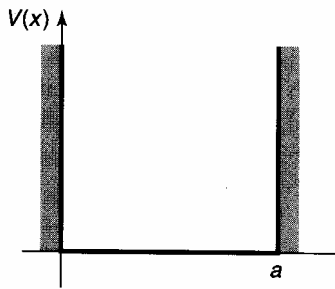**Infinite square well**

We now turn to the most straightforward (and therefore educational) non-zero potentials. We just discussed a free particle; we now turn to a bound particle, and will shortly discuss potentials that can lead to both.

The infinite square well potential is given by:

$$V(x) = \begin{cases} 0, & 0 \leq x \leq a \\ \infty, & x < 0, \ x > a \end{cases}$$

A particle under the influence of such a potential is free (no forces) between x = 0 and x = a, and is completely excluded (infinite potential) outside that region.

Now, the first lesson to take from this problem is that one does not have to solve the TISE everywhere at once – one can solve for the wave function piecemeal in the different regions where the potential is given by one function. However, the wave function must behave as a whole in certain ways as we discussed earlier.

We first look for the wavefunction in the region outside of 0 to a. Here, where the particle is excluded, the wave function must be zero. Great, half of the problem solved.

Inside the region from zero to a, the wavefunction must be a solution of

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

since V(x) = 0. The solution to this simple differential equation is simply the free particle solutions:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

But now we have to apply whatever boundary conditions we have. We know that continuity of the wave function insists that $\psi(0) = \psi(a) = 0$, so,

$$\psi(0) = Ae^{ik0} + Be^{-ik0}$$

$$= A + B \Rightarrow$$

$$B = -A \Rightarrow$$

$$\psi(x) = Ae^{ikx} - Ae^{-ikx} = A\sin(kx)$$

$$\psi(a) = A\sin(ka) = 0 \Rightarrow$$

$$ka = n\pi, \qquad n = 0,1,2\ldots \Rightarrow$$

$$k = \frac{n\pi}{a} \Rightarrow$$

$$\psi_n(x) = A_n \sin\left(\frac{n\pi}{a}x\right), \qquad n = 0,1,2\ldots$$

But, n=0 is a trivial solution, so we have:

$$\psi_n(x) = A_n \sin\left(\frac{n\pi}{a}x\right), \qquad n = 1,2,3\ldots$$

These are our stationary state solutions to the infinite square well potential. We choose to normalize these state solution for reasons that will become evident later:

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = \int_0^a |A_n|^2 \sin^2\left(\frac{n\pi}{a}x\right)dx = 1 \Rightarrow$$

$$|A_n|^2 \frac{a}{2} = 1 \Rightarrow$$

$$|A_n| = |A| = \sqrt{\frac{2}{a}}e^{i\beta}$$

where beta is an arbitrary phase, and since it has no consequence on measurement, we take it to be zero:

$$|A| = \sqrt{\frac{2}{a}}$$

So that the normalized stationary states are:

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right), \qquad n = 1,2,3\ldots}$$

Let's take a moment to study some of the properties of these solutions, as they are in general applicable to solutions to most potentials that you will encounter:

1) These functions are alternatively even and odd about the center of the potential well. This will be true for any symmetric potential.

2) With increasing n, each successive state has one more node in the wavefunction. This is true regardless of the shape of the potential.

3) The states are orthogonal. This means that:

$$\int_{-\infty}^{\infty} \psi_m(x)^* \psi_n(x)\,dx = 0, \qquad m \neq n$$

We show a proof:

$$\int_{-\infty}^{\infty} \psi_m(x)^* \psi_n(x)\,dx = \frac{2}{a}\int_0^a \sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{a}x\right)dx$$

$$= \frac{1}{a}\int_0^a \cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)dx$$

$$= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m+n}{a}\pi x\right)\right\}_0^a$$

$$= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)}\right\} = 0$$

This, together with the fact that when m = n, the same integral gives one (this is why we normalized the state functions) gives:

$$\int_{-\infty}^{\infty} \psi_m(x)^* \psi_n(x)\,dx = \delta_{mn},$$

$$\delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

where δ_{mn} is called the Kronecker delta. These statements are combined to say that the states are orthonormal (both orthogonal and normalized). This is also a general result of state functions regardless of the potential (assuming you normalize them).

4) The state functions form a complete set. This is perhaps the most interesting and useful of the properties. Although not universal, it will usually be the case for potentials you will encounter. This means that any other function f(x) can be written in terms of these functions:

$$\boxed{f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)}$$

Then, finding the values of the constants c_n is straightforward using Fourier's trick (just using the orthonormal nature of the state functions):

$$\int \psi_m(x)^* f(x)dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m \Rightarrow$$

$$c_n = \int \psi_n(x)^* f(x)dx$$

OK, we will get back to these properties of the state functions in a minute, but let's put the whole picture together first. The general state solutions are given by:
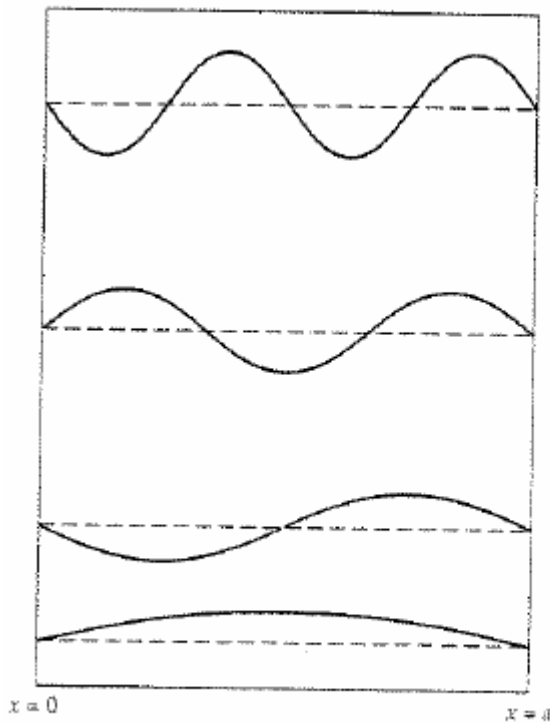
$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-iE_n t/\hbar}, \qquad n = 1,2,3\ldots$$

where we can determine the energies E_n from above:

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} \Rightarrow$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

so that the boundary conditions impose specific, allowed values of the energy.

$E_4 \approx 16 \dfrac{\hbar^2 \pi^2}{2ma^2}$

$E_3 = 9 \dfrac{\hbar^2 \pi^2}{2ma^2}$

$E_2 = 4 \dfrac{\hbar^2 \pi^2}{2ma^2}$

$E_1 = \dfrac{\hbar^2 \pi^2}{2ma^2}$

$x = 0$ $x = a$

Now, if someone asks you: "What is the wavefunction for a particle in an infinite square-well potential?" what would you answer? No, let's say you don't know its energy. The answer is a superposition of all the Ψ_n's:

$$\Psi(x, t) = \sum_n c_n \Psi_n(x, t) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right) e^{-iE_n t/\hbar}, \qquad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

But how do you find the c_n's? To determine these, you have to have an additional boundary condition, namely at some time, call it $t = 0$, you have to know something else about the particle.

Example: A particle in an infinite square well has as an initial wave function

$$\Psi(x,0) = \begin{cases} Ax(a - x), & 0 \le x \le a \\ 0 & 0 < x > a \end{cases} \quad \text{for some constant A. Find } \Psi(x,t).$$
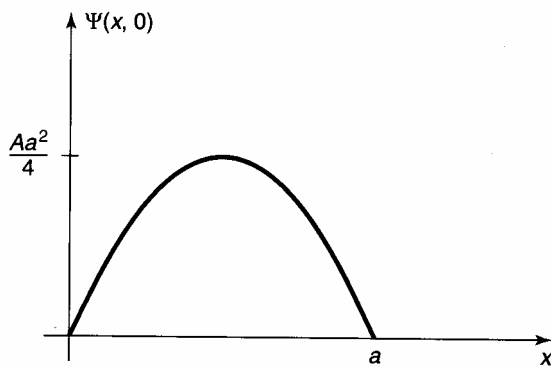
First, we must determine A using the normalization condition (since if $\Psi(x,0)$ is normalized, $\Psi(x,t)$ will stay normalized, as we showed earlier):

$$\int_0^a |\Psi(x,0)|^2 dx = |A|^2 \int_0^a x^2 (a - x)^2 dx = |A|^2 \int_0^a (a^2 x^2 - 2ax^3 + x^4) dx$$

$$= |A|^2 \left(a^2 \frac{x^3}{3} - 2a \frac{x^4}{4} + \frac{x^5}{5} \right)_0^a = |A|^2 \left(\frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5} \right) = |A|^2 \frac{a^5}{30} = 1 \Rightarrow$$

$$|A| = \sqrt{\frac{30}{a^5}}$$

Now we turn to our method for determining the coefficients c_n:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x), \qquad c_n = \int \psi_n(x)^* f(x) dx \qquad \text{so,}$$

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

$$c_n = \int \psi_n(x)^* \Psi(x,0)dx$$

$$= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}} x(a-x)dx$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ a\int_0^a x \sin\left(\frac{n\pi}{a}x\right)dx - \int_0^a x^2 \sin\left(\frac{n\pi}{a}x\right)dx \right\}$$

$$= \frac{2\sqrt{15}}{a^3} \left\{ a\left[\left(\frac{a}{n\pi}\right)^2 \sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]_0^a - \right.$$

$$\left. \left[2\left(\frac{a}{n\pi}\right)^2 x \sin\left(\frac{n\pi}{a}x\right) - \frac{(n\pi x/a)^2 - 2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]_0^a \right\}$$

$$= \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0) \right]$$

$$= \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0) - \cos(n\pi)\right]$$

$$= \begin{cases} 0, & \text{if n even} \\ \dfrac{8\sqrt{15}}{(n\pi)^3}, & \text{if n odd} \end{cases}$$

So that now we can form our time dependent wavefunction by putting this all together:

$$\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5...} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right)e^{-in^2\pi^2\hbar t/2ma^2}$$

Now, let's study this wavefunction, and its implications on measurable quantities. We first ask what the expectation value of the energy is.

$$\langle E \rangle = \int \Psi(x,t)^* \hat{H} \Psi(x,t) dx = \int \left(\sum_m c_m^* \psi_m(x)^* \phi_m(t)^* \hat{H} \sum_n c_n \psi_n(x) \phi_n(t) \right) dx$$

$$= \int \left(\sum_m c_m^* \psi_m(x)^* \phi_m(t)^* \sum_n c_n \hat{H} \psi_n(x) \phi_n(t) \right) dx$$

$$= \int \left(\sum_m c_m^* \psi_m(x)^* \phi_m(t)^* \sum_n c_n E_n \psi_n(x) \phi_n(t) \right) dx$$

$$= \sum_m \sum_n E_n \int c_m^* \psi_m(x)^* c_n \psi_n(x) dx$$

$$= \sum_m \sum_n E_n c_m^* c_n \int \psi_m(x)^* \psi_n(x) dx$$

$$= \sum_m \sum_n E_n c_m^* c_n \delta_{mn} = \sum_n |c_n|^2 E_n$$

So, we can think of the $|c_n|^2$ as the probability that one will measure E_n, remembering again that you will only measure one of these values, and then the total probability to measure one of the E_n's must be one or:

$$\sum_m |c_n|^2 = 1$$

We can show this since the wave function is normalized, each stationary state is normalized and the initial condition is also normalized, then:

$$\int \Psi(x,0)^* \Psi(x,0) dx = \int \left(\sum_m c_m^* \psi_m(x)^* \sum_n c_n \psi_n(x) \right) dx$$

$$= \sum_m \sum_n \int c_m^* \psi_m(x)^* c_n \psi_n(x) dx$$

$$= \sum_m \sum_n c_m^* c_n \int \psi_m(x)^* \psi_n(x) dx$$

$$= \sum_m \sum_n c_m^* c_n \delta_{mn} = \sum_m |c_n|^2 = 1$$

The c_n's can also be thought to tell you the amount of Ψ_n that is in the total wavefunction.

In the example above, you can see that the initial wavefunction closely resembles ψ_1, and if we look at c_1:

$$|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3} \right)^2 = 0.998555\ldots$$

very close to one indicating that the 1st state dominates.