WAVE FUNCTION WITH ARBITRARY INITIAL STATE

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In the solution of the one-dimensional particle in a box problem we find that there are an infinite number of wave functions that satisfy the spatial part of the Schrödinger equation, and that each such solution corresponds to a discrete energy. To summarize, the problem was to solve the spatial equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi = E\psi \tag{1}$$

for the potential

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

We found that the solutions, properly normalized, are

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \tag{3}$$

with $\psi = 0$ outside the box. The energy corresponding to solution ψ_n is

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{4}$$

But this solves only the spatial part of the Schrödinger equation. The full solution requires bringing back the function containing the time dependence that arises from solving the equation using separation of variables. Thus the full, time-dependent solution for a particular energy is

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{5}$$

where ψ_n and E_n are given above.

The probability of finding a particle that is in state $\Psi_n(x,t)$ at location x at time t is therefore $|\Psi_n|^2 = |\psi_n|^2$. That is, if a particle is in one of the states with a definite energy E_n, its probability density is independent of time, since the only time dependence comes from the complex exponential function whose modulus is always 1. The time dependence always disappears when the square modulus is calculated. For this reason, the states $\Psi_n(x,t)$ are called *stationary states*.

This isn't the end of the story, however. Since the Schrödinger equation is linear, once we have found two or more solutions, any linear combination of these solutions gives another solution. Thus the most general solution of the time-independent Schrödinger equation for the particle in a box is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \tag{6}$$

where the c_n are arbitrary complex constants. Solutions that are linear combinations of two or more of the stationary states are, however, not stationary states themselves, since each term in the sum contains its own dependence on time in the form of a complex exponential, and these exponentials will not cancel out when the square modulus is calculated.

To explore the consequences of this general solution, we need first to demonstrate some of the properties of the ψ_n stationary states. We know that ψ_n is normalized, in the sense that

$$\int_0^a |\psi_n(x)|^2 dx = 1 \tag{7}$$

However the set of ψ_n functions is also *orthogonal*, in the sense that if $m \neq n$

$$\int_0^a \psi_n(x)\psi_m(x) dx = 0 \tag{8}$$

(This can be checked by direct integration, using the trigonometric identity $\sin a \sin b = \frac{1}{2}(\cos(a-b) - \cos(a+b))$.) A set of functions that are both orthogonal and normalized is called an *orthonormal* set.

This result may surprise you, but you might also be thinking 'so what?'. The normalization is clearly important if ψ_n is to be used as a probability density, but the orthogonality seems pretty much irrelevant. To see why this property is important, suppose you want a full dynamical description of a particle starting from time $t = 0$ when the particle is in some initial state $\Psi(x,0)$. In general, we should be able to specify this initial state to be anything at all. In the classical case, an analogous situation might be something like this: standing on the Earth's surface we have a rock of mass m which we can throw from any height above the ground. We can aim the rock in any direction and at any speed. All of these things are independent of the law of gravity which takes over after the rock has been thrown. But the theory of motion that we use to describe the motion of the rock must allow us to specify the initial conditions to be anything we like.

It is a similar situation in quantum mechanics. The Schrödinger equation tells us how the particle behaves, but only after we have specified the initial conditions. In this case, we can 'throw' the particle into the potential well by specifying its initial state, and the theory must be able to accept any (within the constraints of the problem) initial state. For the particle in a box, since we have an infinite potential outside the box, there is no way the particle could ever be found outside, so any initial condition must confine the particle to the region $0 \le x \le a$, but apart from that, $\Psi(x,0)$ can be anything at all.

From the general solution above, we can get an expression for $\Psi(x,0)$:

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{9}$$

The problem is therefore, given $\Psi(x,0)$ and $\psi_n(x)$, find the constants c_n. It is here that the orthonormal nature of the set of stationary solutions comes into play. Suppose we want to find c_N for some particular value of N. If we multiply this expression by ψ_N and integrate over the range of the box (from 0 to a), then all integrals where $N \ne n$ are zero because ψ_N is orthogonal to ψ_n, so we are left with just the one term we want:

$$\begin{aligned}\int_0^a \psi_N(x)\Psi(x,0)dx &= \sum_{n=1}^{\infty} c_n \int_0^a \psi_N \psi_n \, dx && (10)\\ &= \sum_{n=1}^{\infty} c_n \delta_{nN} && (11)\\ &= c_N && (12)\end{aligned}$$

where the symbol δ_{nN} is called the *Kronecker delta* and is a shorthand way of writing a quantity that is zero if $n \ne N$, and 1 if $n = N$.

So for *any* initial condition, we now have a way of writing it as a sum over the spatial part of the stationary states at time $t = 0$. The general solution is obtained merely by restoring the time dependence:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} \tag{13}$$

Note that I am *not* saying that *any* function is a solution of the Schrödinger equation - that is clearly absurd. What *is* true, however, is that *any* function of x can be expressed as a linear combination of the solutions of the spatial part of the Schrödinger equation. It is important to note that any of the ψ_n functions on its own is *not* a solution of the Schrödinger equation unless it is multiplied by $e^{-iE_nt/\hbar}$, so the linear combination $\Psi(x,0)=\sum_{n=1}^{\infty}c_n\psi_n(x)$ is *not* in general a solution of the Schrödinger equation. It is only the final form $\Psi(x,t)=\sum_{n=1}^{\infty}c_n\psi_n(x)e^{-iE_nt/\hbar}$ that is a solution.

