# Preface

This book is meant to be a text for a first course in quantum physics. It is assumed that the student has had courses in Modern Physics and in mathematics through differential equations. The book is otherwise self-contained and does not rely on outside resources such as the internet to supplement the material. SI units are used throughout except for those topics for which atomic units are especially convenient.

It is our belief that for a physics major a quantum physics textbook should be more than a one- or two-semester acquaintance. Consequently, this book contains material that, while germane to the subject, the instructor might choose to omit because of time limitations. There are topics and examples included that are not normally covered in introductory textbooks. These topics are not necessarily too advanced, they are simply not usually covered. We have not, however, presumed to tell the instructor which topics must be included and which may be omitted. It is our intention that omitted subjects are available for future reference in a book that is already familiar to its owner. In short, it is our hope that the student will use the book as a reference after having completed the course.

We have included at the end of most chapters a "Retrospective" of the chapter. This is not meant to be merely a summary, but, rather, an overview of the importance of the material and its place in the context of previous and forthcoming chapters. For example, the Retrospective in Chapter 3 we feel is particularly important because, in our experience, students spend so much time learning about eigenstates that they get the impression that physical systems "live" in eigenstates.

We believe that students should, after a very brief review of salient experiments and concepts that led to contemporary quantum physics (Chapter 1), begin solving problems. That is, the formal aspects of quantum physics, operator formalism, should be introduced only after the student has seen quantum mechanics in action. This is certainly not a new approach, but we prefer it to the alternative of the formal mathematical introduction followed by problem solving. More importantly, we believe that the students benefit from this approach. To this end we begin with a derivation (read: rationalization) of the Schrödinger equation in Chapter 2. This chapter continues with a discussion of the nature of the solutions of the Schrödinger equation, particularly the wave function. We discuss at length both the utility of the wave function and its characteristics. It is our observation that the art of sketching wave functions has been neglected. We are led to this conclusion from discussions

with graduate students who have had the undergraduate course, but are unable to sketch wave functions for an arbitrarily drawn potential energy function. We think that such a skill is crucial for understanding quantum mechanics at the introductory level and, thus, we spend a good deal of Chapter 2 discussing qualitative aspects of the wave function.

In Chapter 3 we solve the Schrödinger equation for two of the most important potential energy functions, the infinite square well and the harmonic oscillator. A point of contrast between the these potentials is penetration of oscillator wave functions into the classically forbidden region. We discuss this penetration at length because, in our experience, students have a great deal of difficulty with this concept. We then elaborate upon this concept by presenting the details of a problem not often seen in elementary texts, an infinite square well with a barrier in the middle. This affords the opportunity to see that, for energies less than the barrier height, the particle can be found on either side of the classically impenetrable barrier, thus making the particle's presence inside the barrier undeniable. This problem also sets the stage for solution of the more conventional barrier penetration problems in Chapter 5.

In Chapter 4 we discuss time-dependent states. We choose to do this at this point to contrast these states with those studied in the previous chapter. While we discuss the free particle wave packet (as does virtually every other text), we also present wave packets under the influence of a constant force and of a harmonic force. This discussion will, we believe, relate nicely to a later presentation of harmonic oscillator coherent states (Chapter 7).

Chapter 5 is an extension of Chapter 3 in that we solve the time-independent Schrödinger equation for several different one-dimensional potential energies. Included is one of the most successful analytic potential energy functions for characterizing diatomic molecular vibrations, the Morse potential. The chapter concludes with the WKB method for approximating solutions.

Chapter 6 presents the formalism of quantum physics, the mechanics of quantum mechanics, including a set of postulates. For completeness we also discuss the Schrödinger and Heisenberg pictures. Chapter 7 is devoted to the operator solution of the Schrödinger equation for the harmonic oscillator with emphasis on the properties of the ladder operators. Harmonic oscillator coherent states are also discussed. Chapter 8 introduces three-dimensional problems and is devoted to angular momentum. It is emphasized in this chapter that the concept of angular momentum in quantum mechanics transcends three-dimensional rotations (orbital angular momentum).

Chapters 9 and 10 are devoted to solving the radial Schrödinger equation for several different central potentials. In addition to the common central potentials, Chapter 9 includes a thorough discussion of the isotropic harmonic oscillator using the shell model of the nucleus as an example. The isotropic oscillator also permits introduction the concept of accidental degeneracy. Because they are constituents of oscillator eigenfunctions, an attempt is made to decrypt the different conventions that are used for Laguerre polynomials and associated Laguerre polynomials. In our experience, this is a source of confusion to many students. Also contained in this chapter is an elaboration on the Morse potential in which three-dimensional

molecular motion is considered through rotation–vibration coupling. The discussion of the hydrogen atom, the sole content of Chapter 10, is standard, but, as for the isotropic oscillator, accidental degeneracy is stressed. Chapter 11 is included to demonstrate to the student that there are angular momenta in quantum mechanics other than orbital and spin angular momenta. It includes the introduction of the Lenz vector, its consequences and ramifications. This subject is not usually covered at the introductory level, but it is certainly not beyond the beginning student.

The material in the remaining four chapters depends heavily upon approximation methods. Chapter 12 presents time-independent approximation methods, while Chapter 13 illustrates the use of these methods to solve problems of physical interest. One problem that is included in Chapter 13, albeit superficially, is the effect of fine structure on the shell model of the nucleus. Chapter 14 treats the Stark and Zeeman effects. Particular attention is paid to the consequences of breaking the spherical symmetry of central potentials by application of an external field. Chapter 15 presents time-dependent approximation methods, followed by a discussion of atomic radiation including the Einstein coefficients.

There are more than two hundred problems. A detailed solutions manual is available. There are a number of appendixes to the book, including the answers to all problems for which one is required. Among the other appendixes is one listing the Greek alphabet with notations on common usage of these symbols in the book. There is also a short table of acronyms used in the book. The remaining appendixes contain material that is intended to be quick reference material and helpful with the core material in the book. A list of (the inevitable) corrections can be found at: http://users.stlcc.edu/cburkhardt/ and http://www.umsl.edu/~jjl/homepage/.

