1

INTRODUCTION

This chapter serves as a foundation for the rest of the book. Section 1.1 provides a brief history of the physical observations that led to the development of the Schrödinger equation, which is at the heart of quantum mechanics. Section 1.2 describes a time-domain simulation method that will be used throughout the book as a means of understanding the Schrödinger equation. A few examples are given. Section 1.3 explains the concept of observables, the operators that are used in quantum mechanics to extract physical quantities from the Schrödinger equation. Section 1.4 describes the potential that is the means by which the Schrödinger equation models materials or external influences. Many of the concepts of this chapter are illustrated in Section 1.5, where the simulation method is used to model an electron interacting with a barrier.

1.1 WHY QUANTUM MECHANICS?

In the late nineteenth century and into the first part of the twentieth century, physicists observed behavior that could not be explained by classical mechanics [1]. Two experiments in particular stand out.

1.1.1 Photoelectric Effect

When monochromatic light—that is, light at just one wavelength—is used to illuminate some materials under certain conditions, electrons are emitted from

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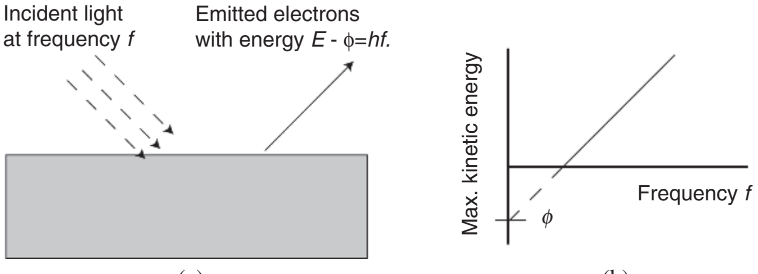


(a) (b)

FIGURE 1.1 The photoelectric effect. (a) If certain materials are irradiated with light, electrons within the material can absorb energy and escape the material. (b) It was observed that the KE of the escaping electron depends on the frequency of the light.

the material. Classical physics dictates that the energy of the emitted particles is dependent on the intensity of the incident light. Instead, it was determined that at a constant intensity, the kinetic energy (KE) of emitted electrons varies linearly with the frequency of the incident light (Fig. 1.1) according to:

$$E - \phi = hf,$$

where, ϕ, the work function, is the minimum energy that the particle needs to leave the material.

Planck postulated that energy is contained in discrete packets called quanta, and this energy is related to frequency through what is now known as Planck's constant, where $h = 6.625 \times 10^{-34}$ J·s,

$$E = hf. \tag{1.1}$$

Einstein suggested that the energy of the light is contained in discrete wave packets called photons. This theory explains why the electrons absorbed specific levels of energy dictated by the frequency of the incoming light and became known as the photoelectric effect.

1.1.2 Wave–Particle Duality

Another famous experiment suggested that particles have wave properties. When a source of particles is accelerated toward a screen with a single opening, a detection board on the other side shows the particles centered on a position right behind the opening as expected (Fig. 1.2a). However, if the experiment is repeated with two openings, the pattern on the detection board suggests points of constructive and destructive interference, similar to an electromagnetic or acoustic wave (Fig. 1.2b).

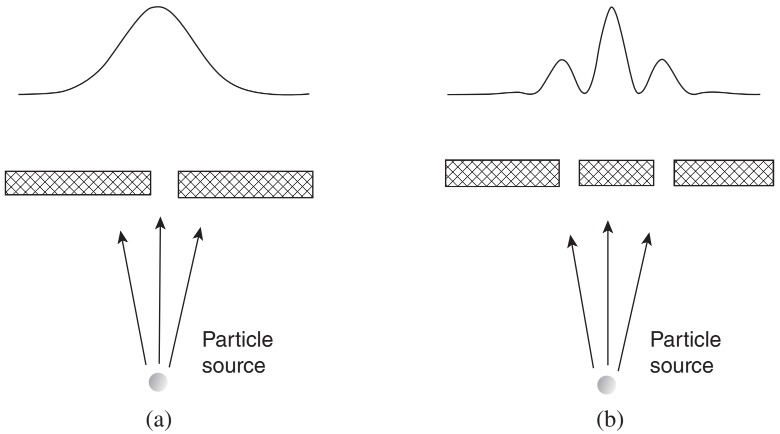


FIGURE 1.2 The wave nature of particles. (a) If a source of particles is directed at a screen with one opening, the distribution on the other side is centered at the opening, as expected. (b) If the screen contains two openings, points of constructive and destructive interference are observed, suggesting a wave.

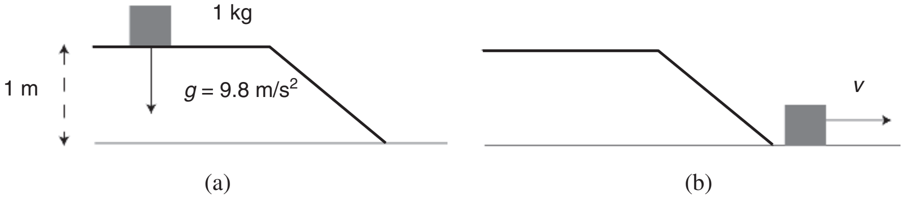


FIGURE 1.3 (a) A block with a mass of 1 kg has been raised 1 m. It has a PE of 9.8 J. (b) The block rolls down the frictionless incline. Its entire PE has been turned into KE.

Based on observations like these, Louis De Broglie postulated that matter has wave-like qualities. According to De Broglie, the momentum of a particle is given by:

$$p = \frac{h}{\lambda}, \tag{1.2}$$

where λ is the wavelength. Observations like Equations (1.1) and (1.2) led to the development of quantum mechanics.

1.1.3 Energy Equations

Before actually delving into quantum mechanics, consider the formulation of a simple energy problem. Look at the situation illustrated in Figure 1.3 and think about the following problem: If the block is nudged onto the incline and rolls to the bottom, what is its velocity as it approaches the flat area, assuming that we can ignore friction? We can take a number of approaches to solve this problem. Since the incline is 45°, we could calculate the gravitational force exerted on the block while it is on the incline. However, physicists like to deal with energy. They would say that the block initially has a potential energy (PE) determined by the mass multiplied by the height multiplied by the acceleration of gravity:

$$\mathrm{PE} = (1\ \mathrm{kg})(1\ \mathrm{m})\left(9.8\frac{\mathrm{m}}{\mathrm{s}^2}\right) = 9.8\frac{\mathrm{kg}-\mathrm{m}^2}{\mathrm{s}^2} = 9.8\ \mathrm{J}.$$

Once the block has reached the bottom of the incline, the PE has been all converted to KE:

$$\mathrm{KE} = 9.8\left(\frac{\mathrm{kg}\cdot\mathrm{m}^2}{\mathrm{s}^2}\right) = \frac{1}{2}(1\ \mathrm{kg})v^2.$$

It is a simple matter to solve for the velocity:

$$v = \left(2\times 9.8\frac{\mathrm{m}^2}{\mathrm{s}^2}\right)^{1/2} = 4.43\frac{\mathrm{m}}{\mathrm{s}}.$$

This is the fundamental approach taken in many physics problems. Very elaborate and elegant formulations, like Lagrangian and Hamiltonian mechanics, can solve complicated problems by formulating them in terms of energy. This is the approach taken in quantum mechanics.

