a moving particle greatly exceeds its rest energy, its de Broglie wavelength is nearly the same as the wavelength of a photon with the same total energy.
12. (*a*) Derive a relativistically correct formula that gives the de Broglie wavelength of a charged particle in terms of the potential difference V through which it has been accelerated. (*b*) What is the nonrelativistic approximation of this formula, valid for $eV \ll mc^2$?

3.4 Phase and Group Velocities

13. An electron and a proton have the same velocity. Compare the wavelengths and the phase and group velocities of their de Broglie waves.
14. An electron and a proton have the same kinetic energy. Compare the wavelengths and the phase and group velocities of their de Broglie waves.
15. Verify the statement in the text that, if the phase velocity is the same for all wavelengths of a certain wave phenomenon (that is, there is no dispersion), the group and phase velocities are the same.
16. The phase velocity of ripples on a liquid surface is $\sqrt{2\pi S/\lambda\rho}$, where S is the surface tension and ρ the density of the liquid. Find the group velocity of the ripples.
17. The phase velocity of ocean waves is $\sqrt{g\lambda/2\pi}$, where g is the acceleration of gravity. Find the group velocity of ocean waves.
18. Find the phase and group velocities of the de Broglie waves of an electron whose speed is 0.900c.
19. Find the phase and group velocities of the de Broglie waves of an electron whose kinetic energy is 500 keV.
20. Show that the group velocity of a wave is given by $v_g = d\nu/d(1/\lambda)$.
21. (*a*) Show that the phase velocity of the de Broglie waves of a particle of mass m and de Broglie wavelength λ is given by

$$v_p = c\sqrt{1 + \left(\frac{mc\lambda}{h}\right)^2}$$

(*b*) Compare the phase and group velocities of an electron whose de Broglie wavelength is exactly 1×10^{-13} m.

22. In his original paper, de Broglie suggested that $E = h\nu$ and $p = h/\lambda$, which hold for electromagnetic waves, are also valid for moving particles. Use these relationships to show that the group velocity v_g of a de Broglie wave group is given by dE/dp, and with the help of Eq. (1.24), verify that $v_g = v$ for a particle of velocity v.

3.5 Particle Diffraction

23. What effect on the scattering angle in the Davisson-Germer experiment does increasing the electron energy have?
24. A beam of neutrons that emerges from a nuclear reactor contains neutrons with a variety of energies. To obtain neutrons with an energy of 0.050 eV, the beam is passed through a crystal whose atomic planes are 0.20 nm apart. At what angles relative to the original beam will the desired neutrons be diffracted?
25. In Sec. 3.5 it was mentioned that the energy of an electron entering a crystal increases, which reduces its de Broglie wavelength. Consider a beam of 54-eV electrons directed at a nickel target. The potential energy of an electron that enters the target changes by 26 eV. (*a*) Compare the electron speeds outside and inside the target. (*b*) Compare the respective de Broglie wavelengths.
26. A beam of 50-keV electrons is directed at a crystal and diffracted electrons are found at an angle of 50° relative to the original beam. What is the spacing of the atomic planes of the crystal? A relativistic calculation is needed for λ.

3.6 Particle in a Box

27. Obtain an expression for the energy levels (in MeV) of a neutron confined to a one-dimensional box 1.00×10^{-14} m wide. What is the neutron's minimum energy? (The diameter of an atomic nucleus is of this order of magnitude.)

28. The lowest energy possible for a certain particle trapped in a certain box is 1.00 eV. (*a*) What are the next two higher energies the particle can have? (*b*) If the particle is an electron, how wide is the box?

29. A proton in a one-dimensional box has an energy of 400 keV in its first excited state. How wide is the box?

3.7 Uncertainty Principle I
3.8 Uncertainty Principle II
3.9 Applying the Uncertainty Principle

30. Discuss the prohibition of $E = 0$ for a particle trapped in a box L wide in terms of the uncertainty principle. How does the minimum momentum of such a particle compare with the momentum uncertainty required by the uncertainty principle if we take $\Delta x = L$?

31. The atoms in a solid possess a certain minimum **zero-point energy** even at 0 K, while no such restriction holds for the molecules in an ideal gas. Use the uncertainty principle to explain these statements.

32. Compare the uncertainties in the velocities of an electron and a proton confined in a 1.00-nm box.

33. The position and momentum of a 1.00-keV electron are simultaneously determined. If its position is located to within 0.100 nm, what is the percentage of uncertainty in its momentum?

34. (*a*) How much time is needed to measure the kinetic energy of an electron whose speed is 10.0 m/s with an uncertainty of no more than 0.100 percent? How far will the electron have traveled in this period of time? (*b*) Make the same calculations for a 1.00-g insect whose speed is the same. What do these sets of figures indicate?

35. How accurately can the position of a proton with $v \ll c$ be determined without giving it more than 1.00 keV of kinetic energy?

36. (*a*) Find the magnitude of the momentum of a particle in a box in its nth state. (*b*) The minimum change in the particle's momentum that a measurement can cause corresponds to a change of ± 1 in the quantum number n. If $\Delta x = L$, show that $\Delta p \, \Delta x \geq \hbar/2$.

37. A marine radar operating at a frequency of 9400 MHz emits groups of electromagnetic waves 0.0800 μs in duration. The time needed for the reflections of these groups to return indicates the distance to a target. (*a*) Find the length of each group and the number of waves it contains. (*b*) What is the approximate minimum bandwidth (that is, spread of frequencies) the radar receiver must be able to process?

38. An unstable elementary particle called the eta meson has a rest mass of 549 MeV/c^2 and a mean lifetime of 7.00×10^{-19} s. What is the uncertainty in its rest mass?

39. The frequency of oscillation of a harmonic oscillator of mass m and spring constant C is $\nu = \sqrt{C/m}/2\pi$. The energy of the oscillator is $E = p^2/2m + Cx^2/2$, where p is its momentum when its displacement from the equilibrium position is x. In classical physics the minimum energy of the oscillator is $E_{\min} = 0$. Use the uncertainty principle to find an expression for E in terms of x only and show that the minimum energy is actually $E_{\min} = h\nu/2$ by setting $dE/dx = 0$ and solving for $E_{\min}$.

40. (*a*) Verify that the uncertainty principle can be expressed in the form $\Delta L \, \Delta\theta \geq \hbar/2$, where ΔL is the uncertainty in the angular momentum of a particle and $\Delta\theta$ is the uncertainty in its angular position. (*Hint*: Consider a particle of mass m moving in a circle of radius r at the speed v, for which $L = mvr$.) (*b*) At what uncertainty in L will the angular position of a particle become completely indeterminate?

CHAPTER 5

Quantum Mechanics

Scanning tunneling micrograph of gold atoms on a carbon (graphite) substrate. The cluster of gold atoms is about 1.5 nm across and three atoms high.

Although the Bohr theory of the atom, which can be extended further than was done in Chap. 4, is able to account for many aspects of atomic phenomena, it has a number of severe limitations as well. First of all, it applies only to hydrogen and one-electron ions such as He^+ and Li^{2+}—it does not even work for ordinary helium. The Bohr theory cannot explain why certain spectral lines are more intense than others (that is, why certain transitions between energy levels have greater probabilities of occurrence than others). It cannot account for the observation that many spectral lines actually consist of several separate lines whose wavelengths differ slightly. And perhaps most important, it does not permit us to obtain what a really successful theory of the atom should make possible: an understanding of how individual atoms interact with one another to endow macroscopic aggregates of matter with the physical and chemical properties we observe.

The preceding objections to the Bohr theory are not put forward in an unfriendly way, for the theory was one of those seminal achievements that transform scientific thought, but rather to emphasize that a more general approach to atomic phenomena is required. Such an approach was developed in 1925 and 1926 by Erwin Schrödinger, Werner Heisenberg, Max Born, Paul Dirac, and others under the apt name of **quantum mechanics.** "The discovery of quantum mechanics was nearly a total surprise. It described the physical world in a way that was fundamentally new. It seemed to many of us a miracle," noted Eugene Wigner, one of the early workers in the field. By the early 1930s the application of quantum mechanics to problems involving nuclei, atoms, molecules, and matter in the solid state made it possible to understand a vast body of data ("a large part of physics and the whole of chemistry," according to Dirac) and—vital for any theory—led to predictions of remarkable accuracy. Quantum mechanics has survived every experimental test thus far of even its most unexpected conclusions.

5.1 QUANTUM MECHANICS

Classical mechanics is an approximation of quantum mechanics

The fundamental difference between classical (or Newtonian) mechanics and quantum mechanics lies in what they describe. In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In the everyday world these quantities can all be determined well enough for the predictions of Newtonian mechanics to agree with what we find.

Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm. Cause and effect are still related in quantum mechanics, but what they concern needs careful interpretation. In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy. As we saw in Sec. 3.7, the more we know about the position of a particle now, the less we know about its momentum and hence about its position later.

The quantities whose relationships quantum mechanics explores are *probabilities.* Instead of asserting, for example, that the radius of the electron's orbit in a ground-state hydrogen atom is always exactly 5.3×10^{-11} m, as the Bohr theory does, quantum mechanics states that this is the *most probable* radius. In a suitable experiment most trials will yield a different value, either larger or smaller, but the value most likely to be found will be 5.3×10^{-11} m.

Quantum mechanics might seem a poor substitute for classical mechanics. However, classical mechanics turns out to be just an approximate version of quantum mechanics. The certainties of classical mechanics are illusory, and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behavior are unnoticeable. Instead of two sets of physical principles, one for the macroworld and one for the microworld, there is only the single set included in quantum mechanics.

Wave Function

As mentioned in Chap. 3, the quantity with which quantum mechanics is concerned is the **wave function** Ψ of a body. While Ψ itself has no physical interpretation, the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ. The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product $\Psi^*\Psi$ of Ψ and its **complex conjugate** Ψ^*. The complex conjugate of any function is obtained by replacing $i(=\sqrt{-1})$ by $-i$ wherever it appears in the function. Every complex function Ψ can be written in the form

Wave function $$\Psi = A + iB$$

where A and B are real functions. The complex conjugate Ψ^* of Ψ is

Complex conjugate $$\Psi^* = A - iB$$

and so $$|\Psi|^2 = \Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$$

since $i^2 = -1$. Hence $|\Psi|^2 = \Psi^*\Psi$ is always a positive real quantity, as required.

Normalization

Even before we consider the actual calculation of Ψ, we can establish certain requirements it must always fulfill. For one thing, since $|\Psi|^2$ is proportional to the probability density P of finding the body described by Ψ, the integral of $|\Psi|^2$ over all space must be finite—the body is *somewhere,* after all. If

$$\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 0$$

the particle does not exist, and the integral obviously cannot be ∞ and still mean anything. Furthermore, $|\Psi|^2$ cannot be negative or complex because of the way it is defined. The only possibility left is that the integral be a finite quantity if Ψ is to describe properly a real body.

It is usually convenient to have $|\Psi|^2$ be *equal* to the probability density P of finding the particle described by Ψ, rather than merely be proportional to P. If $|\Psi|^2$ is to equal P, then it must be true that

Normalization

$$\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 1 \tag{5.1}$$

since if the particle exists somewhere at all times,

$$\int_{-\infty}^{\infty} P \, dV = 1$$

A wave function that obeys Eq. (5.1) is said to be **normalized.** Every acceptable wave function can be normalized by multiplying it by an appropriate constant; we shall shortly see how this is done.

Well-Behaved Wave Functions

Besides being normalizable, Ψ must be single-valued, since P can have only one value at a particular place and time, and continuous. Momentum considerations (see Sec. 5.6) require that the partial derivatives $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ be finite, continuous, and single-valued. Only wave functions with all these properties can yield physically meaningful results when used in calculations, so only such "well-behaved" wave functions are admissible as mathematical representations of real bodies. To summarize:

1 Ψ must be continuous and single-valued everywhere.
2 $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
3 Ψ must be normalizable, which means that Ψ must go to 0 as $x \to \pm\infty$, $y \to \pm\infty$, $z \to \pm\infty$ in order that $\int |\Psi|^2 \, dV$ over all space be a finite constant.

These rules are not always obeyed by the wave functions of particles in model situations that only approximate actual ones. For instance, the wave functions of a particle in a box with infinitely hard walls do not have continuous derivatives at the walls, since $\Psi = 0$ outside the box (see Fig. 5.4). But in the real world, where walls are never infinitely hard, there is no sharp change in Ψ at the walls (see Fig. 5.7) and the derivatives are continuous. Exercise 7 gives another example of a wave function that is not well-behaved.

Given a normalized and otherwise acceptable wave function Ψ, the probability that the particle it describes will be found in a certain region is simply the integral of the probability density $|\Psi|^2$ over that region. Thus for a particle restricted to motion in the x direction, the probability of finding it between x_1 and x_2 is given by

Probability

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 \, dx \tag{5.2}$$

We will see examples of such calculations later in this chapter and in Chap. 6.

5.2 THE WAVE EQUATION

It can have a variety of solutions, including complex ones

Schrödinger's equation, which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of Newtonian mechanics, is a wave equation in the variable Ψ.

