January 9

Energy Spectrum in One Dimension

In the previous lecture, we wrote down the Schrödinger equation and studied its free-particle solutions. Now I would like to study the Schrödinger equation in 1 dimension with a nonzero potential

$$i\hbar \frac{\partial}{\partial t}\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi$$

If $V(x)$ is time-independent, we can look for solutions with definite frequency

$$\psi(x,t) = e^{-i\omega t}\,\psi(x)$$

According to de Broglie, the frequency is to be interpreted as the energy of the quantum state,

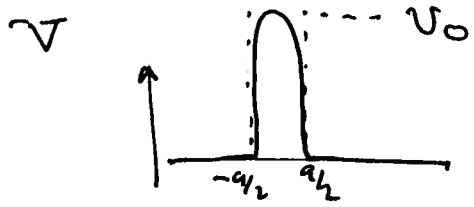
$$E = \hbar\omega$$

Then the equation that we must solve is

$$E\,\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x)$$

This equation is called the *time-independent Schrödinger equation.* It is an ordinary differential equation in one variable. You already have much experience with such equations, and we will gain more in the next few lectures.

The simplest case to study is that of a potential that is only nonzero near $x = 0$



I will study this potential in the limit

$$a \to 0 \qquad V_0 a \to \text{constant} = V$$

(For those of you familiar with the Dirac delta function $\delta(x)$, I am assuming that

$$V(x) = V \cdot \delta(x)$$

If this is not familiar to you, this knowledge is will not be necessary to follow the argument. I will introduce the Dirac delta function formally later in the course.)

Consider first the case $E > 0$. We can easily solve the time-independent Schrödinger equation in any region where the potential is zero. For $x < -a/2$, the most general solution can be written

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

with

$$E = \frac{\hbar^2 k^2}{2m} \qquad \text{or} \qquad k = +(2mE)^{1/2}/\hbar$$

For $x > a/2$, the most general solution is

$$\psi(x) = C e^{ikx} + D e^{-ikx}$$

To finish the solution to the complete equation, we need to find the relationship between A, B and C, D. If the potential were zero, we would simply have $A = C$, $B = D$. That is, we find two independent solutions for each value of E. For the case of nonzero potential, I will solve for the generalization of the first of these solutions by setting

$$C = 1 \qquad D = 0$$

An analysis similar to this can be done for the case

$$C = 0 \qquad D = 1$$

And, since the Schrödinger equation is linear, any linear combination of these solutions is also a solution with the same value of E.

If a is small, it is tempting to say that the wavefunction will be approximately continuous across the potential. This would imply

$$\psi\Big|_{x=-a/2} = \psi\Big|_{x=a/2} + \theta(a) \quad \text{or} \quad A+B = 1 + \theta(a)$$

We will see in a moment that this is a correct statement. It is also tempting to guess that the first derivative of the wavefunction is also continuous across the potential. In fact, this is not correct. To see that, integrate the Schrödinger equation from $x = -a/2$ to $x = a/2$. Assuming that the wavefunction is bounded and its derivatives do not become infinite, the left-hand side and the second term on the right-hand side are approximately proportional to $\psi(x = 0)$. The first term on the right-hand side is the integral of an exact second derivative. Thus, the result is

$$E\,\psi(0)\cdot a = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\psi\Big|_{-a/2}^{a/2} + \left(\int_{-a/2}^{a/2} dx\, V(x)\right)\cdot\psi(0) + \mathcal{O}(a)$$

If we set

$$\int_{-a/2}^{a/2} dx = a\cdot V_0 = \mathbb{V}$$

and then take the limit $a \to 0$, we find

$$\frac{\partial\psi}{\partial x}\Big|_{a/2} - \frac{\partial\psi}{\partial x}\Big|_{-a/2} = \frac{2m}{\hbar^2}\cdot\mathbb{V}\cdot\psi(0)$$

$$ik - (ikA - ikB) = \frac{2m}{\hbar^2}\cdot\mathbb{V}\cdot 1$$

Using $A = 1 - B$, this becomes

$$2ikB = \frac{2m}{\hbar^2}\mathbb{V}$$

or, finally,

$$B = -i\frac{m}{\hbar^2 k}\mathbb{V} \qquad A = 1 + i\frac{m}{\hbar^2 k}\mathbb{V}$$

The expressions for A and B are well-defined for all $E > 0$. The solution we were looking for exists for any such E. Similarly, the solution with $C = 0$, $D = 1$ also exists for all $E > 0$.

