

Physics 228, Lecture 13

Monday, March 7, 2005

Probability, Schrödinger. Ch 39:5, Ch 40:1;

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1 Schrödinger's Equation

According to de Broglie, a freely moving particle with momentum p has an associated wavelength $\lambda = h/p$. This is the wavelength of oscillation of a wavefunction,

$$\Psi_1(x, t) = A \sin\left(\frac{2\pi x}{\lambda}\right) \cos \omega t = A \sin\left(\frac{p}{\hbar}x\right) \cos \omega t,$$

where $\hbar = h/2\pi$. The angular frequency ω is just proportional to the the total energy $E = hf = \hbar\omega$. Of course the phases could be different, and we could have used $\sin \omega t$ instead of $\cos \omega t$

For photons, we know that their wave properties come from the solution of Maxwell's equations in empty space, and in particular from the wave equation for the electric and magnetic fields

$$\frac{\partial^2 \vec{B}}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \vec{B}}{\partial t^2}.$$

For a plane wave with wavelength λ , corresponding to a photon of momentum $p = h/\lambda$ and energy $E = hf = \hbar\omega$, the wave is of the form

$$\vec{B} = \vec{B}_0 \sin\left(\frac{px}{\hbar}\right) \cos\left(\frac{Et}{\hbar}\right),$$

so the partial derivatives are

$$\frac{\partial^2 \vec{B}}{\partial x^2} = -\left(\frac{p}{\hbar}\right)^2 \vec{B}, \quad \frac{\partial^2 \vec{B}}{\partial t^2} = -\left(\frac{E}{\hbar}\right)^2 \vec{B}.$$

and the wave equation is telling us $p^2 = E^2/c^2$. which is just the equation that relates a photon's momentum to its energy.

For a free non-relativistic particle, the corresponding equation is $E = \frac{1}{2}mv^2 = p^2/2m$. So let's see if we can interpret

$$E\Psi = \frac{p^2}{2m}\Psi$$

in terms of a wave-like equation. The p^2 is just like for the photon, so we note that if

$$\begin{aligned}\Psi_1(x, t) &= A \sin\left(\frac{p}{\hbar}x\right) \cos\left(\frac{E}{\hbar}t\right), \\ \frac{\partial^2}{\partial x^2}\Psi_1 &= -\frac{p^2}{\hbar^2}\Psi_1, \quad \text{and so } \frac{p^2}{2m}\Psi_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_1.\end{aligned}$$

For the nonrelativistic particle we only need one power of E , rather than E^2 as we had for the photon. If we apply just one time derivative,

$$\frac{\partial}{\partial t}\Psi_1 = -A\frac{E}{\hbar} \sin\left(\frac{p}{\hbar}x\right) \sin\left(\frac{E}{\hbar}t\right),$$

which is almost enough to write

$$\begin{aligned}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_1 &= \frac{p^2}{2m}\Psi_1 = \frac{p^2}{2m}A \sin\left(\frac{p}{\hbar}x\right) \cos\left(\frac{E}{\hbar}t\right), \\ &\sim \hbar\frac{\partial}{\partial t}\Psi_1 = -EA \sin\left(\frac{p}{\hbar}x\right) \sin\left(\frac{E}{\hbar}t\right), \quad \text{Not quite!},\end{aligned}$$

This doesn't quite work, because we have $-\sin(Et/\hbar)$ instead of $\cos(Et/\hbar)$. What if we had started with a sine? If

$$\begin{aligned}\Psi_2(x, t) &= A \sin\left(\frac{p}{\hbar}x\right) \sin\left(\frac{E}{\hbar}t\right), \\ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_2 &= \frac{p^2}{2m}\Psi_2 \\ \hbar\frac{\partial}{\partial t}\Psi_2 &= EA \sin\left(\frac{p}{\hbar}x\right) \cos\left(\frac{E}{\hbar}t\right) = E\Psi_1.\end{aligned}$$

So that doesn't quite work either. If we rewrite our previous attempt

$$\hbar\frac{\partial}{\partial t}\Psi_1 = -EA \sin\left(\frac{p}{\hbar}x\right) \sin\left(\frac{E}{\hbar}t\right) = -E\Psi_2,$$

we see that neither Ψ_1 nor Ψ_2 provides a neat partial differential equation, but the combination

$$\Psi = \Psi_1 - i\Psi_2 \quad \text{has} \quad \hbar \frac{\partial}{\partial t} \Psi = \hbar \frac{\partial}{\partial t} \Psi_1 - i\hbar \frac{\partial}{\partial t} \Psi_2 = -E(\Psi_2 + i\Psi_1) = -iE\Psi.$$

