Chapter 5: Quantum Mechanics

- The Bohr theory of the atom has a number of severe limitations.
    - It applies only to hydrogen and one-electron ions such as He^+ and Li^{+2}.
    - It cannot explain why certain spectral lines are more intense than others (that is, why certain transitions between energy levels have greater probabilities of occurrence than others).
    - It cannot account for the observation that many spectral lines actually consist of several separate lines whose wavelengths differ slightly.
    - Perhaps most important, it does not permit us to obtain an understanding of how individual atoms interact with one another to endow macroscopic aggregates of matter with the physical and chemical properties we observe.
- A more general approach to atomic phenomena is required. Such an approach was developed in 1925 and 1926 by Erwin Schrödinger, Werner Heisenberg, Max Born, Paul Dirac, and others under the name of quantum mechanics.

5.1 QUANTUM MECHANICS

- Classical mechanics is an *approximation* of quantum mechanics
- The fundamental difference between classical (or Newtonian) mechanics and quantum mechanics lies in what they describe.
    - In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it.
    - Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm.
- In quantum mechanics, the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy.
    - The more we know about the position of a particle now, the less we know about its momentum and hence about its position later.
- The quantities whose relationships quantum mechanics explores are probabilities.
    - The Bohr theory states the radius of the electron's orbit in a ground state hydrogen atom is always exactly 5.3×10^{-11} m.
    - Quantum mechanics states that this is the most probable radius. In a suitable experiment, most trials will yield a different value, either larger or smaller, but the value most likely to be found will be 5.3×10^{-11} m.

Wave Function

- The quantity with which quantum mechanics is concerned is the wave function Ψ of a body.
- The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ.
- The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.
- Wave functions are usually complex with both real and imaginary parts.

$$\text{Wave function} \qquad \Psi = A + iB$$

where A and B are real functions.

- A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex is therefore taken as the product of Ψ and its complex conjugate Ψ^* which is $\Psi^*\Psi$.
- The complex conjugate of any function is obtained by replacing i by -i wherever it appears in the function.

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

and so

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

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

Normalization

- Since $|\Psi|^2$ is proportional to the probability density P of finding the body described by Ψ, the integral of $|\Psi|^2$ over all space must be finite - **the body is somewhere**, after all.
- If $\displaystyle\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 0$ the particle does not exist.
- It is usually convenient to have $|\Psi|^2$ be equal to the probability density P of finding the particle described by Ψ, rather than merely be proportional to P.
- If $|\Psi|^2$ is to equal P, then it must be true that

Normalization	$\displaystyle\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 1$	(5.1)

- A wave function that obeys Eq. (5.1) is said to be normalized. Every acceptable wave function can be normalized by multiplying it by an appropriate constant.

Well-Behaved Wave Functions

- Only wave functions with the properties below can yield physically meaningful results when used in calculations, so only such "well-behaved" wave functions are admissible as mathematical representations of real bodies.

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

- For a particle restricted to motion in the x direction, the probability of finding it between x_1 and x_2 is given by

Probability	$\displaystyle P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 \, dx$	(5.2)

5.2 THE WAVE EQUATION

- It can have a variety of solutions, including complex ones.
- Schrödinger's equation, which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of Newtonian mechanics, is a wave equation in the variable Ψ.

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

- Solutions of the wave equation may be of many kinds, reflecting the variety of waves that can occur.
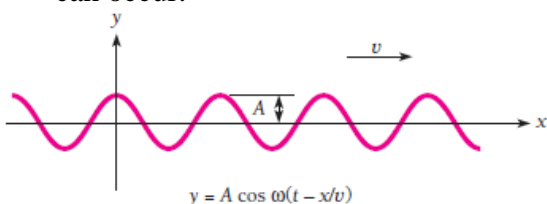

$$y = A \cos \omega(t - x/v)$$

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

All solutions must be of the form

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

where F is any function that can be differentiated.