Now, consider the case $E < 0$. For this case, if we write

$$E = \frac{\hbar^2 k^2}{2m}$$

the value of k is imaginary. It is convenient to define κ by

$$\kappa = (-2mE)^{1/2}/\hbar > 0$$

Then

$$E = -\frac{\hbar^2\kappa^2}{2m}$$

The most general solution of the Schrödinger equation for $x < -a/2$ is

$$\psi(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

and, similarly, the most general solution of the Schrödinger equation for $x > a/2$ is

$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$$

However, there is a serious problem with these expressions unless

$$B = C = 0$$

If these parameters are nonzero, the wavefunction grows exponentially as $x \to \infty$ or $x \to -\infty$. Then all of the weight of the wavefunction would be at ∞, and none would be near the potential. Such solutions do not have physical significance for the problem of a quantum particle with a potential. I will thus reject these solutions as physical solutions of the Schrödinger equation. For the rest of this lecture, I will say that such solutions have *incorrect boundary conditions at infinity.*

Now we can proceed. The most general solutions with correct boundary conditions at infinity are

$$\psi(x) = \begin{cases} A e^{\kappa x} & x < -a/2 \\ D e^{-\kappa x} & x > a/2 \end{cases}$$

continuity across the potential implies

$$A = D \qquad + O(a)$$

and, since the equation is linear, we can set $A = D = 1$ for simplicity. The joining condition for the first derivatives is

$$\left.\frac{\partial \psi}{\partial x}\right|_{a/2} - \left.\frac{\partial \psi}{\partial x}\right|_{-a/2} = \frac{2m}{\hbar^2} V$$

This implies

$$-2\kappa = \frac{2m}{\hbar^2} V$$

or

$$\kappa = -\frac{m}{\hbar^2} V$$

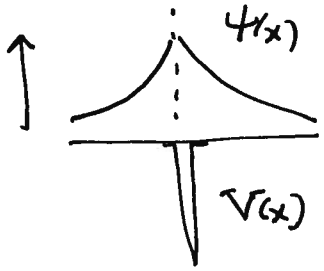
Notice that we have defined κ to be positive, so this equation is consistent only if

$$V < 0$$

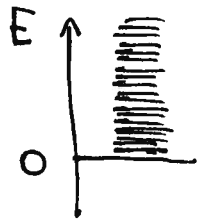
In fact, there is a solution only for *one* negative value of E, namely,

$$E = -\frac{mV^2}{2\hbar^2}$$

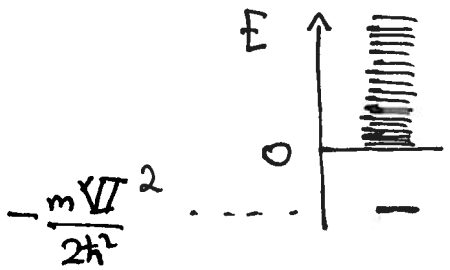
The shape of this wavefunction is



Let's review the results. For a positive potential, there are two solutions for every value of $E >$, and *no* solutions for $E < 0$. We refer to a problem in which the allowed values of E fill a region continuously as having a *continuous spectrum.*



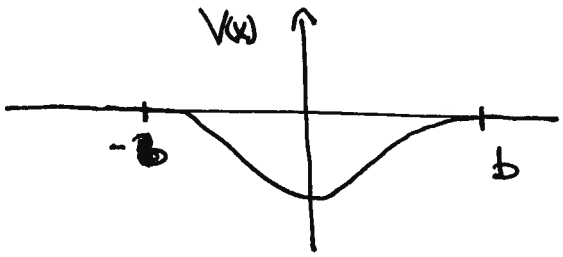
For a negative potential, there is a continuous spectrum for $E > 0$ and also one discrete state for $E < 0$



The situation for $E < 0$ is called a *discrete spectrum*. Since the wavefunction for $E < 0$ is localized near the potential, we also call this state a *bound state* of the potential.

Using methods more sophisticated that those I am discussing here, it is possible to count the states in the continuous spectrum. When this is done, it is possible to show that, in the case of a negative potential, the continuous spectrum has one less solution, which has been sucked down to become the discrete state at $E < 0$.

The problem of a very narrow potential, which we now understand very explicitly, is an example of a more general situation. I would now like to sketch the solution for the allowed values of E for a general potential of the form



This potential is negative in the region between $x = -b$ and $x = b$ and is zero outside this region. For a general form of $V(x)$, it is not possible to solve this problem analytically. However, it is easy to solve the problem numerically, by using software that integrates a first-order differential equation. It is also possible to visualize the form of the solution, and I would like to discuss that analysis now.

