

Lecture 11 - The Schrodinger Equation (Part I)

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11.1 Introduction

In the last chapter, we saw that particles can exhibit wave phenomena. In this chapter we will see that the wave function for a particle is described by a complex-valued function $\Psi(x, t)$. For a free particle whose wave function takes the form of traveling wave, we found that the frequency of the wave function determines the energy of the particle:

$$E = hf \quad \text{or} \quad E = \hbar\omega.$$

Similarly, the wavelength of the wave function determines the momentum of the particle:

$$p = \frac{h}{\lambda} \quad \text{or} \quad p = \hbar k.$$

11.2 Time-Dependent Schrodinger Equation

The question now is how to “do physics” with wave functions. For example, if an electron is trapped inside an atom or a quantum dot, how can we predict how it will behave? Erwin Schrodinger worked out the details when he derived a wave equation controlling the dynamics. This wave equation is called the Schrodinger equation. In one dimension it takes the form:

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

where m is the mass of the particle and $U(x)$ is the potential energy of the system. This equation is essentially a statement of conservation of energy for wave functions. The quantum physicist specifies a potential energy function $U(x)$ defining the system of interest and then works out techniques for solving this equation. The presence of the imaginary unit i on the right-hand-side of the equation means that only complex-valued wave functions are solutions to the time-dependent Schrodinger equation, i.e. real-valued functions are not solutions.

11.3 Harmonic Traveling Waves

We'll start by looking at the following complex, traveling wave:

$$\Psi(x, t) = Ae^{i(kx - \omega t)}.$$

is a solution to the time-dependent Schrodinger equation: First, evaluate the time derivative:

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= -i\omega Ae^{i(kx - \omega t)} \\ &= -i\omega \Psi.\end{aligned}$$

Similarly, the spatial derivatives are:

$$\begin{aligned}\frac{\partial \Psi}{\partial x} &= ikAe^{i(kx - \omega t)} \\ &= ik\Psi\end{aligned}$$

and

$$\begin{aligned}\frac{\partial^2 \Psi}{\partial x^2} &= (ik)^2 Ae^{i(kx - \omega t)} \\ &= -k^2 \Psi\end{aligned}$$

Let's assume the potential energy is constant, $U(x) = U_0$, and substitute these derivatives into the time-dependent Schrodinger equation:

$$-\frac{\hbar^2}{2m}(-k^2\Psi) + U_0\Psi = (i\hbar)(-i\omega\Psi),$$

or

$$\frac{\hbar^2 k^2}{2m} + U_0 = \hbar\omega.$$

What do we make of this result? It will start to look more familiar once we substitute $p = \hbar k$ and $E = \hbar\omega$:

$$\frac{p^2}{2m} + U_0 = E.$$

We see that this result is just a statement of conservation of energy for wave functions. Important note: the relations $p = \hbar k$ and $E = \hbar\omega$ only work for free particles that are spread out as harmonic traveling waves.

11.4 Time-Independent Schrodinger Equation

In many cases, we wish to find standing wave solutions to the Schrodinger equation. Standing waves have the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \quad \text{or} \quad \Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

where $\psi(x)$ contains the spatial form of the wave and the $e^{i\omega t}$ factor contains the time-dependent "phase". We have also written this expression in terms of the total energy of the particle E by

substituting $\omega = E/\hbar$. By plugging this equation into the time-dependent Schrodinger equation, we can cancel out the time dependence to derive the time-independent Schrodinger equation:

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

These standing wave solutions are also called the energy eigenfunctions for the potential $U(x)$. Each unique solution $\psi_n(x)$ will correspond to an energy E_n . The subscript n has been introduced to help us keep track of the solutions. In many cases, a given potential will have an infinite number of energy eigenfunctions and spectrum of energies E_n .

