Chapter 4
Schrödinger's Equation with Potential Energy: Introduction to Operators

The wave equations of electromagnetism are a natural consequence of Maxwell's equations. The time and spatial derivatives of the fields are found to be connected in a simple manner. But what *physical interpretation* can be given to the quantity $\nabla^2\psi(\mathbf{r},t)$ that appears in Schrödinger's equation? To understand the physical significance of this term, I have to introduce the concept of *operators*. Operators play a very important role in quantum mechanics but can be a bit confusing; specifically a distinction must be made between operators and functions. The plan is to look at the free particle Schrödinger equation and to show that the $-\left(\hbar^2/2m\right)\nabla^2$ term can be represented as $\hat{p}^2/2m = \hat{\mathbf{p}}\cdot\hat{\mathbf{p}}/2m$, where $\hat{\mathbf{p}}$ is an operator. I will then be able to generalize Schrödinger's equation to account for situations in which an external potential is present. To simplify matters, I work with the Schrödinger equation in one dimension; in the Appendix, an analogous development is given for the Schrödinger equation in three dimensions.

4.1 Hamiltonian Operator

So far I have been talking about free-particle solutions of Schrödinger's equation, which, in one dimension, is written as

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}. \tag{4.1}$$

The quantity $\partial^2/\partial x^2$ appearing in this equation is an *operator* that acts on functions in coordinate space. The operation simply involves second order differentiation of the function. Operators do just that, they *operate* on a function to produce a new function. For example, you could define the "Chicago operator" that translates the wave function to the top of the Sear's tower in Chicago.

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I've already looked at an integral solution of Eq. (4.1), namely

$$\psi(x,t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} dk\, \Phi(k) \exp[i\left(kx - \hbar k^2 t/2m\right)]. \tag{4.2}$$

Actually I could equally well *guess* this as a solution of the free-particle Schrödinger equation. Substituting this guess into Eq. (4.1), I find

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2}{2m\,(2\pi)^{1/2}} \int_{-\infty}^{\infty} dk\, \Phi(k) k^2 \exp[i\left(kx - \hbar k^2 t/2m\right)] \tag{4.3}$$

and

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{\hbar^2}{2m\,(2\pi)^{1/2}} \int_{-\infty}^{\infty} dk\, \Phi(k) k^2 \exp[i\left(kx - \hbar k^2 t/2m\right)], \tag{4.4}$$

implying that the solution works. I shall assume that $\psi(x,t)$ is normalized,

$$\int_{-\infty}^{\infty} dx\, |\psi(x,t)|^2 = 1. \tag{4.5}$$

Instead of working in coordinate space, I could work equally well in *momentum space*; that is, I can try to get a differential equation for $\Phi(p,t)$, where $\Phi(p,t)$ is the Fourier transform of $\psi(x,t)$ defined by

$$\Phi(p,t) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dx\, \psi(x,t) e^{-ipx/\hbar} \tag{4.6}$$

and

$$p = \hbar k \tag{4.7}$$

is given by the de Broglie relationship. It is *assumed* that $|\Phi(p,t)|^2$ is the probability density in momentum space, that is the probability density to find a momentum p for the particle at time t. Note that I need a factor of $\hbar^{-1/2}$ when momentum rather than k is used in defining the Fourier transform. This assures that $\Phi(p,t)$ has the correct units of $p^{-1/2}$ and that $\int_{-\infty}^{\infty} dp\, |\Phi(p,t)|^2 = 1$ if $|\psi(x,t)|^2$ is normalized.

