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5.112 Principles of Chemical Science, Fall 2005 Transcript – Lecture 4

Where were we last time? Last time we said we were setting aside the problem of the structure of the atom.

We were setting it aside because we were stuck, and what we had to do was to look at another area of discussion. And that is this waveparticle duality of light and matter because it is that discussion that is going to give us the clues about how to proceed.

We are putting aside the discussion of the structure of the atom all the way until next Wednesday, because next Monday I was reminded is a student holiday. [APPLAUSE] And so we started. We talked about the wave-like properties of light.

We said that the property of superposition, the fact that you can put waves at the same point in space and their amplitude add. Since waves have both positive and negative amplitude that means that you have constructive and destructive interference.

And it is those interference phenomena then that are evidence for wave-like property. And we did the two slit experiment to try to give you an example of interference phenomena. We were trying to understand those interference phenomena, and did so in terms of this diagram here.

The interference phenomenon that we saw was an array, actually a row of bright spots, dark spots, bright spots, dark spots. And we drew these semi-circles here around each one of the slits. They represent a little bit of the wave that emanated through those slits.

Because those slits are small then those wave emanated equally in all directions. That is why theses semi-circles represent the wave maxima. And what we discovered is that if we looked along this line here, this line which led to this bright spot, that all of the waves along this line were constructively interfering.

That is we had the maximum of the two waves at the same point in space, or the minimum of the two waves at the same point in space.

And we noticed that everywhere along this line, where we had that constructive interference, the difference in the distance of the waves traveled was 1 lambda.

We noticed here that everywhere along this line, that led to a very bright spot, we had constructive interference. And the difference in distance traveled by those two waves was 2 lambda. And, likewise, up here, along this line the difference in the distance traveled was zero lambda.

And from just that, in a sense, qualitative observation we drew a conclusion. And that conclusion was in order to get maximum constructive interference, a condition that had obtain, is that the difference in the distance traveled by the two waves has to be an integral multiple of the wavelength.

N could be 0, 1, 2, 3, etc. And so, the very bright spot here that always bisects the two slits, since N=0, we call that the zero order interference feature or the zero order fraction feature. The bright spot that is either to the left or to the right or up or down of that center bright spot is the first-order diffraction feature or the first-order interference feature.

And then the second bright spot up or down from the center is a second-order diffraction feature. And so on and so on. And in recitation section, what you also should have done, and you should have reasoned through what the condition was for destructive interference.

That is in between these bright spots you have dark spots as a result of destructive interference. And that results because, say, right here you get a dark spot -- Right here at that point you would see the maximum of one wave at the same point in space as the minimum of the other, and so they exactly cancel.

And so by just analyzing what waves were destructively interfering, you should have come up with a general expression for destructive interference of N plus one-half lambda. That is your general condition for destructive interference, the difference in the distance traveled by the two waves.

This kind of diagram here we are also going to see on Friday, because this interference phenomenon is the property associated with waves. And what we are going to do is see this diagram again when we scatter electrons for particles.

We are going to see that particles also will destructively and constructively interfere. They also have wave-like properties. That is what we will do on Friday. We have established now the wave-like properties of radiation, so I would like to move on and talk about the evidence for the particle-like nature of radiation.

The evidence for the particle-like nature of radiation comes from an effect called the photoelectric effect. Shortly after Thompson discovered the electron, scientists were noticing that if you took a metal and shined radiation on that metal that indeed electrons were emitted.

Electrons came off. These were called photoelectrons. However, the radiation that you shined on the metal had to have a frequency nu that was greater than or equal to some threshold frequency vO. That is if you took radiation of some frequency here, nu, that was less than this threshold frequency, well, you did not get any electrons off.

Well, another way to kind of understand that data or that effect is to just plot the number of the electrons that come off as a function of the frequency of the radiation. And so at low frequency there are no electrons, but all of a sudden you get to vO and then electrons start coming off.

And no matter how high you increase the frequency here, the number of electrons that come off remains the same, remains the constant. And it turned out that for the metals that were looked at, at that time, the threshold frequency here was in the UV range of the electromagnetic spectrum.

Well, in addition to just measuring the number of electrons and generally observing this effect, scientists did not understand what was going on. So they just started measuring everything they could think about measuring.