Before we tackle Schrödinger's equation, let us review the wave equation

Wave equation
$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \qquad (5.3)$$

which governs a wave whose variable quantity is y that propagates in the x direction with the speed v. In the case of a wave in a stretched string, y is the displacement of the string from the x axis; in the case of a sound wave, y is the pressure difference; in the case of a light wave, y is either the electric or the magnetic field magnitude. Equation (5.3) can be derived from the second law of motion for mechanical waves and from Maxwell's equations for electromagnetic waves.

Partial Derivatives

Suppose we have a function $f(x, y)$ of two variables, x and y, and we want to know how f varies with only one of them, say x. To find out, we differentiate f with respect to x while treating the other variable y as a constant. The result is the **partial derivative** of f with respect to x, which is written $\partial f/\partial x$

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx}\right)_{y=\text{constant}}$$

The rules for ordinary differentiation hold for partial differentiation as well. For instance, if $f = cx^2$,

$$\frac{df}{dx} = 2cx$$

and so, if $f = yx^2$,

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx}\right)_{y=\text{constant}} = 2yx$$

The partial derivative of $f = yx^2$ with respect to the other variable, y, is

$$\frac{\partial f}{\partial y} = \left(\frac{df}{dy}\right)_{x=\text{constant}} = x^2$$

Second order partial derivatives occur often in physics, as in the wave equation. To find $\partial^2 f/\partial x^2$, we first calculate $\partial f/\partial x$ and then differentiate again, still keeping y constant:

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)$$

For $f = yx^2$,

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}(2yx) = 2y$$

Similarly
$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial y}(x^2) = 0$$

Solutions of the wave equation may be of many kinds, reflecting the variety of waves that can occur—a single traveling pulse, a train of waves of constant amplitude and wavelength, a train of superposed waves of the same amplitudes and wavelengths, a train of superposed waves of different amplitudes and wavelengths,

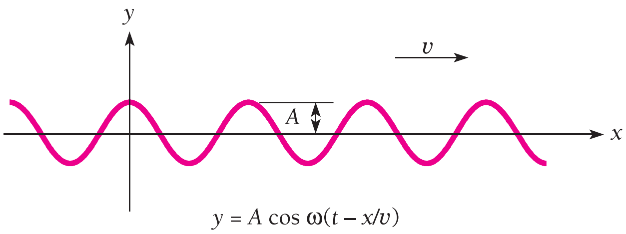


Figure 5.1 Waves in the xy plane traveling in the $+x$ direction along a stretched string lying on the x axis.

a standing wave in a string fastened at both ends, and so on. All solutions must be of the form

$$y = F\left(t \pm \frac{x}{v}\right) \tag{5.4}$$

where F is any function that can be differentiated. The solutions $F(t - x/v)$ represent waves traveling in the $+x$ direction, and the solutions $F(t + x/v)$ represent waves traveling in the $-x$ direction.

Let us consider the wave equivalent of a "free particle," which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed. This wave is described by the general solution of Eq. (5.3) for undamped (that is, constant amplitude A), monochromatic (constant angular frequency ω) harmonic waves in the $+x$ direction, namely

$$y = Ae^{-i\omega(t-x/v)} \tag{5.5}$$

In this formula y is a complex quantity, with both real and imaginary parts.

Because

$$e^{-i\theta} = \cos\theta - i\sin\theta$$

Eq. (5.5) can be written in the form

$$y = A\cos\omega\left(t - \frac{x}{v}\right) - iA\sin\omega\left(t - \frac{x}{v}\right) \tag{5.6}$$

Only the real part of Eq. (5.6) [which is the same as Eq. (3.5)] has significance in the case of waves in a stretched string. There y represents the displacement of the string from its normal position (Fig. 5.1), and the imaginary part of Eq. (5.6) is discarded as irrelevant.

Example 5.1

Verify that Eq. (5.5) is a solution of the wave equation.

Solution

The derivative of an exponential function e^u is

$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$

The partial derivative of y with respect to x (which means t is treated as a constant) from Eq. (5.5) is therefore

$$\frac{\partial y}{\partial x} = \frac{i\omega}{v}y$$

and the second partial derivative is

$$\frac{\partial^2 y}{\partial x^2} = \frac{i^2\omega^2}{v^2}y = -\frac{\omega^2}{v^2}y$$

since $i^2 = -1$. The partial derivative of y with respect to t (now holding x constant) is

$$\frac{\partial y}{\partial t} = -i\omega y$$

and the second partial derivative is

$$\frac{\partial^2 y}{\partial t^2} = i^2\omega^2 y = -\omega^2 y$$

Combining these results gives

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$$

which is Eq. (5.3). Hence Eq. (5.5) is a solution of the wave equation.

5.3 SCHRÖDINGER'S EQUATION: TIME-DEPENDENT FORM

A basic physical principle that cannot be derived from anything else

In quantum mechanics the wave function Ψ corresponds to the wave variable y of wave motion in general. However, Ψ, unlike y, is not itself a measurable quantity and may therefore be complex. For this reason we assume that Ψ for a particle moving freely in the $+x$ direction is specified by

$$\Psi = Ae^{-i\omega(t-x/v)} \tag{5.7}$$

Replacing ω in the above formula by $2\pi\nu$ and v by $\lambda\nu$ gives

$$\Psi = Ae^{-2\pi i(\nu t-x/\lambda)} \tag{5.8}$$

This is convenient since we already know what ν and λ are in terms of the total energy E and momentum p of the particle being described by Ψ. Because

$$E = h\nu = 2\pi\hbar\nu \qquad \text{and} \qquad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

we have

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et-px)} \tag{5.9}$$

Equation (5.9) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction, just as Eq. (5.5) describes, for example, a harmonic displacement wave moving freely along a stretched string.

The expression for the wave function Ψ given by Eq. (5.9) is correct only for freely moving particles. However, we are most interested in situations where the motion of a particle is subject to various restrictions. An important concern, for example, is an electron bound to an atom by the electric field of its nucleus. What we must now do is obtain the fundamental differential equation for Ψ, which we can then solve for Ψ in a specific situation. This equation, which is Schrödinger's equation, can be arrived at in various ways, but it *cannot* be rigorously derived from existing physical principles:

the equation represents something new. What will be done here is to show one route to the wave equation for Ψ and then to discuss the significance of the result.

We begin by differentiating Eq. (5.9) for Ψ twice with respect to x, which gives

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi$$

$$p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial x^2} \tag{5.10}$$

Differentiating Eq. (5.9) once with respect to t gives

$$\frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar}\Psi$$

$$E\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} \tag{5.11}$$

At speeds small compared with that of light, the total energy E of a particle is the sum of its kinetic energy $p^2/2m$ and its potential energy U, where U is in general a function of position x and time t:

$$E = \frac{p^2}{2m} + U(x, t) \tag{5.12}$$

The function U represents the influence of the rest of the universe on the particle. Of course, only a small part of the universe interacts with the particle to any extent; for

---

Erwin Schrödinger (1887–1961) was born in Vienna to an Austrian father and a half-English mother and received his doctorate at the university there. After World War I, during which he served as an artillery officer, Schrödinger had appointments at several German universities before becoming professor of physics in Zurich, Switzerland. Late in November, 1925, Schrödinger gave a talk on de Broglie's notion that a moving particle has a wave character. A colleague remarked to him afterward that to deal properly with a wave, one needs a wave equation. Schrödinger took this to heart, and a few weeks later he was "struggling with a new atomic theory. If only I knew more mathematics! I am very optimistic about this thing and expect that if I can only . . . solve it, it will be *very* beautiful." (Schrödinger was not the only physicist to find the mathematics he needed difficult; the eminent mathematician David Hilbert said at about this time, "Physics is much too hard for physicists.")

The struggle was successful, and in January 1926 the first of four papers on "Quantization as an Eigenvalue Problem" was completed. In this epochal paper Schrödinger introduced the equation that bears his name and solved it for the hydrogen atom, thereby opening wide the door to the modern view of the atom which others had only pushed ajar. By June Schrödinger had applied wave mechanics to the harmonic oscillator, the diatomic molecule, the hydrogen atom in an electric field, the absorption and emission of radiation, and the scattering of radiation by atoms and molecules. He had also shown that his wave mechanics was mathematically equivalent to the more abstract Heisenberg-Born-Jordan matrix mechanics.

The significance of Schrödinger's work was at once realized. In 1927 he succeeded Planck at the University of Berlin but left Germany in 1933, the year he received the Nobel Prize, when the Nazis came to power. He was at Dublin's Institute for Advanced Study from 1939 until his return to Austria in 1956. In Dublin, Schrödinger became interested in biology, in particular the mechanism of heredity. He seems to have been the first to make definite the idea of a genetic code and to identify genes as long molecules that carry the code in the form of variations in how their atoms are arranged. Schrödinger's 1944 book *What Is Life?* was enormously influential, not only by what it said but also by introducing biologists to a new way of thinking—that of the physicist—about their subject. *What Is Life?* started James Watson on his search for "the secret of the gene," which he and Francis Crick (a physicist) discovered in 1953 to be the structure of the DNA molecule.

instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

Multiplying both sides of Eq. (5.12) by the wave function Ψ gives

$$E\Psi = \frac{p^2\Psi}{2m} + U\Psi \tag{5.13}$$

Now we substitute for $E\Psi$ and $p^2\Psi$ from Eqs. (5.10) and (5.11) to obtain the **time-dependent form of Schrödinger's equation:**

Time-dependent Schrödinger equation in one dimension

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U\Psi \tag{5.14}$$

In three dimensions the time-dependent form of Schrödinger's equation is

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + U\Psi \tag{5.15}$$

where the particle's potential energy U is some function of x, y, z, and t.

Any restrictions that may be present on the particle's motion will affect the potential-energy function U. Once U is known, Schrödinger's equation may be solved for the wave function Ψ of the particle, from which its probability density $|\Psi|^2$ may be determined for a specified x, y, z, t.

Validity of Schrödinger's Equation

Schrödinger's equation was obtained here using the wave function of a freely moving particle (potential energy U = constant). How can we be sure it applies to the general case of a particle subject to arbitrary forces that vary in space and time [$U = U(x, y, z, t)$]? Substituting Eqs. (5.10) and (5.11) into Eq. (5.13) is really a wild leap with no formal justification; this is true for all other ways in which Schrödinger's equation can be arrived at, including Schrödinger's own approach.

What we must do is postulate Schrödinger's equation, solve it for a variety of physical situations, and compare the results of the calculations with the results of experiments. If both sets of results agree, the postulate embodied in Schrödinger's equation is valid. If they disagree, the postulate must be discarded and some other approach would then have to be explored. In other words,

> Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

What has happened is that Schrödinger's equation has turned out to be remarkably accurate in predicting the results of experiments. To be sure, Eq. (5.15) can be used only for nonrelativistic problems, and a more elaborate formulation is needed when particle speeds near that of light are involved. But because it is in accord with experience within its range of applicability, we must consider Schrödinger's equation as a valid statement concerning certain aspects of the physical world.

It is worth noting that Schrödinger's equation does not increase the number of principles needed to describe the workings of the physical world. Newton's second law of motion $F = ma$, the basic principle of classical mechanics, can be derived from Schrödinger's equation provided the quantities it relates are understood to be averages rather than precise values. (Newton's laws of motion were also not derived from any other principles. Like Schrödinger's equation, these laws are considered valid in their range of applicability because of their agreement with experiment.)

5.4 LINEARITY AND SUPERPOSITION

Wave functions add, not probabilities

An important property of Schrödinger's equation is that it is linear in the wave function Ψ. By this is meant that the equation has terms that contain Ψ and its derivatives but no terms independent of Ψ or that involve higher powers of Ψ or its derivatives. As a result, a linear combination of solutions of Schrödinger's equation for a given system is also itself a solution. If Ψ_1 and Ψ_2 are two solutions (that is, two wave functions that satisfy the equation), then

$$\Psi = a_1\Psi_1 + a_2\Psi_2$$

is also a solution, where a_1 and a_2 are constants (see Exercise 8). Thus the wave functions Ψ_1 and Ψ_2 obey the superposition principle that other waves do (see Sec. 2.1) and we conclude that interference effects can occur for wave functions just as they can for light, sound, water, and electromagnetic waves. In fact, the discussions of Secs. 3.4 and 3.7 assumed that de Broglie waves are subject to the superposition principle.

Let us apply the superposition principle to the diffraction of an electron beam. Figure 5.2*a* shows a pair of slits through which a parallel beam of monoenergetic electrons pass on their way to a viewing screen. If slit 1 only is open, the result is the intensity variation shown in Fig. 5.2*b* that corresponds to the probability density

$$P_1 = |\Psi_1|^2 = \Psi_1^*\Psi_1$$

If slit 2 only is open, as in Fig. 5.2*c*, the corresponding probability density is

$$P_2 = |\Psi_2|^2 = \Psi_2^*\Psi_2$$

We might suppose that opening both slits would give an electron intensity variation described by $P_1 + P_2$, as in Fig. 5.2*d*. However, this is not the case because in quantum

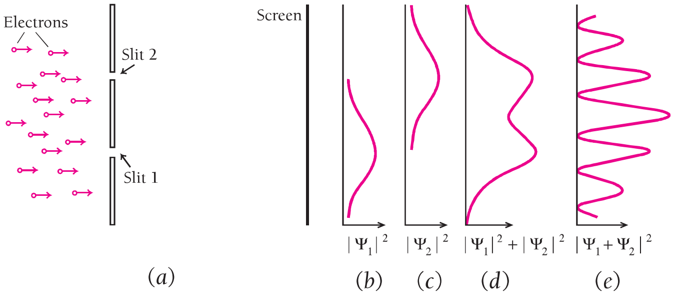


Figure 5.2 (*a*) Arrangement of double-slit experiment. (*b*) The electron intensity at the screen with only slit 1 open. (*c*) The electron intensity at the screen with only slit 2 open. (*d*) The sum of the intensities of (*b*) and (*c*). (*e*) The actual intensity at the screen with slits 1 and 2 both open. The wave functions Ψ_1 and Ψ_2 add to produce the intensity at the screen, not the probability densities $|\Psi_1|^2$ and $|\Psi_2|^2$.

mechanics wave functions add, *not* probabilities. Instead the result with both slits open is as shown in Fig. 5.2*e*, the same pattern of alternating maxima and minima that occurs when a beam of monochromatic light passes through the double slit of Fig. 2.4.