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# Chapter 2
# Elementary Wave Mechanics

## 2.1 What is Doing the Waving?

In nonrelativistic quantum physics, particles are treated as points. That is, they have no finite dimensions (zero volume) so they cannot, for example, spin. We are therefore justified in asking "what is doing the waving?" The answer is that it is the probability of finding the particle in a particular region of space. Actually, it is the probability of finding the particle within a particular range of some physically measurable parameters such as linear momentum or angular momentum, but let us confine our attention to coordinates for now. The application of quantum physics to solve problems thus becomes one of solving the appropriate equation of motion for the function that represents this probability. The mechanics of doing this is called quantum mechanics or, archaically, wave mechanics. The intention of this chapter is to introduce this equation of motion and, using it, to better understand the answer to the question what is doing the waving.

## 2.2 A Gedanken Experiment—Electron Diffraction Revisited

It is reasonable to ask if we can imagine an experiment that will demonstrate the wave nature of the probability and, simultaneously, the pointlike "structure" of the particles. Gedanken is the German word for thought, so a Gedanken experiment is not one that can actually be performed, but one that can be imagined and used to understand a particular phenomenon. Modern technology has, however, made it possible to perform experiments that were envisioned as Gedanken experiments during the development of quantum mechanics. Because of the counterintuitive nature of quantum physics, many Gedanken experiments were imagined, especially in the early development of quantum physics. For the present purpose, we return to the electron diffraction experiment described in Section 1.2.3 and use it to perform a Gedanken experiment.

Imagine the screen to be constructed of a material that phosphoresces when struck by an electron. Phosphorescent materials continue to emit light after being energized and we assume, for the purpose of this experiment, that our screen

phosphoresces indefinitely. Now, let us lower the intensity of the electron beam so we can easily see each electron as it strikes the screen, lights it up, and leaves a signature of its presence in the form of a persistent pinpoint of light. The first electron strikes somewhere, we cannot predict where with certainty. From the known diffraction pattern we know where it is most likely to strike. Perhaps it is a contrary electron and strikes in a region in which the diffraction pattern has low intensity, perhaps not. Bear in mind that it is a single event. Wherever it strikes, it leaves its signature. A second electron arrives. It too leaves its signature. Again, we do not know where it will land, only where it is most likely to land. After perhaps 100 electrons have struck the screen we have a pattern, but it may not look like the known diffraction pattern because 100 is not, statistically speaking, a very large number. When, however, a large number of electrons have struck the screen it is lit up with the known diffraction pattern. This pattern is composed of many points of light representing the point electrons, but the pattern represents the diffraction pattern characteristic of wave motion.

The important point to remember is that the particles are not magically turning into slithering sausages as they make their way through the narrow slit. They maintain their identity as point particles. It is, perhaps, Avogadro's number of them that are required to demonstrate the wavelike properties of matter.

## 2.3 The Wave Function

Paramount to obtaining the probability distribution is the wave function, $\Psi(x, t)$. We use the capital Greek letter to designate the wave function when the time is included and, for now, we work with only one-dimension, $x$. We point out that the wave function need not be written in terms of any coordinates. It could be in terms of another variable (called an observable in quantum mechanics), but we will consider only coordinates and time for now. Now, by postulate, $\Psi(x, t)$ contains all the information that the uncertainty principle permits us to know about the particle. Using an asterisk to signify the complex conjugate, the probability that the particle will be found in the interval $dx$ at time $t$ is given by

$$\Psi^*(x, t)\, \Psi(x, t)\, dx = |\Psi(x, t)|^2\, dx \tag{2.1}$$

provided $\Psi(x, t)$ has been normalized so that

$$\int_{-\infty}^{\infty} \Psi^*(x, t)\, \Psi(x, t)\, dx = 1 \tag{2.2}$$

Normalization assures that the total probability cannot exceed unity. The complex conjugate is required because $\Psi(x, t)$ may very well be a complex function. On the other hand, the probability must be real so the absolute value in Equation 2.1 assures us that the probability will be real. We see then that, while $\Psi(x, t)$ does not give physical information, its absolute square does. The quantity $|\Psi(x, t)|^2$ is

the probability *density* so that, in one-dimension, it has units of probability per unit length.

If we wish to calculate the average value of some quantity that is a function of $x$, say $f(x)$, we multiply this function by the normalized probability distribution $\Psi^*(x, t)\,\Psi(x, t)\,dx$, which weights the values of $f(x)$. We then integrate over all possible values of $x$ to obtain $\langle f(x)\rangle$, the average value of $f(x)$. This procedure is analogous to calculating the class average on an examination by multiplying each possible score by the number of students achieving that score, adding these quantities, and then dividing by the total number of students. Division by the total number has already been accounted for if the wave function is normalized. If not, the integral in Equation 2.2 must be computed, which amounts to normalizing the wave function. In the case of the class average the number of students is a discrete number as are the possible test scores. Clearly the computation of $\langle f(x)\rangle$ requires integration so we define

$$\langle f(x)\rangle \equiv \int_{-\infty}^{\infty} \Psi^*(x, t)\, f(x)\, \Psi(x, t)\, dx = 1 \qquad (2.3)$$

Notice that $\langle f(x)\rangle$ need not be one of the possible values $f(x)$ just as the class average of an examination need not be a score that any particular student actually achieved. In quantum physics the average value as defined in Equation 2.3 is often referred to as the expectation value, a fancy term for average value.

## 2.4 Finding the Wave Function—the Schrödinger Equationö

Just as there are equations of motion in classical physics, there are equations of motion of the wave function in quantum physics. Such equations are called wave equations. In this book we deal with nonrelativistic quantum physics so we will use the Schrödinger wave equation, an equation that cannot be *derived*. It can be rationalized, but it cannot be derived. This is not the first time you have encountered such an equation. Newton's second law, $F = ma$, cannot be derived. It works though, so we accept it as being a law (at least nonrelativistically). It was deduced by Newton. We can presume that he tried others, but settled on $F = ma$ as the correct law of motion because it worked. This is the same approach taken by Erwin Schrödinger who shared the 1933 Nobel Prize in Physics with Paul Adrien Maurice Dirac. The citation for their prize reads: "for the discovery of new productive forms of atomic theory."