And one quantity that they measured was the kinetic energy of these electrons that were being emitted. And so you take kinetic energy here, KE, as a function of the frequency. They found that at low frequency again there is no kinetic energy because there are no electrons. And then at some frequency all of a sudden electrons started coming off. And the kinetic energy of those electrons seemed to increase with the frequency once past that threshold frequency vO. Well, this was really another one of these conundrums here at that time because classical electromagnetism, classical physics had no way of explaining these data.

And, in fact, what classical physics predicted is that the kinetic energy of these electrons should have nothing to do with the frequency of the light. That is the kinetic energy was constant. As you increased the frequency of the light, classical physics would tell you that the kinetic energy should not be affected by the frequency of the light.

There was nothing in the classical way of thinking, classical electromagnetism that connected the frequency of the light to the kind of energy, to the kinetic energy. There was no way for blue light to make the electrons have a larger kinetic energy and for blue light to have an effect on the kinetic energy and red light to not have an effect on the kinetic energy.

In addition, what classical physics predicted is that the kinetic energy of the electrons should be dependent on the intensity of the light. That is the more and more intense the radiation on the metal the more and more kinetic energy those electrons should have.

Because, after all, if you increase the intensity of the light going into the metal, you are putting more and more energy into it. That should be reflected in just how energetic those electrons were picked out.

The more energy in the electrons ought to come out with larger and larger kinetic energy. Of course, the observation was that the kinetic energy of the electrons had nothing to do with the intensity of light.

The kinetic energy of the electrons did not increase as you made the light brighter and brighter. As you put more and more energy in, the kinetic energy remained the same. It didn't have an effect.

This was a real conundrum here. The known classical physics was making predictions really just contrary to what was being observed. These data here of the kinetic energy versus the frequency were around for a few years before Einstein took a look at them in 1905, a hundred years ago. And he looked at these data for many different metals. Here is some data for metal A, for example, and here is some data for metal B. And, in both cases, it certainly looked like the kinetic energy was linearly dependent on the frequency of the radiation.

But what was different for the two different metals was the threshold frequency here vO. What Einstein did was fitted a straight line to these data, y=mx+b. And when he did that, and he went to calculate the slope here, m of these lines, he thought "very interesting".

Because a slope of those lines was 6.626 times 10 to the minus 34 joule seconds. The slope of those lines was something called Planck's constant, h. You say so what? Well, the reason he was so interested in this is because just a few years earlier there was a scientist by the name of Max Planck who was interested in understanding what was called the black-body radiation data.

What is a black-body? Well, let's just, for simplicity purposes, think of the black body as the burner on an electric stove. What you know is that if you turn up the voltage on that burner, the burner gets hot.

It increased in temperature. And you increase the temperature and sooner or later that burner is glowing bright red. And you increase the temperature some more and the burner is glowing a brighter red.

And you increase it some more and it is glowing orange. And you increase it some more, which you shouldn't do, and it glowing yellow. And then if you could increase it some more it glowing white. What is happening, as you increase the temperature, is that the radiation from that black-body, this is the black-body, radiation is increasing in intensity.

But, more importantly, the frequency is getting larger and larger. Dark red, bright red, orange, yellow, white, those are all frequencies. The frequency is shifting to higher and higher values. And what was actually done at that time is that the intensity of that black-body radiation, oh, and this material is not in your notes because you are not responsible for it.

I am just trying to make this surprise that Einstein noticed about the slope. I am just trying to put it in some context, why he was so surprised and amazed at it. This black-body intensity here, people had disbursed that radiation and looked at the frequencies that were coming off. This is intensity versus frequency. Here is a general shape of that intensity versus frequency. That was observed for some temperature T1. That was a low temperature. And then when the temperature was increased and the intensity versus frequency was observed, well, the frequencies generally got higher.

This is higher temperature. Intensity goes up. And you increase the temperature some more and you get even higher frequency. T3 is the highest temperature. And that is what the data was. What Planck was trying to do was understand the origin of that black-body radiation.

What he said was in these black-bodies, in these materials, what there must be are oscillators that are giving off this radiation. But he had another little kick to these oscillators. These oscillators were giving off radiation or energy in chunks, in quanta, in particles.

