Modern Physics notes – Spring 2007

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Lecture 6

- Electrons as waves
- Particle in a box
- Spectral lines

- Feynman, 2.5
- Fowler, "Spectra", "The Bohr atom"

Electrons as waves

Let me summarize the consequences of the experiments we did (electron diffraction and the photoelectric effect). We saw that both light and electrons behave like both particles and waves. They are like particles because they come in discrete bundles. It is possible to talk of a single electron; it is also possible to talk of a photon (a discrete bundle of light). That's their "particle" nature. Their "wave" nature means that they can diffract like waves. The two pictures are related by the formula

$$p = \frac{h}{\lambda}$$

The momentum of the particle is related to the wavelength of the wave by this formula.

The right-hand-side of this equation is weird in the case of the electron: in classical physics an electron does not have a wavelength. The left-hand-side is weird in the case of light: light has momentum classically, but the fact that it comes in these lumps called photons is quantum-mechanical.

But for electrons, what are the waves? A water wave represents regions of greater or lesser height of water. A wave on a guitar string is similar. A light wave is subtler – it's a fluctuating electric and magnetic field. We've noted that electrons are still particles – we still see an integer number of electrons. The wavy nature of the electrons is in their *probability amplitude.* This is the thing whose absolute value you square to get the probability the electron will appear in a given region of space. The probability amplitude is the thing which adds, like the electric field.

In other words, it behaves linearly, like solutions to Maxwell's equations. You might ask if there's a differential equation whose solution determines the probability amplitude. There is – it's called Schrödinger's equation, and we will get to it at the very end of our study of quantum mechanics. But we can understand a lot about quantum mechanics without Schrödinger's equation. In particular, we'll spend a lot of time on the two-state system, where Schrödinger isn't needed.

Particle in a box

The existence of photons was our first reason for the word "quantum" in quantum mechanics. Light at a given frequency occurs in discrete lumps, "quanta". These lumps can be seen easily experimentally, although not quite by the naked eye (although your eye apparently would need to be only about 10 times more sensitive to be able to see individual photons).

A second interesting thing also is apparent in the photoelectric effect experiment we did. You'll notice something about the light which was coming from the mercury vapor. Instead of just giving out light of all colors, there were noticeable lines of distinct frequency (you can check experimentally that these are of distinct frequency, and measure the wavelength, by doing interference experiments). Since we now know that light frequency is proportional to photon energy, this tell us that the mercury atoms are not emitting energy of arbitrary sizes. Instead, the energy seems to be coming out in chunks. Thus again, where classically you might expect something continuous, here you get something quantized.

The last problem on the first homework was I hope very simple to do mathematically. Despite its simple exterior, it is an extremely profound problem. It says two important things happen when you force a particle to be in a box. It says that

1. You get a minimum momentum

$$p_{\text{min}} = \frac{h}{\lambda_{\text{max}}} = \frac{h}{2L}$$

2. The momentum p (and hence the energy $E = p^2/(2m)$) does not take on arbitrary values. They are *quantized*. Since the possible λ are $2L/n$ for n integer, the possible momenta are

$$p = \frac{h}{\lambda} = \frac{nh}{2L}$$

The possible energies are therefore

$$E = \frac{p^2}{2m} = \frac{h^2 n^2}{8mL^2}$$

Both of these are radically new consequences of quantum mechanics. The first can be thought of as a consequence of the uncertainty principle. Since we don't know where the particle in a box is, $\Delta x = L$. Using the uncertainty principle then says that

$$\Delta p \geq \frac{h}{4\pi L}$$

Then it's totally reasonable to assume that if the uncertainty is $\geq h/4\pi L$, then the *actual value* is also $\sim h/L$, where $\sim$ means I'm ignoring all factors of $2, \pi$, etc. Thus we have

$$p \sim h/L$$

This gives the correct answer you derived on the HW to within a factor of 2. In the next lecture I'll use a similar argument to estimate the size of the atom.

The second consequence is one of the reasons for the word "quantum" in "quantum mechanics". So let's explain it in more detail.

