Chapter 3 THE SCHRÖDINGER EQUATION

The discussion in this chapter constructs the ideas that lead to the postulates of quantum mechanics, which are given at the end of the chapter. The overall picture is that quantum mechanical systems such as atoms and molecules are described by mathematical functions that are solutions of a differential equation called the Schrödinger equation.

A *scientific postulate* is a generally accepted statement, which is accepted because it is consistent with experimental observation and serves to predict or explain a variety of observations. These postulates also are known as *physical laws*. Postulates cannot be derived by any other fundamental considerations. Newton's second law, f = ma, is an example of a postulate that is accepted and used because it explains the motion of objects like baseballs, bicycles, rockets, and cars. One goal of science is to find the smallest and most general set of postulates that can explain all observations. A whole new set of postulates was added with the invention of Quantum Mechanics. The Schrödinger equation is the fundamental postulate of Quantum Mechanics. In the previous chapter we saw that many individual quantum postulates were introduced to explain otherwise inexplicable phenomena. We will see that *quantization* and the relations $E = h\nu$ and $p = h/\lambda$, discussed in the last chapter, are consequences of the Schrödinger equation. In other words the Schrödinger equation is a more general and fundamental postulate.

A *differential equation* is a mathematical equation involving one or more derivatives. The analytical solution to a differential equation is the expression or function for the dependent variable that gives an identity when substituted into the differential equation. A mathematical function is a rule that assigns a value to one quantity using the values of other quantities. Any mathematical function can be expressed not only by a mathematical formula, but also in words, as a table of data, or by a graph. Numerical solutions to differential equations also can be obtained. In numerical solutions, the behavior of the dependent variable is expressed as a table of data or by a graph; no explicit function is provided.

Exercise 3.1 The differential equation $\frac{dy(x)}{dx} = 2$ has the solution y(x) = 2 x + b, where b is a constant. This function y(x) defines the family of straight lines on a graph with a slope of 2. Show that this function is a solution to the differential equation by substituting for y(x) in the differential equation. How many solutions are there to this differential equation? For one of these solutions, construct a table of data showing pairs of x and y values, and use the data to sketch a graph of the function. Describe this function in words.

Some differential equations have the property that the derivative of the function gives the function back multiplied by a constant. The differential equation for a first-order chemical reaction is one example. This differential equation and the solution for the concentration of the reactant are given below.

$$\frac{dC(t)}{dt} = -kC(t) \qquad C(t) = C_0 e^{-kt} \qquad \{3\text{-}1\}$$

Exercise 3.2 Show that C(t) is a solution to the differential equation.

Another kind of differential equation, which is illustrated by Equation {3-2}, has the property that the second derivative of the function yields the function multiplied by a constant. Both of these types of differential equations are found in Quantum Mechanics.

$$\frac{d^2\Psi(x)}{dx^2} = k\Psi(x) \qquad \{3\text{-}2\}$$

Exercise 3.3 What is the value of the constant in the above differential equation when Ψ(x) = cos(3x)?

Exercise 3.4 What other functions, in addition to the cosine, have the property that the second derivative of the function yields the function multiplied by a constant?

Since some mathematical functions, such as the sine and cosine, go through repeating periodic maxima and minima, they produce graphs that look like waves. Such functions can themselves be thought of as waves and can be called wavefunctions. We now make a mathematically intuitive leap. If electrons, atoms, and molecules have wave-like properties, then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms, and molecules. This differential equation is called the *wave equation*, and the solution is called the *wavefunction*. Such thoughts may have motivated Erwin Schrödinger to find (i.e. create) the wave equation, which we now accept as the fundamental postulate of Quantum Mechanics.

In this chapter we want to make the Schrödinger equation and other postulates of Quantum Mechanics seem plausible. We follow a *train-of-thought* that could resemble Schrödinger's original thinking. The discussion is not a derivation; it is a *plausibility argument*. In the end we accept and use the Schrödinger equation and associated concepts because they explain the properties of microscopic objects like electrons and atoms and molecules.