The validity of the Schrödinger equation lies in the fact that it satisfactorily explains nonrelativistic quantal phenomena. It is, however, worthwhile to see how this equation can be rationalized because we can see what is built into the Schrödinger equation. The (nonrelativistic) TME $E$ of a particle of mass $m$ in terms of the potential energy $U(x)$, the particle's momentum $p$ is

$$E = \frac{p^2}{2m} + U(x) \tag{2.4}$$

If we incorporate both of the important quantal relations, the Planck relation, Equation 1.2, and the de Broglie wavelength, Equation 1.48, into Equation 2.4, we have

$$\hbar\omega = \frac{(\hbar k)^2}{2m} + U(x) \tag{2.5}$$

where we have replaced the de Broglie wavelength with the wave number $k$ defined as

$$k = 2\pi/\lambda \quad \Rightarrow \quad p = \hbar k \tag{2.6}$$

The term in Equation 2.5 that makes it particularly difficult to write a wave equation for a particle is the potential energy, so we will temporarily ignore it. (We are, after all, only rationalizing, not deriving.) If the particle were massless, for example a photon, then the electromagnetic wave equation would pertain. That is, the equation of motion is

$$\frac{\partial^2 A(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 A(x,t)}{\partial t^2} \tag{2.7}$$

where $A(x,t)$ is the space- and time-dependent amplitude (electric or magnetic field) of the wave, and $c$ is, as usual, the speed of light. Partial derivatives are required because the wave function is a function of two variables. A solution to Equation 2.7 is a plane wave

$$A(x,t) = Ke^{i(kx-\omega t)} \tag{2.8}$$

where $K$ is a constant and $i = \sqrt{-1}$. Before proceeding let us recall that wave motion is always described by a function of $(x - vt)$ where $v$ is the velocity of the wave. Equation 2.8 is such a function with $v = \omega/k$. For electromagnetic waves $v = c$, the speed of light.

Suppose we try to apply Equation 2.7 to the case of a material particle (nonzero mass), but, for simplicity, continue to let $U(x) = 0$. When $U(x) = 0$ we have a "free particle." We then replace the amplitude $A(x,t)$ with the wave function $\Psi(x,t)$, let $c \rightarrow v$ and assume a plane wave solution analogous to Equation 2.8 and insert this solution into Equation 2.7. After dividing by the $\Psi(x,t)$ on both sides of the equation we obtain

$$(ik)^2 = \frac{1}{v^2}(-i\omega)^2 \tag{2.9}$$

Equation 2.9 is, however, inconsistent with Equation 2.5 because, with $U(x) = 0$, $k^2 \propto \omega$, not $\omega^2$. We can see that in order to get only the first power of $\omega$ we must

differentiate $\Psi(x, t)$ only once with respect to time. This results in a modification of Equation 2.7 with $A(x, t) \rightarrow \Psi(x, t)$ and $\partial^2 A(x, t)/\partial t^2 \rightarrow \partial \Psi(x, t)/\partial t$ to yield

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = K \frac{\partial \Psi(x, t)}{\partial t} \tag{2.10}$$

where $K$ is a constant. Inserting Equation 2.8 into Equation 2.10 and solving for $K$ we have

$$K = \frac{k^2}{i\omega} \tag{2.11}$$

But, from Equation 2.5 we see, with $U(x) = 0$,

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \implies \frac{k^2}{\omega} = \frac{2m}{\hbar} \tag{2.12}$$

Therefore,

$$K = -i \frac{2m}{\hbar} \tag{2.13}$$

and we have

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

This equation can be put in its usual form by multiplying both sides by $-\hbar^2/2m$, the advantage of which is that both sides have units of energy. We have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \tag{2.15}$$

This wave equation is applicable only to a free particle, that is, a particle for which the de Broglie wavelength is constant throughout. The de Broglie wavelength is constant because the total energy is presumed constant, so the kinetic energy and therefore the momentum is constant. How do we account for a nonzero potential energy? A constant potential energy is easy because the de Broglie wavelength is constant; $U(x) = 0$ is a special case of $U(x) = U_0 =$ a constant. Thus, we can, without any guilt, write

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_0 \right] \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} \tag{2.16}$$

which is consistent with Equation 2.5 with $U(x)$ replaced by $U_0$. Notice that we have factored the $\Psi(x, t)$ to the right of the bracket on the left-hand side of Equation 2.16. The significance of this is that the quantity in brackets is an operator and

it operates to the right. The first term is a differential operator and must be kept to the left of the function $\Psi(x, t)$. The second term is, however, merely a multiplicative operator, but an operator nonetheless. We will see that, in quantum mechanics, observable quantities such as energy, momentum, and position are represented by operators. We will deal with this in depth in a later chapter touching on it only superficially here. It is not a great leap of faith to replace $U_0$ in Equation 2.16 with the function $U(x)$ thus obtaining the time-*dependent* Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right]\Psi(x, t) = -\frac{\hbar}{i}\frac{\partial \Psi(x, t)}{\partial t} \tag{2.17}$$

which, for brevity, we will refer to as the TDSE.

You may be wondering why we went through all this sleight of hand to arrive at Equation 2.17, after having stated at the outset that it couldn't be derived. After all, you probably never had anyone rationalize $F = ma$. Why then go to all the trouble to rationalize the TDSE? Why not just state it and get down to business solving quantum mechanics problems? The reason lies in Equation 2.5. This equation for the total energy of the particle comprises the two fundamental relations of quantum physics, the de Broglie wavelength and the Planck relation. Thus, these manifestly quantal quantities are incorporated in the TDSE.

There are a few mathematical consequences of using the TDSE as our equation of motion that we should recognize. First, it is a homogeneous linear differential equation. This means that linear combinations of solutions are also solutions, a characteristic that has profound physical consequences. Second, the TDSE is merely a differential equation. As such, it does not quantize anything. It could very well appear at the end of a chapter in a book on differential equations as an exercise asking the student to solve it for a given function $U(x)$. It is the physics of a particular system that imposes quantization on a system, if indeed quantization occurs. In other words, we as physicists must specify the conditions on the wave function that are dictated by the system under consideration. These conditions may or may not quantize the energy levels, as well as other physical parameters.

