6.1: Particle-in-a-Box, Part 1

Bound States

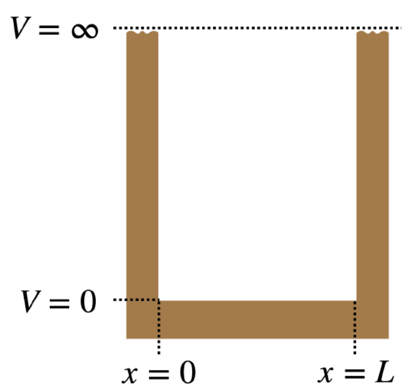
We have discussed at length the case of a free particle, and how we can construct general solutions from plane wave solutions to the Schrödinger equation, but now it's time to have a look at cases where particles are bound to some region by a force. We are staying in one dimension, so this force will need to act in both directions, always acting to keep the particle from straying too far from a central point. [In Physics 9HA, we called such a force a "restoring force."] It is unclear how to use the concept of a force when discussing the effect it has on entities that behave like waves, but since the Schrödinger equation accounts for a potential energy, we can certainly use that. As always, we wish to start as simply as possible, and build our way up to the more complicated cases. As we do this "build-up", we will try to sort out what features of bound states appear to be universal, and what features are special to the model we are examining.

The Infinite Square Well Potential

The simplest conceivable potential well allows us to keep most of the features of the free particle, but simply confines it between two impenetrable potential "walls." We will place these walls at $x=0$ and $x=L$, and make them such that it is impossible for a particle of any finite energy to escape. The full mathematical description is:

$$V(x)=\begin{cases} 0 & 0\le x\le L \\ \infty & x<0,\; x>L \end{cases} \tag{6.1.1}$$

Figure 6.1.1 – Infinite Square Well



When we put this into the Schrödinger equation, we find that the wave function splits up easily into two parts: The part that is inside the well (where $V=0$) which is simply the free particle equation (where the free particle can be traveling in either direction), and the part that is outside the well, which can only satisfy the Schrödinger equation if $\Psi(x,t)$ is identically zero. These two conditions sound very familiar – a wave that can be constructed from harmonic functions (like the free particle plane waves) and has endpoints that must remain fixed at zero – the wave function created by this potential should be similar to a standing wave on a string!

We should also say a word about the classical analog of this potential. Clearly the vertical potential wall corresponds to providing an infinite force, since $F=-\frac{dV}{dx}$. This is exactly what we would assume classically for a rigid ball colliding elastically with a rigid wall – the ball's momentum reverses direction instantly (and keeps the same magnitude), and since this requires a finite net impulse over an infinitesimally-short time period, the force must be infinite. We will come back to classical analogs like this occasionally throughout our study of bound states, to see how the quantum versions differ, and particularly to see how they converge at macroscopic scales.

Stationary-State Solutions

We now follow our prescribed program for finding wave functions from Schrödinger's equation, beginning with the separated stationary-state solutions. We are seeking the wave functions that satisfy:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)=E\psi(x) \tag{6.1.2}$$

Once we have the possible values of E (called the *energy spectrum*), we can use them to compute the oscillation frequencies $\omega=\frac{E}{\hbar}$, and then construct any general wave function solution for this potential by making linear combinations of the $\psi\left(x\right)$'s and their corresponding $e^{-i\omega t}$'s. So for the stationary-state wave functions, we essentially have a differential equation for each region (inside and outside the well):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi\left(x\right)+\left\{\begin{array}{cc} 0 & \text{(inside well)} \\ \infty & \text{(outside well)} \end{array}\right\}\psi\left(x\right)=E\psi\left(x\right) \tag{6.1.3}$$

Let's do the easy part first – outside the well. In this case, we see that an infinite number multiplies the probability amplitude $\psi\left(x\right)$ on the left side of the equation and a finite number multiplies it on the right. The only place where the second derivative cannot have any infinite effect on this equation over the entire outside region, so the only way this can be solved is for $\psi\left(x\right)$ to be identically zero outside the well. This also makes sense from a probability perspective – we would expect to *never* see the particle in the region outside the well, so we would expect this probability to be zero, which means we expect its probability amplitude to also be zero.

