particle inside. This will affect the probability of finding the particle in our specified 1 cm$^3$, according to the specific wave-function intensity $|\psi(x, t)|^2$.

If the wave function $\psi(x, t)$ is to be a representation of a single particle (for example, an electron perceived as a particle), then the intensity $\psi(x, t)\psi^*(x, t)$ relates to probability of finding this particle (electron) at point $x$ and time $t$.

### 2.1.3 Schrödinger Equation

We have used a specific wave function $\psi(x, t)$ to introduce the concept of a wave packet. Clearly, this specifically selected wave function [Eq. (2.14)] cannot be used for any object in any situation. Obviously, we need to be able to find somehow the wave function that would specifically model a particular object (say an electron) in specific conditions.

In 1926, Schrödinger postulated a differential equation, that results with the needed wave function when solved with appropriate boundary and/or initial conditions. The one-dimensional form of the time-dependent Schrödinger equation is given as follows:

$$j\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + E_{pot}(x) \psi(x, t) \tag{2.17}$$

where $E_{pot}(x)$ is the potential-energy function incorporating any influence of the environment on the considered electron. The wave function $\psi(x, t)$ and its first derivative are finite, continuous, and single-valued. The term $\hbar^2/2m$ involves the mass of electrons, $m$, so it relates the wave function to particle properties of electrons.

The three-dimensional form of the time-dependent Schrödinger equation can be written as

$$j\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + E_{pot} \psi \tag{2.18}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, $\psi = \psi(x, y, z, t)$, and $E_{pot} = E_{pot}(x, y, z)$. In the following text we will limit ourselves to the one-dimensional case.

The variables of the time-dependent Schrödinger equation [x and t in Eq. (2.17)] can be separated if the following form of the wave function is used: $\psi(x, t) = \psi(x)\chi(t)$. In this case, Eq. (2.17) can be transformed into

$$j\hbar \frac{\partial \chi(t)}{\partial t} = -\frac{\hbar^2}{2m\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + E_{pot}(x) \tag{2.19}$$

The left-hand side of this equation is a function of time alone, whereas the right-hand side is a function of position alone. This is possible only when the two sides are equal to a constant. The constant is in the units of energy, and it actually represents the total energy $E$:

$$j\hbar \frac{\partial \chi(t)}{\partial t} = E$$

$$-\frac{\hbar^2}{2m\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + E_{pot}(x) = E \tag{2.20}$$
Obviously, the time-independent wave function \( \psi(x) \) has to satisfy the following time-independent Schrödinger equation:

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + E_{pot}(x)\psi(x) = E\psi(x)
\]  

(2.21)

**EXAMPLE 2.1 \( E-k \) Diagram for a Free Electron**

Solve the Schrödinger equation for a free electron to

(a) determine the general wave function for a free electron and
(b) determine and plot the \( E-k \) dependence, and relate this dependence to the classical equation for kinetic energy of a particle \( E_{\text{kin}} = \frac{1}{2}mv^2 \).

**Solution**

(a) For the case of a free electron, \( E_{pot} = 0 \), so the Schrödinger equation is

\[
\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E\psi(x) = 0
\]

The solution of this type of differential equation can be expressed as

\[
\psi(x) = A_+ e^{ix} + A_- e^{-ix}
\]

where \( s_{1,2} \) are the roots of its characteristic equation:\(^3\)

\[
s^2 + \frac{2m}{\hbar^2} E = 0
\]

(2.22)

Given that the solutions of the characteristic equation \( s^2 = -k^2 \) are \( s_{1,2} = \pm jk \), the general solution is expressed as

\[
\psi(x) = A_+ e^{jkx} + A_- e^{-jkx}
\]

(2.23)

Comparing this wave function to the time-independent part of Eq. (2.6), we can see that it consists of two plane waves traveling in the opposite directions: (1) \( A_+ \exp(jkx) \), traveling in the positive \( x \)-direction, and (2) \( A_- \exp(-jkx) \), traveling in the negative \( x \)-direction. Equation (2.23) represents the general solution for the electron wave function in free space \( (E_{pot} = 0) \), as the superposition of the two plane waves can account for any possible situation in terms of boundary conditions.

\(^3\)Here \( s^2 \) represents the second derivative, \( \frac{d^2\psi(x)}{dx^2} \), whereas \( \psi(x) \) itself is represented by \( s^0 = 1 \).
(b) As Eq. (2.22) shows, the wave function given by Eq. (2.23) satisfies the Schrödinger equation when the dependence of the kinetic (and thus total) energy of a free electron is given by

\[ E = \frac{\hbar^2 k^2}{2m} \]  

(2.24)

This \( E-k \) dependence is plotted in Fig. 2.5.