## 2.5 The Equation of Continuity

The TDSE, together with the probability interpretation of $|\Psi(x, t)|^2$ leads to a continuity equation for probability. This means that there is a flux of probability that must be conserved. To take a concrete example, if an electron is moving from, say, left to right, the probability is leaving one region of space and occupying another. Let us be quantitative and examine the time dependence of the normalization of the wave function:

$$\frac{\partial}{\partial t}|\Psi(x, t)|^2 = \Psi^*(x, t)\frac{\partial \Psi(x, t)}{\partial t} + \Psi(x, t)\frac{\partial \Psi^*(x, t)}{\partial t} \tag{2.18}$$

We may, however, replace the partial derivatives with respect to time on the right-hand side of Equation 2.18 using the TDSE Equation 2.17 and its complex conjugate. The potential energy function, being a real function, drops out and we have

$$\frac{\partial}{\partial t}|\Psi(x,t)|^2 = \frac{\hbar}{2im}\left[\Psi(x,t)\frac{\partial^2\Psi^*(x,t)}{\partial x^2} - \Psi^*(x,t)\frac{\partial^2\Psi(x,t)}{\partial x^2}\right]$$

$$\frac{\partial}{\partial t}|\Psi(x,t)|^2 = \frac{\partial}{\partial x}\left\{\frac{\hbar}{2im}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right]\right\} \quad (2.19)$$

Now, define the quantity in curly brackets as the probability current $j(x,t)$:

$$j(x,t) = \frac{\hbar}{2im}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right] \quad (2.20)$$

which leads to

$$\frac{\partial|\Psi(x,t)|^2}{\partial t} + \frac{\partial}{\partial x}j(x,t) = 0 \quad (2.21)$$

which is the desired continuity equation. The analogy with the equation of continuity in electricity is often made. This analogy is more concrete if we imagine the wave function to represent a beam of electrons so that the electronic charge $e$ multiplied by $|\Psi(x,t)|^2$ is, in a very real sense, the charge density. Thus, if we multiply Equation 2.21 by $e$ we recover the continuity equation from electricity inasmuch as we now identify the quantity $ej(x,t)$ with the current density.

## 2.6 Separation of the Schrödinger Equation—Eigenfunctions

The potential energy term in Equation 2.17 does not contain the time. This will almost always be the case (certainly in this book). We attempt to solve the TDSE equation by the time-honored technique of separation of variables assuming a solution of the form

$$\Psi(x,t) = \psi(x)T(t) \quad (2.22)$$

Notice that the Greek psi on the right-hand side is lower-case which we reserve for a function of coordinates only. Inserting Equation 2.22 into Equation 2.17 and dividing by $\psi(x)T(t)$ we have

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right]\psi(x) = -\frac{\hbar}{i}\frac{dT(t)}{dt} \quad (2.23)$$

Note that, on the left-hand side of Equation 2.23, the $\psi(x)$ in the denominator and the $\psi(x)$ in the numerator do not cancel because the one in the numerator must be operated upon by the quantity in square brackets.

Now, the left-hand side of Equation 2.23 contains only coordinates while the right-hand side only time. The only way these quantities, each containing a variable, can be equal is if they are each equal to a constant which we choose to be $E$ (because we know the answer). Now, the equation in $x$ cannot be solved unless we know $U(x)$, but the equation for time can be easily solved. The general solution is

$$T(t) = e^{-i(E/\hbar)t} \tag{2.24}$$

which is the universal time part of the wave function *as long as the potential energy is independent of time*. We need not bother with a normalization constant in Equation 2.24 because that will be absorbed in the normalization for $\psi(x)$.

Setting the left-hand side of Equation 2.23 equal to the separation constant $E$ we have

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi(x) = E\psi(x) \tag{2.25}$$

This is the time-*independent* Schrödinger equation, the TISE. We will devote much of the remainder of this book to the solution of Equation 2.25. It should be noted that, as discussed above, the quantity in square brackets is an operator. This operator represents the total energy of the system and is called the Hamiltonian, the same Hamiltonian as in classical mechanics. If the potential energy does not contain the time, the Hamiltonian, designated by the symbol $\hat{H}$, is the TME. Moreover, since the TME is the sum of kinetic plus potential energies it is clear the the first term is the kinetic energy operator which can be written in terms of the momentum, $\hat{p}_x^2/2m$. The "hat" over the momentum signifies that it is an operator. We will also use a hat to designate a unit vector in any coordinate system, for example, $\hat{\imath}$, $\hat{\jmath}$, $\hat{k}$ in Cartesian coordinates or $\hat{a}_r$, $\hat{a}_\theta$, $\hat{a}_\phi$ in spherical coordinates. This should cause no confusion with the hat designation of operators. Now, the momentum is a vector quantity (operator), so we use the subscript to denote the component even though we are dealing with only one-dimension in this chapter. In terms of the Hamiltonian, the (one-dimensional) TISE may be written as

$$\hat{H}\psi(x) = E\psi(x)$$
$$= \left[ \frac{\hat{p}_x^2}{2m} + U(x) \right] \psi(x) \tag{2.26}$$

and the time-dependent Schrödinger wave equation, the TDSE, is

$$\hat{H}\Psi(x,t) = -\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} \tag{2.27}$$

In general, there will be many solutions of the TISE, each corresponding to a different value of $\psi(x)$ and its corresponding eigenvalue, $E$. We therefore attach subscripts to distinguish the different $\psi_n(x)$ and to correlate them with their corresponding eigenvalues, $E_n$. Equations that have the form of Equation 2.26 are called eigenvalue equations. The different values of $E_n$ are the eigenvalues and the corresponding values of $\psi_n(x)$ are called eigenfunctions. It is also possible that some eigenfunctions can share the same eigenvalue, in which case the eigenfunctions are said to be degenerate. We will ignore degeneracy for now because, for bound states in one-dimension, the eigenfunctions are nondegenerate. It will, however, be an important consideration when we attack three-dimensional problems.

We can actually find the form of the $x$-component of the momentum operator by noting that the square of an operator simply means that we should apply it twice in succession. Thus, comparing the first terms in the brackets of Equations 2.25 and 2.26 we see that

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} \tag{2.28}$$

The appearance of the imaginary number $i$ is not a cause of concern because the wave functions themselves can be complex functions. Recall that it is the absolute squares of the wave functions that must be real. It will, however, be a requirement that the eigenfunctions of any operator that represents an observable quantity, such as momentum or energy, must be real, for it would be absurd to imagine measuring an imaginary momentum.

## 2.7 The General Solution to the Schrödinger Equation

As noted above, an important property of the TISE is that it is a linear differential equation. This means that linear combinations of solutions are also solutions. Moreover, as will be shown later, the eigenfunctions constitute a *complete* set of functions. That is, the eigenfunctions are complete in the sense that any function can be represented as a linear combination of them, much as any vector in three-dimensional space can be represented as a linear combination of the unit vectors $\hat{i}$, $\hat{j}$, and $\hat{k}$. Indeed, the eigenfunctions span a vector space, the "vectors" being any function that can be constructed as a linear combination of the $\psi_n(x)$. Thus, a *general* solution to the TISE, call it $\psi(x)$, the absence of a subscript signifying that it is not an eigenfunction, may be written

$$\psi(x) = \sum_{n=1}^{\infty} a_n \psi_n(x) \tag{2.29}$$

where, because $\psi(x)$ may be complex, as may be the expansion coefficients, the $a_n$. An additional property that will be proven in a later chapter is that the $\psi_n(x)$ are

orthogonal in the same sense that the unit vectors are orthogonal. To designate this orthogonality, the notation can be condensed to

$$\int_{-\infty}^{\infty} \psi_n(x)\psi_m(x)\,dx = 0 \quad m \neq n \tag{2.30}$$

The integral in Equation 2.30 is the equivalent of the dot product for real vectors.