The diffraction pattern of Fig. 5.2*e* arises from the superposition Ψ of the wave functions Ψ_1 and Ψ_2 of the electrons that have passed through slits 1 and 2:

$$\Psi = \Psi_1 + \Psi_2$$

The probability density at the screen is therefore

$$\begin{aligned} P = |\Psi|^2 = |\Psi_1 + \Psi_2|^2 &= (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2) \\ &= \Psi_1^*\Psi_1 + \Psi_2^*\Psi_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \\ &= P_1 + P_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \end{aligned}$$

The two terms at the right of this equation represent the difference between Fig. 5.2*d* and *e* and are responsible for the oscillations of the electron intensity at the screen. In Sec. 6.8 a similar calculation will be used to investigate why a hydrogen atom emits radiation when it undergoes a transition from one quantum state to another of lower energy.

5.5 EXPECTATION VALUES

How to extract information from a wave function

Once Schrödinger's equation has been solved for a particle in a given physical situation, the resulting wave function $\Psi(x, y, z, t)$ contains all the information about the particle that is permitted by the uncertainty principle. Except for those variables that are quantized this information is in the form of probabilities and not specific numbers.

As an example, let us calculate the **expectation value** $\langle x \rangle$ of the position of a particle confined to the x axis that is described by the wave function $\Psi(x, t)$. This is the value of x we would obtain if we measured the positions of a great many particles described by the same wave function at some instant t and then averaged the results.

To make the procedure clear, we first answer a slightly different question: What is the average position $\bar{x}$ of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1, N_2 particles at x_2, and so on? The average position in this case is the same as the center of mass of the distribution, and so

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\Sigma N_i x_i}{\Sigma N_i} \tag{5.16}$$

When we are dealing with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i. This probability is

$$P_i = |\Psi_i|^2\, dx \tag{5.17}$$

where Ψ_i is the particle wave function evaluated at $x = x_i$. Making this substitution and changing the summations to integrals, we see that the expectation value of the position of the single particle is

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x|\Psi|^2\, dx}{\int_{-\infty}^{\infty} |\Psi|^2\, dx} \tag{5.18}$$

If Ψ is a normalized wave function, the denominator of Eq. (5.18) equals the probability that the particle exists somewhere between $x = -\infty$ and $x = \infty$ and therefore has the value 1. In this case

Expectation value for position

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2\, dx \tag{5.19}$$

Example 5.2

A particle limited to the x axis has the wave function $\Psi = ax$ between $x = 0$ and $x = 1$; $\Psi = 0$ elsewhere. (*a*) Find the probability that the particle can be found between $x = 0.45$ and $x = 0.55$. (*b*) Find the expectation value $\langle x \rangle$ of the particle's position.

Solution

(*a*) The probability is

$$\int_{x_1}^{x_2} |\Psi|^2\, dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(*b*) The expectation value is

$$\langle x \rangle = \int_0^1 x|\Psi|^2\, dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

The same procedure as that followed above can be used to obtain the expectation value $\langle G(x) \rangle$ of any quantity—for instance, potential energy $U(x)$—that is a function of the position x of a particle described by a wave function Ψ. The result is

Expectation value

$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x)|\Psi|^2\, dx \tag{5.20}$$

The expectation value $\langle p \rangle$ for momentum cannot be calculated this way because, according to the uncertainty principles, no such function as $p(x)$ can exist. If we specify x, so that $\Delta x = 0$, we cannot specify a corresponding p since $\Delta x\, \Delta p \geq \hbar/2$. The same problem occurs for the expectation value $\langle E \rangle$ for energy because $\Delta E \Delta t \geq \hbar/2$ means that, if we specify t, the function $E(t)$ is impossible. In Sec. 5.6 we will see how $\langle p \rangle$ and $\langle E \rangle$ can be determined.

In classical physics no such limitation occurs, because the uncertainty principle can be neglected in the macroworld. When we apply the second law of motion to the motion of a body subject to various forces, we expect to get $p(x, t)$ and $E(x, t)$ from the solution as well as $x(t)$. Solving a problem in classical mechanics gives us the entire future course of the body's motion. In quantum physics, on the other hand, all we get directly by applying Schrödinger's equation to the motion of a particle is the wave function Ψ, and the future course of the particle's motion—like its initial state—is a matter of probabilities instead of certainties.

5.6 OPERATORS

Another way to find expectation values

A hint as to the proper way to evaluate $\langle p \rangle$ and $\langle E \rangle$ comes from differentiating the free-particle wave function $\Psi = Ae^{-(i/\hbar)(Et-px)}$ with respect to x and to t. We find that

$$\frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} p\Psi$$

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E\Psi$$

which can be written in the suggestive forms

$$p\Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi \tag{5.21}$$

$$E\Psi = i\hbar \frac{\partial}{\partial t} \Psi \tag{5.22}$$

Evidently the dynamical quantity p in some sense corresponds to the differential operator $(\hbar/i)\ \partial/\partial x$ and the dynamical quantity E similarly corresponds to the differential operator $i\hbar\ \partial/\partial t$.

An **operator** tells us what operation to carry out on the quantity that follows it. Thus the operator $i\hbar\ \partial/\partial t$ instructs us to take the partial derivative of what comes after it with respect to t and multiply the result by $i\hbar$. Equation (5.22) was on the postmark used to cancel the Austrian postage stamp issued to commemorate the 100th anniversary of Schrödinger's birth.

It is customary to denote operators by using a caret, so that $\hat{p}$ is the operator that corresponds to momentum p and $\hat{E}$ is the operator that corresponds to total energy E. From Eqs. (5.21) and (5.22) these operators are

Momentum operator

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{5.23}$$

Total-energy operator

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \tag{5.24}$$

Though we have only shown that the correspondences expressed in Eqs. (5.23) and (5.24) hold for free particles, they are entirely general results whose validity is the same as that of Schrödinger's equation. To support this statement, we can replace the equation $E = \mathrm{KE} + U$ for the total energy of a particle with the operator equation

$$\hat{E} = \widehat{\mathrm{KE}} + \hat{U} \tag{5.25}$$

The operator $\hat{U}$ is just $U(\Psi)$. The kinetic energy KE is given in terms of momentum p by

$$\mathrm{KE} = \frac{p^2}{2m}$$

and so we have

Kinetic-energy operator

$$\hat{KE} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{5.26}$$

Equation (5.25) therefore reads

$$i\hbar\frac{\partial}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U \tag{5.27}$$

Now we multiply the identity $\Psi = \Psi$ by Eq. (5.27) and obtain

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U\Psi$$

which is Schrödinger's equation. Postulating Eqs. (5.23) and (5.24) is equivalent to postulating Schrödinger's equation.

Operators and Expectation Values

Because p and E can be replaced by their corresponding operators in an equation, we can use these operators to obtain expectation values for p and E. Thus the expectation value for p is

$$\langle p\rangle = \int_{-\infty}^{\infty} \Psi^*\hat{p}\Psi\,dx = \int_{-\infty}^{\infty} \Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\,dx = \frac{\hbar}{i}\int_{-\infty}^{\infty}\Psi^*\frac{\partial\Psi}{\partial x}\,dx \tag{5.28}$$

and the expectation value for E is

$$\langle E\rangle = \int^{\infty} \Psi^*\hat{E}\Psi\,dx = \int^{\infty} \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi\,dx = i\hbar\int^{\infty}\Psi^*\frac{\partial\Psi}{\partial t}\,dx \tag{5.29}$$

Both Eqs. (5.28) and (5.29) can be evaluated for any acceptable wave function $\Psi(x, t)$.

Let us see why expectation values involving operators have to be expressed in the form

$$\langle p\rangle = \int_{-\infty}^{\infty} \Psi^*\hat{p}\Psi\,dx$$

The other alternatives are

$$\int_{-\infty}^{\infty} \hat{p}\Psi^*\Psi\,dx = \frac{\hbar}{i}\int_{-\infty}^{\infty}\frac{\partial}{\partial x}(\Psi^*\Psi)\,dx = \frac{\hbar}{i}\Big[\Psi^*\Psi\Big]_{-\infty}^{\infty} = 0$$

since Ψ^* and Ψ must be 0 at $x = \pm\infty$, and

$$\int_{-\infty}^{\infty} \Psi^*\Psi\hat{p}\,dx = \frac{\hbar}{i}\int_{-\infty}^{\infty}\Psi^*\Psi\frac{\partial}{\partial x}\,dx$$

which makes no sense. In the case of algebraic quantities such as x and $V(x)$, the order of factors in the integrand is unimportant, but when differential operators are involved, the correct order of factors must be observed.

Every observable quantity G characteristic of a physical system may be represented by a suitable quantum-mechanical operator $\hat{G}$. To obtain this operator, we express G in terms of x and p and then replace p by $(\hbar/i)\,\partial/\partial x$. If the wave function Ψ of the system is known, the expectation value of $G(x, p)$ is

Expectation value of an operator

$$\langle G(x, p)\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{G} \Psi \, dx \tag{5.30}$$

In this way all the information about a system that is permitted by the uncertainty principle can be obtained from its wave function Ψ.

5.7 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

Eigenvalues and eigenfunctions

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U, vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to t.

We begin by noting that the one-dimensional wave function Ψ of an unrestricted particle may be written

$$\Psi = Ae^{-(i/\hbar)(Et-px)} = Ae^{-(iE/\hbar)t}e^{+(ip/\hbar)x} = \psi e^{-(iE/\hbar)t} \tag{5.31}$$

Evidently Ψ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position-dependent function ψ. As it happens, the time variations of *all* wave functions of particles acted on by forces independent of time have the same form as that of an unrestricted particle. Substituting the Ψ of Eq. (5.31) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} e^{-(iE/\hbar)t} \frac{\partial^2\psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

Steady-state Schrödinger equation in one dimension

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \tag{5.32}$$

Equation (5.32) is the **steady-state form of Schrödinger's equation.** In three dimensions it is

Steady-state Schrödinger equation in three dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \tag{5.33}$$

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy E. Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of *all* stable systems.

A familiar and quite close analogy to the manner in which energy quantization occurs in solutions of Schrödinger's equation is with standing waves in a stretched string of length L that is fixed at both ends. Here, instead of a single wave propagating indefinitely in one direction, waves are traveling in both the $+x$ and $-x$ directions simultaneously. These waves are subject to the condition (called a **boundary condition**) that the displacement y always be zero at both ends of the string. An acceptable function $y(x, t)$ for the displacement must, with its derivatives (except at the ends), be as well-behaved as ψ and its derivatives—that is, be continuous, finite, and single-valued. In this case y must be real, not complex, as it represents a directly measurable quantity. The only solutions of the wave equation, Eq. (5.3), that are in accord with these various limitations are those in which the wavelengths are given by

$$\lambda_n = \frac{2L}{n+1} \qquad n = 0, 1, 2, 3, \ldots$$

as shown in Fig. 5.3. It is the *combination* of the wave equation and the restrictions placed on the nature of its solution that leads us to conclude that $y(x, t)$ can exist only for certain wavelengths λ_n.

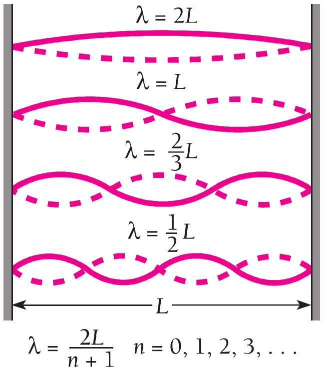


Figure 5.3 Standing waves in a stretched string fastened at both ends.

Eigenvalues and Eigenfunctions

The values of energy E_n for which Schrödinger's steady-state equation can be solved are called **eigenvalues** and the corresponding wave functions ψ_n are called **eigenfunctions.** (These terms come from the German *Eigenwert,* meaning "proper or characteristic value," and *Eigenfunktion,* "proper or characteristic function.") The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots$$

are an example of a set of eigenvalues. We shall see in Chap. 6 why these particular values of E are the only ones that yield acceptable wave functions for the electron in the hydrogen atom.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum **L**. In the case of the hydrogen atom, we shall find that the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)}\,\hbar \qquad l = 0, 1, 2, \ldots, (n-1)$$

Of course, a dynamical variable G may not be quantized. In this case measurements of G made on a number of identical systems will not yield a unique result but instead a spread of values whose average is the expectation value

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\psi|^2 \, dx$$

In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense. This probabilistic statement does not conflict with the fact that experiments performed on hydrogen atoms always show that each one contains a whole electron, not 27 percent of an electron in a certain region and 73 percent elsewhere. The probability is one of *finding* the electron, and although this probability is smeared out in space, the electron itself is not.