Differentiating Eq. (4.6) with respect to time and using Eq. (4.1), I find

$$\begin{aligned} i\hbar \frac{\partial \Phi(p,t)}{\partial t} &= \frac{i\hbar}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dx\, \frac{\partial \psi(x,t)}{\partial t} e^{-ipx/\hbar} \\ &= -\frac{\hbar^2}{2m\,(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar} \frac{\partial^2 \psi(x,t)}{\partial x^2}. \end{aligned} \tag{4.8}$$

I now integrate by parts two times and assume that the wave function and its derivative vanish as x goes to plus or minus infinity (the wave packet is not infinite in extent). In this manner I obtain

$$i\hbar \frac{\partial \Phi(p,t)}{\partial t} = \frac{p^2}{2m\,(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar} \psi(x,t) = \frac{p^2}{2m} \Phi(p,t). \tag{4.9}$$

When this equation is generalized to three dimensions (see Appendix), it becomes

$$i\hbar \frac{\partial \Phi(\mathbf{p},t)}{\partial t} = \frac{p^2}{2m} \Phi(\mathbf{p},t) = \frac{\hat{p}^2}{2m} \Phi(\mathbf{p},t), \tag{4.10}$$

where the *operator* $\hat{p}^2$ is defined such that

$$\hat{p}^2 g(\mathbf{p}) = p^2 g(\mathbf{p}). \tag{4.11}$$

for any function $g(\mathbf{p})$. In other words, the operator $\hat{p}^2$ acting on a function $g(\mathbf{p})$ in momentum space simply *multiplies* $g(\mathbf{p})$ by p^2.

This is an important result. In coordinate space, the free particle Schrödinger equation is

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r},t). \tag{4.12}$$

The right-hand side of the free particle Schrödinger equation in coordinate space is $-\left(\hbar^2/2m\right)\nabla^2$, while it is $\hat{p}^2/2m$ in momentum space. This implies that the operator $\hat{p}^2$ acting on a function $f(\mathbf{r})$ in *coordinate* space results simply in $-\hbar^2\nabla^2 f(\mathbf{r})$; that is,

$$\hat{p}^2 = -\hbar^2 \nabla^2 \tag{4.13}$$

when acting in coordinate space. As a consequence, the Schrödinger equation can be written as

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = \frac{-\hbar^2 \nabla^2 \psi(\mathbf{r},t)}{2m} = \frac{\hat{p}^2}{2m} \psi(\mathbf{r},t). \tag{4.14}$$

Since $p^2/2m$ is equal to the energy of the free particle, I can rewrite Eq. (4.14) as

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = \hat{H} \psi(\mathbf{r},t), \tag{4.15}$$

where $\hat{H}$ is the *Hamiltonian* or energy operator.

I now conjecture that Eq. (4.15) remains valid even when there is a potential $V(\mathbf{r})$ present, with the Hamiltonian operator generalized as

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}. \tag{4.16}$$

In coordinate space, the operator $\hat{V}$ is defined such that

$$\hat{V}f(\mathbf{r}) = V(\mathbf{r})f(\mathbf{r}) \tag{4.17}$$

for any function $f(\mathbf{r})$. In other words, operator $\hat{V}$ acting on a function $f(\mathbf{r})$ in coordinate space simply picks out the value of the potential energy at the position of the function and *multiplies* it by $f(\mathbf{r})$.

Since $\hat{p}^2$ is equal to $-\hbar^2\nabla^2$ in the coordinate representation, I have a complete description of the Hamiltonian operator in the coordinate representation, namely

$$\hat{H}\psi(\mathbf{r},t) = \left[\frac{\hat{p}^2}{2m} + \hat{V}\right]\psi(\mathbf{r},t) = \left[-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})\right]\psi(\mathbf{r},t). \tag{4.18}$$

In the momentum representation, however, things are not so clear, since I do not know the effect of the potential operator in momentum space. To do so, I must use my assumption that $\psi(\mathbf{r},t)$ and $\Phi(\mathbf{p},t)$ are Fourier transforms of one another and make the assumption that the average value of the operators is identical in the coordinate and momentum representations. A derivation of Schrödinger's equation in momentum space is given in Chap. 11.

4.2 Time-Independent Schrödinger Equation

In coordinate space, the time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \hat{H}\psi(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r},t). \tag{4.19}$$

I guess a solution

$$\psi(\mathbf{r},t) = e^{-iEt/\hbar}\psi_E(\mathbf{r}), \tag{4.20}$$

substitute it into Eq. (4.19) and find that it works, *provided*

$$\hat{H}\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}), \tag{4.21}$$

an equation which is known as the *time-independent Schrödinger equation*. There may be many solutions of Eq. (4.21). Since Eq. (4.19) is linear, its general solution is found by forming a linear superposition of all the solutions of Eq. (4.21), namely

$$\psi(\mathbf{r},t) = \sum_E a_E e^{-iEt/\hbar} \psi_E(\mathbf{r}), \tag{4.22}$$

where the expansion coefficients a_E are determined by the initial conditions on $\psi(\mathbf{r},t)$.

