The Schroedinger Equation

From: Modular Series on Solid State Devices Vol. IV

Advanced Semiconductor Fundamentals R.F. Pierret

2.2 BASIC FORMALISM

2.2.1 General Formulation

The accumulation of experimental data and physical explanations in the early 20th century which were at odds with the classical laws of physics emphasized the need for a revised formulation of mechanics. In 1926 Schrödinger not only provided the required revision, but established a unified scheme valid for describing both the microscopic and macroscopic universes. The formulation, called *wave mechanics,* incorporated the physical notions of quantization first advanced by Planck and the wave-like nature of matter hypothesized by de Broglie. It should be mentioned that at almost the same time an alternative formulation called *matrix mechanics* was advanced by Heisenberg. Although very different in their mathematical orientations, the two formulations were later shown to be precisely equivalent and were merged under the general heading of *quantum mechanics*. Herein we will restrict ourselves to the Schrödinger wave mechanical description, which is somewhat simpler mathematically and more readily related to the physics of a particular problem. Nevertheless, the reader should be forewarned that problem-solving using wave mechanics is considerably different, and typically more involved, than a classical analysis. Our general approach will be to present the five basic postulates of wave mechanics and to subsequently discuss the postulates to provide some insight into the formulation.

For a single-particle system, the five basic postulates of wave mechanics are as follows:

(1) There exists a wavefunction, $\Psi = \Psi(x, y, z, t)$, from which one can ascertain the dynamic behavior of the system and all desired system variables. Ψ might be called the "describing function" for the system. Mathematically, Ψ is permitted to

be a complex quantity (with real and imaginary parts) and will, in general, be a function of the space coordinates (x, y, z) and time t.

(2) The Ψ for a given system and specified system contraints is determined by solving the equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U(x, y, z)\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} \tag{2.9}$$

where m is the mass of the particle, U is the potential energy of the system,† and $i = \sqrt{-1}$. Eq. (2.9) is referred to as the time-dependent Schrödinger equation, or simply, the wave equation.

(3) Ψ and $\nabla\Psi$ must be finite, continuous, and single-valued for all values of x, y, z, and t.

(4) $\Psi^*\Psi\, d\mathcal{V} = |\Psi|^2\, d\mathcal{V}$ is to be identified as the probability that the particle will be found in the spatial volume element $d\mathcal{V}$. Hence, by implication,

$$\int_{\mathcal{V}} \Psi^*\Psi\, d\mathcal{V} = 1 \tag{2.10}$$

where $\int_{\mathcal{V}}$ indicates an integration over all space.

(5) One can associate a unique mathematical operator with each dynamic system variable such as position or momentum. The value — or, more precisely, the expectation value — of a given system variable is in turn obtained by "operating" on the wavefunction. Specifically, taking α to be the system variable of interest and α_{op} the associated mathematical operator, the desired expectation value, $\langle\alpha\rangle$, is computed from

$$\langle\alpha\rangle = \int_{\mathcal{V}} \Psi^*\alpha_{op}\Psi\, d\mathcal{V} \tag{2.11}$$

The unique mathematical operator associated with a given system variable has been established by requiring the wave mechanical expectation value to approach the corresponding value derived from classical mechanics in the large-mass/high-energy limit. An abbreviated listing of dynamic variables and associated operators is presented in Table 2.1.

The solution of problems using wave mechanics is in principle quite straightforward. Subject to the constraints (boundary conditions) inherent in a problem and the additional constraints imposed by postulates 3 and 4, one solves Schrödinger's equation for the system wavefunction Ψ. Once Ψ is known, system variables of interest

†In analyses using classical mechanics one normally considers the force, $\mathbf{F}$, acting on a particle. Note that, since $\mathbf{F} = \nabla U$, forces indirectly enter the wave mechanics formulation through the potential energy U.

Table 2.1 Dynamic Variable/Operator Correspondence.

Dynamic Variable (α)		Mathematical Operator (α_{op})	Expectation Value — $\langle\alpha\rangle$
x, y, z	$\leftrightarrow$	x, y, z	$\cdots \quad \langle x\rangle = \int_{\mathcal{V}} \Psi^* x \Psi \, d\mathcal{V}$
$f(x, y, z)$	$\leftrightarrow$	$f(x, y, z)$	
p_x, p_y, p_z	$\leftrightarrow$	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$	$\cdots \langle p_x\rangle = \int_{\mathcal{V}} \Psi^* \frac{\hbar}{i}\frac{\partial \Psi}{\partial x} \, d\mathcal{V}$
E	$\leftrightarrow$	$-\frac{\hbar}{i}\frac{\partial}{\partial t}$	

can be deduced from eq. (2.11) per the postulate 5 recipe. The straightforward approach, however, is often difficult to implement. Except for simple problems of an idealized nature and a very select number of practical problems, it is usually impossible to obtain a closed-form solution to Schrödinger's equation. In many problems, constraints imposed on the solution are used to deduce information about the system variables, notably the allowed system energies, without actually solving for the system wavefunction. Another common approach is to use expansions, trial (approximate) wavefunctions, or limiting-case solutions to deduce information of interest.

Attention should also be drawn to a property of matter inherent in postulates 4 and 5 which is not apparent on a macroscopic scale. Namely, the exact location of a particle and its precise trajectory cannot be specified — one can only ascertain the *probability* of finding the particle in a given spatial volume and the *expectation* values of variables. Consistent with human perception, however, if quantum mechanics is applied to a massive object such as a baseball, $\Psi^*\Psi \, d\mathcal{V}$ is found to be large only within the classical boundaries of the object, and the object is predicted to move in accordance with Newton's laws.

Finally, a comment is in order concerning the "derivation" of Schrödinger's equation and the origin of the other basic postulates. Although excellent theoretical arguments can be presented to justify the form of the equation,[1] Schrödinger's equation is essentially an empirical relationship. Like Newton's laws, Schrödinger's equation and the other basic postulates of quantum mechanics constitute a generalized mathematical description of the physical world extrapolated from specific empirical observations. Relative to the validity of the formulation, it can only be stated that, whenever subject to test by experiment, the predictions of the quantum mechanical formulation have been found to be in agreement with observations to within the limit of experimental uncertainty, which in many cases has been extremely small.[2]

2.2.2 Time-Independent Formulation

If the particle in the system under analysis has a fixed total energy E, the quantum mechanical formulation of the problem is significantly simplified. Consider the general

expression for the energy expectation value as deduced from eq. (2.11) and Table 2.1:

$$\langle E \rangle = \int_{\mathcal{V}} \Psi^* \left(-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} \right) d\mathcal{V} \tag{2.12}$$

By inspection, for the integral to yield $\langle E \rangle = E = \text{constant}$, one must have

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = E\Psi \tag{2.13}$$

Note that the direct substitution of eq. (2.13) into eq. (2.12) yields the desired result

$$\int_{\mathcal{V}} \Psi^* \left(-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} \right) d\mathcal{V} = E \int_{\mathcal{V}} \Psi^* \Psi \, d\mathcal{V} = E = \text{constant} \tag{2.14}$$

where use has been made of postulate 4. Eq. (2.13) is in turn readily shown to have a general solution of the form

$$\boxed{\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}} \tag{2.15}$$

Next substituting eq. (2.15) into the time-dependent Schrödinger equation [eq. (2.9)], canceling the multiplicative factor $\exp(-iEt/\hbar)$ which appears in all terms, and slightly rearranging the resulting equation, one obtains

$$\boxed{\nabla^2 \psi + \frac{2m}{\hbar^2} [E - U(x, y, z)] \psi = 0} \tag{2.16}$$

Eq. (2.16) is referred to as the time-independent Schrödinger equation.

