ROBERT FIELD: Last time, we talked about the photoelectric effect. What was that? And what were the important points? Yes?

AUDIENCE: It's quantized and has energy associated with its frequency.

ROBERT FIELD: Yes. OK, so, the idea of quantization of electromagnetic radiation and photons. And the photon has an energy h times nu. Nu is the frequency. And the evidence was mostly from a plot of what versus what. Somebody else? Yes?

AUDIENCE: Frequency of the incoming photon versus-- or, that's the x-axis. So, kinetic energy of the ejected electron versus frequency.

ROBERT FIELD: Exactly. And the slope of that plot, which was h, is universal. It doesn't matter where the electron came from. And this was really an amazing thing. And then, the other thing we talked about was Compton scattering. And what did Compton scattering tell us? Yes.

AUDIENCE: Photon has a momentum--

ROBERT FIELD: Yes.

AUDIENCE: --transfer.

ROBERT FIELD: We're interested in the particle-like character of what we think of as waves. And we saw that the waves were particles. And particles-- or at least packets. And these packets had definite momentum. And that was a wonderful observation.

So, today, this is the menu of what I'm going to talk about. And at the end, there's a magic word, "spectra." And I like that because what we're going to be discovering today is that the internal structure of atoms and molecules-- we are not allowed to observe it directly, but it's surprising. And it's encoded in something which we can observe, which is a spectrum.

And the spectrum that I will show you at the end is one that is-- contains essentially no

information, but acts as a template for what we really want to know about how things are different from hydrogen atom. And that's the beginning of our exploration of the structure of atoms and molecules. It's through the spectrum and it's how it's different from-- in subtle ways-- the spectrum of the hydrogen atom.

OK, so, we're going to turn our focus today to the electron, as opposed to light. And we're going to play the same game. We know the electron is a particle. Does anyone want to tell me why we know that? Is there any-- anybody who's got a clue? You can-- oh, good. Yes.

AUDIENCE: There's an experiment with the little oil drops, where they suspended them and found that--

ROBERT FIELD: Yes.

AUDIENCE: --charge is quantized.

ROBERT FIELD: I love that experiment. That's the Millikan experiment. One of the reasons I love it is because Millikan and Mulliken are two different people. So I find that it's really easy to come up with one of them. And I remember Mulliken is a spectroscopist and Millikan was a different kind of physicist. But they're both famous and they both have connections to important universities-- University of Chicago for Millikan and Mulliken, MIT and Caltech.

So we're going to be looking at something that we know is a particle. And we're going to show that it has wave characteristics. We want to be able to show that the electron has a wavelength and it follows the same equation that we use to describe the behavior of electromagnetic radiation. So how would we control the momentum of an electron? Yes.

AUDIENCE: So you can control the kinetic energy that it has by putting it through a certain potential.

ROBERT FIELD: OK, so, we know we can easily measure the momentum of a particle. That's not a big challenge. But then how would we measure its wavelength? Yes.

AUDIENCE: Some type of diffraction?

ROBERT FIELD: Yes. We basically use some material, which acts a ruler. We have a thin metal foil and the distances between atoms in the foil are constant. So that's the ruler against which we measure the wavelength of light. And we'll talk about the Davisson-Germer experiment, where we measure the wavelength.

And then we'll talk about the Geiger-Marsden experiment, where we say, well, atoms have

electrons in them. And what is the structure of an atom? Remember, we can't look inside. So we have to use some kind of an experiment to be able to look inside the atom.

Now, physicists have one trick they often use. To find out the internal structure of something, they shoot a particle, or a wave, at it that has a wavelength comparable to the distances you're hoping to measure. So if you have a very high energy probe particle, it will have a very short wavelength and it will look sort of like a bullet. And we know how bullets scatter off of targets or hit targets. We also, if we choose the wavelength to be comparable to the distances we're expecting to measure, then we're going to see diffraction. This is a kind of subject that lends itself to exam questions.