Thus the wave function Ψ which describes a free particle of momentum p and energy E satisfies

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi = \frac{p^2}{2m} \Psi = E\Psi = i\hbar \frac{\partial}{\partial t} \Psi,$$

and more generally any free particle wave function satisfies the differential equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi = i\hbar \frac{\partial}{\partial t} \Psi.$$

Notice that to write down a wave equation we needed to make a **complex** wave function with the combination

$$\Psi = A \sin\left(\frac{p}{\hbar}x\right) (\cos \omega t - i \sin \omega t).$$

In fact the wave equation itself has a complex constant i in it, so no real function can satisfy it (unless the energy is zero).

The combination¹

$$\cos \theta - i \sin \theta = e^{-i\theta},$$

and if you get comfortable using complex numbers in this way, many problems in differential equations become much easier to deal with.

¹Proofs: 1) As

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n, \quad e^{-i\theta} = \sum_{n=0}^{\infty} \frac{1}{n!} (-i)^n \theta^n.$$

But as $(-i)^2 = -1$, we have $(-i)^n = (-1)^{n/2}$ for even n , so

$$e^{-i\theta} = \sum_{\text{even } n} \frac{1}{n!} (-\theta^2)^{n/2} - i \sum_{\text{odd } n} \frac{1}{n!} (-1)^{(n-1)/2} \theta^n = \cos \theta - i \sin \theta.$$

2) For $\theta = 0$ the equation is true because both sides are 1. And each side of the equation satisfies the differential equation

$$\frac{dy(\theta)}{d\theta} = -iy(\theta).$$

That is enough to show the two sides must be equal.

1.1 Adding potential energy

A free particle is nice to understand, but we also need to describe particles that have forces on them, like an electron in an atom. If we have a particle with a definite total energy E in a potential, the momentum will not be the same everywhere, so the wavelength will be varying from point to point. Strictly speaking, the concept of wavelength only applies to a periodic function, for which the wavelength is the same everywhere.

We have just seen how to replace the wavelength by derivatives, which can vary from point to point. Energy conservation tells us that the total energy E is the sum of the kinetic energy $p^2/2m$ and the potential energy $U(x)$. Thus

$$p^2 = 2m[E - U(x)]$$

and

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} [E - U(x)] \psi.$$

This is known as the **time-independent Schrödinger equation**. It applies for a wave function known to have a definite energy E . As before, we can reexpress $E\Psi = i\hbar\partial\Psi/\partial t$, to get the more general **time-dependent Schrödinger equation**²:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t},$$

which we have written for a one dimensional problem³. We will not need this more general form, and shall only ask about states of definite energy which we can treat without worrying about the time dependence of the wave

²The text uses $\Psi(x, t)$ for the time-dependent wave function, to distinguish it from the time-independent function $\psi(x)$. But this is not standard notation.

³For a problem in three dimensional space, Ψ is a function of the full position \vec{r} and t , $\Psi(\vec{r}, t)$, and we need the full momentum squared, $\vec{p}^2 = p_x^2 + p_y^2 + p_z^2$, which turns into a sum of second partial derivatives. Thus the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + U(\vec{r})\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t},$$

where

$$\nabla^2 \Psi(\vec{r}, t) := \frac{\partial^2 \Psi(\vec{r}, t)}{\partial x^2} + \frac{\partial^2 \Psi(\vec{r}, t)}{\partial y^2} + \frac{\partial^2 \Psi(\vec{r}, t)}{\partial z^2}.$$

∇^2 is called the ‘‘Laplacian’’ operator. It is the divergence of the gradient, $\vec{\nabla} \cdot \vec{\nabla}$.

function, using the time-independent Schrödinger equation. For problems in one dimension, the only variable that the wave function depends on is then x , and the partial derivatives are ordinary:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2} [E - U(x)] \psi(x).$$

For a general function $U(x)$, the solution of this equation is a problem of ordinary differential equations and is beyond the scope of this course. We will discuss some simple cases, however. But first, let us discuss the meaning of the wave function.