Suppose that $\psi(x)$, as given by Equation 2.29, represents the total wave function at $t = 0$, that is,

$$\Psi(x, 0) = \psi(x)$$
$$= \sum_{n=1}^{\infty} a_n \psi_n(x) \tag{2.31}$$

then, using the universal time dependence, Equation 2.24, it is a simple matter to write the wave function for all time. We have

$$\Psi(x, t) = \sum_{n=1}^{\infty} a_n \psi_n(x)\,e^{-i(E_n/\hbar)t} \tag{2.32}$$

Equations 2.29 and 2.32 represent one of the most important theorems in quantum mechanics, the superposition theorem. At this stage in our discussion these two equations are merely mathematical constructions, but we will see that they have profound implications for the behavior of physical systems and the states that they occupy.

Because $\Psi(x, t)$, as given in Equation 2.32, is a solution of the TDSE, it is said that the system is in a superposition of states. Moreover, the expansion represented by Equation 2.32 is a *coherent* superposition of states in the sense the "components" of the expansion have definite phase with respect to each other as contained in the expansion coefficients and the time dependence. Suppose we have a large number of identical systems and a measurement of some physical quantity, say the energy, is made on a single one of these systems. The only possible result of this measurement is one of the energy eigenvalues. If an identical measurement is made on another of these systems, again, only one of the eigenvalues could result, but, possibly, a different one than the other measurement. If measurements are made on many of these identical systems (by many we mean *many*, say Avogadro's number), then the absolute squares of the expansion coefficients, the $a_n$, give the probabilities of measuring the corresponding $E_n$'s.

The measurement process described above alters the system and changes the wave function by forcing the system into the particular eigenstate, the eigenstate that corresponds to the measured eigenvalue. In particular, if the energy measurement yielded the $i$th eigenvalue $E_i$, then the wave function of the system becomes the eigenfunction $\psi_i(x)$. The language that goes with this is that the wave function has been "collapsed" into the $i$th state.

Consider a simple example. Suppose we have only two states in the expansion and that the normalized wave function $\Psi(x, t)$ is given by

$$\Psi(x, t) = \frac{1}{\sqrt{3}}\psi_1(x) e^{-i\omega_1 t} + \sqrt{\frac{2}{3}}\psi_2(x) e^{-i\omega_2 t} \qquad (2.33)$$

where $\omega_i = E_i/\hbar$. For simplicity, let $\psi_1(x)$ and $\psi_2(x)$ be real functions. The probability density is

$$|\Psi(x, t)|^2 = \frac{1}{3}\left\{|\psi_1(x)|^2 + 2|\psi_2(x)|^2 \right.$$
$$\left. +2\sqrt{2}\psi_1(x)\psi_2(x)\cos[(\omega_1 - \omega_2)t]\right\} \qquad (2.34)$$

which is oscillatory, the frequency depending upon the difference in the energy and the amplitude depending upon the expansion coefficients. Incidentally, it is clear from Equation 2.34 that if there is only one component of $\Psi(x, t)$ then $|\Psi(x, t)|^2$ does not contain the time, thus justifying its designation as a "stationary state".

Let us assume that we have a large number of identical systems, each described by the wave function of Equation 2.33. Now, what can we expect if we measure the energy of each of these identical systems? We have already stated that the only possible result of such a measurement is one of the eigenvalues. In the present case the measurement can yield only $E_1$ or $E_2$ because the system is in a superposition of only $\psi_1(x)$ and $\psi_2(x)$. What is the probability of measuring each of these eigenvalues? Without resorting to mathematical formalism to which we have not yet been exposed, it is relatively easy to deduce the answer. Suppose, rather than the expansion coefficients used in Equation 2.33, $\Psi(x, t)$ is an equal admixture of $\psi_1(x)$ and $\psi_2(x)$. (For an unknown reason it is customary to use the word admixture here rather than mixture.) For this equal admixture only $E_1$ or $E_2$ could be measured, but with equal probabilities, $\frac{1}{2}$. The normalized wave function must therefore be

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x) e^{-i\omega_1 t} + \frac{1}{\sqrt{2}}\psi_2(x) e^{-i\omega_2 t} \qquad (2.35)$$

Consequently, we conclude that it is the square of the expansion coefficient that gives the probability of measuring the corresponding eigenvalue. If the system is described by the wave function of Equation 2.33, we would therefore measure $E_2$ twice as often as we would measure $E_1$.

The consequence of the above discussion is that the system is indeed in more than one eigenstate—as long as we are not "looking," that is "making a measurement." When we make the measurement (and look), we necessarily perturb the system, immediately collapsing the wave function into one of the eigenstates.

## 2.8 Stationary States and Bound States

Bohr's characterization of the states of hydrogen as stationary states has been broadened and retained in modern quantum physics. It refers to any state $\Psi(x, t)$ for which the expansion, Equation 2.32, consists of a single term. Thus, the probability density $|\Psi(x, t)|^2$ reduces to

$$
\begin{aligned}
|\Psi(x, t)|^2 &= \psi_n(x) \, e^{-i(E_n/\hbar)t} \, \psi_n^*(x) \, e^{+i(E_n/\hbar)t} \\
&= \psi_n(x) \, \psi_n^*(x) \\
&= \text{function of } x \text{ only}
\end{aligned}
\tag{2.36}
$$

Because this probability density is independent of time, it is defined as a "stationary state." On the other hand, if the wave function, $\Psi(x, t)$, contains two or more terms in Equation 2.32, the probability density will be time-dependent and the state does not qualify as a stationary state (see for example Equation 2.34).

If a particle is confined to a region of space by a potential energy function, then the resulting quantum states are referred to as "bound states." Incidentally, physicists often get sloppy and refer to the potential energy function as, simply, the potential. We will follow this custom and use the two interchangeably. Obviously Bohr's stationary states are examples of bound states, but there are many other examples of bound states. The wave function representing a particle confined by such a potential energy function may be a stationary state or it may be a linear combination of them as in Equation 2.32. If there is more than one term in the expansion of the wave function that represents the quantum system, then the system is said to be in "a superposition of states." More will be said about this designation when we discuss the formalism of quantum mechanics. In this chapter we will concentrate on the characteristics of stationary bound states of some simple systems. A great simplification exists for bound states in one-dimensional problems. They are always nondegenerate (see Problem 3).