Example 1.1

An electron, initially at rest, is accelerated through a 1 V potential. What is the resulting velocity of the electron? Assume that the electron then strikes a block of material, and all of its energy is converted to an emitted photon, that is, $\phi = 0$. What is the wavelength of the photon? (Fig. 1.4)

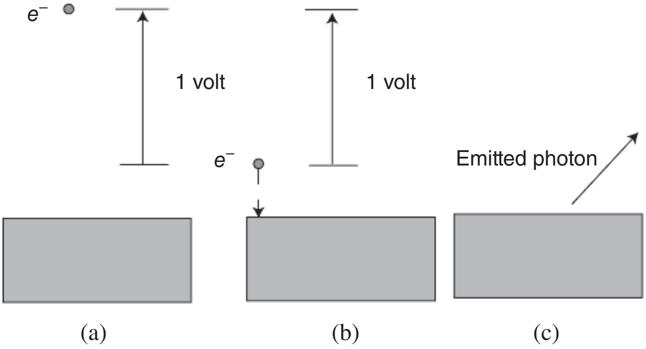


FIGURE 1.4 (a) An electron is initially at rest. (b) The electron is accelerated through a potential of 1 V. (c) The electron strikes a material, causing a photon to be emitted.

Solution. By definition, the electron has acquired energy of 1 electron volt (eV). To calculate the velocity, we first convert to joules. One electron volt is equal to 1.6×10^{-19} J. The velocity of the electron as it strikes the target is:

$$v = \sqrt{\frac{2 \cdot E}{\mathrm{m}_e}} = \sqrt{\frac{2 \cdot 1.6 \times 10^{-19}\ \mathrm{J}}{9.11 \times 10^{-31}\ \mathrm{kg}}} = 0.593 \times 10^6\,\mathrm{m/s}.$$

The emitted photon also has 1 eV of energy. From Equation (1.1),

$$f = \frac{E}{h} = \frac{1\,\mathrm{eV}}{4.135 \times 10^{-15}\ \mathrm{eV \cdot s}} = 2.418 \times 10^{14}\ \mathrm{s}^{-1}.$$

(Note that the Planck's constant is written in *electron volt-second* instead of *joule-second*.) The photon is an electromagnetic wave, so its wavelength is governed by:

$$c_0 = \lambda f,$$

where c_0 is the speed of light in a vacuum. Therefore:

$$\lambda = \frac{c_0}{f} = \frac{3 \times 10^8\ \mathrm{m/s}}{2.418 \times 10^{14}\ \mathrm{s}^{-1}} = 1.24 \times 10^{-6}\ \mathrm{m}.$$

1.1.4 The Schrödinger Equation

Theoretical physicists struggled to include observations like the photoelectric effect and the wave–particle duality into their formulations. Erwin Schrödinger, an Austrian physicist, was using advanced mechanics to deal with these phenomena and developed the following equation [2]:

$$\frac{\partial^2}{\partial t^2}\psi = -\frac{1}{\hbar^2}\left(\frac{\hbar^2}{2m}\nabla^2 - V\right)^2 \psi, \tag{1.3}$$

where $\hbar$ is another version of Planck's constant, $\hbar = h/2\pi$, and m represents the mass. The parameter ψ in Equation (1.3) is called a state variable, because all meaningful parameters can be determined from it even though it has no direct physical meaning itself. Equation (1.3) is second order in time and fourth order in space. Schrödinger realized that so complicated an equation, requiring so many initial and boundary conditions, was completely intractable. Recall that computers did not exist in 1925. However, Schrödinger realized that if he considered ψ to be a complex function, $\psi = \psi_{\mathrm{real}} + i\psi_{\mathrm{imag}}$, he could solve the simpler equation:

$$i\hbar\frac{\partial}{\partial t}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi. \tag{1.4}$$

Putting $\psi = \psi_{\text{real}} + i\psi_{\text{imag}}$ into Equation (1.4) gives:

$$i\hbar\frac{\partial\psi_{\text{real}}}{\partial t} - \hbar\frac{\partial\psi_{\text{imag}}}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi_{\text{real}} + i\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi_{\text{imag}}.$$

Then setting real and imaginary parts equal to each other results in two coupled equations:

$$\frac{\partial\psi_{\text{real}}}{\partial t} = \frac{1}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi_{\text{imag}}, \tag{1.5a}$$

$$\frac{\partial\psi_{\text{imag}}}{\partial t} = \frac{-1}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi_{\text{real}}. \tag{1.5b}$$

If we take the time derivative of Equation (1.5a),

$$\hbar\frac{\partial^2\psi_{\text{real}}}{\partial t^2} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\frac{\partial\psi_{\text{imag}}}{\partial t},$$

and use the time derivative of the imaginary part from Equation (1.5b), we get:

$$\begin{aligned}\frac{\partial^2\psi_{\text{real}}}{\partial t^2} &= \frac{1}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\frac{-1}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi_{\text{real}} \\ &= \frac{-1}{\hbar^2}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)^2 \psi_{\text{real}},\end{aligned}$$

which is the same as Equation (1.3). We could have operated on the two equations in reverse order and gotten the same result for ψ_{imag}. Therefore, both the real and imaginary parts of ψ solve Equation (1.3). (An elegant and thorough explanation of the development of the Schrödinger equation is given in Borowitz [2].)

This probably seems a little strange, but consider the following problem. Suppose we are asked to solve the following equation where a is a real number:

$$x^2 + a^2 = 0.$$

Just to simplify, we will start with the specific example of $a = 2$:

$$x^2 + 2^2 = (x - i2)(x + i2) = 0.$$

We know one solution is $x = i2$ and another solution is $x^* = -i2$. Furthermore, for any a, we can solve the factored equation to get one solution, and the other will be its complex conjugate.

Equation (1.4) is the celebrated *time-dependent Schrödinger equation*. It is used to get a solution of the state variable ψ. However, we also need the complex conjugate ψ^* to determine any meaningful physical quantities. For instance,

$$|\psi(x,t)|^2 \, dx = \psi^*(x,t)\psi(x,t)dx$$

is the probability of finding the particle between x and $x + dx$ at time t. For this reason, one of the basic requirements in finding the solution to ψ is *normalization*:

$$\langle \psi(x)|\psi(x)\rangle = \int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1. \tag{1.6}$$

In other words, the probability that the particle is somewhere is 1.

Equation (1.6) is an example of an *inner product*. More generally, if we have two functions, their inner product is defined as:

$$\langle \psi_1(x)|\psi_2(x)\rangle = \int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)dx.$$

This is a very important quantity in quantum mechanics, as we will see.

The spatial operator on the right side of Equation (1.4) is called the *Hamiltonian*:

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V(x).$$

Equation (1.4) can be written as:

$$i\hbar\frac{\partial}{\partial t}\psi = H\psi. \tag{1.7}$$

1.2 SIMULATION OF THE ONE-DIMENSIONAL, TIME-DEPENDENT SCHRÖDINGER EQUATION

We have seen that quantum mechanics is dictated by the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_e}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t). \tag{1.8}$$

The parameter $\psi(x,t)$ is a state variable. It has no direct physical meaning, but all relevant physical parameters can be determined from it. In general, $\psi(x,t)$

is a function of both space and time. $V(x)$ is the potential. It has the units of energy (usually electron volts for our applications.) $\hbar$ is Planck's constant. m_e is the mass of the particle being represented by the Schrödinger equation. In most instances in this book, we will be talking about the mass of an electron.

