14 The Principles of Quantum Mechanics. I. Classical Waves and the Schrödinger Equation

OBJECTIVES

After studying this chapter, a student should:

1. understand the solution of classical equations of motion;
2. understand the classical wave equation and its solutions and be able to solve problems involving classical wave phenomena;
3. understand the way in which quantization is introduced in the old quantum theory, and be able to solve problems related to that theory;
4. understand the relation of the Schrödinger equation to the classical wave equation and understand the boundary conditions imposed on its solutions;
5. understand and be able to use the method of separation of variables to solve a class of differential equations;
6. be able to solve problems related to the Schrödinger equation.

PRINCIPAL FACTS AND IDEAS

1. Classical mechanics ascribes exact trajectories to particles.
2. The old quantum theory contained quantization as hypotheses but was based on classical mechanics.
3. The "matter waves" of de Broglie led to quantum mechanics.
4. The Schrödinger equation describes the waves that correspond to states of systems.
5. Quantum mechanics contains the concept of wave–particle duality: objects can exhibit wavelike properties as well as particlelike properties.
6. The time-independent Schrödinger equation can be solved for some example systems, and produces quantization as a natural part of the solution.

14.1 Classical Mechanics

Classical mechanics is based on the laws of motion discovered by Sir Isaac Newton, and is also called Newtonian mechanics. Appendix D presents a brief survey of classical mechanics, which is now known to be accurate only for objects of relatively large mass and for relatively high energies.

The Classical Mechanical Analysis of the Harmonic Oscillator

The harmonic oscillator is a model system that represents a mass suspended from a stationary object by a spring as shown in Figure 14.1. Let the vertical coordinate z of the mass equal zero at its equilibrium position and be positive if the mass is above this position and negative below it. The force on a mass suspended by a spring is described for fairly small values of z by **Hooke's law**:

Hooke's law is named for Robert Hooke, 1635–1703, one of Newton's contemporaries and rivals.

$$F_z = -kz \tag{14.1-1}$$

where k is called the **force constant**. The larger the force constant, the stiffer the spring.

The harmonic oscillator obeys Hooke's law exactly for all values of the z coordinate. The mass of the spring suspending the oscillator is assumed to be negligible. From Newton's second law, Eq. (D-1) of Appendix D, the force on an object equals its mass times its acceleration. This gives the **equation of motion** of the harmonic oscillator:

$$-kz = m\frac{d^2z}{dt^2} \tag{14.1-2}$$

This differential equation is called **linear** because the variable z enters only to the first power and is called **second order** because its highest-order derivative is the second derivative.

The **general solution** of a differential equation is a family of functions that includes nearly every solution of the equation. The general solution for Eq. (14.1-2) must contain two arbitrary constants, since this is a property of linear differential equations of second order. A general solution can be written as

$$z(t) = A\sin\left(\sqrt{\frac{k}{m}}t\right) + B\cos\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-3}$$

where A and B are arbitrary constants. The velocity can also be found from Eq. (14.1-3):

$$v_z(t) = \frac{dz}{dt} = \sqrt{\frac{k}{m}}\left[A\cos\left(\sqrt{\frac{k}{m}}t\right) - B\sin\left(\sqrt{\frac{k}{m}}t\right)\right] \tag{14.1-4}$$

To make the general solution apply to a specific case, we apply **initial conditions**. Since there are two arbitrary constants, we require two initial conditions. These conditions can be that at time $t = 0$

$$z(0) = z_0, \qquad v_z(0) = 0 \tag{14.1-5}$$

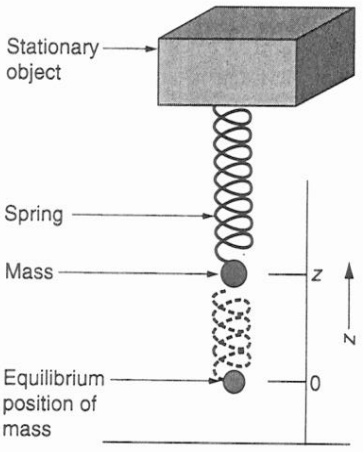


Figure 14.1. A System Represented by a Harmonic Oscillator. This system is a mass on a spring.

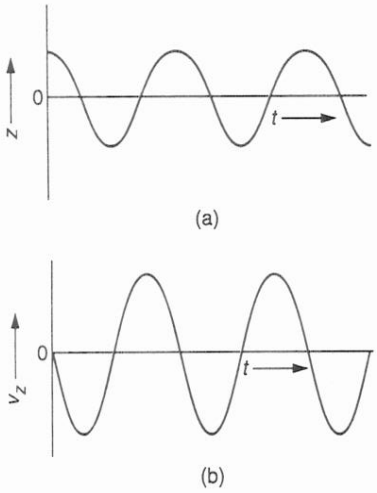


Figure 14.2. The Behavior of a Harmonic Oscillator. (a) **The position as a function of time according to classical mechanics.** (b) **The velocity as a function of time according to classical mechanics.** This motion is called uniform harmonic motion. The position and velocity both vary sinusoidally.

where z_0 is a constant initial displacement. Since $\sin(0) = 0$ and $\cos(0) = 1$, then $v_z(0) = 0$ only if $A = 0$ and $z(0) = z_0$ only if $B = z_0$. The solution that applies to the initial conditions shown in Eq. (14.1-5) is

$$z(t) = z_0 \cos\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-6}$$

$$v_z(t) = -\sqrt{\frac{k}{m}}z_0 \sin\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-7}$$

Figure 14.2a shows the position as a function of time and Figure 14.2b shows the velocity as a function of time. This motion is called **uniform harmonic motion**. It is a **periodic motion**, repeating the same pattern over and over. The constant z_0 is the largest magnitude that z attains and is called the maximum **amplitude** of the oscillation.

The length of time required for the oscillator to go from a certain position and velocity to the next repetition of that position and velocity is called the **period** of the oscillation and is denoted by τ. It is the length of time required for the argument of the sine function in Eq. (14.1-6) or the cosine function in Eq. (14.1-7) to change by 2π:

$$\sqrt{\frac{k}{m}}\tau = 2\pi \tag{14.1-8}$$

or

$$\tau = 2\pi\sqrt{\frac{m}{k}} \tag{14.1-9}$$

The **frequency** ν of the oscillation is the reciprocal of the period, or the number of oscillations per second:

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{14.1-10}$$

The frequency is larger if the force constant is larger and smaller if the mass is larger.

EXAMPLE 14.1

An object of mass 0.250 kg is suspended from a spring with $k = 5.55\,\mathrm{N\,m^{-1}}$. Find the period and the frequency.

Solution

$$\tau = (2\pi)\sqrt{\frac{0.250\,\mathrm{kg}}{5.55\,\mathrm{N\,m^{-1}}}} = 1.33\,\mathrm{s}$$

$$\nu = \frac{1}{1.33\,\mathrm{s}} = 0.750\,\mathrm{s^{-1}} = 0.750\,\mathrm{Hz}$$

The unit of frequency is the reciprocal second, properly called the hertz (Hz).

EXAMPLE 14.2

A typical chemical bond is similar to a spring with a force constant near $500\,\mathrm{N\,m^{-1}}$. Estimate the frequency of oscillation of a hydrogen atom at one end of such a spring with the other end held fixed.

Solution

$$\nu = \frac{1}{2\pi}\sqrt{\frac{500\,\mathrm{N\,m^{-1}}}{1.674 \times 10^{-27}\,\mathrm{kg}}} = 8.7 \times 10^{13}\,\mathrm{Hz}$$

This frequency is typical of vibrational frequencies of molecules.

The kinetic energy of a harmonic oscillator is a state function of the velocity. For our initial conditions,

$$\mathscr{K} = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{k}{m}z_0^2\left[\sin\left(\sqrt{\frac{k}{m}}t\right)\right]^2 = \frac{k}{2}z_0^2\sin^2\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-11}$$

Equation (D-5) of Appendix D relates the potential energy $\mathscr{V}$ and the corresponding force:

$$F_z = -\frac{d\mathscr{V}}{dz} \tag{14.1-12}$$

The potential energy of the harmonic oscillator is

$$\mathscr{V}(z) = \frac{1}{2}kz^2 + \text{constant} \tag{14.1-13}$$

An arbitrary constant can be added to a potential energy without any physical effect, since it does not change the forces. We set the constant in Eq. (14.1-13) equal to zero so that $\mathscr{V}0) = 0$. Figure 14.3a shows the potential energy for the harmonic oscillator as a function of z, and Figure 14.3b shows the force due to this potential energy. For our initial conditions, the potential energy is given as a function of time by

$$\mathscr{V} = \frac{k}{2}z_0^2\cos^2\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-14}$$

The total energy, E, is given by

$$E = \mathscr{K} + \mathscr{V} = \frac{1}{2}kz_0^2\left[\sin^2\left(\sqrt{\frac{k}{m}}t\right) + \cos^2\left(\sqrt{\frac{k}{m}}t\right)\right] = \frac{1}{2}kz_0^2 \tag{14.1-15}$$

since $\sin^2(x) + \cos^2(x) = 1$ for all values of x. The total energy does not change during the oscillation, corresponding to **conservation of energy**.

The kinetic energy becomes equal to zero at the extreme of an oscillation (the **turning point**) as the object changes direction, so the total energy equals the potential energy:

$$E = \mathscr{V}(z_t) = \frac{1}{2}kz_t^2 \tag{14.1-16}$$

The displacement at the turning point is denoted by z_t,

$$z_t = \sqrt{\frac{2E}{k}} \tag{14.1-17}$$

For our initial conditions, $z_t = z_0$.

The harmonic oscillator is used as a model for a vibrating diatomic molecule. Since both nuclei move, the model oscillator consists of two movable masses connected by a

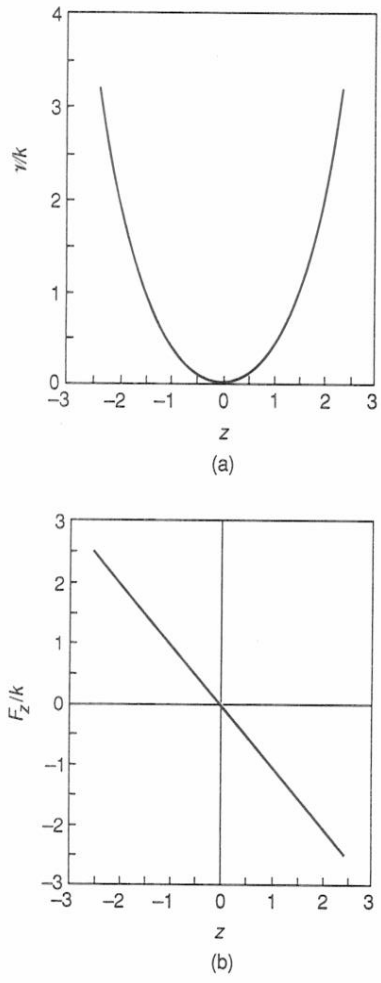


Figure 14.3. Mechanical Variables of a Harmonic Oscillator. (a) **The potential energy.** (b) **The force on the oscillator.** The force is given as the negative derivative of the potential energy.

spring, as depicted in Figure 14.4. As shown in Appendix D, it is necessary to replace the mass in the harmonic oscillator formulas by the **reduced mass** μ:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{14.1-18}$$

where m_1 and m_2 are the masses of the two nuclei. The frequency of oscillation of a diatomic molecule is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{14.1-19}$$

14.2 Classical Waves

There are various wave phenomena that are adequately described by classical mechanics. These include sound waves, light waves, waves on the surface of bodies of water, and vibrations of the strings in musical instruments. A wave consists of an oscillating displacement. In a water wave the displacement is the distance to a point on the surface from the equilibrium position of this part of the surface. A region of positive displacement is called a **crest**, and a region of negative displacement is called a **trough**. A location where the displacement of a wave equals zero is called a **node**. Most waves are periodic waves, with a number of crests and troughs having the same shape. The distance from one crest to the next is called the **wavelength** λ. The **period** of a wave is the time for the first return of the oscillating object to an initial state. The **frequency** is the reciprocal of the period, or the number of oscillations per unit time, and it is denoted by ν. A wave is inherently delocalized (cannot exist at a single point in space).

There are two principal types of waves. A **traveling wave** propagates (moves along) like the waves on the surface of a body of water. A **standing wave**, such as the vibration of a string in a musical instrument, does not propagate but has stationary nodes. Figure 14.5 represents some features of traveling and standing waves. It shows how the traveling wave in Figure 14.5a moves to the right without changing shape, while the standing wave in Figure 14.5b oscillates between stationary nodes.

One important property of waves is **interference**. When two waves come to the same location, their displacements add. If two crests or two troughs coincide, a displacement of larger magnitude results. This addition is called **constructive interference**. If a crest of one wave and a trough of another wave coincide, they will partially or completely cancel each other. This cancellation is called **destructive interference**. Constructive and destructive interference are qualitatively depicted in Figure 14.6a, which shows the sum of two waves of different wavelengths.

A property that arises from interference is **diffraction**. If a water wave encounters a post, there will be a reflected wave that moves out in all directions with crests that are circles or arcs of circles. The reflected waves from a row of equally spaced posts can interfere to produce a diffracted wave with straight crests, which travels in a direction different from that of the incident wave. Figure 14.6b illustrates diffraction by a set of equally spaced scattering centers. The broken straight lines represent the crests of a plane wave moving from left to right. The arcs represent the crests of diffracted waves moving outward from the scattering centers. At a distance from the scattering centers that is large compared to a wavelength, these crests combine to produce a diffracted

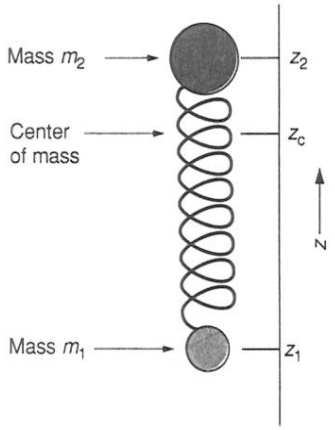


Figure 14.4. A Second System Represented by a Harmonic Oscillator. This system consists of two masses connected by a spring.