## 2.9 Characteristics of the Eigenfunctions $\psi_n(x)$

What must be the character of an eigenfunction $\psi_m(x)$? First, it may be a real, imaginary, or complex function because it is the absolute square of $\psi_n(x)$ that gives the probability density. It must, however, be single valued and it must be continuous. Even in the mysterious world of quantum mechanics a particle cannot be in two places at once. If $\psi_n(x)$ had, say, two different values at a given value of $x$, then $|\psi_n(x)|^2$ would be similarly double valued and there would be two *different* probabilities of finding the particle at a given value of $x$. Accepting that this is absurd, even in quantum physics, we require that $\psi_n(x)$ is single valued. A similar incongruity would occur if the wave function were discontinuous. These are, in fact, characteristics of any general solution to the TISE $\psi(x)$, not just eigenfunctions. Figure 2.1 illustrates three hypothetical wave functions $\psi(x)$ that are unacceptable.

**Fig. 2.1** Hypothetical wave
functions $\psi(x)$ that, for the
indicated reasons, would be
unacceptable bound state
wave functions
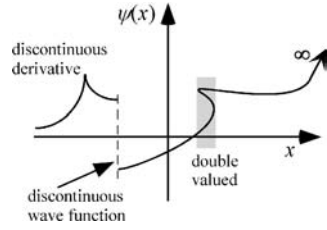


In addition to these general conditions on $\psi(x)$, we are also interested in the
important case in which $U(x)$ supports bound states. This means that the particle
motion is restricted to a particular region of space by the potential energy func-
tion, similar to the way the planets are bound by the potential energy of the sun.
In such cases the particle is confined by the potential energy function and, as a
consequence, the probability density and therefore the wave function must approach
zero as $|x| \to \infty$. The language that goes with this is to say that the wave function
is "normalizable" or "square integrable." This means that the wave function can be
multiplied by a constant such that

$$\int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = 1 \tag{2.37}$$

Equation 2.37 is called the normalization integral and it signifies that the probability
of finding the particle somewhere is unity. Moreover, for bound states it cannot be
found at infinity because the nature of the potential localizes it in space. Notice that
multiplication of the eigenfunction by a constant does not change the magnitude of
the corresponding eigenvalue because the eigenfunction $\psi(x)$ occurs in each term of
the TISE, Equation 2.25. Combining the orthogonality property with normalization,
we may write for eigenfunctions

$$\int_{-\infty}^{\infty} \psi_n^*(x)\,\psi_m(x)\,dx = \delta_{mn} \tag{2.38}$$

where $\delta_{mn}$ is the Kronecker delta defined as

$$\begin{aligned}
\delta_{mn} &= 0 \quad \text{if} \quad m \neq n \\
&= 1 \quad \text{if} \quad m = n
\end{aligned} \tag{2.39}$$

Eigenfunctions that obey Equation 2.38 are said to be orthonormal.

Now we must ask about the derivative of $\psi(x)$. The TISE contains the second
derivative, so that if $U(x)$ is a continuous function, both $\psi(x)$ and $d\psi(x)/dx$ must
be continuous. Even if $U(x)$ has a finite discontinuity, both $\psi(x)$ and $d\psi(x)/dx$
must be continuous. This is so because, from the TISE, $d^2\psi(x)/dx^2$ will then have
a finite discontinuity (imagine solving Equation 2.23 for $d^2\psi(x)/dx^2$) from which
it follows that $d\psi(x)/dx$ must be continuous and that $\psi(x)$ is continuous. An

**Fig. 2.2** Sketch of a
hypothetical potential energy
with a discontinuity that
occurs as $\varepsilon \to 0$
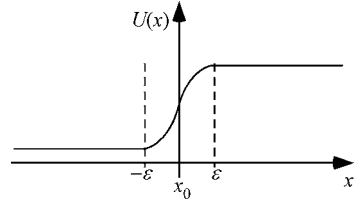


unacceptable discontinuity of the derivative is illustrated in Fig. 2.1. To place this
on a more mathematical foundation we may imagine a potential energy function that
has a finite discontinuity at some value of $x$, say $x = x_0$ as illustrated in Fig. 2.2.

We simply integrate the TISE across the discontinuity from $x_0 - \varepsilon$ to $x_0 + \varepsilon$:

$$\int_{-\varepsilon}^{\varepsilon} \frac{d}{dx} \left[ \frac{d\psi_n(x)}{dx} \right] dx = \left( -\frac{2m}{\hbar^2} \right) \int_{-\varepsilon}^{\varepsilon} [E - U(x)] \psi_n(x) dx \qquad (2.40)$$

and take the limit as $\varepsilon \to 0$:

$$\lim_{\varepsilon \to 0} \frac{d\psi_n(x)}{dx} \bigg|_{x=\varepsilon} - \lim_{\varepsilon \to 0} \frac{d\psi_n(x)}{dx} \bigg|_{x=-\varepsilon}$$

$$= \left( -\frac{2m}{\hbar^2} \right) \lim_{\varepsilon \to 0} \int_{-\varepsilon}^{\varepsilon} [E - U(x)] \psi_n(x) dx \qquad (2.41)$$

As long as the discontinuity in $U(x)$ that occurs when $\varepsilon \to 0$ is finite, the integral
on the right-hand side of Equation 2.41 vanishes in the limit and $d\psi/dx$ must be
continuous at $x = x_0$. If, on the other hand, the discontinuity is infinite, as would
occur if $U \to \infty$, then the integral on the right-hand side does not necessarily vanish
in the limit and the derivative need not be continuous.

There is a great deal that we can learn about the nature of the eigenfunctions, the
$\psi_n(x)$, without ever actually solving the TISE. Let us solve Equation 2.25 for the
second derivative and, again, for simplicity, imagine $\psi_n(x)$ to be a real function:

$$\frac{d^2 \psi_n(x)}{dx^2} = \left( -\frac{2m}{\hbar^2} \right) [E - U(x)] \psi_n(x) \qquad (2.42)$$

Now, recall that the second derivative of a function is a measure of the curvature of
the function. A high value of the second derivative means a "tight" curve, while
a low value means a gentle curve. Moreover, the sign of the second derivative
indicates the direction of curvature. (Recall that this is the basis for determining
whether a zero of the first derivative is a maximum or a minimum.) A negative
second derivative means that the function is concave down while a positive second
derivative is concave up. These features of the second derivative are summarized in
Fig. 2.3 for an arbitrary function $f(x)$.