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

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

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

5.3 SCHRÖDINGER'S EQUATION: TIME-DEPENDENT FORM

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

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

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

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

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

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

we have

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

- Equation (5.9) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the +x- direction.
- The expression for the wave function Ψ given by Eq. (5.9) is correct only for freely moving particles.
- However, we are most interested in situations where the motion of a particle is subject to various restrictions. An important concern, for example, is *an electron bound to an atom by the electric field of its nucleus*.
- What we must now do is obtain the fundamental differential equation for Ψ, which we can then solve for in a specific situation. This equation is Schrödinger's equation.
- We begin by differentiating Eq. (5.9) for Ψ twice with respect to x, which gives

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

$$p^2\Psi = -\hbar^2\frac{\partial^2 \Psi}{\partial x^2} \qquad (5.10)$$

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

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

$$E\Psi = -\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} \qquad (5.11)$$

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

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

- The function U represents the influence of the rest of the universe on the particle.
  - Of course, only a small part of the universe interacts with the particle to any extent; for instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.
- Multiplying both sides of Eq. (5.12) by the wave function Ψ.
- Now we substitute for E Ψ and p^2 Ψ from Eqs. (5.10) and (5.11) to obtain the **time dependent form of Schrödinger's equation**:

Time-dependent Schrödinger equation in one dimension

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

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

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

where the particle's potential energy U is some function of x, y, z, and t.
- Any restrictions that may be present on the particle's motion will affect the potential energy function U.
- Once U is known, Schrödinger's equation may be solved for the wave function Ψ of the particle, from which its probability density $|\Psi|^2$ may be determined for a specified x, y, z, t.
- Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

Erwin Schrödinger (1887–1961) Nobel Prize in Physics in 1933

5.4 LINEARITY AND SUPERPOSITION

- Wave functions add, not probabilities.

- An important property of Schrödinger's equation is that it is linear in the wave function. By this is meant that the equation has terms that contain and its derivatives but no terms independent of or that involve higher powers of or its derivatives.
- As a result, a linear combination of solutions of Schrödinger's equation for a given system is also itself a solution. If Ψ_1 and Ψ_2 are two solutions (that is, two wave functions that satisfy the equation), then $\Psi = a_1\Psi_1 + a_2\Psi_2$ is also a solution, where a_1 and a_2 are constants. Superposition principle.
- We conclude that interference effects can occur for wave functions just as they can for light, sound, water, and electromagnetic waves. Let us apply the superposition principle to the diffraction of an electron beam.
  - Figure 5.2a shows a pair of slits through which a parallel beam of monoenergetic electrons pass on their way to a viewing screen.
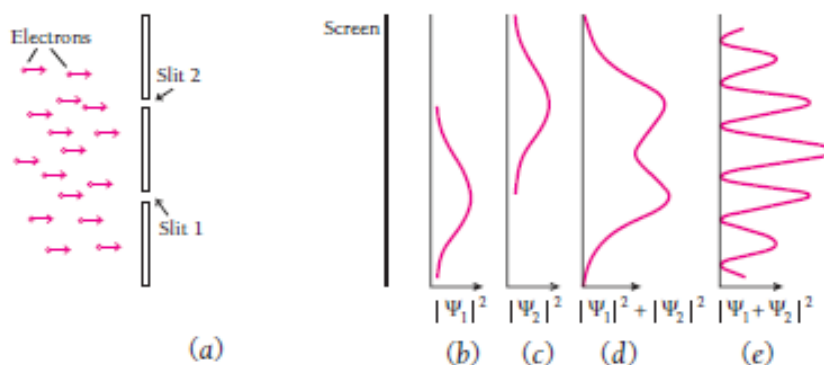

Figure 5.2 (a) Arrangement of double-slit experiment. (b) The electron intensity at the screen with only slit 1 open. (c) The electron intensity at the screen with only slit 2 open. (d) The sum of the intensities of (b) and (c). (e) The actual intensity at the screen with slits 1 and 2 both open. The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