Let's first think about classical waves. The amplitude of a guitar string (the maximum distance it is stretched) must be zero at the ends, but otherwise can form any pattern inside. You may remember from math class that you can write this as a sum of waves. Specifically, in a box of length L with vanishing amplitude at the ends, you can have waves of wavelength $2L, L, 2L/3, \ldots$. Any wave vanishing on both ends can be written as a sum of waves of wavelengths $2L/n$, where n is an integer. (This was your HW problem 5.) This is called a *standing wave.*

Now let's think about light trapped in a 1d box. You saw in the first problem of the homework that light obeys the wave equation. The spatial dependence of light of a given wavelength λ is either

$$e^{-2\pi ix/\lambda} \quad \text{or} \quad e^{+2\pi ix/\lambda}$$

(the correct answer to the first problem is that $\omega = \pm kc$). Remember, we can always add two solutions of Maxwell's equations in a vacuum and get another, so we can add these two together with arbitrary coefficients $\vec{A}$ and $\vec{B}$. In a equation:

$$\vec{E} = \vec{A}e^{-2\pi ix/\lambda} + \vec{B}e^{+2\pi ix/\lambda}$$

However, here we need to take into account the presence of the box. This says that $\vec{A}$, $\vec{B}$ and λ are not arbitrary. Since no light is escaping, there can be no light at the edges of the box, which we put at $x = 0$ and $x = L$. This means $\vec{E} = 0$ at the edges. To satisfy this, we need to make

$$\vec{E} \propto \sin\left(\frac{\pi n}{L}x\right)$$

where n is some integer. Because $\sin n\pi$ vanishes for any integer n, this $\vec{E}$ behaves appropriately at the edges. So note that we have $\vec{A} = -\vec{B}$, and more importantly

$$\lambda = \frac{2L}{n}$$

for some integer n. The wavelength is quantized in units of the size of the box. This is a standing wave like the guitar string: you can think of it as the light just bouncing back and forth off of mirrors.

Note that this is a little easier to write out if instead of using wavelength, we use the wavenumber $k = 2\pi/\lambda$. Then our wave is $\propto \sin(kx)$, and the boundary conditions require that

$$k = \frac{\pi n}{L}.$$

The two ways of writing this are obviously equivalent; you'll notice that Feynman tends to use k instead of λ. To get rid of the factors of 2π this introduces, people introduced the constant $\hbar$. In terms of these new variables,

$$p = \frac{h}{\lambda} = \hbar k$$

Once we start using $\hbar$, then it's easier to to use

$$\omega \equiv 2\pi\nu$$

for frequency so that for photons

$$E = \hbar\omega$$

You should have seen ω before, when you were doing rotational motion. There ω is the angular frequency as measured in radians. The point of all of these definitions is to absorb factors of 2π: in terms of k, ω and $\hbar$, you don't see any factors of 2π in $E = \hbar\omega$, $p = \hbar k$ and a wave looks like $e^{ikx-i\omega t}$.

Spectral lines

The fact that the wavelength and hence the momentum and energy of a particle in a box are quantized is quite important. It explains why we saw those lines coming from the mercury lamp.

Classically, you can think of an atom as being a mini-solar system. There are neutrons and protons in the middle (the nucleus). Orbiting the nucleus are the electrons, which are much less massive. They don't feel the force (the "strong" force) which holds the nucleus together. Instead, they are bound by electric forces, just like the planets are bound by gravity. Because electromagnetism is different from gravity, this picture ends up not working classically. I explained how an accelerating electron radiates classically, and so would emit all its energy and crash into the nucleus. You need quantum mechanics to fix this up, and we'll explain how.

Think of an orbit at some radius a. Since we are now in quantum mechanics, this is a probability wave going around the atom. Instead of demanding that the probability vanish at the edges, we demand that the probability be periodic: if you go around once, the probability must be the same. Put another way, one must have an integer number of wavelengths n around the orbit. Thus

$$n\lambda \sim 2\pi a$$

where a is the radius of electron's orbit. So it's just like a particle in a box. The difference you see that when you do this carefully, is that here it's *angular momentum* which is quantized.