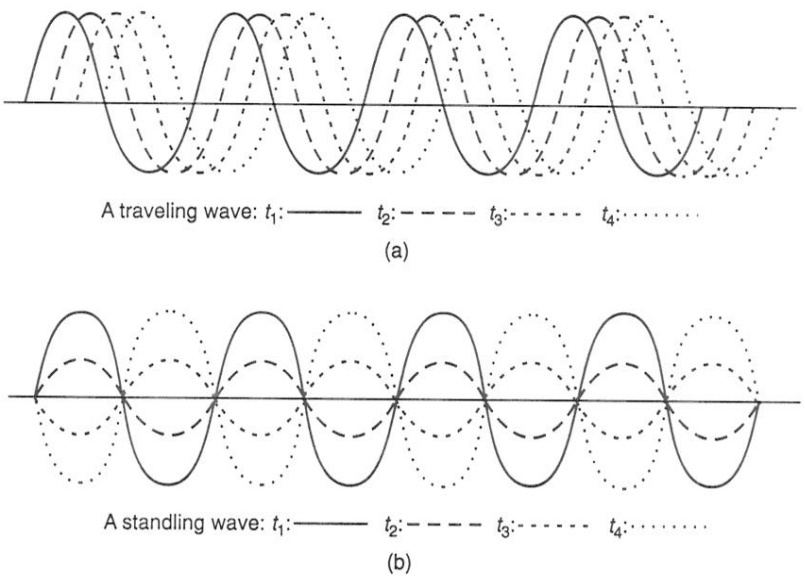


Figure 14.5. Traveling and Standing Waves. (a) **A traveling wave at times $t_1 < t_2 < t_3 < t_4$.** The nodes of the traveling wave move along (from left to right in this diagram). (b) **A standing wave at times $t_1 < t_2 < t_3 < t_4$.** The nodes of the standing wave remain at fixed positions.

plane wave. The wave nature of light was established experimentally when interference and diffraction of light were observed.

Waves in a Flexible String

The flexible string is a model system that represents a real vibrating string. It is defined to be uniform (all parts have the same mass per unit length, denoted by ρ); there is a tension force of magnitude T pulling at each end of the string; the string is perfectly

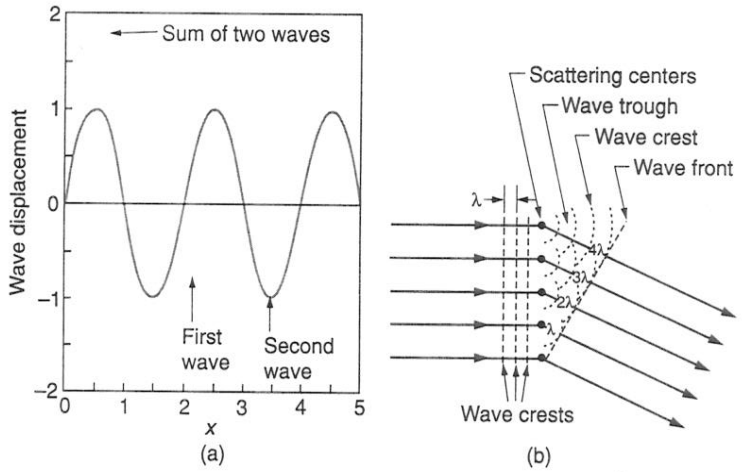


Figure 14.6. (a) **The superposition of two waves of different wavelengths.** This figure illustrates constructive and destructive interference at one time. (b) **The diffraction of a wave by a row of scattering centers.** The direction of the diffracted wave depends on the wavelength.

flexible; there is no friction; the string undergoes only small displacements, so that the total length of the string remains nearly constant and the magnitude of the tension force T is nearly constant; the equilibrium position of the string is a straight line segment on the x axis, with its ends fixed on the x axis at $x = 0$ and $x = L$.

At some initial time the string is displaced into some position in the x–z plane and released to vibrate freely in this plane. The state of the string is specified by giving the displacement and velocity at each point of the string as a function of t:

$$z = z(x, t) \tag{14.2-1}$$

$$v_z = v_z(x, t) = \frac{\partial z}{\partial t} \tag{14.2-2}$$

The classical wave equation of the string is derived from Newton's second law in Appendix D. Equation (D-9) of Appendix D is

$$\frac{\partial^2 z}{\partial x^2} = \frac{\rho}{T}\frac{\partial^2 z}{\partial t^2} = \frac{1}{c^2}\frac{\partial^2 z}{\partial t^2} \tag{14.2-3}$$

where $c^2 = T/\rho$. We will show later that c is equal to the speed of propagation of the wave in the string.

Standing Waves in a Flexible String

Equation (14.2-3) is a partial differential equation whose solution is a function of x and t. We begin by seeking a solution that represents a standing wave by separating the variables.

1. The first step in the separation of variables is to assume a **trial solution** that is a product of functions of one independent variable:

$$z(x, t) = \psi(x)\zeta(t) \tag{14.2-4}$$

2. The second step of the method is to substitute the trial solution into the differential equation and to perform whatever algebraic operations that result in an equation with terms that are functions of only one independent variable. We substitute the trial function of Eq. (14.2-4) into Eq. (14.2-3):

$$\zeta\frac{d^2\psi}{dx^2} = \frac{1}{c^2}\psi\frac{d^2\zeta}{dt^2} \tag{14.2-5}$$

The derivatives are ordinary derivatives since ζ and ψ each depends on a single variable. We divide Eq. (14.2-5) by $\psi\zeta$:

$$\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} = \frac{1}{c^2\zeta(t)}\frac{d^2\zeta}{dt^2} \tag{14.2-6}$$

Each term depends on only one independent variable, so the variables are separated.

3. The third step in the method is to set each side of the equation equal to a constant since each side is a function of a different independent variable. This gives the two equations:

$$\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} = \text{constant} = -\kappa^2 \tag{14.2-7}$$

$$\frac{1}{c^2\zeta(t)}\frac{d^2\zeta}{dt^2} = -\kappa^2 \tag{14.2-8}$$

The constant must be negative to give an oscillatory solution. We denote it by $-\kappa^2$ so that κ will be a real quantity.

Multiplying Eq. (14.2-7) by ψ and Eq. (14.2-8) by $c^2\zeta$ gives

$$\frac{d^2\psi}{dx^2} + \kappa^2\psi(x) = 0 \tag{14.2-9}$$

$$\frac{d^2\zeta}{dt^2} + \kappa^2 c^2\zeta(t) = 0 \tag{14.2-10}$$

These equations have the same form as Eq. (14.1-2). The general solutions are obtained by transcribing the solution to that equation with appropriate changes in symbols:

$$\psi(x) = B\cos(\kappa x) + D\sin(\kappa x) \tag{14.2-11}$$

$$\zeta(t) = F\cos(\kappa ct) + G\sin(\kappa ct) \tag{14.2-12}$$

where B, D, F, and G are arbitrary constants. The product of these two functions is a wave function that satisfies the wave equation, Eq. (14.2-3).

However, the solution does not yet apply to a string with fixed ends. It must obey the **boundary conditions** that z vanishes at $x = 0$ and at $x = L$. The function ψ must vanish at these points, since it contains all of the x dependence of z. The condition that $\psi(0) = 0$ requires that $B = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The sine function vanishes if its argument is an integral multiple of π, so that

$$\kappa L = n\pi \tag{14.2-13}$$

where n is an integer. We have the values of B and κ, and can write

$$\psi(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{14.2-14}$$

Now that we have satisfied the boundary conditions, the constants D, F, and G are chosen to match **initial conditions**. A classical equation of motion generally requires two initial conditions, one related to the initial position and one related to the initial velocity. We specify the first initial condition that the string is passing through its equilibrium position ($z = 0$ for all x) at the time $t = 0$. This requires that $F = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The solution can now be written as

$$\begin{aligned} z(x, t) = \psi(x)\zeta(t) &= DG\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \\ &= A\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \end{aligned} \tag{14.2-15}$$

We have replaced the product DG by a constant A.

We now choose as the second initial condition that the maximum value that z achieves is equal to z_0. We call z_0 the maximum displacement or **amplitude** of the wave. This condition determines the initial velocity of the string. The solution now contains no unknown constants:

$$z(x, t) = z_0\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \tag{14.2-16}$$

The velocity of any point of the string is

$$v_z = \frac{\partial z}{\partial t} = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi ct}{L}\right) \tag{14.2-17}$$

The velocity at $t = 0$ is

$$v_z(0) = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right) \tag{14.2-18}$$

The function $z(x, t)$ is a **wave function** that represents the motion of the flexible string for all values of x and t.

Exercise 14.1

a. Show by substitution that Eq. (14.2-15) satisfies Eq. (14.2-3).
b. What is the effect on the wave function of replacing n by its negative?
***c.** What is the relationship between the value of n and the number of nodes?

The relationship between L and the wavelength λ for a standing wave is

$$n\lambda = 2L \qquad \text{or} \qquad \lambda = \frac{2L}{n} = \frac{2\pi}{\kappa} \tag{14.2-19}$$

The **period** τ of the motion is the time for the string to return to an initial state. It is the time necessary for the argument of $\sin(n\pi ct/L)$ to change by 2π, so that

$$2\pi = \frac{n\pi c\tau}{L} \qquad \text{or} \qquad \tau = \frac{2L}{nc} \tag{14.2-20}$$

The **frequency** ν is the number of oscillations per unit time or the reciprocal of the period:

$$\nu = \frac{nc}{2L} = \frac{n}{2L}\sqrt{\frac{T}{\rho}} \tag{14.2-21}$$

A different frequency results for each value of n. For a fixed value of n, the frequency can be increased by increasing the tension force, by decreasing the length of the string, or decreasing the mass per unit length of the string.

The wave function shown in Eq. (14.2-15) represents a different standing wave for each value of n, so there is a set of wave functions. Figure 14.7 represents the wave functions for several values of n. Each wave function corresponds to a different frequency and wavelength. The frequencies and wavelengths are **quantized** (take on values from a discrete set). In musical acoustics, the standing wave with $n = 1$ is called the **fundamental** or the **first harmonic**, the standing wave with $n = 2$ is called the **first overtone** to the **second harmonic** and so on. A string does not usually move as described by a single harmonic. A **linear combination** (sum with coefficients) of harmonics can satisfy the wave equation, and such a linear combination represents a typical motion of a flexible string:

$$z(x, t) = \sum_{n=1}^{\infty} a_n(t) \sin\left(\frac{n\pi x}{L}\right) \tag{14.2-22}$$

The fact that a linear combination of solutions can be a solution to the wave equation is called the **principle of superposition**. The sum shown in Eq. (14.2-22) is called a **Fourier sine series**. Fourier cosine series also exist, which are linear combinations of cosine functions, and a more general Fourier series contains both sine and cosine terms.

The Fourier series is named for Jean Baptiste Joseph Fourier, 1768–1830, famous French mathematician and physicist.

The **Fourier coefficients** $a_1, a_2, \ldots$ must depend on t to satisfy the wave equation. With the initial condition that the string is passing through its equilibrium position at $t = 0$, the following sum is a solution:

$$z(x, t) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi ct}{L}\right) \tag{14.2-23}$$

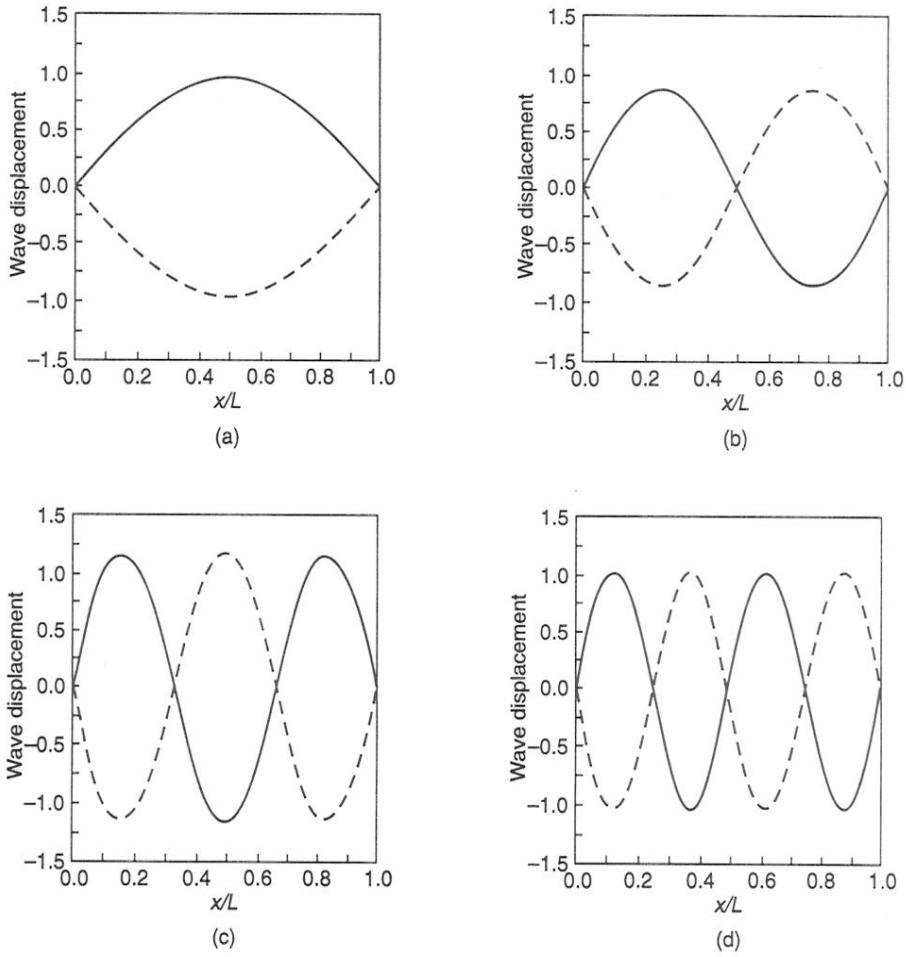


Figure 14.7. Standing Waves in a Flexible String. (a) **The wave function for $n = 1$.** (b) **The wave function for $n = 2$.** (c) **The wave function for $n = 3$.** (d) **The wave function for $n = 4$.** These are the first few standing waves which satisfy the condition that the ends of the string are fixed. The nodes are fixed. Between the nodes the string oscillates.

Exercise 14.2

Show by substitution that the series in Eq. (14.2-23) satisfies Eq. (14.2-3).

The constants $A_1, A_2, \ldots$, can have any values. Any harmonic whose coefficient does not vanish makes a contribution to the motion of the string, with constructive and destructive interference that continually changes because the different harmonics have different frequencies. Figure 14.8 shows a linear combination of three harmonics with $A_1 = 1$, $A_2 = 0.2$, and $A_3 = 0.1$. Figure 14.8a shows the sum at time $t = L/(4c)$, and Figure 14.8b shows the sum at $t = 3L/(4c)$.