Rewrite the time-independent Schrödinger equation as

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

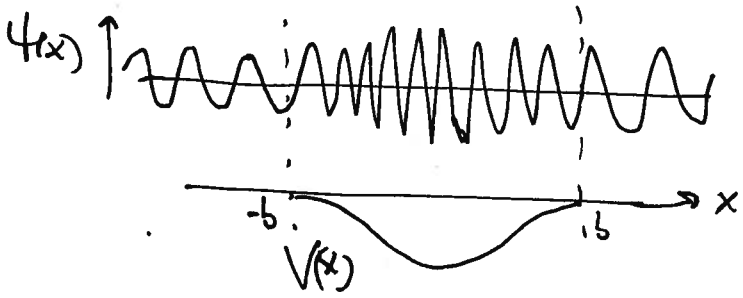
We can try to gain intuition by treating the right-hand side of this equation as approximately constant. Then the solution is a wave with wavenumber

$$k \sim \left[\frac{2m}{\hbar^2}(E - V(x))\right]^{\frac{1}{2}}$$

The wave oscillates more rapidly for larger values of $(E - V(x))$. For $|x| > b$, the solution is exactly an oscillation at the wavenumber

$$k = \left(\frac{2m}{\hbar^2} E\right)^{1/2}$$

Then we can sketch the form of the solution for a general $E > 0$



As before, there are two solutions for every E. We can write these as one with $\psi = \sin(kx)$ for $x < -b$, the other with $\psi = \cos(kx)$ for $x < b$. The wave oscillates through the potential in a way that is hard to predict, so in both cases the wave acquires a phase shift as it passes through the potential. But it is clear that the two solutions exist for every $E > 0$, so we have a continuous spectrum also in this more general situation. You can check all of these statements by writing down an explicit form for $V(x)$ and integrating the time-independent Schrödinger equation using MatLab or Mathematica.

For $E < 0$, the situation is more complicated. For a region to the left that includes $E < -b$, the quantity $(E - V(x))$ is negative. In this region, the solution of the Schrödinger equation has exponential behavior, that is (in the same intuitive approximation as above),

$$\psi(x) \sim A e^{\chi(x)\cdot x} + B e^{-\chi(x)\cdot x}$$

with

$$\chi(x) = +\left[\frac{2m}{\hbar^2}(V(x) - E)\right]^{1/2}$$

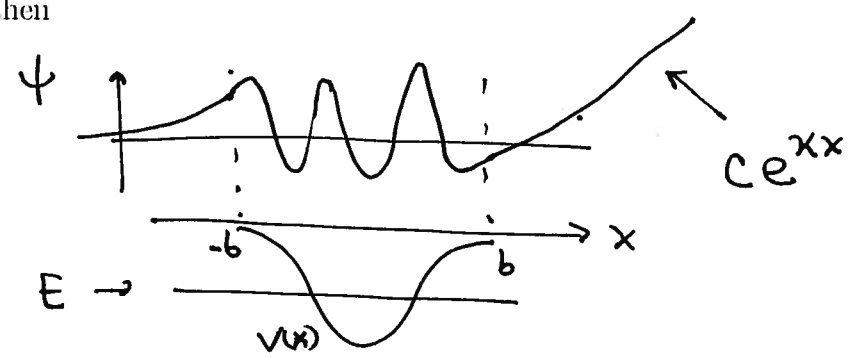
Notice that, if B is nonzero, this function has incorrect boundary conditions as $x \to -\infty$, in the sense described earlier. So we must begin from a solution with $B = 0$

and κ nonzero. The solution of the Schrödinger equation has similar exponential behavior a the region to the right of the potential that includes $x > b$. For $x > b$, the general solution is

$$\psi(x) = C e^{\kappa x} + D e^{-\kappa x}, \quad \kappa = \left[\frac{-2mE}{\hbar^2}\right]^{\frac{1}{2}}$$

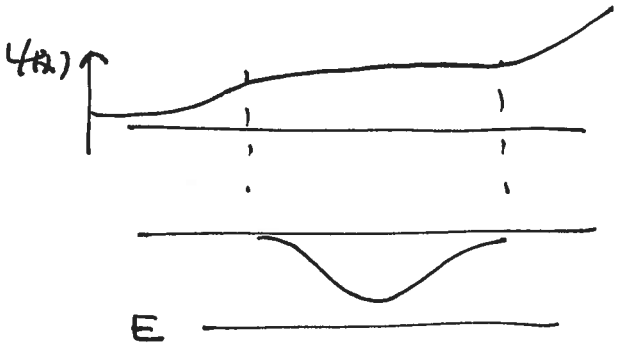
In between these regions, there might be a region where $(E - V(x)) > 0$ in which the wavefunction has oscillatory behavior.

