

Chapter 5. The Schrödinger Wave Equation Formulation of Quantum Mechanics

Notes:

- *Most of the material in this chapter is taken from Thornton and Rex, Chapter 6.*

5.1 The Schrödinger Wave Equation

There are several formalisms available to the quantum physicists. As stated in the previous chapter, the two original and independent formulations were those of Heisenberg and Schrödinger. Heisenberg's approach is often referred to as *matrix mechanics*, as the description of a quantum system is expressed through the time evolution of matrix operators for the different quantities characterizing the state of the system (e.g., position, momentum, angular momentum, etc.). On the other hand, Schrödinger's version of quantum mechanics is based on the evolution of a *wave function* characterizing the system, a notion previously introduced in Chapter 4, as dictated by the *Schrödinger wave equation*. This is the approach we will take here. It is interesting to note, however, that **Richard Feynman** (1918-1988) introduced in the late 1940's another very successful approach to quantum mechanics based on so-called *path integrals* or *sum over histories*. Whatever the case, all of these versions of quantum mechanics are equivalent and make the same predictions for the outcome of measurements.

Since our analyses of quantum mechanical systems will be conducted through the intermediary of wave functions it would seem natural to also have at hand a corresponding wave equation to determine how the wave functions evolve through time and space. The Schrödinger wave equation, which serves this purpose, is not something that can be rigorously derived from first principles. Like many other instances in physics, it is usually postulated and tested against experiments; its successes then justify its acceptance. Although it is indeed the fact that the Schrödinger equation is generally simply postulated as a starting point in quantum mechanics, we can still provide elements of a derivation to make it plausible that our eventual choice for the wave equation is correct. In order to guide us in that regard we can postulate some conditions to be fulfilled by the wave equation:

1. The equation should be *linear* and *homogeneous*, which is a condition met by waves in general. That is, if the wave functions ψ_1 and ψ_2 are solutions of the wave equation, then $a_1\psi_1 + a_2\psi_2$ must also be a solution, with a_1 and a_2 some constants.
2. Because we want that knowledge of the wave function at a given instant be sufficient to specify it at any other later time, then the wave equation must be a differential equation of first order with respect to time. If, for example, the wave equation were of second order with respect to time (as is the wave equation in electromagnetism; see equation (1.24) in Chapter 1), then knowledge of the first time derivative of the initial wave function would also be needed.
3. Finally, we require the wave equation to conform to Bohr's correspondence principle (see Section 3.3.1 in Chapter 3).

Let us first consider the simplest case possible, i.e., that of a free particle of mass m , where we know that the following classical relation must exist between the energy and momentum

$$E = \frac{p^2}{2m}. \quad (5.1)$$

In accordance with the material covered in Chapter 4, we express the particle's wave function with the Fourier transform

$$\psi(x, t) = \int A(p) e^{j(px - Et)/\hbar} dp, \quad (5.2)$$

limiting ourselves to a one-dimensional problem, for simplicity. We also made a change of variables in order to have the energy and momentum appear in the wave function, which is straightforward from $E = \hbar\omega$ and $p = \hbar k$ (see equation (4.9) in Chapter 4). Let us now calculate the time and spatial derivatives of the wave function

$$\begin{aligned} \frac{\partial}{\partial t} \psi(x, t) &= \frac{\partial}{\partial t} \int A(p) e^{j(px - Et)/\hbar} dp \\ &= -\frac{j}{\hbar} \int E A(p) e^{j(px - Et)/\hbar} dp, \end{aligned} \quad (5.3)$$

and

$$\begin{aligned} \frac{\partial}{\partial x} \psi(x, t) &= \frac{\partial}{\partial x} \int A(p) e^{j(px - Et)/\hbar} dp \\ &= \frac{j}{\hbar} \int p A(p) e^{j(px - Et)/\hbar} dp. \end{aligned} \quad (5.4)$$

From the last equation we also have

$$\begin{aligned} \frac{\partial^2}{\partial x^2} \psi(x, t) &= \frac{\partial^2}{\partial x^2} \int A(p) e^{j(px - Et)/\hbar} dp \\ &= -\frac{1}{\hbar^2} \int p^2 A(p) e^{j(px - Et)/\hbar} dp. \end{aligned} \quad (5.5)$$

Slightly rearranging and combining equations (5.3) and (5.5) then yield

$$\begin{aligned} \left(j\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi(x, t) &= \int \left(E - \frac{p^2}{2m} \right) A(p) e^{j(px - Et)/\hbar} dp \\ &= 0, \end{aligned} \quad (5.6)$$

where the second line follows from equation (5.1). We are then left with

$$j\hbar \frac{\partial}{\partial t} \psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x,t), \quad (5.7)$$

which can easily be shown to verify our three earlier conditions. We therefore postulate that equation (5.7) is the *Schrödinger wave equation for a free particle*.