2 Probability Density

Last time we discussed that the wave function ψ is the probability amplitude, whose square gives the probability density, the probability that the particle is found in a small region divided by the volume of that region. Let's consider just motion in one dimension, so we may ask what the probability is that the particle will be in the range $[x, x + dx]$. For infinitesimal dx , the answer is

Show Fig. 41.8,
 Δx added

3" x 3"

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

provided $\psi(x)$ is the **normalized** wave function. What does that mean? The Schrödinger equation does not determine a scale for ψ — if $\psi(x)$ satisfies it, so does $2\psi(x)$, or any other multiple. But we do know that the probability that the particle is *somewhere* must be one, so

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

This last condition is called the **normalization condition**, and ψ is said to be normalized if it satisfies that condition. Then the more interesting question is what the probability is that the particle be between a and $b > a$. That is

$$P([a, b]) = \int_a^b |\psi(x)|^2 dx.$$

If we know a quantum mechanical system is in the state ψ and want to know where the particle is, we do not have a definite answer. We can do some measurement that determines where it is, but we will get different answers,

with various probabilities, if we repeat the experiment many times. Knowing the wave function does not enable you to predict the answer you will get from one measurement, but it can tell you the average you will get if you repeat the experiment many times. This is called the **expectation value**, which physicists denote with angle brackets. To get the expectation value, one must multiply the result x by the probability of getting that result, $P(x)$, and sum over all possible results. With a continuum of possible results, this is

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

Note the extra x in the integrand, compared to the normalization condition.

3 Wave packets

We have seen that the Schrödinger equation determines the wave function for a particle, and in particular for a free particle with no forces or potential, we have

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

This is a linear differential equation which has the particular solutions

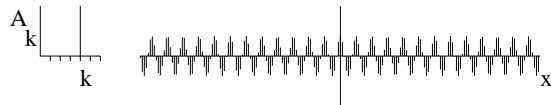
$$\Psi_k(x, t) = e^{i(kx - \omega t)}, \quad \text{with } \omega = \hbar \frac{k^2}{2m},$$

because

$$p = \frac{h}{\lambda} = \hbar k, \quad E = hf = \hbar\omega = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}.$$

As the Schrödinger equation is linear, an arbitrary linear combination of these particular solutions is also a solution.

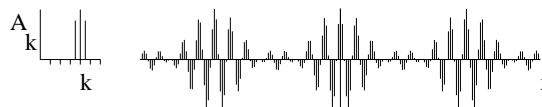
Now if we look at the solution $\Psi_k(x, t)$, it doesn't look much like a particle moving in the positive x direction. The



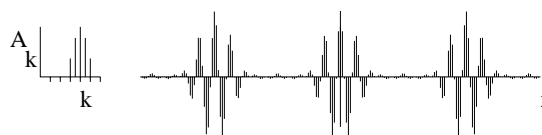
real part is a sine wave throughout space, so the particle is not localized at all.

This should not be a surprise, because this particle has its momentum exactly determined to be the one value $p = \hbar k$. If we want to localize the particle we will need to make the momentum a bit uncertain.

Let's add in to the $k = 4$ amplitude some $k = 3.5$ and some $k = 4.5$ wave, with amplitudes as shown:

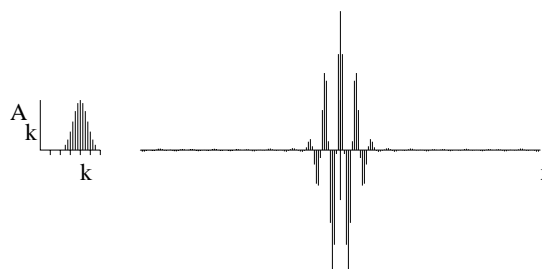


These give “beats” which localize the particle somewhat, but not to one localized location. If we want to do better, let's throw in some $k = 3$ and $k = 5$ stuff:



We see that each location is a bit better localized, because Δp has increased, but we still have repeats.

To do something about that, we need to use more intermediate values of k , so let's throw in contributions at intervals of 0.25 in k -space, as shown.



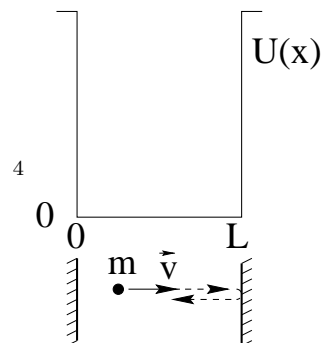
That seemed to work, but in fact there will still be repeats, beyond the values of x we have plotted, unless we use a continuum of k values, so we need to use an integral,

$$\psi(x) = \int_{-\infty}^{\infty} A(k)e^{ikx} dk,$$

where $A(k)$ is some smooth function of k , such as the envelope of the discrete values shown, which for our example is $A(k) = e^{-(k-4)^2}$. This will then have no recurrences, and just the uncertainty in x visible on the graph.