For a generic value of E, the result of integrating the Schrödinger equation through the potential is then

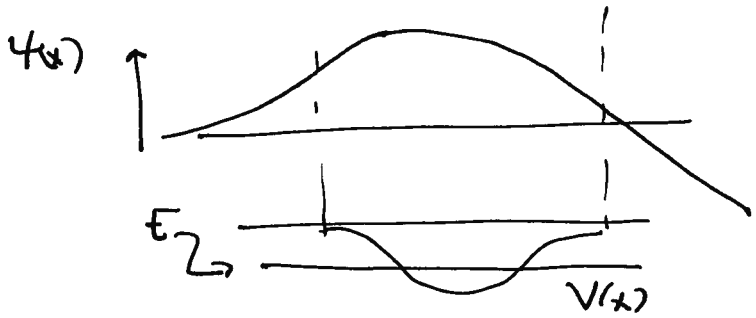


This solution has an incorrect boundary condition as $x \to \infty$.

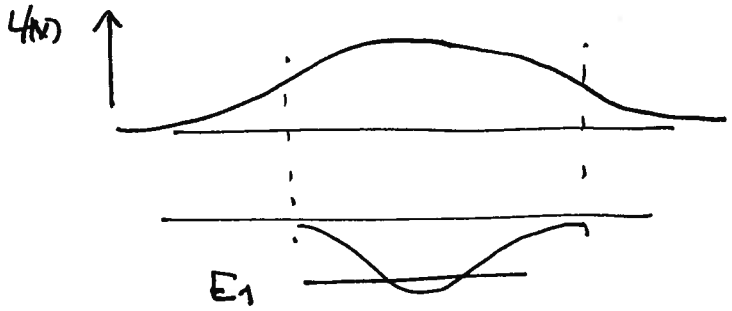
However, there are solutions with correct boundary conditions. We can find them in the following way: Start at a value of E less than the minimum of $V(x)$. In this case, the solution of the Schrödinger equation is always exponential and always increasing,



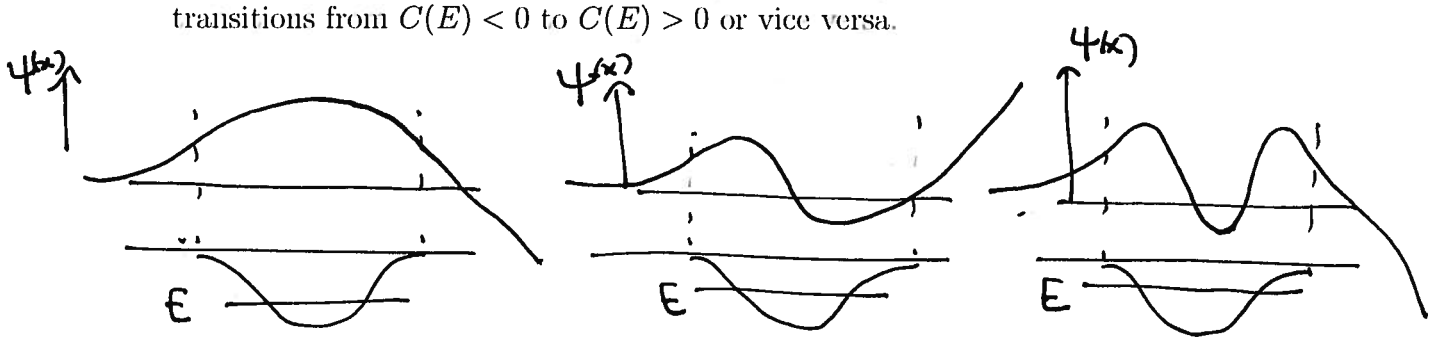
For this solution, for $x > b$, the coefficient $C(E)$ is positive. Now increase E above the minimum of the potential. If the wavefunction oscillates sufficiently, we will find a solution of the form



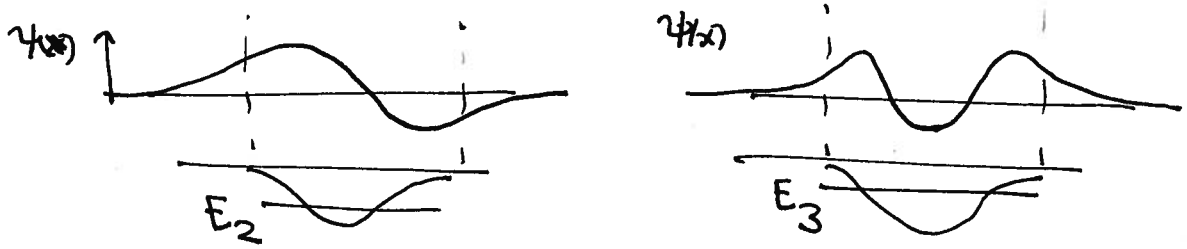
for which the coefficient $C(E)$ is negative. There must be some energy in between these values where, by continuity, $C(E) = 0$. Then we have a solution to the Schrödinger equation with correct boundary conditions.



As we continue to raise the value of E, still keeping $E < 0$, we might find additional transitions from $C(E) < 0$ to $C(E) > 0$ or vice versa.

