

Schrödinger's Equation – 1

Eigenfunctions and Eigenvalues

Introduction

You should be familiar with the time-dependent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)+V(\mathbf{r})\Psi(\mathbf{r},t)=i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}.$$

This is a *partial differential equation* for the wave function $\Psi(\mathbf{r},t)$. You should recall that the first term represents the *kinetic energy*, the second term represents the *potential energy*, and the term on the right hand side represents the total energy.

In the general three dimensional case in rectangular cartesian coordinates the arguments of Ψ are x, y, z , and t . The Laplacian, in the kinetic energy term, is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

A given problem is specified by the potential energy function $V(\mathbf{r})$. We set up the quantum mechanical problem by writing a Schrödinger equation and putting in the corresponding classical expression for the potential energy.

1d case – separating the time dependence

For simplicity we shall consider an example where there is only one spatial variable. Realistic one-dimensional problems include the simple harmonic oscillator and some tunneling problems. In such cases the Schrödinger equation will have one space variable and one time variable:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

and Ψ is a function of x and t only:

$$\Psi = \Psi(x,t);$$

we have two independent variables.

Separation of variables

By using the method of separation of variables we should be able to split this Schrödinger equation into two differential equations, one in x and one in t . Thus we write

$$\Psi(x,t) = \psi(x)T(t)$$

and substitute this into the time dependent Schrödinger equation.

Since

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi(x)}{dx^2} T(t)$$

$$\frac{\partial \Psi}{\partial t} = \psi(x) \frac{dT(t)}{dt}$$

the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} T(t) + V(x) \psi(x) T(t) = i\hbar \psi(x) \frac{dT(t)}{dt}.$$

This is simplified (in the usual way) by dividing through by $\Psi(x, t) = \psi(x)T(t)$, giving

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x) = i\hbar \frac{1}{T(t)} \frac{dT(t)}{dt}.$$

The left hand side depends only on x and the right hand side depends only on t . Since these variables are independent the sides of this equation must be constant. Let us denote this constant by E . We are motivated in this designation since on physical grounds we identify this as the energy of the system. Thus we obtain two equations:

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

$$i\hbar \frac{dT(t)}{dt} = ET(t).$$

The first equation is called the *time independent* Schrödinger equation. The second equation is solved easily.

The time-independent Schrödinger equation

The bulk of the effort goes into solving this equation. Only certain values of E will solve this equation; these are the *energy eigenvalues*. Corresponding to a given energy eigenvalue, the solution $\psi(x)$ is called the *eigenfunction* and we can denote it by $\psi_E(x)$.

$$\psi_E \quad \text{called the eigenfunction}$$

$$E \quad \text{called the eigenvalue}$$

The existence of a discrete set of allowed solutions is called *quantisation*.

Solving the time equation

If we write the time equation as

$$\frac{1}{T(t)} \frac{dT(t)}{dt} = \frac{E}{i\hbar}$$

then we identify the left hand side as the derivative of a logarithm

$$\frac{d \ln T(t)}{dt} = \frac{E}{i\hbar} = -\frac{iE}{\hbar}$$

and this may be integrated immediately, giving

$$\ln T(t) = -iEt / \hbar + \text{const.}$$

or

$$T(t) = e^{-iEt/\hbar},$$

where we have dropped the arbitrary (now multiplicative) constant.

For a give allowed energy eigenvalue E

$$T_E(t) = e^{-iEt/\hbar}$$

so the solution to the time dependent Schrödinger equation corresponding to this E is

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

and the general solution will be a superposition of these for all allowed energy eigenvalues

$$\Psi(x,t) = \sum_E A_E \psi_E(x)e^{-iEt/\hbar}.$$

The coefficients A_E are chosen to satisfy the *initial conditions*.

When the system is in an energy eigenstate the only time dependence of the wave function is in the exponential $e^{-iEt/\hbar}$. Probabilities are given by the *square of the modulus* of Ψ , so in an energy eigenstate the time variation cancels. For this reason the energy eigenstates are called *stationary states*.

So the properties of stationary states are determined entirely from solutions to the time independent Schrödinger equation. The problem is to find the energy eigenstates and eigenvalues.

Generalisation

In the general case the Schrödinger equation will depend on more than one spatial variable. One can still separate off the time part using the energy as the separation variable. The same time equation (ODE) must be solved, giving the same oscillatory solution. The time independent Schrödinger equation which results, however, still depends on the three spatial variables, so it is still a partial differential equation. Further separations must be performed to yield solvable ODEs.

The important points of this section are:

- The time dependent Schrödinger equation is a partial differential equation in spatial and time variables.
- The physical problem is specified by the potential energy function.
- The mathematical problem is specified by the potential energy function and the coordinate system.
- The rule to set up a quantum mechanical problem is to write down a Schrödinger equation and to put in the classical potential energy expression.
- Separation of variables enables the time variation to be factored out; the separation constant is the energy E .
- Eigenfunctions and eigenvalues are obtained from the time independent Schrödinger equation when the boundary conditions are imposed.
- Energy eigenfunctions are stationary states.
- The general solution will be a superposition of different energy eigenstates, each with its own time dependence and the appropriate amplitude.
- The amplitudes of the different eigenstate solutions are determined by the initial conditions.