Electron in a Box
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Plane Wave Solutions

The best way to gain understanding of Schrödinger’s equation is to solve it for various potentials. The simplest is a one-dimensional “particle in a box” problem. The appropriate potential is $V(x) = 0$ for $x$ between 0, $L$ and $V(x) = \infty$ otherwise—that is to say, there are infinitely high walls at $x = 0$ and $x = L$, and the particle is trapped between them. This turns out to be quite a good approximation for electrons in a long molecule, and the three-dimensional version is a reasonable picture for electrons in metals.

Between $x = 0$ and $x = L$ we have $V = 0$, so the wave equation is just

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2}. $$

A possible plane wave solution is

$$\psi(x,t) = Ae^{i(px-Et)}. $$

On inserting this into the zero-potential Schrödinger equation above we find $E = p^2/2m$, as we expect.

It is very important to notice that the complex conjugate, proportional to $e^{-i(px-Et)}$, is not a solution to the Schrödinger equation! If we blindly put it into the equation we get

$$E = -p^2/2m, $$

an unphysical result.

However, a wave function proportional to $e^{-i\hbar(mx+Et)}$ gives $E = p^2/2m$, so this plane wave is a solution to the equation.

Therefore, the two allowed plane-wave solutions to the zero-potential Schrödinger equation are proportional to $e^{i\hbar(px-Et)}$ and $e^{-i\hbar(px+Et)}$ respectively.

Note that these two solutions have the same time dependence $e^{iEt/\hbar}$. 
To decide on the appropriate solution for our problem of an electron in a box, of course we have to bring in the walls—what they mean is that \( \psi = 0 \) for \( x < 0 \) and for \( x > L \) because remember \( |\psi|^2 \) tells us the probability of finding the particle anywhere, and, since it’s in the box, it’s trapped between the walls, so there’s zero probability of finding it outside.

The condition \( \psi = 0 \) at \( x = 0 \) and \( x = L \) reminds us of the vibrating string with two fixed ends—the solution of the string wave equation is standing waves of sine form. In fact, taking the difference of the two permitted plane-wave forms above gives a solution of this type:

\[
\psi(x, t) = A \sin \left( \frac{p x}{\hbar} e^{-\frac{d t}{\hbar}} \right).
\]

This wave function satisfies the Schrödinger equation between the walls, it vanishes at the \( x = 0 \) wall, it will also vanish at \( x = L \) provided that the momentum variable satisfies:

\[
\frac{p L}{\hbar} = \pi, \ 2\pi, \ 3\pi...
\]

Thus the allowed values of \( p \) are \( \hbar n/2L \), where \( n = 1, 2, 3 \ldots \), and from \( E = p^2/2m \) the allowed energy levels of the particle are:

\[
E = \frac{p^2}{2m} = \frac{1}{2m} \left( \frac{\hbar}{2L} \right)^2, \ \frac{4}{2m} \left( \frac{\hbar}{2L} \right)^2, \ \frac{9}{2m} \left( \frac{\hbar}{2L} \right)^2, \ldots
\]

Note that these energy levels become more and more widely spaced out at high energies, in contrast to the hydrogen atom potential. (As we shall see, the harmonic oscillator potential gives equally spaced energy levels, so by studying how the spacing of energy levels varies with energy, we can learn something about the shape of the potential.)

What about the overall multiplicative constant \( A \) in the wave function? This can be real or complex. To find its value, note that at a fixed time, say \( t = 0 \), the probability of the electron being between \( x \) and \( x + dx \) is \( |\psi|^2 dx \) or

\[
|A|^2 \sin^2 \left( \frac{p x}{\hbar} \right) dx.
\]

The total probability of the particle being somewhere between 0, \( L \) must be unity:

\[
\int_{x=0}^{x=L} \left| A \right|^2 \sin^2 \left( \frac{p x}{\hbar} \right) dx = 1, \text{ so } \frac{1}{2} \left| A \right|^2 = 1.
\]

Hence
\[ \psi(x,t) = \sqrt{\frac{2}{L}} \sin \left( \frac{px}{\hbar} e^{-\frac{i\varepsilon t}{\hbar}} \right). \]

When \( A \) is fixed in this way, by demanding that the total probability of finding the particle somewhere be unity, it is called the **normalization constant**.

### Stationary States

Notice that at a later time the probability distribution for the wave function

\[ \psi(x,t) = \sqrt{\frac{2}{L}} \sin \left( \frac{px}{\hbar} e^{-\frac{i\varepsilon t}{\hbar}} \right) \]

is **the same**, because **time only appears as a phase factor** in this time-dependent function, and so does not affect \( |\psi|^2 \).