3.1 A Classical Wave Equation

The easiest way to find a differential equation that will provide wavefunctions as solutions is to start with a wavefunction and work backwards. We will consider a sine wave, take its first and second derivatives, and then examine the results. The amplitude of a sine wave can depend upon position, x, in space,

$$A(x) = A_0 \sin\left(\frac{2\pi x}{\lambda}\right) \qquad \{3\text{-}3\}$$

or upon time, t,

$$A(t) = A_0 \sin(2\pi\nu t) \qquad \{3\text{-}4\}$$

or upon both space and time,

$$A(x,t) = A_0 \sin\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right) \qquad \{3\text{-}5\}$$

We can simplify the notation by using the definitions of a wave vector, $k = 2\pi/\lambda$, and the angular frequency, $\omega = 2\pi\nu$ to get

$$A(x,t) = A_0 \sin(kx - \omega t) \qquad \{3\text{-}6\}$$

When we take partial derivatives of A(x,t) with respect to both x and t, we find that the second derivatives are remarkably simple and similar.

$$\frac{\partial^2 A(x,t)}{\partial x^2} = -k^2 A_0 \sin(kx - \omega t) = -k^2 A(x,t) \qquad \{3\text{-}7\}$$

$$\frac{\partial^2 A(x,t)}{\partial t^2} = -\omega^2 A_0 \sin(kx - \omega t) = -\omega^2 A(x,t) \qquad \{3\text{-}8\}$$

By looking for relationships between the second derivatives, we find that both involve A(x,t); consequently an equality is revealed.

$$k^{-2} \frac{\partial^2 A(x,t)}{\partial x^2} = -A(x,t) = \omega^{-2} \frac{\partial^2 A(x,t)}{\partial t^2} \qquad \{3\text{-}9\}$$

Recall that ν and λ are related; their product gives the velocity of the wave, $\nu\lambda = v$. Be careful to distinguish between the similar but different symbols for frequency ν, and the velocity v. If in $\omega = 2\pi\nu$ we replace ν with v/λ, then

$$\omega = \frac{2\pi v}{\lambda} = vk \qquad \{3\text{-}10\}$$

and Equation {3-9} can be rewritten to give what is known as the classical wave equation in one dimension. This equation is very important. It is a differential equation whose solution describes all waves in one dimension that move with a constant velocity (e.g. the vibrations of strings in musical instruments), and it can be generalized to three dimensions. The classical wave equation in one dimension is

$$\frac{\partial^2 A(x,t)}{\partial x^2} = v^{-2}\frac{\partial^2 A(x,t)}{\partial t^2} \qquad \{3\text{-}11\}$$

Exercise 3.5 Complete the steps leading from Equation {3-5} to Equations {3-7} and {3-8} and then to Equation {3-11}.

3.2 Invention of the Schrödinger Equation

Although we used a sine function to obtain the classical wave equation, functions other than the sine function can be substituted for A in Equation {3-11}. Our goal as chemists is to seek a method for finding the wavefunctions that are appropriate for describing electrons, atoms, and molecules. In order to reach this objective, we need the appropriate wave equation.

Exercise 3.6 Show that the functions $e^{i(kx + \omega t)}$ and $\cos(kx - \omega t)$ also satisfy the classical wave equation. Note that i is a constant equal to $\sqrt{-1}$.

We start our search for the quantum mechanical wave equation by thinking about how to find the solutions to differential equations. We apply these thoughts to the classical wave equation and suggest a wavefunction that has the necessary properties. After incorporating the de Broglie relationship and the total energy as a sum of kinetic and potential energy terms, we will arrive at the one-dimensional Schrödinger equation.

A general method for finding solutions to differential equations that depend on more than one variable (x and t in this case) is to separate the variables into different terms. This separation makes it possible to write the solution as a product of two functions, one that depends on x and one that depends on t. This important technique is called the *Method of Separation of Variables*. This technique is used in most of the applications that we will be considering.

For the classical wave equation (Equation {3-11}), separating variables is very easy because x and t do not appear together in the same term in the differential equation. In fact, they are on opposite sides of the equation. The variables already have been separated, and we only have to see what happens when we substitute a product function into this equation. It is common in Quantum Mechanics to symbolize the functions that are solutions to Schrödinger's equation as Ψ (upper-case psi), ψ (lower-case psi) or ϕ (lower-case phi), so we use $\psi(x)$ as the x-function, and examine the consequences of using $\cos(\omega t)$ as one possibility for the t-function. (▲Greek Alphabet)

$$\Psi(x,t) = \psi(x)\ \cos(\omega t) \qquad \{3-12\}$$

After substituting Equation {3-12} into the classical wave equation (3-11) and differentiating, we obtain

$$\cos(\omega t)\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{\omega^2}{v^2}\psi(x)\cos(\omega t) \qquad \{3\text{-}13\}$$

which yields, after simplifying and rearranging,

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{\omega^2}{v^2}\psi(x) = 0 \qquad \{3\text{-}14\}$$

We now include the idea that we are trying to find a wave equation for a particle. We introduce the particle momentum by using de Broglie's relation to replace ω^2/v^2 with $p^2/\hbar^2$, where $\hbar = h/2\pi$ (called h-bar).