In essence, when the particle has a fixed total energy E, the time-dependence is completely specified and the problem reduces to solving the time-independent Schrödinger equation for the time-independent wavefunction $\psi = \psi(x, y, z)$. The remainder of the basic postulates can also be restated in terms of the time-independent wavefunction. Specifically,

(3′) ψ and $\nabla\psi$ must be finite, continuous, and single-valued for all values of x, y and z.

(4′) Since $\Psi^*\Psi = \psi^*\psi$, $\psi^*\psi\, d\mathcal{V} = |\psi|^2\, d\mathcal{V}$ is to be identified as the probability the particle will be found in the spatial volume element $d\mathcal{V}$. Likewise,

$$\int_{\mathcal{V}} \psi^*\psi\, d\mathcal{V} = 1 \tag{2.17}$$

(5′) The expectation value of the system variable α is given by

$$\langle\alpha\rangle = \int_{\mathcal{V}} \psi^*\alpha_{op}\psi\, d\mathcal{V} \tag{2.18}$$

where α_{op} is the mathematical operator associated with α. α_{op} in eq. (2.18) cannot explicitly depend on time.

All of the problems to be considered herein and most of the problems encountered in practice employ the foregoing time-independent formulation.

2.3 SIMPLE PROBLEM SOLUTIONS

The following simple problem solutions serve a threefold purpose: First, they help illustrate use of the quantum mechanical formalism and the interpretation of results. Second, the problems introduce additional formalism and a number of concepts which will prove to be of general utility. Finally, the problem solutions are of interest in themselves. The solutions, or reference to the results, can be found in the later chapters and in a number of solid-state device analyses.

The reader should be alerted to the fact that each of the first two problems contains a "violation" of the basic quantum mechanical postulates. These arise as a direct result of unrealistic idealizations which are introduced to make the problems tractable. Fortunately, neither violation poses a serious difficulty.

2.3.1 The Free Particle

PROBLEM SPECIFICATION:

The first problem to be addressed is the quantum mechanical characterization of a free particle. By definition, a free particle is an entity (say an electron) which finds itself alone in the universe. The particle is assumed to have a mass m and a fixed total energy E. Being alone, the particle will experience no forces and the potential energy of the system must likewise be a constant everywhere. The potential energy is of course arbitrary to within a constant, and we can therefore choose $U(x, y, z) = \text{constant} = 0$. For simplicity, let us also take the universe to be one-dimensional.

SOLUTION:

To obtain the desired solution, we must clearly solve the time-independent Schrödinger equation. With $U(x, y, z) = 0$ and the particle restricted to one-dimensional motion ($\nabla^2 \rightarrow d^2/dx^2$), eq. (2.16) simplifies to

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \tag{2.19}$$

By introducing the constant

$$k \equiv \sqrt{2mE/\hbar^2} \qquad \left(\text{or equivalently, } E = \frac{\hbar^2 k^2}{2m}\right) \tag{2.20}$$

the equation to be solved can be manipulated into the form

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{2.21}$$

Eq. (2.21) is a well-known differential equation whose general solution can be alternatively expressed in terms of sines and cosines, the hyperbolic functions, or exponentials. The last cited form of the solution is the most convenient in this particular problem. We therefore rapidly obtain the general solution

$$\psi(x) = A_+ e^{ikx} + A_- e^{-ikx} \tag{2.22}$$

where A_+ and A_- are solution constants. Furthermore, making use of eq. (2.15), we conclude

$$\Psi(x, t) = A_+ e^{i(kx - Et/\hbar)} + A_- e^{-i(kx + Et/\hbar)} \tag{2.23}$$

DISCUSSION:

The interpretation of the foregoing result is reasonably straightforward to those familiar with classical wave theory. In classical analyses dealing with electromagnetic waves, sound waves, and even mass waves on a vibrating string,

$e^{i(kx-\omega t)}$ . . . corresponds to a wave traveling in the $+x$ direction

and

$e^{-i(kx+\omega t)}$ . . . corresponds to a wave traveling in the $-x$ direction

where

$$\boxed{k \equiv \frac{2\pi}{\lambda}} \quad \ldots \text{is the } \textit{wavenumber} \tag{2.24}$$

and ω is the angular frequency of the traveling wave. Thus, by analogy, the free-particle wavefunction [eq. (2.23)] is interpreted to be a traveling wave. If the particle is assumed to be moving in the $+x$ direction, it follows that $A_- = 0$. Likewise, A_+ would be zero for a free particle moving in the $-x$ direction. Also note that the introduction of $k = \sqrt{2mE/\hbar^2}$ in the wavefunction solution anticipated this constant being identified as the wavenumber.

Let us next see what can be deduced about the free particle itself. Assuming the particle is moving in the $+x$ direction, we note first of all that $\psi^*\psi\,dx = A_+^*A_+\,dx =$ constant for all values of x. Thus one has an equal probability of finding the particle in any dx spatial segment. The probability of finding the particle integrated over all space must be equal of course to unity according to postulate 4. Integration of the probability density over all space is the usual means whereby one "normalizes" the wavefunction—i.e., determines the multiplicative constant in the wavefunction solution. However, a constant probability integrated between infinite limits technically requires $A_+^*A_+ = |A_+|^2$ and the associated wavefunction to become vanishingly small. The paradox here (which keeps us from determining A_+) arises because of the non-physical size of the assumed universe. Simply limiting the size of the universe to some large but finite value would resolve the paradox without affecting any of the results or conclusions presented herein.

Another property of the free particle which we wish to investigate is its $+x$ direction momentum. Making use of postulate 5′ and Table 2.1, we find

$$\langle p \rangle = \langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \frac{\hbar}{i} \frac{d\psi}{dx}\,dx = \hbar k \int_{-\infty}^{\infty} \psi^*\psi\,dx \tag{2.25a}$$

or, in light of postulate 4′ and eq. (2.24),

$$[\langle p \rangle = \hbar k = h/\lambda] \tag{2.25b}$$

Note that eq. (2.25b) is a restatement of the de Broglie relationship [eq. (2.8)] and its derivation here was based solely on wave mechanical arguments. Thus the de Broglie free-particle hypothesis is implicitly contained in the postulates of wave mechanics.

Finally, let us examine the energy of the free particle. Expressing k in terms of the momentum using eq. (2.25b), and substituting into the equivalent form of eq. (2.20),

one obtains

$$\left[E = \frac{\langle p \rangle^2}{2m}\right] \tag{2.26}$$

Now the energy of a *classical* free particle is equal to $mv^2/2$, $p = mv$, and therefore $E_{\text{classical}} = p^2/2m$. Hence, the quantum mechanical and classical free particles exhibit precisely the same energy–momentum relationship. This important E–$\langle p \rangle$ relationship is pictured in Fig. 2.3 for future reference. Also note that the quantum mechanical free particle, like its classical analog, can take on a continuum of energies: the energy of the free particle is not restricted to a quantized set of values.