Operators and Eigenvalues

The condition that a certain dynamical variable G be restricted to the discrete values G_n—in other words, that G be quantized—is that the wave functions ψ_n of the system be such that

Eigenvalue equation

$$\hat{G}\psi_n = G_n\psi_n \tag{5.34}$$

where $\hat{G}$ is the operator that corresponds to G and each G_n is a real number. When Eq. (5.34) holds for the wave functions of a system, it is a fundamental postulate of quantum mechanics that any measurement of G can only yield one of the values G_n. If measurements of G are made on a number of identical systems all in states described by the particular eigenfunction ψ_k, each measurement will yield the single value G_k.

Example 5.3

An eigenfunction of the operator d^2/dx^2 is $\psi = e^{2x}$. Find the corresponding eigenvalue.

Solution

Here $\hat{G} = d^2/dx^2$, so

$$\hat{G}\psi = \frac{d^2}{dx^2}(e^{2x}) = \frac{d}{dx}\left[\frac{d}{dx^2}(e^{2x})\right] = \frac{d}{dx}(2e^{2x}) = 4e^{2x}$$

But $e^{2x} = \psi$, so

$$\hat{G}\psi = 4\psi$$

From Eq. (5.34) we see that the eigenvalue G here is just $G = 4$.

In view of Eqs. (5.25) and (5.26) the total-energy operator $\hat{E}$ of Eq. (5.24) can also be written as

Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U \tag{5.35}$$

and is called the **Hamiltonian operator** because it is reminiscent of the Hamiltonian function in advanced classical mechanics, which is an expression for the total energy of a system in terms of coordinates and momenta only. Evidently the steady-state Schrödinger equation can be written simply as

Schrödinger's equation

$$\hat{H}\psi_\mathrm{n} = E_n\psi_n \tag{5.36}$$

Table 5.1 Operators Associated with Various Observable Quantities

Quantity	Operator
Position, x	x
Linear momentum, p	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Potential energy, $U(x)$	$U(x)$
Kinetic energy, $\mathrm{KE} = \frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Total energy, E	$i\hbar\frac{\partial}{\partial t}$
Total energy (Hamiltonian form), H	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$

so we can say that the various E_n are the eigenvalues of the Hamiltonian operator $\hat{H}$. This kind of association between eigenvalues and quantum-mechanical operators is quite general. Table 5.1 lists the operators that correspond to various observable quantities.

5.8 PARTICLE IN A BOX

How boundary conditions and normalization determine wave functions

To solve Schrödinger's equation, even in its simpler steady-state form, usually requires elaborate mathematical techniques. For this reason the study of quantum mechanics has traditionally been reserved for advanced students who have the required proficiency in mathematics. However, since quantum mechanics is the theoretical structure whose results are closest to experimental reality, we must explore its methods and applications to understand modern physics. As we shall see, even a modest mathematical background is enough for us to follow the trains of thought that have led quantum mechanics to its greatest achievements.

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. In Sec. 3.6 we saw how a quite simple argument yields the energy levels of the system. Let us now tackle the same problem in a more formal way, which will give us the wave function ψ_n that corresponds to each energy level.

We may specify the particle's motion by saying that it is restricted to traveling along the x axis between $x = 0$ and $x = L$ by infintely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant. From a formal point of view the potential energy U of the particle is infinite on both sides of the box, while U is a constant—say 0 for convenience—on the inside (Fig. 5.4). Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function ψ is 0 for $x \leq 0$ and $x \geq L$. Our task is to find what ψ is within the box, namely, between $x = 0$ and $x = L$.

Within the box Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \qquad (5.37)$$

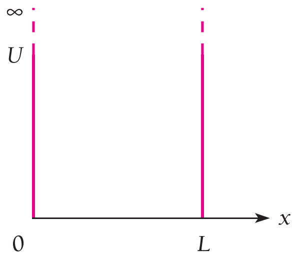


Figure 5.4 A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.

since $U = 0$ there. (The total derivative $d^2\psi/dx^2$ is the same as the partial derivative $\partial^2\psi/\partial x^2$ because ψ is a function only of x in this problem.) Equation (5.37) has the solution

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \tag{5.38}$$

which we can verify by substitution back into Eq. (5.37). A and B are constants to be evaluated.

This solution is subject to the boundary conditions that $\psi = 0$ for $x = 0$ and for $x = L$. Since $\cos 0 = 1$, the second term cannot describe the particle because it does not vanish at $x = 0$. Hence we conclude that $B = 0$. Since $\sin 0 = 0$, the sine term always yields $\psi = 0$ at $x = 0$, as required, but ψ will be 0 at $x = L$ only when

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \qquad n = 1, 2, 3, \ldots \tag{5.39}$$

This result comes about because the sines of the angles π, 2π, 3π, . . . are all 0.

From Eq. (5.39) it is clear that the energy of the particle can have only certain values, which are the eigenvalues mentioned in the previous section. These eigenvalues, constituting the **energy levels** of the system, are found by solving Eq. (5.39) for E_n, which gives

Particle in a box

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1, 2, 3, \ldots \tag{5.40}$$

Equation (5.40) is the same as Eq. (3.18) and has the same interpretation [see the discussion that follows Eq. (3.18) in Sec. 3.6].

Wave Functions

The wave functions of a particle in a box whose energies are E_n are, from Eq. (5.38) with $B = 0$,

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x \tag{5.41}$$

Substituting Eq. (5.40) for E_n gives

$$\psi_n = A \sin \frac{n\pi x}{L} \tag{5.42}$$

for the eigenfunctions corresponding to the energy eigenvalues E_n.

It is easy to verify that these eigenfunctions meet all the requirements discussed in Sec. 5.1: for each quantum number n, ψ_n is a finite, single-valued function of x, and ψ_n and $\partial\psi_n/\partial x$ are continuous (except at the ends of the box). Furthermore, the integral of $|\psi_n|^2$ over all space is finite, as we can see by integrating $|\psi_n|^2\,dx$ from $x = 0$ to $x = L$ (since the particle is confined within these limits). With the help of the trigonometric identity $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$ we find that

$$\begin{aligned}\int_{-\infty}^{\infty} |\psi_n|^2\,dx &= \int_0^L |\psi_n|^2\,dx = A^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right)dx\right] \\ &= \frac{A^2}{2}\left[x - \left(\frac{L}{2n\pi}\right)\sin\frac{2n\pi x}{L}\right]_0^L = A^2\left(\frac{L}{2}\right) \qquad (5.43)\end{aligned}$$

To normalize ψ we must assign a value to A such that $|\psi_n|^2\,dx$ is *equal* to the probability $P\,dx$ of finding the particle between x and $x + dx$, rather than merely proportional to $P\,dx$. If $|\psi_n|^2\,dx$ is to equal $P\,dx$, then it must be true that

$$\int_{-\infty}^{\infty} |\psi_n|^2\,dx = 1 \qquad (5.44)$$

Comparing Eqs. (5.43) and (5.44), we see that the wave functions of a particle in a box are normalized if

$$A = \sqrt{\frac{2}{L}} \qquad (5.45)$$

The normalized wave functions of the particle are therefore

Particle in a box

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n = 1, 2, 3, \ldots \qquad (5.46)$$

The normalized wave functions ψ_1, ψ_2, and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig. 5.5. Although ψ_n may be negative as well as positive, $|\psi_n|^2$ is never negative and, since ψ_n is normalized, its value at a given x is equal to the probability density of finding the particle there. In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, the boundaries of the box.

At a particular place in the box the probability of the particle being present may be very different for different quantum numbers. For instance, $|\psi_1|^2$ has its maximum value of $2/L$ in the middle of the box, while $|\psi_2|^2 = 0$ there. A particle in the lowest energy level of $n = 1$ is most likely to be in the middle of the box, while a particle in the next higher state of $n = 2$ is *never* there! Classical physics, of course, suggests the same probability for the particle being anywhere in the box.

The wave functions shown in Fig. 5.5 resemble the possible vibrations of a string fixed at both ends, such as those of the stretched string of Fig. 5.2. This follows from the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that when identical restrictions are placed upon each kind of wave, the formal results are identical.

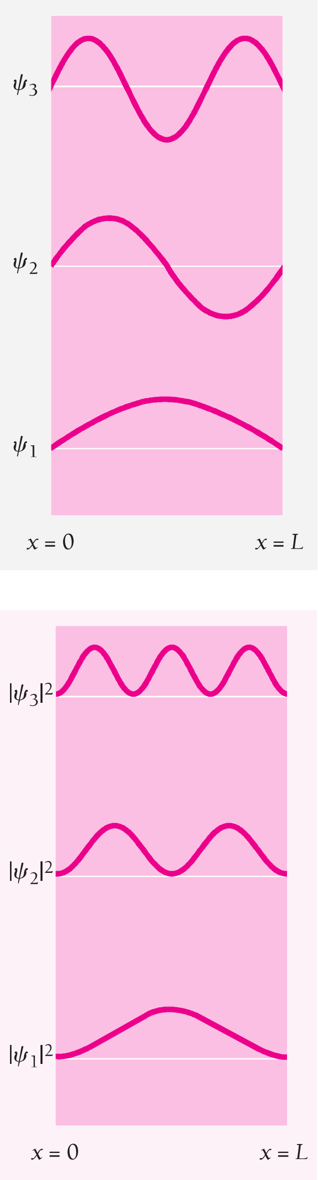


Figure 5.5 Wave functions and probability densities of a particle confined to a box with rigid walls.

Example 5.4

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.6). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.46) the probability of finding the particle between x_1 and x_2 when it is in the nth state is

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\psi_n|^2\,dx = \frac{2}{L}\int_{x_1}^{x_2} \sin^2\frac{n\pi x}{L}\,dx$$
$$= \left[\frac{x}{L} - \frac{1}{2n\pi}\sin\frac{2n\pi x}{L}\right]_{x_1}^{x_2}$$

Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1,x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have

$$P_{x_1,x_2} = 0.0065 = 0.65 \text{ percent}$$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

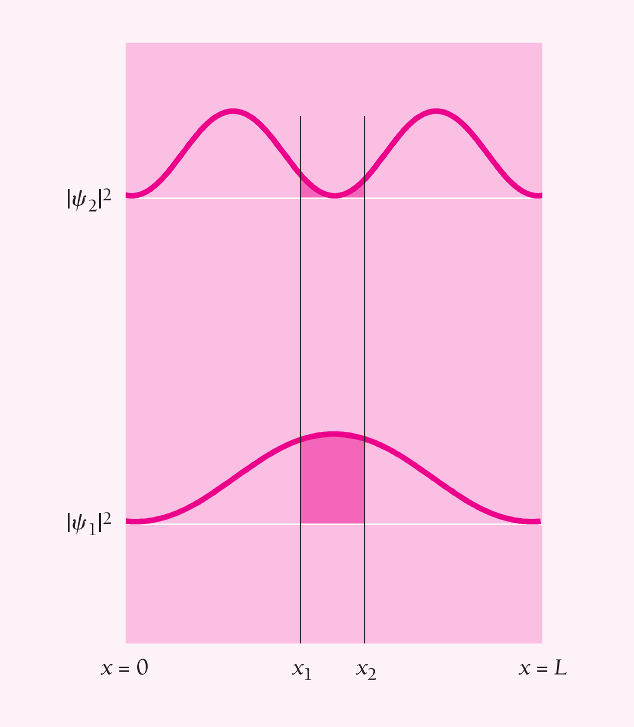


Figure 5.6 The probability P_{x_1,x_2} of finding a particle in the box of Fig. 5.5 between $x_1 = 0.45L$ and $x_2 = 0.55L$ is equal to the area under the $|\psi|^2$ curves between these limits.

Example 5.5

Find the expectation value $\langle x\rangle$ of the position of a particle trapped in a box L wide.

Solution

From Eqs. (5.19) and (5.46) we have

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2\,dx = \frac{2}{L}\int_0^L x\sin^2\frac{n\pi x}{L}\,dx$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2}\right]_0^L$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x\rangle = \frac{2}{L}\left(\frac{L^2}{4}\right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \ldots$ states because $\langle x\rangle$ is an *average*, not a probability, and it reflects the symmetry *of* $|\psi|^2$ about the middle of the box.

Momentum

Finding the momentum of a particle trapped in a one-dimensional box is not as straightforward as finding $\langle x\rangle$. Here

$$\psi^* = \psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$\frac{d\psi}{dx} = \sqrt{\frac{2}{L}}\frac{n\pi}{L}\cos\frac{n\pi x}{L}$$

and so, from Eq. (5.30),

$$\langle p\rangle = \int_{-\infty}^{\infty}\psi^*\hat{p}\psi\,dx = \int_{-\infty}^{\infty}\psi^*\left(\frac{\hbar}{i}\frac{d}{dx}\right)\psi\,dx$$

$$= \frac{\hbar}{i}\frac{2}{L}\frac{n\pi}{L}\int_0^L \sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}\,dx$$

We note that

$$\int \sin ax\cos ax\,dx = \frac{1}{2a}\sin^2 ax$$

With $a = n\pi/L$ we have

$$\langle p \rangle = \frac{\hbar}{iL}\left[\sin^2 \frac{n\pi x}{L}\right]_0^L = 0$$

since $$\sin^2 0 = \sin^2 n\pi = 0 \qquad n = 1, 2, 3, \ldots$$

The expectation value $\langle p \rangle$ of the particle's momentum is 0.