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{p^2}{\hbar^2}\psi(x) = 0 \qquad \{3\text{-}15\}$$

Exercise 3.7 Show that $\omega^2/v^2 = p^2/\hbar^2$.

Next we will use the total energy of a particle as the sum of the kinetic energy and potential energy to replace the momentum in Equation {3-15}.

$$E = T + V(x) = \frac{p^2}{2m} + V(x) \qquad \{3\text{-}16\}$$

Note that we have included the idea that the potential energy is a function of position. Each atomic or molecular system we will consider in the following chapters will have different potential energy functions.

Solving Equation {3-16} for p^2 and substituting it into Equation {3-15} gives us **the Schrödinger Equation**,

$$\frac{\partial^2\psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0 \qquad \{3\text{-}17\}$$

which usually is written in rearranged form,

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \qquad \{3\text{-}18\}$$

Notice that the left side of Equation {3-18} consists of the two terms corresponding to the kinetic energy and the potential energy. When we look at the left side of Equation {3-18}, we can deduce a method of extracting the total energy from a known wavefunction, or we can use Equation {3-18} to find the wavefunction. Finding wavefunctions for models of interesting chemical phenomena will be one of the tasks we will accomplish in this text.

Exercise 3.8 Show the steps that lead from Equations {3-11} and {3−12} to Equation {3-18}.

More precisely, Equation {3-18} is the Schrödinger equation for a particle of mass m moving in one dimension (x) in a potential field specified by V(x). Since this equation does not contain time, it often is called the *Time-Independent Schrödinger Equation*. As mentioned previously, functions like $\psi(x)$ are called wavefunctions because they are solutions to this wave equation. The term, *wave*, simply denotes oscillatory behavior or properties. The significance of the wavefunction will become clear as we proceed. For now, $\psi(x)$ is the wavefunction that accounts for or describes the wave-like properties of particles.

The Schrödinger equation for a particle moving in three dimensions (x, y, z) is obtained simply by adding the other second derivative terms and by including the three-dimensional potential energy function. The wavefunction ψ then depends on the three variables x, y, and z.

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z) \qquad \{3\text{-}19\}$$

Exercise 3.9 Write the Schrödinger equation for a particle of mass m moving in a 2-dimensional space with the potential energy given by $V(x, y) = -(x^2 + y^2)/2$.

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) \qquad \{3\text{-}20\}$$

The del operator,

$$\nabla = \vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z} \qquad \{3\text{-}21\}$$

also is used in Quantum Mechanics. Remember, symbols with arrows over them are unit vectors.

Exercise 3.10 Write the del-operator and the Laplacian operator for two dimensions and rewrite your answer to Exercise 3.9 in terms of the Laplacian operator.

3.3 Operators, Eigenfunctions, Eigenvalues, and Eigenstates

The Laplacian operator is called an operator because it does something to the function that follows: namely, it produces or generates the sum of the three second-derivatives of the function. Of course, this is not done automatically; you must do the work, or remember to use this operator properly in algebraic manipulations. Symbols for operators are denoted by a caret ^ over the symbol, unless the symbol is used exclusively for an operator, e.g. ∇ (del/nabla), or does not involve differentiation, e.g. **r** for position.

From Equation {3-19}, we can identify the total energy operator, which is called the *Hamiltonian operator*, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \qquad \{3\text{-}22\}$$

Using this notation we write the Schrödinger Equation (Equation {3-19}) as

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z) \qquad \{3\text{-}23\}$$

The term *Hamiltonian*, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, H = T + V, rather than Newton's second law, f = ma. Equation {3-23} says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an *eigenvalue equation*. The function is called an *eigenfunction*, and the resulting numerical value is called the *eigenvalue*. *Eigen* here is the German word meaning *self* or *own*.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A *physical observable* is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the *eigenvalue*, and the system is said to be in an *eigenstate*. Equation {3-23} states this principle mathematically for the case of energy as the observable.