So let's start out by talking about the Geiger-Marsden experiment-- I mean, the Davisson-Germer experiment. So we have a beam of X-rays or a beam of electrons-- either one. And we have an aluminum foil. And we have-- it's just an intense beam. We want to stop most of it before it hits a detector. And, so, this is some kind of a screen or--

So what we're looking for is, when the X-rays or the electrons scatter off of this ruler, we get something that appears on the screen as pairs of circles. This is the powder pattern because this is a multi-crystalline object. But in each object, we have a bunch of equally-spaced atoms, where this is the lattice constant and this is the square root of 2 times the lattice constant.

So each atom has nearest neighbors and second-nearest neighbors. So we have two rulers going on. And one ruler will give one set of rings and the other ruler will give a different set of rings. And because these particles are randomly oriented, instead of having spots, you have circles. And there's all sorts of information in these powder patterns.

But basically, they're saying, well, we're seeing a structure which is related to something we know. How would we know the distance between atoms in a foil? Using macroscopic measurements? Yes. You're hot today.

AUDIENCE: You have access to density and you have access to the non-atomic weight.

ROBERT FIELD: That's it, yes. So it's a simple matter to know at least what is the magnitude of the distance. There is an issue of what is the crystal structure. And there are different structures and that will give rise to different features in the powder pattern.

But the important thing is we do this. We look at the pattern that emerges when we shoot X-rays at this screen. And we already know that X-rays have wavelengths. And we know that

they have momentum. We know about the scattering of photons. And as a result, we know that we can predict exactly what the pattern associated with the X-ray scattering is going to be.

And then we do the same thing with electrons. And now for the electrons, we can control the momentum. That's easy. And what we want to know is what is the wavelength. And we have the wavelength of the X-rays.

And so what we do is we vary the momentum of the electrons until the powder pattern for the electron-- the diffraction pattern for the electron-- is exactly the same as the diffraction pattern for the X-ray. And we discover that, for the electron, we have the same result.

OK, so, we have, now, photons. They have wavelengths. And the momentum was the surprise for the photons. And we have particles, which have wavelengths and momentum. And the wavelength was a surprise for the particle. So it doesn't matter. Everything follows this equation.

And this equation was anticipated by de Broglie who, in his PhD thesis-- you know, he's a person about your age-- and he wrote his thesis in 1924. And, among other brilliant things, he said that everything should follow this simple equation. And that was a brave statement. And it predicted that de Broglie was going to make a lot of brilliant statements in his career. And this was just the first of-- and one of the nicest-- but we'll hear a little bit more about de Broglie by the time I'm finished with this lecture.

So, we're now worried about atoms. And we already know that atoms have a diameter, roughly. We know that from the density, the typical size we like to have-- quantities that describe macroscopic objects. Which are not like 10 to the minus 20, but like 1 to 100. And so, the angstrom unit, which is 10 to the minus 10 meters, is a very useful thing for talking about sizes of atoms and molecules.

So if we have an atom of a size about one angstrom, we can use this equation to say, well, what would it take for an electron to fit inside an atom? So we specify this-- we know this, we know that-- and that determines what the momentum would have to be. And these are all simple calculations.

And since I don't like doing calculations on the board, and I don't really need to do this now-- you need to be able to do them, quickly, if I ask you on the exam. But basically, what we end up finding out is that the velocity of the electron would have to be 7.25 times 10 to the 6

meters per second. Which is OK, it's pretty fast. It's a few percent of the speed of light.

But that would correspond to a kinetic energy, which is 2.4 times 10 to the minus 7 joules. Remember, I don't like these kinds of units. But it also corresponds to-- doing a unit conversion-- 149 electron volts. Electron volts are a good unit for energy for atoms because the ionization energy-- the energy it takes to pull an electron off of an atom-- is always somewhere between five and 15 electron volts. So you always want to calibrate yourself, your insight, in terms of numbers which are in the small scale, rather than having to remember the exponent.

All right, 149 electron volts. Should that bother you? Well, it can't bother you yet because you don't know about what the ionization energy is.