The solution for inside the well is not much tougher than outside, as it is the same differential equation that we had for the free particle. Stationary-state solutions consist of plane waves, which can be traveling in either direction. As the Schrödinger equation only takes into account energy, it doesn't select one direction over another, and the general stationary-state solution is a linear combination of both:

$$\psi\left(x\right)=Ae^{+ikx}+Be^{-ikx} \tag{6.1.4}$$

Now we have to apply the boundary conditions. The wave function *must* be continuous everywhere, most notably at the walls $x=0$ and $x=L$. Since $\psi\left(x\right)$ vanishes just on the other side of the walls, we have that $\psi\left(0\right)=\psi\left(L\right)=0$. Plugging this in gives:

$$\left.\begin{array}{l} \psi\left(0\right)=0=A+B \\ \psi\left(L\right)=0=Ae^{+ikL}+Be^{-ikxL} \end{array}\right\}\;\;\Rightarrow\;\; e^{+2ikL}=1\;\;\Rightarrow\;\; k_n=\frac{n\pi}{L}\;,\;\;n=0,\;1,\;2,\dots \tag{6.1.5}$$

We have subscripted the wave number $k\rightarrow k_n$ to distinguish the solutions from each other. The $n=0$ solution leads to the trivial solution of $\psi\left(x\right)\equiv 0$, so we discard that case. Plugging back in for B, we get for our n^{th} solution (which we also subscript with an n):

$$\psi_n\left(x\right)=A\left(e^{+ik_nx}-e^{-ik_nx}\right)=2iA\sin\left(\frac{n\pi x}{L}\right)\;,\;\;\;n=1,\;2,\dots \tag{6.1.6}$$

Well this certainly looks familiar! As we predicted, harmonic (plane wave) solutions inside the well, coupled with the requirement of nodes (vanishing probability) at the endpoints leads to a standing wave solution, with the harmonics determined by the n-values. We will see later that the interpretation of this "standing wave" is quite different from that of a standing wave on a string, but the math certainly matches.

Normalization

The reader may be troubled by the appearance of the "i" in the amplitude of our solution above. But there is no reason why A can't be complex as well. Keep in mind that all wave functions are equivalent up to a factor of a complex number with magnitude of 1, since all such wave functions give the same probability density. In any case, we *can* do better than just leaving the solution in this form, by using the normalization condition. Given that the wave function vanishes outside the well, the integral that usually goes from $x=-\infty$ to $x=+\infty$ can be reduced to an integral from 0 to L:

$$1=\int\limits_0^L\psi_n^*\left(x\right)\psi_n\left(x\right)dx=\int\limits_0^L\left[-2iA^*\sin\left(\frac{n\pi x}{L}\right)\right]\left[2iA\sin\left(\frac{n\pi x}{L}\right)\right]dx=4\left|A\right|^2\int\limits_0^L\sin^2\left(\frac{n\pi x}{L}\right)dx \tag{6.1.7}$$

Performing the integral and solving for $\left|A\right|^2$ gives:

$$\left|A\right|^2=\frac{1}{2L} \tag{6.1.8}$$

As we have said, the value of A is free to be anything that has this magnitude-squared, but it is traditional to choose the value of A that gives a real-valued amplitude for the standing wave, so choosing $A=\frac{-i}{\sqrt{2}}$ we get for the wave function that is the n_{th} harmonic:

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad n = 1,\ 2, \dots \tag{6.1.9}$$

Energy Spectrum

Now that we have the wave function for the stationary states, we can look into what measurable physical values we can expect to see. Highest on this list of observables is energy. Recall that the stationary-state solution gives us all of the eigenstates of energy, and the measurable values of energy are the eigenvalues associated with these states. We can therefore plug the wave function back into the Schrödinger equation for stationary states and solve for the possible values of E (the constant that appears in this equation:

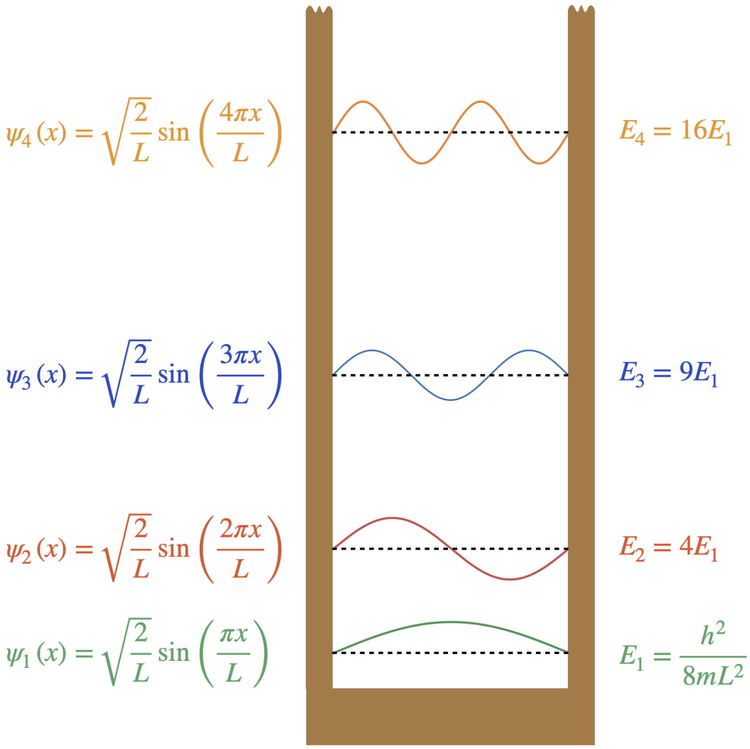
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right] = +\frac{\hbar^2 n^2}{2\pi^2 mL^2}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right] \tag{6.1.10}$$