At first glance this conclusion seems strange. After all, $E = p^2/2m$, and so we would anticipate that

Momentum eigenvalues for trapped particle

$$p_n = \pm\sqrt{2mE_n} = \pm\frac{n\pi\hbar}{L} \tag{5.47}$$

The ± sign provides the explanation: The particle is moving back and forth, and so its *average* momentum for any value of n is

$$p_{\text{av}} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

which is the expectation value.

According to Eq. (5.47) there should be two momentum eigenfunctions for every energy eigenfunction, corresponding to the two possible directions of motion. The general procedure for finding the eigenvalues of a quantum-mechanical operator, here $\hat{p}$, is to start from the eigenvalue equation

$$\hat{p}\psi_n = p_n\psi_n \tag{5.48}$$

where each p_n is a real number. This equation holds only when the wave functions ψ_n are eigenfunctions of the momentum operator $\hat{p}$, which here is

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

We can see at once that the energy eigenfunctions

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

are not also momentum eigenfunctions, because

$$\frac{\hbar}{i}\frac{d}{dx}\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right) = \frac{\hbar}{i}\frac{n\pi}{L}\sqrt{\frac{2}{L}}\cos\frac{n\pi x}{L} \neq p_n\psi_n$$

To find the correct momentum eigenfunctions, we note that

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i}e^{i\theta} - \frac{1}{2i}e^{-i\theta}$$

Hence each energy eigenfunction can be expressed as a linear combination of the two wave functions

Momentum eigenfunctions for trapped particle

$$\psi_n^+ = \frac{1}{2i}\sqrt{\frac{2}{L}}\,e^{in\pi x/L} \tag{5.49}$$

$$\psi_n^- = \frac{1}{2i}\sqrt{\frac{2}{L}}\,e^{-in\pi x/L} \tag{5.50}$$

Inserting the first of these wave functions in the eigenvalue equation, Eq. (5.48), we have

$$\hat{p}\psi_n^+ = p_n^+\psi_n^+$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi_n^+ = \frac{\hbar}{i}\frac{1}{2i}\sqrt{\frac{2}{L}}\frac{in\pi}{L}e^{in\pi x/L} = \frac{n\pi\hbar}{L}\psi_n^+ = p_n^+\psi_n^+$$

so that

$$p_n^+ = +\frac{n\pi\hbar}{L} \tag{5.51}$$

Similarly the wave function ψ_n^- leads to the momentum eigenvalues

$$p_n^- = -\frac{n\pi\hbar}{L} \tag{5.52}$$

We conclude that ψ_n^+ and ψ_n^- are indeed the momentum eigenfunctions for a particle in a box, and that Eq. (5.47) correctly states the corresponding momentum eigenvalues.

5.9 FINITE POTENTIAL WELL

The wave function penetrates the walls, which lowers the energy levels

Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart. However, potential wells with barriers of finite height certainly do exist. Let us see what the wave functions and energy levels of a particle in such a well are.

Figure 5.7 shows a potential well with square corners that is U high and L wide and contains a particle whose energy E is less than U. According to classical mechanics, when the particle strikes the sides of the well, it bounces off without entering regions I and III. In quantum mechanics, the particle also bounces back and forth, but now it has a certain probability of penetrating into regions I and III even though $E < U$.

In regions I and III Schrödinger's steady-state equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

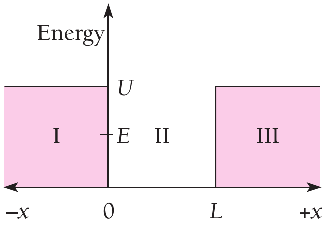


Figure 5.7 A square potential well with finite barriers. The energy E of the trapped particle is less than the height U of the barriers.

which we can rewrite in the more convenient form

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \qquad \begin{array}{l} x < 0 \\ x > L \end{array} \tag{5.53}$$

where

$$a = \frac{\sqrt{2m(U - E)}}{\hbar} \tag{5.54}$$

The solutions to Eq. (5.53) are real exponentials:

$$\psi_{\mathrm{I}} = Ce^{ax} + De^{-ax} \tag{5.55}$$

$$\psi_{\mathrm{III}} = Fe^{ax} + Ge^{-ax} \tag{5.56}$$

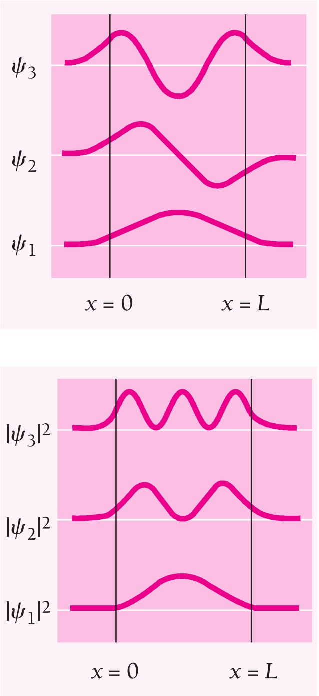


Figure 5.8 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

Both ψ_{I} and ψ_{III} must be finite everywhere. Since $e^{-ax} \to \infty$ as $x \to -\infty$ and $e^{ax} \to \infty$ as $x \to \infty$, the coefficients D and F must therefore be 0. Hence we have

$$\psi_{\mathrm{I}} = Ce^{ax} \tag{5.57}$$

$$\psi_{\mathrm{III}} = Ge^{-ax} \tag{5.58}$$

These wave functions decrease exponentially inside the barriers at the sides of the well.

Within the well Schrödinger's equation is the same as Eq. (5.37) and its solution is again

$$\psi_{\mathrm{II}} = A \sin\frac{\sqrt{2mE}}{\hbar}x + B \cos\frac{\sqrt{2mE}}{\hbar}x \tag{5.59}$$

In the case of a well with infinitely high barriers, we found that $B = 0$ in order that $\psi = 0$ at $x = 0$ and $x = L$. Here, however, $\psi_{\mathrm{II}} = C$ at $x = 0$ and $\psi_{\mathrm{II}} = G$ at $x = L$, so both the sine and cosine solutions of Eq. (5.59) are possible.

For either solution, both ψ and $d\psi/dx$ must be continuous at $x = 0$ and $x = L$: the wave functions inside and outside each side of the well must not only have the same value where they join but also the same slopes, so they match up perfectly. When these boundary conditions are taken into account, the result is that exact matching only occurs for certain specific values E_n of the particle energy. The complete wave functions and their probability densities are shown in Fig. 5.8.

Because the wavelengths that fit into the well are longer than for an infinite well of the same width (see Fig. 5.5), the corresponding particle momenta are lower (we recall that $\lambda = h/p$). Hence the energy levels E_n are lower for each n than they are for a particle in an infinite well.

5.10 TUNNEL EFFECT

A particle without the energy to pass over a potential barrier may still tunnel through it

Although the walls of the potential well of Fig. 5.7 were of finite height, they were assumed to be infinitely thick. As a result the particle was trapped forever even though it could penetrate the walls. We next look at the situation of a particle that strikes a potential barrier of height U, again with $E < U$, but here the barrier has a finite width (Fig. 5.9). What we will find is that the particle has a certain probability—not

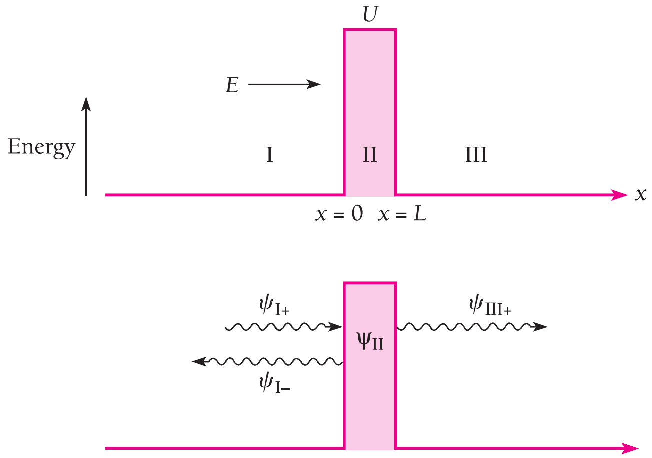


Figure 5.9 When a particle of energy $E < U$ approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.

necessarily great, but not zero either—of passing through the barrier and emerging on the other side. The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it, so to speak. Not surprisingly, the higher the barrier and the wider it is, the less the chance that the particle can get through.

The **tunnel effect** actually occurs, notably in the case of the alpha particles emitted by certain radioactive nuclei. As we shall learn in Chap. 12, an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high. The probability of escape is so small that the alpha particle might have to strike the wall 10^{38} or more times before it emerges, but sooner or later it does get out. Tunneling also occurs in the operation of certain semiconductor diodes (Sec. 10.7) in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

Let us consider a beam of identical particles all of which have the kinetic energy E. The beam is incident from the left on a potential barrier of height U and width L, as in Fig. 5.9. On both sides of the barrier $U = 0$, which means that no forces act on the particles there. The wave function $\psi_{\mathrm{I}+}$ represents the incoming particles moving to the right and $\psi_{\mathrm{I}-}$ represents the reflected particles moving to the left; ψ_{III} represents the transmitted particles moving to the right. The wave function ψ_{II} represents the particles inside the barrier, some of which end up in region III while the others return to region I. The transmission probability T for a particle to pass through the barrier is equal to the fraction of the incident beam that gets through the barrier. This probability is calculated in the Appendix to this chapter. Its approximate value is given by

Approximate transmission probability

$$T = e^{-2k_2 L} \tag{5.60}$$

where

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \tag{5.61}$$

and L is the width of the barrier.

Example 5.6

Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50 nm wide. (*a*) Find their respective transmission probabilities. (*b*) How are these affected if the barrier is doubled in width?

Solution

(*a*) For the 1.0-eV electrons

$$
\begin{aligned}
k_2 &= \frac{\sqrt{2m(U - E)}}{\hbar} \\
&= \frac{\sqrt{(2)(9.1 \times 10^{-31}\ \text{kg})[(10.0 - 1.0)\ \text{eV}](1.6 \times 10^{-19}\ \text{J/eV})}}{1.054 \times 10^{-34}\ \text{J} \cdot \text{s}} \\
&= 1.6 \times 10^{10}\ \text{m}^{-1}
\end{aligned}
$$

Since $L = 0.50\ \text{nm} = 5.0 \times 10^{-10}\ \text{m}$, $2k_2L = (2)(1.6 \times 10^{10}\ \text{m}^{-1})(5.0 \times 10^{-10}\ \text{m}) = 16$, and the approximate transmission probability is

$$T_1 = e^{-2k_2L} = e^{-16} = 1.1 \times 10^{-7}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average. For the 2.0-eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$. These electrons are over twice as likely to tunnel through the barrier.

(*b*) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T_1' = 1.3 \times 10^{-14} \qquad T_2' = 5.1 \times 10^{-14}$$

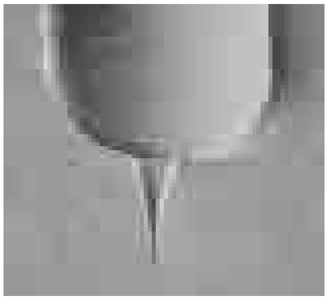
Evidently T is more sensitive to the width of the barrier than to the particle energy here.

Scanning Tunneling Microscope

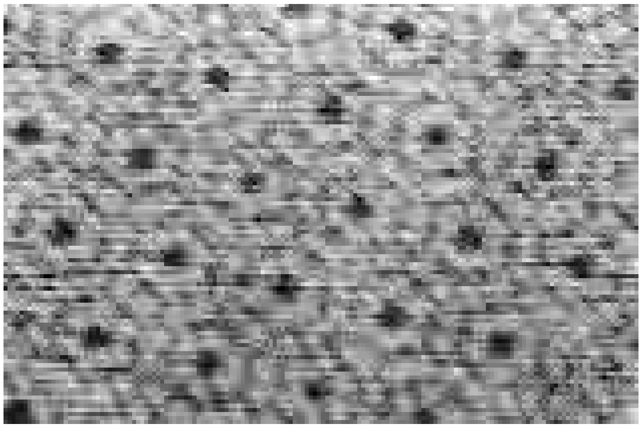
The ability of electrons to tunnel through a potential barner is used in an ingenious way in the **scanning tunneling microscope** (STM) to study surfaces on an atomic scale of size. The STM was invented in 1981 by Gert Binning and Heinrich Rohrer, who shared the 1986 Nobel Prize in physics with Ernst Ruska, the inventor of the electron microscope. In an STM, a metal probe with a point so fine that its tip is a single atom is brought close to the surface of a conducting or semiconducting material. Normally even the most loosely bound electrons in an atom on a surface need several electron-volts of energy to escape—this is the work function discussed in Chap. 2 in connection with the photoelectric effect. However, when a voltage of only 10 mV or so is applied between the probe and the surface, electrons can tunnel across the gap between them if the gap is small enough, a nanometer or two.

