6.1: The Schrödinger Wave Equation

The Schrödinger wave equation in its time-dependent form for a particle of energy $E$ moving in a potential $V$ in one dimension is:

\[ i \hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t) \Psi(x,t) \]

where $\Psi = \Psi(x,t)$

where $i$ is the square root of -1.

The Schrodinger Equation is THE fundamental equation of Quantum Mechanics.

General Solution of the Schrödinger Wave Equation when $V = 0$

In free space (with $V = 0$), the general form of the wave function is:

\[ \Psi(x,t) = A e^{ikx} e^{-\omega t} + A^* e^{-ikx} e^{+\omega t} \]

which also describes a wave moving in the $x$ direction. In general the amplitude may also be complex.

The wave function is also not restricted to being real. Notice that this function is complex.

Only the physically measurable quantities must be real. These include the probability, momentum and energy.

Normalization and Probability

The probability $P(x) \, dx$ of a particle being between $x$ and $x + dx$ is given in the equation

\[ P(x) \, dx = \Psi^* (x,t) \Psi(x,t) \, dx \]

The probability of the particle being between $x_i$ and $x_f$ is given by

\[ P = \int_{x_i}^{x_f} \Psi^* (x,t) \Psi(x,t) \, dx \]

The wave function must also be normalized so that the probability of the particle being somewhere on the $x$ axis is 1.

\[ \int_{-\infty}^{\infty} \Psi^* (x,t) \Psi(x,t) \, dx = 1 \]
Properties of Valid Wave Functions

Conditions on the wave function:
1. In order to avoid infinite probabilities, the wave function must be finite everywhere.
2. The wave function must be single valued.
3. The wave function must be twice differentiable. This means that it and its derivative must be continuous. (An exception to this rule occurs when \(V\) is infinite.)
4. In order to normalize a wave function, it must approach zero as \(x\) approaches infinity.

Solutions that do not satisfy these properties do not generally correspond to physically realizable circumstances.

Time-Independent Schrödinger Wave Equation

The potential in many cases will not depend explicitly on time. The dependence on time and position can then be separated in the Schrödinger wave equation. Let:

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

This equation is known as the time-independent Schrödinger wave equation, and it is as fundamental an equation in quantum mechanics as the time-dependent Schrödinger equation.

So often physicists write simply:

\[
\hat{H} \psi = E \psi
\]

where:

\[
\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V
\]

\(\hat{H}\) is an operator.

6.2: Expectation Values

In quantum mechanics, we'll compute expectation values. The expectation value \(\langle x \rangle\) of a given quantity is:

\[
\langle x \rangle = \int \psi(x) x \psi^* dx
\]

If there are an infinite number of possibilities, and \(x\) is continuous:

\[
\langle x \rangle = \int \psi(x) x \psi^* dx
\]

Quantum-mechanically:

\[
\langle x \rangle = \int \psi(x) \phi(x) x dx = \int \psi^* (x) \phi(x) dx
\]

And the expectation of some function \(g(x)\) of \(x\):

\[
\langle g(x) \rangle = \int \psi^* (x) g(x) \psi(x) dx
\]
To find the expectation value of $p$, we first need to represent $p$ in terms of $x$ and $t$. Consider the derivative of the wave function of a free particle with respect to $x$:

$$\frac{d\Psi(x,t)}{dx} = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

With $k = p/\hbar$ we have

$$\frac{d\Psi(x,t)}{dx} = \frac{p}{\hbar} \Psi(x,t)$$

This yields

$$\hbar i \frac{\partial \Psi(x,t)}{\partial x} = \frac{p}{\hbar} \Psi(x,t)$$

This suggests we define the momentum operator as $\hat{p} = -i\hbar \frac{\partial}{\partial x}$.

The expectation value of the momentum is

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} \psi^* (x,t) \frac{\partial \Psi (x,t)}{\partial x} \, dx$$

### Deriving the Schrödinger Equation using operators

The energy is: $E = K + V = \frac{p^2}{2m} + V$ which yields $E\Psi = \frac{p^2}{2m} \Psi + V\Psi$

Substituting operators:

$$E: \quad E\Psi = \hbar^2 k^2 m \Psi = \frac{p^2}{2m} \Psi + V\Psi$$

$$K + V: \quad \frac{p^2}{2m} \Psi + V\Psi = \frac{1}{2m} (-i\hbar \frac{\partial}{\partial t})^2 \Psi + V\Psi$$

$$= \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial t^2} + V\Psi$$

Substituting:

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial t^2} + V\Psi$$

### 6.3: Infinite Square-Well Potential

The simplest such system is that of a particle trapped in a box with infinitely hard walls that the particle cannot penetrate. This potential is called an infinite square well and is given by:

$$V(x) = \begin{cases} \infty & 0 < x < L \\ 0 & x < 0, x > L \end{cases}$$

Clearly the wave function must be zero where the potential is infinite. Where the potential is zero (inside the box), the time-independent Schrödinger wave equation becomes:

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

The general solution is:

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

Quantization conditions of the potential dictate that the wave function must be zero at $x = 0$ and $x = L$. This yields valid solutions for integer values of $n$ such that $nk = n\pi$.