  - If slit 1 only is open, the result is the intensity variation shown in Fig. 5.2b that corresponds to the probability density $P = |\Psi_1|^2 = \Psi_1^*\Psi_1$
  - If slit 2 only is open, as in Fig. 5.2c, the corresponding probability density is $P = |\Psi_2|^2 = \Psi_2^*\Psi_2$
  - We might suppose that opening both slits would give an electron intensity variation described by $P_1 + P_2$, as in Fig. 5.2d.
  - However, this is not the case because in quantum mechanics wave functions add, not probabilities.
  - Instead the result with both slits open is as shown in Fig. 5.2e, the same pattern of alternating maxima and minima that occurs when a beam of monochromatic light passes through the double slit of Fig. 2.4. Superposition of the wave functions.

5.5 EXPECTATION VALUES

- How to extract information from a wave function.
- Once Schrödinger's equation has been solved for a particle in a given physical situation, the resulting wave function $\Psi(x, y, z, t)$ contains all the information about the particle that is permitted by the uncertainty principle.
- Let us calculate the **expectation value** $<x>$ of the position of a particle confined to the x axis that is described by the wave function $\Psi(x, t)$.
  - This is the value of x we would obtain if we measured the positions of a great many particles described by the same wave function at some instant t and then averaged the results.
- What is the average position x of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1, N_2 particles at x_2, and so on? The average position in this case is the same as the center of mass of the distribution, and so

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\Sigma N_i x_i}{\Sigma N_i} \qquad (5.16)$$

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

$$P_i = |\Psi_i|^2 \, dx \qquad (5.17)$$

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

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

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

Expectation value for position
$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2 \, dx \qquad (5.19)$$

Example 5.2
A particle limited to the x axis has the wave function $\Psi = ax$ between $x=0$ and $x=1$; $\Psi = 0$ elsewhere. (a) Find the probability that the particle can be found between $x=0.45$ and $x=0.55$. (b) Find the expectation value $<x>$ of the particle's position.

Solution

(a) The probability is

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

(b) The expectation value is

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

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

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

5.6 OPERATORS
- Another way to find expectation values.
- A hint as to the proper way to evaluate $<p>$ and $<E>$ comes from differentiating the free particle wave function $\Psi = A \exp(-i/h(Et - px))$ with respect to x and to t. We find that

$$p\Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi \qquad (5.21)$$

$$E\Psi = i\hbar \frac{\partial}{\partial t} \Psi \qquad (5.22)$$

- An operator tells us what operation to carry out on the quantity that follows it.
- Thus, the operator E instructs us to take the partial derivative of what comes after it with respect to t and multiply the result by i.
- It is customary to denote operators by using a caret, so that ˆp is the operator that corresponds to momentum p and ˆE is the operator that corresponds to total energy E.
- From Eqs. (5.21) and (5.22) these operators are

Momentum operator
$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad (5.23)$$

Total-energy operator
$$\hat{E} = i\hbar\frac{\partial}{\partial t} \qquad (5.24)$$

- They are entirely general results whose validity is the same as that of Schrödinger's equation.
- Replace the equation E=KE+U for the total energy of a particle with the operator equation

$$\hat{E} = \hat{KE} + \hat{U} \qquad (5.25)$$

- The kinetic energy KE is given in terms of momentum p by

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

and so we have

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

Equation (5.25) therefore reads

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

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

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

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

Operators and Expectation Values

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

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

and the expectation value for E is

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

- Every observable quantity G characteristic of a physical system may be represented by a suitable quantum-mechanical operator ˆG. To obtain this operator, we express G in terms of x and p. If the wave function Ψ of the system is known, the expectation value of G(x, p) is

Expectation value of an operator

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

5.7 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

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

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

- Ψ is now the product of a time-dependent function exp(-(iE/h)t) and a position dependent function ψ. Substituting the Ψ of Eq. (5.31) into the time-dependent form of Schrödinger's equation, we find that

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

Dividing through by the common exponential factor gives

Steady-state Schrödinger equation in one dimension

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

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

Steady-state Schrödinger equation in three dimensions

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

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

Eigenvalues and Eigenfunctions

- The values of energy E_n for which Schrödinger's steady-state equation can be solved are called eigenvalues and the corresponding wave functions ψ_n are called eigenfunctions.
- The discrete energy levels of the hydrogen atom are an example of a set of eigenvalues.

