3.2: Infinite Square Well

Basic Features

Let's take a moment to briefly review the basic features of the square well ("particle-in-a-box"). We will use as our model potential a box with sides (infinitely-steep and tall potentials) at \( x = \pm \frac{L}{2} \) The energy eigenstate wave functions (solutions to the stationary state Schrödinger equation with the proper boundary conditions) are sines and cosines:

\[
\psi_n(x) = \begin{cases} 
\sqrt{\frac{2}{L}} \cos\frac{n\pi x}{L} & n = 1, 3, 5 \ldots \\
\sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} & n = 2, 4, 6 \ldots 
\end{cases}
\]

The energy spectrum is the description of the eigenvalue for the \( n^{th} \) eigenstate, which can be found by plugging this wave function back into the stationary-state Schrödinger equation, and comes out to be:

\[
E_n = n^2 E_1, \quad E_1 = \frac{\hbar^2 \pi^2}{2mL^2}
\]

A typical diagram which combines the energy levels with their corresponding wave functions is given in the figure below.

Figure 3.2.1 – Typical Energy Level / Wave Function Diagram
Incorporating Time

Now that we know there is more to quantum mechanics than the spatial part of the stationary state wave functions, let's expand our understanding, first by incorporating the time evolution of these stationary states. A first treatment of this subject typically involves equating these eigenstates with standing waves on strings. The analogy is a close one, but unfortunately breaks down when time is included. A standing wave on a string has a time-varying amplitude, meaning that if you take snapshots of its motion, you will get pictures of a wave with all sorts of displacements from the central line, including zero displacement, as the antinodes are flipping over. The displacement of the wave in quantum mechanics is the probability amplitude. These wave functions are stationary states, which means that if we look at different times, we will not see different probabilities of finding the particle at various positions, and there certainly won't be a moment in time when the probability of finding the particle is zero everywhere!

The problem with the standing-wave-on-a-string analogy is that the time dependence of such a standing wave is inherently different from that of a wave function. The time-changing phase of the wave function does not affect its spatial amplitude, as it does with a string. We can thank the fact that the wave function is complex-valued for this. The time evolution for quantum systems has the wave function oscillating between real and imaginary numbers. The figure below gives a nice description of the first excited state, including the time evolution – it's more of a "jump rope" model than a standing wave model.

Figure 3.2.2 – Improved Energy Level / Wave Function Diagram
The real and imaginary axes indicated give us a picture of a wave that is circling around the \(\langle x \rangle\)-axis, not through it. The displacement of the wave from the axis at a given value of \(\langle x \rangle\) doesn’t change over time – only its orientation within the complex plane evolves. The shape of the wave function is determined by \(\langle \psi_2 \rangle \langle x | \right\rangle\), and the orientation as it rotates is determined by the time portion, \(\langle e^{i \omega_2 t} \rangle\), with \(\langle \omega_2 \rangle\) equal to the speed of the "jump rope's" rotation, which is determined by the energy of the state, \(\langle E_2 \rangle\).

Non-Stationary States

In a first treatment of particle-in-a-box, so much emphasis is given to the stationary states, that it is understandable if the student comes away thinking that the particle cannot be in any quantum state other than the stationary states, but now we know that this is not true. A particle can be "prepared" into any state we like that can be constructed from a linear combination of the stationary states. Doing so ensures that the boundary conditions at the ends are maintained, but of course the "stationary" nature is lost. Let’s see if we can get a better handle on this by considering what happens if we superpose the ground state and first excited state in equal proportions.

The full eigenstates (including time dependence) are given by:

\[
|\psi_n\rangle = |E_n\rangle e^{-i\omega_n t}
\]

The mixed state is prepared at \(t=0\) with equal weights given to the two states, which after normalization gives us this state function:

\[
|\psi(t=0)\rangle = \frac{1}{\sqrt{2}} |E_1\rangle + \frac{1}{\sqrt{2}} |E_2\rangle
\]

There is no time dependence shown here, because it is just the starting state. As time passes, the evolution of the state is determined by the superposition of the time-dependent eigenstates:

\[
|\psi(t)\rangle = \frac{1}{\sqrt{2}} |E_1\rangle e^{-i\omega_1 t} + \frac{1}{\sqrt{2}} |E_2\rangle e^{-i\omega_2 t}
\]

The key thing to note here is that the phasors associated with the two states rotate at different rates. Let’s return to our jump rope model to see the effect this has.
Imagine two separate jump ropes turning at the same time, one with a single antinode (the ground state), and the other with two antinodes (the first excited state). The superposition of these two jump ropes is the total state. Suppose that at one moment both jump ropes lie in the vertical plane (i.e. the values are all real), and the antinode of the \((n=1)\) jump rope is above the \((x)\)-axis, while the left antinode of the \((n=2)\) jump rope is above the \((x)\)-axis (and its other antinode is below). At this moment, the superposition of the states results in constructive interference on the left side of the box, and destructive interference on the right side of the box. If we calculate the probabilities of finding the particle in various regions of the box, we find that it is more probable that it will be found in the left half of the box.

But now we wait a little while. The two jump ropes rotate at different rates. Specifically, the \((n=2)\) jump rope rotates 4 times faster than the \((n=1)\) jump rope, since its energy is 4 times as great. If we wait the period of time necessary for the \((n=2)\) jump rope to make 2 full rotations, it comes back to its original orientation. The \((n=1)\) jump rope, on the other hand is only turning at one-fourth the rate, and only gets halfway around in this period of time. The result of the superposition at this moment is that the particle is now more likely to be in the right half of the box than the left half. The probabilities are not "stationary."

