

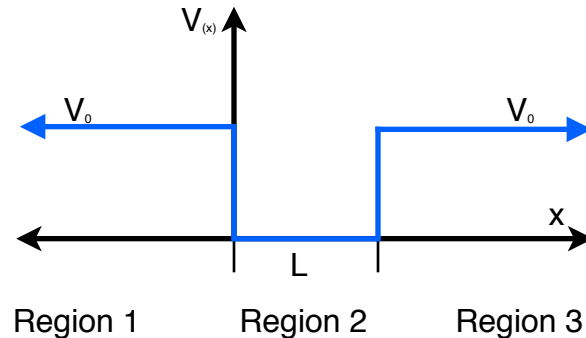
## Particle in a Box

This is our first example of a bound state system. A bound state is an eigenstate of the Hamiltonian with eigenvalue  $E$  that has asymptotically  $E < V(x)$  as  $x \rightarrow \infty$

Couple of general theorems, (for single dimension)

- if  $V(x)$  dips below its asymptotic values at  $x \rightarrow \pm\infty$  then there exists a bound state
- bound states are not degenerate

We are looking for solution to the general problem;



(if  $V_0 \rightarrow \infty$  then retrieve the classical particle in a box)

Hamiltonian:

$$H = \frac{P^2}{2m} + \int dx |x\rangle V(x) \langle x|$$

(solutions are a basis of Hilbert space)

where  $P^2$  is the momentum operator squared.

To solve the general problem we look for stationary solutions  $|\Psi\rangle$  to Schrödinger's equation.

$$H|\Psi\rangle = E|\Psi\rangle$$

Find solutions in x-space  $\rightarrow$  multiply by  $\langle x|$  on the right to construct

$$\begin{aligned} \langle x| E |\Psi\rangle &= \langle x| H |\Psi\rangle = \langle x| \frac{P^2}{2m} |\Psi\rangle + V(x) \langle x|\Psi\rangle \\ \parallel & \\ E \Psi_{(x)} &= H \Psi_{(x)} \end{aligned} \quad \begin{array}{l} \downarrow \text{Express in x-space} \\ \langle x| P |x\rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \end{array}$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_{(x)} + V(x) \Psi_{(x)}$$

Which we should remember is not the Schrödinger equation, it's just a representation of the Schrödinger equation. It is a good representation if  $V$  is independent of  $x$ , (example of a  $V$  that is dependent of  $x$  would be a constant force)

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi_{(x)} = \begin{cases} (V_0 - E) \Psi_{(x)} & \text{if } x < 0 \text{ or } x > L \\ -E \Psi_{(x)} & \text{if } 0 \leq x \leq L \end{cases}$$

We require  $E < V$  at  $\infty$ , and  $E < V_0$ , for a bound state system. If not then the system is closer to a scattering state or an unbound state.

!  $E > 0$ , else any solutions would grow without bounds as  $x \rightarrow \infty$

(If a solution were to be positive then the 2<sup>nd</sup> derivative would also be positive meaning it would grow both for negative and positive  $x$  and the system would not be square integrable, a requirement of our Hilbert space.)

How ever this is not a major problem as if the well's bottom is not located at zero then we can always re-normalize (define) the potential at the bottom of the well to be zero, ( $\epsilon = E - V_1$ )

$$\text{Then the solutions would be } \begin{cases} (V_0 - V_1 - \epsilon) \Psi_{(x)} & \text{if } x < 0 \text{ or } x > L \\ -\epsilon \Psi_{(x)} & \text{if } 0 \leq x \leq L \end{cases}$$

But the eigenfunction would look the same. Similarly the well doesn't have to start at  $x = 0$  but a change of coordinates ( $\Psi'_{(x)} = \Psi_{(x + \Delta x)}$ ) would yield a more familiar construction. While there exists an even more general problem, where the potential on the right of the well doesn't equal the potential on the left, this problem can be solved using principles constructed here.

Can we find a dimensionless version of the problem? If we can find a constant inherent in the problem such that  $E$  becomes unit-less.