The wave function is:

$$\psi_n(x) = A \sin \left( \frac{n\pi x}{L} \right)$$

We normalize the wave function:

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{L}}$$

The normalized wave function becomes:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)$$

These functions are identical to those obtained for a vibrating string with fixed ends.

### Quantized Energy

The quantized wave number now becomes:

$$n = \frac{nk}{L} = \frac{n\pi}{L}$$

Solving for the energy yields:

$$E_n = \frac{n^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$$

Note that the energy depends on integer values of $n$. Hence the energy is quantized and nonzero.

The special case of $n = 1$ is called the ground state.
6.4: Finite Square-Well Potential

The finite square-well potential is:

\[ V(x) = \begin{cases} V_0 & \text{if } |x| < L/2 \\ 0 & \text{otherwise} \end{cases} \]

The Schrödinger equation outside the finite well in regions I and III is:

\[ \frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} \left( E - V_0 \right) \psi = 0 \]

Letting: \( \alpha = \sqrt{\frac{2m}{\hbar^2} \left( E - V_0 \right)} \)

Considering that the wave function must be zero at infinity, the solutions for this equation are:

\[ \psi(x) = \begin{cases} A e^{\alpha x} + B e^{-\alpha x} & \text{if } x > L \\ A e^{\alpha x} & \text{if } -L < x < 0 \\ B e^{-\alpha x} & \text{if } 0 < x < L \\ 0 & \text{otherwise} \end{cases} \]

Finite Square-Well Solution

Inside the square well, where the potential \( V \) is zero, the wave equation becomes:

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

The solution here is:

\[ \psi(x) = C_1 e^{i \sqrt{2mE/\hbar^2} x} + C_2 e^{-i \sqrt{2mE/\hbar^2} x} \]

The boundary conditions require that:

\[ \psi_0 = \psi_L, \quad \psi_0 = 0 \quad \text{and} \quad \psi_0 = 0, \quad \text{as} \quad x = L \]

so the wave function is smooth where the regions meet.

Note that the wave function is nonzero outside of the box.

Penetration Depth

The penetration depth is the distance outside the potential well where the probability significantly decreases. It is given by:

\[ \delta = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \]

The penetration distance that violates classical physics is proportional to Planck’s constant.

6.5: Simple Harmonic Oscillator

Simple harmonic oscillators describe many physical situations: springs, diatomic molecules and atomic lattices.

Consider the Taylor expansion of a potential function:

\[ V(x) = \frac{1}{2} k x^2 + \frac{1}{4} k x^4 + \frac{1}{6} k x^6 + \cdots \]

Substituting this into Schrödinger’s equation:

\[ \frac{d^4 \psi}{dx^4} + \frac{2m}{\hbar^2} \left( E - \frac{1}{2} k x^2 \right) \psi = 0 \]

Let \( \frac{d^4 \psi}{dx^4} = 0 \), which yields:

\[ \frac{d^4 \psi}{dx^4} = 0 \]

The Parabolic Potential Well

The wave function solutions are:

\[ \psi_n(x) = H_n(x) \sqrt{\frac{2}{L}} e^{-\frac{x^2}{2L^2}} \]

where \( H_n(x) \) are Hermite polynomials of order \( n \).
The Parabolic Potential Well

Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center. Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

The energy levels are given by:

\[ E_n = (n + \frac{1}{2}) \hbar \omega \]

The zero point energy is called the Heisenberg limit:

\[ E_0 = \frac{1}{2} \hbar \omega \]

Analysis of the Parabolic Potential Well

As the quantum number increases, however, the solution approaches the classical result.

\[ \Psi \psi^2 \]

6.7: Barriers and Tunneling

Consider a particle of energy \( E \) approaching a potential barrier of height \( V_0 \), and the potential everywhere else is zero.

First consider the case of the energy greater than the potential barrier. In regions I and III the wave numbers are:

In the barrier region we have

\[ k = \frac{\sqrt{2m(E-V_0)}}{\hbar} \]

Reflection and Transmission

The wave function will consist of an incident wave, a reflected wave, and a transmitted wave.