**Fig. 2.3** Illustrations of various possible second derivatives of the function $f(x)$. The curves labeled 1 and 2 have positive values of $d^2 f(x)/dx^2$ and are therefore concave up. Curve 3 is concave down. The second derivative of curve 1 is greater than that of curve 2
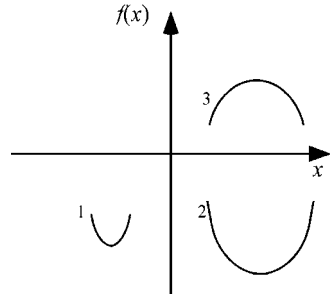
If the curvature of a wave function $\psi(x)$ is high as, for example, the curve labeled number 1 in Fig. 2.3, then the de Broglie wavelength of the particle that it represents is short and the momentum and kinetic energy are high. This is characteristic of a high-energy state. Thus, we expect the lowest energy states to have the longest de Broglie wavelengths and their eigenfunctions to have the gentlest curvatures. In such a case the wave function will not go through zero (a node) except at $\pm\infty$ so the lowest state, the ground state, will have no nodes. The first excited state, having slightly higher energy, has one node, and so on. In essence, we are fitting de Broglie waves into the region of space that is dictated by the potential energy function. In this sense the ground state is the fundamental and the first excited state the first overtone.

There is still more that we can learn from Equation 2.42. Figure 2.4 shows a sketch of a fictitious potential energy curve.

The horizontal line represents $E$, the TME of a particle. Let us temporarily assume classical motion so that $E$ can take on any value as determined by the initial conditions. Because $U(x)$ (in the illustration) extends to values higher than $E$, the motion will be bound. The limits of this motion will be $x_{c1}$ and $x_{c2}$. These points are known as classical turning points. At these points the particle has zero kinetic energy and it turns around. Classically, the particle cannot move beyond the classical turning points because this would require a negative kinetic energy and, thus, an imaginary speed. Nevertheless, quantum mechanics, being the contrary branch of physics that it is, permits motion into this "classically forbidden region." Let us
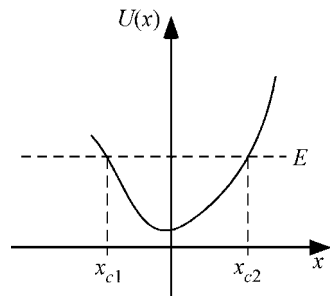
**Fig. 2.4** A hypothetical potential energy curve with a presumed total mechanical energy (TME) showing the classical turning points $x_{c1}$ and $x_{c2}$

examine the nature of $\psi(x)$ in both the classically allowed and forbidden regions of space.

In the classically allowed region $E$ is always greater than $U(x)$ so the the quantity in square brackets in Equation 2.42 is necessarily positive. Thus, if $\psi(x)$ is positive, the second derivative is negative. On the other hand, if $\psi(x)$ is negative, then $d^2\psi(x)/dx^2 > 0$. The consequence of this is that, in the classically allowed region, the wave function always curves toward the $x$-axis as illustrated in Fig. 2.5 where we have superposed a presumed wave function on the potential function of Fig. 2.4 using the line representing the TME as the zero of $\psi(x)$. Thus, the second derivative is shown to be positive on the left-hand side where $\psi(x)$ is negative and negative on the right-hand side where it is positive. At the $x_{c2}$, where the wave function crosses into the classically forbidden region, the wave function undergoes an inflection point and the second derivative changes from negative to positive.

These characteristics of the second derivative are typical of sinusoidal functions for the classically allowed region and exponentially decaying functions for the forbidden regions. Indeed, the wave functions in the forbidden regions must decrease as $x \rightarrow \pm\infty$ in order for the wave function to be normalizable, as it must be to correctly describe a bound state.

There is yet another bit of general information that can be obtained in certain cases from the TISE equation. Let us make the assumption that the potential function is an even function so that $U(x) = U(-x)$. Recall that functions *may* have definite parity. That is, they may be even or they may be odd. They may also be neither. To check the parity of a function $f(x)$ simply let $x \rightarrow -x$. If $f(x)$ has definite parity, then one of the conditions

$$f(x) = f(-x) \qquad \text{even}$$
$$f(x) = -f(x) \qquad \text{odd} \tag{2.43}$$

will prevail. An easy way to think of these functions is that even functions are symmetric with respect to the ordinate, while odd functions are symmetric with respect to the origin as illustrated in Fig. 2.6.

We let $x \rightarrow -x$ in the TISE, Equation 2.25 with the condition that $U(x) = U(-x)$ and obtain
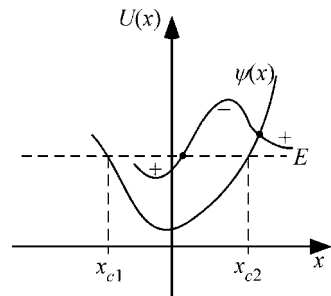
**Fig. 2.5** A hypothetical wave function sketched on the potential curve shown in Fig. 2.4. The signs of the second derivative of the wave function, the curvature, in different regions are displayed; inflection points are indicated by solid circles

**Fig. 2.6** Even and odd functions of $x$, $f(x)$
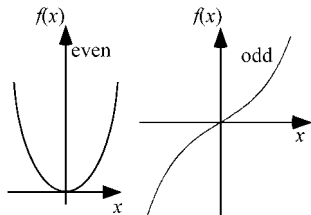


$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi_n(-x) = E \psi_n(-x) \tag{2.44}$$

where we have used the subscripts on the wave function to emphasize that they are eigenfunctions. Clearly $\psi_n(-x)$ and $\psi_n(x)$ are solutions of the same TISE, and, importantly, have the same eigenvalue $E_n$. Because $\psi_n(-x)$ and $\psi_n(x)$ have the same eigenvalue, they can differ only by a constant. That is,

$$\psi_n(-x) = \beta \psi_n(x) \tag{2.45}$$

We can, however, change the sign of $x$ again so that

$$\begin{aligned} \psi_n(x) &= \beta \psi_n(-x) \\ &= \beta \left[ \beta \psi_n(x) \right] \\ &= \beta^2 \psi_n(x) \end{aligned} \tag{2.46}$$

from which it is clear that $\beta = \pm 1$. The conclusion is, therefore, that in the not so special case in which the potential energy is an even function, the eigenfunctions of the TISE have definite parity. That is, if $U(x) = U(-x)$, then the eigenfunctions $\psi_n(x)$ are such that they have definite parity, $\psi_n(x) = \pm \psi_n(-x)$. We note that the ground state must have no nodes so it must have even parity.