Equation (4.22) is a *critically important* result. *If* we can solve the *time-independent* Schrödinger equation, we can build a solution to the time-dependent problem. This is why so much time is spent in quantum mechanics courses on the time-independent Schrödinger equation. However you should not forget that the interesting dynamics of a quantum system is obtained only through a solution of the *time-dependent* Schrödinger equation. In order to solve equations of the type given in Eq. (4.21), I will need the additional ammunition to be provided in Chap. 5.

4.3 Summary

The concept of an operator in quantum mechanics has been introduced. I found that the square of the momentum operator is proportional to the Laplacian operator in coordinate space. We have seen that it is possible to obtain a solution of the time-dependent Schrödinger equation if we are able to solve the time-independent Schrödinger equation. The formal method for solving the time-independent Schrödinger is given in the next chapter, where I discuss the properties of operators in a more systematic fashion.

4.4 Appendix: Schrödinger Equation in Three Dimensions

Schrödinger's equation in three dimensions is

$$i\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r},t). \tag{4.23}$$

As in the one-dimensional case, I *guess* a solution of the form

$$\psi(\mathbf{r},t) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{k}\, \Phi(\mathbf{k}) \exp[i\left(\mathbf{k}\cdot\mathbf{r} - \hbar k^2 t/2m\right)], \tag{4.24}$$

which is easily shown to be a solution of Eq. (4.23).

In three dimensions, $\Phi(\mathbf{p},t)$ is defined by

$$\Phi(\mathbf{p},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{r}\, \psi(\mathbf{r},t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{4.25}$$

where

$$\mathbf{p} = \hbar \mathbf{k} \tag{4.26}$$

is given by the de Broglie relationship.

Differentiating Eq. (4.25) with respect to time and using Eq. (4.23), I find

$$\begin{aligned} i\hbar \frac{\partial \Phi(\mathbf{p}, t)}{\partial t} &= \frac{i\hbar}{(2\pi\hbar)^{3/2}} \int d\mathbf{r} \, \frac{\partial \psi(\mathbf{r}, t)}{\partial t} e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \\ &= -\frac{\hbar^2}{2m\,(2\pi\hbar)^{3/2}} \int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \nabla^2 \psi(\mathbf{r}, t). \end{aligned} \tag{4.27}$$

I now use the vector identity

$$\begin{aligned} \nabla^2 \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] = &-\frac{p^2}{\hbar^2} \psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} - 2i e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \frac{\mathbf{p}}{\hbar} \cdot \nabla \psi(\mathbf{r}, t) \\ &+ e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \nabla^2 \psi(\mathbf{r}, t) \end{aligned} \tag{4.28}$$

to rewrite the integral appearing in Eq. (4.27) as

$$\begin{aligned} \int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \nabla^2 \psi(\mathbf{r}, t) &= \int d\mathbf{r}\, \nabla^2 \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] \\ &+ \frac{p^2}{\hbar^2} \int d\mathbf{r}\, \psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} + 2i \frac{\mathbf{p}}{\hbar} \cdot \int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \nabla \psi(\mathbf{r}, t). \end{aligned} \tag{4.29}$$

The first integral on the right-hand side (rhs) of Eq. (4.29) can be evaluated using the divergence theorem as

$$\begin{aligned} \int d\mathbf{r}\, \nabla^2 \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] &= \int d\mathbf{r}\, \nabla \cdot \nabla \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] \\ &= \oint_S \nabla \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] \cdot d\mathbf{a}. \end{aligned} \tag{4.30}$$