Traveling Waves

In a string of finite length, stationary nodes are required at the ends of the string, which prevents the occurrence of traveling waves. Traveling waves can occur in an infinitely

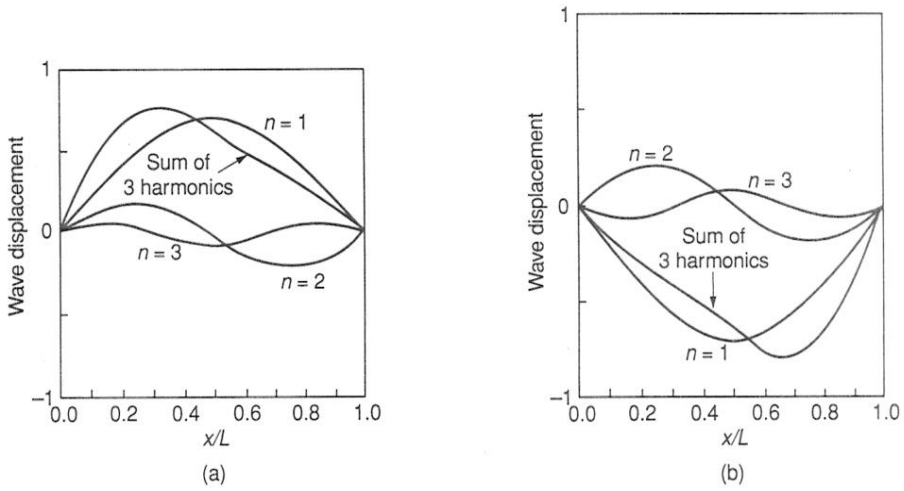


Figure 14.8. The Superposition of Three Harmonics of a Flexible String. (a) **At time $t = L/(4c)$.** (b) **At time $t = 3L/(4c)$.** By the principle of superposition, a sum of the three harmonics satisfies the wave equation. Constructive and destructive interference produces waves that are not sinusoidal and do not maintain a fixed shape.

long string. A wave function that satisfies Eq. (14.2-3) and corresponds to a traveling wave is

$$z(x, t) = a \sin(\kappa x - \kappa c t) \tag{14.2-24}$$

Exercise 14.3

Show by substitution that the function in Eq. (14.2-24) satisfies Eq. (14.2-3).

We can find the speed of a traveling wave by following the motion of one of the nodes. At time $t = 0$ there is a node at $x = 0$. As time passes this node will be located at the point where $x - ct = 0$. Thus

$$x(\text{node}) = ct \tag{14.2-25}$$

The node is moving toward the positive end of the x axis with a speed equal to c, as stated earlier. Since $c = \sqrt{T/\rho}$, increasing the mass per unit length decreases the speed and increasing the tension force increases the speed.

*Exercise 14.4

What change would have to be made in the mass per unit length to quadruple the speed of propagation? What change would have to made in the tension force to double the speed of propagation?

If the function of Eq. (14.2-24) is replaced by

$$z(x, t) = A \sin(\kappa x + \kappa c t) \tag{14.2-26}$$

the wave travels toward the negative end of the x axis with speed c. This function satisfies the same wave equation as the function shown in Eq. (14.3-24).

Exercise 14.5

a. Show that the function of Eq. (14.2-26) satisfies Eq. (14.2-3).
b. Show that the speed of the wave is equal to c.

In one wavelength, the argument of the sine function changes by 2π for fixed t, so that the same relationship occurs as in Eq. (14.2-19) for a standing wave:

$$\kappa = \frac{2\pi}{\lambda} \tag{14.2-27}$$

The relationship between the frequency and the wavelength can be obtained by observing that in time t, the length of the wave "train" that passes a fixed point is

$$\text{Length} = ct$$

where c is the speed. The number of wavelengths in this wave train is equal to

$$\text{Number} = \frac{ct}{\lambda}$$

In time t, the number of oscillations is equal to

$$\text{Number} = \nu t$$

so that $\nu t = ct/\lambda$, or

$$\nu = \frac{c}{\lambda} \tag{14.2-28}$$

Equation (14.2-28) is the general relation between wavelength and frequency. This important equation holds for all kinds of waves, including sound waves and electromagnetic waves.

***Exercise 14.6**

The speed of sound in air at sea level and room temperature is approximately equal to $338\ \text{m s}^{-1}$. Find the wavelength of a sound wave with a frequency of $440\ \text{s}^{-1}$, or 440 Hertz. (This frequency is the frequency of "A" above "middle C" in a musical scale.)

Two traveling waves moving in opposite directions can interfere to produce a standing wave. The two waves

$$z_{\text{R}}(x, t) = A \sin(\kappa x - \kappa ct) \tag{14.2-29a}$$

and

$$z_{\text{L}}(x, t) = A \sin(\kappa x + \kappa ct) \tag{14.2-29b}$$

interfere to give

$$z(x, t) = A[\sin(\kappa x + \kappa ct) + \sin(\kappa x - \kappa ct) \tag{14.2-30}$$

which is the same as

$$z(x, t) = 2A \sin(\kappa x) \cos(\kappa ct) \tag{14.2-31}$$

Exercise 14.7

Use trigonometric identities to obtain Eq. (14.2-31) from Eq. (14.2-30).

The Classical Wave Theory of Light

James Clerk Maxwell, 1831–1879, made fundamental contributions to electrodynamics, gas kinetic theory and thermodynamics.

In 1865, Maxwell developed a mathematical theory of electromagnetism. In this theory, there are four important vector quantities, the electric field $\mathscr{E}$, the electric displacement **D**, the magnetic field strength $\mathscr{H}$, and the magnetic induction **B**. The dependence of these quantities on time and position is described by **Maxwell's equations**, which Maxwell deduced from empirical laws. He found that the electric and magnetic fields can oscillate like waves, constituting electromagnetic radiation. Example of such radiation are visible light, infrared radiation, ultraviolet radiation, X-rays, radio waves, microwaves, etc., which differ from each other only in having different wavelengths and frequencies. At first it was thought that light consisted of oscillations in a medium called "the luminiferous ether." The assumption that such a medium exists was abandoned after Michelson and Morley demonstrated that the speed of light has the same value for observers moving with different velocities. We now think of light and other electromagnetic waves as oscillations that do not require any supporting medium.

Albert A. Michelson, 1852–1931, was an American physicist who was the first American to win a Nobel Prize in science (in 1907) and Edward W. Morley, 1838–1923, was an American chemist.

A **plane polarized** wave traveling in the y direction can have an electric field that oscillates in the y–z plane and a magnetic field that oscillates in the x–y plane. In a medium with zero electrical conductivity (a perfect insulator or a vacuum), the following equations for such a wave follow from Maxwell's equations.[1]

$$\frac{\partial^2 \mathscr{E}_z}{\partial y^2} - \frac{1}{c^2}\frac{\partial^2 \mathscr{E}_z}{\partial t^2} = 0 \tag{14.2-32}$$

$$\frac{\partial^2 \mathscr{H}_x}{\partial y^2} - \frac{1}{c^2}\frac{\partial^2 \mathscr{H}_x}{\partial t^2} = 0 \tag{14.2-33}$$

where

$$c = \frac{1}{\sqrt{\varepsilon\mu}} \tag{14.2-34}$$

and where ε is called the **permittivity** of the medium and μ is called the **permeability** of the medium. The values of these quantities for a vacuum are denoted by ε_0 and μ_0. In SI units, the permeability of a vacuum has the value

$$\begin{aligned}\mu_0 &= 4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}} \quad \text{(exact value by definition)}\\ &= 12.566370614\ldots \times 10^{-7}\,\mathrm{N\,A^{-2}}\end{aligned} \tag{14.2-35a}$$

and the permittivity of a vacuum is

$$\varepsilon_0 = 8.8542 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}} \tag{14.2-35b}$$

There is an additional condition from Maxwell's equations that makes Eqs. (14.2-32) and (14.2-33) interdependent:

$$\frac{\mathscr{E}_z}{\mathscr{H}_x} = \pm\sqrt{\frac{\mu}{\varepsilon}} \tag{14.2-36}$$

[1] See J. C. Slater and N. H. Frank, *Electromagnetism*, McGraw-Hill, New York, 1947, pp 90ff, or any other textbook on electricity and magnetism.

The electric field cannot oscillate without oscillation of the magnetic field, and vice versa. Equations (14.2-32) and (14.2-33) have the same form as Eq. (14.2-3), in which c is the speed of propagation of the wave. The theory of Maxwell correctly predicts the value of the speed of light.

EXAMPLE 14.3

Use the value of the permittivity of the vacuum and the permeability of the vacuum to show that Eq. (14.2-34) gives a value for the speed of light in a vacuum that agrees with experiment.

Solution

$$c_{\text{vacuum}} = \frac{1}{\sqrt{(8.8542 \times 10^{-12}\,\text{C}^2\,\text{N}^{-1}\,\text{m}^{-2})(4\pi \times 10^{-7}\,\text{N A}^{-2})}}$$
$$= 2.9979 \times 10^{8}\,\text{m s}^{-1}$$

Exercise 14.8

Show that the units in Eq. (14.2-34) are correct, using the fact that an ampere (A) is the same as a coulomb per second.

A traveling-wave solution to Eqs. (14.2-32) and (14.2-33) is

$$\mathscr{E}_z(y, t) = \mathscr{E}_0 \sin[2\pi(y - ct)/\lambda] \tag{14.2-37}$$

$$\mathscr{H}_x(y, t) = \mathscr{H}_0 \sin[2\pi(y - ct)/\lambda] \tag{14.2-38}$$

where $\mathscr{E}_0$ and $\mathscr{H}_0$ are constants that obey Eq. (14.2-36). The wavelength λ can take on any real value.

Figure 14.9 shows $\mathscr{E}$ and $\mathscr{H}$ as functions of y at time $t = 0$ with $\mathscr{E}$ and $\mathscr{H}$ plotted in the directions in which they point. As time passes, the traveling wave moves to the right without changing its shape or wavelength. Since oscillating electric and magnetic fields put oscillating forces on charged particles such as the electrons and nuclei in molecules,

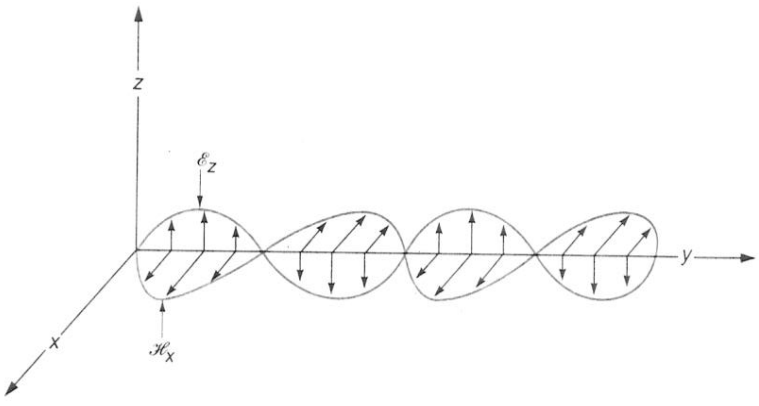


Figure 14.9. The Electric and Magnetic Fields in an Electromagnetic Wave. The wave is propagating to the right in the y direction. The electric field is oscillating in the z direction, and the magnetic field is oscillating in the x direction. The nodes of the electric field and those of the magnetic field coincide.

molecules can absorb electromagnetic radiation. The converse is also true. According to Maxwell's equations, oscillating electric charges emit electromagnetic radiation.

An electromagnetic wave cannot penetrate a perfect conductor. Therefore, electromagnetic waves must have nodes at perfectly conducting walls, and will approximately vanish at a real conducting wall. Reflection between walls in a conducting cavity can produce standing electromagnetic waves.

14.3 The Old Quantum Theory

Near the end of the nineteenth century, several important phenomena were discovered that classical physics was unable to explain. Three of these were explained early in the twentieth century by new theories: Planck's theory of blackbody radiation, Einstein's theory of the photoelectric effect, and Bohr's theory of the hydrogen atom. These theories are the major parts of what is called the "old quantum theory." They were based on assumptions of **quantization**, which is the idea that the value of a physical quantity can equal one of a discrete set of values, but not any of the values between those in the discrete set. We will discuss these theories for historical perspective, and this section can be skipped without loss of continuity.

Planck's Theory of Blackbody Radiation

If an object has a temperature of 1000°C, it glows with a red color, no matter what material it is made of. At higher temperatures, it glows orange, yellow, white, or even blue if the temperature is high enough. At any temperature an object with a lower reflectivity glows more intensely at every wavelength, so that a **black body**, a model system that reflects no radiation at any wavelength, has the maximum emissivity at every wavelength.

The best laboratory approximation to a black body is not an object, but a small hole in a hollow box. If the inside of the box (the "cavity") is made fairly nonreflective, any light falling on the hole from outside will be absorbed as it is reflected around in the box. Measurements on the light emitted through the hole when such a box is heated show that the amount of light emitted and its spectral distribution depend only on the temperature of the walls of the box. Figure 14.10 shows the **spectral radiant emittance** η of a black body as a function of wavelength for several temperatures. This quantity is defined such that $\eta(\lambda)\, d\lambda$ is the energy per unit time per unit area emitted in the wavelengths lying between λ and $\lambda + d\lambda$. The visible part of the electromagnetic spectrum, which ranges from about 400 nm to 750 nm, is labeled in the figure.

At 2000 K, only the red part of the visible spectrum (around 650 to 750 nm) is represented, but at higher temperature the other visible wavelengths are also represented. At around 6000 K the maximum in the curve is in the middle (green) portion of the visible region, and black-body radiation of this temperature is similar to sunlight. Near room temperature, almost all of the radiation is in the infrared region. It is this radiation from the surface of the earth that is involved in the greenhouse effect in the earth's atmosphere, which is the absorption in the upper atmosphere of infrared radiation emitted by the earth. It is principally due to CO_2, H_2O, CH_4, and various chlorofluorocarbons.