3.4 Momentum Operators

One of the tasks we must be able to do as we develop the quantum mechanical representation of a physical system is to replace the classical variables in mathematical expressions with the corresponding quantum mechanical operators. In the preceding section, operators were identified for the total energy and the kinetic energy. Potential energy operators will be introduced case by case in the following chapters. In the remaining paragraphs, we will focus on the momentum operator.

Momentum operators now can be obtained from the kinetic energy operator. Since the classical expression for the kinetic energy of a particle moving in one dimension, along the x-axis, is

$$T_x = \frac{p_x^2}{2m} \qquad \{3\text{-}24\}$$

we expect from Equation {3-18} that

$$\hat{T}_x = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \{3\text{-}25\}$$

so we can identify the operator for the square of the x-momentum as

$$\hat{p}_x{}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2} \qquad \{3\text{-}26\}$$

Since $\hat{p}_x{}^2$, can be interpreted to mean $\hat{p}_x \cdot \hat{p}_x$, there are two possibilities for $\hat{p}_x$, namely

$$\hat{p}_x = i\hbar \frac{\partial}{\partial x} \quad \text{or} \quad \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \qquad \{3\text{-}27\}$$

where $i = \sqrt{-1}$. The second possibility is the best choice, as explained below.

In making this choice, consider the e^{ikx} function. This function is an eigenfunction of both possible forms for the momentum operator. This fact can be used to choose which form of the momentum operator to use. You can make this decision yourself in Exercise 3.11.

Exercise 3.11 Demonstrate that the function e^{ikx} is an eigenfunction of either momentum operator.
Plan: Start with $\hat{p}_x \psi(x) = p_x \psi(x)$ where $\psi(x) = e^{ikx}$.
Operate on $\psi(x) = e^{ikx}$ with $\pm i\hbar \frac{\partial}{\partial x}$ to show that $p_x = \mp\hbar k$ $p_x = \mp \hbar k$.
Which do you prefer, $p_x = +\hbar k$ or $p_x = -\hbar k$?

If we use the momentum operator that has the - sign, we get the momentum and the wave vector pointing in the same direction, $p_x = +\hbar k$, which is the preferred result corresponding to the de Broglie relation.

The review of vectors and scalar products ▲ may help you with the following exercises.

Exercise 3.12 Show graphically, using a unit vector diagram, that $\vec{x} \cdot \vec{x} = 1$ and $\vec{x} \cdot \vec{y} = 0$.

Exercise 3.13 Consider a particle moving in three dimensions. The total momentum, which is a vector, is

$$p = \vec{x}p_x + \vec{y}p_y + \vec{z}p_z$$

where $\vec{x}$, $\vec{y}$, and $\vec{z}$ are unit vectors pointing in the x, y, and z directions, respectively. Write the operators for the momentum of this particle in the x, y, and z directions, and show that the total momentum operator is $-i\hbar\nabla = -i\hbar\left(\vec{x}\frac{\partial}{\partial x} + \vec{y}\frac{\partial}{\partial y} + \vec{z}\frac{\partial}{\partial z}\right)$ and ∇ is the vector operator called del. Show that the scalar product $\nabla \cdot \nabla$ produces the Laplacian operator.

Exercise 3.14 Following Exercise 3.11, show that the de Broglie relation $p = h/\lambda$ follows from the definition of the momentum operator and the momentum eigenfunction for a one-dimensional space.

Exercise 3.15 Write the wavefunction for an electron moving in the z-direction with an energy of 100 eV. The form of the wavefunction is e^{ikz}. You need to find the value for k. Obtain the electron's momentum by operating on the wavefunction with the momentum operator.

3.5 The Time-Dependent Schrödinger Equation

A second Schrödinger equation, called the time-dependent Schrödinger equation, is used to find the time dependence of the wavefunction. This equation relates the energy to the first time derivative analogous to the classical wave equation that involved the second time derivative. This equation,

$$\hat{H}(r,t)\Psi(r,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,t) \qquad \{3\text{-}28\}$$

where **r** represents the spatial coordinates (x, y, z), must be used when the Hamiltonian operator depends on time, e.g. when a time dependent external field causes the potential energy to change with time.