According to Eq. (5.60) the electron transmission probability is proportional to e^{-L}, where L is the gap width, so even a small change in L (as little as 0.01 nm, less than a twentieth the diameter of most atoms) means a detectable change in the tunneling current. What is done is to move the probe across the surface in a series of closely spaced back-and-forth scans in about the same way an electron beam traces out an image on the screen of a television picture tube. The height of the probe is continually adjusted to give a constant tunneling current, and the adjustments are recorded so that a map of surface height versus position is built up. Such a map is able to resolve individual atoms on a surface.

How can the position of the probe be controlled precisely enough to reveal the outlines of individual atoms? The thickness of certain ceramics changes when a voltage is applied across them, a property called **piezoelectricity.** The changes might be several tenths of a nanometer per volt. In an STM, piezoelectric controls move the probe in x and y directions across a surface and in the z direction perpendicular to the surface.



The tungsten probe of a scanning tunneling microscope.



Silicon atoms on the surface of a silicon crystal form a regular, repeated pattern in this image produced by an STM.

Actually, the result of an STM scan is not a true topographical map of surface height but a contour map of constant electron density on the surface. This means that atoms of different elements appear differently, which greatly increases the value of the STM as a research tool.

Although many biological materials conduct electricity, they do so by the flow of ions rather than of electrons and so cannot be studied with STMs. A more recent development, the **atomic force microscope** (AFM) can be used on any surface, although with somewhat less resolution than an STM. In an AFM, the sharp tip of a fractured diamond presses gently against the atoms on a surface. A spring keeps the pressure of the tip constant, and a record is made of the deflections of the tip as it moves across the surface. The result is a map showing contours of constant repulsive force between the electrons of the probe and the electrons of the surface atoms. Even relatively soft biological materials can be examined with an AFM and changes in them monitored. For example, the linking together of molecules of the blood protein fibrin, which occurs when blood clots, has been watched with an AFM.

5.11 HARMONIC OSCILLATOR

Its energy levels are evenly spaced

Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be an object supported by a spring or floating in a liquid, a diatomic molecule, an atom in a crystal lattice—there are countless examples on all scales of size. The condition for harmonic motion is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed. The inertia of the masses involved causes them to overshoot equilibrium, and the system oscillates indefinitely if no energy is lost.

In the special case of simple harmonic motion, the restoring force F on a particle of mass m is linear; that is, F is proportional to the particle's displacement x from its equilibrium position and in the opposite direction. Thus

Hooke's law

$$F = -kx$$

This relationship is customarily called Hooke's law. From the second law of motion, $\mathbf{F} = m\mathbf{a}$, we have

$$-kx = m\frac{d^2x}{dt^2}$$

Harmonic oscillator

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \tag{5.62}$$

There are various ways to write the solution to Eq. (5.62). A common one is

$$x = A\cos(2\pi\nu t + \phi) \tag{5.63}$$

where

Frequency of harmonic oscillator

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{5.64}$$

is the frequency of the oscillations and A is their amplitude. The value of ϕ, the phase angle, depends upon what x is at the time $t = 0$ and on the direction of motion then.

The importance of the simple harmonic oscillator in both classical and modern physics lies not in the strict adherence of actual restoring forces to Hooke's law, which is seldom true, but in the fact that these restoring forces reduce to Hooke's law for small displacements x. As a result, any system in which something executes small vibrations about an equilibrium position behaves very much like a simple harmonic oscillator.

To verify this important point, we note that any restoring force which is a function of x can be expressed in a Maclaurin's series about the equilibrium position $x = 0$ as

$$F(x) = F_{x=0} + \left(\frac{dF}{dx}\right)_{x=0} x + \frac{1}{2}\left(\frac{d^2F}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3F}{dx^3}\right)_{x=0} x^3 + \cdots$$

Since $x = 0$ is the equilibrium position, $F_{x=0} = 0$. For small x the values of $x^2, x^3, \ldots$ are very small compared with x, so the third and higher terms of the series can be neglected. The only term of significance when x is small is therefore the second one. Hence

$$F(x) = \left(\frac{dF}{dx}\right)_{x=0} x$$

which is Hooke's law when $(dF/dx)_{x=0}$ is negative, as of course it is for any restoring force. The conclusion, then, is that *all* oscillations are simple harmonic in character when their amplitudes are sufficiently small.

The potential-energy function $U(x)$ that corresponds to a Hooke's law force may be found by calculating the work needed to bring a particle from $x = 0$ to $x = x$ against such a force. The result is

$$U(x) = -\int_0^x F(x)\,dx = k\int_0^x x\,dx = \frac{1}{2}kx^2 \tag{5.65}$$

which is plotted in Fig. 5.10. The curve of $U(x)$ versus x is a parabola. If the energy of the oscillator is E, the particle vibrates back and forth between $x = -A$ and $x = +A$, where E and A are related by $E = \frac{1}{2}kA^2$. Figure 8.18 shows how a nonparabolic potential energy curve can be approximated by a parabola for small displacements.

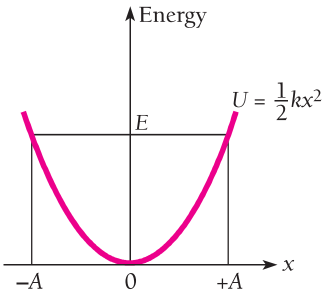


Figure 5.10 The potential energy of a harmonic oscillator is proportional to x^2, where x is the displacement from the equilibrium position. The amplitude A of the motion is determined by the total energy E of the oscillator, which classically can have any value.

Even before we make a detailed calculation we can anticipate three quantum-mechanical modifications to this classical picture:

1 The allowed energies will not form a continuous spectrum but instead a discrete spectrum of certain specific values only.
2 The lowest allowed energy will not be $E = 0$ but will be some definite minimum $E = E_0$.
3 There will be a certain probability that the particle can penetrate the potential well it is in and go beyond the limits of $-A$ and $+A$.

Energy Levels

Schrödinger's equation for the harmonic oscillator is, with $U = \frac{1}{2}kx^2$,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \tag{5.66}$$

It is convenient to simplify Eq. (5.75) by introducing the dimensionless quantities

$$y = \left(\frac{1}{\hbar}\sqrt{km}\right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}}\,x \tag{5.67}$$

and

$$\alpha = \frac{2E}{\hbar}\sqrt{\frac{m}{k}} = \frac{2E}{h\nu} \tag{5.68}$$

where ν is the classical frequency of the oscillation given by Eq. (5.64). In making these substitutions, what we have done is change the units in which x and E are expressed from meters and joules, respectively, to dimensionless units.

In terms of y and α Schrödinger's equation becomes

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0 \tag{5.69}$$

The solutions to this equation that are acceptable here are limited by the condition that $\psi \rightarrow 0$ as $y \rightarrow \infty$ in order that

$$\int_{-\infty}^{\infty} |\psi|^2\, dy = 1$$

Otherwise the wave function cannot represent an actual particle. The mathematical properties of Eq. (5.69) are such that this condition will be fulfilled only when

$$\alpha = 2n + 1 \qquad n = 0, 1, 2, 3, \ldots$$

Since $\alpha = 2E/h\nu$ according to Eq. (5.68), the energy levels of a harmonic oscillator whose classical frequency of oscillation is ν are given by the formula

Energy levels of harmonic oscillator

$$E_n = (n + \tfrac{1}{2})h\nu \qquad n = 0, 1, 2, 3, \ldots \tag{5.70}$$

The energy of a harmonic oscillator is thus quantized in steps of $h\nu$.

We note that when $n = 0$,

Zero-point energy

$$E_0 = \tfrac{1}{2}h\nu \tag{5.71}$$

which is the lowest value the energy of the oscillator can have. This value is called the **zero-point energy** because a harmonic oscillator in equilibrium with its surroundings would approach an energy of $E = E_0$ and not $E = 0$ as the temperature approaches 0 K.

Figure 5.11 is a comparison of the energy levels of a harmonic oscillator with those of a hydrogen atom and of a particle in a box with infinitely hard walls. The shapes of the respective potential-energy curves are also shown. The spacing of the energy levels is constant only for the harmonic oscillator.

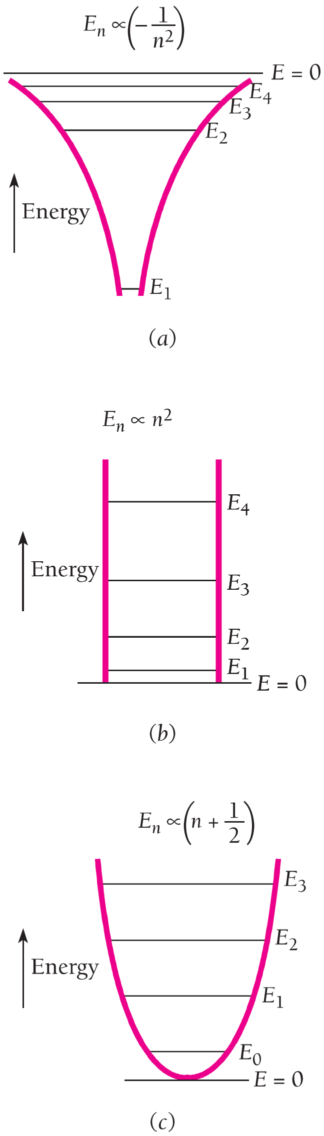


Figure 5.11 Potential wells and energy levels of (*a*) a hydrogen atom, (*b*) a particle in a box, and (*c*) a harmonic oscillator. In each case the energy levels depend in a different way on the quantum number *n*. Only for the harmonic oscillator are the levels equally spaced. The symbol ∝ means "is proportional to."

Wave Functions

For each choice of the parameter α_n there is a different wave function ψ_n. Each function consists of a polynomial $H_n(y)$ (called a **Hermite polynomial**) in either odd or even powers of y, the exponential factor $e^{-y^2/2}$, and a numerical coefficient which is needed for ψ_n to meet the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n|^2\, dy = 1 \qquad n = 0, 1, 2 \ldots$$

The general formula for the *n*th wave function is

Harmonic oscillator

$$\psi_n = \left(\frac{2m\nu}{\hbar}\right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2} \tag{5.72}$$

The first six Hermite polynomials $H_n(y)$ are listed in Table 5.2.

The wave functions that correspond to the first six energy levels of a harmonic oscillator are shown in Fig. 5.12. In each case the range to which a particle oscillating classically with the same total energy E_n would be confined is indicated. Evidently the particle is able to penetrate into classically forbidden regions—in other words, to exceed the amplitude A determined by the energy—with an exponentially decreasing probability, just as in the case of a particle in a finite square potential well.

It is interesting and instructive to compare the probability densities of a classical harmonic oscillator and a quantum-mechanical harmonic oscillator of the same energy. The upper curves in Fig. 5.13 show this density for the classical oscillator. The probability P of finding the particle at a given position is greatest at the endpoints of its motion,

Table 5.2 Some Hermite Polynomials

n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}h\nu$
1	$2y$	3	$\frac{3}{2}h\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}h\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}h\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}h\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}h\nu$

where it moves slowly, and least near the equilibrium position ($x = 0$), where it moves rapidly.

Exactly the opposite behavior occurs when a quantum-mechanical oscillator is in its lowest energy state of $n = 0$. As shown, the probability density $|\psi_0|^2$ has its maximum value at $x = 0$ and drops off on either side of this position. However, this disagreement becomes less and less marked with increasing n. The lower graph of Fig. 5.13 corresponds to $n = 10$, and it is clear that $|\psi_{10}|^2$ when averaged over x has approximately the general character of the classical probability P. This is another example of the correspondence principle mentioned in Chap. 4: In the limit of large quantum numbers, quantum physics yields the same results as classical physics.

It might be objected that although $|\psi_{10}|^2$ does indeed approach P when smoothed out, nevertheless $|\psi_{10}|^2$ fluctuates rapidly with x whereas P does not. However, this objection has meaning only if the fluctuations are observable, and the smaller the spacing of the peaks and hollows, the more difficult it is to detect them experimentally. The exponential "tails" of $|\psi_{10}|^2$ beyond $x = \pm A$ also decrease in magnitude with increasing n. Thus the classical and quantum pictures begin to resemble each other more and more the larger the value of n, in agreement with the correspondence principle, although they are very different for small n.

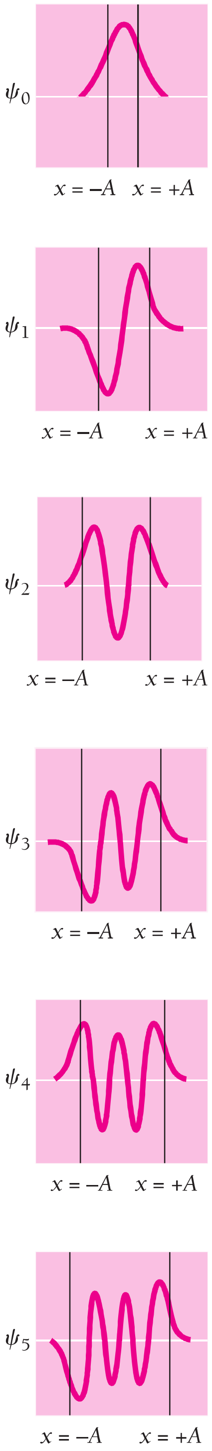


Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits $-A$ and $+A$ between which a classical oscillator with the same energy would vibrate.