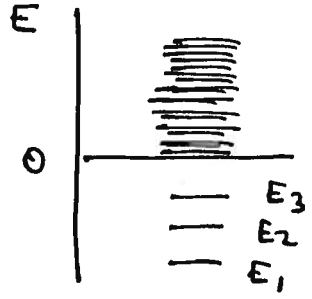


At the energies of the transitions, we find additional solutions with correct boundary conditions



These solutions occur at discrete energies and are finite in number. When we go above $E = 0$, there are two solutions for every energy, as described above.

The spectrum of values of E for which there are solutions of the time-independent Schrödinger equation then has the form



with a continuous spectrum above $E = 0$ and a finite number of discrete bound states below $E = 0$. This is the form of the spectrum of energy levels in a typical atom. So, somehow, we seem to be on the right track to explain the discrete energy levels seen in atoms.

For a potential that extends out to infinity, it is also possible to have an accumulation of bound states as E approaches 0 from below. We will see later that this happens for the Coulomb potential.

The mathematical problem that we are solving here has the form of a linear equation

$$E\psi(x) = \mathcal{O}\psi(x)$$

where $\mathcal{O}$ is a differential operator. Here

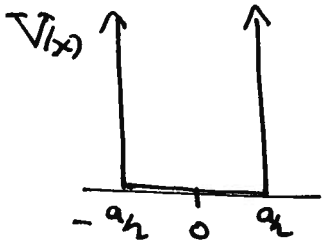
$$\mathcal{O} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

The problem is solvable, not for every value of E, but only for some particular values of E. Part of the problem is to find the values of E for which solutions exist. This type of problem is called an *eigenvalue problem*. The values of E for which solutions exist are called the *eigenvalues* of $\mathcal{O}$. The corresponding solutions for ψ are called *eigenfunctions* or *eigenstates*.

In this lecture and the next few, I will study some examples in which the eigenfunctions and eigenvalues of the Schrödinger equation can be found analytically. In the first, simplest, problems that we will solve, the continuous spectrum is pushed to high energies, so only the discrete spectrum remains. Of course, this is the part of the spectrum that is most difficult to understand. So I hope that these examples will help you understand how discrete eigenvalues arise. These examples will also develop mathematical materials that we will use to assemble a deeper understanding of quantum mechanics.

The first of these problems is the *infinite square well*, otherwise known as the *particle in a box*. The potential is

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



For this potential, at any finite energy E, the wavefunction must go to zero exponentially in the region $|x| > a/2$, and, in fact, it must go to zero extremely rapidly. In the idealization in which the potential is truly infinite for $|x| > a/2$, the wavefunction is *zero* in the region $|x| > a/2$. Then, by continuity,

$$\psi(x) = 0 \quad \text{at} \quad x = -a/2 \,, \, a/2$$

This is a set of two boundary conditions to be imposed in solving the Schrödinger equation. The derivative of the wavefunction can change discontinuously at $x = \pm a/2$, in fact, it must change from a finite value to zero.

From the arguments just given, there are no solutions with $E < 0$. For $E > 0$, the Schrödinger equation takes the form

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

for $|x| < a/2$. The most general solution of this equation is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{or} \quad \psi(x) = F\sin kx + G\cos kx$$

with

$$k = \left[\frac{2mE}{\hbar^2}\right]^{\frac{1}{2}}$$

To solve the condition $\psi(x) = 0$ at $x = -a/2$, the solution must be proportional to

$$\psi(x) = \sin k\left(x + \tfrac{a}{2}\right)$$

To solve the condition $\psi(x) = 0$ at $x = a/2$, we must also impose

$$0 = \psi\left(x = \tfrac{a}{2}\right) = \sin ka$$

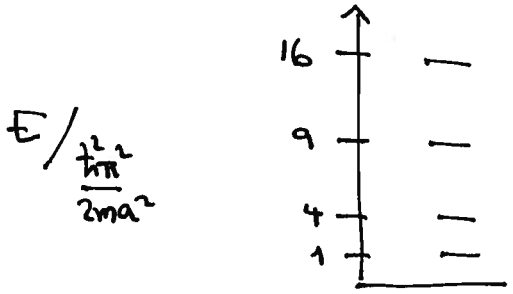
This equation can be satisfied only for a discrete set of values of k,

$$k = \frac{n\pi}{a} \qquad n = 1, 2, 3, \cdots$$

Then the allowed energies also must be a discrete set

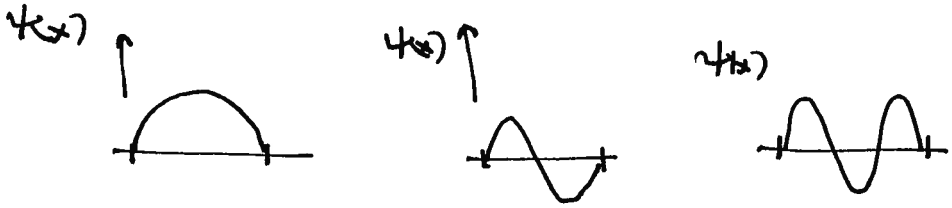
$$E = \frac{\hbar^2\pi^2}{2ma^2} \cdot n^2$$

The spectrum contains only discrete eigenvalues



On the problem set 1, you will study the case of a square well in which the potential has a large but not infinite value V_* for $|x| > a/2$. You can check explicitly that this potential has a continous spectrum beginning from V_*.