The total radiant emittance (emission per unit area per unit time, summed over all wavelengths) is equal to the area under the curve. The **Stefan–Boltzmann law** is an

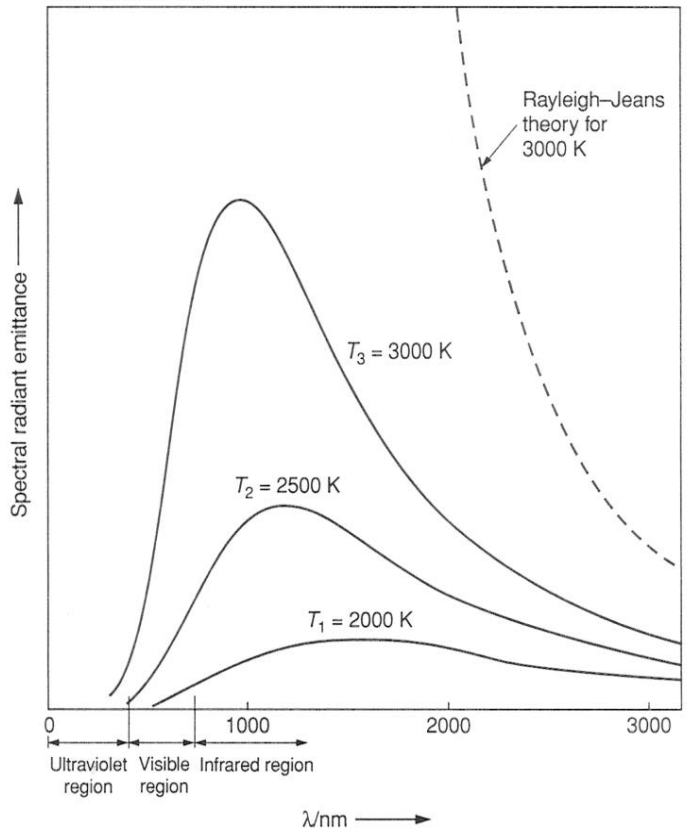


Figure 14.10. The Spectral Radiant Emittance of a Black Body for $T_1 = 2000\,\text{K}$, $T_2 = 2500\,\text{K}$, and $T_3 = 3000\,\text{K}$. The maximum in the curve shifts to shorter wavelengths as the temperature is raised. The Rayleigh–Jeans curve and the experimental curve coincide for sufficiently long wavelengths.

empirical law that relates the total radiant emittance to the absolute temperature of the black body:

$$(\text{Total radiant emittance}) = \sigma T^4 \tag{14.3-1}$$

The **Stefan–Boltzmann constant** σ has the value

$$\sigma = 5.67051 \times 10^{-8}\,\text{J m}^{-2}\,\text{s}^{-1}\,\text{K}^{-4} = 5.67051 \times 10^{-8}\,\text{W m}^{-2}\,\text{K}^{-4} \tag{14.3-2}$$

John William Strutt, third Baron Rayleigh, 1842–1919, was the 1904 Nobel Prize winner in physics, and Sir James Jeans, 1877–1946, was a British astronomer and physicist.

Rayleigh and Jeans constructed a classical theory of black-body radiation. They defined as their system the set of standing electromagnetic waves that could exist inside a cavity. For a rectangular cavity, they counted the possible standing waves of various wavelengths that could exist in the cavity with nodes at the walls and computed the average energy of each standing wave as a function of temperature using statistical mechanics (see Chapters 21 and 22). Their result was

$$\eta(\lambda)\,d\lambda = \frac{2\pi c k_B T}{\lambda^4}\,d\lambda \tag{14.3-3}$$

where c is the speed of light, k_B is Boltzmann's constant, and T is the absolute temperature.

Max Planck, 1858–1947, received the Nobel Prize in physics in 1918 for this theory, although at first most other physicists were reluctant to believe that it was correct.

Equation (14.3-3) agrees well with experiment for large values of the wavelength (much larger than visible wavelengths), but predicts that the spectral radiant emittance becomes large without bound in the limit of short wavelength. This failure of the Rayleigh–Jeans theory was called the "ultraviolet catastrophe." In 1900, Planck devised a new theory of black-body radiation that eliminated the ultraviolet catastrophe. Although he was working to obtain a result in agreement with experimental data, his theory is based on assumptions (hypotheses) that at the outset had no direct evidence to support them. The following statements are a simplified version of assumptions that lead to his result:[2]

1. In the walls of the cavity there exist oscillating electric charges. Each such oscillator has a characteristic fixed frequency of oscillation, but many oscillators are present and every frequency is represented.
2. The standing waves in the cavity are equilibrated with the oscillators in such a way that the average energy of standing waves of a given frequency equals the average energy of the oscillators of the same frequency.
3. The energy of a wall oscillator is **quantized**. That is, it is capable of assuming only one of the values

$$E = 0, h\nu, 2h\nu, 3h\nu, 4h\nu, \ldots, nh\nu, \ldots \tag{14.3-4}$$

where ν is the frequency of the oscillator and where h is a new constant, now known as **Planck's constant**. The quantity n, which can take on any nonnegative integral value, is called a **quantum number**. A quantum number is an integer or some other value that can be used to specify which state occurs from a set of possible states. Figure 14.11 schematically shows this energy quantization. Quantization has been compared to a ladder. A person can stand on any rung of a ladder, but nowhere between the rungs. The energy can take on any of the values in Eq. (14.3-4), but no value between these values.
4. The probability of any energy is given by the Boltzmann probability distribution, Eq. (1.8-25).

The result of Planck's derivation is that the spectral radiant emittance is given by

$$\eta(\lambda)\,d\lambda = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_B T} - 1)}\,d\lambda \tag{14.3-5}$$

This formula agrees accurately with experimental measurements of blackbody radiation at all temperatures and wavelengths if an optimum value of the constant h is taken. By fitting data available at the time, Planck was able to get a value of h approximately equal to the presently accepted value, 6.62608×10^{-34} J s. Planck's formula agrees with an empirical law known as Wien's law, with the result of Rayleigh and Jeans for large wavelengths and with the Stefan–Boltzmann law.

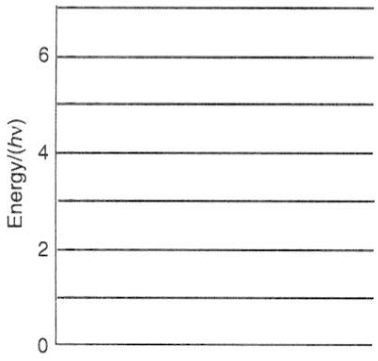


Figure 14.11. The Quantized Energies of an Oscillator as Postulated by Planck. The horizontal line segments are plotted at the heights of the assumed energy values, 0, $h\nu$, $3h\nu$, $4h\nu$, $5h\nu$, $6h\nu$, $7h\nu$, etc.

EXAMPLE 14.4

Find the relation of the wavelength of maximum spectral radiant emittance to the temperature.

[2] M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966, pp. 10ff.

Solution

We set the derivative of the function of Eq. (14.3-5) equal to zero:

$$\frac{d\eta}{d\lambda} = 2\pi hc^2 \frac{(hc/\lambda k_B T)e^{hc/\lambda k_B T} - 5(e^{hc/\lambda k_B T} - 1)}{\lambda^6[e^{hc/\lambda k_B T} - 1]} = 0$$

This expression can vanish only if the numerator vanishes, which is equivalent to

$$\frac{hc}{\lambda_{max} k_B T} = 5(1 - e^{-hc/\lambda_{max} k_B T})$$

This equation must be solved by numerical approximation. The result is the Wien displacement law,

$$\lambda_{max} = (0.2014)\frac{hc}{k_B T} = \frac{2.898 \times 10^{-3}\,\text{m K}}{T} \tag{14.3-6}$$

***Exercise 14.9**

Find the temperature that corresponds to a wavelength of maximum spectral emittance in the red part of the visible spectrum at 650. nm.

Exercise 14.10

Show that in the limit as $\lambda \to \infty$, Eq. (14.3-5) agrees with Eq. (14.3-3).

***Exercise 14.11**

Use the definite integral

$$\int_0^\infty \frac{x^3}{e^x - 1}\,dx = \frac{\pi^4}{15} \tag{14.3-7}$$

to derive the Stefan–Boltzmann law, Eq. (14.3-1). Calculate the theoretical value of the Stefan–Boltzmann constant.

Einstein's Theory of the Photoelectric Effect

Albert Einstein, 1879–1955, was a German-Swiss-American physicist who received the 1921 Nobel Prize in physics for this work. He was the greatest physicist of the twentieth century and made fundamental contributions in almost every area of theoretical physics.

When a metal plate inside an evacuated glass tube is illuminated with light of sufficiently short wavelength, it emits electrons. Electrons are not ejected unless the wavelength of the incident light is at least as small as a threshold wavelength, and the maximum energy of the ejected electrons depends only on the wavelength. There was no explanation for this behavior until 1905, when Einstein published a theory for the photoelectric effect. This theory is based on the hypothesis that the energy in a beam of light consists of discrete "quanta," and that each quantum has an energy

$$E = h\nu = \frac{hc}{\lambda} \tag{14.3-8}$$

where h is Planck's constant and c is the speed of light. Equation (l4.3-8) is known as the **Planck–Einstein relation**. The quanta of light are called **photons**.

Einstein obtained the quantitative explanation for the photoelectric effect from Eq. (14.3-8). The energy of an electron ejected from the metal is equal to the energy of the

photon minus the energy required to detach the electron from the metal. The **work function** W is the minimum energy required to detach an electron from a given substance. The maximum electron energy is

$$E_{\max}(\text{electron}) = h\nu - W = \frac{hc}{\lambda} - W \tag{14.3-9}$$

Robert A. Millikan, 1868–1953, was an American physicist who received the Nobel Prize in physics in 1923 for his measurement of the charge on the electron.

In 1916 Millikan made accurate measurements of the photoelectric effect that agreed well with Eq. (14.3-9).

Since light exhibits a particlelike nature in some experiments and wavelike properties in other experiments, we say that it has a **wave–particle duality**. This terminology means that light appears in some circumstances to act like a wave and in other circumstances to act like a particle. We cannot adequately answer the question: "What is light *really* like?" We use the wave description when it explains the observations of a particular experiment, and use the particle description when it explains the observations of another experiment.

***Exercise 14.12**

The work function of nickel equals 5.0 eV. Find (a) the threshold wavelength for nickel and (b) the maximum electron speed for a wavelength of 195 nm.

Bohr's Theory of the Hydrogen Atom

Excited hydrogen atoms emit light when electrons in higher energy states drop to lower energies. However, only certain wavelengths are emitted. Four wavelengths are present in the visible light and other wavelengths occur in the ultraviolet and in the infrared. When viewed in a spectroscope, each wavelength produces an image of the slit of the spectroscope, resembling a line segment. Such a set of separated lines is called a **line spectrum** and the slit images are called **spectral lines**.

Johannes Robert Rydberg, 1854–1919, was a Swedish physicist.

Rydberg was able to represent the wavelengths of all of the spectral lines of hydrogen atoms with a single empirical formula:

$$\frac{1}{\lambda} = \Re_{\text{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-10}$$

Ernest Rutherford, first Baron Rutherford of Nelson, 1871–1937, was a British physicist originally from New Zealand who won the 1908 Nobel Prize in chemistry, and who coined the terms α, β, and γ radiation.

Niels Henrik David Bohr, 1885–1962, was a Danish physicist who received the Nobel Prize in physics in 1922 for this work. He was responsible for much of the accepted physical interpretation of quantum mechanics and for the quantum mechanical explanation of the form of the periodic table of the elements.

where n_1 and n_2 are two positive integers and $\Re_{\text{H}}$ is a constant known as **Rydberg's constant** for the hydrogen atom, equal to $1.09677581 \times 10^7\ \text{m}^{-1}$. Using classical physics, no explanation for this relationship could be found.

In 1911, Rutherford scattered α-particles from a thin piece of gold foil. From the way in which the α-particles were scattered, he concluded that atoms contained a very small positive nucleus containing almost all of the mass of the atom, with the negative electrons orbiting around the nucleus. However, according to the electrodynamics of Maxwell, an orbiting electron would emit electromagnetic radiation, losing energy and falling onto the nucleus and collapsing the atom. Classical physics was unable to explain either the line spectrum of the hydrogen atom or its continuing existence.

In 1913, Bohr published a theory of the hydrogen atom, based on unproven assumptions. A simplified version of Bohr's assumptions is:

1. The hydrogen atom consists of a positive nucleus of charge e and an electron of charge $-e$ moving around it in a circular orbit. The charge e had been determined by Millikan to have the value $1.6022 \times 10^{-19}\ \text{C}$.

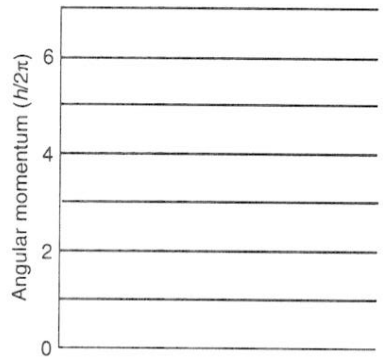


Figure 14.12. The Quantized Angular Momentum Values of Electronic Motion in a Hydrogen Atom as Postulated by Bohr. The horizontal line segments are plotted at the heights of the assumed angular momentum values, $h/2\pi$, $2h/2\pi$, $3h/2\pi$, $4h/2\pi$, $5h/2\pi$, $6h/2\pi$, $7h/2\pi$, etc.

2. The angular momentum (see Appendix D) of the electron is quantized: its magnitude can take on one of the values $h/2\pi$, $2h/2\pi$, $3h/2\pi$, $4h/2\pi$, etc., where h is Planck's constant. No other values are possible. Figure 14.12 schematically shows the quantization of the angular momentum.
3. Maxwell's equations do not apply. Radiation is emitted or absorbed only when a sudden transition is made from one quantized value of the angular momentum to another.
4. The wavelength of emitted or absorbed light is given by the Planck–Einstein relation, Eq. (14.3-8), with the energy of the photon equal to the difference in energy of the initial and final states of the atom.
5. In all other regards, classical mechanics is valid.

We now derive the consequences of Bohr's assumptions. For simplicity, we assume that the electron orbits around a stationary nucleus. This is a good approximation, but it can be removed if desired by replacing the mass of the orbiting electron by the reduced mass of the electron and the nucleus (see Appendix D). To maintain a circular orbit, there must be a centripetal force on the electron:

$$F_r = -\frac{mv^2}{r} \tag{14.3-11}$$

where v is the speed of the electron, m is its mass, and r is its distance from the nucleus (see Eq. (D-13) of Appendix D).

*Exercise 14.13

Find the centripetal force on an object of mass 1.50 kg if you swing it on a rope so that the radius of the orbit is 2.50 m and the time required for one orbit is 1.00 s (a speed of 9.43 m s^{-1}).

The centripetal force is provided by the electrostatic attraction of the positive nucleus for the negative electron:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \tag{14.3-12}$$

where ε_0 is the permittivity of the vacuum.

The angular momentum of the electron in a circular orbit is given by Eq. (D-15) of Appendix D. It is quantized, according to assumption 2:

$$L = rmv = \frac{nh}{2\pi} \tag{14.3-13}$$

where the **quantum number** n is a positive integer.

Equation (14.3-13) is solved for the speed v and the result is substituted into Eq. (14.3-12). The resulting equation is solved for r to give

$$r = \frac{h^2 4\pi\varepsilon_0}{4\pi^2 me^2} n^2 = a_0 n^2 \tag{14.3-14}$$

where a_0 is equal to 5.29×10^{-11} m 52.9 pm and is called the **Bohr radius**. Figure 14.13 depicts the first few Bohr orbits.

