

## 5.1: The Free Particle

We obtain the Schrödinger equation for the free particle using the following steps. First write

$$\hat{H}\psi = E\psi \quad (5.1.1)$$

Next define the Hamiltonian,

$$\hat{H} = \hat{T} + \hat{V} \quad (5.1.2)$$

and substitute the potential energy operator

$$\hat{V} = 0 \quad (5.1.3)$$

and the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (5.1.4)$$

to obtain the Schrödinger equation for a free particle

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (5.1.5)$$

A major problem in Quantum Mechanics is finding solutions to differential equations, e.g. Equation 5.1.5. Differential equations arise because the operator for kinetic energy includes a second derivative. We will solve the differential equations for some of the more basic cases, but since this is not a course in Mathematics, we will not go into all the details for other more complicated cases. The solutions that we consider in the greatest detail will illustrate the general procedures and show how the physical concept of quantization arises mathematically.

We already encountered Equation 5.1.5 in the last chapter Chapter 4. There, we used our knowledge of some basic functions to find the solution. Now we solve this equation by using some algebra and mathematical logic. First we rearrange Equation 5.1.5 and make the substitution

$$k^2 = \frac{2mE}{\hbar^2}. \quad (5.1.6)$$

The substitution in Equation 5.1.6 is only one way of making a simplification. You could also use a different formulation for the substitution

$$\alpha = \frac{2mE}{\hbar^2}$$

but then you would find later that  $(\alpha)^{1/2}$  corresponds to the wavevector  $k$  which equals  $\frac{2\pi}{\lambda}$  and  $\frac{P}{\hbar}$ . So choosing a squared variable like  $k^2$  in Equation 5.1.6 is a choice made with foresight. Trial-and-error is one method scientists use to solve problems, and the results often look sophisticated and insightful after they have been found, like choosing  $k^2$  rather than  $\alpha$ .

Since  $E$  is the kinetic energy,

$$E = \frac{p^2}{2m} \quad (5.1.7)$$

and we saw in previous chapters that the momentum  $p$  and the wavevector  $k$  are related,

$$p = \hbar k \quad (5.1.8)$$

we also could recognize that  $\frac{2mE}{\hbar^2}$  is just  $k^2$  as shown here in Equation 5.1.11.

$$\frac{2mE}{\hbar^2} = \left( \frac{2m}{\hbar^2} \right) \left( \frac{p^2}{2m} \right) \quad (5.1.9)$$

$$= \left( \frac{\cancel{2m}}{\cancel{\hbar^2}} \right) \left( \frac{\cancel{\hbar^2} k^2}{\cancel{2m}} \right) \quad (5.1.10)$$

$$= k^2 \quad (5.1.11)$$

The result for Equation 5.1.5 after rearranging and substitution of result from Equation 5.1.11 is

$$\left( \frac{d^2}{dx^2} + k^2 \right) \psi(x) = 0 \quad (5.1.12)$$

This linear second-order differential equation can be solved in the same way that a algebraic quadratic equation is solved. It is separated into two factors, and each is set equal to 0. This factorization produces two first-order differential equations that can be integrated. The details are shown in the following equations.

$$\left( \frac{d^2}{dx^2} + k^2 \right) \psi(x) = \left( \frac{d}{dx} + ik \right) \left( \frac{d}{dx} - ik \right) \psi(x) = 0 \quad (5.1.13)$$

Equation 5.1.13 will be true if either

$$\left( \frac{d}{dx} + ik \right) \psi(x) = 0 \quad (5.1.14)$$

or

$$\left( \frac{d}{dx} - ik \right) \psi(x) = 0 \quad (5.1.15)$$

Rearranging and designating the two equations and the two solutions simultaneously by a + sign and a – sign produces

$$\frac{d\psi_{\pm}(x)}{\psi_{\pm}(x)} = \pm ik dx \quad (5.1.16)$$

which leads to

$$\ln \psi_{\pm}(x) = \pm ikx + C_{\pm} \quad (5.1.17)$$

and finally

$$\psi_{\pm}(x) = A_{\pm} e^{\pm ikx} \quad (5.1.18)$$

The constants  $A_+$  and  $A_-$  result from the constant of integration. The values of these constants are determined by some physical constraint that is imposed upon the solution. Such a constraint is called a boundary condition. For the particle in a box, discussed previously, the boundary condition is that the wavefunction must be zero at the boundaries where the potential energy is infinite. The free particle does not have such a boundary condition because the particle is not constrained to any one place. Another constraint is normalization, and here the integration constants serve to satisfy the normalization requirement.