To relate the obtained \( E-k \) dependence to the classical equation for \( E_{kin} \), we notice first that \( E = E_{kin} \) (given that a free electron has no potential energy). Then, we apply the fundamental link between the wave number and momentum \( (p = \hbar k) \) and convert the momentum into velocity \( (p = mv) \):

\[ E_{kin} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = \frac{mv^2}{2} \]

This equation shows that the \( E-k \) dependence of a free electron is identical to the classical dependence of kinetic energy on velocity.

**EXAMPLE 2.2 Electron in a Potential Well**

The infinite potential well, illustrated in Fig. 2.6a, is mathematically defined as

\[ E_{pot}(x) = \begin{cases} 
0 & \text{for } 0 < x < W \\
\infty & \text{for } x \leq 0 \text{ and } x \geq W
\end{cases} \]

For an electron inside the potential well, determine

(a) the possible energy values and
(b) the wave functions corresponding to the possible energy levels.
The Schrödinger equation for this case is

\[
\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad \text{for } 0 < x < W
\]

\[
\psi(x) = 0 \quad \text{for } x \leq 0 \text{ and } x \geq W
\]

Mathematically, this problem is reduced to solving the Schrödinger equation for a free particle \(E_{\text{tot}} = 0\) with the following boundary conditions: \(\psi(0) = 0\) and \(\psi(W) = 0\). Therefore, the general solution is given by Eq. (2.23).

(a) In the case when the electron is trapped between two walls, the plane waves moving in either direction are relevant as the electron is reflected backwards and forwards by the walls. Time-independent solutions (steady states) are still possible, but only in the form of standing waves, as illustrated in Fig. 2.6b. Obviously, the standing waves are formed only for specific values of \(k = 2\pi/\lambda\) that correspond to integer multiples of half-wavelengths \(\lambda/2\). Therefore,

\[
h \frac{k_n}{2} = W \quad (n = 1, 2, 3, \ldots)
\]

\[
k_n = \frac{2\pi}{\lambda_n} = \frac{\pi}{W} n
\]
Using the relationship between the total energy and the wave number from Eq. (2.22),

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mW^2} \quad (n = 1, 2, 3, \ldots) \]  

we obtain

\[ E_n = \hbar^2 \frac{\pi^2 n^2}{2mW^2} \]

With this result the following important conclusion is reached: the electrons in a potential well cannot have an arbitrary value of total energy. Only specific energy values are possible (Fig. 2.6a). This effect is called energy quantization.

(b) The two constants in the general solution (2.23), \( A_+ \) and \( A_- \), have to be determined so to obtain the particular wave function \( \psi(x) \) representing the specifically defined case (electrons inside a potential well of width \( W \) and infinitely high walls). Applying the boundary condition \( \psi(0) = 0 \), we find the following relationship between the constants \( A_+ \) and \( A_- \):

\[ A_+ e^0 + A_- e^0 = 0 \Rightarrow A_+ = -A_- \]

After this, Eq. (2.23) can be transformed as

\[ \psi(x) = A_+ \cos(kx) + jA_+ \sin(kx) - A_+ \cos(-kx) - jA_+ \sin(-kx) = 2jA_+ \sin(kx) \]

where \( A \) is a new constant, involving the constant \( A_- \).

The second boundary condition is \( \psi(W) = 0 \). With exception of the trivial case \( A = 0 \), no other value for \( A \) in Eq. (2.27) can satisfy this boundary condition. However, \( \sin(kW) \) can be zero for a number of \( kW \) values, which means that the possible solutions are determined by specific (and discrete) \( k \) values. Because \( k \) is related to the total energy [Eq. (2.22)], this means that the possible solutions are determined by specific (and discrete) energy values. This is the same conclusion related to the energy quantization effect, only it is reached in a different way. Given that \( \sin(kW) = 0 \) for \( kW = n\pi \), where \( n = 1, 2, 3, \ldots \), the possible energy levels are according to Eq. (2.26).

There is an additional condition that has to be satisfied by the wave function that is to represent electrons in the potential well. It relates to the probability of finding an electron at \( x \): \( |\psi(x)|^2 = \psi(x)\psi^*(x) \). If an electron is trapped inside the potential well, then it has to be somewhere between 0 and \( W \), which means

\[ \int_0^W \psi(x)\psi^*(x) \, dx = 1 \]
This is called normalization condition. The normalization condition determines a specific value of the constant $A$, as

$$\int_0^W A^2 \left( \sin \frac{n\pi}{W} x \right)^2 dx = 1 \Rightarrow A = \sqrt{\frac{2}{W}}$$

Therefore, the final solution is

$$\psi_n(x) = \sqrt{\frac{2}{W}} \sin \frac{n\pi}{W} x \quad (n = 1, 2, 3, \ldots)$$

where $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$, \ldots ($n = 1, 2, 3, \ldots$) represent different electron states (electrons at different energy levels $E_n$). The wave functions $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ are illustrated in Fig. 2.6b.