We will use computer simulation to illustrate the Schrödinger equation. In particular, we will use a very simple method called the finite-difference time-domain (FDTD) method. The FDTD method is one of the most widely used in electromagnetic simulation [3] and is now being used in quantum simulation [4].

1.2.1 Propagation of a Particle in Free Space

The advantage of the FDTD method is that it is a "real-time, real-space" method—one can observe the propagation of a particle in time as it moves in a specific area. The method will be described briefly.

We will start by rewriting the Schrödinger equation in one dimension as:

$$\frac{\partial \psi}{\partial t} = i\frac{\hbar}{2m_e}\frac{\partial^2 \psi(x,t)}{\partial x^2} - \frac{i}{\hbar}V(x)\psi(x,t). \tag{1.9}$$

To avoid using complex numbers, we will split $\psi(x,t)$ into two parts, separating the real and imaginary components:

$$\psi(x,t) = \psi_{\text{real}}(x,t) + i\cdot\psi_{\text{imag}}(x,t).$$

Inserting this into Equation (1.9) and separating into the real and imaginary parts leads to two coupled equations:

$$\frac{\partial \psi_{\text{real}}(x,t)}{\partial t} = -\frac{\hbar}{2m_e}\frac{\partial^2 \psi_{\text{imag}}(x,t)}{\partial x^2} + \frac{1}{\hbar}V(x)\psi_{\text{imag}}(x,t), \tag{1.10a}$$

$$\frac{\partial \psi_{\text{imag}}(x,t)}{\partial t} = \frac{\hbar}{2m_e}\frac{\partial^2 \psi_{\text{real}}(x,t)}{\partial x^2} - \frac{1}{\hbar}V(x)\psi_{\text{real}}(x,t). \tag{1.10b}$$

To put these equations in a computer, we will take the finite-difference approximations. The time derivative is approximated by:

$$\frac{\partial \psi_{\text{real}}(x,t)}{\partial t} \cong \frac{\psi_{\text{real}}(x,(m+1)\cdot\Delta t) - \psi_{\text{real}}(x,(m)\cdot\Delta t)}{\Delta t}, \tag{1.11a}$$

where Δt is a time step. The Laplacian is approximated by:

$$\begin{aligned}\frac{\partial^2 \psi_{\text{imag}}(x,t)}{\partial x^2} \cong \frac{1}{(\Delta x)^2}\big[&\psi_{\text{imag}}(\Delta x\cdot(n+1), m\cdot\Delta t)\\ &- 2\psi_{\text{imag}}(\Delta x\cdot n, m\cdot\Delta t) + \psi_{\text{imag}}(\Delta x\cdot(n-1), m\cdot\Delta t)\big]\end{aligned}. \tag{1.11b}$$

where Δx is the size of the cells being used for the simulation. For simplicity, we will use the following notation:

$$\psi(n\cdot\Delta x, m\cdot\Delta t)=\psi^{m}(n), \tag{1.12}$$

that is, the superscript ^{m} indicates the time in units of time steps ($t = m\cdot\Delta t$) and n indicates position in units of cells ($x = n\cdot\Delta x$).

Now Equation (1.10a) can be written as:

$$\frac{\psi_{\text{real}}^{m+1}(n)-\psi_{\text{real}}^{m}(n)}{\Delta t}=-\frac{\hbar}{2m}\frac{\psi_{\text{imag}}^{m+1/2}(n+1)-2\psi_{\text{imag}}^{m+1/2}(n)+\psi_{\text{imag}}^{m+1/2}(n-1)}{(\Delta x)^2}$$
$$+\frac{1}{\hbar}V(n)\psi_{\text{imag}}^{m+1/2}(n),$$

which we can rewrite as:

$$\begin{aligned}\psi_{\text{real}}^{m+1}(n)&=\psi_{\text{real}}^{m}(n)-\frac{\hbar}{2m_e}\frac{\Delta t}{(\Delta x)^2}\left[\psi_{\text{imag}}^{m+1/2}(n+1)-2\psi_{\text{imag}}^{m+1/2}(n)+\psi_{\text{imag}}^{m+1/2}(n-1)\right]\\&\quad+\frac{\Delta t}{\hbar}V(n)\psi_{\text{imag}}^{m+1/2}(n).\end{aligned} \tag{1.13a}$$

A similar procedure converts Equation (1.10b) to the same form

$$\begin{aligned}\psi_{\text{imag}}^{m+3/2}(n)&=\psi_{\text{imag}}^{m+1/2}(n)+\frac{\hbar}{2m_e}\frac{\Delta t}{(\Delta x)^2}\left[\psi_{\text{real}}^{m+1}(n+1)-2\psi_{\text{real}}^{m+1}(n)+\psi_{\text{real}}^{m+1}(n-1)\right]\\&\quad-\frac{\Delta t}{\hbar}V(n)\psi_{\text{real}}^{m+1}(n).\end{aligned} \tag{1.13b}$$

Equation (1.13) tells us that we can get the value of ψ at time $(m + 1)\Delta t$ from the previous value and the surrounding values. Notice that the real values of ψ in Equation (1.13a) are calculated at integer values of m while the imaginary values of ψ are calculated at the half-integer values of m. This represents the leapfrogging technique between the real and imaginary terms that is at the heart of the FDTD method [3]. $\hbar$ is Planck's constant and m_e is the mass of a particle, which we will assume is that of an electron. However, Δx and Δt have to be chosen. For now, we will take $\Delta x = 0.1$ nm. We still have to choose Δt. Look at Equation (1.13). We will define a new parameter to combine all the terms in front of the brackets:

$$ra\equiv\frac{\hbar}{2m_e}\frac{\Delta t}{(\Delta x)^2}. \tag{1.14}$$

To maintain stability, this term must be small, no greater than about 0.15. All of the terms in Equation (1.14) have been specified except Δt. If $\Delta t = 0.02$

femtoseconds (fs), then $ra = 0.115$, which is acceptable. Actually, Δt must also be small enough so that the term $(\Delta t \cdot V(n)/h)$ is also less than 0.15, but we will start with a "free space" simulation where $V(n) = 0$. This leaves us with the equations:

$$\psi_{\text{real}}^{m+1}(n) = \psi_{\text{real}}^{m}(n) - ra \cdot \left[\psi_{\text{imag}}^{m+1/2}(n+1) - 2\psi_{\text{imag}}^{m+1/2}(n) + \psi_{\text{imag}}^{m+1/2}(n-1)\right], \tag{1.15a}$$

$$\psi_{\text{imag}}^{m+3/2}(n) = \psi_{\text{imag}}^{m+1/2}(n) + ra \cdot \left[\psi_{\text{real}}^{m+1}(n+1) - 2\psi_{\text{real}}^{m+1}(n) + \psi_{\text{real}}^{m+1}(n-1)\right], \tag{1.15b}$$

which can easily be implemented in a computer.