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

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

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

- In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense.

Operators and Eigenvalues

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

Eigenvalue equation $\qquad\qquad \hat{G}\psi_n = G_n\psi_n \qquad\qquad\qquad (5.34)$

where $\hat{G}$ is the operator that corresponds to G and each G_n is a <u>real number</u>.

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

Example 5.3

An eigenfunction of the operator d^2/dx^2 is $\psi = \exp(2x)$. Find the corresponding eigenvalue.

Solution

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

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

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

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

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

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

Hamiltonian operator $\qquad\qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U \qquad\qquad (5.35)$

and is called the Hamiltonian operator. Evidently the steady-state Schrödinger equation can be written simply as

Schrödinger's equation $\qquad\qquad \hat{H}\psi_n = E_n\psi_n \qquad\qquad\qquad (5.36)$

Table 5.1 Operators Associated with Various Observable Quantities

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

Table 5.1 lists the operators that correspond to various observable quantities.

5.8 PARTICLE IN A BOX

- *How boundary conditions* and *normalization* determine **wave functions.**
- The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls.
  - We may specify the particle's motion by saying that it is restricted to traveling along the x axis between x=0 and x=L by infinitely hard walls.
  - A particle does not lose energy when it collides with such walls, so that its total energy stays constant.

    Figure 5.4 A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.
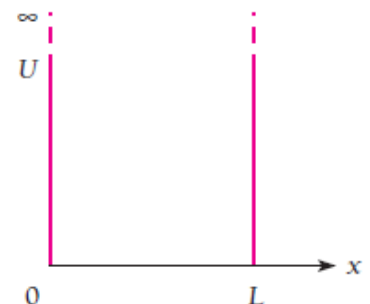
  - From a formal point of view the potential energy U of the particle is infinite on both sides of the box, while U is a constant -say 0 for convenience- on the inside (Fig. 5.4).

- Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function ψ is 0 for x≤0 and x≥L.
- Our task is to find what ψ is within the box, namely, between x=0 and x=L. Within the box Schrödinger's equation becomes

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

  since U=0 there. Equation (5.37) has the solution

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

  A and B are constants to be evaluated
- This solution is subject to the boundary conditions that
  - ψ=0 for x=0 and for x=L. Since cos 0=1, the second term cannot describe the particle because it does not vanish at x=0. Hence, we conclude that B=0.
  - Since sin0=0, the sine term always yields ψ=0 at x=0, as required, but ψ will be 0 at x=L only when

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

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

$$\text{Particle in a box} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1, 2, 3, \ldots \qquad (5.40)$$

Wave Functions

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

$$\psi_n = A \sin\frac{\sqrt{2mE_n}}{\hbar}x \qquad (5.41)$$

Substituting Eq. (5.40) for E_n gives

$$\psi_n = A \sin\frac{n\pi x}{L} \qquad (5.42)$$

for the eigenfunctions corresponding to the energy eigenvalues E_n.

- Normalization. With the help of the trigonometric identity $\sin^2\theta = 1/2(1-\cos2\theta)$ we find that

$$\int_{-\infty}^{\infty} |\psi_n|^2\, dx = \int_0^L |\psi_n|^2\, dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right) dx\right]$$

$$= \frac{A^2}{2}\left[x - \left(\frac{L}{2n\pi}\right)\sin\frac{2n\pi x}{L}\right]_0^L = A^2\left(\frac{L}{2}\right) \qquad (5.43)$$