*An** *a* **state with a time-independent probability distribution is called a stationary state**.

### States with Moving Probability Distributions

Recall that the Schrodinger equation is a **linear** equation, and *the sum of any two solutions is also a solution* to the equation. That means that we can add two solutions having different energies, and still have a legal wave function. We shall establish that in this case, *the probability distribution varies in time*.

The simplest way to see how this must be is to look at an example. Let’s add the ground state to the first excited state, and normalize the sum:

\[ \psi(x,t) = \sqrt{\frac{1}{L}} \left( \sin \frac{\pi x}{L} e^{\frac{i\varepsilon t}{\hbar}} + \sin \frac{2\pi x}{L} e^{\frac{i\varepsilon t}{\hbar}} \right). \]

*note: \( h \), not \( \hbar \).*

(You can check the normalization constant at \( t = 0 \)). For general \( x \), the two terms rotate in the complex plane at different rates, so their sum has a time-varying magnitude. That is to say, \( |\psi(x,t)|^2 \) varies in time, so the particle must be moving around—this is *not* a stationary state.

**Exercise:** To see this, note that at \( t = 0 \) the wave function is:

\[ \psi(x,0) = \sqrt{\frac{1}{L}} \left( \sin \frac{\pi x}{L} + \sin \frac{2\pi x}{L} \right) \]

and sketch this function: the particle is more likely to be found in the left-hand half of the box.
Now, suppose the time is $t = 4 mL^2 / \hbar$, so $e^{-i \hbar t / 4mL^2} = -1$. At this time,

$$\psi(x, 2L^2 / \hbar) = \sqrt{\frac{1}{L}} \left(-\sin \frac{\pi x}{L} + \sin \frac{2\pi x}{L}\right)$$

and it’s easy to see that the particle is more likely to be found in the right-hand half.

That is to say, this wave function, a linear sum of wave functions corresponding to different energies, has a probability distribution that sloshes back and forth in the box: and, any attempt to describe a classical-type particle motion, bouncing back and forth, necessarily involves adding quantum wave functions of different energies. Note that the frequency of the sloshing motion depends on the difference of the two energies: how constructively the two components interfere depends on the difference of the phases in the energies at the time. A single energy wave function always has a static probability distribution.

Of course, the total probability of finding the particle somewhere in the box remains unity: the normalization constant is time-independent.

The Time-Independent Schrödinger Equation: Eigenstates and Eigenvalues

The only way to prevent $|\psi(x, t)|^2$ varying in time is to have all its parts changing phase in time at the same rate. This means they all correspond to the same energy. If we restrict our considerations to such stationary states, the wave function can be factorized

$$\psi(x, t) = \psi(x) e^{iEt / \hbar}$$

and putting this wave function into the Schrödinger equation we find

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

This is the time-independent Schrödinger equation, and its solutions are the spatial wave functions for stationary states, states of definite energy. These are often called eigenstates of the equation.

The values of energy corresponding to these eigenstates are called the eigenvalues.

An Important Point: What, Exactly, Happens at the Wall?

Consider again the wavefunction for the lowest energy state of a particle confined between walls at $x = 0$ and $x = L$. The reader should sketch the wavefunction from some point to the left of $x = 0$ over to the right of $x = L$. To the left of $x = 0$, the wavefunction is exactly zero, then at $x = 0$ it takes off to the right (inside the box) as a sine curve. In other
words, at the origin the slope of the wavefunction $\psi$ is zero to the left, nonzero to the right. There is a discontinuity in the slope at the origin: this means the second derivative of $\psi$ is infinite at the origin. On examining the time-independent Schrödinger equation above, we see the equation can only be satisfied at the origin because the potential becomes infinite there—the wall is an infinite potential. (And, in fact, since $\psi$ becomes zero on approaching the origin from inside the box, the limit must be treated carefully.)

It now becomes obvious that if the box does not have infinite walls, but merely high ones, $\psi$ describing a confined particle cannot suddenly go to zero at the walls: the second derivative must remain finite. For non-infinite walls, $\psi$ and its derivative must be continuous on entering the wall. This has the important physical consequence that $\psi$ will be nonzero at least for some distance into the wall, even if classically the confined particle does not have enough energy to “climb the wall”. (Which it doesn’t, if it’s confined.) Thus, in quantum mechanics, there is a non-vanishing probability of finding the particle in a region which is “classically forbidden” in the sense that it doesn’t have enough energy to get there.