



Erwin Schrödinger (1887–1961)
Established quantum mechanical wave equation

6

The Schrödinger equation

6.1 The time-dependent Schrödinger equation

The Schrödinger equation is the key equation of quantum mechanics (Schrödinger 1925, 1926a, 1926b). This second order, partial differential equation determines the spatial shape and the temporal evolution of a wave function in a given potential and for given boundary conditions. The one-

dimensional Schrödinger equation is used when the particle of interest is confined to one spatial dimension, for example the x axis. Here, we restrict our considerations to such one-dimensional cases. Due to the one-dimensional nature of many semiconductor heterostructures, the one-dimensional Schrödinger equation is sufficient for most applications. To derive the one-dimensional Schrödinger equation, we start with the total-energy equation, i. e. the sum of kinetic and potential energy

$$\frac{p^2}{2m} + U(x) = E_{\text{total}} . \quad (6.1)$$

Substitution of the dynamical variables by their quantum mechanical operators which act on the wave function $\Psi(x, t)$ yields the **one-dimensional time-dependent Schrödinger equation**

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + U(x) \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(x, t) \quad (6.2)$$

The left side of this equation can be rewritten by using the Hamilton or total-energy operator

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) . \quad (6.3)$$

Using the notation of the Hamilton operator, the time-dependent Schrödinger equation can be written as

$$H \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(x, t) \quad (6.4)$$

Since the Schrödinger equation is a *partial differential equation*, the **product method** can be used to separate the equation into a **spatial** and a **temporal** part

$$\Psi(x, t) = \psi(x) f(t) \quad (6.5)$$

where $\psi(x)$ depends only on x and $f(t)$ depends only on t . Insertion of Eq. (6.5) into the Schrödinger equation yields

$$\frac{1}{\psi(x)} H \psi(x) = \frac{i \hbar}{f(t)} \frac{d}{dt} f(t) . \quad (6.6)$$

The left side of this equation depends on x only, while the right side depends only on t . Because x and t are completely independent variables, the equation can be true, only if both sides are constant.

$$\frac{i \hbar}{f(t)} \frac{d}{dt} f(t) = \text{const.} \quad (6.7)$$

Tentatively this constant is designated as $\text{const.} = E$ where the meaning of E will become evident below. Integration of Eq. (6.7) yields

$$f(t) = e^{-iEt/\hbar} . \quad (6.8)$$

Insertion of this result into Eq. (6.5) yields the time-dependent wave function

$$\Psi(x, t) = \psi(x) e^{-iEt/\hbar} \quad (6.9)$$

If E is real, then the wave function has an *amplitude* $\psi(x)$ and a *phase* $\exp(-iEt/\hbar)$. The amplitude and phase representation is convenient for many applications. To find the physical meaning of the real quantity E , we calculate the expectation value of the total energy using the wave function obtained from the product method.

$$\langle E_{\text{total}} \rangle = \int_{-\infty}^{\infty} \psi^*(x) f^*(t) \left(-\frac{\hbar}{i} \frac{\partial}{\partial t} \right) \psi(x) f(t) dx = e^{\frac{iEt}{\hbar}} e^{-\frac{iEt}{\hbar}} E \int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = E .$$

(6.10)

Because the wave function is normalized, that is $\langle \psi(x) | \psi(x) \rangle = 1$, the constant designated as E is the expectation value of the total energy.

6.2 The time-independent Schrödinger equation

The time-independent Schrödinger equation is obtained by inserting the wave function obtained from the product method, Eq. (6.9) into the time-dependent Schrödinger equation (see Eq. 6.2). One obtains

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

(6.11)

which is the **time-independent Schrödinger equation**. Using the hamiltonian operator, one obtains

$$H \psi(x) = E \psi(x) .$$

(6.12)

Since H is an operator and E is a real number, the Schrödinger equation has the form of an eigenvalue equation. The eigenfunctions $\psi_n(x)$ and the eigenvalues E_n are found by solving the Schrödinger equation.

The eigenvalues of the Schrödinger equation, E_n , are *discrete*, that is only certain energy values are allowed, all other energies are disallowed or forbidden. The energy eigenvalues are also called **eigenenergies** or **eigenstate energies**. The lowest eigenstate energy is the **ground state energy**. All higher energies are called of **excited state energies**.

The solution of the Schrödinger equation and the eigenstate energies and wave functions of a physical system are of great importance, because the knowledge of $\psi_n(x)$ and E_n implies the knowledge of *all* relevant physical parameters. It is the purpose of the next sections to get familiar with the properties of the Schrödinger equation and its solutions.

6.3 The superposition principle

Mathematically speaking the Schrödinger equation is a *linear*, second order, partial differential equation. Any linear differential equation allows for the superposition of its solutions. That is, if Ψ_n and Ψ_m are solutions of the Schrödinger equation, then any *linear combination* of Ψ_n and Ψ_m are solutions as well. That is, a new solution of Schrödinger's equation is given by

$$\Psi(x,t) = A \Psi_n(x,t) + B \Psi_m(x,t) \quad (6.13)$$

where, A and B are real constants. For practical physical problems, the Schrödinger equation has always more than one solution. Thus, the superposition principle can be applied to all physical problems in order to obtain a new solution. The new solution $\Psi(x, t)$ must be normalized as well, that is $\langle \Psi | \Psi \rangle = 1$.