2.3.2 Particle in a 1-D Box

PROBLEM SPECIFICATION:

The "particle-in-a-box" analysis, or characterization of a spatially confined entity, is more typical of wave mechanical problems. As pictured in Fig. 2.4a, we envision a particle of mass m with fixed total energy E confined to a relatively small segment of one-dimensional space between $x = 0$ and $x = a$. In terms of the potential energy (see Fig. 2.4b), the particle may be viewed as being trapped in an infinitely deep one-dimensional potential well with $U(x) =$ constant for $0 < x < a$. Since the potential energy is arbitrary to within a constant, we can choose $U = 0$ for $0 < x < a$ without

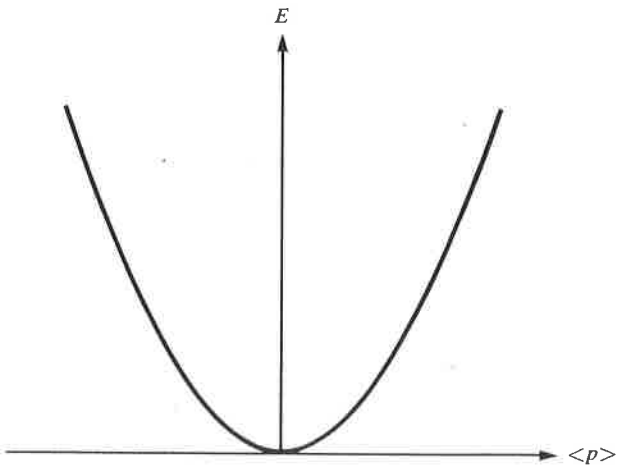

Fig. 2.3 Energy–momentum relationship for a free particle.

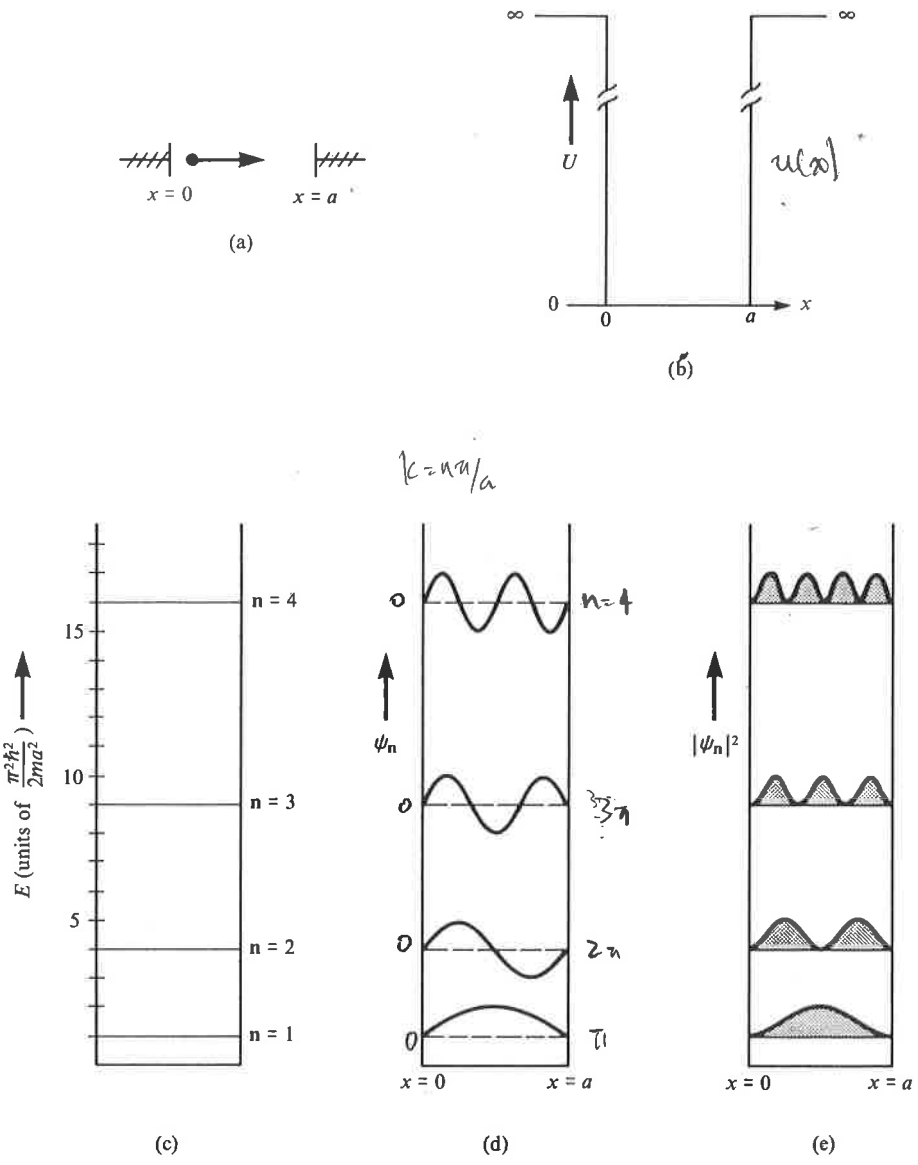

Fig. 2.4 Particle in an infinitely deep one-dimensional potential well. (a) Spatial visualization of the particle confinement. (b) The assumed potential energy versus position dependence. (c) First four allowed energy levels. (d) Wavefunctions and (e) $|\psi|^2$ associated with the first four energy levels. $|\psi|^2$ is proportional to the probability of finding the particle at a given point in the potential well.

any loss in generality. Clearly, the formulation of the particle-in-a-box and free-particle problems are identical except for the size of the confining "box."

SOLUTION:

With $U = 0$ in the region of particle confinement, and given the one-dimensional nature of the problem, the time-independent Schrödinger equation again reduces to

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots 0 < x < a \tag{2.27}$$

where, as before,

$$k \equiv \sqrt{2mE/\hbar^2} \quad \text{or} \quad E = \frac{\hbar^2 k^2}{2m} \tag{2.28}$$

Since the particle cannot stray into the regions external to $0 < x < a$, the wavefunction in these regions must be identically zero. The wavefunction, however, must also be continuous at the region boundaries (postulate 3′), which imposes the boundary conditions

$$\psi(0) = 0 \tag{2.29a}$$

and

$$\psi(a) = 0 \tag{2.29b}$$

The general solution of eq. (2.27), written in the form most convenient for this particular problem, is

$$\psi(x) = A \sin kx + B \cos kx \tag{2.30}$$

Next, applying the boundary conditions yields

$$\psi(0) = B = 0 \tag{2.31a}$$

and

$$\psi(a) = A \sin ka = 0 \tag{2.31b}$$

Other than the trivial $\psi = 0$ result obtained by setting $A = 0$, the eq. (2.31b) condition is satisfied only when ka is a multiple of π. We therefore conclude that k is re-

stricted to the values

$$[k = \mathbf{n}\pi/a \qquad \mathbf{n} = \pm 1, \pm 2, \pm 3, \cdots] \tag{2.32}$$

with the wavefunction corresponding to a given k (or $\mathbf{n}$) being

$$\left[\psi_{\mathbf{n}}(x) = A_{\mathbf{n}} \sin \frac{\mathbf{n}\pi x}{a}\right] \tag{2.33}$$

Likewise, making use of eq. (2.28), we further conclude that the energy of the particle can only assume the quantized values

$$\left[E_{\mathbf{n}} = \frac{\mathbf{n}^2\pi^2\hbar^2}{2ma^2}\right] \tag{2.34}$$

DISCUSSION:

Perhaps the most striking feature of the foregoing results is the direct prediction of energy quantization, a quantization which arises in turn as a direct result of the particle confinement. The four lowest-lying energy levels are pictured in Fig. 2.4c, while the wavefunctions and $|\psi|^2$ associated with the first four levels are shown, respectively, in Fig. 2.4d and e.