Of course, not all particles are free... Indeed, a more general equation for the classical energy of a particle, or a system of particles, is

$$E = \frac{p^2}{2m} + V(x,t), \quad (5.8)$$

where $V(x,t)$ is the potential energy, which we assume to be a function of the position and time. We need to find a way to incorporate the potential energy in our previous analysis. This could be problematic as V is not a function of the momentum and cannot be easily included in the integrand like previously p and p^2 were in equations (5.4) and (5.5). We can, however, make the approximation that the spatial extent of the wave function $\psi(x,t)$ is much smaller than the extent over which $V(x,t)$ varies significantly. This is not an unreasonable assumption if we consider the fact that, according to de Broglie's idea of matter waves, the size of the wave function should more or less correspond to that of the (classical) particle associated to it. One could consider the electron of a hydrogen atom as an example; this assumption is certainly well verified in this case. We therefore approximate $V(x,t)$ as being constant over the spatial extent of $\psi(x,t)$, and we can thus write

$$\begin{aligned} V(x,t)\psi(x,t) &= V(x,t) \int A(p) e^{j(px-Et)/\hbar} dp \\ &\approx \int V(x,t) A(p) e^{j(px-Et)/\hbar} dp. \end{aligned} \quad (5.9)$$

We can then generalize equation (5.6) to

$$\begin{aligned} \left[j\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V(x,t) \right] \psi(x,t) &\approx \int \left[E - \frac{p^2}{2m} - V(x,t) \right] A(p) e^{j(px-Et)/\hbar} dp \\ &\approx 0, \end{aligned} \quad (5.10)$$

or alternatively

$$j\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right] \psi(x,t). \quad (5.11)$$

This equation is readily generalized to the three-dimensional case by implementing the following replacements

$$x \rightarrow \mathbf{r}$$

$$\frac{\partial^2}{\partial x^2} \rightarrow \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \quad (5.12)$$

(remember that $\nabla^2 = \nabla \cdot \nabla$), which yield

$$j\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \psi(\mathbf{r}, t). \quad (5.13)$$

This is the (non-relativistic) *time-dependent Schrödinger wave equation* for a particle subjected to a potential $V(\mathbf{r}, t)$.

It is interesting and important to note that according to equations (5.3) and (5.4) we can make the following correspondence between the classical and quantum mechanical representations of energy and linear momentum

$$E \leftrightarrow j\hbar \frac{\partial}{\partial t} \quad (5.14)$$

$$\mathbf{p} \leftrightarrow -j\hbar \nabla.$$

We further preserve the interpretation of the wave function as providing a probability density through the square of its norm, and the constraint on it being normalized over all space

$$P(\mathbf{r}, t) d^3r = |\psi(\mathbf{r}, t)|^2 d^3r \quad (5.15)$$

$$\int_{-\infty}^{\infty} |\psi(\mathbf{r}, t)|^2 d^3r = 1,$$

but we also add the following properties

1. It must be finite everywhere in space and through time, in order to yield sensible predictions on probabilities.
2. It must be single-valued, in order to be physically unambiguous.
3. Its value $\psi(\mathbf{r}, t)$ and spatial derivative $\nabla \psi(\mathbf{r}, t)$ must be continuous wherever the potential $V(\mathbf{r}, t)$ does not have any discontinuity. It is not surprising that the spatial derivative must be specified since the Schrödinger equation contains the second-order spatial derivative of the wave function.
4. Finally, the wave function must tend to zero as $r = |\mathbf{r}|$ goes to infinity, i.e.,

$$\lim_{r \rightarrow \infty} \psi(\mathbf{r}, t) = 0. \quad (5.16)$$

Exercises

1. Determine if (a) $\psi(x, t) = \sqrt{2\ell^{-1}} \cos(kx - \omega t)$ and (b) $\psi(x, t) = \ell^{-1/2} e^{j(kx - \omega t)}$ are viable solutions for the time-dependent Schrödinger equation when $0 \leq x \leq \ell$.