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

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

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

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

The normalized wave functions of the particle are therefore

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

- The normalized wave functions ψ_1, ψ_2, and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig. 5.5.
  - Although ψ_n may be negative as well as positive, $|\psi_n|^2$ is never negative
  - Since ψ_n is normalized, its value at a given x is equal to the probability density of finding the particle there.
  - In every case $|\psi_n|^2=0$ at x=0 and x=L, the boundaries of the box.
    Figure 5.5 Wave functions and probability densities of a particle confined to a box with rigid walls.
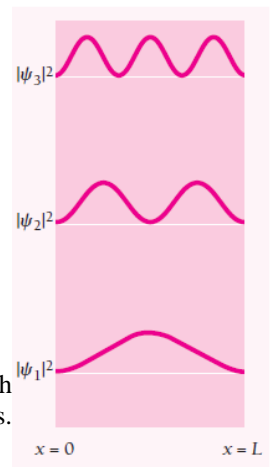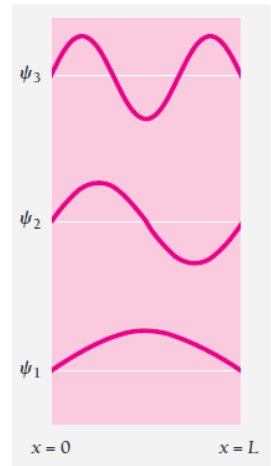
Example 5.4
Find the probability that a particle trapped in a box L wide can be found between 0.45L and 0.55L for the ground and first excited states.

Solution

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

$$P_{x_1, x_2} = \int_{x_1}^{x_2} |\psi_n|^2\, dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L}\, dx$$

$$= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2}$$

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

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

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

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

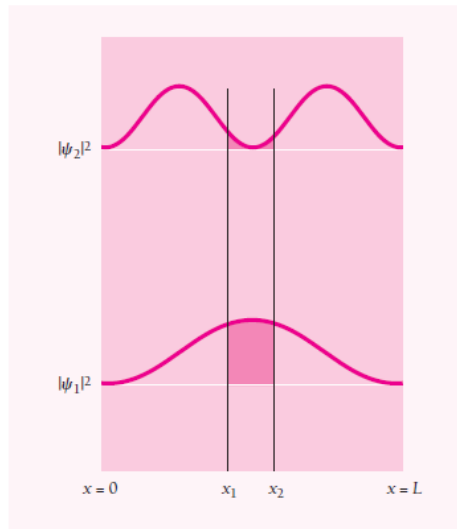This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

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

Example 5.5

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

Solution

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

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

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

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

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

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

5.9 FINITE POTENTIAL WELL

- The wave function penetrates the walls, which lowers the energy levels
- Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart.
- However, potential wells with barriers of finite height certainly do exist.
- Figure 5.7 shows a potential well with square corners that is U high and L wide and contains a particle whose energy E is less than U
  - According to classical mechanics, when the particle strikes the sides of the well, it bounces off without entering regions I and III.
  - In quantum mechanics, the particle also bounces back and forth, but now it has a certain probability of penetrating into regions I and III even though E<U.
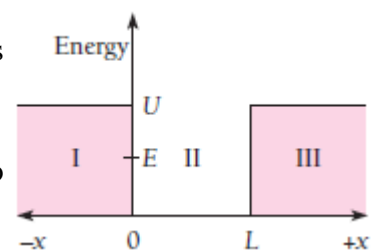 -

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

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

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

which we can rewrite in the more convenient form

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

where

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

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

$$\psi_I = Ce^{ax} + De^{-ax} \tag{5.55}$$

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

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

$$\psi_I = Ce^{ax} \tag{5.57}$$

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

- These wave functions decrease exponentially inside the barriers at the sides of the well.
- In regions II (within the well). Schrödinger's equation is the same as Eq. (5.37) and its solution is

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

   Here, $\psi_{II} = C$ at x=0 and $\psi_{II} = G$ at x =L, so both the sine and cosine solutions of Eq. (5.59) are possible.