Figure 1.5 shows a simulation of an electron in free space traveling to the right in the positive x direction. It is initialized at time $T = 0$. (See program Se1_1.m in Appendix D.) After 1700 iterations, which represents a time of

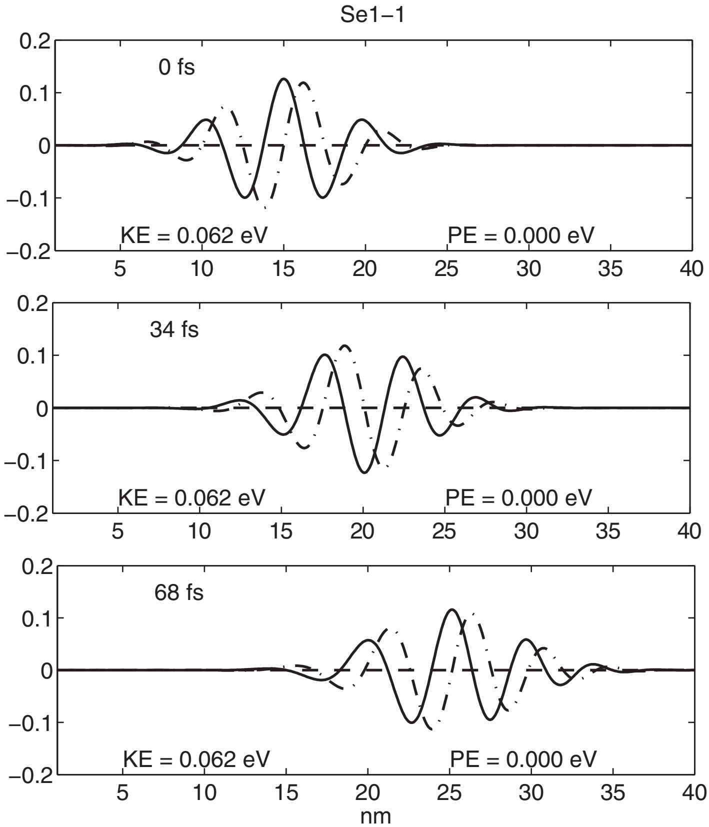


FIGURE 1.5 A particle propagating in free space. The solid line represents the real part of ψ and the dashed line represents the imaginary part.

$$T = 1700 \times \Delta T = 34 \text{ fs},$$

we see the electron has moved about 5 nm. After another 1700 iterations the electron has moved a total of about 10 nm. Notice that the waveform has real and imaginary parts and the imaginary part "leads" the real part. If it were propagating the other way, the imaginary part would be to the left of the real part.

Figure 1.5 indicates that the particle being simulated has 0.062 eV of KE. We will discuss how the program calculates this later. But for now, we can check and see if this is in general agreement with what we have learned. We know that in quantum mechanics, momentum is related to wavelength by Equation (1.2). So we can calculate KE by:

$$\text{KE} = \frac{1}{2} m_e v^2 = \frac{p^2}{2m_e} = \frac{1}{2m_e}\left(\frac{h}{\lambda}\right)^2.$$

In Figure 1.5, the wavelength appears to be 5 nm. The mass of an electron in free space is 9.1×10^{-31} kg.

$$\begin{aligned}
\text{KE} &= \frac{1}{2(9.1\times10^{-31}\ \text{kg})}\left(\frac{6.625\times10^{-34}\ \text{J}\cdot\text{s}}{5\times10^{-9}\ \text{m}}\right)^2 \\
&= \frac{1}{2(9.1\times10^{-31}\ \text{kg})}\left(1.325\times10^{-25}\frac{\text{J}\cdot\text{s}}{\text{m}}\right)^2 = \frac{1.756\times10^{-50}\ \text{J}^2\text{s}^2}{18.2\times10^{-31}\ \text{kg}\cdot\text{m}^2} \\
&= 9.65\times10^{-21}\ \text{J}\left(\frac{1\ \text{eV}}{1.6\times10^{-19}\ \text{J}}\right) = 0.0603\ \text{eV}.
\end{aligned}$$

Let us see if simulation agrees with classical mechanics. The particle moved 10 nm in 68 fs, so its velocity is:

$$v = \frac{10\times10^{-9}\ \text{m}}{68\times10^{-15}\ \text{s}} = 0.147\times10^{6}\ \text{m/s},$$

$$\begin{aligned}
\text{KE} &= \frac{1}{2}m_e v^2 = \frac{1}{2}(9.1\times10^{-31}\ \text{kg})(1.47\times10^{5}\ \text{m/s})^2 \\
&= 9.83\times10^{-21}\ \text{J}\left(\frac{1\ \text{eV}}{1.6\times10^{-19}}\right) = 0.0614\ \text{eV}.
\end{aligned}$$

1.2.2 Propagation of a Particle Interacting with a Potential

Next we move to a simulation of a particle interacting with a potential. In Section 1.4 we will discuss what might cause this potential, but we will ignore that for right now. Figure 1.6 shows a particle initialized next to a barrier that is 0.1 eV high. The potential is specified by setting $V(n)$ of Equation (1.13) to 0.1 eV for those value of n corresponding to the region between 20 and 40 nm.

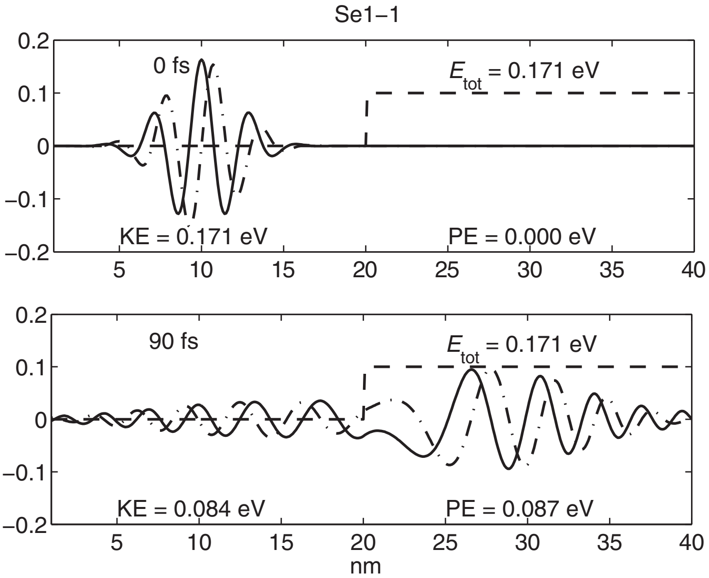


FIGURE 1.6 A particle is initialized in free space and strikes a barrier with a potential of 0.1 eV.

After 90 fs, part of the waveform has penetrated into the potential and is continuing to propagate in the same direction.

Notice that part of the waveform has been reflected. You might assume that the particle has split into two, but it has not. Instead, there is some probability that the particle will enter the potential and some probability that it will be reflected. These probabilities are determined by the following equations:

$$\mathrm{P}_{\text{reflected}} = \int_0^{20\text{ nm}} |\psi(x)|^2 \, dx, \tag{1.16a}$$

$$\mathrm{P}_{\text{penetrated}} = \int_{20\text{ nm}}^{40\text{ nm}} |\psi(x)|^2 \, dx. \tag{1.16b}$$

Also notice that as the particle enters the barrier it exchanges some of its KE for PE. However, the total energy remains the same.