The first few eigenfunctions have the form



These functions have some interesting properties that I would like to discuss.

First, these functions are symmetrical about $x = 0$, even for odd n and odd for even n. We can show this explicitly.

$$\sin\frac{n\pi}{a}(x+\tfrac{a}{2}) = \sin\left(\frac{n\pi x}{a} + \frac{n\pi}{2}\right)$$

$$= \sin\frac{n\pi x}{a}\cos\frac{n\pi}{2} + \cos\frac{n\pi x}{a}\sin\frac{n\pi}{2}$$

For n odd, $\cos(\pi n/2) = 0$, so

$$\psi_n(x) \sim \cos\frac{n\pi x}{a}$$

and the wavefunction is even about $x = 0$. For n even, $\sin(\pi n/2) = 0$, so

$$\psi_n(x) \sim \sin \frac{n\pi}{a} x$$

and the function is odd about $x = 0$.

It is a general property of a symmetric potential

$$V(x) = V(-x)$$

that all discrete eigenfunctions are either even or odd about $x = 0$. Here is a proof. Write the Schrödinger equation

$$E\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x)$$

Replace x by $(-x)$

$$E\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial(-x)^2} + V(-x)\right]\psi(-x)$$

The term with two derivatives has two minus signs. Using this and the symmetry of the potential, this equation becomes

$$E\psi(-x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(-x)$$

so $\psi(-x)$ is an eigenfunction of the original problem with the same eigenvalue. If there is a unique discrete state at the energy E, it must be true that

$$\psi(-x) = c\,\psi(x)$$

Repeating the argument, we find that

$$\psi(x) = c^2\,\psi(x)$$

so

$$c = \pm 1$$

and so the eigenfunction must be either even or odd. If there are two independent eigenfunctions at the energy E, we can form the even and odd linear combinations

$$[\psi(x) + \psi(-x)] \qquad [\psi(x) - \psi(-x)]$$

Thus, it is always possible to write the discrete eigenfunctions of a symmetric potential as linear combinations of even and odd eigenfunctions.

Second, the zeros of successive eigenfunctions neatly interleave one another. You can see intuitively why this should happen using the argument about integrating the Schrödinger equation given above. It is possible to prove this statement rigorously, but the proof is not so simple.

This aspect of the form of the eigenfunctions suggests another relation that is easier to prove and also is a very fundamental part of the struction of an eigenvalue problem. I claim that, if $\psi_n(x)$ and $\psi_m(x)$ are eigenfunctions of the Schrödinger equation with energies E_n and E_m, respectively, and $E_n \neq E_m$, then

$$\int_{-\infty}^{\infty} dx \; \psi_n^*(x)\, \psi_m(x) = 0$$

We say that $\psi_n(x)$ and $\psi_m(x)$ are *orthogonal*. In the problem we are studying now, the discrete eigenfunctions can be taken to be real, but in more general situations, the Schrödinger wavefunction can be complex, and then the indicated complex conjugation is needed.

It is not so difficult to check this relation for the explicit eigenfunctions that we have found. It is easy to see, just by symmetry, that

$$\int_{-a/2}^{a/2} dx \; \cos\frac{\pi x}{a} \; \sin\frac{2\pi x}{a} = 0$$

But, also, for example

$$\int_{-a/2}^{a/2} dx \; \cos\frac{\pi x}{a} \; \cos\frac{3\pi x}{a} = 0$$

Indeed, the integral is equal to

$$\int_{-a/2}^{a/2} dx \; \frac{1}{4}\left(e^{i\pi x/a} + e^{-i\pi x/a}\right)\left(e^{3\pi i x/a} + e^{-3\pi i x/a}\right)$$

$$= \frac{1}{4}\int_{-a/2}^{a/2} dx \left(e^{4\pi i x/a} + e^{2\pi i x/a} + e^{-2\pi i x/a} + e^{-4\pi i x/a}\right)$$

$$= \frac{1}{4}\,\frac{a}{2\pi}\int_{-\pi}^{\pi} dy \left(e^{2iy} + e^{iy} + e^{-iy} + e^{-2iy}\right) \qquad y = \frac{2\pi x}{a}$$

In the last expression, each term integrates to zero.