But I just told you. It's between five and 15. This is a factor of 10-- too big. So this is going to be a problem. How is it possible for things so small to have an electron fitting in that small size without it just leaving because it's just way too high energy?

And so that leads us to ask questions about, well, what is the internal structure of an atom? How can an atom somehow accommodate this electron which needs to somehow fit inside? So that was the basis for the Geiger-Marsden experiment.

Now, the Geiger-Marsden experiment looks very similar to the previous experiment. And here we have-- whoops-- alpha particles. Alpha particles are helium-2 plus ions. And they're produced by radioactive decay. And they have a tremendous amount of energy. More energy than was possible in the days these experiments we're doing to create for a particle.

In fact, one of the earliest experiments, or apparatuses, capable of producing very high energy electrons was built by Robert Van de Graaff, here at MIT. And this was in the form of cylindrical towers, right near the parking garage. And it was there for the first 10 years I was at MIT. I'm very old, but that's still fairly recent.

But anyway, Van de Graaff could make high energy particles and it was really neat. And what he could do was dwarfed by what can be done in electron accelerators, now. But in the days when the Geiger-Marsden experiment was done, which was 1911, there was no way of making and controlling the energy of an electron-- or of any particle.

And here we have some particles which are produced by radioactive decay, which have

tremendous energy. So they're heavy and they have high energy. And so that means the wavelength is very small. We want to use these helium ions. Yes?

AUDIENCE: Could you not also control the energy of each particle as they're passing through, right?

ROBERT FIELD: Yes. But you would need a very high voltage. And though that is something we could imagine doing now, but in 1911, the ability to do that sort of thing with control was not there. There needed to be advances in vacuum technology. There needed to be advances in power supplies.

I mean, we're talking about very high voltages. And you wouldn't want to do that in your laboratory, even now with the capability. I remember when I was a graduate student, we had these things called Spellman power supplies. And they could produce 40 kilovolts. They were really scary. But that's nothing compared to what you need.

OK, so, we want bullets. We want to have these helium particles interacting with a thin metal foil. We have a whole array of atoms here. And we have a little hole here.

And what's going to happen is this radiation is going to hit these atoms. And there's going to be backscatter and forward scattering. And the crucial experiment was to measure the ratio of backscattering to forward scattering.

Now, if we have a target that looks sort of like a smear, then the forward and backward scattering would be similar. If we have a target that looked like a bunch of tiny points, there would very rarely be backscattering. All of the scattering would be forward because most of the particles don't hit anything.

And so what was found, and what was the surprise, is that there was very little backscattering. And that implied that the ratio of the size of the target to the size of the particle was enormous. The particles that scattered-- the alpha particles-- were tiny. They had a size-- something like 10 to the minus 4 times the typical dimension of an atom.

So this is jellium. And this is a perfectly reasonable approach. That the positive and negative charges that make up an atom are distributed uniformly. This was the surprise.

How do we explain, now, if atoms that are scattering the alpha particles are really small, even compared to the one angstrom? Well, how do they stick together? Why is matter not compressable? So what is going on here?

Now, I'm not exactly sure of the genealogy here, but Geiger and Marsden were workers, or students, in the Rutherford lab. And the old man wanted to save face or to say, oh, here's an experiment. We learned something from this. You know, this is what we do-- this is my job.

But anyway, Rutherford said, well, maybe it's like this. We have a nucleus and we have the electrons. So we have a nucleus where all the positive charge of the atom, and most of the mass, resides. And we have electrons in circular orbits.

So maybe these circular orbits explain why you can't compress atoms to something that would be commensurate with the size of the nuclei. That the electrons cause a repulsion and the structure is stable.

So this is a pretty reasonable hypothesis until one analyzes it. So what we have is a positive charge here, negative charge here. And so, there is Coulomb attraction and there's centrifugal force, or centripetal acceleration. And we have to have these two things match. So the inward force is minus the charge on the electron squared over 4 by epsilon 0 and 1 over r squared. And the centrifugal, it's--

OK, this is-- you know all this. You know to do this. Have known it since high school, probably.