Solution.

(a) We first calculate

$$\begin{aligned} \frac{\partial}{\partial t} \psi(x, t) &= \sqrt{\frac{2}{\ell}} \omega \sin(kx - \omega t) \\ \frac{\partial}{\partial x} \psi(x, t) &= -\sqrt{\frac{2}{\ell}} k \sin(kx - \omega t) \\ \frac{\partial^2}{\partial x^2} \psi(x, t) &= -\sqrt{\frac{2}{\ell}} k^2 \cos(kx - \omega t) \\ &= -k^2 \psi(x, t), \end{aligned} \quad (5.17)$$

and from equation (5.13)

$$j\hbar \cdot \sqrt{\frac{2}{\ell}} \omega \sin(kx - \omega t) \neq \left[\frac{\hbar^2 k^2}{2m} + V(x, t) \right] \cdot \sqrt{\frac{2}{\ell}} \cos(kx - \omega t). \quad (5.18)$$

The function $\psi(x, t) = \sqrt{2\ell^{-1}} \cos(kx - \omega t)$ is therefore not a viable solution for the time-dependent Schrödinger equation.

(b) We again calculate the derivatives

$$\begin{aligned} \frac{\partial}{\partial t} \psi(x, t) &= -\frac{j\omega}{\sqrt{\ell}} e^{j(kx - \omega t)} \\ &= -j\omega \psi(x, t) \\ \frac{\partial}{\partial x} \psi(x, t) &= \frac{jk}{\sqrt{\ell}} e^{j(kx - \omega t)} \\ \frac{\partial^2}{\partial x^2} \psi(x, t) &= -\frac{k^2}{\sqrt{\ell}} e^{j(kx - \omega t)} \\ &= -k^2 \psi(x, t), \end{aligned} \quad (5.19)$$

which when inserted in the time-dependent Schrödinger equation yield

$$\hbar\omega\psi(x,t) = \left[\frac{\hbar^2 k^2}{2m} + V(x,t) \right] \psi(x,t). \quad (5.20)$$

If we now use $E = \hbar\omega$ and $p = \hbar k$ for the energy and linear momentum, then we find that equation (5.20) verifies that $E = p^2/2m + V$, which is correct. Also, we find that

$$\begin{aligned} \int_0^\ell |\psi(x,t)|^2 dx &= \frac{1}{\ell} \int_0^\ell \sin^2(kx - \omega t) dx \\ &= 1, \end{aligned} \quad (5.21)$$

and this function is properly normalized. Since it further verifies all other needed properties for a wave function, we conclude that it is a solution of the time-dependent Schrödinger equation.

5.1.1 Separation of Variables and the Time-independent Schrödinger Equation

It is often the case in physics that functions of several variables that are solutions to differential equations can be separated in a product of one-variable functions. For example, let us assume that the wave function $\psi(x,t)$ is such that

$$\psi(x,t) = \varphi(x)f(t). \quad (5.22)$$

Insertion in the time-dependent Schrödinger equation (5.11) for a *conservative* quantum mechanical system, when the potential energy is not a function of time (i.e., $V = V(x)$), yields

$$\begin{aligned} j\hbar \frac{\partial}{\partial t} [\varphi(x)f(t)] &= \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \varphi(x)f(t) \\ j\hbar \varphi(x) \frac{d}{dt} f(t) &= f(t) \left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \varphi(x). \end{aligned} \quad (5.23)$$

Dividing both sides of the last equation by $\varphi(x)f(t)$ results in

$$j\hbar \frac{1}{f(t)} \frac{d}{dt} f(t) = \frac{-\hbar^2}{2m} \frac{1}{\varphi(x)} \frac{d^2}{dx^2} \varphi(x) + V(x). \quad (5.24)$$

Since both sides of the equality sign are functions of only one variable, i.e., a function of time on the left and position on the right, then it must be that they are equal to a constant, which we denote by E . Concentrating on the left side, we have that

$$j\hbar \frac{1}{f(t)} \frac{d}{dt} f(t) = E, \quad (5.25)$$

or

$$\frac{df(t)}{f(t)} = -j \frac{E}{\hbar} dt. \quad (5.26)$$

Integrating on both sides yields

$$\ln f(t) = -j \frac{E}{\hbar} dt + C, \quad (5.27)$$

with C a constant of integration. Equation (5.27) can then easily be transformed to

$$f(t) = A e^{-jEt/\hbar}, \quad (5.28)$$

with again a constant $A = e^C$. We note that we also have from equation (5.24)

$$E = \frac{-\hbar^2}{2m} \frac{1}{\varphi(x)} \frac{d^2}{dx^2} \varphi(x) + V(x), \quad (5.29)$$

which, from the second of equations (5.14) allows us to establish that E is indeed the energy of the system, hence our notation.