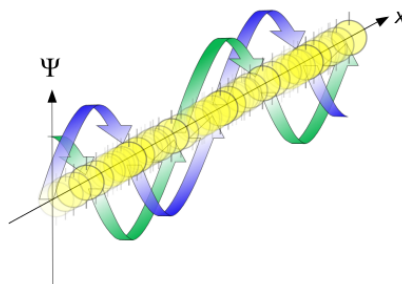


Figure 5.1.1: Propagation of free particle waves in 1d - real part of the complex amplitude is blue, imaginary part is green. The probability (shown as the color opacity) of finding the particle at a given point x is spread out like a waveform, there is no definite position of the particle. (public domain).

### ? Exercise 5.1.1

Show that the operator  $\left(\frac{d^2}{dx^2} + k^2\right)$  equals  $\left(\frac{d}{dx} + ik\right)\left(\frac{d}{dx} - ik\right)$  and that the two factors commute since  $k$  does not depend on  $x$ . The answer is Equation 5.1.13

### ✓ Example 5.1.1: Normalizing the wavefunction of a free particle

Use the normalization constraint to evaluate  $A_{\pm}$  in Equation 5.1.18

#### Solution

Since the integral of  $|\psi|^2$  over all values of  $x$  from  $-\infty$  to  $+\infty$  is infinite, it appears that the wavefunction  $\psi$  cannot be normalized. We can circumvent this difficulty if we imagine the particle to be in a region of space ranging from  $-L$  to  $+L$  and consider  $L$  to approach infinity.

The normalization then proceeds in the usual way as shown below. Notice that the normalization constants are **real** even though the wavefunctions are complex.

$$\int_{-L}^{+L} \psi^*(x)\psi(x)dx = A_{\pm}^* A_{\pm} \int_{-L}^{+L} e^{\mp ikx} e^{\pm ikx} dx = 1$$

$$|A_{\pm}|^2 \int_{-L}^{+L} dx = |A_{\pm}|^2 2L = 1$$

$$A_{\pm} = [2L]^{-1/2}$$

### ? Exercise 5.1.2

Write the wavefunctions,  $\psi^+$  and  $\psi^-$ , for the free particle, explicitly including the normalization factors found in Example 5.1.1.

### ? Exercise 5.1.3

Find solutions to each of the following differential equations.

$$\frac{d^2 y(x)}{dx^2} + 25y(x) = 0$$

$$\frac{d^2 y(x)}{dx^2} - 3y(x) = 0$$

A neat property of linear differential equations is that sums of solutions also are solutions, or more generally, linear combinations of solutions are solutions. A linear combination is a sum with constant coefficients where the coefficients can be positive, negative, or imaginary. For example

$$\psi(x) = C_1 \psi_+(x) + C_2 \psi_-(x) \quad (5.1.19)$$

where  $C_1$  and  $C_2$  are the constant coefficients. Inserting the functions from Equation 5.1.18, one gets

$$\psi(x) = \frac{C_1}{\sqrt{2L}} e^{+ikx} + \frac{C_2}{\sqrt{2L}} e^{-ikx} \quad (5.1.20)$$

By using Euler's formula,

$$e^{\pm ikx} = \cos(kx) \pm i \sin(kx) \quad (5.1.21)$$

Equation 5.1.19 is transformed into

$$\psi(x) = C \cos(kx) + D \sin(kx) \quad (5.1.22)$$

where we see that  $k$  is just the wavevector  $\frac{2\pi}{\lambda}$  in the trigonometric form of the solution to the Schrödinger equation. This result is consistent with our previous discussion regarding the choice of  $k^2$  to represent  $\frac{2mE}{\hbar^2}$ .

#### ? Exercise 5.1.4

Find expressions for  $C$  and  $D$  in Equation 5.1.22 for two cases: when  $C_1 = C_2 = +1$  and when  $C_1 = +1$  and  $C_2 = -1$ .

#### ? Exercise 5.1.5

Verify that Equations 5.1.20 and 5.1.22 are solutions to the Schrödinger Equation (Equation 5.1.5) with the eigenvalue  $E = \frac{\hbar^2 k^2}{2m}$ .

#### ? Exercise 5.1.6

Demonstrate that the wavefunctions you wrote for Exercise 5.1.2 are eigenfunctions of the momentum operator with eigenvalues  $\hbar k$  and  $-\hbar k$ .

#### ? Exercise 5.1.7

Determine whether  $\psi(x)$  in Equation 5.1.20 is an eigenfunction of the momentum operator.

#### ? Exercise 5.1.8

The probability density for finding the free particle at any point in the segment  $-L$  to  $+L$  can be seen by plotting  $\psi^* \psi$  from  $-L$  to  $+L$ . Sketch these plots for the two wavefunctions,  $\psi_+$  and  $\psi_-$ , that you wrote for Exercise 5.1.2. Demonstrate that the area between  $\psi^* \psi$  and the x-axis equals 1 for any value of  $L$ . Why must this area equal 1 even as  $L$  approaches infinity? Are all points in the space equally probable or are some positions favored by the particle?