And using that idea, plus some statistical mechanics, he was able to calculate the shapes of these curves. That is he indeed got, for the lowest temperature here, a curve that looked like this. And for T2 he got a curve that looked like this.

And for T3 he got a curve that looked like this. He got the shape right, but he wanted to get the intensity right, too. What he realized he had to do was he essentially needed to have a scaling factor actually in front of his frequencies of his oscillators.

He wanted a constant. And so he said what constant do I have to have in order to make all of these data fit the observation? That constant is Planck's constant, his own 6.626 times 10 to the minus 34 joule seconds.

There it is. That is Planck's constant. That is it. There is nothing deeper here. It is a natural constant. It comes from our observations of the world, of nature. That is it. It is a fitting constant.

And so that is why Einstein was so amazed here when he realized this number is the same as what comes out of here. There must be something very fundamental about this Planck's constant. That is the story.

Isn't that amazing? What Einstein then proceeded to do, of course, is to write down the equation of the straight line that he just put through

these data. And so that equation is the kinetic energy equal to nu, which is our x, h, which is the slope.

And then what he found was that the intercept here, of course, is hv0. This is plus -hv0. And that is the equation of a straight line. Of course, he realized if this is energy on this side, boy, there better be energy on this side.

And so this hv0 better be an energy. And since this nu was the frequency of the incident radiation, therefore, hv0 better be the energy of the incident radiation Ei. That is where this expression, E=hv0 comes from.

Nothing more. That is where it comes from, the photoelectric effect. This was the first time that there was any relationship between the frequency of the radiation and the energy of the radiation.

In classical electromagnetism there is no relationship between the frequency and the energy. This was the first time in which that relationship was observed. And what this is saying is the following.

This is saying that you can have any frequency of radiation you want, but the corresponding energy comes in the chunks of hv. H is a quantization constant, radiation, nu is continuous, but the energy that corresponds to any given frequency of radiation is h times nu.

This E=hv here is thought of as a quantum of energy. A particle of energy. A chunk of energy. Later on it became the energy of a photon. If this hv here was an energy, well, this hv0 also better be an energy.

It is the threshold energy. Let's draw an energy level diagram to try to understand that. I am going to plot an energy here. Let's draw an energy level for an electron. This is an electron here bound to the metal.

And we know that it takes some energy to rip this electron off of the metal. Up here, at higher energy, is going to be our free electron. I will just call it electron-free, not bound to the metal anymore.

And the energy that is required to pull the electron off from the bound state to its free state is this threshold energy, hv0. This threshold energy is like an ionization potential. You know what the ionization potential is.

Just the energy required to pull an electron off an atom or a molecule. However, when we are pulling an electron off a chunk of a metal, we actually have another name for it. It is called the work function.

That is just historical, but it is the same thing as an ionization potential. And we often give it the symbol phi. That threshold energy, ionization energy for a metal is the work function here, hv0.

The important point here is this. In order to get an electron off of the metal, what you have to have is energy, Ei. That Ei has to be equal to at least the threshold energy, hv0. If you come in with energy of this radiation, of this wavelength and that frequency, you pulled the electron off and then the electron is off the metal and it just kind of stays there.

It doesn't move away. But you can also come in with energy here, Ei, that is greater than this work function, than the threshold energy. And you can pull the electron off. But then the electron is actually going to move away from the metal, and the energy with which it moves away from the metal, its kinetic energy is just the incident energy minus this threshold energy.

It is the excess energy here. And I am going to write it as the kinetic energy. From that energy level diagram, this energy, the incident energy has to be equal to the work function hv0 plus the kinetic energy.

Or, if I turned this around, the kinetic energy is equal to the incident energy -hv0. The actual expression for the energy that Einstein down, I just turned that equation around. This is an equation that you have to know.

I will not give this to you on an exam. Now, you don't have to memorize. You just have to reason it. Draw yourself an energy diagram. You know conservation of energy. The sum of these two energies has to equal the incident energy.

Then you will be all set. Now, what is very important here is the following. If I come in with radiation that is, say, a half of the threshold energy. Suppose I come in with two photons where each photon is $\Omega hv0$ -- The bottom line is that you are not going to get an electron off.

Even though you are coming in with two photons, which together are going to give you the threshold energy, you won't get a photon off. You have to come in with at least the energy of the work function.