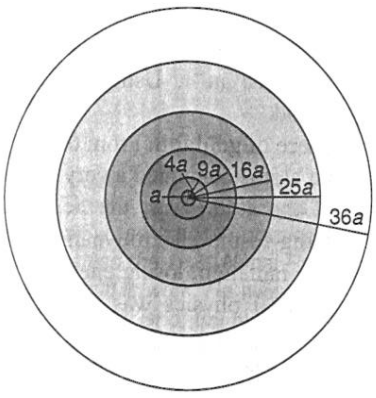


Figure 14.13. The Quantized Bohr Orbits. The radius of an electron orbit can take on only the values a, $4a, \ldots, n^2a, \ldots$ where n is a positive integer.

Exercise 14.14

a. Obtain Eq. (14.3-14) from Eqs. (14.3-12) and (14.3-13).
b. Using the accepted values of the physical constants, verify the value of the Bohr radius.

The energy of the electron is also quantized. The potential energy for an electron of charge $-e$ in an orbit of radius r around a nucleus of charge e is

$$\mathscr{V} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{14.3-15}$$

where we choose a value of zero for the potential energy at $r \to \infty$.

Exercise 14.15

Using Eq. (D-6) of Appendix D and Eq. (B-41) of Appendix B, show that the potential energy of Eq. (14.3-15) leads to the force expression of Eq. (14.3-12).

The kinetic energy is given by

$$\mathscr{K} = \frac{1}{2}mv^2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} = \frac{1}{2}|\mathscr{V}| \tag{14.3-16}$$

where Eq. (14.3-12) has been used to replace v^2. The kinetic energy is equal to half of the magnitude of the potential energy. This is one of the consequences of the **virial theorem** of mechanics that holds for any system acted upon only by electrostatic forces.[3]

The total energy of the hydrogen atom is

$$E = E_n = \mathscr{K} + \mathscr{V} = -\frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^2 n^2} \tag{14.3-17}$$

where we have used Eq. (14.3-14) for the value of r. The energy is determined by the value of the quantum number, n. Figure 14.14 depicts the first few energy levels. Each horizontal line segment is placed at a height proportional to the energy value.

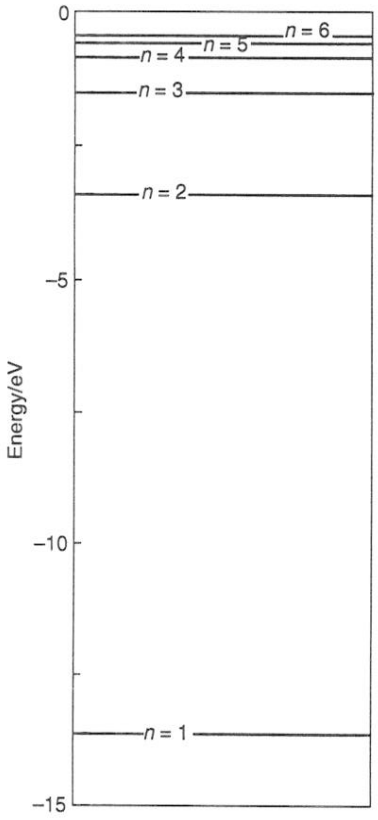


Figure 14.14. **The Quantized Electron Energies by the Bohr Theory.** The energy values are all negative, since an energy value of zero corresponds to enough energy barely to remove the electron from the atom.

The energy of an emitted or absorbed photon is equal to the difference between two quantized energies of the atom:

$$E_{(\text{photon})} = E_{n_2} - E_{n_1} = \frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-18}$$

Figure 14.15 depicts the first few transitions corresponding to emission of photons. Using the Planck–Einstein relation for the energy of the photon, Eq. (14.3-8),

$$\frac{1}{\lambda} = \frac{E_{n_2} - E_{n_1}}{hc} = \frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-19}$$

This is the formula of Rydberg, Eq. (14.3-10), with the constant $\Re$ given by the expression in front of the bracket. The first set of transitions shown in Figure 14.15, in which the lower-energy state (n_1 state) is the $n = 1$ state, corresponds to the series of spectral lines known as the Lyman series. The second set of transitions, in which

[3] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1991, pp. 434ff.

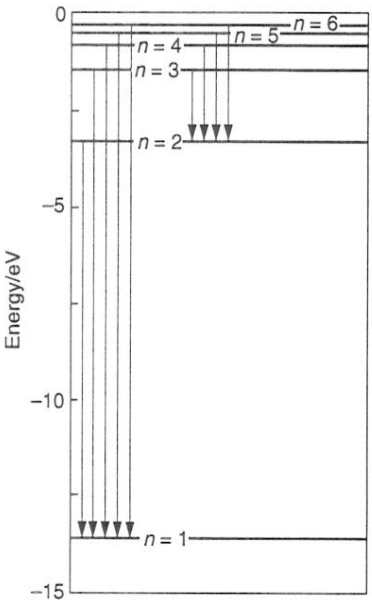


Figure 14.15. The Transitions between Bohr Theory Energies for the Hydrogen Atom. These are some of the transitions that lead to the wavelengths given by the Rydberg formula.

$n_1 = 2$, is the Balmer series. The next series, which is not shown, is the Paschen series. When the values of the physical constants are substituted into Eq. (14.3-19), we get

$$\Re_\infty = 1.097373 \times 10^7\ \mathrm{m}^{-1} \tag{14.3-20}$$

This value is labeled with the subscript ∞, corresponding to the assumption that the nucleus is stationary, as it would be if infinitely heavy. if we replace the mass of the electron by the reduced mass of the electron and proton to correct for the actual motion of the nucleus as in Eq. (D-27) of Appendix D, we get

$$\Re_\mathrm{H} = 1.09678 \times 10^7\ \mathrm{m}^{-1} \tag{14.3-21}$$

which is in agreement with the experimental value. This value of Rydberg's constant is for wavelengths measured in a vacuum. Wavelengths measured in air are slightly shorter than vacuum wavelengths, so the value of $\Re$ in air is larger by a factor of 1.00027, the refractive index of air for visible wavelengths.

Exercise 14.16

a. Substitute the values of the constants into the expression of Eq. (14.3-19) to verify the value of $\Re_\infty$.

b. Use the value of the reduced mass of the proton and electron to calculate the value of $\Re_\mathrm{H}$ from the value of $\Re_\infty$.

***c.** Calculate the wavelength and frequency of the light emitted when n changes from 4 to 2. What color does this correspond to?

14.4 De Broglie Waves and the Schrödinger Equation

Even though the Bohr theory gave the correct values for the energies of the hydrogen atom, it failed when applied to any other atoms or to any molecule. The theories of Planck, Einstein, and Bohr are now known as the "old quantum theory," and have been supplanted by the quantum theory of Schrödinger and Heisenberg, based on the "matter waves" of de Broglie.

De Broglie Waves

Prince Louis Victor de Broglie, 1892–1977, was a graduate student in 1923 and won the Nobel Prize in physics in 1929 for this work.

In 1923 de Broglie was trying to find a physical justification for Bohr's hypothesis of quantization of angular momentum. In classical physics, one thing that is quantized is the wavelength of standing waves, given for example by Eq. (14.2-19). De Broglie sought a way to relate this to Bohr's theory of the hydrogen atom, and came up with the idea that a moving particle such as an electron might somehow be accompanied by a "fictitious wave."[4]

According to Einstein's theory of relativity, a photon of energy E has a mass m such that

$$E = mc^2 \tag{14.4-1}$$

[4] Jammer, *op. cit.*, pp. 243ff (Note 2).

where c is the speed of light, even though it has no rest-mass. If the Planck–Einstein relation, Eq. (14.3-8), is used for the energy and if mc is replaced by the momentum p, Eq. (14.4-1) becomes

$$\frac{hc}{\lambda} = pc \qquad \text{or} \qquad \lambda = \frac{h}{p} \tag{14.4-2}$$

where λ is the wavelength. De Broglie deduced that the velocity of the wave accompanying a particle was the same as the velocity of the particle if the wavelength is given by Eq. (14.4-2).

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{14.4-3}$$

We omit most of de Broglie's argument, which is more complicated than simply saying that Eq. (14.4-3) is analogous to Eq. (14.4-2).

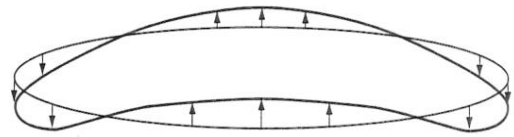
The quantization assumption of Bohr's theory arises naturally from Eq. (14.4-3) if one assumes that the circumference of a circular electron orbit in a hydrogen atom is equal to an integral number of wavelengths. This assumption means that the wave repeats itself with the same phase (with crests in the same positions) on each trip around the orbit, as depicted in Figure 14.16a. The situation depicted in Figure 14.16b is assumed not to occur. For a circular orbit

$$2\pi r = n\lambda = \frac{nh}{mv} \tag{14.4-4}$$

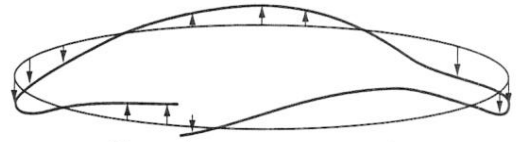
This equation is the same as Eq. (14.3-13), the hypothesis of Bohr.

$$mvr = \frac{nh}{2\pi} \tag{14.4-5}$$

Although he had established his wave–particle relation only for the motion of electrons in the hydrogen atom, de Broglie hypothesized this relation to hold for any motion of any particle. This proposal of **matter waves** was revolutionary. When



As assumed by de Broglie
(a)



Mismatch–contrary to assumption
(b)

Figure 14.16. De Broglie Waves around a Closed Orbit. (a) **An integral number of wavelengths on the circumference.** Only if the circumference is an integral multiple of the wavelength. (b) **Not an integral number of wavelengths on the circumference.** In this case, a unique point occurs at which there is a discontinuity in the wave.

de Broglie presented his doctoral thesis containing this proposal, the examining committee refused to believe that it might correspond to physical reality.

EXAMPLE 14.5

Calculate the de Broglie wavelength of a baseball of mass 5.1 ounces thrown at 95 miles per hour.

Solution

$$\lambda = \frac{6.6261 \times 10^{-34}\,\text{J s}}{(5.1\,\text{oz})(59\,\text{mi/h})}\left(\frac{16\,\text{oz}}{1\,\text{lb}}\right)\left(\frac{1\,\text{lb}}{0.4536\,\text{kg}}\right)\left(\frac{3600\,\text{s}}{1\,\text{h}}\right)\left(\frac{1\,\text{mi}}{1609\,\text{m}}\right)$$

$$= 1.1 \times 10^{-34}\,\text{m}$$

This value suggests why matter waves are not observed for objects of ordinary size.

De Broglie suggested at his final oral examination that electron diffraction by crystals could verify his theory. In 1927, Davisson and Germer[5] accidentally grew a single crystal while heating a piece of nickel. When they irradiated this piece of nickel with a beam of electrons, they observed diffraction effects, verifying the existence of de Broglie's matter waves.

*Exercise 14.17

Find the speed of electrons with a de Broglie wavelength equal to 2.15×10^{-10} m, the lattice spacing in a nickel crystal.

The notion of a wave moving along with a particle as it traces out a classical trajectory has been abandoned. We now speak of a wave–particle duality for electrons and other particles, with the wavelike properties inherently belonging to the object and not to an accompanying wave. This wave–particle duality is illustrated by a hypothetical experiment.[6] A beam of electrons, all with the same speed, is allowed to stream toward a partition with two slits in it, as depicted in Figure 14.17a. At some distance from the other side of the partition is a screen coated with a material such as zinc sulfide, which glows when an electron strikes it.

A glowing pattern of bands is observed on the screen when an intense beam of electrons is passed through the slits. This pattern is schematically depicted in Figure 14.17b, where the intensity of the glow is plotted as a function of position on the screen. The pattern is explained by the constructive and destructive interference of waves appearing to pass through the two slits, since the waves are diffracted by the slits and produce waves moving in various directions from the slits. If the difference in the path lengths from the two slits to a given point on the screen equals an integral number of wavelengths, there is constructive interference and a glowing band. Between the bands, there is destructive interference and little or no glow.

If the intensity of the source is decreased so that electrons pass through the slits one at a time, it can be observed that each electron lands at a single point on the screen. There is a tiny localized flash when each electron arrives. If the flashes are recorded and summed up, exactly the same pattern of diffraction bands appears as with an intense

[5] C. J. Davisson and L. H. Germer, *Phys. Rev.* **30**, 705 (1927).

[6] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. 3, Addison-Wesley, Reading Mass. 1965, Ch. 1.

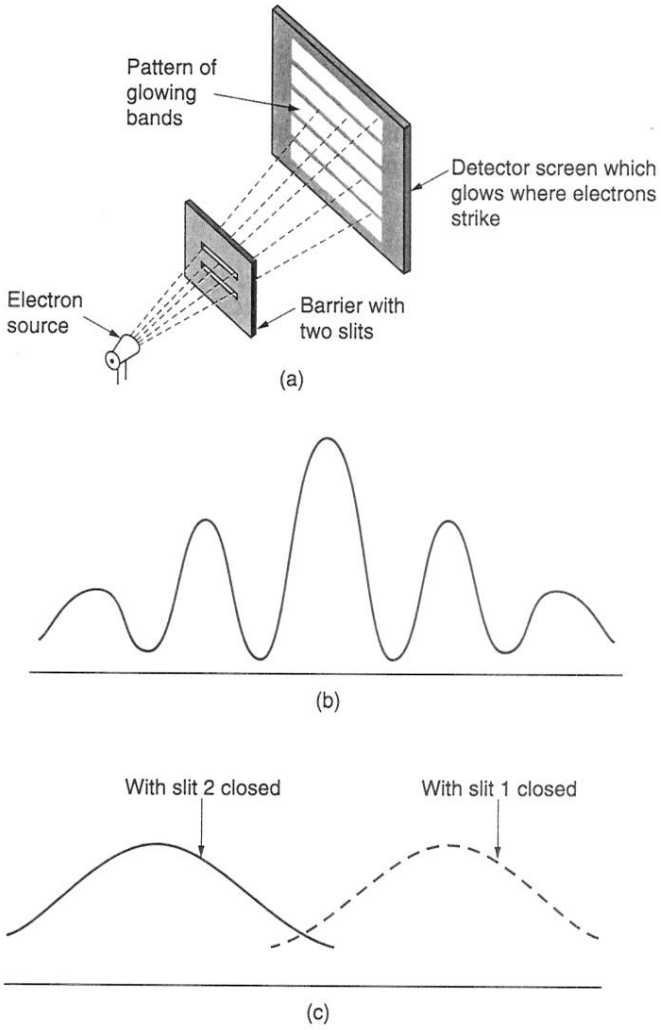


Figure 14.17. A Hypothetical Experiment with Electrons Passing through Two Slits. (a) **The apparatus.** (b) **The intensity of the glow due to electrons arriving at the screen in (a) with both slits open.** This diagram shows the diffraction pattern that proves that the particles have a wavelike character. (c) **The intensity of the glow due to electrons arriving at the screen in (a) with one slit open at a time.** If only one slit is open at a time, no diffraction pattern occurs.

beam of electrons. If one slit is covered while the electrons continue to pass through the second slit, there is a single band distributed on the screen. If the first slit is uncovered and the second slit is covered another single band is observed. The sum of these two single bands shows no interference effect, as shown schematically in Figure 14.17c.