The surface integral is taken over a surface whose radius approaches infinity; this integral vanishes if the wave function falls off more rapidly than r^{-2} as $r \to \infty$, that is,

$$\oint_S \nabla \left[\psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \right] \cdot d\mathbf{a} \sim 0. \tag{4.31}$$

The third integral on the rhs Eq. (4.29) can be written as

$$
\begin{aligned}
&2i\frac{\mathbf{p}}{\hbar}\cdot\int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\nabla\psi(\mathbf{r},t) \\
&= 2i\frac{\mathbf{p}}{\hbar}\cdot\int d\mathbf{r}\left\{\nabla\left[e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{r},t)\right]+\left(\frac{i\mathbf{p}}{\hbar}\right)e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{r},t)\right\} \\
&= 2i\frac{\mathbf{p}}{\hbar}\cdot\left\{\oint_S \psi(\mathbf{r},t)e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}d\mathbf{a}+\left(\frac{i\mathbf{p}}{\hbar}\right)\int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{r},t)\right\} \\
&= -2\frac{p^2}{\hbar^2}\int d\mathbf{r}\,\psi(\mathbf{r},t)e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar},
\end{aligned}
\tag{4.32}
$$

where the generalized Gauss' theorem given in Eq. (2.21b) was used to convert the integral containing $\nabla\left[e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\psi(\mathbf{r},t)\right]$ into a surface integral that vanishes as the radius of the surface approaches infinity. Combining Eqs. (4.29)–(4.32) and using Eq. (4.25), I find

$$
\int d\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\nabla^2\psi(\mathbf{r},t) = -\frac{p^2}{\hbar^2}\int d\mathbf{r}\,\psi(\mathbf{r},t)e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} = -\frac{p^2}{\hbar^2}(2\pi\hbar)^{3/2}\,\Phi(\mathbf{p},t).
\tag{4.33}
$$

Substituting this result into Eq. (4.27), I finally arrive at

$$
i\hbar\frac{\partial\Phi(\mathbf{p},t)}{\partial t} = \frac{p^2}{2m}\Phi(\mathbf{p},t),
\tag{4.34}
$$

which is Eq. (4.10).

4.5 Problems

1. Given a Hamiltonian of the form

$$
\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)
$$

in coordinate space, show that the most general solution of the time-dependent Schrödinger equation is

$$
\psi(x,t) = \sum_E a_E\psi_E(x)e^{-iEt/\hbar} = \sum_E a_E(t)\psi_E(x)
$$

provided $a_E(t) = a_E e^{-iEt/\hbar}$ and

$$\hat{H}\psi_E(x) = E\psi_E(x).$$

Prove that the probability to be in a given quantum state, given by $|a_E(t)|^2$, is constant in time, but that, in general, the probability $|\psi(x,t)|^2$ varies in time.

2. Why doesn't the momentum distribution change in time for a free particle, even though the coordinate space distribution changes? How would you expect the wave function in momentum space to change for a particle falling in a uniform gravitational field? Explain. What is the difference between the operator $\hat{p}^2$ in momentum space and in coordinate space?

3. Suppose you are given a Hamiltonian of the form

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x),$$

with $\psi(x,0) = f(x)$. In terms of the eigenfunctions and eigenenergies of $\hat{H}$, derive an expression for $\psi(x,t)$.

4. Prove that

$$\int \psi^*(x,t)\hat{H}\psi(x,t)dx$$

is constant in time. Why must this be the case?

5. Consider a wave function for a free particle having mass m of the form

$$\psi(x) = Ne^{-x^2/a^2}\Theta(b-x)\Theta(b+x),$$

where $b \gg a > 0$, N is a normalization constant, and $\Theta(x)$ is a Heaviside function equal to 0 for $x < 0$ and 1 for $x \geq 1$. For $b \gg a$, you might think that it would be an excellent approximation to consider the wave function as a Gaussian packet having average energy $\langle E \rangle = \left\langle \hat{p}^2 \right\rangle / 2m = \hbar^2 / \left(4ma^2\right)$. Use the result of Problem 2.9 to show that this is *not* the case—for any finite b, the average energy is infinite. This occurs because of the point jump discontinuity in the wave function.