Even if the Hamiltonian does not depend on time, we can use this equation to find the time dependence $\phi(t)$ of the eigenfunctions of $\hat{H}(\mathbf{r})$. First we write the wavefunction $\Psi(\mathbf{r},t)$ as a product of a space function and a time function, $\psi(\mathbf{r})\phi(t)$, and substitute into Equation {3-28}.

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})\varphi(t) \qquad \{3\text{-}29\}$$

We use a product function because the space and time variables are separated in Equation {3-28} when the Hamiltonian operator does not depend on time. Since $\psi(\mathbf{r})$ is an eigenfunction of $\hat{H}(\mathbf{r})$ with eigenvalue E, this substitution leads to Equation {3-31}

$$\begin{aligned} \hat{H}(r)\psi(r)\varphi(t) &= i\hbar\frac{\partial}{\partial t}\psi(r)\varphi(t) \\ E\psi(r)\varphi(t) &= i\hbar\psi(r)\frac{\partial}{\partial t}\varphi(t) \end{aligned} \qquad \{3\text{-}30\}$$

which rearranges to

$$\frac{d\varphi(t)}{\varphi(t)} = \frac{-iE}{\hbar}dt \qquad \{3\text{-}31\}$$

Integration gives

$$\varphi(t) = e^{-i\omega t} \qquad \{3\text{-}32\}$$

by setting the integration constant to 0 and using the definition $\omega = E/\hbar$. Thus, we see the time dependent Schrödinger equation contains the condition $E = \hbar\omega$ proposed by Planck and Einstein.

The eigenfunctions of a time-independent Hamiltonian therefore have an oscillatory time dependence given by a complex function, i.e. a function that involves $\sqrt{-1}$.

$$\Psi(r,t) = \psi(r)e^{-i\omega t} \qquad \{3\text{-}33\}$$

When molecules are described by such an eigenfunction, they are said to be in an eigenstate of the time-independent Hamiltonian operator. We will see that all observable properties of a molecule in an eigenstate are constant or independent of time because the calculation of the properties from the eigenfunction is not affected by the time dependence of the eigenfunction. A wavefunction with this oscillatory time dependence $e^{-i\omega t}$ therefore is called a *stationary-state function*.

When a system is not is a stationary state, the wavefunction can be represented by a sum of eigenfunctions like those above. In this situation, the oscillatory time dependence does not cancel out in calculations, but rather accounts for the time dependence of physical observables. Examples are provided in Chapter 4, Activity 2, and Chapter 5, Activity 1.

Exercise 3.16 Complete the steps leading from Equation {3-28} to Equation{3-33}.

Exercise 3.17 Show that Equation {3-33} is a solution to Equation {3-28} when the Hamiltonian operator does not depend on time and ψ(r) is an eigenfunction of the Hamiltonian operator.

This might be a good time to review complex numbers ▲

3.6 Meaning of the Wavefunction

Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the square of the modulus.

$$\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) = |\Psi(\mathbf{r},t)|^2 \qquad \{3\text{-}34\}$$

where **r** is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field.

At one time it was thought that for an electron described by the wavefunction $\psi(\mathbf{r})$, the quantity $e\psi^*(\mathbf{r}_i)\psi(\mathbf{ri})d\tau$ was the amount of charge to be found in the volume $d\tau$ located at $\mathbf{r}_i$. However, Max Born found this interpretation to be inconsistent with the results of scattering experiments. The Born interpretation, which generally is accepted today, is that $\psi^*(\mathbf{r}_i)\psi(\mathbf{r}_i)d\tau$ is the probability that the electron is in the volume $d\tau$, located at $\mathbf{r}_i$. The Born interpretation therefore calls the wavefunction the *probability amplitude*, the absolute square of the wavefunction is called the *probability density*, and the probability density times a volume element in three-dimensional space ($d\tau$) is the *probability*. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

Exercise 3.18 Show that the square of the modulus of $\Psi(\mathbf{r},t) = \psi(\mathbf{r})\, e^{-i\,\omega\, t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Exercise 3.19 According to the Born interpretation, what is the physical significance of $e\psi^*(\mathbf{r}_0)\psi(\mathbf{r}_0)d\tau$?