6.4 The orthogonality of eigenfunctions

If two eigenfunctions $\psi_n = \psi_n(x)$ and $\psi_m = \psi_m(x)$ are solutions of the Schrödinger equation and the two eigenfunctions belong to different energies E_n and E_m (so that $E_n \neq E_m$), then the eigenfunctions are **orthogonal**:

$$\langle \psi_n | \psi_m \rangle = 0. \quad (6.14)$$

This equation can be proven by starting with the Schrödinger equation for $\psi_n(x)$ and the complex conjugate equation for ψ_m , that is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n + U \psi_n = E_n \psi_n \quad (6.15)$$

and

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_m^* + U \psi_m^* = E_m \psi_m^* . \quad (6.16)$$

Multiplication of Eq. (6.15) with ψ_m^* and of Eq. (6.16) with ψ_n and subtraction of the two resulting equations yields

$$\frac{\hbar^2}{2m} \left(\psi_n \frac{d^2}{dx^2} \psi_m^* - \psi_m^* \frac{d^2}{dx^2} \psi_n \right) = (E_n - E_m) \psi_n \psi_m^* . \quad (6.17)$$

Using the identity

$$\frac{d}{dx} \left(\psi_n \frac{d}{dx} \psi_m^* - \psi_m^* \frac{d}{dx} \psi_n \right) = \psi_n \frac{d^2}{dx^2} \psi_m^* - \psi_m^* \frac{d^2}{dx^2} \psi_n \quad (6.18)$$

and integrating over x yields

$$\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{d}{dx} \left(\psi_n \frac{d}{dx} \psi_m^* - \psi_m^* \frac{d}{dx} \psi_n \right) dx = (E_n - E_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx. \quad (6.19)$$

The integral on the left side of the equation simplifies to

$$\int_{-\infty}^{\infty} \frac{d}{dx} \left(\psi_n \frac{d}{dx} \psi_m^* - \psi_m^* \frac{d}{dx} \psi_n \right) dx = \left[\psi_n \frac{d}{dx} \psi_m^* - \psi_m^* \frac{d}{dx} \psi_n \right]_{-\infty}^{+\infty} \quad (6.20)$$

This expression is zero due to the normalization condition which requires that $\psi(x \rightarrow \pm \infty) = 0$. Hence, we obtain the following condition for the eigenvalues and eigenfunctions

$$\frac{2m}{\hbar^2} (E_n - E_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0. \quad (6.21)$$

Because $E_n \neq E_m$, this equation can be true, only if

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (m \neq n) \quad (6.22)$$

which concludes the proof that ψ_m and ψ_n are orthogonal. Together with the normalization condition, one obtains

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \begin{cases} 0 & (m \neq n) \\ 1 & (m = n). \end{cases} \quad (6.23)$$

This result can be also written as

$$\langle \psi_m | \psi_n \rangle = \delta_{mn} \quad (6.24)$$

where δ_{mn} is the **Kronecker delta** which is defined as

$$\delta_{mn} = \begin{cases} 0 & (m \neq n) \\ 1 & (m = n). \end{cases} \quad (6.25)$$

6.5 The complete set of eigenfunctions

Consider a practical physical problem given by the potential energy $U(x, y, z)$. Assume further that at least one solution of the Schrödinger equation exists for the potential energy $U(x, y, z)$. Generally, the number of solutions is large

but finite. The solutions of the Schrödinger equation are designated a set of solutions. Such a set of solutions is a **complete set of solutions**, if it contains all possible solutions. If, in addition, each solution of the set is normalized and if the solutions are orthogonal, then the solutions are called an orthogonal, normal, complete set or, abbreviated, a **orthonormal complete set** of solutions. Such an orthonormal complete set of solutions provides *any* solution of a physical problem by superposition (linear combination) of the individual solutions.

Exercise: Solutions of the Schrödinger equation in a constant potential. Assume that the potential $U(x)$ is a *constant*. What are the mathematical functions that are possible solutions of the one-dimensional Schrödinger equation in such a potential?

Solution: For $U(x) = \text{constant}$, the Schrödinger equation has the form $(d^2 / dx^2) \psi(x) \propto \pm \psi(x)$. This equation has either an exponential or a sinusoidal solution. An example is shown in **Fig. 6.1**.

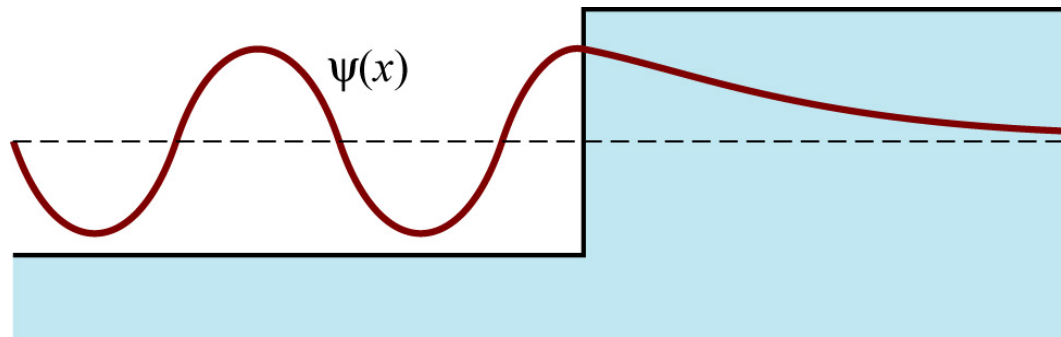


Fig. 6.1. Sinusoidal (left) and exponential (right) solution of the Schrödinger equation in a constant potential.