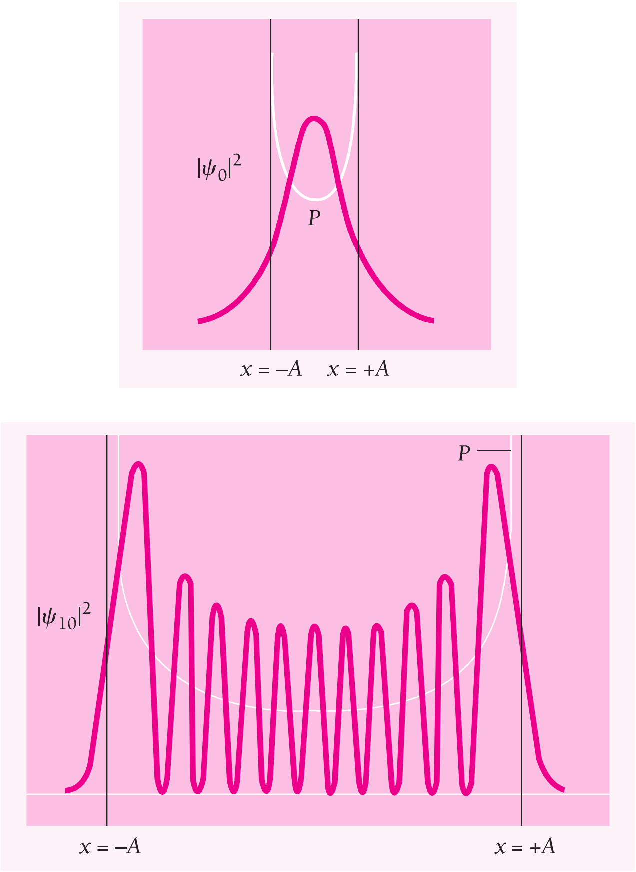


Figure 5.13 Probability densities for the $n = 0$ and $n = 10$ states of a quantum-mechanical harmonic oscillator. The probability densities for classical harmonic oscillators with the same energies are shown in white. In the $n = 10$ state, the wavelength is shortest at $x = 0$ and longest at $x = -A$.

Example 5.7

Find the expectation value $\langle x \rangle$ for the first two states of a harmonic oscillator.

Solution

The general formula for $\langle x \rangle$ is

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\psi|^2\,dx$$

In calculations such as this it is easier to begin with y in place of x and afterward use Eq. (5.67) to change to x. From Eq. (5.72) and Table 5.2,

$$\psi_0 = \left(\frac{2m\nu}{\hbar}\right)^{1/4} e^{-y^2/2}$$

$$\psi_1 = \left(\frac{2m\nu}{\hbar}\right)^{1/4}\left(\frac{1}{2}\right)^{1/2}(2y)\,e^{-y^2/2}$$

The values of $\langle x \rangle$ for $n = 0$ and $n = 1$ will respectively be proportional to the integrals

$$n = 0\text{:} \int_{-\infty}^{\infty} y|\psi_0|^2\,dy = \int_{-\infty}^{\infty} ye^{-y^2}\,dy = -\left[\frac{1}{2}e^{-y^2}\right]_{-\infty}^{\infty} = 0$$

$$n = 1\text{:} \int_{-\infty}^{\infty} y|\psi_1|^2\,dy = \int_{-\infty}^{\infty} y^3e^{-y^2}\,dy = -\left[\left(\frac{1}{4} + \frac{y^2}{2}\right)e^{-y^2}\right]_{-\infty}^{\infty} = 0$$

The expectation value $\langle x \rangle$ is therefore 0 in both cases. In fact, $\langle x \rangle = 0$ for *all* states of a harmonic oscillator, which could be predicted since $x = 0$ is the equilibrium position of the oscillator where its potential energy is a minimum.

Appendix to Chapter 5

The Tunnel Effect

We consider the situation that was shown in Fig. 5.9 of a particle of energy $E < U$ that approaches a potential barrier U high and L wide. Outside the barrier in regions I and III Schrödinger's equation for the particle takes the forms

$$\frac{d^2\psi_{\mathrm{I}}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{\mathrm{I}} = 0 \tag{5.73}$$

$$\frac{d^2\psi_{\mathrm{III}}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{\mathrm{III}} = 0 \tag{5.74}$$

The solutions to these equations that are appropriate here are

$$\psi_{\mathrm{I}} = Ae^{ik_1x} + Be^{-ik_1x} \tag{5.75}$$

$$\psi_{\mathrm{III}} = Fe^{ik_1x} + Ge^{-ik_1x} \tag{5.76}$$

where

Wave number outside barrier

$$k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} \tag{5.77}$$

is the wave number of the de Broglie waves that represent the particles outside the barrier.

Because

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{-i\theta} = \cos\theta - i\sin\theta$$

these solutions are equivalent to Eq. (5.38)—the values of the coefficients are different in each case, of course—but are in a more suitable form to describe particles that are not trapped.

The various terms in Eqs. (5.75) and (5.76) are not hard to interpret. As was shown schematically in Fig. 5.9, Ae^{ik_1x} is a wave of amplitude A incident from the left on the barrier. Hence we can write

Incoming wave

$$\psi_{\mathrm{I}+} = Ae^{ik_1x} \tag{5.78}$$

This wave corresponds to the incident beam of particles in the sense that $|\psi_{\mathrm{I}+}|^2$ is their probability density. If $v_{\mathrm{I}+}$ is the group velocity of the incoming wave, which equals the velocity of the particles, then

$$S = |\psi_{\mathrm{I}+}|^2 v_{\mathrm{I}+}$$

is the flux of particles that arrive at the barrier. That is, S is the number of particles per second that arrive there.

At $x = 0$ the incident wave strikes the barrier and is partially reflected, with

Reflected wave
$$\psi_{\mathrm{I}-} = Be^{-ik_1x} \tag{5.79}$$

representing the reflected wave. Hence

$$\psi_{\mathrm{I}} = \psi_{\mathrm{I}+} + \psi_{\mathrm{I}-} \tag{5.80}$$

On the far side of the barrier ($x > L$) there can only be a wave

Transmitted wave
$$\psi_{\mathrm{III}+} = Fe^{ik_1x} \tag{5.81}$$

traveling in the $+x$ direction at the velocity $\boldsymbol{v}_{\mathrm{III}+}$ since region III contains nothing that could reflect the wave. Hence $G = 0$ and

$$\psi_{\mathrm{III}} = \psi_{\mathrm{III}+} = Fe^{ik_1x} \tag{5.82}$$

The transmission probability T for a particle to pass through the barrier is the ratio

Transmission probability
$$T = \frac{|\psi_{\mathrm{III}+}|^2\boldsymbol{v}_{\mathrm{III}+}}{|\psi_{\mathrm{I}+}|^2\boldsymbol{v}_{\mathrm{I}+}} = \frac{FF^*\boldsymbol{v}_{\mathrm{III}+}}{AA^*\boldsymbol{v}_{\mathrm{I}+}} \tag{5.83}$$

between the flux of particles that emerges from the barrier and the flux that arrives at it. In other words, T is the fraction of incident particles that succeed in tunneling through the barrier. Classically $T = 0$ because a particle with $E < U$ cannot exist inside the barrier; let us see what the quantum-mechanical result is.

In region II Schrödinger's equation for the particles is

$$\frac{d^2\psi_{\mathrm{II}}}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi_{\mathrm{II}} = \frac{d^2\psi_{\mathrm{II}}}{dx^2} - \frac{2m}{\hbar^2}(U - E)\psi_{\mathrm{II}} = 0 \tag{5.84}$$

Since $U > E$ the solution is

Wave function inside barrier
$$\psi_{\mathrm{II}} = Ce^{-k_2x} + De^{k_2x} \tag{5.85}$$

where the wave number inside the barrier is

Wave number inside barrier
$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \tag{5.86}$$

Since the exponents are real quantities, ψ_{II} does not oscillate and therefore does not represent a moving particle. However, the probability density $|\psi_{\mathrm{II}}|^2$ is not zero, so there is a finite probability of finding a particle within the barrier. Such a particle may emerge into region III or it may return to region I.

Applying the Boundary Conditions

In order to calculate the transmission probability T we have to apply the appropriate boundary conditions to ψ_{I}, ψ_{II}, and ψ_{III}. Fig. 5.14 shows the wave functions in regions I, II, and III. As discussed earlier, both ψ and its derivative $\partial\psi/\partial x$ must be continuous everywhere. With reference to Fig. 5.14, these conditions mean that for a perfect fit at each side of the barrier, the wave functions inside and outside must have the same value and the same slope. Hence at the left-hand side of the barrier

Boundary conditions at $x = 0$

$$\left.\begin{aligned} \psi_{\mathrm{I}} &= \psi_{\mathrm{II}} && (5.87)\\ \frac{d\psi_{\mathrm{I}}}{dx} &= \frac{d\psi_{\mathrm{II}}}{dx} && (5.88)\end{aligned}\right\} x = 0$$

and at the right-hand side

Boundary conditions at $x = L$

$$\left.\begin{aligned} \psi_{\mathrm{II}} &= \psi_{\mathrm{III}} && (5.89)\\ \frac{d\psi_{\mathrm{II}}}{dx} &= \frac{d\psi_{\mathrm{III}}}{dx} && (5.90)\end{aligned}\right\} x = L$$

Now we substitute ψ_{I}, ψ_{II}, and ψ_{III} from Eqs. (5.75), (5.81), and (5.85) into the above equations. This yields in the same order

$$A + B = C + D \tag{5.91}$$

$$ik_1A - ik_1B = -k_2C + k_2D \tag{5.92}$$

$$Ce^{-k_2L} + De^{k_2L} = Fe^{ik_1L} \tag{5.93}$$

$$-k_2Ce^{-k_2L} + k_2De^{k_2L} = ik_1Fe^{ik_1L} \tag{5.94}$$

Equations (5.91) to (5.94) may be solved for (A/F) to give

$$\left(\frac{A}{F}\right) = \left[\frac{1}{2} + \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right]e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right]e^{(ik_1-k_2)L} \tag{5.95}$$

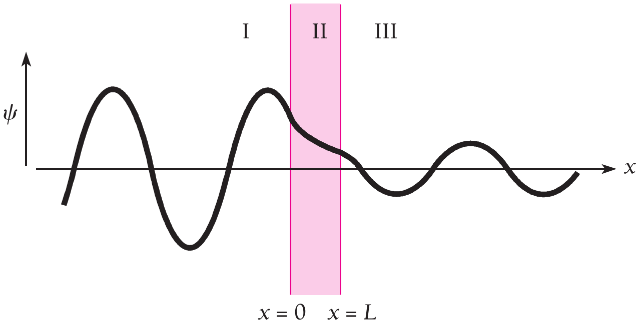


Figure 5.14 At each wall of the barrier, the wave functions inside and outside it must match up perfectly, which means that they must have the same values and slopes there.

Let us assume that the potential barrier U is high relative to the energy E of the incident particles. If this is the case, then $k_2/k_1 > k_1/k_2$ and

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1} \tag{5.96}$$

Let us also assume that the barrier is wide enough for ψ_{II} to be severely weakened between $x = 0$ and $x = L$. This means that $k_2L \gg 1$ and

$$e^{k_2L} \gg e^{-k_2L}$$

Hence Eq. (5.95) can be approximated by

$$\left(\frac{A}{F}\right) = \left(\frac{1}{2} + \frac{ik_2}{4k_1}\right) e^{(ik_1+k_2)L} \tag{5.97}$$

The complex conjugate of (A/F), which we need to compute the transmission probability T, is found by replacing i by $-i$ wherever it occurs in (A/F):

$$\left(\frac{A}{F}\right)^* = \left(\frac{1}{2} - \frac{ik_2}{4k_1}\right) e^{(-ik_1+k_2)L} \tag{5.98}$$

Now we multiply (A/F) and $(A/F)^*$ to give

$$\frac{AA^*}{FF^*} = \left(\frac{1}{4} + \frac{k_2^2}{16k_1^2}\right) e^{2k_2L}$$

Here $\boldsymbol{v}_{\text{III}+} = \boldsymbol{v}_{\text{I}+}$ so $\boldsymbol{v}_{\text{III}+}/\boldsymbol{v}_{\text{I}+} = 1$ in Eq. (5.83), which means that the transmission probability is

Transmission probability

$$T = \frac{FF^*\boldsymbol{v}_{\text{III}+}}{AA^*\boldsymbol{v}_{\text{I}+}} = \left(\frac{AA^*}{FF^*}\right)^{-1} = \left[\frac{16}{4 + (k_2/k_1)^2}\right] e^{-2k_2L} \tag{5.99}$$

From the definitions of k_1, Eq. (5.77), and of k_2, Eq. (5.86), we see that

$$\left(\frac{k_2}{k_1}\right)^2 = \frac{2m(U-E)/\hbar^2}{2mE/\hbar^2} = \frac{U}{E} - 1 \tag{5.100}$$

This formula means that the quantity in brackets in Eq. (5.99) varies much less with E and U than does the exponential. The bracketed quantity, furthermore, always is of the order of magnitude of 1 in value. A reasonable approximation of the transmission probability is therefore

Approximate transmission probability

$$T = e^{-2k_2L} \tag{5.101}$$

as stated in Sec. 5.10.