3.7 Expectation Values

An important deduction can be made if we multiply the left-hand side of the Schrödinger equation by $\psi^*(x)$, integrate over all values of x, and examine the potential energy term that arises. We can deduce that the potential energy integral provides the average value for the potential energy. Likewise we can deduce that the kinetic energy integral provides the average value for the kinetic energy. This is shown in Equation {3-35}. If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral. In the equation below, the symbol $\langle H \rangle$ is used to denote the average value for the total energy.

$$\langle H \rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)\,dx \quad = \quad \int_{-\infty}^{\infty} \psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)\,dx \; + \int_{-\infty}^{\infty} \psi^*(x)\,V(x)\,\psi(x)\,dx$$

kinetic energy term + potential energy term

{3-35}

Exercise 3.20 Evaluate the two integrals in Equation {3-35} for the wavefunction ψ(x) = sin(kx) and the potential function V(x) = x.

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum. The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation {3-35}. For example, the harmonic potential in one dimension is $\frac{1}{2}kx^2$. (Note: here k is the force constant and not the wave vector. Unfortunately just like words, a symbol can have more than one meaning, and the meaning must be gotten from the context.) The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the *commutative property*. The potential energy integral therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \qquad \{3\text{-}36\}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is ψ*(x)ψ(x)dx, multiply this probability by the potential energy at x, and sum (i.e. integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle. This integral therefore is called the *average-value integral* or the *expectation-value integral* because it gives the average result of a large number of measurements of the particle's potential energy.

When an operator involves differentiation, it does not commute with the wavefunctions, e.g.

$$\psi^*(x)\frac{\partial^2}{\partial x^2}\psi(x) \neq \psi^*(x)\psi(x)\frac{\partial^2}{\partial x^2} \neq \frac{\partial^2}{\partial x^2}\left(\psi^*(x)\psi(x)\right) \qquad \{3\text{-}37\}$$

but the interpretation of the kinetic energy integral in Equation {3-35} is the same as for the potential energy. This integral gives the average kinetic energy of the particle.

These expectation value integrals are very important in Quantum Mechanics. They provide us with the average values of physical properties (e.g. like energy, momentum, or position) because in many cases precise values cannot, even in principle, be determined. If we know the average of some quantity, it also is important to know whether the distribution is narrow, i.e. all values are close to the average, or broad, i.e. many values differ considerably from the average. The width of a distribution is characterized by its *variance*.

3.8 Postulates of Quantum Mechanics

We now summarize Chapter 3 by formally stating the postulates of Quantum Mechanics that have been introduced. The application of these postulates will be illustrated in subsequent chapters. A summary of the Postulates is available through a hyperlink on the left navigation bar.

1. The properties of a quantum mechanical system are determined by a wavefunction $\Psi(\mathbf{r},t)$ that depends upon the spatial coordinates of the system and time, $\mathbf{r}$ and t. For a single particle system, $\mathbf{r}$ is the set of coordinates of that particle $\mathbf{r} = (x_1, y_1, z_1)$. For more than one particle, $\mathbf{r}$ is used to represent the complete set of coordinates $\mathbf{r} = (x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_n, y_n, z_n)$. Since the state of a system is defined by its properties, Ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

2. The wavefunction is interpreted to be the probability amplitude and the absolute square of the wavefunction, $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)$, is interpreted to be the probability density at time t. A probability density times a volume is a probability, so for one particle $\Psi^*(x_1,y_1,z_1,t)\Psi(x_1,y_1,z_1,t)dx_1dy_1dz_1$ is the probability that the particle is in the volume $dx_1dy_1dz_1$ located at x_1,y_1,z_1 at time t. For a many particle system, we write the volume element as $d\tau = dx_1dy_1dz_1 \dots dx_ndy_ndz_n$; and $\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)d\tau$ is the probability that particle 1 is in the volume $dx_1dy_1dz_1$ at $x_1y_1z_1$ and particle 2 is in the volume $dx_2dy_2dz_2$ at $x_2y_2z_2$, etc. Because of this probabilistic interpretation, the wavefunction must be normalized.

$$\int_{\text{all space}} \Psi^*(r,t)\Psi(r,t)d\tau = 1 \qquad \{3\text{-}38\}$$

The integral sign here represents a multi-dimensional integral involving all coordinates: $x_1 \dots z_n$.