Now let us look at the situation where the particle is initialized at a potential of 0.1 eV, as shown in the top of Figure 1.7. This particle is also moving left to right. As it comes to the interface, most of the particle goes to the zero potential region, but some is actually reflected and goes back the other way. This is another purely quantum mechanical phenomena. According to classical

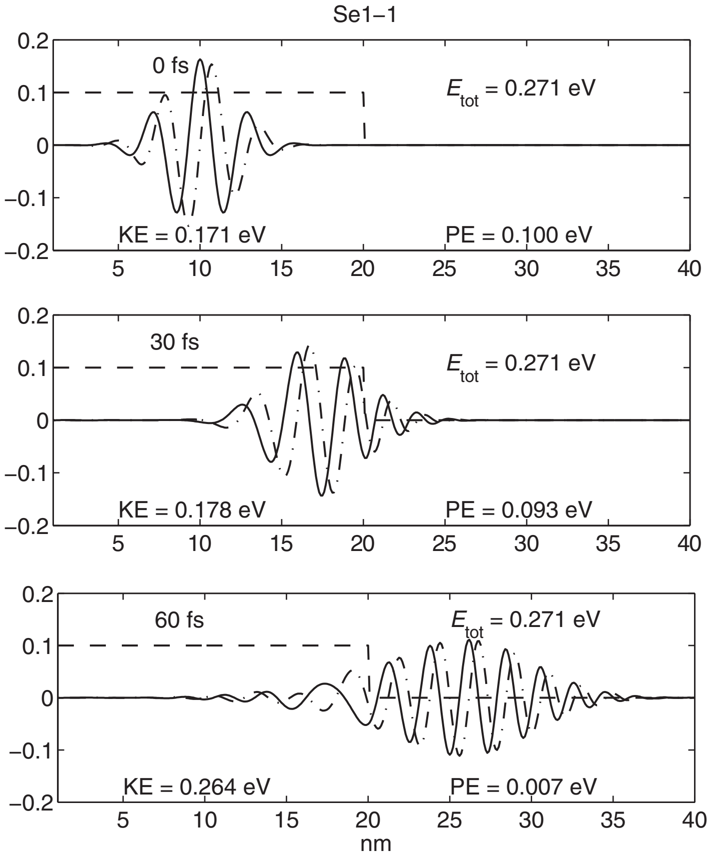
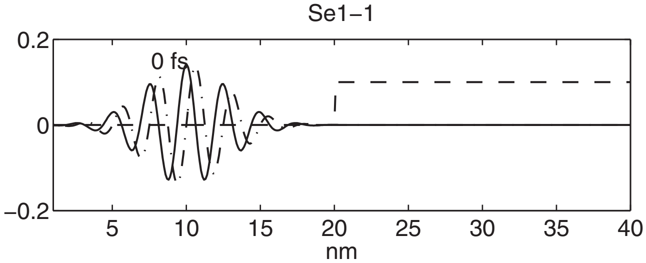


FIGURE 1.7 A particle moving left to right is initialized at a potential of 0.1 eV. Note that the particle initially has both KE and PE, but after most of the waveform moves to the zero potential region, it has mostly KE.

physics, a particle coming to the edge of a cliff would drop off with 100% certainty. Notice that by 60 fs, most of the PE has been converted to KE, although the total energy remains the same.

Example 1.2

The particle in the figure is an electron moving toward a potential of 0.1 eV. If the particle penetrates into the barrier, explain how you would estimate its total energy as it keeps propagating. You may write your answer in terms of known constants.



Solution. The particle starts with only KE, which can be estimated by:

$$\mathrm{KE} = \frac{(h/\lambda)^2}{2m_e} = 3.84 \times 10^{-20}\ \mathrm{J} = 0.24\ \mathrm{eV}.$$

In this case, $\lambda = 2.5$ nm and $m = 9.11 \times 10^{-31}$ kg the mass of an electron. If the particle penetrates into the barrier, 0.1 eV of this KE is converted to PE, but the total energy remains the same.

1.3 PHYSICAL PARAMETERS: THE OBSERVABLES

We said that the solution of the Schrödinger equation, the state variable ψ, contains all meaningful physical parameters even though its amplitude had no direct physical meaning itself. To find these physical parameters, we must do something to the waveform $\psi(x)$. In quantum mechanics, we say that we apply an *operator* to the function. It may seem strange that we have to do something to a function to obtain the information, but this is not as uncommon as you might first think. For example, if we wanted to find the total area under some waveform $F(x)$ we would apply the integration operator to find this quantity. That is what we do now. The operators that lead to specific physical quantities in quantum mechanics are called *oberservables*.

Let us see how we would go about extracting a physical property from $\psi(x)$. Suppose we have a waveform like the one shown in Figure 1.5, and that we can write this function as:

$$\psi(x) = A(x)e^{ikx}. \tag{1.17}$$

The e^{ikx} is the oscillating complex waveform and $A(x)$ describes the spatial variation, in this case a Gaussian envelope. Let us assume that we want to determine the momentum. We know from Equation (1.2) that in quantum mechanics, momentum is given by:

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

So if we could get that k in the exponential of Equation (1.17), we could just multiply it by $\hbar$ to have momentum. We can get that k if we take the derivative with respect to x. Try this:

$$\frac{\partial}{\partial x}\psi(x)=\left(\frac{\partial}{\partial x}A(x)\right)e^{ikx}+ikA(x)e^{ikx}.$$

We know that the envelope function $A(x)$ is slowly varying compared to e^{ik}, so we will make the approximation

$$\frac{d}{dx}\psi(x)\cong ikA(x)e^{ikx}.$$

Similar to the way we multiplied a state variable with its complex conjugate and integrated to get the normalization factor in Equation (1.6), we will now multiply the above function with the complex conjugate of $\psi(x)$ and integrate:

$$\int_{-\infty}^{\infty}A^{*}(x)e^{-ikx}ikA(x)e^{ikx}dx=ik\int_{-\infty}^{\infty}A^{*}(x)A(x)e^{-ikx}e^{ikx}dx=ik.$$

We know that last part is true because $\psi(x)$ is a normalized function. If instead of just the derivative, we used the operator

$$p=\frac{\hbar}{i}\frac{d}{dx}, \tag{1.18}$$

when we take the inner product, we get $\hbar k$, the momentum. The p in Equation (1.18) is the momentum observable and the quantity we get after taking the inner product is the *expectation value* of the momentum, which has the symbol $\langle p\rangle$.

If you were to guess what the KE operator is, your first guess might be

$$\mathrm{KE}=\frac{p^{2}}{2m_{e}}=\frac{1}{2m_{e}}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^{2}=-\frac{\hbar^{2}}{2m_{e}}\frac{\partial^{2}}{\partial x^{2}}. \tag{1.19}$$

You would be correct. The *expectation value* of the KE is actually the quantity that the program calculates for Figure 1.6.

We can calculate the KE in the FDTD program by taking the Laplacian, similar to Equation (1.11b),

$$Lap\_\psi(k)=\psi(k+1)-2\psi(k)+\psi(k-1),$$

and then calculating:

$$\langle \mathrm{KE} \rangle = -\frac{\hbar^2}{2m_e \cdot \Delta x^2} \sum_{k=1}^{NN} \psi^*(k) Lap\_\psi(k). \tag{1.20}$$

The number *NN* is the number of cells in the FDTD simulation.

What other physical quantities might we want, and what are the corresponding observables? The simplest of these is the *position operator*, which in one dimension is simply x. To get the expectation value of the operator x, we calculate

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x) x \psi(x) dx. \tag{1.21}$$

To calculate it in the FDTD format, we use

$$\begin{aligned} \langle x \rangle &= \sum_{n=1}^{NN} [\psi_{\mathrm{real}}(n) - i\psi_{\mathrm{imag}}(n)](n \cdot \Delta x)[\psi_{\mathrm{real}}(n) + i\psi_{\mathrm{imag}}(n)] \\ &= \sum_{n=1}^{NN} [\psi_{\mathrm{real}}^2(n) + \psi_{\mathrm{imag}}^2(n)](n \cdot \Delta x), \end{aligned}$$

where Δx is the cell size in the program and *NN* is the total number of cells. This can be added to the FDTD program very easily.

The expectation value of the PE is also easy to calculate:

$$\langle \mathrm{PE} \rangle = \int_{-\infty}^{\infty} \psi^*(x) V(x) \psi(x) dx. \tag{1.22}$$

The potential $V(x)$ is a real function, so Equation (1.22) simplifies to

$$\langle \mathrm{PE} \rangle = \int_{-\infty}^{\infty} |\psi(x)|^2 V(x) dx,$$

which is calculated in the FDTD program similar to $\langle x \rangle$ above,

$$\langle \mathrm{PE} \rangle = \sum_{n=1}^{NN} [\psi_{\mathrm{real}}^2(n) + \psi_{\mathrm{imag}}^2(n)] V(n). \tag{1.23}$$

These expectation values of KE and PE are what appear in the simulation in Figure 1.6.

Probably the most important observable is the Hamiltonian itself, which is the sum of the KE and PE observable. Therefore, the expectation value of the Hamiltonian is the expectation of the total energy

$$\langle H \rangle = \langle \text{KE} \rangle + \langle \text{PE} \rangle.$$

1.4 THE POTENTIAL *V* (*x*)

Remember that we said that the Schrödinger equation is an energy equation, and that $V(x)$ represents the PE. In this section we will give two examples of how physical phenomena are represented through $V(x)$.

1.4.1 The Conduction Band of a Semiconductor

Suppose our problem is to simulate the propagation of an electron in an n-type semiconductor. The electrons travel in the conduction band [5]. A key reference point in a semiconductor is the Fermi level. The more the n-type semiconductor is doped, the closer the Fermi level is moved toward the conduction band. If two n-type semiconductors with different doping levels are placed next to each other, the Fermi levels will align, as shown in Figure 1.8. In this case, the semiconductor to the right of the junction is more lightly doped than the one on the left. This results in the step in the conduction band. An electron going from left to right will see this potential, and there will be some chance it will penetrate and some chance it will be reflected, similar to the simulation of Figure 1.6.

In actuality, one more thing must be changed to simulate Figure 1.8. If the simulation is in a semiconductor material, we can no longer use the free space mass of the electron, given by $m_e = 9.109 \times 10^{-31}$ kg. It must be altered by a quantity called the effective mass. We will discuss this in Chapter 6. For now, just understand that if the material we are simulating is silicon, which has an effective mass of 1.08, we must use a mass of $m_e = 1.08 \times (9.109 \times 10^{-31}\ \text{kg})$ in determining the parameters for the simulation. Figure 1.9 is a simulation of a particle interacting with the junction of Figure 1.8.

1.4.2 A Particle in an Electric Field

Suppose we have the situation illustrated in Figure 1.10 on the following page. The voltage of U_0 volts results in an electric field through the material of

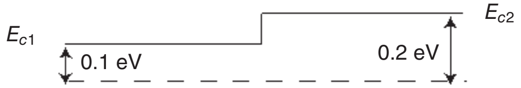


FIGURE 1.8 A junction formed by two n-type semiconductors with different doping levels. The material on the left has heavier doping because the Fermi level (dashed line) is closer to the conduction band.

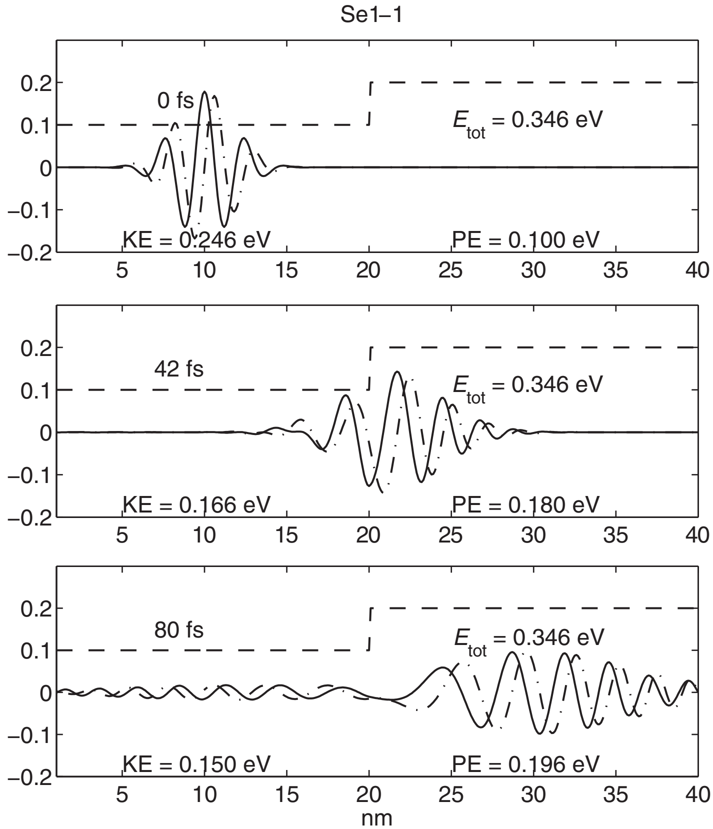


FIGURE 1.9 A simulation of a particle in the conduction band of a semiconductor, similar to the situation shown in Fig. 1.8. Note that the particle initially has a PE of 0.1 eV because it begins in a conduction band at 0.1 eV. After 80 fs, most of the waveform has penetrated to the conduction band at 0.2 eV, and much of the initial KE has been exchanged for PE.

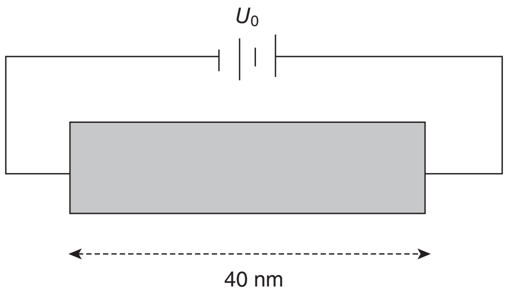


FIGURE 1.10 A semiconductor material with a voltage across it.

$$\boldsymbol{E_e} = -\frac{U_0}{40\ \text{nm}}.$$

This puts the right side at a higher potential of U_0 volts.

