

### 3.3: Invention of the Schrödinger Equation

From the previous section, the the classical wave equation in one-dimension was discussed:

$$\frac{\partial^2 A(x, t)}{\partial x^2} = \nu^{-2} \frac{\partial^2 A(x, t)}{\partial t^2} \quad (3.3.1)$$

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 3.3.1. 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 3.3.1

Show that the functions  $e^{i(kx+\omega t)}$  and  $\cos(kx - \omega t)$  also satisfy the classical wave equation (Equation 3.3.1). Note that  $i$  is a constant equal to  $\sqrt{-1}$ .

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 3.3.1, 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  $\psi$ ,  $\psi$ , or  $\phi$ , so we use  $\Phi(x)$  as the  $x$ -function, and examine the consequences of using  $\cos(\omega t)$  as one possibility for the  $t$ -function.

$$\psi(x, t) = \psi(x)\cos(\omega t) \quad (3.3.2)$$

After substituting Equation 3.3.2 into the classical wave Equation 3.3.1 and differentiating, we obtain

$$\cos(\omega t) \frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{\omega^2}{\nu^2} \psi(x) \cos(\omega t) \quad (3.3.3)$$

which yields, after simplifying and rearranging,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{\omega^2}{\nu^2} \psi(x) = 0 \quad (3.3.4)$$

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  $\frac{\omega^2}{\nu^2}$  with  $\frac{p^2}{\hbar^2}$ , where  $\hbar = \frac{h}{2\pi}$  (called h-bar).

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{p^2}{\hbar^2} \psi(x) = 0 \quad (3.3.5)$$

#### Exercise 3.3.2

Show that  $\frac{\omega^2}{\nu^2} = \frac{p^2}{\hbar^2}$ .

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.

$$E = T + V(x) = \frac{p^2}{2m} + V(x) \quad (3.3.6)$$

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 3.3.6 for  $p^2$  and substituting it into Equation 3.3.5 gives us **the Schrödinger Equation**,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (E - V(x)) \psi(x) = 0 \quad (3.3.7)$$

which usually is written in rearranged form,

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \psi(x) = E \psi(x) \quad (3.3.8)$$

Notice that the left side of Equation 3.3.8 consists of the two terms corresponding to the kinetic energy and the potential energy. When we look at the left side of Equation 3.3.8, we can deduce a method of extracting the total energy from a known wavefunction, or we can use Equation 3.3.8 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 3.3.3

Show the steps that lead from Equations 3.3.1 and 3.3.2 to Equation 3.3.8.

More precisely, Equation 3.3.8 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  $\psi$  then depends on the three variables  $x, y$ , and  $z$ .

$$\frac{-\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + V(x, y, z) \psi(x, y, z) = E \psi(x, y, z) \quad (3.3.9)$$

### Exercise 3.3.4

Write the Schrödinger equation for a particle of mass  $m$  moving in a 2-dimensional space with the potential energy given by

$$V(x, y) = -\frac{(x^2 + y^2)}{2}. \quad (3.3.10)$$

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

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (3.3.11)$$

with the del operator,

$$\nabla = \left( \vec{x} \frac{\partial}{\partial x} + \vec{y} \frac{\partial}{\partial y} + \vec{z} \frac{\partial}{\partial z} \right) \quad (3.3.12)$$

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

### Exercise 3.3.5

Write the del-operator and the Laplacian operator for two dimensions and rewrite your answer to Exercise 3.3.4 in terms of the Laplacian operator.

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