Combining equations (5.22), (5.28), and (5.29) we find that for a conservative quantum mechanical system (generalizing to three dimensions)

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r}) e^{-jEt/\hbar} \quad (5.30)$$

is a solution to the time-dependent Schrödinger equation (note that we have redefined $\varphi(\mathbf{r})$ such that it now includes the constant A), and the equation for which $\varphi(\mathbf{r})$ is a solution is

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \varphi(\mathbf{r}) = E \varphi(\mathbf{r}), \quad (5.31)$$

the so-called *time-independent Schrödinger wave equation*.

Exercises

2. What mathematical form does the one-dimensional wave function of a free particle take (i.e., set $V(x) = 0$ in equation (5.31))?

Solution.

The time-independent Schrödinger equation is in this case

$$\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \varphi(x) = E \varphi(x), \quad (5.32)$$

or

$$\begin{aligned} \frac{d^2}{dx^2} \varphi(x) &= -\frac{2mE}{\hbar^2} \varphi(x) \\ &= -\frac{p^2}{\hbar^2} \varphi(x). \end{aligned} \quad (5.33)$$

This is a differential equation that is readily solved, yielding

$$\varphi(x) = A e^{jpx/\hbar}, \quad (5.34)$$

with A a constant that will ensure the normalization of the wave function. For example, if $V(x) = 0$ only over a range of length ℓ , then $A = \ell^{-1/2}$ since we have

$$\begin{aligned} \int_0^\ell |\varphi(x)|^2 dx &= \int_0^\ell \frac{1}{\sqrt{\ell}} e^{jpx/\hbar} \cdot \frac{1}{\sqrt{\ell}} e^{-jpx/\hbar} dx \\ &= \frac{1}{\ell} \int_0^\ell dx \\ &= 1. \end{aligned} \quad (5.35)$$

Please note that the functions $\cos(px/\hbar)$ and $\sin(px/\hbar)$ are also solutions. Although they are not allowed when ωt is part of their argument (see Exercise 1), they can be viable solutions for the spatial part of the wave function.

5.2 Expectation Values

We have previously established the fact that, when considering a particle, the square of the norm of its wave function $|\psi(x,t)|^2$ yields the probability density of finding that particle at position x for a measurement effected at time t . It follows that we could use the wave function to calculate the *expectation* or *mean value* for the particle's position through

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi(x,t)|^2 dx. \quad (5.36)$$

In the same manner, we could calculate the expectation value for the square of the position with

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 |\psi(x,t)|^2 dx, \quad (5.37)$$

etc. Although these particular equations are perfectly adequate, it is more prudent in quantum mechanics to generally write such expectation values in the following manner

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) x \psi(x,t) dx. \quad (5.38)$$

Evidently equations (5.36) and (5.38) are equal for $\langle x \rangle$ ($|\psi(x,t)|^2 = \psi^*(x,t)\psi(x,t)$), but care must be taken when calculating the expectation value of other physical observables. For example, what would the expectation value for the energy $\langle E \rangle$ be? Before answering this question we should ask ourselves what representation does the energy *operator*¹ \hat{E} take when acting on the wave function $\psi(x,t)$? We know from the discussion leading to derivation of the time-dependent Schrödinger equation that, from the first of equations (5.14),

$$\hat{E} = j\hbar \frac{\partial}{\partial t} \quad (5.39)$$

since from equation (5.3)

$$\hat{E}\psi(x,t) = j\hbar \frac{\partial}{\partial t} \psi(x,t). \quad (5.40)$$

Because the energy operator modifies the wave function through the action of a time derivative, unlike x that leaves it unchanged, we cannot use a relation similar to equation (5.36) to calculate its mean value. We rather write

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) \hat{E}\psi(x,t) dx \\ &= j\hbar \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\partial}{\partial t} \psi(x,t) dx. \end{aligned} \quad (5.41)$$

¹ From now on, we will associate an operator to any physical observables that can act on the wave function and denote it with a “caret” when it is not only a function of x (or \mathbf{r} in three dimensions).