A photon has to have at least this energy to get an electron off. That is the particle-like nature of radiation. Energy comes in chunks, in particles of energy, in quantum of energy. Likewise, if I came in here with a photon that had twice the energy of the work function or the threshold energy, I would still only get one electron off.

I would not get two electrons off, even though energetically you would be able, in principle, to get two electrons off. But you won't. You will only get one electron off. Whenever you send a photon in, if it has enough energy, that is if its energy is equal to or greater than the work function you will get an electron off.

There is one electron for every photon. You never get two electrons for every photon or you can never get one electron for two photons that are lower energy. That is the particle quantum nature of radiation.

That is important. Yes? What is the form of the photon? What do you mean by form? Oh, you want a picture of the photon. You're looking at them. You cannot draw a picture of a photon because you want to relate it to something that is within your classical experience.

And you cannot do that. It isn't a classical particle. That is what you're working with right here. You are trying to use your experiences, that are everyday experiences, to explain something that isn't within your everyday experiences.

You don't have a frame or a format to do that. Yeah? Yes. If you have a constant flux of photons onto the surface, you will have a constant flux of electrons. Now, there is a probability. It is not necessarily the case that every photon gets in, will eject electrons, because there are other kinds of competing processes.

Whatever the rate with which the photons come in. It depends on the flux of the photon. And we will have some problems like that where we are going to assume that the probability of the electron coming off is going to be one, so one electron for every photon.

But, in reality, there are competing processes. Are all electrons being ejected? Actually, some electrons. Again, this goes to the probability. Some are actually kind of going in, too, into deeper the metal.

Not the probability, right. The rate at which the electrons come out with is dependent on the intensity. The more photons you send in, the larger the number of photons per second coming in, the larger the number of electrons per second coming out.

This is a plot here of the energy of the electrons. That's all right. Other questions? Yeah? Eventually. Yes. Absolutely. There are other problems that will come in. Usually your light source isn't so energetic that you could possibly do that.

Now, also usually what happens is that you've got your metal grounded so that as you lose electrons new electrons come in and fill it up to the level. And so you don't charge up your sample. In an experiment, if you had your metal just not grounded and you did shine some radiation, what would happen is the metal would start to charge up.

Then that would make it difficult to get electrons off. Yes? Yes. How strongly those electrons are bound to the metal depends on the electronic structure of the metal. And we are going to talk a little bit about what determines the strength of the interaction for electrons on atoms and molecules, but it is similar to what it is for metals.

That is coming in a few days. Yes? Yes, there is. Right. You don't actually have to have a metal. You could do it. There are usually higher frequencies on insulators and semiconductors, right.

It is harder to see the effect, but it can be done and has been done. Well, what I want to do right now is to show you an experiment we are going to do. We are going to do a photoelectron experiment.

And the experiment is this. We have a device up here. What we have is an aluminum plate. And that aluminum plate is mounted on this blue metal rod. And in the middle of this rod is a needle on a pivot.

And this is a fairly frictionless pivot. This back ring here is just a support structure, an insulating support structure. What we are going to do is put some excess charge on this aluminum plate.

And that excess charge is going to run down this metal rod and then onto this needle. And because that excess charge, the electrons on the needle and the electrons on the metal rod are repulsive, since this is rather frictionless, that needle is going to move because of the repulsive interactions between these electrons.

What we're then going to do is try to do the photoelectron experiment. We are going to take some UV radiation and shine it on this metal and drive the electrons off. And we should see then the needle swing back to its original position.

I need a couple of volunteers in order to do this experiment here. Come on up. All right. Fantastic. I think that is all right. Good. OK. One of you needs to be the charger and the other needs to be the discharger.

Which one? You want to discharge? Discharge, OK. You come over here. And what you are going to do is discharge the aluminum plate after we get some excess charge on it. You are going to do it just by holding it up to here.

You have to get it kind of close because it is not a very intense UV source. Could you get the video cam on the side or on the center to get where we are putting it? I get we are putting it on the side, right? OK.

There we go. There is the device. You are the charger. What we are going to do, to get the excess charge, we are taking a piece of natural fur. We are going to rub it on this Lucite rod. You have to keep your fingers on the yellow tape here.