Our observations are interpreted as follows: The path of any electron from the source to the screen cannot be specified when no attempt is made to detect its location along the path. The position of the electron can be determined only by doing something to it such as stopping it with a screen. Only when the screen is placed at the slits is it possible to say which slit the electron passes through. When the screen is some distance from the slits, there is no way to say whether the electron went through slit 1 or slit 2, and wavelike interference properties are observed as though the electron passed through both slits in a delocalized wavelike fashion.

The Schrödinger Equation

Erwin Schrödinger, 1887–1961, was an Austrian physicist who shared the 1933 Nobel Prize in physics with P. A. M. Dirac, who pioneered the development of relativistic quantum mechanics.

In 1926, Schrödinger published a series of four papers containing a wave equation for de Broglie waves. The first three papers presented the time-independent version of the Schrödinger equation and applied it to the hydrogen atom, rotation and vibration of diatomic molecules, and the effect of an external electric field on energy levels. The time-dependent version of the equation was reported in the fourth paper at the end of 1926.[7]

Nonrigorous Derivation of the Schrödinger Equation

In the formal theory of quantum mechanics, the Schrödinger wave equation is taken as a postulate (fundamental hypothesis). In order to demonstrate a relationship with the classical wave equation, we obtain the time-independent Schrödinger equation nonrigorously for the case of a particle that moves parallel to the x axis. For a wave along the x axis, the classical coordinate wave equation of Eq. (14.2-9) is

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \tag{14.4-6}$$

where we have used Eq. (14.2-19) to replace the wave constant κ in terms of the wavelength λ. Use of the de Broglie relation, Eq. (14.4-3), to replace λ gives

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}m^2v^2\psi = 0 \tag{14.4-7}$$

This equation now represents a matter wave moving along the x axis.

We eliminate the speed v from our equation, using the relation

$$E = \mathscr{K} + \mathscr{V} = \tfrac{1}{2}mv^2 + \mathscr{V}(x) \tag{14.4-8}$$

where $\mathscr{K}$ is the kinetic energy, $\mathscr{V}(x)$ is the potential energy, and E is the total energy. The result is the **time-independent Schrödinger equation** for one-dimensional motion:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathscr{V}(x)\psi = E\psi \tag{14.4-9}$$

where ψ is the coordinate wave function or time-independent wave function. We introduce the symbol $\hbar$ ("h-bar"):

$$\hbar = \frac{h}{2\pi} \tag{14.4-10}$$

Exercise 14.18

Carry out the algebra to obtain Eq. (14.4-9) from Eq. (14.4-7).

The left-hand side of Eq. (14.4-9) can be abbreviated by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathscr{V}(x) \tag{14.4-11}$$

[7] The time-independent equations are presented in *Ann. Physik*, **79**, 361 (1926), **79**, 489 (1926), and **80**, 437 (1926), and the time-dependent equation is presented in *Ann. Physik*, **81**, 109 (1926).

so that

$$\hat{H}\psi = E\psi \tag{14.4-12}$$

The quantity $\hat{H}$ is a **mathematical operator**, since it stands for the carrying out of mathematical operations. It is called the **Hamiltonian operator**. Mathematical operators will be discussed in Chapter 15.

The Time-Dependent Schrödinger Equation

For motion in the x direction, the time-dependent Schrödinger equation is postulated to be

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{14.4-13}$$

where i is the imaginary unit

$$i = \sqrt{-1} \tag{14.4-14}$$

There is no way to construct the time-dependent Schrödinger equation from the classical wave equation because that wave equation is second order in time while the Schrödinger equation is first order in time. A first-order differential equation requires one initial condition to apply a general solution to a specific case, while a second-order differential equation requires two initial conditions. Equation (14.2-12) required one initial condition related to the position of the string and one related to its velocity in order to assign values to the two constants F and G. The uncertainty principle of quantum mechanics (to be discussed later) implies that positions and velocities cannot be specified simultaneously to arbitrary accuracy. For this reason only one initial condition is possible, which requires the Schrödinger equation to be first order in time. The fact that the equation is first order in time also requires that the imaginary unit must occur in the equation in order for oscillatory solutions to exist. The function Ψ is the **time-dependent wave function**, or the displacement of the matter wave as a function of position and time. In this chapter and the next we will use a capital psi (Ψ) for a time-dependent wave function, and a lower-case psi (ψ) for a coordinate wave function.

The time-independent Schrödinger equation, Eq. (14.4-12), can be obtained from the time-dependent equation by separation of variables. We assume a trial solution of the same type as with the classical wave function:

$$\Psi(x, t) = \psi(x)\zeta(t) \tag{14.4-15}$$

We use the same symbols as for the factors in the classical wave function, Eq. (14.2-4), but do not mean to imply that they are the same functions. We substitute (14.4-15) into Eq. (14.4-13) and divide by $\psi(x)\zeta(t)$, obtaining

$$\frac{1}{\psi}\hat{H}\psi = \frac{i\hbar}{\zeta}\frac{d\zeta}{dt} \tag{14.4-16}$$

The variables x and t are separated in this equation. Each side is equal to the same constant, which we denote by E:

$$\frac{1}{\psi}\hat{H}\psi = E \tag{14.4-17}$$

and

$$\frac{i\hbar}{\zeta}\frac{d\zeta}{dt} = E \tag{14.4-18}$$

Multiplication of the first equation by ψ and of the second equation by $\zeta/i\hbar$ gives

$$\hat{H}\psi = E\psi \tag{14.4-19}$$

and

$$\frac{d\zeta}{dt} = \frac{E}{i\hbar}\zeta \tag{14.4-20}$$

Equation (l4.4-19) is the same as the time-independent Schrödinger equation, Eq. (14.4-12), so ψ is the same coordinate wave function as in that equation and E is the constant energy of the system. Equation (14.4-20) has the solution

$$\zeta(t) = Ce^{Et/i\hbar} = Ce^{-iEt/\hbar} \tag{14.4-21}$$

where C is a constant. Since the Schrödinger equation is satisfied for any value of C, we take $C = 1$ and the complete wave function is

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \tag{14.4-22}$$

If we have a solution to the time-independent Schrödinger equation, including knowledge of the value of the energy E, we can immediately write a solution to the time-dependent equation by multiplying the coordinate wave function by the function ζ. This type of solution, with the coordinate and time dependence in separate factors, corresponds to a standing wave, as in the classical wave. There are also solutions of the time-dependent Schrödinger equation that correspond to traveling waves, and the time-independent Schrödinger equation does not necessarily apply to such solutions. The time-dependent equation applies to all cases.

The coordinate wave function can in many cases be chosen to be a real function. The function ζ is always complex, and can be written as a real part plus an imaginary part (see Appendix B):

$$e^{-iEt/\hbar} = \cos(-Et/\hbar) + i\sin(-Et/\hbar) = \cos(Et/\hbar) - i\sin(Et/\hbar) \tag{14.4-23}$$

where we have used the fact that the cosine is an even function and the sine is an odd function. For an even function, $f(-x) = f(x)$, and for an odd function, $f(-x) = -f(x)$. The real part and the imaginary parts oscillate with the same frequency, but out of phase. If the coordinate wave function is real, the real and imaginary parts of the complete wave function have stationary nodes in the same locations, since they have the same coordinate factor.

The Schrödinger Equation in Three Dimensions

For a single particle moving in three dimensions, the Hamiltonian operator is

$$\hat{H} = \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathcal{V}(x, y, z) = -\frac{\hbar^2}{2m}\nabla^2 + \mathcal{V}(x, y, z) \tag{14.4-24}$$

where the potential energy $\mathscr{V}$ can depend on x, y, and z. The operator ∇^2 is the **Laplacian operator**, introduced in Eq. (11.2-13) and in Eq. (B-40) of Appendix B. In cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{14.4-25}$$

Since the Hamiltonian operator depends on x, y, and z, the coordinate wave function will depend on x, y, and z. To write the Schrödinger equation for a particular system, one must find an expression for the potential energy function that applies to that system. If it is convenient to express the potential energy in coordinates other than cartesian coordinates, the Laplacian operator can also be expressed in those coordinates in order to obtain a solution (see Appendix B).

The Schrödinger Equation for a Mutiparticle System

If the system consists of n point-mass particles moving in three dimensions, the potential energy can depend on $3n$ coordinates. The Hamiltonian operator for such a system is

$$\hat{H} = -\sum_{j=1}^{n} \frac{\hbar^2}{2m_j} \nabla_j^2 + \mathscr{V}(q) \tag{14.4-26}$$

where ∇_j^2 is the Laplacian operator for the coordinates of particle number j and where we use the abbreviation q to stand for the coordinates of all n particles. Since the Hamiltonian operator contains the coordinates of all of the particles, the solution to the Schrödinger equation must depend on all of these coordinates. Just as with the Schrödinger equation of a single particle, a solution to the time-independent Schrödinger equation for a system of many particles gives a solution to the time-dependent Schrödinger equation when multiplied by the time-dependent function of Eq. (14.4-21), but there can be other solutions of the time-dependent Schrödinger equation that are not of this form.

Exercise 14.19

Carry out the steps to show that equations analogous to Eqs. (14.4-19) and (14.4-20) hold for a system of n particles.

Eigenvalue Equations

The time-independent Schrödinger equation is one of a class of equations called **eigenvalue equations**. The word "eigenvalue" is a partial translation of the German word **Eigenwert**. A full translation is "characteristic value." An eigenvalue equation has on one side an operator operating on a function, and on the other side a constant (the **eigenvalue**) multiplying the same function, which is called the **eigenfunction**. In the time-independent Schrödinger equation, the eigenvalue is E, the value of the energy, and is called the **energy eigenvalue**. The coordinate wave function is often called the **energy eigenfunction**.

There is generally a set of eigenfunctions to a given eigenvalue equation, with each eigenfunction corresponding to a specific eigenvalue. Two common cases occur: (1) the

eigenvalue can take on any value within some range of values (a **continuous spectrum** of eigenvalues); (2) the eigenvalue can take on values only from a discrete set, with the values between the allowed values not permitted (a **discrete spectrum** of eigenvalues). The occurrence of a discrete spectrum of eigenvalues corresponds to quantization.

In addition to satisfying the Schrödinger equation, the wave function must satisfy other conditions. Since it represents a wave, we assume that it has the properties that are shared by all waves: (1) *the wave function is single-valued*, (2) *the wave function is continuous*, and (3) *the wave function is finite*. These properties will lead to boundary conditions that have important consequences.

14.5 The Particle in a Box. The Free Particle

In this section we solve the time-independent Schrödinger equation for the two simplest cases. This analysis will show how the wave function and the values of the energy are determined by the Schrödinger equation and the three conditions obeyed by the wave function.

The Particle in a One-Dimensional Box

The particle in a one-dimensional box is a model system that consists of a single structureless particle that can move parallel to the x axis. The particle moves without friction, but is confined to a finite segment of the x axis, from $x = 0$ to $x = a$. Inside this interval (the box) there is no force on the particle. This model system could represent a particle sliding in a tight-fitting (but frictionless) tube with closed ends or a bead sliding on a frictionless wire between barriers. The principal chemical system represented by this model is an electron moving in a conjugated system of single and double bonds. The model only very crudely represents this system since the electron interacts with the other electrons and with nuclei, but we will discuss this application in Chapter 18. Since the particle experiences no force inside the box, its potential energy is constant inside the box, and we choose the value zero for this constant. In order to represent absolute confinement within the box we say that this potential energy outside the box is made to approach infinity.

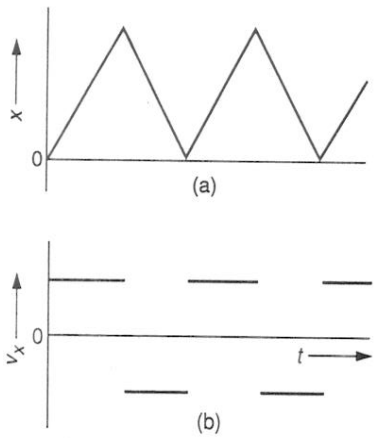


Figure 14.18. Mechanical Variables of a Particle in a Hard One-Dimensional Box. (a) **The position according to classical mechanics.** (b) **The velocity according to classical mechanics.** This diagram shows that the particle in a box moves back and forth at constant speed, according to classical mechanics.

Figure 14.18a shows the position of the particle as a function of time according to classical mechanics, and Figure 14.18b shows the velocity of the particle as a function of time. We will see that the quantum mechanics solution is qualitatively very different from this behavior. The time-independent Schrödinger equation for the system is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathcal{V}(x)\psi(x) = E\psi(x) \qquad (14.5\text{-}1)$$

where $\psi(x)$ is the coordinate wave function (energy eigenfunction) and E is the energy eigenvalue. We divide the x axis into three regions and solve separately in each region:

Region I: $x < 0$
Region II: $0 \leq x \leq a$
Region III: $a < x$

We will adjust the three solutions so that ψ is continuous at the boundaries between the regions.