For example, let us take the case of a conservative system where

$$\psi(x,t) = \varphi(x)e^{-jEt/\hbar}. \quad (5.42)$$

Equation (5.41) then yields

$$\begin{aligned} \langle E \rangle &= j\hbar \int_{-\infty}^{\infty} \varphi^*(x) e^{jEt/\hbar} \frac{\partial}{\partial t} \varphi(x) e^{-jEt/\hbar} dx \\ &= j\hbar \int_{-\infty}^{\infty} \varphi^*(x) \varphi(x) e^{jEt/\hbar} \frac{\partial}{\partial t} e^{-jEt/\hbar} dx \\ &= j\hbar \int_{-\infty}^{\infty} |\varphi(x)|^2 e^{jEt/\hbar} \left(-j \frac{E}{\hbar} \right) e^{-jEt/\hbar} dx \\ &= E \int_{-\infty}^{\infty} |\varphi(x)|^2 dx \\ &= E, \end{aligned} \quad (5.43)$$

which was expected since this energy is explicitly defined in the wave function. A simple calculation using an equation similar to (5.36) would have given a zero value for the mean energy, which is clearly erroneous.

Likewise, the expectation value of the linear momentum is given by

$$\begin{aligned} \langle p_x \rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) \hat{p}_x \psi(x,t) dx \\ &= -j\hbar \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\partial}{\partial x} \psi(x,t) dx, \end{aligned} \quad (5.44)$$

where we used

$$\hat{p}_x = -j\hbar \frac{\partial}{\partial x} \quad (5.45)$$

from the last of equations (5.14). In general, the expected value for a physical observable Q (with an associated operator \hat{Q}) is

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \hat{Q} \psi(x,t) dx. \quad (5.46)$$

Exercises

3. The Infinite Square-well Potential – The Particle in a Box Revisited

In an example in Chapter 4 we postulated that a quantum mechanical particle was confined in the interior of a one-dimensional box. We can relate this to the time-

independent Schrödinger equation by considering a situation where a particle is subjected to an infinite potential everywhere except in a spatial interval where the particle is free. That is, the potential is mathematically defined with

$$V(x) = \begin{cases} \infty, & \text{for } x \leq 0 \text{ and } x \geq \ell \\ 0, & \text{for } 0 < x < \ell. \end{cases} \quad (5.47)$$

Our goal is then to solve the time-independent Schrödinger equation in the two regions and ensure that the two solutions are consistent with one another. Let us start with the region where $V(x) = \infty$. In this case, the Schrödinger equation can be simplified with

$$\begin{aligned} E\varphi(x) &= \left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \varphi(x) \\ &= V(x)\varphi(x), \end{aligned} \quad (5.48)$$

for $x \leq 0$ and $x \geq \ell$. But since we require the energy of the system E to be finite, in order to be physically meaningful, while $V(x) = \infty$, then it must be that

$$\varphi(x) = 0, \quad \text{for } x \leq 0 \text{ and } x \geq \ell. \quad (5.49)$$

We then find that, as in the case of the particle in a box, the particle is confined to evolve within the region $0 < x < \ell$. Within that region the particle is free and the Schrödinger equation previously studied with equation (5.32) and solved to yield the more general wave function

$$\varphi(x) = A \cos\left(\frac{px}{\hbar}\right) + B \sin\left(\frac{px}{\hbar}\right), \quad \text{for } 0 < x < \ell, \quad (5.50)$$

with A and B some constants. However, we are also constrained by equation (5.49), which implies that $A = 0$ (because $\cos(0) = 1$) and

$$\frac{p\ell}{\hbar} = n\pi, \quad (5.51)$$

with $n = 1, 2, 3, \dots$. This is exactly the same solution we found for the particle in a box in Section 4.5 of Chapter 4. We then found that the admissible solutions are

$$\varphi_n(x) = \begin{cases} \sqrt{\frac{2}{\ell}} \sin\left(\frac{n\pi x}{\ell}\right), & \text{for } 0 < x < \ell \\ 0, & \text{elsewhere,} \end{cases} \quad (5.52)$$

with the associated energies

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2m\ell^2}, \quad (5.53)$$

for $n = 1, 2, 3, \dots$. It can be verified that the wave functions (5.52) are normalized when the square of their respective norm are integrated over all space.