First we divide by  $\hbar^2$  over  $2m$ .

$$\frac{\partial^2}{\partial x^2} \Psi_{(x)} = \begin{cases} (V_0 - E) / (\hbar^2 / 2m) \Psi_{(x)} & \text{if } x < 0 \text{ or } x > L \\ -E / (\hbar^2 / 2m) \Psi_{(x)} & \text{if } 0 \leq x \leq L \end{cases}$$

Notice that the 2<sup>nd</sup> derivative has units of length squared. So next we divide [multiply] by 2 powers of a 'natural' length. It is inherent in this problem that the natural length is the length of the well,  $L$

$$\frac{L^2 \partial^2}{\partial x^2} \Psi_{(x)} = \begin{cases} (V_0 - E) / (\hbar^2 / 2mL^2) \Psi_{(x)} & \text{if } x < 0 \text{ or } x > L \\ -E / (\hbar^2 / 2mL^2) \Psi_{(x)} & \text{if } 0 \leq x \leq L \end{cases}$$

By examining the term  $(\hbar^2 / 2mL^2)$ , we can see that it has units of energy, this reveals another inherent unit of the problem, namely  $E_0 = (\hbar^2 / 2mL^2)$

$$\frac{L^2 \partial^2}{\partial x^2} \Psi_{(x)} = \begin{cases} \left( \frac{V_0}{E_0} - \frac{E}{E_0} \right) \Psi_{(x)}, & \text{if } x < 0 \text{ or } x > L \\ \left( \frac{E}{E_0} \right) \Psi_{(x)}, & \text{if } 0 \leq x \leq L \end{cases}$$

Particle in a Box

The term  $\frac{V_0}{E_0}$  characterizes the problem.

The two solutions are 2nd order differential equations, therefore the answer is;

$$\Psi_{1(x)} = Ae^{Kx} + Be^{-Kx} \quad \text{where, } K = \left( \sqrt{\frac{V_0 - E}{E_0}} \right) \left( \frac{1}{L} \right)$$

For region 1 we require  $Be^{-Kx}$  to go to zero, therefore we set  $B = 0$  and our solution becomes  $\Psi_{1(x)} = Ae^{Kx}$ , similarly for region 3,  $\Psi_{3(x)} = De^{-Kx}$ ,

For region 2, the general solution has the form

$$\Psi_{2(x)} = B \cos(kx) + C \sin(kx) \quad \text{where, } k = \left( \sqrt{\frac{E}{E_0}} \right) \left( \frac{1}{L} \right)$$

At this stage we have 4 unknowns to find. The first can be eliminated by realizing that we can multiply the entire wave function by a constant and still retrieve an eigen solution, namely by multiplying by  $1/A$ .

We cannot solve the system for all 3 unknowns, but we can use the boundary conditions to find relationships between them.

First condition, at  $x = 0$

$$\Psi_{1(0)} = \Psi_{2(0)} \Rightarrow 1 = B$$

Second condition, at  $x = L$

$$\Psi_{2(L)} = \Psi_{3(L)} \Rightarrow \cos(kL) + C \sin(kL) = De^{-KL}$$

Since the potential is finite everywhere, the 2nd derivative is finite anywhere.

$$\Psi' \rightarrow \Psi'_{(\varepsilon)} - \Psi'_{(-\varepsilon)} = \int_{-\varepsilon}^{\varepsilon} \Psi'' dx$$

$\hookrightarrow$  finite  $\therefore = 0$  in the lim as  $\varepsilon \rightarrow 0$

If  $V$  jumps to  $\infty$  values, (a delta function, classical particle in a box) there is no guarantee that  $\Psi'$  is continuous. This gives us another boundary condition,

$$\Psi'_{1(0)} = \Psi'_{2(0)} \Rightarrow K = Ck$$

$$\therefore C = K/k$$

$\therefore \Psi_{2(x)} = \cos(kx) + (K/k)\sin(kx)$  evaluating  $\Psi_{2(x)}$  at  $x = L$  we find

$$\therefore \Psi_{2(L)} = \Psi_{3(L)} \Rightarrow \cos(kL) + (K/k)\sin(kL) = De^{-KL}$$

$$\therefore D = [\cos(kL) + (K/k)\sin(kL)]e^{KL}$$

Note, if  $V_0$  and  $E$  are known then  $K$  and  $k$  are known.