The Fig. 2.4d wavefunction plots are highly suggestive of standing waves, and indeed the particle can be thought of as bouncing back and forth between the walls of the potential well. Since the particle periodically changes direction, it should come as no surprise that the expectation or average value of the particle's momentum, $\langle p \rangle = \langle p_x \rangle$, is precisely zero for all energy states. However, a standing wave can always be decomposed into two counterpropagating traveling waves. If this be done, the momentum associated with the component waves is readily shown to be $+\mathbf{n}\pi\hbar/a$ and $-\mathbf{n}\pi\hbar/a$ for $+x$ and $-x$ propagation, respectively. A plot of allowed particle energies [eq. (2.34)] versus the counterpropagating wave momentum is shown in Fig. 2.5. Note that the discrete E–p points derived from the particle-in-a-box analysis all lie along the continuous $E = \langle p \rangle^2/2m$ curve characteristic of a free particle. Conceptually increasing the width a of the potential well would cause the discrete points in Fig. 2.5 to move closer together and slide toward the origin of coordinates. In the limit where $a \to \infty$, the discrete points would form a quasi-continuum, thereby essentially replicating the free-particle curve. This is of course consistent with the particle-in-a-box becoming a free particle as $a \to \infty$.

We should point out that the $\mathbf{n}$-integer which appears in the k, $E_{\mathbf{n}}$, and $\psi_{\mathbf{n}}$ relationships is called a *quantum number*. Strictly speaking, as noted in eq. (2.32), $\mathbf{n}$ can take on both positive and negative integer values. However, substituting into eq. (2.33),

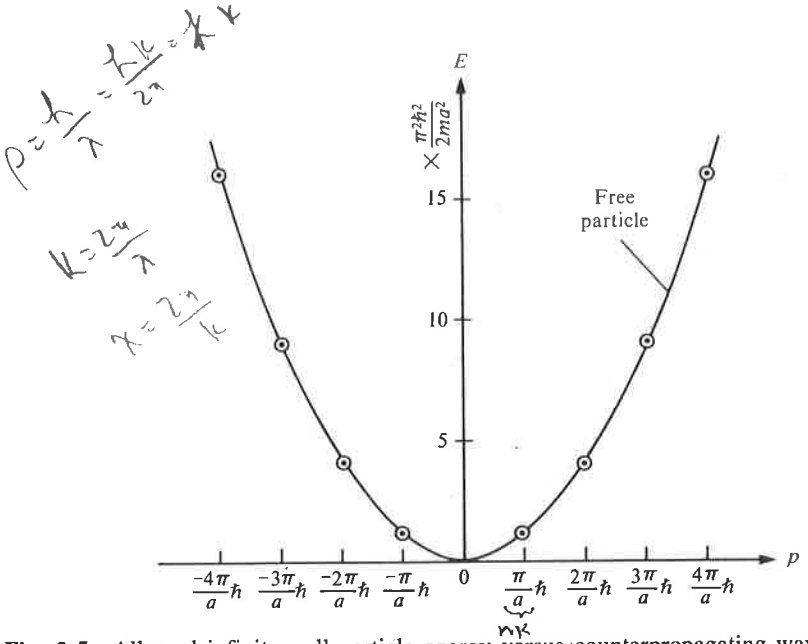

Fig. 2.5 Allowed infinite-well particle energy versus counterpropagating wave momentum (discrete points) referenced against the free particle E–$\langle p \rangle$ relationship.

one finds that the wavefunctions corresponding to the negative and positive values of the same whole number differ by only a minus sign—i.e., $\psi_{-\mathbf{n}} = -\psi_{+\mathbf{n}}$. As can be deduced from eq. (2.11) or eq. (2.18), when two wavefunctions differ only in sign, the expectation values for all system observables will be identical. In other words, one cannot physically distinguish between the $-\mathbf{n}$ and $+\mathbf{n}$ states; they actually refer to one and the same state. For this reason it is common practice to simply neglect the negative quantum numbers in the preceding analysis.

In many quantum mechanics problems the analysis is considered complete when the allowed energy spectrum has been determined; the multliplicative constants in the wavefunction solutions are often left unspecified. Nevertheless, it is a relatively easy matter to normalize the wavefunction in the particular problem at hand. Substituting the $\psi_{\mathbf{n}}$ expression into eq. (2.17), one rapidly deduces $A_{\mathbf{n}} = \sqrt{2/a}$. We should also mention that our wavefunction solutions for a particle in an infinitely deep potential well are not in strict compliance with postulate 3′. As is evident from Fig. 2.4d, the derivative of the wavefunctions is not continuous at the well boundaries ($d\psi/dx = 0$ for $x < 0$ and $x > a$). The source of the discrepancy is the unrealistic specification of an *infinite* well depth. Fortunately, it is possible to verify the results which we have presented by alternatively considering a particle in a finite potential well and examining the limit as the well depth goes to infinity. The finite potential well problem is addressed in the next subsection.

2.3.3 Finite Potential Well

PROBLEM SPECIFICATION:

The "particle in a finite potential well" is the last problem we will consider to illustrate the general procedures and concepts of quantum mechanics. The potential energy is taken to be as specified in Fig. 2.6, with $U(x) = 0$ for $0 < x < a$ and $U(x) = U_0$ for $x < 0$ and $x > a$. The particle under consideration has a mass m and a fixed total energy E.

SOLUTION ($0 < E < U_0$):

A classical particle with an energy $0 < E < U_0$ would be confined to the envisioned potential well, while the same particle with an energy $E > U_0$ would be free to roam throughout all space. The behavior of a quantum mechanical particle is likewise distinctly different when $E < U_0$ and $E > U_0$. The quantitative analysis to be presented treats the $E < U_0$ situation, with comments on the particle's $E > U_0$ behavior being included in the ensuing discussion.