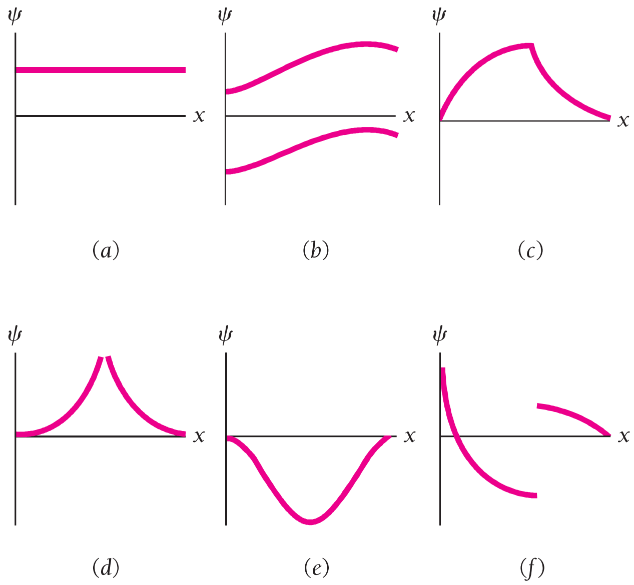
EXERCISES

Press on, and faith will catch up with you. —Jean D'Alembert

5.1 Quantum Mechanics

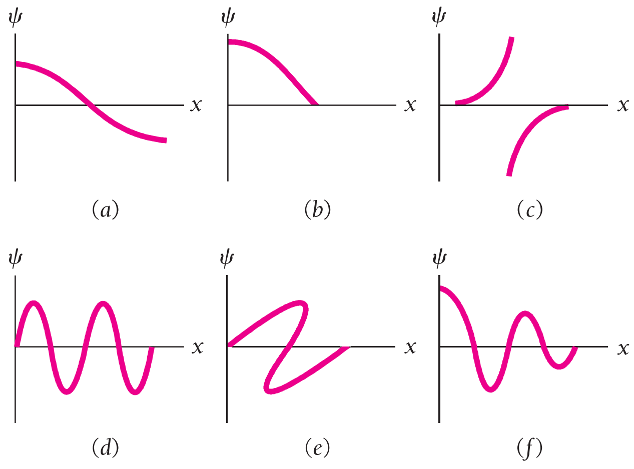
1. Which of the wave functions in Fig. 5.15 cannot have physical significance in the interval shown? Why not?

2. Which of the wave functions in Fig. 5.16 cannot have physical significance in the interval shown? Why not?



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 5.15



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 5.16

3. Which of the following wave functions cannot be solutions of Schrödinger's equation for all values of x? Why not? (*a*) $\psi = A \sec x$; (*b*) $\psi = A \tan x$; (*c*) $\psi = Ae^{x^2}$; (*d*) $\psi = Ae^{-x^2}$.

4. Find the value of the normalization constant A for the wave function $\psi = Axe^{-x^2/2}$.

5. The wave function of a certain particle is $\psi = A\cos^2 x$ for $-\pi/2 < x < \pi/2$. (*a*) Find the value of A. (*b*) Find the probability that the particle be found between $x = 0$ and $x = \pi/4$.

5.2 The Wave Equation

6. The formula $y = A\cos\omega(t - x/v)$, as we saw in Sec. 3.3, describes a wave that moves in the $+x$ direction along a stretched string. Show that this formula is a solution of the wave equation, Eq.(5.3).

7. As mentioned in Sec. 5.1, in order to give physically meaningful results in calculations a wave function and its partial derivatives must be finite, continuous, and single-valued, and in addition must be normalizable. Equation (5.9) gives the wave function of a particle moving freely (that is, with no forces acting on it) in the $+x$ direction as

$$\Psi = Ae^{-(i/\hbar)(Et-px)}$$

where E is the particle's total energy and p is its momentum. Does this wave function meet all the above requirements? If not, could a linear superposition of such wave functions meet these requirements? What is the significance of such a superposition of wave functions?

5.4 Linearity and Superposition

8. Prove that Schrödinger's equation is linear by showing that

$$\Psi = a_1\Psi_1(x, t) + a_2\Psi_2(x, t)$$

is also a solution of Eq. (5.14) if Ψ_1 and Ψ_2 are themselves solutions.

5.6 Operators

9. Show that the expectation values $\langle px\rangle$ and $\langle xp\rangle$ are related by

$$\langle px\rangle - \langle xp\rangle = \frac{\hbar}{i}$$

This result is described by saying that p and x do not **commute** and it is intimately related to the uncertainty principle.

10. An eigenfunction of the operator d^2/dx^2 is $\sin nx$, where $n = 1, 2, 3, \ldots$. Find the corresponding eigenvalues.

5.7 Schrödinger's Equation: Steady-State Form

11. Obtain Schrödinger's steady-state equation from Eq. (3.5) with the help of de Broglie's relationship $\lambda = h/mv$ by letting $y = \psi$ and finding $\partial^2\psi/\partial x^2$.

5.8 Particle in a Box

12. According to the correspondence principle, quantum theory should give the same results as classical physics in the limit of large quantum numbers. Show that as $n \to \infty$, the probability of finding the trapped particle of Sec. 5.8 between x and $x + \Delta x$ is $\Delta x/L$ and so is independent of x, which is the classical expectation.

13. One of the possible wave functions of a particle in the potential well of Fig. 5.17 is sketched there. Explain why the wavelength and amplitude of ψ vary as they do.

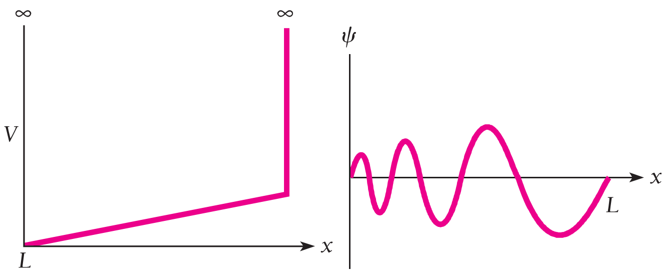


Figure 5.17

14. In Sec. 5.8 a box was considered that extends from $x = 0$ to $x = L$. Suppose the box instead extends from $x = x_0$ to $x = x_0 + L$, where $x_0 \neq 0$. Would the expression for the wave functions of a particle in this box be any different from those in the box that extends from $x = 0$ to $x = L$? Would the energy levels be different?

15. An important property of the eigenfunctions of a system is that they are **orthogonal** to one another, which means that

$$\int_{-\infty}^{\infty} \psi_n \psi_m \, dV = 0 \qquad n \neq m$$

Verify this relationship for the eigenfunctions of a particle in a one-dimensional box given by Eq. (5.46).

16. A rigid-walled box that extends from $-L$ to L is divided into three sections by rigid interior walls at $-x$ and x, where $x < L$. Each section contains one particle in its ground state. (*a*) What is the total energy of the system as a function of x? (*b*) Sketch $E(x)$ versus x. (*c*) At what value of x is $E(x)$ a minimum?

17. As shown in the text, the expectation value $\langle x \rangle$ of a particle trapped in a box L wide is $L/2$, which means that its average position is the middle of the box. Find the expectation value $\langle x^2 \rangle$.

18. As noted in Exercise 8, a linear combination of two wave functions for the same system is also a valid wave function. Find the normalization constant B for the combination

$$\psi = B\left(\sin\frac{\pi x}{L} + \sin\frac{2\pi x}{L}\right)$$

of the wave functions for the $n = 1$ and $n = 2$ states of a particle in a box L wide.

19. Find the probability that a particle in a box L wide can be found between $x = 0$ and $x = L/n$ when it is in the nth state.

20. In Sec. 3.7 the standard deviation σ of a set of N measurements of some quantity x was defined as

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - x_0)^2}$$

(*a*) Show that, in terms of expectation values, this formula can be written as

$$\sigma = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

(*b*) If the uncertainty in position of a particle in a box is taken as the standard deviation, find the uncertainty in the expectation value $\langle x \rangle = L/2$ for $n = 1$. (*c*) What is the limit of Δx as n increases?

21. A particle is in a cubic box with infinitely hard walls whose edges are L long (Fig. 5.18). The wave functions of the particle are given by

$$\psi = A \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L} \qquad \begin{aligned} n_x &= 1, 2, 3, \ldots \\ n_y &= 1, 2, 3, \ldots \\ n_z &= 1, 2, 3, \ldots \end{aligned}$$

Find the value of the normalization constant A.

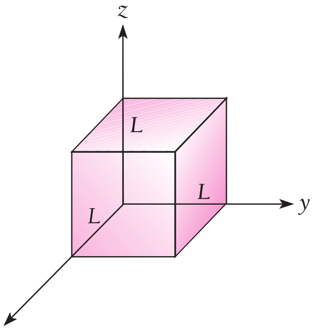


Figure 5.18 A cubic box.

22. The particle in the box of Exercise 21 is in its ground state of $n_x = n_y = n_z = 1$. (*a*) Find the probability that the particle will be found in the volume defined by $0 \leq x \leq L/4$, $0 \leq y \leq L/4$, $0 \leq z \leq L/4$. (*b*) Do the same for $L/2$ instead of $L/4$.

23. (*a*) Find the possible energies of the particle in the box of Exercise 21 by substituting its wave function ψ in Schrödinger's equation and solving for E. (*Hint*: Inside the box $U = 0$.) (*b*) Compare the ground-state energy of a particle in a one-dimensional box of length L with that of a particle in the three-dimensional box.

5.10 Tunnel Effect

24. Electrons with energies of 0.400 eV are incident on a barrier 3.00 eV high and 0.100 nm wide. Find the approximate probability for these electrons to penetrate the barrier.

25. A beam of electrons is incident on a barrier 6.00 eV high and 0.200 nm wide. Use Eq. (5.60) to find the energy they should have if 1.00 percent of them are to get through the barrier.

5.11 Harmonic Oscillator

26. Show that the energy-level spacing of a harmonic oscillator is in accord with the correspondence principle by finding the ratio $\Delta E_n/E_n$ between adjacent energy levels and seeing what happens to this ratio as $n \rightarrow \infty$.

27. What bearing would you think the uncertainty principle has on the existence of the zero-point energy of a harmonic oscillator?

28. In a harmonic oscillator, the particle varies in position from $-A$ to $+A$ and in momentum from $-p_0$ to $+p_0$. In such an oscillator, the standard deviations of x and p are $\Delta x = A/\sqrt{2}$ and $\Delta p = p_0/\sqrt{2}$. Use this observation to show that the minimum energy of a harmonic oscillator is $\frac{1}{2}h\nu$.

29. Show that for the $n = 0$ state of a harmonic oscillator whose classical amplitude of motion is A, $y = 1$ at $x = A$, where y is the quantity defined by Eq. (5.67).

30. Find the probability density $|\psi_0|^2\,dx$ at $x = 0$ and at $x = \pm A$ of a harmonic oscillator in its $n = 0$ state (see Fig. 5.13).

31. Find the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$ for the first two states of a harmonic oscillator.

32. The potential energy of a harmonic oscillator is $U = \frac{1}{2}kx^2$. Show that the expectation value $\langle U \rangle$ of U is $E_0/2$ when the oscillator is in the $n = 0$ state. (This is true of all states of the harmonic oscillator, in fact.) What is the expectation value of the oscillator's kinetic energy? How do these results compare with the classical values of $\overline{U}$ and $\overline{\mathrm{KE}}$?

33. A pendulum with a 1.00-g bob has a massless string 250 mm long. The period of the pendulum is 1.00 s. (*a*) What is its zero-point energy? Would you expect the zero-point oscillations to be detectable? (*b*) The pendulum swings with a very small amplitude such that its bob rises a maximum of 1.00 mm above its equilibrium position. What is the corresponding quantum number?

34. Show that the harmonic-oscillator wave function ψ_1 is a solution of Schrödinger's equation.

35. Repeat Exercise 34 for ψ_2.

36. Repeat Exercise 34 for ψ_3.

Appendix: The Tunnel Effect

37. Consider a beam of particles of kinetic energy E incident on a potential step at $x = 0$ that is U high, where $E > U$ (Fig. 5.19). (*a*) Explain why the solution $De^{-ik'x}$ (in the notation of appendix) has no physical meaning in this situation, so that $D = 0$. (*b*) Show that the transmission probability here is $T = CC^*\boldsymbol{v}'/AA^*\boldsymbol{v}_1 = 4k_1^2/(k_1 + k')^2$. (*c*) A 1.00-mA beam of electrons moving at 2.00×10^6 m/s enters a region with a sharply defined boundary in which the electron speeds are reduced to 1.00×10^6 m/s by a difference in potential. Find the transmitted and reflected currents.

38. An electron and a proton with the same energy E approach a potential barrier whose height U is greater than E. Do they have the same probability of getting through? If not, which has the greater probability?

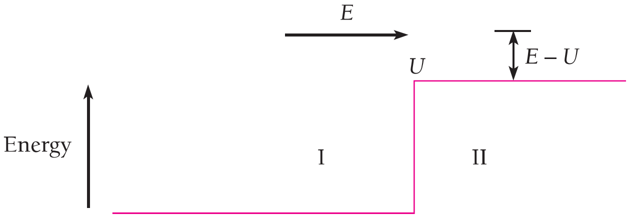


Figure 5.19