11.5 Properties of Wave Functions

Before we explore solutions to the time-independent Schrodinger equation, we will first outline some general properties of the wave function:

1. $\Psi(x, t) =$ complex-valued wave function. The wave function is also called the “probability amplitude” for reasons that will be seen shortly. The wave function itself cannot be directly observed. What can be observed is the probability density (see next item).
2. $|\Psi(x, t)|^2 =$ probability density associated with the wave function. It is a real-valued function that tells you the probability of where you will find the particle. Just like any complex valued function, the modulus squared is equal to the product of the function with its complex conjugate: $|\Psi(x, t)|^2 = \Psi^*\Psi$.
3. All wave functions must be normalized, meaning

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1.$$

This integral gives the probability that the particle exists anywhere, so assuming the particle exists, the probability must be unity. We can also calculate the probability of finding the particle in a particular region, say on the interval $x \in (a, b)$. This probability is

$$P(a, b) = \int_a^b |\Psi(x, t)|^2 dx = 1.$$

4. The wave function must be continuous and single valued.
5. The wave function must be smooth, meaning the first spatial derivative of the wave function, $d\Psi/dx$ must be continuous, if the underlying potential is smooth.
6. The wave function must go to zero when $x \rightarrow \pm\infty$.
7. The wave function must be zero wherever the potential energy is infinite: $\Psi(x) = 0$ when $U(x) = \infty$.

11.6 Method for Solving the Time-Independent Schrodinger Equation

Typically, you will have a potential energy function $U(x)$ that defines the problem. The goal is to find the energy eigenfunctions $\psi_n(x)$ and corresponding energy eigenvalues E_n that are solutions to the Schrodinger equation. If you have taken a course on linear algebra, you may recognize this type of problem as an eigenvalue problem. Here are some general steps:

Step 1. Begin by writing the time-independent Schrodinger equation with the potential energy $U(x)$ included.

Step 2. Magically come up with the general solution to the equation. Different solutions may apply to different regions in space. For example, classically allowed and classically forbidden regions may have different solutions. This process takes experience and/or knowledge ODEs. Typically, you will be guided through this step.

Step 3. Use boundary conditions such as $\lim_{x \rightarrow \pm\infty} \psi(x) = 0$ to exclude or restrict the general solutions. Boundary conditions also may be used to join piece-wise continuous functions.

Step 4. Solve for the allowed energy eigenvalues E_n by using results from the boundary constraints.

Step 5. Use the normalization condition to evaluate unknown constants.

Step 6. Collect your results including the wave functions $\psi_n(x)$ and energy eigenvalues E_n . All done, although its always a good idea to sit back and contemplate what it all means.

11.7 Constant Potential Energy

A number of interesting problems can be constructed using piece-wise constant potentials. Let the potential energy of the particle be a constant U_0 in some region of interest. The Schrodinger equation may then be rewritten as

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m(E - U_0)}{\hbar^2}\psi(x).$$

When the energy of the particle is greater than the potential energy, i.e. $E > U_0$, the solution is

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad \text{where } k = \frac{\sqrt{2m(E - U_0)}}{\hbar}$$

When the energy of the particle is less than the potential energy, i.e. $E < U_0$, the solution is

$$\psi(x) = A'e^{k'x} + B'e^{-k'x} \quad \text{where } k' = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$$

When $E > U_0$, the particle is in a classically allowed region and the wave function exhibits oscillatory behavior. The wavelength of the oscillations grows in proportion to $\lambda \propto (E - U_0)^{-1/2}$. Thus, as the energy of the particle increases, the wavelength decreases.

When $E < U_0$, the particle is in a classically forbidden region and the wave function exhibits exponentially decaying behavior. The farther the energy drops below the potential U_0 , the quicker the function decays causing it to penetrate less into the forbidden region.