To put this in the Schrödinger equation, we have to express this in terms of energy. For an electron to be at a potential of V_0 volts, it would have to have a PE of

$$V_e = -eU_0. \tag{1.24}$$

What are the units of the quantity V_e? Volts have the units of joules per coulomb, so V_e has the units of joules. As we have seen, it is more convenient to work in electron volts: to convert V_e to electron volts, we divide by $1/1.6 \times 10^{-19}$. That means the application of U_0 volts lowers the potential by V_e electron volts. That might seem like a coincidence, but it is not. We saw earlier that an electron volt is defined as the energy to move charge of one electron through a potential difference of 1 V. To quantify our discussion we will say that $U_0 = 0.2$ V. With the above reasoning, we say that the left side has a PE that is 0.2 eV higher than the right side. We write this as:

$$V_e(x) = 0.2 - \frac{0.2}{40} x\text{eV}, \tag{1.25}$$

as shown by the dashed line in Figure 1.11 (x is in nanometers). This potential can now be incorporated into the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t}\psi = \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_e(x)\right)\psi. \tag{1.26}$$

Note that the potential induces an electric field given by [6]:

$$\mathsf{E} = -\nabla V_e(x) = -\frac{\partial V_e(x)}{dx}.$$

If we take $U_0 = 0.2$ V, then

$$\mathsf{E} = -\frac{0.02\ \text{V}}{40 \times 10^{-9}\,\text{m}} = -10^6\ \text{V/m}. \tag{1.27}$$

This seems like an extremely intense E field but it illustrates how intensive E fields can appear when we are dealing with very small structures.

Figure 1.11 is a simulation of a particle in this E field. We begin the simulation by placing a particle at 10 nm. Most of its energy is PE. In fact, we see that PE = 0.15 eV, in keeping with its location on the potential slope. After

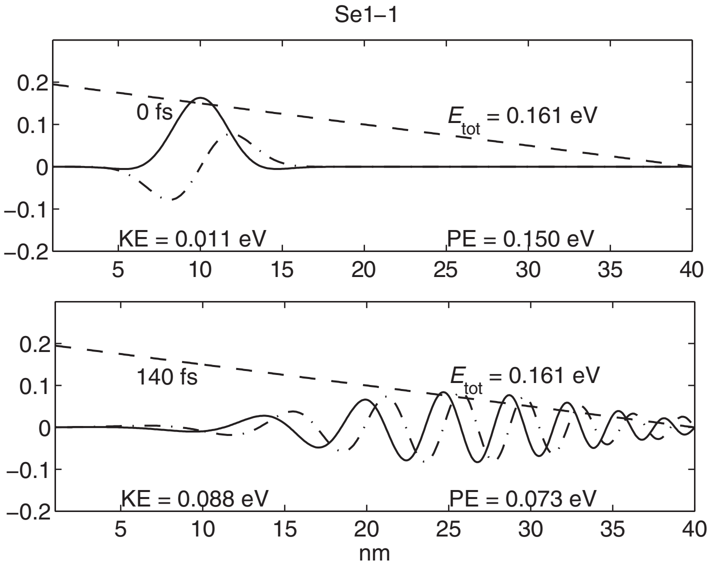


FIGURE 1.11 An electric field is simulated by a slanting potential (top). The particle is initialized at 10 nm. After 140 fs the particle has moved down the potential, acquiring more KE.

140 fs, the particle has started sliding down the potential. It has lost much of its PE and exchanged it for KE. Again, the total energy remains constant.

Note that the simulation of a particle in an E field was accomplished by adding the term $-eV_0$ to the Schrödinger equation of Equation (1.25). But the simulation illustrated in Figure 1.11 looks as if we just have a particle rolling down a graded potential. This illustrates the fact that all phenomena incorporated into the Schrödinger equation must be in terms of energy.

1.5 PROPAGATING THROUGH POTENTIAL BARRIERS

The state variable ψ is a function of both space and time. In fact, it can often be written in separate space and time variables

$$\psi(x,t) = \psi(x)\theta(t). \tag{1.28}$$

Recall that one of our early observations was that the energy of a photon was related to its frequency by

$$E = hf.$$

In quantum mechanics, it is usually written as:

$$E = (2\pi f)\left(\frac{h}{2\pi}\right) = \hbar\omega.$$

The Schrödinger equation is first order in time so we can assume that the time-dependent parameter $\theta(t)$ is in a time-harmonic form,

$$\theta(t) = e^{-i\omega t} = e^{-i(E/\hbar)t}. \tag{1.29}$$

When we put this in the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\left\{\psi(x)e^{-i(E/\hbar)t}\right\} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{\psi(x)e^{-i(E/\hbar)t}\right\} + V(x)\left\{\psi(x)e^{-i(E/\hbar)t}\right\},$$

the left side becomes

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left\{\psi(x)e^{-i(E/\hbar)t}\right\} &= i\hbar\left(-i\frac{E}{\hbar}\right)\left\{\psi(x)e^{-i(E/\hbar)t}\right\} \\ &= E\left\{\psi(x)e^{-i(E/\hbar)t}\right\}. \end{aligned}$$

If we substitute this back into the Schrödinger equation, there are no remaining time operators, so we can divide out the term $e^{-i(E/\hbar)t}$, which leaves us with the *time-independent Schrödinger* equation

$$E\psi(x) = -\frac{\hbar^2}{2m_e}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x). \tag{1.30}$$

We might find it more convenient to write it as:

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0,$$

or even

$$\frac{\partial^2\psi(x)}{\partial x^2} + k^2\psi(x) = 0, \tag{1.31a}$$

with

$$k = \frac{1}{\hbar}\sqrt{2m_e(E - V(x))}. \tag{1.31b}$$

Equation (1.31a) now looks like the classic Helmholtz equation that one might find in electromagnetics or acoustics. We can write two general types of solutions for Equation (1.31a) based on whether k is real or imaginary. If $E > V$, k will be real and solutions will be of the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

or

$$\psi(x) = A\cos(kx) + B\sin(kx);$$

that is, the solutions are propagating. Notice that for a given value of E, the value of k changes for different potentials V. This was illustrated in Figure 1.6.