We can now calculate the expectation values for x , p , and p^2 for any wave function $\varphi_n(x)$. The calculations for $\langle x \rangle$ give

$$\begin{aligned} \langle x \rangle &= \frac{2}{\ell} \int_0^\ell x \sin^2\left(\frac{n\pi x}{\ell}\right) dx \\ &= \frac{1}{\ell} \int_0^\ell x \left[1 - \cos\left(\frac{2n\pi x}{\ell}\right) \right] dx \\ &= \frac{1}{\ell} \left\{ \frac{x^2}{2} \Big|_0^\ell - \left[\frac{x\ell}{2n\pi} \sin\left(\frac{2n\pi x}{\ell}\right) \right]_0^\ell - \frac{\ell}{2n\pi} \int_0^\ell \sin\left(\frac{2n\pi x}{\ell}\right) dx \right\} \\ &= \frac{1}{\ell} \left\{ \frac{\ell^2}{2} - \left[0 + \left(\frac{\ell}{2n\pi}\right)^2 \cos\left(\frac{2n\pi x}{\ell}\right) \Big|_0^\ell \right] \right\} \\ &= \frac{\ell}{2}, \end{aligned} \quad (5.54)$$

where we integrated by parts with $u = x$ and $dv = \cos(2n\pi x/\ell)$ to go from the second to the third equation. For $\langle p \rangle$ we have (please note where the momentum operator is located)

$$\begin{aligned} \langle p \rangle &= \frac{2}{\ell} \int_0^\ell \sin\left(\frac{n\pi x}{\ell}\right) \left(-j\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{\ell}\right) dx \\ &= -\frac{2j\hbar}{\ell} \int_0^\ell \frac{n\pi}{\ell} \sin\left(\frac{n\pi x}{\ell}\right) \cos\left(\frac{n\pi x}{\ell}\right) dx \\ &= -\frac{jn\pi\hbar}{\ell^2} \int_0^\ell \sin\left(\frac{2n\pi x}{\ell}\right) dx \\ &= 0. \end{aligned} \quad (5.55)$$

We thus find that, although the mean position of the particle is $\ell/2$, its linear momentum is zero. This lends itself to the picture of a particle going back and forth within the box. On the other hand, we also have from the last of equations (5.55)

$$\begin{aligned}
\langle p^2 \rangle &= \frac{2}{\ell} \int_0^\ell \sin\left(\frac{n\pi x}{\ell}\right) \left(-\hbar^2 \frac{d^2}{dx^2}\right) \sin\left(\frac{n\pi x}{\ell}\right) dx \\
&= \frac{2}{\ell} \left(\frac{n\pi\hbar}{\ell^2}\right)^2 \int_0^\ell \sin\left(\frac{n\pi x}{\ell}\right) \sin\left(\frac{n\pi x}{\ell}\right) dx \\
&= \frac{1}{\ell} \left(\frac{n\pi\hbar}{\ell^2}\right)^2 \int_0^\ell \left[1 - \cos\left(\frac{2n\pi x}{\ell}\right)\right] dx \\
&= \left(\frac{n\pi\hbar}{\ell^2}\right)^2.
\end{aligned} \tag{5.56}$$

This equation is consistent with, and come have been guessed from, equation (5.53) for the energy since $p_n^2 = 2mE_n^2$ for a free particle.

5.3 Measurement and Commutators

Whenever a measurement is made on a quantum system, say, to determine its energy, the result must yield an energy level associated with one of the stationary states. For example, in the preceding problem of the infinite square-well potential the energy measured would be one of the different values E_n of equation (5.53) with the probability associated of having the function φ_n . As we saw in Exercise 7 at the end of Chapter 4, if the total wave function is given by

$$\psi(x) = \frac{1}{\sqrt{2}} [\varphi_m(x) + \varphi_n], \tag{5.57}$$

then the probability of funding E_m or E_n is $(1/\sqrt{2})^2 = 0.5$ for each, and zero for any other energy. The same would be true if we measured the momentum p .

The measurement process is a fairly complex, and not completely understood, process in quantum mechanics, but it is directly related to the application of the operator associated to the physical observable we intend to measure on the wave function of the system. As we just studied, measuring the expected value of the linear momentum when the system is in a given state n can be expressed mathematically with

$$\langle p \rangle = \int_{-\infty}^{\infty} \varphi_n^*(x) \hat{p} \varphi_n(x) dx, \tag{5.58}$$

where we clearly see that the operator \hat{p} for the linear momentum is acting on the wave function $\varphi_n(x)$.

