

# Stationary States and Quantization of Energy

Podcast Learn & Fun \*

January 23, 2025

In quantum mechanics, the behavior of a system is described by the *wavefunction*  $\Psi(\mathbf{r}, t)$ , which encodes the probabilities of finding a particle at position  $\mathbf{r}$  and time  $t$ . For many systems of interest, we are specifically concerned with solutions to the Schrödinger equation that do not explicitly depend on time. These solutions describe *stationary states*, where the probability distribution of the particle does not change with time.

## 0.1 Separation of Variables

The Schrödinger equation in quantum mechanics is given by:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t)$$

where  $\Psi(\mathbf{r}, t)$  is the wavefunction, and  $\hat{H}$  is the Hamiltonian operator, which represents the total energy (kinetic + potential) of the system. To look for solutions that describe stationary states, we assume that the wavefunction can be separated into a spatial part and a temporal part:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \cdot \phi(t)$$

where  $\psi(\mathbf{r})$  is the spatial part of the wavefunction, and  $\phi(t)$  is the temporal part. Substituting this into the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} (\psi(\mathbf{r}) \cdot \phi(t)) = \hat{H} (\psi(\mathbf{r}) \cdot \phi(t))$$

Since  $\psi(\mathbf{r})$  depends only on position, it functions as a constant in time derivatives:

$$i\hbar \psi(\mathbf{r}) \frac{\partial \phi(t)}{\partial t} = \hat{H} (\psi(\mathbf{r}) \phi(t))$$

For potential energies that do not explicitly depend on time, the Hamiltonian operator  $\hat{H}$  acts only on the spatial part  $\psi(\mathbf{r})$ . We can therefore factor out the time-dependent part  $\phi(t)$ :

$$i\hbar \psi(\mathbf{r}) \frac{\partial \phi(t)}{\partial t} = \phi(t) \hat{H} \psi(\mathbf{r})$$

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Now, divide both sides by  $\psi(\mathbf{r})\phi(t)$  (assuming neither is zero):

$$i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = \frac{\hat{H}\psi(\mathbf{r})}{\psi(\mathbf{r})}$$

The left side depends only on time, and the right side depends only on position. Therefore, both sides must equal a constant, which we'll call  $E$ , which will turn out to be the energy of the system. This results in two separate equations:

1. *The temporal equation:*

$$i\hbar \frac{\partial \phi(t)}{\partial t} = E\phi(t)$$

2. *The spatial equation:*

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The temporal equation is a simple first-order differential equation in time, whose solution is:

$$\phi(t) = e^{-iEt/\hbar}$$

This solution represents the time evolution of the system, where  $E$  is the energy eigenvalue.

The spatial wavefunction is the *eigenfunction* of the Hamiltonian:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The equation is also known as the time-independent Schrödinger equation. The solution  $\psi(\mathbf{r})$  is the *stationary state wavefunction*, and the associated energies  $E$  are called the *eigenvalues*. These eigenvalues determine the allowed energy levels of the system.

The equation  $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$  is thus a fundamental equation in quantum mechanics, and it leads to the quantization of energy in many systems, meaning that only specific, discrete energy values are possible. This is in stark contrast to classical systems, where energy can vary continuously.

## 0.2 Particle in a 1D Infinite Square Well

As an illustrative example, consider a particle confined in a one-dimensional infinite square well. The potential  $V(x)$  is given by:

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L \\ \infty & \text{if } x < 0 \text{ or } x > L \end{cases}$$

In this case, the particle is free to move within the well (where the potential is zero) but cannot escape, as the potential is infinite outside the well. The Schrödinger equation inside the well ( $0 \leq x \leq L$ ) becomes:

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

where  $m$  is the mass of the particle, and  $\hbar$  is the reduced Planck's constant. This equation is the stationary Schrödinger equation for the spatial part of the wavefunction. The boundary conditions for this problem are that the wavefunction must vanish at the edges of the well, i.e.,  $\psi(0) = 0$  and  $\psi(L) = 0$ , because the particle cannot exist outside the well due to the infinite potential there.

To solve this equation, we assume a solution of the form  $\psi(x) = A \sin(kx)$ , where  $k$  is the wave number. Substituting this form into the Schrödinger equation and applying the boundary conditions gives a discrete set of allowed wave numbers  $k_n = n\pi/L$ , where  $n$  is a positive integer. Consequently, the corresponding wavefunctions inside the well are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \dots$$

These wavefunctions represent the stationary-state solutions to the Schrödinger equation, and they are associated with discrete energy levels. The energies corresponding to these solutions are found by substituting the allowed wave numbers  $k_n$  into the expression for the energy of the particle:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \dots$$

These energies are quantized, meaning that only specific, discrete energy values are possible, corresponding to the integer values of  $n$ . This is a clear example of energy quantization, a fundamental feature of quantum mechanics.

In summary, the time-independent Schrödinger equation provides the framework for understanding stationary states, where the system's wavefunction is time-independent and the energy is quantized. The quantization arises from the boundary conditions and the nature of the Hamiltonian operator, which, for a confined system, leads to discrete energy eigenvalues.