Earlier, we saw how to determine the energy eigenstates for a particle in an infinite square well. We can extend the methods developed there to particles in arbitrary "square" potentials, i.e., those where the potential is piecewise constant. So we could consider

The strategy here is:

- pick a value of energy $E$
- find a solution in each region where $V$ is constant. This gives

$$\Psi_1(x) \text{ \ if \ } x < x_1,$$
$$\Psi_2(x) \text{ \ if \ } x_1 \leq x \leq x_2,$$

- apply continuity conditions for $\Psi$ at boundaries

$$\Psi_1(x_1) = \Psi_2(x_1)$$
$$\Psi_2(x_2) = \Psi_3(x_2) \text{ etc...}$$

- apply matching conditions for $\frac{d\Psi}{dx}$ at boundaries. These must be continuous unless $V(x) \to \infty$ at a boundary.
It's relatively straightforward to solve in each region since $V$ is constant. Thus

$$
\hat{H}\psi = E\psi \Rightarrow \frac{-\hbar^2}{2m} \psi'' + V\psi = E\psi
$$

and in the position space representation

$$
\langle x | \hat{p}^2 | \psi \rangle = -\frac{\hbar^2}{2} \frac{\partial^2 \psi}{\partial x^2}
$$

This gives:

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

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

and there are two circumstances to consider:

**Case A:** \( E < V \)

\[
\frac{\partial^2 \psi}{\partial x^2} = q^2 \psi \quad \text{where} \quad q = \sqrt{\frac{2m(V-E)}{\hbar^2}}
\]

\[\psi(x) = A e^{qx} + B e^{-qx}\]

\[V\]

\[E\]

/ decays here.
Case B: \[ E > V \implies \frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi. \]

where \[ k = \sqrt{\frac{2m(E-V)}{\hbar^2}}. \]

\[ \implies \psi(x) = Ae^{ikx} + Be^{-ikx}. \]

which gives sinusoidal type solutions

Once this is done, applying matching conditions at the boundaries starts to relate the constants \( A, B \) for each section. In some cases we require that \( \psi(x) \to 0 \) as \( x \to \pm \infty \) and this fixes some of these two and imposes restrictions on the possible values of \( E \). Normalization usually fixes any remaining constants.

Example: Finite Square Well.

Suppose that a particle is free within \( -\frac{a}{2} \leq x \leq \frac{a}{2} \) but outside this range. \( V = V_0 > 0 \). Thus

\[ V(x) = \begin{cases} V_0 & x \leq -\frac{a}{2} \\ 0 & -\frac{a}{2} < x < \frac{a}{2} \\ V_0 & x \geq \frac{a}{2}. \end{cases} \]
A sketch of the potential is:

\[ \begin{align*}
\text{Region I} & \quad \text{Region II} & \quad \text{Region III} \\
-\frac{q}{2} & \quad & \frac{q}{2}
\end{align*} \]

First consider cases where \( E > V_0 \). Clearly we have oscillatory solutions in all three regions. Note that for regions I, III the constant

\[ k_I = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \]

is the same and smaller than that for region II:

\[ k_II = \sqrt{\frac{2mE}{\hbar^2}}. \]

Thus the solution has the form:

\[ \text{Region I} \quad \text{Region II} \quad \text{Region III} \]

\[ \begin{align*}
\text{such solutions exist for any energy } E > V_0. \text{ The relative amplitudes in the regions will depend on } E, V_0 \text{ and } m. \text{ Thus for } E > V_0 \\
\text{the possible energies are continuous.}
\end{align*} \]
Now consider $E < V_0$. In regions I, III the solutions will be exponential, while in region II it will be oscillatory. But the exponential solutions must decay as $x \to \pm \infty$. Thus we get:

Region I: $\psi_1(x) = A e^{q x} + F e^{-q x}$  \quad \quad \quad \quad q = \sqrt{\frac{2m(V_0 - E)}{k^2}}$

Region II: $\psi_2(x) = C e^{i k x} + D e^{-i k x}$  \quad \quad \quad \quad k = \sqrt{\frac{2mE}{h^2}}$

Region III: $\psi_3(x) = B e^{-q x} + G e^{q x}$

These have form:

\begin{center}
\begin{tabular}{c|c|c}
Region I & Region II & Region III \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c|c|c}
Symmetric & & \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c|c|c}
& & Antisymmetric \\
\end{tabular}
\end{center}

One can show that applying matching conditions results in only certain values of $E$ that will work. Note also that these states are bound. The probability densities are concentrated within the well. There is still a probability of finding the particle outside the well but this is generally small.
So the energies of the bound states are discrete. Thus the energy spectrum is:

\[ E \]

\[ V_0 \]

\[ \text{continuum} \rightarrow \text{free states} \]

\[ \text{discrete} \rightarrow \text{bound states} \]

Bound state energies vs infinite square well energy states

Some simple physical arguments all one to compare the energies of bound states in finite square wells to those in an infinite square well. Note that for an infinite square well of width \( a \), the energies are:

\[ E_n = \frac{n^2 \hbar^2}{2ma^2} \]

where \( n \) labels the eigenstate. How do the energies for finite wells compare? Consider the lowest state:

\[ V = \infty \quad 0 \quad \infty \]

Then in the well

- wavelength \( \lambda = 2a \)
- wavenumber \( k = \frac{2\pi}{\lambda} = \frac{\pi}{a} \)
- momentum \( p = \hbar k = \frac{\hbar \pi}{a} \)
- energy \( E = \frac{p^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2} \)

\[ \lambda > 2a \]

\[ k < \frac{\pi}{a} \]

\[ p < \frac{\hbar \pi}{a} \]

\[ E < \frac{\hbar^2 \pi^2}{2ma^2} \]