THE INFINITE SQUARE WELL (PARTICLE IN A BOX)

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Sec 2.2.

Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Section 5.2, Exercise 5.2.5.

To get the feel of how to solve the time-independent Schrödinger equation in one dimension, the most commonly used example is that of the infinite square well, sometimes known as the 'particle in a box' problem. First, recall the Schrödinger equation itself:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V(x)\Psi \;=\; i\hbar\frac{\partial\Psi}{\partial t} \tag{1}$$

Remember that the 'time-independent' bit refers to the potential function V which is taken to be a function of position only; the wave function itself, which is the solution of the equation, will in general be time-dependent.

The infinite square well is defined by a potential function as follows:

$$V(x)=\begin{cases}0 & 0<x<a\\ \infty & \text{otherwise}\end{cases} \tag{2}$$

An area with an infinite potential means simply that the particle is not allowed to exist there. In classical physics, you can think of an infinite potential as an infinitely high wall, which no matter how much kinetic energy a particle has, it can never leap over. Although examples from classical physics frequently break down when applied to quantum mechanics, in this case, the comparison is still valid: an infinitely high potential barrier is an absolute barrier to a particle in both cases.

We saw in our study of the time independent Schrödinger equation that separation of variables reduces the problem to solving the spatial part of the equation, which is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi \;=\; E\psi \tag{3}$$

where the constant E represents the possible energies that the system can have. It is important to note that both E and $V(x)$ are unknown before we solve the equation. In classical physics, we would be allowed to specify E since it is just the kinetic energy that the particle has inside the well. Classically, E can be any positive quantity, and the particle would just bounce around inside the well without ever changing its speed (assuming the walls were perfectly elastic and there was no friction). In quantum physics, as we will see, E can have only certain discrete values, and these values arise in the course of solving the equation.

In an infinite square well, the infinite value that the potential has outside the well means that there is zero chance that the particle can ever be found in that region. Since the probability density for finding the particle at a given location is $|\Psi|^2$, this condition can be represented in the mathematics by requiring $\psi(x) = 0$ if $x < 0$ or $x > a$. This condition is forced from the Schrödinger equation since if $V(x) = \infty$, any non-zero value for $\psi(x)$ would result in an infinite term in the equation. However, it is certainly not rigorous mathematics, since multiplying infinity by zero can be done properly only by using a limiting procedure, which we haven't done here. A proper treatment of the infinite square well is as a limiting case of the *finite* square well, where $V(x)$ can have a large but finite value outside the well. However, the mathematics for solving the finite square well is considerably more complicated and tends to obscure the physics. Readers who are worried, however, can be reassured that the energy levels in the finite square well do become those in the infinite square well when the proper limit is taken.

Inside the well, $V(x) = 0$ so the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{4}$$

$$\frac{d^2\psi}{dx^2} = -k^2\psi \tag{5}$$

$$\text{with } k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{6}$$

This differential equation has the general solution

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{7}$$

for unspecified (yet) constants A and B. If you don't believe this, just substitute the solution back into the equation.

How can we determine A and B? To do this, we need to appeal to Born's conditions on the wave function. Born's first condition is clearly satisfied here: ψ is single-valued. The second condition of ψ being square integrable we'll leave for a minute. The third condition is that ψ must be continuous. We have argued above that $\psi = 0$ outside the well, so in particular, this means that at the boundaries $x = 0$ and $x = a$ we must have $\psi = 0$. If we impose that condition on our general solution above, we get:

$$\begin{aligned}
\psi(0) &= 0 && (8)\\
A\sin(0) + B\cos(0) &= 0 && (9)\\
B &= 0 && (10)\\
\psi(a) &= 0 && (11)\\
A\sin(ka) &= 0 && (12)\\
ka &= n\pi && (13)\\
\frac{\sqrt{2mE}}{\hbar} &= \frac{n\pi}{a} && (14)\\
E &= \frac{n^2\pi^2\hbar^2}{2ma^2} && (15)
\end{aligned}$$

where n is an integer. The useful values of n are just the positive integers. To see this, note that if $n = 0$, then $\psi(x) = 0$ everywhere which besides being very boring, is also no good as a probability density since its square modulus cannot integrate to 1. Negative integers don't really give new solutions, since $\sin(-x) = -\sin x$, so the negative sign can be absorbed into the (still undetermined) constant A. Also, the energies depend only on the square of n so the sign of n doesn't matter physically.

We can now return to the square-integrable condition and use it to determine A. Remember that the integral is over all space in which the particle can be found, so in this case we are interested in $0 \leq x \leq a$.

$$\int_0^a |\psi|^2 dx = 1 \tag{16}$$

$$A^2 \int_0^a \sin^2 kx = 1 \tag{17}$$

$$= A^2 \frac{1}{2} \int_0^a [1 - \cos(2kx)]\, dx \tag{18}$$

$$= \frac{A^2}{2} \left[x - \frac{1}{2k} \sin(2kx) \right]_0^a \tag{19}$$

$$= A^2 \frac{a}{2} \tag{20}$$

$$A = \pm \sqrt{\frac{2}{a}} \tag{21}$$

where we used 13 in 19 to eliminate the sine term.

Since it is only the square modulus of the wave function that has physical significance, we can ignore the negative root and take the final form of the wave function as

$$\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \tag{22}$$

Notice what has happened here. Applying the first boundary condition at $x = 0$ allowed us to eliminate B. But the other boundary condition at $x = a$ ended up giving us a condition on E rather than A. (Well, ok, we *could* have used the second boundary condition to set $A = 0$ but then we would have $\psi(x) = 0$ everywhere again.) Not only that, but the energy levels are discrete; thus the infinite square well is the first case in which the Schrödinger equation has actually *predicted* quantization in a system.

So the boundary conditions on the differential equation have put restrictions on the allowable energies. The acceptable solutions for ψ are determined by the condition $ka = n\pi$ and so the various ψ functions are just lobes of the sine function. The lowest energy, called the *ground state*, occurs when $n = 1$ and ψ is half a sine wave, consisting of the bit between $x = 0$ and $x = \pi$. The next state at $n = 2$ corresponds to a single complete cycle of the sine wave; $n = 3$ contains 1.5 cycles and so on.

Eagle-eyed readers will have noticed that in all the excitement over discovering quantization, we have neglected to look at Born's fourth condition: that of continuous first derivatives. Clearly this condition is violated, since the derivative of ψ outside the well is 0 (since $\psi = 0$ outside the well), but inside the derivative is $kA\cos(kx)$,which is kA at $x = 0$ and $\pm kA$ at $x = a$

(the sign depends on whether n is odd or even). Neither of these derivatives is zero.

The reason is, of course, because of the infinite potential function which is not physically realistic. In fact, what happens in the (real-world) finite square well is that the wave function inside the potential barrier (that is, just off the ends of the well) is *not* zero, but a decaying exponential which tends to zero the further into the barrier you go. In that case, it *is* possible to make both the wave function and its first derivative continuous at both ends of the well (and it is precisely that condition which makes the mathematics so much more complicated in the finite square well).

In fact, this effect happens in any potential where the energy of the particle is less than that of a (finite) potential barrier: the particle's wave function extends into the barrier region. So does that mean that the particle has a probability of appearing *inside* a barrier? Technically yes, but in practice it usually doesn't do the particle much good, since the probability of being outside the barrier is usually a lot greater. However, there is one case where this barrier penetration effect does occur, and that is if the barrier is thin enough for the wave function to have a significant magnitude on the *other* side of the barrier. That is, if we have a particle in a finite well, but the wall of the well is fairly thin and there is another well (or just open space) on the other side of the barrier, then the wave function starts off with a respectable magnitude inside the main well, extends into the barrier (but gets attentuated exponentially in doing so), but before the attenuation gets so severe that the wave function becomes very small, it bursts through to the other side of the barrier. *That* means that, yes, there is a definite probability that the particle can spontaneously appear *outside* the well *without* having to jump over the barrier. In effect, it tunnels through the barrier and escapes. The effect, not surprisingly, is known as *quantum tunneling* and is one of the main causes of some forms of radioactive decay. But that's a topic for another post.

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