Here is a general proof of the orthogonality relation: Write the Schrödinger equation

$$E_m \psi_m = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi_m$$

and write the complex conjugate of this equation

$$E_m^* \psi_m^* = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi_m^*$$

By assumption, $V(x)$, a potential energy, is real-valued. Consider the integrals over the whole domain

$$\int_{-\infty}^{\infty} dx \; \psi_n^* \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi_m = E_m \int_{-\infty}^{\infty} dx \; \psi_n^* \psi_m$$

$$\int_{-\infty}^{\infty} dx \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi_n^* \cdot \psi_m = E_n^* \int_{-\infty}^{\infty} dx \; \psi_n^* \psi_m$$

For a smooth potential, the wavefunction will extend to infinity and go to zero as $|x| \to \infty$. Then we can integrate by parts

$$\int_{-\infty}^{\infty} dx \; \psi_n^* \frac{\partial^2}{\partial x^2} \psi_m = - \int_{-\infty}^{\infty} dx \; \frac{\partial \psi_n}{\partial x} \frac{\partial \psi_m}{\partial x} = \int_{-\infty}^{\infty} dx \; \frac{\partial^2 \psi_n}{\partial x^2} \psi_m$$

and then rearrange the terms in the second integral so that it becomes identical to the first integral. This implies

$$E_m \int_{-\infty}^{\infty} dx \; \psi_n^* \psi_m = E_n^* \int dx \; \psi_n^* \psi_m$$

First consider the case $m = n$. The integral is

$$\int_{-\infty}^{\infty} dx \, |\psi_n|^2$$

which is manifestly positive. We see that

$$E_n = E_n^*$$

Then consider $m \neq n$. If $E_m \neq E_n$, the equation is consistent only if

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

This proves the result claimed above.

The positive quantity found in the case $m = n$ plays a rather important role in quantum mechanics. To understand its significance, consider a general time-dependent Schrödinger wavefunction $\psi(x,t)$, obeying the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x,t)$$

Using this equation, we can compute the time derivative of the integral of the square of the wavefunction

$$\frac{\partial}{\partial t} \int dx \, \psi^*(x) \psi(x)$$

$$= \int dx \left(\frac{1}{-i\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi^* \right) \psi + \psi^* \left(\frac{1}{i\hbar} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi \right)$$

Note that the coefficient in the first term is

$$\left(\frac{1}{i\hbar}\right)^* = -\frac{1}{i\hbar}$$

After integration by parts as above and rearrangement of terms, we find

$$\int dx\ \psi^* \left\{ -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi + \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi \right\} = 0$$

Then, for any solution to the Schrödinger equation,

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx\ |\psi(x,t)|^2 = 0$$

It is very useful to set

$$\int_{-\infty}^{\infty} dx\ |\psi(x,t)|^2 = 1$$

A wavefunction satisfying this condition is said to be *normalized*. A wavefunction that is normalized at one initial value of t remains normalized at any value of t.

The normalized eigenfunctions of the infinite square well problem are

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\cos\frac{\pi n x}{a} & n \text{ odd} \\ \sqrt{\frac{2}{a}}\sin\frac{\pi n x}{a} & n \text{ even} \end{cases}$$

In discussing the interpretation of the Schrödinger equation, I told you that a quantum particle such as an electron was described by a Schrödinger wavefunction,

with the actual particle located somewhere in the wave. The results above make it is reasonable to propose that the quantity

$$P(x) = |\psi(x)|^2$$

is the *probability distribution* of the particle within the wave. That is, the probability to find the particle in a small box of size Δx about $x = x_0$ is

$$\Delta P = |\psi(x_0)|^2 \Delta x$$

The total probability to find the particle is conveniently

$$\int_{-\infty}^{\infty} dx\, P(x) = \int_{-\infty}^{\infty} dx\, |\psi(x)|^2 = 1$$

for a normalized wavefunction, and this total probability is indepedent of time. The average or *expected* position of the particle $\langle x \rangle$ is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} dx\, |\psi(x)|^2 \cdot x$$

Notice that, for every eigenfunction of the square well problem

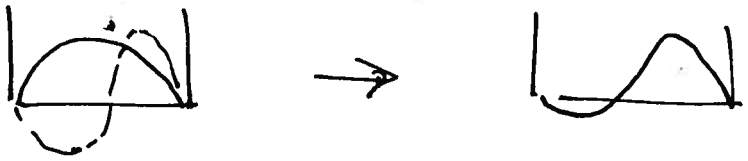
$$\langle x \rangle = \int_{-\infty}^{\infty} dx\, |\psi_n(x)|^2 \cdot x = 0$$

That is, the particle is equally likely to be to the left or to the right of $x = 0$. This is the expectation from the symmetry of the problem.