4 Particle in a box

We will consider next one very simplified problem using Schrödinger's equation. Suppose we have a particle that is free (*i.e.* has no forces on it) except that it is confined to a box. In one dimension that means there is a wall, say at $x = 0$, which prevents the particle from being to its left, and another wall, at $x = L$, preventing the particle from being to its right. This is called the infinite square well. These walls exert an infinite force from an infinite⁴ confining potential (no matter how hard the particle hits, it cannot penetrate.) Thus there is zero probability that the particle will be outside the box, and



$$\psi(x) = \begin{cases} 0 & \text{for } x \leq 0 \\ A \sin(kx) & \text{for } 0 \leq x \leq L \\ 0 & \text{for } x \geq L \end{cases}$$

The function in the region $x \in [0, L]$ is a sine because it has to be zero to match the wavefunction values outside the box. We can assume $U = 0$ inside the box, so from the Schrödinger equation

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} &= -\frac{2mE}{\hbar^2}\psi(x) \\ &= -k^2\psi(x) \end{aligned}$$

so we see that

$$k = \frac{\sqrt{2mE}}{\hbar},$$

but also, because ψ must be continuous and thus zero at $x = L$, we must have $\sin kL = 0$, or $kL = n\pi$ for some integer n . This means that not all energies are possible — for each positive integer n we have one state with energy E_n given by

Show fig 41.12
 E levels in
box ($3^{\circ} \times 3 \ 1/4^{\circ}$)

$$\frac{\sqrt{2mE_n}}{\hbar} L = n\pi, \quad \text{or } E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{h^2}{8mL^2} n^2.$$

⁴There would be an infinite force even if the potential outside the box were finite, as long as there is a discontinuity in $U(x)$. But that “finite square well” would not necessarily be enough to confine a particle, because if it has enough energy, $E > U(x > L)$ the particle could overcome this force. We will discuss the finite square well next time.

Each state has a wave function

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right).$$

Classically, the particle would be moving back and forth with constant speed, and would spend an equal amount of time in each region of the box. Quantum mechanically, the probability of being at any particular spot is given by the square of the wave function. Here we show the wave function and the probability density for the lowest three states.

show fig 41.11
 $\psi, |\psi^2|$ in box
 7 1/4" × 3 3/4"

There is some strange stuff going on here. The particle is never found right at the wall, and for the $n = 2$ state it is never in the middle, even though it is equally likely to be on either side of the middle.

Notice that the momentum $p = \frac{h}{\lambda} = \frac{h}{2L/n} = \frac{nh}{2L}$ also only takes on discrete values. It would appear to have a definite value for the n 'th state, which would contradict the Heisenberg uncertainty principle coupled with the fact that we know its position,

$$0 \leq x \leq L \quad \text{so } \Delta x = L.$$

But in fact the above value for the momentum is actually its magnitude only, the momentum is equally likely to be positive or negative (in the x -direction), so $\Delta p = 2nh/2L$, and

$$\Delta x \Delta p = L \frac{nh}{L} = nh > \hbar/2.$$

Note also that the lowest state is $n = 1$. $n = 0$ is not possible for several reasons. One is that $\psi = A \sin(0 \cdot x) = 0$ cannot be normalized. Another is that then $p = \pm 0$ would violate the Heisenberg principle. So a particle in a box cannot be completely at rest — it has a minimum possible energy called the **zero-point energy**.

Schrödinger's equation is the basis of non-relativistic quantum mechanics, and many important physical problems, like the harmonic oscillator or the hydrogen atom, can be worked out in detail. There are many interesting effects, such as the fact that there is some probability of finding a particle in a region in which its potential energy is higher than its total energy,

which cannot happen classically. This also permits particles to “tunnel” through small regions which, classically, they could not get through, and this is responsible for such things as the long half-lives of radioactive nuclei. It is also the principle behind an electronic device called a tunnel diode. But you will have to take a more advanced course if you want to see those things worked out.

5 Summary

- The time-independent Schrödinger Equation (in one dimension)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2m}{\hbar^2} [E - U(x)] \psi(x)$$

gives the wave function for a stationary state, that is a state of definite energy.

- The probability density is given by $|\psi|^2$, and the expectation value for the position is

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

- a particle trapped in a box with infinitely strong walls has states labelled by a positive integer n with wave functions and energies

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{h^2}{8mL^2} n^2.$$