If however, $E < V$, k will be imaginary and solutions will be of the form

$$\psi(x) = Ae^{-kx} + Be^{kx}; \tag{1.32}$$

that is, the solutions are decaying. The first term on the right is for a particle moving in the positive x-direction and the second term is for a particle moving in the negative x-direction. Figure 1.12 illustrates the different wave behaviors

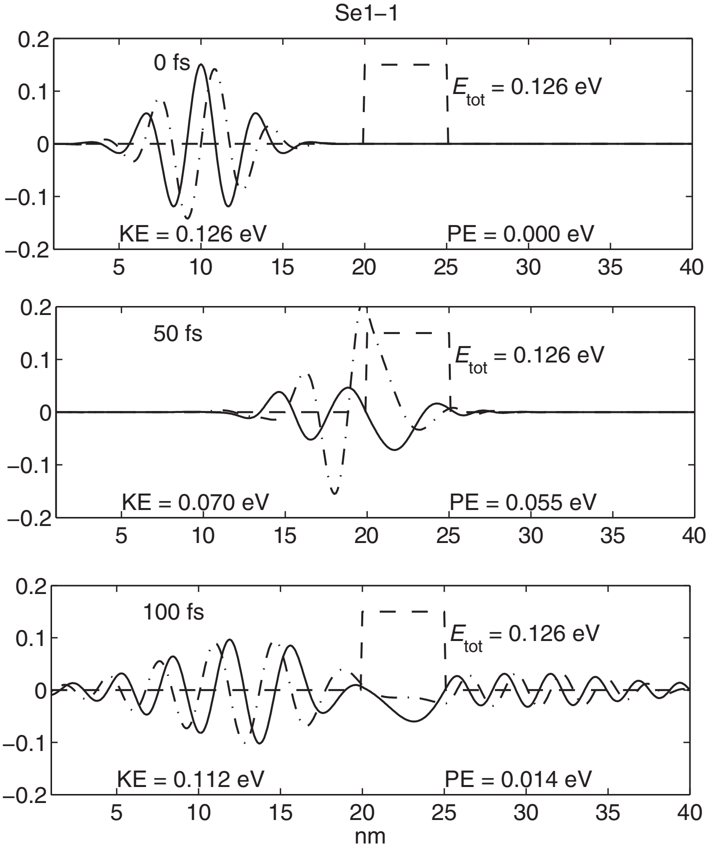


FIGURE 1.12 A propagating pulse hitting a barrier with a PE of 0.15 eV.

for different values of k. A particle propagating from left to right with a KE of 0.126 eV encounters a barrier, which has a potential of 0.15 eV. The particle goes through the barrier, but is attenuated as it does so. The part of the waveform that escapes from the barrier continues propagating at the original frequency. Notice that it is possible for a particle to move through a barrier of higher PE than it has KE. This is a purely quantum mechanical phenomenon called "tunneling."

1.6 SUMMARY

Two specific observations helped motivate the development of quantum mechanics. The photoelectric effect states that energy is related to frequency

$$E = hf. \tag{1.33}$$

The wave–particle duality says that momentum and wavelength are related

$$p = \frac{h}{\lambda}. \tag{1.34}$$

We also made use of two classical equations in this chapter. When dealing with a particle, like an electron, we often used the formula for KE:

$$\mathrm{KE} = \frac{1}{2} m_e v^2, \tag{1.35}$$

where m is the mass of the particle and v is its velocity. When dealing with photons, which are packets of energy, we have to remember that it is electromagnetic energy, and use the equation

$$c_0 = f\lambda, \tag{1.36}$$

where c_0 is the speed of light, f is the frequency, and λ is the wavelength.

We started this chapter stating that quantum mechanics is dictated by the *time-dependent Schrödinger* equation. We subsequently found that each of the terms correspond to energy:

$$\underset{\text{Total energy}}{i\hbar \frac{\partial}{\partial t} \psi(x,t)} = \underset{\text{Kinetic energy}}{-\frac{\hbar^2}{2m} \nabla^2 \psi(x,t)} + \underset{\text{Potential energy}}{V(x)\psi(x,t)} \tag{1.37}$$

However, we can also work with the *time-independent Schrödinger* equation:

$$E\psi(x,t) = \underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi(x,t)}_{} + V(x)\psi(x,t) \tag{1.38}$$

Total energy Kinetic energy Potential energy

EXERCISES

1.1 Why Quantum Mechanics?

1.1.1 Look at Equation (1.2). Show that h/λ has units of momentum.

1.1.2 Titanium has a work function of 4.33 eV. What is the maximum wavelength of light that I can use to induce photoelectron emission?

1.1.3 An electron with a center wavelength of 10 nm is accelerated through a potential of 0.02 V. What is its wavelength afterward?

1.2 Simulation of the One-Dimensional, Time-Dependent Schrödinger Equation

1.2.1 In Figure 1.6, explain why the wavelength changes as it goes into the barrier. Look at the part of the waveform that is reflected from the barrier. Why does the imaginary part appear slightly to the left of the real, as opposed to the part in the potential?

1.2.2 You have probably heard of the Heisenberg uncertainty principle. This says that we cannot know the position of a particle and its momentum with unlimited accuracy at any given time. Explain this in terms of the waveform in Figure 1.5.

1.2.3 What are the units of $\psi(x)$ in Figure 1.5? (Hint: The "1" in Eq. 1.6 is dimensionless.) What are the units of ψ in two dimensions? In three dimensions?

1.2.4 Suppose an electron is represented by the waveform in Figure 1.13 and you have an instrument that can determine the position to within 5 nm. Approximate the probability that a measurement will find the particle: (a) between 15 and 20 nm, (b) between 20 and 25 nm, and (c) between 25 and 30 nm. Hint: Approximate the magnitude in each region and remember that the magnitude

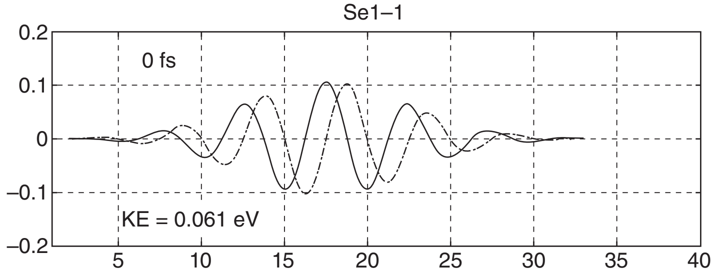


FIGURE 1.13 A waveform representing an electron.

squared gives the probability that the particle is there and that the total probability of it being somewhere must be 1.

1.2.5 Use the program se1_1.m and initialize the wave in the middle (set nc = 200). Run the program with a wavelength of 10 and then a wavelength of 20. Which propagates faster? Why? Change the wavelength to –10. What is the difference? Why does this happen?

1.3 Physical Parameters: The Observables

1.3.1 Add the calculation of the expectation value of position $\langle x \rangle$ to the program se1_1.m. It should print out on the plots, like KE and PE expectation values. Show how this value varies as the particle propagates. Now let the particle hit a barrier as in Figure 1.7. What happens to the calculation of $\langle x \rangle$? Why?

1.4 The Potential $V(x)$

1.4.1 Simulate a particle in an electric field of strength $E = 5 \times 10^6$ V/m. Initialize a particle 10 nm left of center with a wavelength of 4 nm and $\sigma = 4$ nm. (Sigma represents the width of the Gaussian shape.) Run the simulation until the particle reaches 10 nm right of center. What has changed and why?

1.4.2 Explain how you would simulate the following problem: A particle is moving along in free space and then encounters a potential of –0.1 eV.

1.5 Propagation through Barriers

1.5.1 Look at the example in Figure 1.12. What percentage of the amplitude is attenuated as the wave crosses through the barrier? Simulate this using se1_1.m and calculate the probability that the particle made it through the barrier using a calculation similar to Equation (1.15). Is your calculation of the transmitted amplitude in qualitative agreement with this?

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