Let us now suppose that our quantum system is composed of a single particle, on which we first measure the momentum and then the position. The expected value for this measuring sequence is then

$$\langle xp \rangle = \int_{-\infty}^{\infty} \varphi_n^*(x) x \hat{p} \varphi_n(x) dx. \quad (5.59)$$

This raises an important question. We saw, when discussing Young's double-slit experiment, that attempting to measure through which slit an electron went destroyed the interference pattern that would otherwise be measured. We are then justified to ask if measuring the momentum and then the position would yield the same result as measuring the position and then the momentum? That is, if the measuring process is known to alter a quantum mechanical system, then wouldn't the order of measurements matter? We can answer these questions by considering the following expectation value

$$\begin{aligned} \langle xp - px \rangle &= \int_{-\infty}^{\infty} \varphi_n^*(x) (x \hat{p} - \hat{p} x) \varphi_n(x) dx \\ &= -j\hbar \left\{ \int_{-\infty}^{\infty} \varphi_n^*(x) x \frac{d}{dx} \varphi_n(x) dx - \int_{-\infty}^{\infty} \varphi_n^*(x) \frac{d}{dx} [x \varphi_n(x)] dx \right\} \\ &= -j\hbar \left\{ \int_{-\infty}^{\infty} \varphi_n^*(x) x \frac{d}{dx} \varphi_n(x) dx \right. \\ &\quad \left. - \int_{-\infty}^{\infty} \varphi_n^*(x) \varphi_n(x) dx - \int_{-\infty}^{\infty} \varphi_n^*(x) x \frac{d}{dx} \varphi_n(x) dx \right\} \\ &= j\hbar \int_{-\infty}^{\infty} |\varphi_n(x)|^2 dx \\ &= j\hbar. \end{aligned} \quad (5.60)$$

It thus becomes apparent that *the order of the measurements is of paramount importance in quantum mechanics*, since $\langle xp - px \rangle \neq 0$. This result is entirely general and can be shown to be at the root of the Heisenberg inequality. The difference between such inverted sequences of measurements is so important in quantum mechanics that the following fundamental quantity is introduced for two operators \hat{a} and \hat{b}

$$[\hat{a}, \hat{b}] \equiv \hat{a}\hat{b} - \hat{b}\hat{a}. \quad (5.61)$$

The left-hand side of equation (5.61) is referred to the *commutator* of \hat{a} and \hat{b} . For the position and momentum operator we have

$$[x, \hat{p}] = j\hbar \hat{1}, \quad (5.62)$$

where $\hat{1}$ is the unit operator (like a unit matrix). It follows that we can rewrite equation (5.60) as

$$\begin{aligned}
\langle xp - px \rangle &= \int_{-\infty}^{\infty} \varphi_n^*(x) [x, \hat{p}] \varphi_n(x) dx \\
&= j\hbar \int_{-\infty}^{\infty} \varphi_n^*(x) \hat{1} \varphi_n(x) dx \\
&= j\hbar \int_{-\infty}^{\infty} \varphi_n^*(x) \varphi_n(x) dx \\
&= j\hbar.
\end{aligned}
\tag{5.63}$$

It is important to note that not all commutators equal $j\hbar$. For example, for a system exhibiting more than one dimension we have

$$[x, \hat{p}_y] = [y, \hat{p}_z] = 0, \tag{5.64}$$

etc.

5.4 Quantum Tunneling

Let us now consider the case of a particle of energy E incident on a potential barrier of level V_0 over the region $0 < x < L$, as shown in Figure 1. The particle is free in Regions I and III, and will have solutions

$$\begin{aligned}
\varphi_{\text{I}}(x) &= Ae^{jk_1x} + Be^{-jk_1x} \\
\varphi_{\text{III}}(x) &= Fe^{jk_1x} + Ge^{-jk_1x},
\end{aligned}
\tag{5.65}$$

where

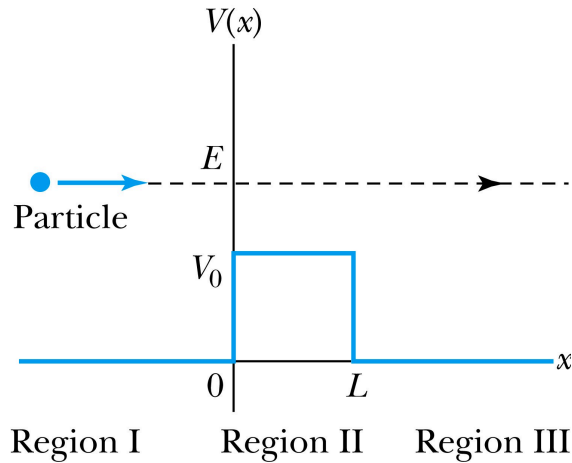


Figure 1 – A particle of energy E incident on a potential barrier of level V_0 over the region $0 < x < L$. Both cases $E < V_0$ and $E > V_0$ are possible.