And so, you can combine all these things, say the inward and outward-- the inward force is exactly canceling the outward force. And you can solve for the velocity. And the velocity is q over the electron squared over 4 by epsilon 0 mass of the electron and the radius of the orbit, square root. This is a trivial derivation. I won't insult you by attempting to do it and try to increase your understanding of the equation, because you already understand it.

So this is the requirement for the radius of the circular orbit. And it has the mass-- I mean, this is the requirement for the velocity. And this is the radius, here. So we know all that. There is nothing about quantization, yet. We know that for any radius, the electron will have a certain velocity. And we can choose whatever radius, we want whatever velocity we want. And that corresponds to whatever energy we get.

What we're interested in is the frequency of the orbit. And so that will be 1 over the time it takes for the electron to go around. And 1 over the time it takes for electron to go around is 2 pi r, the circumference, divided by the velocity. So we have the velocity is equal to-- I mean, the frequency is equal to 1 over 2 pi r. And we can write an equation for this.

And that's in the notes. In fact, there was a typo in the notes. Which has been corrected and read. But I don't need to tell you what it is.

We can calculate this frequency. The reason we calculate the frequency is because we know if we have electrons moving back and forth at some frequency, they're going to radiate electromagnetic radiation at that frequency. Well, where did that energy come from? It came from the motion of the electron. So it has to give up kinetic energy.

Now, the energy is the kinetic energy plus the potential energy. So if it gives up energy, some of these two things has to decrease. And what happens is this decreases faster that this increases. And what ends up happening is that the electron has a death spiral. What happens will be that the electron will go in a spiral, going faster and faster as it goes to smaller and smaller radius, and annihilate itself.

So this is garbage. This can't be true. It violates laws that everybody knows are right. So one needs to find a way to live with this.

Now, one really doesn't need to find a way to live with it until you realize what happens. Because this picture, subject to a couple of hypotheses, predicts an infinite number of 10-digit numbers. It's not an accident. Maybe one prediction would be fine. But all of the lines in the spectra of hydrogen atom, helium ion, lithium doubly-charged ion, all of those are predicted with no adjustable parameters to measurement accuracy.

Now, at the time this was being done, the measurement accuracy might have been only a part in 1,000, or maybe a part in a million. But a part in 10 to the 10th, beyond that we're starting to get into fundamental physics. But this is an astonishing thing. And so I have to explain what the additional assumptions were because we've got something that predicts things we have no business knowing. And there was no explanation for the spectrum before these experiments, or this picture, was developed.

So we have to first find a way, whether it's believable or not, of getting rid of the radiative collapse. So Bohr proposed that angular momentum, l vector r cross p is conserved. Well, we know that angular momentum is conserved. But for a microscopic system, what it means to be conserved may be a little bit more subtle.

He proposed that angular momentum is conserved and that the angular momentum, the magnitude of the angular momentum, had to have a particular value. And that value was

integer times h bar. h bar is the Planck's constant divided by 2 pi. Now, this is complete nonsense. Why should it be conserved? Why should it be restricted to this set of values?

Well, the reason we accept that it's restricted is because it gives the energy levels that are observed. Now, before I get to energy level-- well, I do. OK, we have energy levels. We find that the energy is equal to minus some constant over n squared. Same n as in here.

This is the Rydberg constant. And it's something that you can measure. It's basically a whole bunch of fundamental constants combined. And so, it has a value.

This is one of the numbers in my permanent memory. And that's the value of the Rydberg constant in reciprocal centimeter units. And to get it into energy units you multiply by h times c, or to get it into frequency, you just multiply it by the speed of light. So, anyway, this is a number that is known to many decimal places. And it is generated by this idea that the angular momentum has to be certain values.

Conservation is good, that's easy. This is weird. And it's also wrong because we find out later that the possible values of n include 0. Which would completely mess up the Bohr model.