We can see all this mathematically as well, simply by forming the probability density function. Start by getting the full wave function:

\[
\psi(x,t) = \frac{1}{\sqrt{2}} \left< x | E_1 \right> e^{-i \omega_1 t} + \frac{1}{\sqrt{2}} \left< x | E_2 \right> e^{-i \omega_2 t} = \frac{1}{\sqrt{2}} \left[ \psi_1(x) e^{-i \omega_1 t} + \psi_2(x) e^{-i \omega_2 t} \right]
\]

Now the probability density is:

\[
P(x,t) = \psi^*(x,t) \psi(x,t) = \frac{1}{2} \left[ \psi_1^*(x) e^{+i \omega_1 t} + \psi_2^*(x) e^{+i \omega_2 t} \psi_1(x) e^{-i \omega_1 t} + \psi_2(x) e^{-i \omega_2 t} \right]
\]

We can now plug in the wave functions from Equation 3.2.1, but it should be clear from here that the time dependence is not going away – the probability density changes with time.

**Spectral Decomposition**

The other aspect of quantum mechanics that we have covered that we can incorporate into the particle-in-a-box discussion is what it all looks like in the momentum basis. We can do this by taking fourier transforms of the eigenstates given in Equation 3.2.1. This momentum-space "recipe" for these wave functions is also known as the spectral content.

Until the particle in an energy eigenstate encounters a wall, it "thinks" it is a free particle – its energy comes entirely in the kinetic variety. Although this particle is not free, let's take a moment to see what the momentum space wave function would look like if it was just a combination of two opposite-moving-but-otherwise-identical plane waves with wave numbers \((k')\). In momentum space, each plane wave looks like a delta function (one momentum only!), so we get:
\( \Phi_E(k) = \frac{1}{\sqrt{2}} \delta(k-k') + \frac{1}{\sqrt{2}} \delta(k+k') \)

So what makes this different from the momentum-space wave function of the particle-in-a-box? The particle-in-a-box wave function is zero outside the box, while the wave function described above exists everywhere. This may seem like a trivial difference, but in fact it is not. We can see the role that confining the particle in a region of space has on the spectral content by considering the simpler case of a wave function that results in a uniform probability distribution over a finite region.

Example \( \PageIndex{1} \)

Consider a particle confined to a region between \( \left( x = -\frac{L}{2} \right) \) and \( \left( x = +\frac{L}{2} \right) \), and which has an equal probability of being at any point within that region.

a. Write a normalized wave function for this particle.

b. Find the momentum-space wave function of this particle.

Solution

a. The wave function is a simple block:

The only question is, how tall is the block? Well, to normalize it, we need it to be such that if we square the height and compute the area under that new block, it equals one. This is satisfied with this wave function:

\[
\psi(x) = \begin{cases} \frac{1}{\sqrt{L}} & -\frac{L}{2} < x < +\frac{L}{2} \\ 0 & \text{elsewhere} \end{cases}
\]

b. We find the momentum-space wave function through a Fourier transform of the position-space wave function:

\[
\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}} \int_{-\frac{L}{2}}^{\frac{L}{2}} \left( \frac{1}{\sqrt{L}} \right) e^{-ikx} dx = \sqrt{\frac{L}{2\pi}} \left( \frac{\sin \frac{KL}{2}}{kL} \right)
\]

A graph of the probability density in momentum space looks like this:
The similarity of this graph with that of a single-slit diffraction pattern is no accident. As photons pass through a single slit, they are confined in the dimension transverse to their motion, and the probability density of a photon being anywhere in the slit as it passes through is uniform. The distribution of transverse momenta of the photon is therefore given by this graph. After traveling to the screen, this transverse momentum distribution will be reflected in a distribution of photon events – the interference pattern.

Okay, so now that the above example makes it clear that the mere existence of confining limits affects the spectral content of the wave function (even if the wave function is totally flat between the walls), let's compute the spectral content for an energy eigenstate of the particle-in-a-box, where there are only two plane waves present between the walls. We will do the computation for the ground state, and extension of the process to the excited states will be apparent. Writing the fourier transform of the ground state:

\[
\phi (k) = \frac{1}{\sqrt {2\pi } } \int_{-\infty }^{+\infty } \psi (x) e^{-ikx} dx
\]

Now substitute the exponentials for the cosine with the Euler identity (Equation 1.1.7):

\[
\phi (k) = \frac{1}{\sqrt {\pi L} } \int_{-\frac{L}{2}}^{+\frac{L}{2}} \left[ \frac{e^{+i\pi x/L} + e^{-i\pi x/L}}{2} \right] e^{-ikx} dx
\]

The integral is not difficult, so other than keeping the constants straight and using the Euler identity again, it is not difficult to simplify it to:

\[
\phi (k) = \frac{\sqrt{L\pi}}{2}\left( \frac{\cos \alpha}{\frac{\pi^2}{4}-\alpha^2}\right), \quad \alpha = \frac{kL}{2}
\]

This is a far cry from a sum of two delta functions, and the influence of the confinement inside the box on the spectral content is evident in the graph:
Integrating the square of this function (numerically) from \(k=-\frac{2\pi}{L}\) to \(k=+\frac{2\pi}{L}\) reveals that the probability of the momentum lying between the two momenta associated with the ground state energy eigenvalue is 97% (and over 99% falls within the central bump).