41.2 Solving the Schrödinger Equation

The Schrödinger equation is a second-order differential equation, meaning that it is a differential equation for $\psi(x)$ involving its second derivative. However, this textbook does not assume that you know how to solve differential equations. As we did with Newton's laws, we will restrict ourselves to situations where the mathematical skills are those you have been developing in calculus.

The solution to an algebraic equation is simply a number. For example, $x = 3$ is the solution to the equation $2x = 6$. In contrast, the solution to a differential equation is a *function*. You saw this idea in the preceding section, where Equation 41.6 was constructed so that the function $\psi(x) = \psi_0 \sin(2\pi x/\lambda)$ was a solution.

The Schrödinger equation can't be solved until the potential-energy function $U(x)$ has been specified. Different potential-energy functions result in different wave functions, just as different forces lead to different trajectories in classical mechanics. Once $U(x)$ has been specified, the solution of the differential equation is a *function* $\psi(x)$. We will usually display the solution as a graph of $\psi(x)$ versus x.

Restrictions and Boundary Conditions

Not all functions $\psi(x)$ make *acceptable* solutions to the Schrödinger equation. That is, some functions may satisfy the Schrödinger equation but not be physically meaningful. We have previously encountered restrictions in our solutions of algebraic equations. We insist, for physical reasons, that masses be positive rather than negative numbers, that positions be real rather than imaginary numbers, and so on. Mathematical solutions not meeting these restrictions are rejected as being unphysical.

Because we want to interpret $|\psi(x)|^2$ as a probability density, we have to insist that the function $\psi(x)$ be one for which this interpretation is possible. The conditions or restrictions on acceptable solutions are called the **boundary conditions.** You will see, in later examples, how the boundary conditions help us choose the correct solution for $\psi(x)$. The primary conditions the wave function must obey are:

1. $\psi(x)$ is a continuous function.
2. $\psi(x) = 0$ if x is in a region where it is physically impossible for the particle to be.
3. $\psi(x) \to 0$ as $x \to +\infty$ and $x \to -\infty$.
4. $\psi(x)$ is a normalized function.

The last is not, strictly speaking, a boundary condition but is an auxiliary condition we require for the wave function to have a useful interpretation. Boundary condition 3 is needed to enable the normalization integral $\int |\psi(x)|^2 dx$ to converge.

Once boundary conditions have been established, there are general approaches to solving the Schrödinger equation: Use general techniques for solving second-order differential equations, solve the equation numerically on a computer, or guess.

More advanced courses make extensive use of the first and second approaches. However, we are not assuming a knowledge of differential equations, so you will not be asked to use these methods. The third, although it sounds almost like cheating, is widely used in simple situations where we can use physical arguments to infer the functional form of the wave function. The upcoming examples will illustrate this third approach.

A quadratic algebraic equation has two different solutions. Similarly, a second-order differential equation has two independent solutions $\psi_1(x)$ and $\psi_2(x)$. By "independent solutions" we mean that $\psi_2(x)$ is not just a constant multiple of $\psi_1(x)$, such as $3\psi_1(x)$, but that $\psi_1(x)$ and $\psi_2(x)$ are totally different functions.

Suppose that $\psi_1(x)$ and $\psi_2(x)$ are known to be two independent solutions of the Schrödinger equation. A theorem you will learn in differential equations states that a *general solution* of the equation can be written as

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \tag{41.8}$$

where A and B are constants whose values are determined by the boundary conditions. Equation 41.8 is a powerful statement, although one that will make more sense after you see it applied in upcoming examples. The main point is that **if we can find two independent solutions $\psi_1(x)$ and $\psi_2(x)$ by guessing, then Equation 41.8 is the general solution to the Schrödinger equation.**

Quantization

We've asserted that the Schrödinger equation is the law of quantum mechanics, but thus far we've not said anything about quantization. Although the particle's total energy E appears in the Schrödinger equation, it is treated in the equation as an unspecified constant. However, it will turn out that there are *no* acceptable solutions for most values of E. That is, there are no functions $\psi(x)$ that satisfy both the Schrödinger equation *and* the boundary conditions. Acceptable solutions exist only for *discrete* values of E. The energies for which solutions exist are the quantized energies of the system. Thus, as you'll see, the Schrödinger equation has quantization as a built-in feature.

Problem Solving in Quantum Mechanics

Our problem-solving strategy for classical mechanics focused on identifying and using forces. In quantum mechanics we're interested in *energy* rather than forces. The critical step in solving a problem in quantum mechanics is to determine the particle's potential-energy function $U(x)$. Identifying the interactions that cause a potential energy is the *physics* of the problem. Once the potential-energy function is known, it is "just mathematics" to solve for the wave function.

PROBLEM-SOLVING STRATEGY 41.1 Quantum-mechanics problems (MP)

MODEL Determine a potential-energy function that describes the particle's interactions. Make simplifying assumptions.

VISUALIZE The potential-energy curve is the pictorial representation.

- Draw the potential-energy curve.
- Identify known information.
- Establish the boundary conditions that the wave function must satisfy.

SOLVE The Schrödinger equation is the mathematical representation.

- Utilize the boundary conditions.
- Normalize the wave functions.
- Draw graphs of $\psi(x)$ and $|\psi(x)|^2$.
- Determine the allowed energy levels.
- Calculate probabilities, wavelengths, or other specific quantities.

ASSESS Check that your result has the correct units, is reasonable, and answers the question.

The solutions to the Schrödinger equation are the stationary states of the system. Bohr had postulated the existence of stationary states, but he didn't know how to find them. Now we have a strategy for finding them.

Bohr's idea of transitions, or quantum jumps, between stationary states remains very important in Schrödinger's quantum mechanics. The system can jump from one stationary state, characterized by wave function $\psi_i(x)$ and energy E_i, to another state, characterized by $\psi_f(x)$ and E_f, by emitting or absorbing a photon of frequency

$$f = \frac{\Delta E}{h} = \frac{|E_f - E_i|}{h}$$

Thus the solutions to the Schrödinger equation will allow us to predict the emission and absorption spectra of a quantum system. These predictions will test the validity of Schrödinger's theory.