In regions I and III the potential energy must approach an infinite value, so we write Eq. (14.5-1) as

$$\frac{d^2\psi}{dx^2} - \lim_{\mathcal{V}\to\infty} \frac{2m\mathcal{V}}{\hbar^2}\psi = -\frac{2mE}{\hbar^2}\psi \tag{14.5-2}$$

We assume that E is finite, so the right-hand side of this equation is finite. The left-hand side would be infinite unless ψ vanished, so the solution is

$$\psi^{(\mathrm{I})}(x) = \psi^{(\mathrm{III})}(x) = 0 \tag{14.5-3}$$

For region II

$$\frac{d^2\psi^{(\mathrm{II})}}{dx^2} = -\kappa^2\psi^{(\mathrm{II})} \tag{14.5-4}$$

where κ is given by

$$\kappa^2 = \frac{2mE}{\hbar^2} \tag{14.5-5}$$

Equation (14.5-4) is of the same form as Eq. (14.2-9). Its general solution is

$$\psi^{(\mathrm{II})}(x) = B\cos(\kappa x) + C\sin(\kappa x) \tag{14.5-6}$$

In order for ψ to be continuous at $x = 0$ and $x = a$, we must have the boundary conditions

$$\psi^{(\mathrm{II})}(0) = \psi^{(\mathrm{I})}(0) = 0; \qquad \psi^{(\mathrm{II})}(a) = \psi^{(\mathrm{III})}(a) = 0 \tag{14.5-7}$$

These conditions are similar to the boundary conditions for the vibrations of a string described in Section 14.2. In order for $\psi^{(\mathrm{II})}(0)$ to vanish, the constant B must vanish, because cos(0) equals unity while sin(0) equals zero. Thus

$$\psi^{(\mathrm{II})}(x) = C\sin(\kappa x) \tag{14.5-8}$$

The condition that $\psi^{(\mathrm{II})}(a)$ vanishes imposes a condition on κ, as in Eq. (14.2-14). The sine function vanishes when its argument is an integral multiple of π, so that

$$n\pi = \kappa a \qquad \text{or} \qquad \kappa = \frac{n\pi}{a} \tag{14.5-9}$$

where n is a quantum number that can take on integral values. Specifying a value of n is equivalent to specifying which energy eigenfunction is "occupied" by the system. We can now write a formula for the set of energy eigenfunctions:

$$\psi_n(x) = C\sin\left(\frac{n\pi x}{a}\right) \tag{14.5-10}$$

where we now omit the superscript (II).

The energy eigenvalues are quantized, with values determined by the value of n:

$$E = E_n = \frac{\hbar^2\kappa^2}{2m} = \frac{\hbar^2 n^2\pi^2}{2ma^2} = \frac{h^2 n^2}{8ma^2} \tag{14.5-11}$$

We disregard negative values of n, because replacing a value of n by its negative does not change the energy eigenvalue and is equivalent to changing the sign of C since the sine is an odd function. We also disregard $n = 0$ since $n = 0$ corresponds to $\psi = 0$. The value of C is unimportant at this stage since the Schrödinger equation is satisfied for any value of C and since the energy eigenvalue does not depend on C. We will later introduce a normalization procedure to assign convenient values to such constants.

There is a single energy eigenfunction for each energy eigenvalue. This is called the **nondegenerate** case. In the **degenerate** case there is more than one energy eigenfunc-

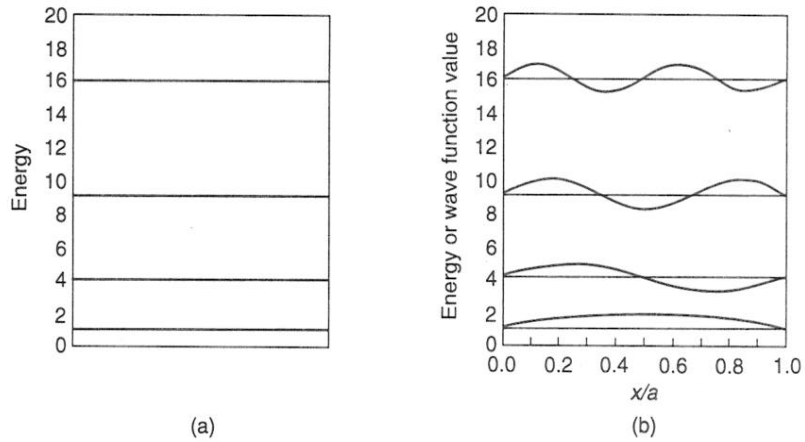


Figure 14.19. The Solutions to the Schrödinger Equation for a Particle in a One-Dimensional Box. (a) **The energy eigenvalues.** (b) **The energy eigenfunctions.** Compare the information about the motion of the particle in this figure with that in Figure 14.18.

tion corresponding to a given eigenvalue, and the number of eigenfunctions for a given eigenvalue is called its **degeneracy**. A single eigenfunction never corresponds to more than one eigenvalue. Figure 14.19a represents the energy eigenvalues by horizontal line segments at heights proportional to their energy values and Figure 14.19b shows the wave functions (energy eigenfunctions). Each wave function is plotted on a separate axis, placed at a height in the diagram corresponding to its energy eigenvalue. Equation (14.5-10) resembles Eq. (14.2-14) for the vibrating string and each wave function in Figure 14.19b resembles one of the standing waves in Figure 14.7.

The quantization of the energy eigenvalues comes not only from solving the Schrödinger equation but also from the boundary condition that the wave function must vanish at the ends of the box. Unlike the quantization by hypothesis of the old quantum theory, quantization has arisen from the mathematical analysis of the eigenvalue equation.

The energy in Eq. (14.5-11) is kinetic energy, since we set the potential energy inside the box equal to zero. Since we do not allow $n = 0$, the minimum possible kinetic energy is positive and is called the **zero-point energy**. It is not possible for the particle in a box to have zero kinetic energy. This result is very different from classical mechanics, which allows a particle to be at rest with zero kinetic energy.

EXAMPLE 14.6

Find the energy of an electron in a box of length 1.000 nm for $n = 1$.

Solution

$$E = \frac{(6.6261 \times 10^{-34}\,\text{J s})^2(1)^2}{(8)(14.109 \times 10^{-31}\,\text{kg})(1.000 \times 10^{-9}\,\text{m})^2} = 6.025 \times 10^{-20}\,\text{J}$$

*Exercise 14.20

How does the energy for a given value of n change if the length of the box is doubled? How does it change if the mass of the particle is doubled?

The Schrödinger Equation and De Broglie Waves

The particle in a box model provides the clearest illustration of the fact that the Schrödinger equation is the wave equation for de Broglie waves. In the case of zero potential energy, the total energy is equal to the kinetic energy so that

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{14.5-12}$$

where we use the definition of the momentum, $\mathbf{p} = m\mathbf{v}$. From Eq. (14.4-3) and Eq. (14.5-12),

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \tag{14.5-13}$$

which is the same as

$$E = \frac{h^2}{2m\lambda^2} \tag{14.5-14}$$

The energy of a de Broglie wave is inversely proportional to the square of its wavelength. When the relationship between the wavelength and the length of the box is used, this becomes the same as the energy expression in Eq. (14.5-11).

Exercise 14.21

a. Show that the value of the wavelength corresponding to ψ_n is equal to $2a/n$.

b. Show that the same formula for the energy as in Eq. (14.5-11) is obtained by substituting the result of part (a) into Eq. (14.5-14).

As the value of n increases, the energy increases, the wavelength decreases, and the number of nodes increases. *It is an important general fact that a wave function with more nodes corresponds to a higher energy.*

If the potential energy inside the box is assigned a nonzero constant value $\mathcal{V}_0$ instead of zero, the energy eigenfunction is unchanged and the energy eigenvalue is increased by the value of $\mathcal{V}_0$.

Exercise 14.22

a. Carry out the solution of the time-independent Schrödinger equation for the particle in a one-dimensional box with constant potential $\mathcal{V}_0$ in the box. Show that the energy eigenvalue is

$$E_n = \mathcal{V}_0 + \frac{h^2n^2}{8ma^2}$$

but that the wave function is unchanged.

b. The result of part (a) is generally true. That is, adding a constant to the potential energy adds the same constant to the energy eigenvalues. Write the time-independent Schrödinger equation for a general system of n particles, Eq. (14.4-26), and show that this statement is correct.

If a particle in a box is electrically charged, it can absorb or emit photons. The energy of a photon that is emitted or absorbed is equal to the difference in energy of the initial and final states of the particle.

***Exercise 14.23**

Calculate the wavelength and frequency of the photon emitted if an electron in a one-dimensional box of length 10.0 Å (1.00×10^{-9} m) makes a transition from $n = 3$ to $n = 2$ and the energy difference is entirely converted into the energy of the photon.

Equation (14.4-22) can be used to obtain the time-dependent wave function for a particle in a one-dimensional box:

$$\Psi_n(x, t) = C \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar}$$

$$= C \sin\left(\frac{n\pi x}{a}\right)(\cos(-iE_n t/\hbar) + i \sin(-iE_n t/\hbar)) \qquad (14.5\text{-}15)$$

It is generally possible to choose a real energy eigenfunction for a particle confined in a finite region, but the time-dependent wave function is always complex. We will usually refer to the energy eigenfunction as the coordinate wave function and the time-dependent wave function as the complete wave function. At times when we do not need to discuss the complete wave function we will simply call the energy eigenfunction "the wave function."

Exercise 14.24

***a.** Calculate the frequency of the de Broglie wave for the $n = 2$ and $n = 3$ states of an electron in a box of length 1.000 nm.

b. Calculate the difference between these frequencies.

c. Compare these frequencies and their difference with the photon frequency in Exercise 14.23. Do you think there is any simple relationship between these frequencies?

Specification of the State of a Particle in a Box

Instead of specifying the position and velocity of the particle, the state of the quantum-mechanical particle is specified by saying which wave function and energy eigenvalue correspond to the state of the particle. We recognize two cases:

1. The wave function of the system is known to be an energy eigenfunction times the appropriate time-dependent factor as in Eq. (14.5-15). Chemists are usually interested in this case. When a photon is absorbed or emitted by a molecule, the initial and final molecule states correspond to energy eigenfunctions.
2. The wave function is some function other than an energy eigenfunction times the appropriate time-dependent factor. Such a function must obey the time-dependent Schrödinger equation and the same boundary conditions as the energy eigenfunctions. It can be represented by a linear combination analogous to that of Eq. (14.2-23):

$$\Psi(x, t) = \sum_{n=1}^{\infty} A_n \psi_n(x) e^{-iE_n t/\hbar} \qquad (14.5\text{-}16)$$

where $A_1, A_2, \ldots$ are a set of time-independent constants. As in the classical case, this equation expresses the principle of superposition.

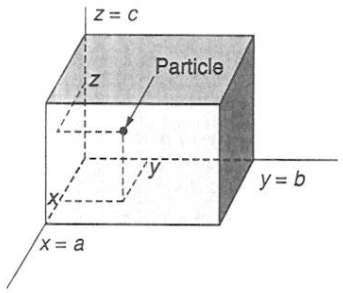


Figure 14.20. A Particle in a Hard Three-Dimensional Box. This system contains a single particle that moves freely so long as it remains in the box.

Exercise 14.25

Show that the function of Eq. (14.5-16) satisfies the time-dependent Schrödinger equation for the particle in a one-dimensional box.

The Particle in a Three-Dimensional Box

We now consider a model system consisting of a single point-mass particle confined in a three-dimensional rectangular box, which is placed so that its lower left rear corner is at the origin of coordinates and its walls are perpendicular to the coordinate axes, as depicted in Figure 14.20. Denote the length of the box in the x direction by a, the length in the y direction by b, and the length in the z direction by c. We will use this model system to represent the motion of an electron or of a gas molecule in a container.

The solution of the Schrödinger equation is carried out in Appendix F. The energy eigenfunction (coordinate wave function) is a product of three wave functions for particles in one-dimensional boxes

$$\psi_{n_x n_y n_z}(x, y, z) = C \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \tag{14.5-17}$$

where C is a constant. The energy eigenvalue is the sum of three energy eigenvalues for particles in one-dimensional boxes:

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{14.5-18}$$

There are three quantum numbers n_x, n_y, and n_z, which we will sometimes denote by the three values in parentheses, as for example (1,1,2), etc. A particular energy eigenfunction and its energy eigenvalue are specified by giving the values of the three quantum numbers.

If $a = b = c$ (a cubical box) the energy eigenvalue is

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{14.5-19}$$

There can be several states that correspond to the same energy eigenvalue in this case. The two sets of quantum numbers (1,2,3) and (3,2,1) both correspond to the same energy although they correspond to different states. A set of states with equal energies is called an **energy level**, and the number of states making up the energy level is called the **degeneracy** of the energy level.

EXAMPLE 14.7

For an electron in a cubical box of side 1.00×10^{-9} m, find the energy and the degeneracy of the level in which the state corresponding to (1,2,3) occurs.

Solution

The energy eigenvalue is

$$E_{123} = \frac{14h^2}{8ma^2} = \frac{(14)(6.6261 \times 10^{-34}\,\text{J s})^2}{(8)(14.109 \times 10^{-31}\,\text{kg})(1.00 \times 10^{-9}\,\text{m})^2}$$
$$= 8.43 \times 10^{-19}\,\text{J}$$

There are six permutations of the three distinct numbers: (1,2,3), (2,3,1), (3,1,2), (3,2,1), (1,3,2) and (2,1,3). There are no other sets of three integers whose squares add up to 14, so the degeneracy is 6.

***Exercise 14.26**

For an electron in the cubical box of Example 14.7 find the energy eigenvalues and degeneracies of all energy levels of lower energy than that in Example 14.7.

The Free Particle in One Dimension

The free particle is an object on which no forces act. The potential energy of the particle is equal to a constant, which we set equal to zero. If a point-mass particle can move only parallel to the x axis, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{14.5-20}$$

Equation (14.5-20) is the same as Eq. (14.5-4) for the motion of a particle in a box, but the boundary conditions are different. The general solution to Eq. (14.5-20) is the same as that in Eq. (14.5-6). We write this solution (the energy eigenfunction) in a different way:

$$\psi(x) = De^{i\kappa x} + Fe^{-i\kappa x} \tag{14.5-21}$$

where the constant κ is given by Eq. (14.5-5).

***Exercise 14.27**

Use the identity

$$e^{ix} = \cos(x) + i\sin(x) \tag{14.5-22}$$

to find the relations between the constants B, C, D and F that cause Eq. (14.5-6) and Eq. (14.5-21) to represent the same function.

There are now no walls at which the wave function must vanish. We must still conform our solution to the assumptions that the wave function be continuous and finite. The finiteness condition requires that κ be real. We let

$$\kappa = a + ib$$

where a and b are real. The solution is now

$$\psi(x) = De^{iax}e^{-bx} + Fe^{-iax}e^{bx} \tag{14.5-23}$$

If b is positive, the second term grows without bound for large positive values of x. If b is negative the first term grows without bound if x becomes large and negative. To keep

the wave function finite, b must vanish and κ must be real. The energy eigenvalues are given by Eq. (14.5-5):

$$E = \frac{\hbar^2\kappa^2}{2m} \tag{14.5-24}$$

There is no restriction on the values of the parameter κ except that it must be real, so E can take on any real nonnegative value. The energy is not quantized and there is no zero-point energy.