Beginning the $0 < E < U_0$ analysis we note that the $x < 0$, $0 < x < a$ and $x > a$ solutions of the time-independent Schrödinger equation must be handled on an individual basis. The subscripts $-$, 0, and $+$ will therefore be used to identify the wavefunctions and solution constants in these regions respectively. Invoking the simplifications inherent in the problem, one obtains

$$\frac{d^2\psi_0}{dx^2} + k^2\psi_0 = 0 \qquad 0 < x < a \tag{2.35}$$

$$k \equiv \sqrt{2mE/\hbar^2} \tag{2.36}$$

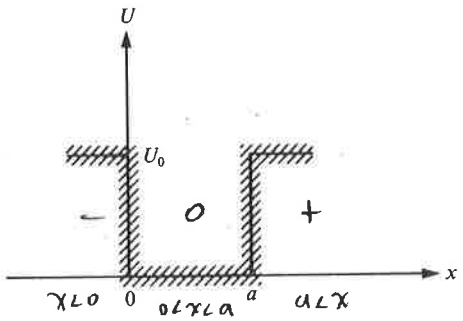

Fig. 2.6 Finite potential well.

and

$$\frac{d^2\psi_\pm}{dx^2} - \alpha^2\psi_\pm = 0 \qquad x < 0;\, x > a \tag{2.37}$$

$$\alpha \equiv \sqrt{2m(U_0 - E)/\hbar^2} \qquad (0 < E < U_0) \tag{2.38}$$

The general solutions to eqs. (2.35) and (2.37) are

$$\psi_-(x) = A_-e^{\alpha x} + B_-e^{-\alpha x} \qquad \ldots x < 0 \tag{2.39a}$$

$$\psi_0(x) = A_0\sin kx + B_0\cos kx \qquad \ldots 0 < x < a \tag{2.39b}$$

$$\psi_+(x) = A_+e^{\alpha x} + B_+e^{-\alpha x} \qquad \ldots x > a \tag{2.39c}$$

Far from the well boundaries the wavefunction must vanish. Likewise, the wavefunction and its derivative must be continuous at $x = 0$ and $x = a$. These requirements translate into six boundary conditions—namely,

$$\psi_-(-\infty) = 0; \qquad \psi_+(+\infty) = 0 \qquad (\psi \to 0 \text{ as } x \to \pm\infty) \tag{2.40a}$$

$$\psi_-(0) = \psi_0(0); \qquad \psi_0(a) = \psi_+(a) \qquad (\text{continuity of } \psi) \tag{2.40b}$$

$$\left.\frac{d\psi_-}{dx}\right|_0 = \left.\frac{d\psi_0}{dx}\right|_0; \qquad \left.\frac{d\psi_0}{dx}\right|_a = \left.\frac{d\psi_+}{dx}\right|_a \qquad \left(\text{continuity of } \frac{d\psi}{dx}\right) \tag{2.40c}$$

The eq. (2.40a) boundary conditions can only be satisfied by setting $B_- = 0$ and $A_+ = 0$. The remaining boundary conditions give rise to a set of four simultaneous equations:

$$A_- = B_0 \tag{2.41a}$$

$$A_0\sin ka + B_0\cos ka = B_+e^{-\alpha a} \tag{2.41b}$$

$$\alpha A_- = kA_0 \tag{2.41c}$$

$$kA_0\cos ka - kB_0\sin ka = -\alpha B_+e^{-\alpha a} \tag{2.41d}$$

Seeking a solution to these equations, we note that B_0 can be readily expressed in terms of A_0 using eqs. (2.41a) and (2.41c). After the B_0 expression is substituted into eqs. (2.41b) and (2.41d), the resulting equations can be appropriately combined to obtain an equation involving only A_0. The net result is

$$A_0[(k^2 - \alpha^2)\sin ka - 2\alpha k\cos ka] = 0 \tag{2.42}$$

To satisfy eq. (2.42), either $A_0 = 0$ or the bracketed expression must be equal to zero. However, if $A_0 = 0$, all the other solution constants are likewise equal to zero, and

one obtains the trivial $\psi = 0$ result. A non-trivial solution is therefore obtained if and only if

$$(k^2 - \alpha^2)\sin ka - 2\alpha k \cos ka = 0 \tag{2.43a}$$

or

$$\tan ka = \frac{2\alpha k}{k^2 - \alpha^2} \tag{2.43b}$$

To recast eq. (2.43b) into a form more amenable to examination, let us introduce

$$\alpha_0 \equiv \sqrt{2mU_0/\hbar^2} \qquad (\alpha_0 = \text{constant}) \tag{2.44}$$

and

$$\xi \equiv E/U_0 \qquad (0 < \xi < 1) \tag{2.45}$$

One can then write

$$\alpha = \alpha_0\sqrt{1 - \xi} \tag{2.46}$$

$$k = \alpha_0\sqrt{\xi} \tag{2.47}$$

and therefore

$$\tan(\alpha_0 a\sqrt{\xi}) = \frac{2\sqrt{\xi(1 - \xi)}}{2\xi - 1} \tag{2.48}$$

Since α_0 and a are system constants, the normalized particle energy ξ is the only unknown in eq. (2.48); the ξ values satisfying eq. (2.48) correspond to the allowed particle energies. To solve eq. (2.48) for the desired energy eigenvalues one must resort to numerical or graphical techniques. One approach would be to locate intersection points on superimposed plots of the tangent function versus ξ and $f(\xi) \equiv 2\sqrt{\xi(1 - \xi)}/(2\xi - 1)$ versus ξ. $f(\xi)$ versus ξ is plotted in Fig. 2.7.

DISCUSSION:

Let us first investigate the allowed particle energies as a function of potential well depth. For very shallow wells where $\alpha_0 a < \pi$ or $U_0 < \hbar^2\pi^2/2ma^2$, we find that there is one and only one allowed energy level. The $\tan\theta$ is a multi-branch function which monotonically increases from zero at $\theta = 0$ to $+\infty$ as $\theta \to \pi/2$, changes discontinuously to $-\infty$ at $\pi/2$, and then monotonically increases again to 0 at $\theta = \pi$. The described functional behavior is repeated for all subsequent $n\pi \leq \theta \leq (n + 1)\pi$

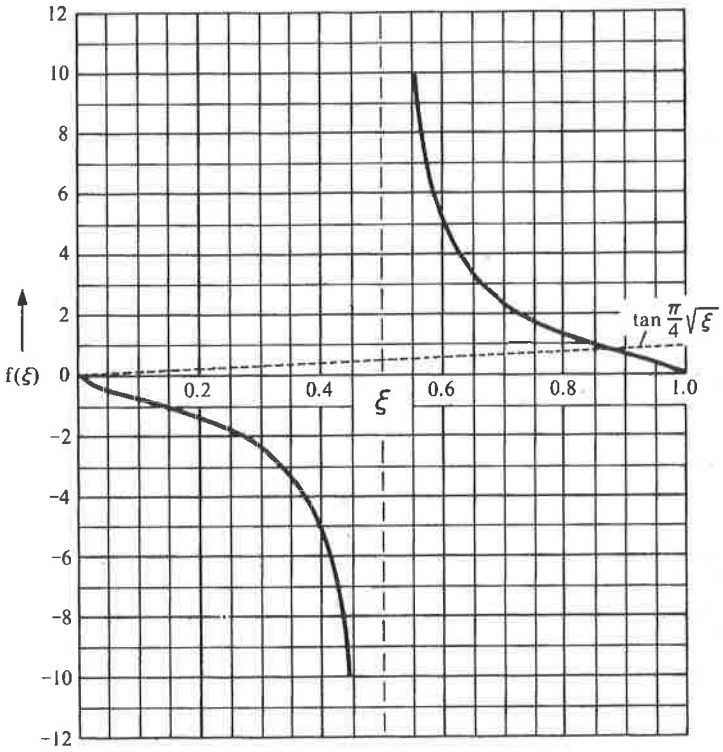

Fig. 2.7 The f(ξ) function used to determine the allowed energies of a particle in a finite potential well.

increments (n = $1, 2, 3, \cdots$). If $\alpha_0 a < \pi$ the tanθ is restricted to a portion of one repetitive unit and intercepts f(ξ) at only one point, yielding the one allowed level. The specific case where $\alpha_0 a = \pi/4$ is illustrated in Fig. 2.7, from which one deduces the single allowed energy of $E = 0.87\ U_0$. This result is pictured in Fig. 2.8a. Extending the preceding argument, one finds two allowed levels when $\pi \leq \alpha_0 a < 2\pi$, three allowed levels when $2\pi \leq \alpha_0 a < 3\pi$, four levels for $\alpha_0 a = 3\pi + \pi/4$ as shown in Fig. 2.8b, etc. In the limit where $U_0 \rightarrow \infty$ (but E remains finite), the right-hand side of eq. (2.43b) vanishes, tan$ka = 0$, and one must have $ka = \mathbf{n}\pi$ ($\mathbf{n} = 1, 2, 3, \cdots$). Note that the limiting case solution here is identical to the result obtained in the infinite well analysis. Moreover, for a potential well of finite depth the energy levels always lie below the corresponding infinite well levels, with E_n(finite) $\rightarrow E_n$(infinite) at the lower energies (see Fig. 2.8c). Naturally, the deeper the finite well, the better the infinite well approximation for the lower-lying energy values.

Although we have not obtained explicit expressions for the wavefunction solution constants, it is still possible to deduce the shape of the wavefunctions from the general

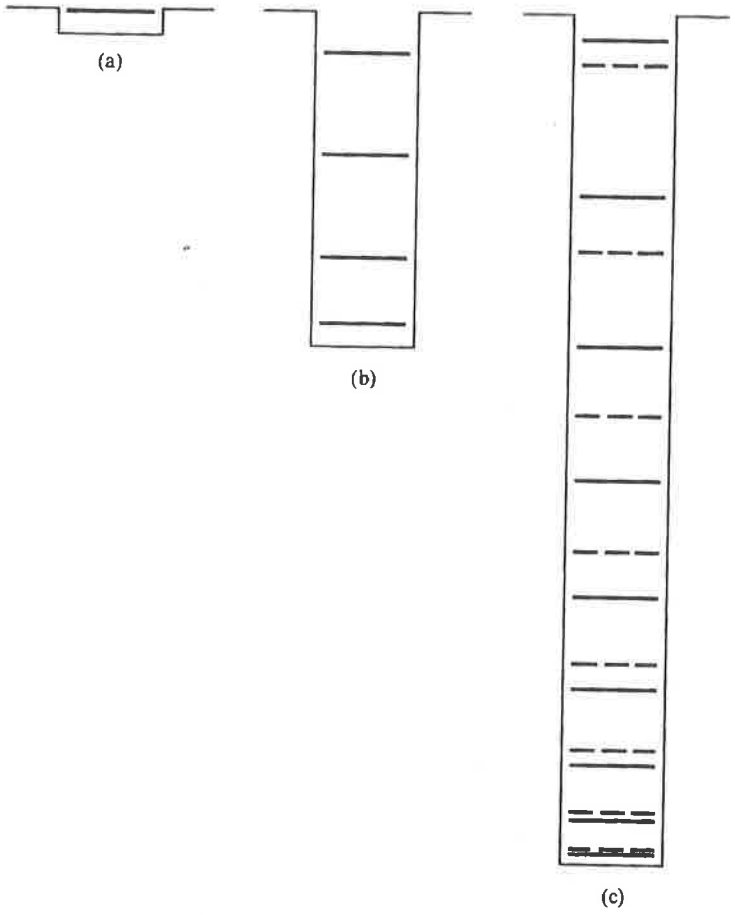

Fig. 2.8 Allowed particle energies as a function of potential well depth. (a) Shallow well with single allowed level ($\alpha_0 a = \pi/4$). (b) Increase of allowed levels when $\alpha_0 a$ exceeds π ($\alpha_0 a = 3\pi + \pi/4$). (c) Comparison of the finite-well (———) and infinite-well (- - - -) energies ($\alpha_0 a = 8\pi + \pi/4$). All plots are drawn to scale.

form solutions and the earlier infinite well solutions. In particular, one would expect the wavefunction associated with the lowest energy state to exhibit the general form shown in Fig. 2.9a. The wavefunction is roughly a half-period sinusoid within the well and falls exponentially to zero external to the well. The most interesting feature of the finite well wavefunction is its non-zero value external to the well. Since $|\psi|^2 dx$ is interpreted as the probability of finding the particle in a given dx region, a non-zero wavefunction external to the well implies a finite probability of finding the particle outside the well in the classically "forbidden" region. (Classically, a particle with an energy

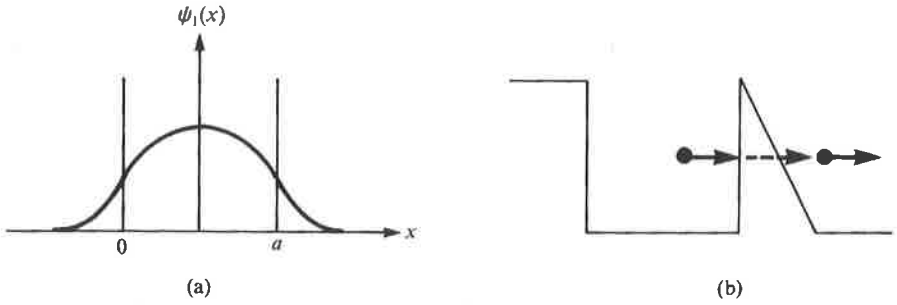

Fig. 2.9 (a) Sketch of the wavefunction associated with the lowest energy state of a particle in a finite potential well. The sketch emphasizes the finite value of the wavefunction external to the well. (b) Visualization of tunneling through a thin barrier.

$E < U_0$ cannot exist external to the well.) The significance of this observation is not readily apparent in relationship to the finite potential well problem. However, if the potential well is slightly modified as envisioned in Fig. 2.9b, the significance becomes self-evident. Given the finite value of the wavefunction in classically forbidden regions, the particle has a finite probability of "passing through" the Fig. 2.9b barrier and appearing as a free particle on the other side of the barrier. The quantum mechanical phenomenon of "passing through" a thin barrier, a phenomenon having no classical analog, is called *tunneling*. Tunneling provides the phenomenological basis for the tunnel diode and plays an important role in the operational behavior of a number of other solid-state devices.

As we have seen, a particle classically confined to a finite potential well ($0 < E < U_0$) is subject to energy quantization. On the other hand, repeating the finite potential well analysis for particle energies $E > U_0$, energies which would permit a classical particle to roam throughout all space, one finds a continuum of allowed energies. These results are consistent with a pattern of results that can be formulated into a general rule. Whenever a particle is classically confined to a small spatial region, as was the case in the infinite potential well and finite $0 < E < U_0$ potential well problems, the particle will exhibit "bound" states with a discrete set of allowed energies. Conversely, whenever a particle is classically permitted to move unimpeded throughout a large spatial region, as exemplified by the free-particle and finite $E > U_0$ potential well problems, the particle will assume a continuum of allowed energies.

Finally, it should be mentioned that the finite potential well particle with $E > U_0$ does exhibit behavioral properties distinct from a free particle. Notably, since the wavefunction is different within and exterior to the potential well region, there is a finite probability that the particle will be reflected at the well boundaries as pictured in Fig. 2.10. Quantum mechanical reflection at a potential discontinuity comes into play, for example, in the detailed analysis of the Schottky diode current–voltage characteristics. Again, there is no classical analog for quantum mechanical reflection.