$$k_1 = \frac{\sqrt{2mE}}{\hbar}. \quad (5.66)$$

Please note that the first terms on the right-hand side of both of equations (5.65) with the positive exponent are for propagation in the positive x direction (since the total wave function is of the type $\varphi_1(x)e^{-j\omega t}$). These are thus for the incident and transmitted waves in Regions I and III, respectively. It follows that the other two terms on the right-hand side are for propagation in the negative x direction, and therefore imply reflected waves. It is clear that it must be that $G = 0$ since there is nothing against which the particle could reflect in region III.

In Region II the Schrödinger equation becomes

$$E\varphi_{II}(x) = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0 \right) \varphi_{II}(x), \quad (5.67)$$

or

$$\frac{d^2}{dx^2} \varphi_{II}(x) + \frac{2m}{\hbar^2} (E - V_0) \varphi_{II}(x) = 0, \quad (5.68)$$

when $0 < x < L$. The solution for equation (5.68) is similar to the previous ones with

$$\varphi_{II}(x) = Ce^{jk_{II}x} + De^{-jk_{II}x}, \quad (5.69)$$

but with

$$k_{II} = \frac{\sqrt{2m(E - V_0)}}{\hbar}. \quad (5.70)$$

Since the wave function must be continuous at $x=0$ and $x=L$ we find that $\varphi_I(0) = \varphi_{II}(0)$ and $\varphi_{II}(L) = \varphi_{III}(L)$. Equations (5.65) and (5.69) then imply that

$$\begin{aligned} A + B &= C + D \\ Ce^{jk_{II}L} + De^{-jk_{II}L} &= Fe^{jk_1L}. \end{aligned} \quad (5.71)$$

Likewise, the derivatives of the wave function must also be continuous at $x=0$ and $x=L$. We therefore find that

$$\begin{aligned} jk_1(A - B) &= jk_{II}(C - D) \\ jk_{II}(Ce^{jk_{II}L} - De^{-jk_{II}L}) &= jk_1Fe^{jk_1L}. \end{aligned} \quad (5.72)$$

The solution to this problem consists in using the four equations in (5.71) and (5.72) to evaluate B , C , D , and F a function of A . We will not go through the details here and simply state the results.

Case when $E > V_0$

In classical mechanics, a particle going through a potential barrier when $E > V_0$ would be slowed down as it passed through it but would recover its initial velocity on its far side. This is simply accounted by the conservation of energy: the initial speed of the particle is simply $v_I = \sqrt{2E/m}$, changing to $v_{II} = \sqrt{2(E - V_0)/m}$ within the barrier in Region II, and finally recovering $v_{III} = v_I = \sqrt{2E/m}$ in Region III. We then find that a classical particle is transmitted with certainty from Region I to Region III. On the other hand, the quantum mechanical *transmission coefficient* obtained from equations (5.71) and (5.72) yields

$$T = \frac{|F|^2}{|A|^2} = \left[1 + \frac{V_0^2 \sin^2(k_{II}L)}{4E(E - V_0)} \right]^{-1}. \quad (5.73)$$

We therefore find the peculiar result that the particle is transmitted with a probability lower than one.

Case when $E < V_0$

Here a classical particle could never penetrate the barrier since this would require that $v_{II}^2 < 0$, which is impossible. Instead the conservations of linear momentum and energy imply that the particle is reflected back with a speed that is approximately v_I , but in the opposite direction. In the quantum mechanical case, however, we find from equation (5.70) that

$$k_{II}^2 = \frac{2m(E - V_0)}{\hbar^2} < 0, \quad (5.74)$$

and we write $k_{II} = j\kappa = j\sqrt{2m(V_0 - E)}/\hbar$. The transmission coefficient becomes

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)} \right]^{-1}. \quad (5.75)$$

We then find that the particle is able to *tunnel* through the barrier and be transmitted on its far side. Again this unexpected result is purely quantum mechanical.