EXAMPLE 2.3 Tunneling

Another important quantum-mechanical effect, observed in semiconductor devices, is tunneling. To illustrate the effect of tunneling, determine the wave function $\psi(x)$ for the case when electrons are approaching a potential-energy barrier, as in Fig. 2.7. This potential barrier is mathematically defined as

$$E_{\text{pot}}(x) = \begin{cases} 0 & \text{for } x < 0 \\ E_{\text{pot}} & \text{for } 0 \leq x \leq W \\ 0 & \text{for } x > W \end{cases}$$

Consider both cases: (a) the electron energy is higher than the barrier height, $E > E_{\text{pot}}$, and (b) the electron energy is smaller than the barrier height, $E < E_{\text{pot}}$.

**SOLUTION**

Writing the Schrödinger equation in the following forms:

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad \text{for } x < 0 \text{ and } x > W$$
and

\[
\frac{d^2 \psi(x)}{dx^2} - \frac{2m}{\hbar^2} (E_{\text{pot}} - E) \psi(x) = 0 \quad \text{for } 0 \leq x \leq W
\]

the general solution can be expressed as

\[
\psi(x) = \begin{cases} 
    A_+ e^{ikx} + A_- e^{-ikx} & \text{for } x < 0 \\
    B_+ e^{ikx} + B_- e^{-ikx} & \text{for } 0 \leq x \leq W \\
    C_+ e^{ikx} + C_- e^{-ikx} & \text{for } x > W 
\end{cases}
\]

(2.28)

Again, the electron wave function appears as a superposition of two plane waves traveling in the opposite directions when \(E_{\text{pot}} = 0\) [the first and third rows in Eq. (2.28)]. In the region where \(E_{\text{pot}} \neq 0\), two different cases have to be considered: \(E > E_{\text{pot}}\) and \(E < E_{\text{pot}}\).

(a) \(E > E_{\text{pot}}\): In this case, the classical mechanics predicts that a particle with energy \(E\) should go over the lower barrier, \(E_{\text{pot}}\), without any interference. However, the wave function inside the barrier region (\(B_+ e^{ikx}\) if we limit ourselves to the wave traveling in the positive \(x\) direction) is different from the incident wave (\(A_+ e^{ikx}\)). Because \(k^2 = \frac{2m}{\hbar^2} (E_{\text{pot}} - E)\) is negative, \(k\) can be expressed as \(k = jk_E\), where \(k_E = \sqrt{\frac{2m}{\hbar^2} (E - E_{\text{pot}})}\) is the wave number inside the barrier region. This means that the incident plane wave continues to travel as a plane wave through the barrier region (\(B_+ e^{jk_E x}\)), but with an increased wavelength \(\lambda_E = 2\pi/k_E\) (\(k_E < k\)). In addition to that, the intensity of the wave (\(|B_+|^2\)) is reduced because there is a finite probability (\(|A_-|^2\)) that the particle is reflected by the barrier.
2.2 ENERGY LEVELS IN ATOMS AND ENERGY BANDS IN CRYSTALS

2.2.7 Atomic Structure

The potential-well problem from the previous section introduced the quantization concept—the fact that electrons can only have discrete values of energy when appearing inside a potential well. This concept will be applied to the case of electrons in an atom and in a crystal in the following text. To be able to describe how electrons populate these levels, we need to know the fundamental properties of electrons. In addition to being negatively charged, electrons possess intrinsic angular momentum called spin. The spin can take two values, $s = \pm 1/2$ in the units of $\hbar$. Another fundamental property of electrons is that only two electrons, with different spins, can occupy the same energy level if their wave functions overlap. This is known as the Pauli exclusion principle.

The electrons of an atom appear in a potential well created by the electric field of the positive core. The potential energy has spherical symmetry:

$$E_{pot}(r) = -\frac{(Ze)^2}{4\pi \varepsilon_0 r}$$  \hspace{1cm} (2.29)

---

\(^{1}\)In the specific case of $E_{pot} = \infty$ (infinite barrier height), the wave function is equal to zero inside the barrier region as $\kappa = -\sqrt{\frac{2m}{\hbar^2}}(E_{pot} - E) = -\infty$ and $\exp(-\kappa x) = 0$.

\(^{2}\)When there is an overlap in the wave functions, we say that the electrons belong to the same system (an atom, molecule, or crystal).