The potentials and the Schrödinger wave equation for the three regions are as follows:

Region I (\( x < 0 \))

\[ \psi_{inc} = \psi_{ref} = \psi_{trans} = 0 \]

Region II (\( 0 < x < L \))

\[ \psi_{inc} = \psi_{ref} = \psi_{trans} = 0 \]

Region III (\( x > L \))

\[ \psi_{inc} = \psi_{ref} = \psi_{trans} = 0 \]

The corresponding solutions are:

Region I (\( x < 0 \))

\[ \psi_{inc} = A e^{ikx} + B e^{-ikx} \]

Region II (\( 0 < x < L \))

\[ \psi_{inc} = A e^{ikx} + B e^{-ikx} \]

Region III (\( x > L \))

\[ \psi_{inc} = A e^{ikx} + B e^{-ikx} \]

As the wave moves from left to right, we can simplify the wave functions to:

\[ \psi_{inc} = \psi_{ref} = \psi_{trans} = 0 \]

Probability of Reflection and Transmission

The probability of the particles being reflected \( R \) or transmitted \( T \) is:

\[ R = \frac{|\psi_{ref}|^2}{|\psi_{ref}|^2 + |\psi_{trans}|^2} \]

\[ T = \frac{|\psi_{trans}|^2}{|\psi_{ref}|^2 + |\psi_{trans}|^2} \]

Because the particles must be either reflected or transmitted we have: \( R + T = 1 \).

By applying the boundary conditions \( x = 0, x = L, \) and \( x = -L \), we arrive at the transmission probability:

\[ 2 \left( \frac{\sin^2 \left( \frac{n \pi x}{L} \right)}{\frac{n \pi x}{L}} \right) \]

Note that the transmission probability can be 1.
The quantum mechanical result is one of the most remarkable features of modern physics. There is a finite probability that the particle can penetrate the barrier and even emerge on the other side!

The wave function in region II becomes:

\[ \psi(x) = \begin{cases} \begin{array}{ll} \frac{1}{\sqrt{2L}} \sin \left( \frac{\pi x}{L} \right) & \text{for } x > L \\ \frac{1}{\sqrt{2L}} \sin \left( \frac{\pi x}{L} \right) & \text{for } x < L \end{array} \end{cases} \]

The transmission probability that describes the phenomenon of tunneling is:

\[ T = \left| \frac{\sin \left( \frac{\pi x}{L} \right)}{\frac{\pi x}{L}} \right|^2 \]

This violation of classical physics is allowed by the uncertainty principle. The particle can violate classical physics by \(\Delta E = \hbar / \Delta t\) for a short time.

### Analogy with Wave Optics

If light passing through a glass prism reflects from an internal surface with an angle greater than the critical angle, total internal reflection occurs. However, the electromagnetic field is not exactly zero just outside the prism. If we bring another prism very close to the first one, experiments show that the electromagnetic wave (light) appears in the second prism. The situation is analogous to the tunneling described here. This effect was observed by Newton and can be demonstrated with two prisms and a laser. The intensity of the second light beam decreases exponentially as the distance between the two prisms increases.

### Potential Well

Consider a particle passing through a potential well, rather than a barrier. Classically, the particle would speed up in the well region because

\[ K = \frac{mv^2}{2} = E + V_0 \]

Quantum mechanically, reflection and transmission may occur, but the wavelength decreases inside the well. When the width of the potential well is precisely equal to half-integral or integral units of the wavelength, the reflected waves may be out of phase or in phase with the original wave, and cancellations or resonances may occur. The reflection/cancellation effects can lead to almost pure transmission or pure reflection for certain wavelengths. For example, at the second boundary \((x = L)\) for a wave passing to the right, the wave may reflect and be out of phase with the incident wave. The effect would be a cancellation inside the well.

### Alpha-Particle Decay

The phenomenon of tunneling explains alpha-particle decay of heavy, radioactive nuclei. Inside the nucleus, an alpha particle feels the strong, short-range attractive nuclear force as well as the repulsive Coulomb force. The nuclear force dominates inside the nuclear radius where the potential is a square well. The Coulomb force dominates outside the nuclear radius. The potential barrier at the nuclear radius is several times greater than the energy of an alpha particle.

In quantum mechanics, however, the alpha particle can tunnel through the barrier. This is observed as radioactive decay.

### 6.5: Three-Dimensional Infinite-Potential Well

The wave function must be a function of all three spatial coordinates. Now consider momentum as an operator acting on the wave function. In this case, the operator must act twice on each dimension. Given:

\[ p_x^2 + p_y^2 + p_z^2 + V(x, y, z) = E \]

So the three-dimensional Schrödinger wave equation is

\[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + V(x, y, z) \right) \psi = E \psi \]

or

\[ \frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi \]
The 3D infinite potential well

It’s easy to show that:

\[ \psi(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z) \]

where: \( k_x = \pi n_x / L_x \) \( k_y = \pi n_y / L_y \) \( k_z = \pi n_z / L_z \)

and:

\[ E = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \]

When the box is a cube:

\[ E = \frac{\pi^2 \hbar^2}{2mL^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \]

Note that more than one wave function can have the same energy.

Degeneracy

The Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy. And the same energy can be obtained by different sets of quantum numbers.

A quantum state is called degenerate when there is more than one wave function for a given energy.

Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy.