

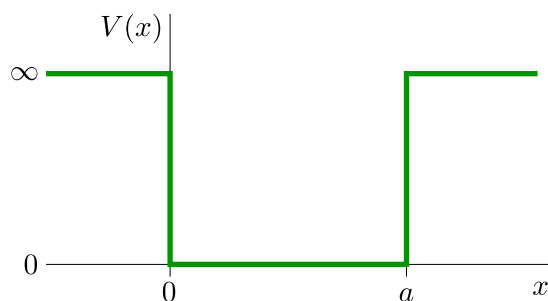
4. The Infinite Square Well

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In the previous lesson I emphasized the *free* particle, for which $V(x) = 0$, because its energy eigenfunctions are so simple: they're the same as the momentum eigenfunctions, e^{ikx} . The next-simplest example is a particle that's free within a certain limited region (say from $x = 0$ to $x = a$), but absolutely confined to that region by powerful forces on each side. In the most idealized model, this system would have zero potential energy inside the region and infinite potential energy outside:

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a, \\ \infty & \text{elsewhere.} \end{cases} \quad (1)$$

This potential energy function is called an infinite square well or a one-dimensional “box.” We can visualize $V(x)$ like this:



Of course, any confining forces in the real world would be neither infinitely strong nor infinitely abrupt. But this model is still useful for understanding a variety of real-world potential wells (e.g., electrons in long organic molecules, or in fabricated semiconductor layers), and provides a good starting point for understanding the general properties of quantum particles that are trapped within a finite region.

The infinite potential energy outside the box means that there is zero probability of ever finding the particle there, so all of the allowed wavefunctions for this system are exactly zero at $x < 0$ and $x > a$. Inside the box the wavefunction can have any shape at all, so long as it is normalized. The wavefunction could be localized in a region much smaller than a , or spread over the full width of the box, and of course it can have both real and imaginary parts.

Energy eigenfunctions

The most important wavefunctions, however, are the energy eigenfunctions, whose shapes and formulas are not hard to guess. Inside the box there is no potential energy, so definite momentum would imply definite energy, just as for a free particle.

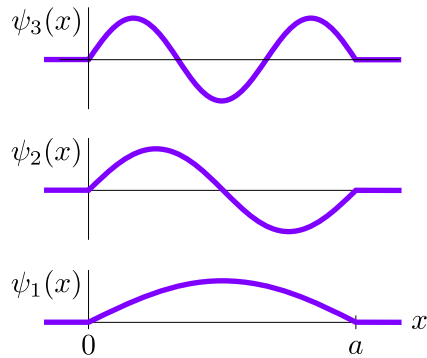
The difference here is that the wavefunction must go to zero at each end, and the momentum eigenfunctions, e^{ikx} , don't go to zero anywhere. The way out of this difficulty is to realize that for a given kinetic energy there are actually *two* possible momenta, one positive and one negative. If we superimpose the two corresponding wavefunctions we get a standing wave, analogous to a standing wave on a string, with the same wavelength (and hence the same $|p_x|$ and the same kinetic energy) as the traveling waves, but with nodes where the wavefunction goes to zero. In our case the correct superposition is proportional to

$$e^{ikx} - e^{-ikx} \propto \sin(kx), \quad (2)$$

which is automatically zero at $x = 0$, at the left end of the box. To make the wavefunction go to zero at the right end as well, we must restrict the values of k so that some integer number of half-wavelength “bumps” fits in the box:

$$\lambda = 2a, a, \frac{2a}{3}, \frac{2a}{4}, \dots = \frac{2a}{n}, \quad (3)$$

where n can be any positive integer (and is equal to the number of bumps). The first three wavefunctions look like this:



The corresponding k values are just $2\pi/\lambda = n\pi/a$, so the corresponding momentum magnitudes are

$$|p_x| = \hbar k = \frac{h}{\lambda} = \frac{hn}{2a}. \quad (4)$$

The formula for the wavefunctions themselves is therefore

$$\psi_n(x) = \begin{cases} A \sin\left(\frac{n\pi x}{a}\right) & \text{for } 0 < x < a, \\ 0 & \text{elsewhere,} \end{cases} \quad (5)$$

where the normalization constant A equals $\sqrt{2/a}$ (as you can easily show), times an arbitrary unit-modulus phase factor $e^{i\phi}$, which we might as well take to be 1. Again, these are eigenfunctions of energy but *not* momentum; they are mixtures of positive-momentum and negative-momentum eigenstates, in equal parts.

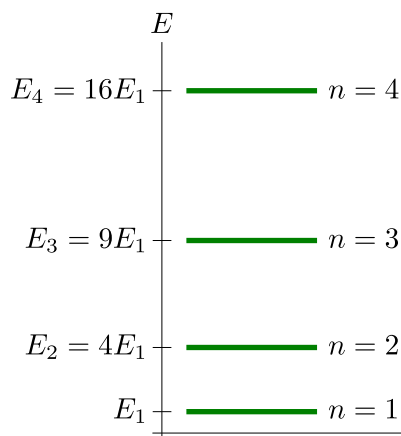
Quantized energies

To find the energy values that correspond to these eigenfunctions, we need to know the formula for kinetic energy in terms of momentum. If the particle is nonrelativistic, we have simply

$$E = K = \frac{p_x^2}{2m} = \frac{h^2 n^2}{8ma^2}, \quad (6)$$

where the first equals sign holds only inside the box, but the result must be valid for the wavefunction as a whole. Thus, we have a series of *discrete* allowed energy values, with intermediate values not allowed. We say that the energy is *quantized*; this is where the “quantum” in quantum mechanics comes from.

Here is an energy level diagram (that is, a plot of energy vs. nothing) showing the four lowest states of this system:



Such a diagram is sometimes called a *quantum ladder*, and in this case the rungs get farther and farther apart as you go up. The lowest energy level is called the *ground state*, while the rest are called *excited states*.

The *reason* why the energy is quantized is easy enough to understand: In order to fit within the box, a sinusoidal wavefunction must have an integer number of bumps. Partial bumps are not allowed, because the wavefunction must go to zero at both ends of the box (and a discontinuity at either end of the wavefunction would be equivalent to an infinitely short wavelength at that point, and hence an infinitely high energy—subverting our goal of finding wavefunctions for which the energy is well defined and finite).

Notice also that the energy of the ground state is nonzero; in fact it is $h^2/8ma^2$. This is the lowest possible energy for a (nonrelativistic) particle trapped inside an infinite square well of width a . It is nonzero because the wavefunction must have at least one full bump inside the box, and therefore the longest possible wavelength is $2a$. If you squeeze the particle into a smaller box (that is, reduce the value of a), the maximum wavelength decreases and therefore the ground-state energy

increases. This inverse relation between size and energy is quite general in quantum mechanics, and is ultimately responsible for the stability of matter.

I wish I could now show you an *experimental* energy level diagram for a real particle trapped in a real potential that approximates an infinite square well. Perhaps there's a good example out there somewhere, but so far I've been unable to find it. As I mentioned above, the one-dimensional infinite square well can be used to model electrons in certain organic molecules, or in semiconductor layers. If you shine light on these systems, the wavelengths absorbed will correspond to electron transitions from one rung on the quantum ladder up to a higher rung. Typically, however, the data show only a single transition—not enough to decode the full structure of the energy level diagram or even to show that the levels get farther apart as you go up. Many of the experiments verify the dependence on the well width a in equation 6, but even extracting this information involves quite a few real-world complications that I'd rather not spend time on now.

So please be patient. The real reason to study the one-dimensional infinite square well is not because of its direct, real-world applications, but because it serves as a foundation and starting point for understanding quantum systems in general.

Time dependence

If a particle in a box starts out in one of the energy eigenfunctions $\psi_n(x)$, what happens as time passes? I told you the answer—for energy eigenfunctions in general—in the previous lesson: Just multiply ψ_n by the usual time-dependent wobble factor to obtain

$$\psi(x, t) = \psi_n(x) e^{-iE_n t/\hbar}. \quad (7)$$

In other words, the magnitude of the wavefunction remains unchanged at every x , but the phase oscillates clockwise in the complex plane, at a rate proportional to the energy E_n .

Things get more interesting if we start out in a mixture of two or more stationary states. Again, the general prescription was given in the previous lesson: If $\psi(t = 0)$ is a sum of stationary-state terms, then $\psi(t)$ is given by the same formula with the corresponding wobble factor, $e^{-iE_n t/\hbar}$, multiplying each term. That is, each term oscillates sinusoidally at a frequency proportional to its energy. The Infinite Square Well simulation, linked from our course web page, animates the time dependence of an arbitrary mixture of the eight lowest-energy eigenfunctions. Please spend some time playing with that simulation now.

But what if a system starts in a wavefunction that *isn't* a mixture of energy eigenstates? Well, it turns out that no such wavefunctions exist! To see how this works (and why), we need to investigate some of the mathematical properties of the energy eigenfunctions.

Completeness and orthogonality

The claim that I just made can be stated as a mathematical theorem: *Any* function $\psi(x)$, within the interval from 0 through a , can be written as a linear combination of the energy eigenfunctions, for some set of coefficients c_n :

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right). \quad (8)$$

This theorem is sometimes called *Dirichlet's theorem*, and you may recognize this formula as the *Fourier series* for $\psi(x)$. I won't try to prove the theorem, but I hope you've had at least a little bit of experience with it before. Notice that in general the sum requires an infinite number of terms, although it's common in physics to stop after a finite number of terms as an approximation (since we never know the wavefunction *exactly* anyway). If the function $\psi(x)$ is complex, then so are at least some of the constants c_n . The formal name for this property of the ψ_n functions is *completeness*: they form a *complete set*, from which any other wavefunction can be built as a linear combination.

You might wonder, though, how to *find* all the c_n values for a given $\psi(x)$. Before I tell you how, I need to mention another mathematical property of the energy eigenfunctions: they are *orthogonal*, in the sense that

$$\int_0^a \psi_m(x) \psi_n(x) dx = 0 \quad \text{for } m \neq n. \quad (9)$$

I like to think of this integral as a kind of infinite-dimensional dot-product, where we multiply the “components” of ψ_m and ψ_n together at each x , then add them all up. In fact, we define the *inner product* of any two one-dimensional wavefunctions as

$$\langle \psi_a, \psi_b \rangle = \int_{-\infty}^{\infty} \psi_a^*(x) \psi_b(x) dx, \quad (10)$$

where the complex conjugation is needed to ensure that any normalized wavefunction's inner product with itself equals 1. You can find a general proof of the orthogonality of the infinite-square-well energy eigenfunctions in Griffiths or almost any other quantum mechanics textbook. I'll let you work out a few special cases in the homework.

We usually combine equation 9 with the normalization condition to write

$$\int_0^a \psi_m(x) \psi_n(x) dx = \delta_{mn}, \quad (11)$$

where δ_{mn} is an abbreviation called the *Kronecker delta symbol*, defined as

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n, \\ 0 & \text{if } m \neq n. \end{cases} \quad (12)$$

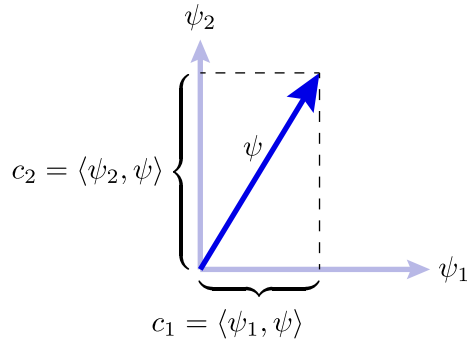
The verbal way of expressing equation 11 is then to say that the energy eigenfunctions are *orthonormal*. This property is not unique to the infinite square well; it actually applies to any quantum system whose energy levels are discrete.

I'm now ready to tell you how to find the coefficients c_n in equation 8. Griffiths calls the method by the apt name *Fourier's trick*: Multiply equation 8 by an arbitrary $\psi_m(x)$, and integrate from 0 to a :

$$\int_0^a \psi_m(x)\psi(x) dx = \sum_{n=1}^{\infty} c_n \int_0^a \psi_m(x)\psi_n(x) dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m. \quad (13)$$

In mathematical language, we're taking the inner product of our function $\psi(x)$ with one of the "basis" functions $\psi_m(x)$, to project out the "component" of $\psi(x)$ along this basis function. After moving the integral inside the sum, we obtain the same integral as in equation 11, and then the Kronecker delta kills every term in the sum except one, leaving us with a formula for c_m . The formula involves an integral, and you might feel daunted by the prospect of having to carry out an infinite number of such integrals to find the whole list of c_m values. But even if this process would be tedious, at least it's straightforward—and often we can get computers to do the tedious work for us.

The term "inner product" is supposed to remind you of an ordinary dot product of vectors. In fact, everything we're doing here is analogous to the more familiar example of expanding an arbitrary vector in terms of an orthonormal set of unit-length "basis" vectors. Here's the picture for ordinary vectors in two dimensions:



In the analysis above, the energy eigenfunctions ψ_n are our basis "vectors," which must be orthogonal to each other and normalized to unit length (equation 11). Because these basis functions form a complete set, any other wavefunction ψ can be expanded in terms of its components c_n in this basis. And to find any particular component c_n , you just "dot" the corresponding basis function ψ_n into the function ψ .

Of course my little two-dimensional picture leaves out two important complications: (1) we're actually working in an *infinite*-dimensional vector space, with an

infinite number of mutually orthogonal basis functions ψ_n ; and (2) our components c_n can be *complex* numbers. I can't really visualize either of these complications, but I still find my little two-dimensional picture to be far better than no picture at all.

Probabilities for energy measurements

If a particle in an infinite square well starts out in an energy eigenfunction and then you measure its position, you know how to calculate the probabilities of the various possible outcomes: the method is the same as for any other wavefunction, as described in Lesson 2. In general, the position probability density is spread over the whole width of the well, and varies sinusoidally between 0 at the nodes and $2/a$ at the antinodes.

But what if, on the other hand, the particle starts out in some arbitrary wavefunction and you try to measure its *energy*? If the wavefunction is an energy eigenfunction ψ_n , then of course you will obtain the corresponding E_n value with 100% certainty. If the wavefunction is a mixture of two energy eigenfunctions, such as

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x), \quad (14)$$

then presumably you could obtain either E_1 or E_2 as your result, with probabilities that somehow depend on the sizes of the coefficients c_1 and c_2 . But the probabilities can't be *equal* to c_1 and c_2 , because these coefficients could be negative or even complex; in fact the probabilities are equal to the *square moduli* of these coefficients, $|c_1|^2$ and $|c_2|^2$, respectively. To see why, let's check the normalization of $\psi(x)$:

$$1 = \int_0^a |\psi(x)|^2 dx = \int_0^a \left[|c_1|^2\psi_1^2 + |c_2|^2\psi_2^2 + (c_1^*c_2 + c_2^*c_1)\psi_1\psi_2 \right] dx. \quad (15)$$

Integrating the three terms separately, we find that the first two give simply $|c_1|^2$ and $|c_2|^2$, because ψ_1 and ψ_2 themselves are normalized, while the third term integrates to zero, because ψ_1 and ψ_2 are orthogonal. Therefore the squared coefficients must obey the relation $|c_1|^2 + |c_2|^2 = 1$, just as you would expect for probabilities.

The formulas in the previous paragraph generalize straightforwardly to superpositions of three or more energy eigenfunctions. If you measure the energy for a particle with *any* (normalized) wavefunction $\psi(x)$, the probability of obtaining the result E_n is the square modulus of the expansion coefficient c_n , when the wavefunction is expanded in terms of energy eigenfunctions as in equation 8. Therefore, according to the result of Fourier's trick (equation 13), the probability is

$$\text{(Probability of } E_n) = |c_n|^2 = \left| \int_0^a \psi_n(x)\psi(x) dx \right|^2. \quad (16)$$

Moreover, normalization of $\psi(x)$ implies that the sum of all these probabilities equals 1:

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \quad (17)$$

Finally, I should mention that *after* your measurement, now that you have a definite energy E_n for the particle, the wavefunction will have “collapsed” to $\psi_n(x)$.