And we are going to transfer some of the natural oils here onto this rod. And there are plenty of negative ions around here and free electrons. That oil likes those negative charges, and so there are going to be excess negative charges on this Lucite rod.

And then you are going to come over here and just touch the edge of this and let the electrons flow onto there. Are you right-handed? You have to rub that really, really hard. [LAUGHTER] Great. Go over there.

Touch the end. Cool. Why don't you give it another jolt here and we will really move that needle over. OK. Discharger. We have to give it

another jolt. That is OK. You may have touched it with something else and discharge rule.

No, that's OK. You have to get the hang of this here. You are doing fantastic. Take it off. That's what it is. You are holding it on too long. OK, that is pretty good. Put it in front there. Get it a little bit closer.

Here comes the UV radiation. We did it. Try it again really hard. Just touch it. Take it off. Do it again. You need to do it again. You've got to get it right here. Not too much, not too little.

OK. It is doing it. Discharge in front. Electrons off. Now we have to do a control experiment. That is you have got to charge it up again, but now, when you put the light there, what I am going to is hold up a Pyrex plate in between the light and the metal.

It is going to block the radiation and it should not discharge. You need to get on there. Fantastic. There it goes. Here is the plate. Get it to a little bit lower. Do a good discharge. [APPLAUSE] Fantastic.

Thank you very much. Thank you for being a good sport. That is the photoelectron experiment. Hey, it works. Well, what I want to do now is just spend a few minutes working on a few problems. I think these are pretty straightforward, but I just want to make sure that everybody is on the same page here in terms of being able to do the homework.

Here is the first problem. The first problem says how many photons? And remember what we said a photon was? E=hv. This is the number of joules. Implied is the number of joules per photon, although we don't usually write this but that is what that is, joules per photon.

You may want to write it as you do these problems. How many photons associated with radiation of a wavelength lambda equals one picometer, which is 1.0 times 10 to the minus 12 meters, do you need in order to create, say, a laser pulse of energy that is one joule? Lasers are pulsed, so I am talking about a pulse of energy one joule.

You want to draw yourself a picture here. We are drawing a picture of one pulse of energy, one joule. Now, we have not been given the frequency here of this radiation, but we know the wavelength and we know the relationship between frequency and wavelength. It is just C/?. I know what lambda is. I can calculate nu. And, when I do that, I find that the energy of the photon, hC over lambda, that energy of the photon is 1.99 times 10 to the minus 13 joules per photon.

And I am using one more figure than is significant since this an intermediate step in the calculation. If I want a pulse of one joule of energy and I am asked how many photons do I need to get that, and each photon is 1.99 times 10 to the minus 13 joules, well, that means that I am going to need 5.0 times 10 to the 12 photons.

There was a question here? All right. Let's work another one. Here we want to define what we mean by power. This says the power of radiation from the continuous laser is three milliwatts. We have some laser and the power of that radiation coming out is three milliwatts.

Well, what is power? Power is energy per unit time. It is the energy delivered or the energy expended per unit time. The unit of power that we are going to use is a watt. A watt is a joule per second.

We are told that we have radiation of three milliwatts. That is 3.0 times 10 to the minus 3 joules per second. And the question asks how long will it take for a total energy of one joule to be supplied? Well, one joule.

And we have the rate of energy supply as 3 times 10 to the minus 3 joules per second. That gives us 330 seconds. That is straightforward. Finally, we have one more. It says how many photons per second of, again, the same radiation of the wavelength of one picometer? That means, again, we are dealing with photons that have an energy of 1.99 times 10 to the minus 13 joules per photon.

How many photons per second, the rate of photons at the wavelength do you have to have, or do you have if the power of the radiation is three milliwatts? Well, the power of the radiation is 3.0 times 10 to the minus 3 joules per second.

And we have 1.99 times 10 to the minus 13 joules per photon. In order to have this kind of power, what we have to have being emitted is 1.5 times 10 to the 10 photons per second. All right. The photoelectric effect is one of the experiments that demonstrated the particle-like nature of light, of radiation. Particle-like nature because you have to have these chunks of energy to make some process occur. Next time we are going to look at and will just talk briefly about the other experiments that demonstrated the particle-like nature of radiation.

And that other experiment is the demonstration that a photon has momentum, even though it doesn't have any mass. See you Wednesday. See you Friday.