

## Lecture 3: Particle in a 1D Box

First we will consider a free particle moving in 1D so  $V(x) = 0$ . The TDSE now reads

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

which is solved by the function

$$\psi = Ae^{ikx}$$

where

$$k = \pm \frac{\sqrt{2mE}}{\hbar}$$

A general solution of this equation is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where  $A$  and  $B$  are arbitrary constants. It can also be written in terms of sines and cosines as

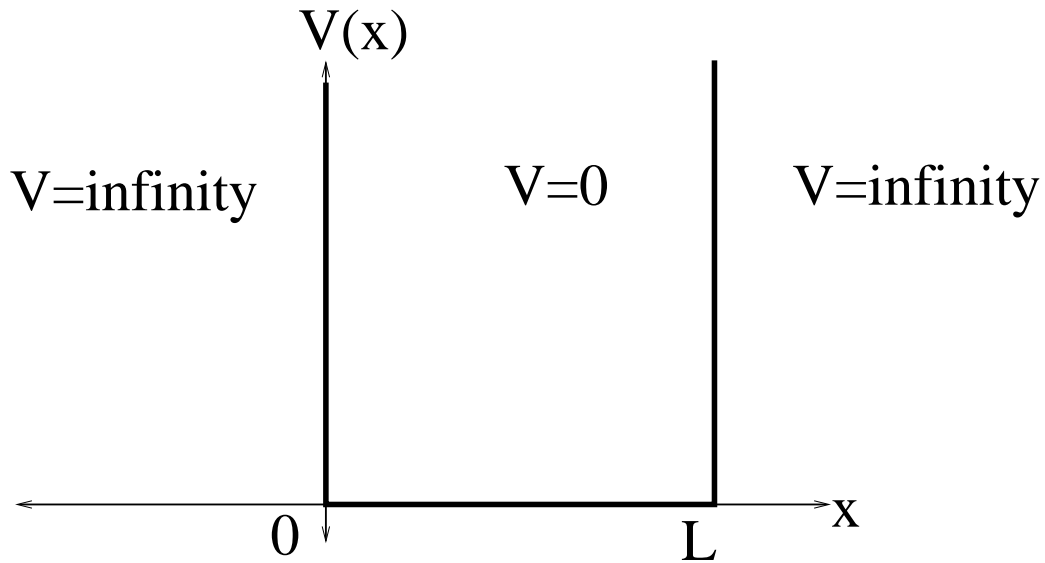
$$\psi(x) = C \sin(kx) + D \cos(kx)$$

The constants appearing in the solution are determined by the boundary conditions. For a free particle that can be anywhere, there is no boundary conditions, so  $k$  and thus  $E = \hbar^2 k^2 / 2m$  can take any values. The solution of the form  $e^{ikx}$  corresponds to a wave travelling in the +x direction and similarly  $e^{-ikx}$  corresponds to a wave travelling in the -x direction. These are eigenfunctions of the momentum operator. Since the particle is free, it is equally likely to be anywhere so  $\psi^*(x)\psi(x)$  is independent of  $x$ . Incidentally, it cannot be normalized because the particle can be found anywhere with equal probability.

Now, let us confine the particle to a region between  $x = 0$  and  $x = L$ . To do this, we choose our interaction potential  $V(x)$  as follows

$$\begin{aligned} V(x) &= 0 & \text{for } 0 \leq x \leq L \\ &= \infty & \text{otherwise} \end{aligned}$$

It is always a good idea to plot the potential energy, when it is a function of a single variable, as shown in Fig.1. The TISE is now given by



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

First consider the region outside the box where  $V(x) = \infty$ . Since  $V(x)\psi(x)$  has to be finite for finite energy, we insist that  $\psi(x) = 0$ . In other words, the particle cannot go outside the box.

In the box, we have the TISE given by the free particle term

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

now subjected to the boundary conditions given by

$$\psi(0) = \psi(L) = 0$$

Thus, we take the general solution

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

If we put  $x = 0$ , we get  $\psi(0) = B = 0$ . If we now put  $\psi(L) = 0$ , we get

$$A \sin(kL) = 0 \quad \text{or } k = \frac{n\pi}{L}$$

where  $n$  is any integer. Clearly  $n = 0$  is not valid as the wavefunction vanishes. Also, we see that changing the sign of  $n$  simply changes the sign of the wavefunction and as we said before, it does not produce a new wavefunction.

Thus the solution of the TISE that satisfies the boundary condition is written as

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad \text{where } n = 1, 2, 3, \dots$$

The constant  $A$  is determined by the normalization condition to be  $\sqrt{2/L}$ . The corresponding energy is given by

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \hbar^2}{8mL^2}$$

so we have quantization of energy with

$$E_1 = \frac{\hbar^2 k^2}{2m} \quad E_2 = \frac{4\hbar^2 k^2}{2m}$$

and so on. Notice that the lowest possible energy is not zero. This is referred to as zero point energy. The first few wavefunctions are plotted schematically as shown below. Notice that as the quantum number increases, the wavefunction becomes more oscillatory. For  $n = 2$ , the wavefunction is zero at the midpoint of the box  $x = L/2$ . This point is a node of this wavefunction. A node refers to a point (other than boundary points) where the wavefunction goes to zero. For the particle in a 1D box, we see that the number of nodes is equal to  $n - 1$ .

Though the particle in a 1D box is a simple model system, it illustrates the important features of a quantum mechanical description. It is a very useful first approximation to the behavior of  $\pi$  electrons in conjugated alkenes.