If we were to somehow set up a situation in which the particle started in the right-hand side of the well, we would expect that it would oscillate back and forth from $x > 0$ to $x < 0$. I would like to demonstrate this in a simple example. Consider choosing as the initial condition for the Schrödinger equation

$$\psi_0(x) = a_1\sqrt{\frac{2}{a}}\cos\frac{\pi x}{a} + a_2\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

where $a_1^2 + a_2^2 = 1$ if the function is to be normalized. This wavefunction has the form



We can now solve the time-dependent Schrödinger equation to find the time evolution of this state. The time-dependence of each eigenfunction is

$$\psi_n(x,t) = e^{-iE_nt/\hbar}\psi_n(x)$$

and a linear combination of solutions to the Schrödinger equation gives another solution. Thus, the solution with the above initial condition is

$$\psi(x,t) = a_1\sqrt{\frac{2}{a}}\cos\frac{\pi x}{a}\,e^{-i\frac{\hbar\pi^2}{2ma^2}t} + a_2\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\,e^{-i\frac{4\hbar\pi^2}{2ma^2}t}$$

The value of the expectation value of x, $\langle x\rangle$, as a function of time is given by

$$\langle x\rangle = \frac{2}{a}\int_{-a/2}^{a/2} dx\, x\left\{a_1^2\cos^2\frac{\pi x}{a} + a_1a_2\left(e^{\frac{3i\hbar\pi^2}{2ma^2}t} + e^{-\frac{3i\hbar\pi^2}{2ma^2}t}\right)\cos\frac{\pi x}{a}\sin\frac{2\pi x}{a} + a_2^2\sin^2\frac{2\pi x}{a}\right\}$$

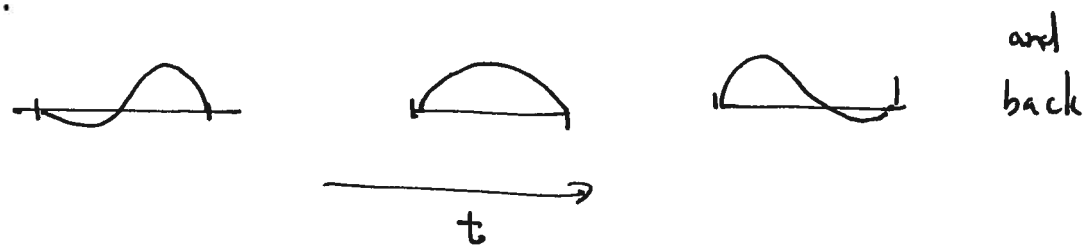
The first and third terms vanish by symmetry. The second term contains the integral

$$I = \int_{-a_2}^{a_2} dx \; x \cos\frac{\pi x}{a} \sin\frac{2\pi x}{a} = \frac{8}{9\pi^2} a^2$$

Then

$$\langle x \rangle = \frac{4 a_1 a_2}{} \cdot \frac{8}{9\pi^2} \cdot a \cdot \cos\left[\frac{3\hbar\pi^2}{2ma^2} t\right]$$

So, very nicely, $\langle x \rangle$ oscillates back and forth between positive and negative values! The evolution of the wavefunction is



The method of solution used here can actually be used to find a general time-dependent solution to the square well problem. I would like to sketch the method here. We will come back to these ideas later in the course and discuss some of the concepts used in more detail.

We wish to solve the Schrödinger equation with initial condition give by a general function $\psi_0(x)$, which must of course vanish at $x = \pm a/2$. To begin, hypothesize that this function can be written as a linear combination of the eigenfunctions,

$$\psi_0(x) = \sum_n c_n \psi_n(x)$$

Then we can immediately write down the solution

$$\psi(x,t) = \sum_n c_n \psi_n(x)\, e^{-i\frac{\hbar\pi^2 n^2}{2ma^2}t}$$

The big question that remains is, can we always apply the expansion used here? For the problem of the square well, we already know the answer. A smooth function on a finite interval can always be approximated arbitrarily accurately by a Fourier series, that is, by a series of sines and cosines. The eigenfunctions of the square well problem are precisely those sine and cosine functions that vanish at $x = \pm a/2$. OK, we are done!

Our formalism has also given us an algorithm for computing the coefficients a_n. Integrate the initial condition $\psi_0(x)$ with an eigenfunction $\psi_m^*(x)$

$$\int dx\, \psi_m^*(x)\, \psi_0(x) = \sum_n \int dx\, \psi_m^*(x) \cdot c_n \psi_n(x)$$

by orthogonality, only the term with $n = m$ on the right hand side is nonzero. If $\psi_m(x)$ is also normalized,

$$\int dx\, \psi_m^*(x)\, \psi_0(x) = c_n$$

Then we can work out all of the expansion coefficients by doing integrals. This is a small piece of a more general theory that we will discuss further later in the course.