To finish apply the last boundary condition,

$$\Psi'_{2(L)} = \Psi'_{3(L)}$$

$$-k\sin(kL) + \left(\frac{k}{K}\right)K\cos(kL) = -K(\cos(kL) + (K/k)\sin(kL))(e^{kL})(e^{-kL})$$

$$-k\sin(kL) + K\cos(kL) = -K(\cos(kL) + (K/k)\sin(kL))$$

$$F_1(E) = F_2(E) \text{ [one function of energy equal to another]}$$

In general we can not find a closed solution. In fact, there must be multiple solutions. However, it is clear that only a countable number of values for  $E$  can solve this equation, so  $E$  cannot take on any arbitrary value:  $E$  is quantized  $\Rightarrow$  for any bound state we have a discrete spectrum of bound state energies

$$2K\cos(kL) = k\sin(kL) - (K^2/k)\sin(kL)$$

$$2Kk\cos(kL) = k^2\sin(kL) - K^2\sin(kL)$$

$$2Kk\cos(kL) = (k^2 - K^2)\sin(kL)$$

$$2Kk = (k^2 - K^2)\tan(kL)$$

$$0 = K^2\tan(kL) + 2kK - k^2\tan(kL)$$

$$0 = K^2 + [(2k)/\tan(kL)]K - k^2$$

$$K = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\text{where } a = 1, b = [(2k)/\tan(kL)], c = -k^2$$

$$K = \frac{1}{2} \left( \frac{-2k}{\tan(kL)} \pm \sqrt{\frac{4k^2}{\tan^2(kL)} + 4k^2} \right)$$

$$K = \frac{-k}{\tan(kL)} \pm k \sqrt{\frac{1}{\tan^2(kL)} + 1}$$

$$K = \frac{-k}{\tan(kL)} \pm k \sqrt{\frac{\tan^2(kL) + 1}{\tan^2(kL)}}$$

$$K = \frac{-k}{\tan(kL)} \pm k \sqrt{\frac{\sec^2(kL)}{\tan^2(kL)}}$$

$$K = k \left( \frac{-1}{\tan(kL)} \pm k \sqrt{\csc^2(kL)} \right)$$

$$K = k [-\cot(kL) \pm \csc(kL)]$$

from  $\tan(\theta/2) = \csc(\theta) - \cot(\theta)$  and  $\cot(\theta/2) = \csc(\theta) + \cot(\theta)$  we come to

$$K = \begin{cases} k \tan(kL/2) \\ -k \cot(kL/2) \end{cases}$$

2 positive solutions, at least 1 of these equations has a solution,  $K = k \tan(kL/2)$ :  
As  $K$  goes down,  $k \tan(kL/2)$  increases; this implies that at some point they will be equal to each other: A ground state bound solution can always be found!

Numerical and graphical solutions of these equations can be found in the spreadsheet posted on our website. Higher energy solutions can only be found if  $V_0$  is high enough; solutions for the first equation for  $K$  are interleaved with solutions for the 2nd one.

Note that as  $V_0 \rightarrow \infty$ ,  $K$  becomes  $\infty$  also. This means we require  $kL/2 = (2n+1)\pi/2$  (first equation) or  $kL/2 = (2n)\pi/2$  (2nd equation) for integer  $n$ . In other words, the solutions are  $kL = n\pi$  for  $n = 1, 2, \dots$  and the corresponding energies are  $E_n = E_0(kL)^2 = E_0 n^2 \pi^2$ . From our solution for the wave function, we see that the term containing  $\sin(kx)$  increases without bound beyond the other terms, so it will be the only surviving term in this limit. With other words, the wave function becomes strictly zero outside of zone 2 and proportional to  $\sin(kx)$  inside zone 2. (The normalization constant turns out to be  $(2/L)^{1/2}$ .)