## 2.10 Retrospective

The statistical nature of the quantum description of matter is the most important distinction between quantum physics and classical physics. The concept of a wave function from which all allowable information can be extracted is new to most students and the idea that probabilities, averages, and other statistical quantities must be employed to describe a physical system is novel. The Schrödinger equation, which is the equation of motion for the wave function, incorporates the Planck relation and the de Broglie wavelength, neither of which have classical analogs. Thus, one

can, in principle, find the wave function for a given set of conditions. But, what is this wave function? It isn't something that we can measure. Obviously though, it is important. From our current perspective, the perspective that the wave function is a solution to the TDSE and is a function of position and time, we must regard it as a function, such that when its absolute square is taken, it yields the probability of finding the particle between $x$ and $x + dx$ during the time interval between $t$ and $t + dt$. We can say no more. This is, however, a great deal—quantum mechanically speaking. It should thus be borne in mind when going through the mathematical gymnastics required to solve the TDSE that we ultimately seek these probabilities.

## Problems

1. A particle of mass $m$ that is confined in a potential well is known to be in an eigenstate having eigenfunction $\psi(x) = Ae^{-\alpha^2 x^2/2}$ and energy $(\alpha\hbar)^2/(2m)$.

   (a) Find the potential energy function $U(x)$ that confines the particle.
   (b) What is the force that confines the particle?
   (c) Find the value of the constant $A$ that is required to normalize this eigen-function.

2. The normalized wave function of a particle of mass $m$ is given by

$$\Psi(x, t) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-\alpha^2 x^2/2} e^{i(kx-\omega t)}$$

   (a) What is the probability of finding the particle between $x$ and $x + dx$ at time $t$?
   (b) What is the probability of finding the particle in the range $-\infty < x < \infty$?

3. Prove that for bound states in one-dimension the energy eigenfunctions are non-degenerate. Note that it is crucial that this proof applies only to one-dimension and to bound states.

4. A particle is represented by the wave function $\psi(x) = Ae^{i(kx-\omega t)}$ where $k = p/\hbar = 2\pi/\lambda$ where $\lambda$ is the de Broglie wavelength and $p$ is the momentum.

   (a) Calculate the probability current density $j(x, t)$.
   (b) The particle encounters a rise in potential energy that causes $p$ to decrease by a factor of 2. Find the resulting change in amplitude of the wave after the encounter.

5. Six potential wells with possible wave functions $\psi(x)$ sketched on the wells are shown. The dashed lines are located at the energy of the state that $\psi(x)$ is intended to represent. The dashed lines also represent $\psi(x) = 0$. Which $\psi(x)$ are acceptable wave functions and which are unacceptable? Give reasons.
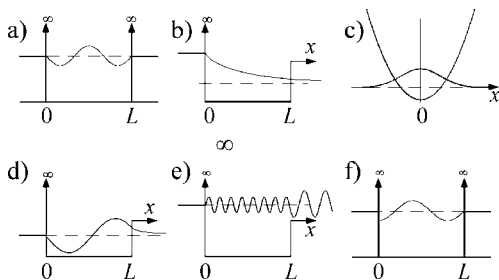
Potential wells and possible wave functions for Problem 5

6. Assume that the TISE has been solved for a potential energy function that supports bound states and the orthonormal energy eigenfunctions are denoted by $\psi_n(x)$ with corresponding energy eigenvalues $E_n$. A large number of energy measurements are made, but only three different values of the energy are actually observed, $E_1$, $E_2$, and $E_3$. The ratio of occurrences of these values is (in order) $3 : 4 : 5$.

   (a) What is the normalized wave function $\Psi(x, 0)$ at $t = 0$?
   (b) What is the normalized wave function $\Psi(x, t)$?
   (c) What is the expectation value of the energy at $t = 0$?
   (d) What is the expectation value of the energy for $t > 0$?

7. A free particle having wave number $k_{\mathrm{I}}$ is traveling in the $+x$ direction when it encounters a sudden change in the potential energy to some constant lower value. After a finite distance the potential energy increases to its original value. Sketch the wave function that represents this particle in all three regions of space. Pay particular attention to the de Broglie wavelengths in each region. Note the properties of this wave function such as amplitude, continuity, and derivatives.

8. A particle of mass $m$ is subjected to a potential energy such that at $t = 0$ the wave function that describes the particle is given by

$$\Psi(x, 0) = \left[ \frac{\sqrt{2}}{3} \psi_1(x) + \frac{\sqrt{6}}{3} \psi_2(x) + \frac{1}{3} \psi_3(x) \right]$$

   where the $\psi_n(x)$ are eigenfunctions of the Hamiltonian $\hat{H}$, each of which has energy eigenvalue $-\left(1/n^2\right) E_0$ where $E_0$ is a positive constant.

   (a) If an energy measurement is made, what are the possible results of the measurement?
   (b) What is the probability of measuring each of these energies?
   (c) What is the expectation value of the energy?
   (d) Suppose there is another physical quantity that may be measured, a quantity that is represented mathematically by $Q$. Assume that the $\psi_n(x)$ are also eigenfunctions of the operator that represents this quantity, $\hat{Q}$, with

eigenvalues $n\,Q_0$. If the energy is measured first and found to be $-\left(1/9\right)E_0$ and then a measurement of $Q$ is made, what will be the value of $Q$ that is measured?

9. A one-dimensional potential energy function is given in a.u. by

$$U\left(x\right) = \infty \quad x \leq 0$$
$$= -\frac{1}{x} \quad x > 0$$

(a) Sketch the potential energy. Is it possible that this potential will support bound states?
(b) Only one of the wave functions listed below is the eigenfunction that represents the ground state. Which one?

$$\psi_1\left(x\right) = Ae^{-\alpha x}; \quad \psi_2\left(x\right) = Axe^{-\alpha x}$$
$$\psi_3\left(x\right) = Ae^{-\alpha^2 x^2}; \quad \psi_4\left(x\right) = A\left(x - 2x^2\right)e^{-\alpha^2 x^2}$$

(c) What is the ground state energy in a.u.?
(d) What is $\langle x \rangle$ for the ground state?