Example 1. A particle in the infinite square well starts off with a wave function as follows:

$$\Psi(x,0)=\begin{cases}Ax & 0\le x\le a/2\\ A(a-x) & a/2\le x\le a\end{cases}\tag{14}$$

The initial wave function is thus a triangle with its peak at $x=a/2$ and a height of $Aa/2$. We can normalize the wave function first

$$\int_0^a|\Psi|^2dx=A^2\left(\int_0^{a/2}x^2dx+\int_{a/2}^a(a-x)^2dx\right)\tag{15}$$

$$=A^2\frac{a^3}{12}=1\tag{16}$$

$$A=\frac{2\sqrt{3}}{a^{3/2}}\tag{17}$$

Next, we can find $\Psi(x,0)$ in terms of the ψ_n. We need to calculate the c_n, so:

$$c_n=\int_0^a\Psi(x,0)\psi_ndx\tag{18}$$

$$=\frac{2\sqrt{3}}{a^{3/2}}\sqrt{\frac{2}{a}}\left(\int_0^{a/2}x\sin\frac{n\pi x}{a}dx+\int_{a/2}^a(a-x)\sin\frac{n\pi x}{a}dx\right)\tag{19}$$

$$=\frac{4\sqrt{6}}{n^2\pi^2}\sin\frac{n\pi}{2}\tag{20}$$

(The integral is straightforward, if a bit tedious. I used mathematical software to do it on a computer.) Thus we get

$$\Psi(x,0)=\frac{4\sqrt{6}}{\pi^2}\sum_{n=1}^{\infty}\frac{\sin(n\pi/2)}{n^2}\psi_n(x)\tag{21}$$

$$=\frac{4\sqrt{6}}{\pi^2}\left[\sum_{n=1,5,9\ldots}\frac{\psi_n}{n^2}-\sum_{n=3,7,11\ldots}\frac{\psi_n}{n^2}\right]\tag{22}$$

The term $\sin(n\pi/2)$ is zero if n is even, and ±1 for odd values of n, giving the sums shown in the last line. The series consists of odd n only, with half the terms being positive and the other half negative. The full solution is found by replacing the exponentials containing the time dependence:

$$\Psi(x,t)=\frac{4\sqrt{6}}{\pi^2}\left[\sum_{n=1,5,9\ldots}\frac{\psi_n}{n^2}e^{-iE_nt/\hbar}-\sum_{n=3,7,11\ldots}\frac{\psi_n}{n^2}e^{-iE_nt/\hbar}\right] \tag{23}$$

The probability that the energy is E_1 is

$$c_1^2=\left(\frac{4\sqrt{6}}{\pi^2}\right)^2=\frac{96}{\pi^4}=0.9855 \tag{24}$$

[Incidentally, since we know that $\sum_n |c_n|^2=1$, we get from 20 that

$$\sum_{n\ odd}\frac{1}{n^4}=\frac{\pi^4}{96} \tag{25}$$

The average energy can be found by using the energy levels for the infinite square well:

$$E_n=\frac{(n\pi\hbar)^2}{2ma^2} \tag{26}$$

We then have

$$\begin{aligned}\langle H\rangle &= \sum_{n=0}^{\infty}|c_n|^2E_n &(27)\\ &= \frac{96}{\pi^4}\frac{\pi^2\hbar^2}{2ma^2}\sum_{n\ odd}\frac{1}{n^2} &(28)\\ &= \frac{96}{\pi^4}\frac{\pi^2\hbar^2}{2ma^2}\frac{\pi^2}{8} &(29)\\ &= \frac{6\hbar^2}{ma^2} &(30)\\ &\approx 1.216E_1 &(31)\end{aligned}$$

The sum

$$\sum_{n\ odd}\frac{1}{n^2}=\frac{\pi^2}{8} \tag{32}$$

is not commonly found in tables, but a link (live at the time of writing) showing a derivation is here. The derivation requires knowledge of either the Riemann zeta function or the residue theorem from complex variable theory.

To summarize, the situation with the particle in a box is:

1. Using separation of variables, we can split the solution $\Psi(x,t)$ into a spatial function $\psi(x)$ and a temporal factor $e^{-iEt/\hbar}$.
2. When we solve the spatial equation with appropriate boundary conditions and normalization, we get the set of functions $\psi_n(x)$. Each of these functions is associated with a specific discrete energy E_n.
3. The set of functions $\psi_n(x)$ is orthonormal.
4. The full solution of the Schrödinger equation for a particular energy E_n is $\psi_n(x)e^{-iE_nt/\hbar}$. The square modulus of this solution is independent of time, so it is a stationary state.
5. The general solution of the Schrödinger equation is a linear combination of the set of stationary states. The square modulus of a general solution will not, in general, be stationary (time-independent).
6. The constants c_n in the general solution can be obtained using the initial condition $\Psi(x,0)$ and the orthonormality of the $\psi_n(x)$.

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