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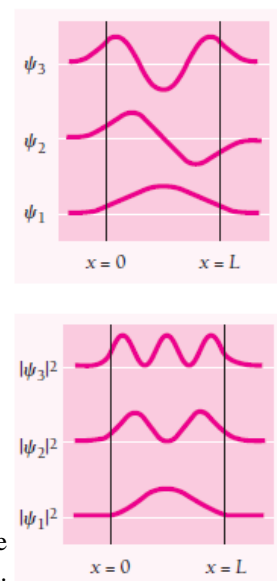

Figure 5.8 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

- A particle without the energy to pass over a potential barrier may still tunnel through it
- Although the walls of the potential well of Fig. 5.7 were of finite height, they were assumed to be infinitely thick.

    ◦ As a result, the particle was trapped forever even though it could penetrate the walls.

- We next look at the situation of a particle that strikes a potential barrier of height U, again with E<U, but here the barrier has a finite width (Fig. 5.9).
- What we will find is that the particle has a certain probability -not necessarily great, but not zero either- of passing through the barrier and emerging on the other side.
- The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it, so to speak.
- Not surprisingly, the higher the barrier and the wider it is, the less the chance that the particle can get through.
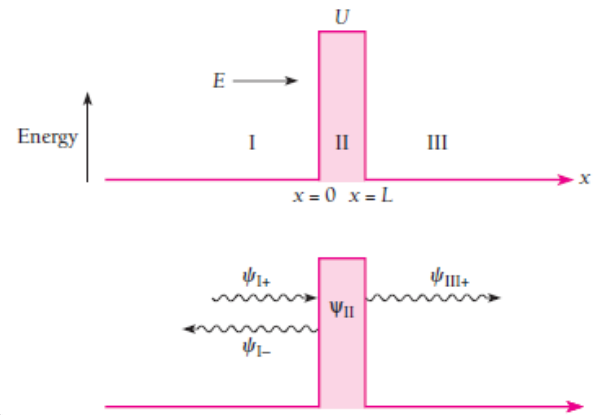
Figure 5.9 When a particle of energy E< U approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.

- The tunnel effect actually occurs, notably in the case of the alpha particles emitted by certain radioactive nuclei.

    ◦ An alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high.

    ◦ The probability of escape is so small that the alpha particle might have to strike the wall 1038 or more times before it emerges, but sooner or later it does get out.

- Tunneling also occurs in the operation of certain semiconductor diodes in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

Scanning Tunneling Microscope

- The ability of electrons to tunnel through a potential barner is used in an ingenious way in the scanning tunneling microscope (STM) to study surfaces on an atomic scale of size.

    ◦ In an STM, a metal probe with a point so fine that its tip is a single atom is brought close to the surface of a conducting or semiconducting material.

    ◦ Normally even the most loosely bound electrons in an atom on a surface need several electron-volts of energy to escape -this is the work function.

    ◦ However, when a voltage of only 10 mV or so is applied between the probe and the surface, electrons can tunnel across the gap between them if the gap is small enough, a nanometer or two.

    ◦ What is done is to move the probe across the surface in a series of closely spaced back-and-forth scans.

    ◦ The height of the probe is continually adjusted to give a constant tunneling current, and the adjustments are recorded so that a map of surface height versus position is built up.

The tungsten probe of a scanning tunneling microscope.

- Such a map is able to resolve individual atoms on a surface.
  - Actually, the result of an STM scan is not a true topographical map of surface height but a contour map of constant electron density on the surface. This means that atoms of different elements appear differently.
- Although many biological materials conduct electricity, they do so by the flow of ions rather than of electrons and so cannot be studied with STMs.
- The atomic force microscope (AFM) can be used on any surface, although with somewhat less resolution than an STM.
  - In an AFM, the sharp tip of a fractured diamond presses gently against the atoms on a surface.
  - A spring keeps the pressure of the tip constant, and a record is made of the deflections of the tip as it moves across the surface.
  - The result is a map showing contours of constant repulsive force between the electrons of the probe and the electrons of the surface atoms.