11.8 Infinite Potential Well (a.k.a. Particle in a Box)

We imagine a 1D potential well with $U = 0$ between $0 < x < L$ and $U = \infty$ outside of that region:

$$U(x) = \begin{cases} +\infty & \text{for } x \leq 0 \\ 0 & \text{for } 0 < x < L \\ +\infty & \text{for } x \geq L \end{cases}$$

We follow the steps outlined in section 5.6:

Step 1. Inside the well, $U(x) = 0$ so the Schrodinger equation may be written as

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

Step 2. The general solution was given in section 5.6:

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar}$$

Step 3. Because the potential equals infinity at the edges of the well, we have two boundary conditions:

$$\text{Left: } \psi(0) = 0$$

$$\text{Right: } \psi(L) = 0.$$

Apply the left boundary condition, $\psi(0) = 0$:

$$\begin{aligned} \psi(0) &= A \sin(0) + B \cos(0) \\ 0 &= B. \end{aligned}$$

Thus we see that $B = 0$ and the solution is reduced from the general case to:

$$\psi(x) = A \sin(kx).$$

Apply the right boundary condition, $\psi(L) = 0$:

$$\psi(L) = A \sin(kL) = 0$$

This is true when

$$k = \frac{n\pi}{L}.$$

Step 4. Solve for energy eigenvalues by equating the values of k found in steps 2 and 3:

$$\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L}$$

gives the energies to be

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}.$$

Step 5. We evaluate the constant A using normalization:

$$\int_0^L |\Psi(x, t)|^2 dx = 1.$$

The integral is evaluated over the domain on which the wave function is defined, i.e. from 0 to L .

$$\begin{aligned} \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx &= A^2 \left[\frac{x}{2} - \frac{\sin(2(n\pi/L)x)}{4(n\pi/L)} \right]_0^L \\ &= A^2 \left[\frac{L}{2} \right] \end{aligned}$$

Thus, we find that

$$A = \sqrt{\frac{2}{L}}.$$

Step 6. Finally, we combine our results. The standing wave solutions called energy eigenfunctions are

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

and the corresponding energy eigenvalues are

$$E_n = \frac{\hbar^2 n^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

And now for the most important step: interpreting the results and understanding what it all means. We have derived an infinite set of standing waves. Each standing wave $\psi_n(x)$ has a corresponding energy E_n . These solutions are called the **quantum states** (or **energy eigenstates**) of the infinite potential well. The integer n is the **quantum number** that labels the states. These allowed energy values E_n are also called **energy levels**. The energies of the quantum states increase as $E_n \propto n^2$. The smallest energy corresponding to $n = 1$ is called the **ground state** and the other states are called **excited states**. Notice that for each step up the “ladder” of quantum states, the wave function is compressed a bit more to make room for one more half wavelength: i.e. the number of half wavelengths in the wave function just equals the quantum number n .

Imagine placing a marble in a frictionless box. If we give it an initial velocity it will roll back and forth in the box bouncing off the walls indefinitely. We can give the marble any amount of kinetic energy by starting it off with any velocity we choose $K = \frac{1}{2}mv^2$. However, quantum mechanics says something strange happens when we shrink the marble and size of the box down to an atomic scale. We see that the “marble” bounces around in the box with a predetermined and **quantized** set of energies.

For example, the energy levels of an electron placed inside a 1 nm wide box are $E_n = 0.376 \text{ eV } n^2$. We see that $E_1 = 0.376 \text{ eV}$, $E_2 = 0.376 \cdot 2^2 = 1.50 \text{ eV}$, $E_3 = 0.376 \cdot 3^2 = 3.37 \text{ eV}$, etc. In other words, an electron can be placed into a quantum state with a kinetic energy of 0.376 eV or 1.50 eV but nothing in between, i.e. a kinetic energy of 1.0 eV is not allowed by quantum physics. This weirdness is a direct result of the “waviness” of quantum particles. Also notice that in the lowest state E_1 , i.e. the ground state, the electron still has kinetic energy. In other words, if you place an electron in a box it cannot just sit at rest with zero kinetic energy, it has to bounce around!! This fact is a direct result of the Heisenberg uncertainty relation: because the particle is trapped in the box $\Delta x \approx L$ and $\Delta p > \hbar/\Delta x$.