The two derivatives on the sine function changed its sign, and brought out two factors of $\frac{n\pi x}{L}$. We can peel-off the constant in front of the wave function on the right-hand side of the equation, and set it equal to the energy. We see that the energy depends upon the harmonic n:

$$E_n = \frac{\hbar^2 n^2}{2\pi^2 mL^2} = \frac{h^2 n^2}{8mL^2} \tag{6.1.11}$$

We will abandon the use of the word "harmonic" in favor of *energy level*. The lowest energy level is referred-to as the *ground state*, and the energy levels above that are called *excited states*. So $n = 1$ corresponds to the ground state, $n = 2$ the first excited state, and so on.

Figure 6.1.2 – Energy Eigenstates and Eigenvalues of the Infinite Square Well



Physical Interpretation

Nothing seems particularly unusual about this solution until we think about how the result differs from what we expect to see classically. The first thing that comes to mind is that a we can start a ball bouncing elastically between two walls at any speed we wish, and therefore it can have any kinetic energy whatsoever. Certainly we would not expect to be able to only be able to measure certain allowable kinetic energies. While it is not yet clear why, it will turn out that this *quantization* of the energy spectrum is a general feature of all particles in bound states.

Another thing we find about the energy (and another thing that is true for bound states in general) is that the minimum energy level for the particle can never be the minimum potential energy of the well (i.e. it can never be found at the "bottom" of the well). One might be tempted to claim that the ground state can never have a zero value, but this is actually a silly statement, since we can set the zero-point of energy wherever we like. If we redefine our energy scale as $E' = E_n - E_1$, then the energy is zero at the ground state. But with this scale, the minimum potential energy is negative, so the ground state still doesn't get that low.

Next we consider momentum. For a ball bouncing back-and-forth elastically, we would expect to find it moving in either direction with equal probability, and with a fixed magnitude of momentum. We also see this in the quantum-mechanical case. However, considering what we found for kinetic energy, it's clear that we can't prepare the system with whatever fixed magnitude of momentum that we wish. Put another way, we will only measure certain magnitudes of momentum for the particle – half the time moving left and half the time moving right with a momentum magnitude of $|p_n| = \frac{hn}{2L}$.

In case you are wondering why it seems like we *can* start a ball bouncing back-and-forth between two walls with any momentum/KE we want, consider the tolerances we would need to measure to in order to prove it. A ball with a mass of $0.1kg$ can change its momentum in increments of $\frac{h}{2L}$, so if it is bouncing between walls separated by $20cm$, its "jump" in speed from one level to the next is:

$$v = \frac{p}{m} = \frac{h}{2mL} = \frac{6.63\times10^{-34}Js}{2\left(0.1kg\right)\left(0.2m\right)} = 1.66\times10^{-32}\frac{m}{s} \tag{6.1.12}$$

With such small increments of quantized speeds, it's no wonder it seems to us in the classical world that we can make the speed anything we want.

Possibly the strangest comparison between the classical and quantum results is the particle's position. Randomly measuring the position of a ball bouncing back-and-forth results in an uniform probability distribution. The ball moves at a constant speed, so naturally it spends the same amount of time in every small region Δx between the walls, making all these regions equally likely to find the ball. But a quantum particle in the ground state has a higher probability density at the center of the well than anywhere else, which means it is more likely to be found in a small region Δx near the center than in an equal-sized region closer to the walls. Stranger still, this behavior changes *dramatically* when the energy state is instead the first excited state. In this case, there is a node in the wave function at the center of the well, which means that unlike the ground state, for which the probability density is a maximum there, the probability density is actually *zero*.