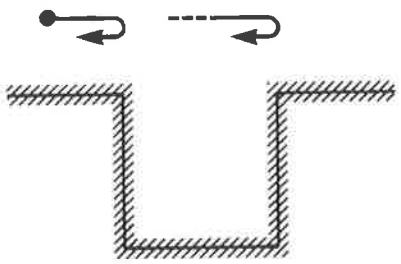

Fig. 2.10 Visualization of quantum mechanical reflection.

REFERENCES

[1] Mathematical arguments justifying the form of Schrödinger's equation can be found in any text on quantum mechanics and in a number of books treating solid-state device physics. For example, see J. L. Powell and B. Crasemann, *Quantum Mechanics*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1961 (pp. 86-95) or H. E. Talley and D. G. Daugherty, *Physical Principles of Semiconductor Devices*, Iowa State University Press, Ames, 1976 (pp. 32-37).

[2] J. P. McKelvey, *Solid-State and Semiconductor Physics*, Harper and Row, New York, 1966; p. 75.

SOURCE LISTING

(1) J. P. McKelvey, *Solid State and Semiconductor Physics*, Harper and Row, New York, 1966.

(2) J. L. Powell and B. Crasemann, *Quantum Mechanics*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1961.

(3) H. E. Talley and D. G. Daugherty, *Physical Principles of Semiconductor Devices*, Iowa State University Press, Ames, 1976.

PROBLEMS

2.1 The *exciton* is a hydrogen atom-like entity encountered in advanced semiconductor work. It consists of an electron bound to a $+q$ charged particle (a hole) of approximately equal mass. Bohr atom results can be used in computing the allowed energy states of the exciton provided the reduced mass, $m_r = m_+m_-/(m_+ + m_-) \simeq m_0/2$, replaces the electron mass in the Bohr atom formulation. In addition, the distance between the components of the exciton is always such that there are intervening semiconductor atoms. Thus ε_0 in the Bohr formulation must also be replaced by $K_S\varepsilon_0$, where K_S is the semiconductor dielectric constant. Using $K_S = 11.8$, determine the ground state ($\mathbf{n} = 1$) energy of an exciton in Si.

2.2 Reflection High Energy Electron Diffraction (RHEED) has become a commonplace technique for probing the atomic surface structures of materials. Under vacuum conditions an elec-

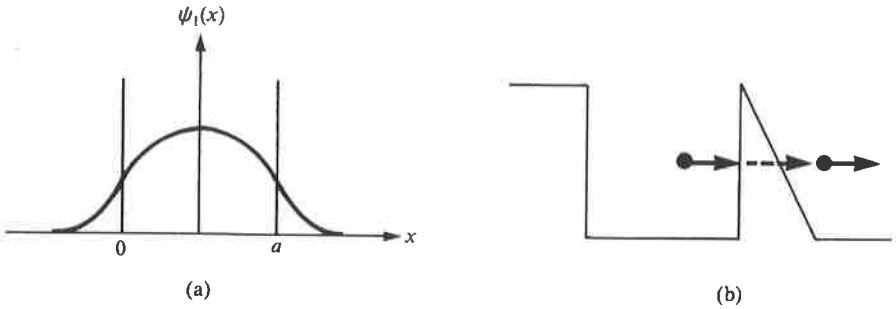

Fig. 2.9 (a) Sketch of the wavefunction associated with the lowest energy state of a particle in a finite potential well. The sketch emphasizes the finite value of the wavefunction external to the well. (b) Visualization of tunneling through a thin barrier.

$E < U_0$ cannot exist external to the well.) The significance of this observation is not readily apparent in relationship to the finite potential well problem. However, if the potential well is slightly modified as envisioned in Fig. 2.9b, the significance becomes self-evident. Given the finite value of the wavefunction in classically forbidden regions, the particle has a finite probability of "passing through" the Fig. 2.9b barrier and appearing as a free particle on the other side of the barrier. The quantum mechanical phenomenon of "passing through" a thin barrier, a phenomenon having no classical analog, is called *tunneling*. Tunneling provides the phenomenological basis for the tunnel diode and plays an important role in the operational behavior of a number of other solid-state devices.

As we have seen, a particle classically confined to a finite potential well ($0 < E < U_0$) is subject to energy quantization. On the other hand, repeating the finite potential well analysis for particle energies $E > U_0$, energies which would permit a classical particle to roam throughout all space, one finds a continuum of allowed energies. These results are consistent with a pattern of results that can be formulated into a general rule. Whenever a particle is classically confined to a small spatial region, as was the case in the infinite potential well and finite $0 < E < U_0$ potential well problems, the particle will exhibit "bound" states with a discrete set of allowed energies. Conversely, whenever a particle is classically permitted to move unimpeded throughout a large spatial region, as exemplified by the free-particle and finite $E > U_0$ potential well problems, the particle will assume a continuum of allowed energies.

Finally, it should be mentioned that the finite potential well particle with $E > U_0$ does exhibit behavioral properties distinct from a free particle. Notably, since the wavefunction is different within and exterior to the potential well region, there is a finite probability that the particle will be reflected at the well boundaries as pictured in Fig. 2.10. Quantum mechanical reflection at a potential discontinuity comes into play, for example, in the detailed analysis of the Schottky diode current–voltage characteristics. Again, there is no classical analog for quantum mechanical reflection.

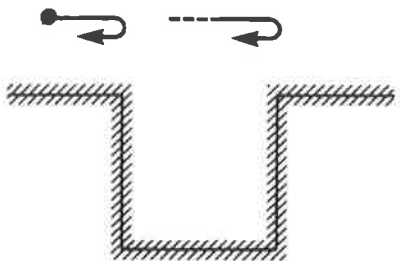

Fig. 2.10 Visualization of quantum mechanical reflection.

REFERENCES

[1] Mathematical arguments justifying the form of Schrödinger's equation can be found in any text on quantum mechanics and in a number of books treating solid-state device physics. For example, see J. L. Powell and B. Crasemann, *Quantum Mechanics*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1961 (pp. 86-95) or H. E. Talley and D. G. Daugherty, *Physical Principles of Semiconductor Devices*, Iowa State University Press, Ames, 1976 (pp. 32-37).

[2] J. P. McKelvey, *Solid-State and Semiconductor Physics*, Harper and Row, New York, 1966; p. 75.

SOURCE LISTING

(1) J. P. McKelvey, *Solid State and Semiconductor Physics*, Harper and Row, New York, 1966.

(2) J. L. Powell and B. Crasemann, *Quantum Mechanics*, Addison-Wesley Publishing Co., Inc., Reading, MA, 1961.

(3) H. E. Talley and D. G. Daugherty, *Physical Principles of Semiconductor Devices*, Iowa State University Press, Ames, 1976.

Current Density Operator - Continuity Equation
A. F. J. Levi - Applied Quantum Mechanics
pp 128-131

3.5 Current flow

If one were to place an electron in the one-dimensional potential well with infinite barrier energy we have been discussing one might reasonably expect there to be circumstances under which it is able to move around. Of course, as a particle moves around there must be a corresponding current flow. To find the current density, we start by making the reasonable and simplifying assumption that the electron moves in a potential which is real.