5.11 HARMONIC OSCILLATOR
- Its energy levels are evenly spaced.
- Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be
  - an object supported by a spring
  - floating in a liquid,
  - a diatomic molecule,
  - an atom in a crystal lattice … on all scales of size.
- The condition for harmonic motion is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed.

Hooke's law
$$F = -kx$$

This relationship is customarily called Hooke's law. From the second law of motion, $F = ma$, we have

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

Harmonic oscillator
$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \qquad (5.62)$$

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

$$x = A \cos(2\pi\nu t + \phi) \qquad (5.63)$$

where

Frequency of harmonic oscillator
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (5.64)$$

is the frequency of the oscillations and A is their amplitude. The value of ϕ, the phase angle, depends upon what x is at the time t=0 and on the direction of motion then.
- The importance of the simple harmonic oscillator in both classical and modern physics lies not in the strict adherence of actual restoring forces to Hooke's law, which is seldom true, but in the fact that *these restoring forces reduce to Hooke's law for small displacements x.*

- *As a result, any system in which something executes small vibrations about an equilibrium position* behaves very much like a simple harmonic oscillator.
- The potential-energy function U(x) that corresponds to a Hooke's law force may be found by calculating the work needed to bring a particle from x=0 to x=x against such a force.
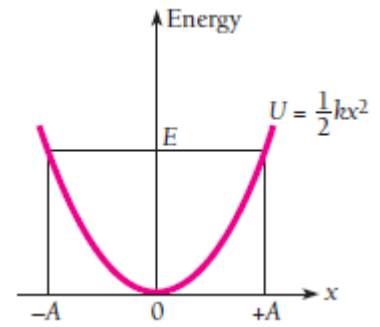
Figure 5.10 The potential energy of a harmonic oscillator is proportional to x^2, where x is the displacement from the equilibrium position. The amplitude A of the motion is determined by the total energy E of the oscillator, which classically can have any value.

- Three quantum mechanical modifications to this classical picture:
- The allowed energies will not form a continuous spectrum but instead a discrete spectrum of certain specific values only.
- The lowest allowed energy will not be E=0 but will be some definite minimum E=E_0.
- There will be a certain probability that the particle can penetrate the potential well it is in and go beyond the limits of -A and +A.

Energy Levels

Schrödinger's equation for the harmonic oscillator is, with U=1/2kx^2,

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

Energy levels of harmonic oscillator

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

- The energy of a harmonic oscillator is thus quantized in steps of hν. Note that when n=0,

Zero-point energy

$$E_0 = \tfrac{1}{2}h\nu \qquad (5.71)$$

which is the lowest value the energy of the oscillator can have.

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

- Figure 5.11 is a comparison of the energy levels of a harmonic oscillator with those of a hydrogen atom and of a particle in a box with infinitely hard walls.
  - The shapes of the respective potential-energy curves are also shown.
  - The spacing of the energy levels is constant only for the harmonic oscillator.
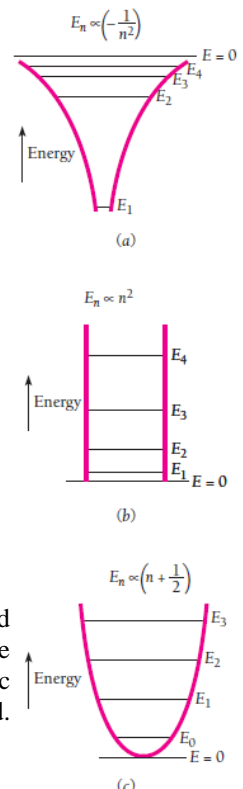
Figure 5.11 Potential wells and energy levels of (a) a hydrogen atom, (b) a particle in a box, and (c) a harmonic oscillator. In each case the energy levels depend in a different way on the quantum number n. Only for the harmonic oscillator are the levels equally spaced.