3. For every observable property of a system there is a quantum mechanical operator. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector

$$r = (x,y,z) = x\vec{x} + y\vec{y} + z\vec{z} \qquad \{3\text{-}39\}$$

The operator for a component of momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \{3\text{-}40\}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \qquad \{3\text{-}41\}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \qquad \{3\text{-}42\}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m} \right) \nabla^2 \qquad \{3\text{-}43\}$$

The Hamiltonian operator $\hat{H}$ is the operator for the total energy. In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

4. The time-independent wavefunctions of a time-independent Hamiltonian are found by solving the time-independent Schrödinger equation.

$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \{3\text{-}44\}$$

These wavefunctions are called stationary-state functions because the properties of a system in such a state, i.e. a system described by the function $\psi(\mathbf{r})$, are time independent.

5. The time evolution or time dependence of a state is found by solving the time-dependent Schrödinger equation.

$$\hat{H}(r,t)\Psi(r,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,t) \qquad \{3\text{-}45\}$$

For the case where $\hat{H}$ is independent of time, the time dependent part of the wavefunction is $e^{-i\omega t}$ where $\omega = E/\hbar$ or equivalently $\nu = E/h$, which shows that the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation. This oscillatory time dependence of the probability amplitude does not affect the probability density or the observable properties because in the calculation of these quantities, the imaginary part cancels in multiplication by the complex conjugate.

6. If a system is described by the eigenfunction Ψ of an operator Â then the value measured for the observable property corresponding to Â will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}\Psi = a\Psi \qquad \{3\text{-}46\}$$

7. If a system is described by a wavefunction Ψ, which is not an eigenfunction of an operator Â, then a distribution of measured values will be obtained, and the average value of the observable property is given by the expectation value integral,

$$\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau} \qquad \{3\text{-}47\}$$

where the integration is over all coordinates involved in the problem. The average value ⟨A⟩, also called the expectation value, is the average of many measurements. If the wavefunction is normalized, then the normalization integral in the denominator of Equation {3-47} equals 1.

Exercise 3.21 What does it mean to say a wavefunction is normalized? Why must wavefunctions be normalized?

Exercise 3.22 Rewrite Equations {3-42} and {3-43} using the definitions of $\hbar$, ∇, and ∇^2.

Exercise 3.23 Write a definition for a stationary state. What is the time dependence of the wavefunction for a stationary state?

Exercise 3.24 Show how the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation.

Exercise 3.25 Show how the de Broglie relation follows from the postulates of Quantum Mechanics using the definition of the momentum operator.

Exercise 3.26 What quantity in Quantum Mechanics gives you the probability density for finding a particle at some specified position in space? How do you calculate the average position of the particle and the uncertainty in the position of the particle from the wavefunction?

Problems

1. Prove Euler's formula is correct by expanding $e^{\pm i\theta}$, $\cos\theta$, and $\sin\theta$ each in terms of a Maclaurin series and showing that corresponding terms are identical.

2. The following table gives the results of many measurements of the length of a laser cavity. Complete the table by calculating the probability for each value. Use the probabilities that you calculated to compute the average value for the length, the average of the length squared, the variance, and the standard deviation in the measurements.

length (cm)	number of times the value was obtained	probability
100.05	4	
100.04	3	
100.03	6	
100.02	9	
100.01	8	
100.00	9	
99.99	9	
99.98	8	
99.97	2	
99.96	3	

3. Consider an electron trapped by a positively charged point defect in a one-dimensional world. The following wavefunction with α = 20/nm describes the distance x of the electron from the point defect located at x=0. Note that in 1, 2, and 3 dimensions, $r = |x|$, $(x^2+y^2)^{1/2}$, and $(x^2+y^2+z^2)^{1/2}$, respectively.

$$\psi(r) = Ne^{-\alpha|x|} \qquad \{3\text{-}48\}$$

a) Evaluate the normalization constant N.

b) Graph the probability density for this electron.

c) Calculate the expectation value for x and |x|.

d) If the electron were in a two or three-dimensional world, such as on the surface of a crystal or in a free atom, would the average distance of the electron from the origin $\langle r \rangle$ be less, the same, or larger than the value you found for one dimension?

e) Determine whether the expectation value for r depends upon the dimensionality of the world (1, 2, or 3) in which the atom lives.

Symbolic Mathematics Activity

Study the examples of common quantum mechanical procedures and calculations carried out in Mathcad using the following files.

Example_QM_calculations.xmcd
Example_QM_calculations.pdf

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