From Maxwell's equations or by elementary consideration of current conservation, the change in charge density ρ is related to the divergence of current density $\mathbf{J}$ through

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}(\mathbf{r}, t) \tag{3.47}$$

This is the classical expression for *current continuity*. The time dependence of charge density (the *temporal* dependence of a scalar field) is related to net current into or out of a region of space (the *spatial* dependence of a vector field). For a particle of charge e, we identify $\rho = e|\psi|^2$, so that

$$\frac{\partial \rho}{\partial t} = e\frac{\partial}{\partial t}(\psi^*\psi) = e\left(\psi^*\frac{\partial \psi}{\partial t} + \psi\frac{\partial \psi^*}{\partial t}\right) \tag{3.48}$$

There are two terms in the parentheses on the right-hand side of the equation that we wish to find. To obtain these terms one makes use of the fact that the time-dependent Schrödinger equation for a particle of mass m is

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}, t) = \hat{H}\psi(\mathbf{r}, t) \tag{3.49}$$

Multiplying both sides by $\psi^*(\mathbf{r}, t)$ gives

$$i\hbar\psi^*(\mathbf{r}, t)\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\psi^*(\mathbf{r}, t)\nabla^2\psi(\mathbf{r}, t) + \psi^*(\mathbf{r}, t)V(\mathbf{r})\psi(\mathbf{r}, t) \tag{3.50}$$

which, when multiplied by $e/i\hbar$, is the first term in our expression for $\partial\rho/\partial t$. To find the second term one takes the complex conjugate of Eq. (3.49) and multiplies both sides by $\psi(\mathbf{r}, t)$. In effect, we interchange $\psi(\mathbf{r}, t)$ and $\psi^*(\mathbf{r}, t)$ and change the sign of i in Eq. (3.50). Now, because $V(\mathbf{r})$ is real, one may write $\psi^*(\mathbf{r}, t)V(\mathbf{r})\psi(\mathbf{r}, t) = \psi(\mathbf{r}, t)V(\mathbf{r})\psi^*(\mathbf{r}, t)$, giving the rate of change of charge density

$$\frac{\partial \rho}{\partial t} = -\psi^*\frac{e\hbar}{i2m}\nabla^2\psi + \psi\frac{e\hbar}{i2m}\nabla^2\psi^* + \frac{e\psi^*\psi}{i\hbar}(V(\mathbf{r}) - V(\mathbf{r})) \tag{3.51}$$

$$\frac{\partial \rho}{\partial t} = \frac{ie\hbar}{2m}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) = \frac{ie\hbar}{2m}\nabla \cdot (\psi^*\nabla\psi - \psi\nabla\psi^*) = -\nabla \cdot \mathbf{J} \tag{3.52}$$

Hence, the *current density* for a particle described by state ψ is

$$\boxed{\mathbf{J} = -\frac{ie\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*)} \tag{3.53}$$

or in one-dimension

$$J_x = -\frac{ie\hbar}{2m}\left(\psi^*(x)\frac{\partial}{\partial x}\psi(x) - \psi(x)\frac{\partial}{\partial x}\psi^*(x)\right) \tag{3.54}$$

The above derivation of the current density requires that the potential be real. If the potential is complex, it can have the effect of absorbing or creating particles. This is a useful feature that helps in solving some types of problems. However, we are not going to consider complex potentials in this book.

A point worth highlighting is the obvious symmetry in the expression for the current operator. This symmetry has an important influence on the types of wave functions that can carry current. We explore this in the next two sections.

3.5.1 Current in a rectangular potential well with infinite barrier energy

Initially, we are interested in finding the current carried by the lowest energy state of a one-dimensional, rectangular potential with infinite barrier energy and well width L. In Section 3.3.1 we chose the one-dimensional, rectangular potential well with infinite barrier energy to be centered at $x = 0$. Our calculations identified the $n = 1$ ground-state energy as

$$E_1 = \hbar\omega_1 = \frac{\hbar^2\pi^2}{2mL^2} \tag{3.55}$$

and the ground-state wave function appeared as a standing wave

$$\psi_1(x,t) = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi}{L}\left(x+\frac{L}{2}\right)\right)e^{-i\omega_1 t} \tag{3.56}$$

To find the current due to this state, we substitute the wave function into the expression for the current density. The current density in this case is

$$J_x = -\frac{ie\hbar}{2m}\left(\psi_1^*(x)\frac{\partial}{\partial x}\psi_1(x) - \psi_1(x)\frac{\partial}{\partial x}\psi_1^*(x)\right) = 0 \tag{3.57}$$

from which we conclude that current is not carried by a single standing wave. This should come as no surprise, since a standing wave can be thought of as a resonance consisting of two counter-propagating traveling waves whose individual contributions to current flow exactly cancel each other out.

We are still left with the question of how particles are transported in the one-dimensional potential well. The answer is that a superposition of electron states is required. This is easily illustrated by example.

Let us consider current flow in a linear superposition state consisting of a simple combination of the ground-state wave function, ψ_1, and the first excited-state wave function, ψ_2, so that

$$\psi(x,t) = \frac{1}{\sqrt{2}}(\psi_1(x,t) + \psi_2(x,t)) \tag{3.58}$$

Substituting this into our expression for current density gives the result

$$J_x = -\frac{2e\pi\hbar}{mL^2}\left(\cos\left(\frac{\pi x}{L}\right)\cos\left(\frac{2\pi x}{L}\right)+\frac{1}{2}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\right)\sin((\omega_2-\omega_1)t) \tag{3.59}$$

This equation shows that current is carried by a superposition of stationary bound states. The ability of a linear superposition of stationary states to carry current is due to the symmetry embedded in Eq. (3.54). We can also see how current flows in the one-dimensional potential well as a function of time. The current has an oscillatory time dependence, which in our particular example is given by the difference frequency, $\omega_2-\omega_1$, between the ψ_1 and ψ_2 eigenstates.

In the next section we consider current flow for an unbound state. In this situation the symmetry that gave zero current for a stationary bound state is broken, and we may evaluate the current in unbound, plane-wave traveling states.

3.5.2 Current flow due to a traveling wave

Consider the simple case of a particle with charge e and mass m that is in an unbound state. The particle is described by a wave function that is a plane-wave traveling from left to right of the form $\psi(x) = e^{i(kx-\omega t)}$. To calculate the current flow associated with this state, we substitute into our expression for the current density

$$J_x = -\frac{ie\hbar}{2m}\left(\psi^*(x)\frac{\partial}{\partial x}\psi(x)-\psi(x)\frac{\partial}{\partial x}\psi^*(x)\right) \tag{3.60}$$

$$J_x = -\frac{ie\hbar}{2m}(e^{-ikx}ike^{ikx}+e^{ikx}ike^{-ikx}) = -\frac{ie\hbar}{2m}2ik = \frac{e\hbar k}{m} \tag{3.61}$$

Since momentum in the x-direction is $p_x = mv_x = \hbar k$, the current associated with the traveling wave may be written in the familiar form $J_x = ev_x$, where e is the particle charge and v_x is its velocity.

If we were to construct an electron wave function consisting of a plane wave traveling from left to right and an identical but counter-propagating wave, then the individual contributions to current flow exactly cancel and there is zero net current flow. The symmetry that gives rise to zero net current flow for a superposition of two identical but counter propagating traveling waves is the same symmetry that creates the standing-wave state or stationary state previously discussed in Sections 3.1 and 3.5.1.