We found wavefunctions that describe the free particle, which could be an electron, an atom, or a molecule. Each wavefunction is identified by the wavevector  $k$ . A wavefunction tells us three things about the free particle: the energy of the particle, the momentum of the particle, and the probability density of finding the particle at any point. You have demonstrated these properties in Exercises 5.1.5, 5.1.6, and 5.1.8. These ideas are discussed further in the following paragraphs.

We first find the momentum of a particle described by  $\psi_+(x)$ . We also can say that the particle is in the state  $\psi_+(x)$ . The value of the momentum is found by operating on the function with the momentum operator. Remember this problem is one-dimensional so vector quantities such as the wavevector or the momentum appear as scalars. The result is shown in Example 5.1.1.

#### ✓ Example 5.1.2

Extract the momentum from the wavefunction for a free electron.

##### Solution

First we write the momentum operator and wavefunction as shown by I and II. The momentum operator tells us the mathematical operation to perform on the function to obtain the momentum. Complete the operation shown in II to get III, which simplifies to IV.

$$-i\hbar \frac{d}{dx} \psi_+(x) = -i\hbar \frac{d}{dx} A_+ e^{ikx} = (-i\hbar)(ik) A_+ e^{ikx} = \hbar k \psi_+(x)$$

I
II
III
IV

Example 5.1.2 is another way to conclude that the momentum of this particle is

$$p = \hbar k. \quad (5.1.23)$$

Here the Compton-de Broglie momentum-wavelength relation  $p = \hbar k$  appears from the solution to the Schrödinger equation and the definition of the momentum operator! For an electron in the state  $\psi_{-}(x)$ , we similarly find  $p = -\hbar k$ . This particle is moving in the minus x direction, opposite from the particle with momentum  $+\hbar k$ .

Since  $k = \frac{2\pi}{\lambda}$ , what then is the meaning of the wavelength for a particle, e.g. an electron? The wavelength is the wavelength of the wavefunction that describes the properties of the electron. We are not saying that an electron is a wave in the sense that an ocean wave is a wave; rather we are saying that a wavefunction is needed to describe the wave-like properties of the electron. Why the electron has these wave-like properties, remains a mystery.

We find the energy of the particle by operating on the wavefunction with the Hamiltonian operator as shown next in Equation 5.1.26. Examine each step and be sure you see how the eigenvalue is extracted from the wavefunction.

$$\hat{H}\psi_{\pm}(x) = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} A_{\pm} e^{\pm i k x} \quad (5.1.24)$$

$$= \frac{-\hbar^2}{2m} (\pm i k)^2 A_{\pm} e^{\pm i k x} \quad (5.1.25)$$

$$= \frac{\hbar^2 k^2}{2m} A_{\pm} e^{\pm i k x} \quad (5.1.26)$$

Notice again how the operator works on the wavefunction to extract a property of the system from it. We conclude that the energy of the particle is

$$E = \frac{\hbar^2 k^2}{2m} \quad (5.1.27)$$

Which is just the classical relation between energy and momentum of a free particle,  $E = \frac{p^2}{2m}$ . Note that an electron with momentum  $+\hbar k$  has the same energy as an electron with momentum  $-\hbar k$ . When two or more states have the same energy, the states and the energy level are said to be degenerate.

We have not found any restrictions on the momentum or the energy. These quantities are not quantized for the free particle because there are no boundary conditions. Any wave with any wavelength fits into an unbounded space. Quantization results from boundary conditions imposed on the wavefunction, as we saw for the particle-in-a-box.

### ? Exercise 5.1.9

Describe how the wavelength of a free particle varies with the energy of the particle.

### ? Exercise 5.1.10

Summarize how the energy and momentum information is contained in the wavefunction and how this information is extracted from the wavefunction.

The probability density of a free particle at a position in space  $x_0$  is

$$\psi_{\pm}^*(x_0)\psi_{\pm}(x_0) = (2L)^{-1} e^{\mp i k x_0} e^{\pm i k x_0} = (2L)^{-1} \quad (5.1.28)$$

From this result we see that the probability density has units of 1/m; it is the probability per meter of finding the electron at the point  $x_0$ . This probability is independent of  $x_0$ , the electron can be found any place along the x axis with equal probability. Although we have no knowledge of the position of the electron, we do know the electron momentum exactly. This relationship between our knowledge of position and momentum is a manifestation of the [Heisenberg Uncertainty Principle](#), which says that as the uncertainty in one quantity is reduced, the uncertainty in another quantity increases. For this case, we know the momentum exactly and have no knowledge of the position of the particle. The uncertainty in the momentum is zero; the uncertainty in the position is infinite.

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