If one then assumes that for a given n, the electrons are in orbits of a fixed radius a_n, the possible *energies* of an electron in an atom are quantized as well. Using this assumption along with the quantization of angular momentum describes what is usually called the "Bohr" atom. It gives the correct formula for the energy levels in hydrogen; you'll work this out on HW#3. It turns out when you do the whole thing properly using Schrödinger's equation that the assumption of fixed radii is wrong. But the result is correct, and extremely important. **The energy levels of the electron in an atom are quantized.** To illustrate this, physicists often draw the diagrams of the type you see in Fig. 2-9 of Feynman.

So how do discrete energy levels translate into what we saw in the mercury lamp? The mercury vapor we saw in the lamp is fairly dilute, so the atoms are far enough apart so that they can be treated individually. When you heat a gas, or run an electrical current through the gas, it puts energy into the system. This "excites" the atom. This means that the energy you put in lifts the electrons out of the lowest energy levels and into higher ones. But the electron won't stay there, if it can. It will fall down into the levels with lower energy. So what happens to the now-excess energy. When falling down levels, a photon is emitted! The energy of this photon is not arbitrary: when an electron falls from energy E_1 to the lowest-energy state (the "ground" state) with energy E_0, the photon emitted must have energy $E_1 - E_0$. But now quantum mechanics comes in again: we know that this photon of fixed energy must have a fixed frequency. Thus this transition will emit a photon of frequency

$$\nu = \frac{E_1 - E_0}{h}.$$

The discrete lines we saw in mercury arise from the various transitions in mercury.

Quantum mechanics therefore explains something completely obscure classically: the existence of spectral lines. One of many ways of exploiting this fact in technology is the laser. In physics, it enables one to to do very accurate interferometry experiments to measure distances and time. In fact, this measure is so accurate that the second is now defined in terms of the frequency of the photon emitted by a certain transition in the cesium-133 atom. Namely, the second consists of 9,192,631,770 periods (inverse frequency) of the photon emitted by this transition. To give just a few of the many examples, knowing such numbers with such incredible accuracy was one of the key ways quantum mechanics was first understood, and measuring the Doppler shift of these lines from distant stars and galaxies is still used heavily today in understanding cosmology.

Typically, the spacing between these levels in an atom is on the order of an eV. This is because the values of these energies are related to the size of the atom, *not* the size of the box the mercury vapor is in. If they were related to the size of the system, you wouldn't see the quantization. Remember that $p \propto 1/L$ for a system in a box of size L, while $p \propto 1/a$ for the atom. Since a/L is around 10^{-10}, the levels due to the size of the box would be spaced much closer together than the levels due to the size of the atom.

Another thing to note is that if the atoms are close enough together so that different atoms interact with each other, the behavior can change dramatically. For example, in a metal, there are electrons which are not bound to a given atom. This is why metals conduct current!

A digression

Probably you're not yet used to hearing "hand-waving" arguments like the ones I just given, so let me digress and say what I mean by that. These are arguments where you're not being very precise, but rather are more along the lines of a plausibility argument. In some sciences, that's pretty much all you can ever do (biology is in an interesting transitional period). In physics, we often can go much farther: we can write down precise mathematical equations which describe the experimental reality. And in probably all of your physics classes so far were done in this fashion. But all scientists, including physicists, give plausibility arguments all the time.

One reason is that when you're doing research, it's usually a good idea to try to know the answer before you find it. Of course, the best researchers are prepared for when they don't get the answer they were looking for – often the greatest discoveries (e.g. the X-ray, and we'll see, the cosmic microwave background) were made this way. But knowing what to expect is important in these cases – previously-unknown physics is necessary to explain why you didn't see what you thought you would see.

A second reason for giving plausibility arguments is that before you understand the math describing what's going on, you need to decided what's going on. (Even good mathematicians do it this way, by the way.) So you have to take a plausibility argument the way it is intended: to give you a short-cut to the right answer. As long as you don't take it too seriously (i.e. get upset if it ends up giving the wrong answer), it's a useful thing.

In this case we know the hand-waving argument is essentially correct because we know how to do the computations correctly, and will explain this later in the course. Trouble starts in research when people don't know the correct answer, but write papers anyway containing only the hand-waving argument! Then you get to have fun yelling at your colleagues whose hand-waving arguments give a different answer than yours. You then all go to conferences in nice parts of the world to continue the arguments, so we all win.