If F vanishes, the complete wave function is

$$\Psi(x, t) = De^{i\kappa x - iEt/\hbar} = De^{i(\kappa x - Et/\hbar)} \tag{14.5-25}$$

where E is given by Eq. (14.5-24). Separating the real and imaginary parts, we obtain

$$\Psi(x, t) = D\left[\cos\left(\kappa x - \frac{Et}{\hbar}\right) + i\sin\left(\frac{\kappa x - Et}{\hbar}\right)\right] \tag{14.5-26}$$

Comparison of this with Eq. (14.2-24) shows both the real and imaginary parts to be traveling waves moving to the right with a speed given by

$$c = \frac{\hbar\kappa}{2m} \tag{14.5-27}$$

A nonzero value of the constant F corresponds to a traveling wave moving to the left.

Exercise 14.28

Show that Eq. (14.5-27) is correct.

***Exercise 14.29**

Show that the function

$$\Psi(x, t) = Fe^{-i\kappa x - iEt/\hbar} \tag{14.5-28}$$

represents a traveling wave moving to the left, and find its speed.

If D and F are equal, the two traveling waves can produce a standing wave:

$$\psi(x) = D(e^{i\kappa x} + e^{-i\kappa x}) = 2D\cos(\kappa x) \tag{14.5-29}$$

Exercise 14.30

Use Eq. (14.5-22) to verify Eq. (14.5-29).

The complete wave function corresponding to Eq. (14.5-29) is

$$\Psi(x, t) = 2D\cos(\kappa x)e^{-iEt/\hbar} \tag{14.5-30}$$

Exercise 14.31

Show that if $D = -F$, a different standing wave results. How does it compare with that of Eq. (14.5-30)?

If the constants D and F are both nonzero but have unequal magnitudes, the complete wave function becomes

$$\Psi(x, t) = De^{i(\kappa x - Et/\hbar)} + Fe^{-i(\kappa x + Et/\hbar)} \tag{14.5-31}$$

which represents a combination of traveling waves with different amplitudes, one moving to the right and one moving to the left. This behavior is rather different from that found in classical mechanics, in which one state always corresponds to only one kind of behavior. The idea that a single particle can have a single state corresponding to motion in two different directions at the same time seems impossible, but it is allowed in quantum mechanics. A possible interpretation is that since some predictions of quantum mechanics are statistical in nature, a wave function should be thought of as representing the behavior of a large collection (an ensemble) of objects, all in the same state but capable of different outcomes of a particular measurement. We will return to this question in the next chapter.

The Free Particle in Three Dimensions

From the Hamiltonian operator in Eq. (14.4-24), the time-independent Schrödinger equation for a free particle moving in three dimensions is

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = -\frac{2mE}{\hbar^2}\psi \tag{14.5-32}$$

This is the same as for a particle inside a three-dimensional box, and it can be solved in the same way by separation of variables. For the special case of a traveling wave moving in a definite direction with a definite energy (definite values of κ_x, κ_y, and κ_z) the energy eigenfunction is

$$\psi(x, y, z) = De^{i\kappa_x x}e^{i\kappa_y y}e^{i\kappa_z z} \tag{14.5-33}$$

where

$$\kappa_x^2 = \frac{2mE_x}{\hbar^2}, \qquad \kappa_y^2 = \frac{2mE_y}{\hbar^2}, \qquad \kappa_z^2 = \frac{2mE_z}{\hbar^2} \tag{14.5-34}$$

The vector $\boldsymbol{\kappa}$ with components κ_x, κ_y, and κ_z points in the direction in which the traveling wave moves and is called the **wave vector**. The three components of the wave vector can take on any real values.

The energy eigenvalue is given by

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) = \frac{\hbar^2\kappa^2}{2m} \tag{14.5-35}$$

The energy is not quantized and there is no zero-point energy. Just as Eq. (14.5-31) represents a linear combination of waves moving in opposite directions, an energy eigenfunction for a three-dimensional free particle can consist of a linear combination of waves moving in various directions as long as the wave vectors have the same magnitude.

14.6 The Harmonic Oscillator

The time-independent Schrödinger equation of the harmonic oscillator is

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + \frac{1}{2}kz^2\psi = E\psi \tag{14.6-1}$$

where we continue to use the letter z for the coordinate as in Section 14.1. We define the constants

$$b = \frac{2mE}{\hbar^2}, \qquad a = \frac{\sqrt{km}}{\hbar} \tag{14.6-2}$$

so that the Schrödinger equation can be written

$$\frac{d^2\psi}{dz^2} + (b - a^2z^2)\psi = 0 \tag{14.6-3}$$

Charles Hermite, 1822–1901, was a great French mathematician who made many contributions to mathematics, including the proof that e (2.71828...) is a transcendental irrational number.

This differential equation is of the form of a well-known equation known as the Hermite equation (see Appendix F). The solutions to the Hermite equation are of the form

$$\psi(z) = e^{-az^2/2}S(z) \tag{14.6-4}$$

where $S(z)$ is a power series

$$S(z) = c_0 + c_1z + c_2z^2 + c_3z^3 + \cdots = \sum_{n=0}^{\infty} c_nz^n \tag{14.6-5}$$

with constant coefficients $c_1, c_2, c_3, \ldots$ Hermite showed that the series must terminate in order to keep ψ from becoming infinite as $|z|$ becomes large. The series S becomes one of a set of polynomials known as **Hermite polynomials**. Appendix F contains some information about the solution. As is shown in Appendix F, the termination of the polynomials determines the energy eigenvalues, which are given by

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right) \tag{14.6-6}$$

where v is the frequency of the oscillator predicted by classical mechanics, (see Eq. (14.1-10)) and where $v = 0, 1, 2, 3, \ldots$. The energy is quantized and there is a zero-point energy:

$$E_0 = \tfrac{1}{2}h\nu \quad \text{(zero-point energy)} \tag{14.6-7}$$

With the particle in a box the quantization was produced by the condition that the wave function must be continuous. With the harmonic oscillator system, the energy quantization is produced by the condition that the wave function must be finite.

Exercise 14.32

***a.** Find a formula for the frequency of a photon with energy equal to the difference in energy between the $v = 0$ state and the $v = 1$ state.

b. How does this frequency compare with the classical frequency of the oscillator? How do you interpret this comparison?

For $v = 0$, the energy eigenfunction of the harmonic oscillator is

$$\psi_0 = S_0 e^{-az^2/2} = c_0 e^{-az^2/2} = \left(\frac{a}{\pi}\right)^{1/4} e^{-az^2/2} \tag{14.6-8}$$

where the choice for the value of c_0 will be discussed later. For $v = 1$, the energy eigenfunction is

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} z e^{-az^2/2} \tag{14.6-9}$$

and for $v = 2$, the wave function is

$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2az^2 - 1) e^{-az^2/2} \tag{14.6-10}$$

The factor $(2az^2 - 1)$ is proportional to the Hermite polynomial $H_2(\sqrt{a}\,z)$. Other energy eigenfunctions can be generated from formulas for the Hermite polynomials in Appendix F.

Exercise 14.33

Obtain a formula for ψ_3 for the harmonic oscillator. Do not evaluate the constant c_0.

Figure 14.21 shows the energy eigenfunctions for $v = 0$, $v = 1$, $v = 2$, and $v = 3$. Each wave function is plotted on a separate axis at a height representing the energy eigenvalue. The potential energy as a function of z is also plotted with the same energy scale. The classical turning point for any given energy is the point at which the potential energy is equal to the total energy, and the wave function is nonzero in the regions past the turning points. A comparison of these graphs with those for the particle in a one-dimensional box in Figure 14.19b shows that the general pattern of the nodes is the same, with more nodes corresponding to higher energy. In addition to the nodes at infinite $|z|$ for the harmonic oscillator and at the ends of the box for the particle in a box, the lowest-energy wave function has no nodes, the next-lowest-energy wave function has one node, and so on.

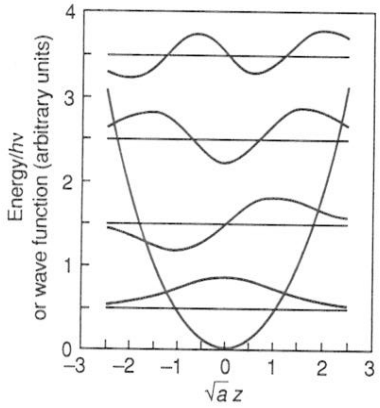


Figure 14.21. Harmonic Oscillator Wave Functions. This diagram shows the first four energy eigenfunctions for the harmonic oscillator, superimposed on a diagram of the energy eigenvalues.

We can now compare the classical and quantum-mechanical solutions for the harmonic oscillator. The classical solution gives the position and velocity of the oscillator as a function of time, as shown in Figure 14.2, and the state of the oscillator at any instant is specified by giving the value of the position and the velocity. The quantum-mechanical state is specified by stating which wave function corresponds to the state of the system. The wave function describes a de Broglie wave and, if the wave function corresponds to a standing wave, the de Broglie wave oscillates with a certain frequency but does not move. The de Broglie wave oscillates over all values of the coordinate, including values beyond the classical turning points. As we will show in the next chapter, this behavior corresponds to possible penetration of the particle into a classically forbidden region, which is called **tunneling**.

EXAMPLE 14.8

Calculate the frequency of oscillation of the wave function corresponding to the $v = 0$ state of the oscillating hydrogen atom of Example 14.2.

Solution

From Eq. (14.4-21) the time-dependent factor of the wave function is

$$\zeta(t) = e^{-iE_0 t/\hbar} = e^{-ihvt/2\hbar} = e^{-\pi ivt}$$

Inspection of this equation shows that the frequency is $v/2$, where v is the classical frequency of the oscillator, or $4.35 \times 10^{13}\ s^{-1}$. It is interesting that this frequency is not the same as that of the classical oscillator, and is also not the same as that of the other wave functions.

*Exercise 14.34

a. Find a formula for the frequency of oscillation of the harmonic oscillator wave function for the $v = 1$ state.

b. Find a formula for the frequency of oscillation of the harmonic oscillator wave function for the $v = 2$ state.

c. Compare the frequencies from parts (a) and (b) and the frequency from Example 14.8 with the frequency of the photon in Exercise 14.32 and with the frequency of oscillation of the classical oscillator.

d. Compare the difference between the frequencies of the $v = 2$ state and the $v = 1$ state with the frequency of the photon.

EXAMPLE 14.9

Find the classical amplitude of oscillation for a hydrogen atom attached to a chemical bond as in Example 14.2 if the energy is equal to that of the $v = 0$ quantum state.

Solution

For a classical energy equal to the $v = 0$ quantum energy, the turning point is given by

$$z_t^2 = \frac{hv}{k} = \frac{h}{2\pi}\sqrt{\frac{1}{km}} = \frac{6.6261 \times 10^{-34}\ \text{J s}}{\sqrt{(500\ \text{N m}^{-1})(1.674 \times 10^{-27}\ \text{kg})}}$$

$$= 1.15 \times 10^{-22}\ \text{m}^2$$

$$z_t = 1.07 \times 10^{-11}\ \text{m} = 0.107\ \text{Å}$$

*Exercise 14.35

Find the classical amplitude of oscillation of a hydrogen molecule with an energy equal to that of the $v = 0$ quantum state. Express it as a percentage of the bond length, 0.74×10^{-10} m. The molecule vibrates like a harmonic oscillator with a mass equal to the reduced mass of the two nuclei (see Eq. (D-30) of Appendix D). The force constant is equal to $576\ \text{N m}^{-1}$, and the reduced mass is equal to 8.369×10^{-28} kg (half the mass of a hydrogen atom).

Summary of the Chapter

The solution of the classical equation of motion for the harmonic oscillator provides formulas for the position and velocity of the mass as functions of time. The solution of the classical equation of motion for a flexible string prescribes the position and velocity of each point of the string as a function of time.

The "old quantum theory" consists of theories with arbitrary assumptions of quantization, devised to explain phenomena that classical physics could not explain. This theory consists primarily of the black-body radiation theory of Planck, the photoelectric effect theory of Einstein, and the hydrogen atom theory of Bohr.

De Broglie sought a physical justification for Bohr's assumption of quantization, and hypothesized that all particles move with a wavelike character with a wavelength given by

$$\lambda = \frac{h}{mv}$$

where h is Planck's constant, m is the mass of the particle, and v is its speed. According to the concept of wave–particle duality, electrons and other objects have some of the properties of classical waves and some of the properties of classical particles. Schrödinger discovered a wave equation for these matter waves. The time-independent equation is an eigenvalue equation given by

$$\hat{H}\psi = E\psi$$

where E is the energy of the system, ψ is a wave function, and $\hat{H}$ is the Hamiltonian operator. The time-dependent Schrödinger equation is

$$\hat{H}\psi = i\hbar \frac{\partial \Psi}{\partial t}$$

By assuming that the wave function Ψ is a product of a coordinate factor ψ and a time factor ζ, the coordinate factor is found to obey the time-independent Schrödinger equation.

The solutions to the time-independent Schrödinger equation for three example systems were presented: the particle in a hard box (in one dimension and in three dimensions), the free particle, and the harmonic oscillator. Sets of energy eigenfunctions and energy eigenvalues were obtained, and in the cases of the particle in a box and the harmonic oscillator, we found a discrete spectrum of energies, corresponding to energy quantization. Two new phenomena occurred. First, the particle in a box and harmonic oscillator exhibited a zero-point energy. Second, the harmonic oscillator has a nonzero wave function in regions where classical mechanics predicts that the particle cannot enter.

PROBLEMS

Problems for Section 14.1

14.36. The vibrational frequency of a $^{12}C^{16}O$ molecule is $6.5405 \times 10^{13}\ s^{-1}$. The atomic masses are: ^{12}C, 12.00000 amu; ^{16}O, 15.994915 amu.

a. Find the value of the force constant.
b. Find the vibrational frequency of a $^{13}C^{16}O$ molecule.
c. Find the vibrational frequency of a $^{12}C^{17}O$ molecule.

***14.37.** Assume that a $^{12}C^{16}O$ is adsorbed on a platinum surface in such a way that the carbon atom is held stationary. Find the vibrational frequency of the vibrating oxygen atom. See the previous problem for data.

14.38. The frequency of vibration of a $^{1}H^{35}Cl$ molecule is $8.966 \times 10^{13}\ s^{-1}$. What would the frequency be if the chlorine atom were infinitely massive?

Problems for Section 14.2

14.39. a. If a violin string has a fundamental frequency of $264\ s^{-1}$, find the frequency of each of the first three overtones.

b. If the speed of sound is $338\ m\ s^{-1}$, find the wavelength of the sound wave with frequency $264\ s^{-1}$.

14.40. a. In a closed organ pipe, the wavelength of the fundamental corresponds to twice the length of the pipe.