But, anyway, this, then, in combination with this amazing statement that-- OK, we have the nth energy and the n prime-th energy. And the spectrum corresponds to the frequency, corresponds to e n minus e n prime, over h. So everything we see in the emission spectrum of the hydrogen atom, or in a gas-- which is mostly H2-- there are transitions associated with the free atoms. And they're always around this simple equation, based on the Rydberg equation.

This says the spectra are telling us about the energy level differences. And it's a simple equation. And it's true. It's true at incredibly high accuracy.

And it tells you nothing except the mass of the particle. Because the mass of the particle-- for this Rydberg equation-- we have it expressed in terms of the mass of the electron. But it really should be the reduced mass of the mass of the nucleus times the mass of the electron, or the mass of the nucleus plus the mass of the electron.

And this is something we know for all two-body interactions. That was known well before the time of these experiments. If you have two things interacting, the reduced mass is what you want rather than the individual masses. And so, the only information in these one-electron spectra is the mass of the nucleus. And there's not much difference in this reduced mass effect. But it's enough to say this is a spectrum of hydrogen, as opposed to lithium 2 plus.

OK, but we still have a problem-- a very serious problem. Why is the angular momentum conserved? Why is the angular momentum forced to have a certain value?

Well, I've really finished this lecture pretty fast. Let me just get to the end and I will go back.

All right, so, the problem is this electron is assumed to be a particle and it's assumed to be moving. So the equation-- Maxwell's equations-- all of the equations about motion of charged particles say if it's moving it's going to radiate, whereas if it's oscillating, it's going to radiate. So maybe the problem is that it's not moving.

Remember, the particles are both particles and waves. So we could imagine that, around this circular orbit, we have standing waves-- no motion. And this led to this Schrodinger equation, which talks about the states of the electrons that are allowed. It's basically the classical wave equation, with a couple little twists. And the thing about waves, you remember, we can have constructive and destructive interference. We can have standing waves.

So there doesn't need to be a motion of our particle. There could be some static description of the probability of finding the electron everywhere around this orbit. And that's the Schrodinger equation.

In the next lecture, I'm going to talk about the classical wave equation, which will be the warm-up for the Schrodinger equation. And the Schrodinger equation explains everything. People have made some really fantastic philosophical statements about the Schrodinger.

It contains everything that we need to know. The problem is we can't solve the equation exactly. But it's true. And it contains everything that we'd ever want to know about the microscopic structure of atoms and molecules.

So we've been led by these very simple experiments, which, now, you could do-- really trivially. You wouldn't have to be a smart student of a smart advisor, or stupid advisor. You would be able to do these experiments. And you could say, yeah, this is all very weird, but know now we know that spectra are everything.

And I'm a spectroscopist. I'm very proud of this because the idea that you can make a few measurements and say something about the internal structure of an atom or molecule-- that's a fantastic thing. And what we've seen-- the spectrum of one-electron atoms-- is something which is really simple. It's the template for understanding all complexity. Because everything is

different from hydrogen.

Hydrogen has a point charge at the center. It's not quite a point charge, and that's actually a subject of even modern physics. And other atoms are not a point charge because they have electrons.

And so there is a concentration of charge-- the thing to which the electron is attached is space filling. So that results in a shift at the energy levels. And the shift at the energy levels, and how that shift depends on the orbital angular momentum, tells you something about the shape of this charge distribution-- the radial shape.

So everything we do in spectroscopy is somehow referenced to something we understand perfectly, but which is not of much interest. But it's a template for building up our understanding of everything. And this is a kind of a radical statement. And I get to say this because I'm up here and I do this for a living. I mean-- not teaching, but research.

And I really believe that the things that we are enabled to observe about the microscopic structure of things are encoded in something completely unlike looking at it. And our job is to figure out how to break that code. And that's what I've done for the last 50 years and it's fun.

OK, so, what more could I say to amuse you for five-- six minutes? Not much, because I've skipped a lot of really great stuff. But go back to de Broglie.

De Broglie had the hypothesis that there is an integer number of wavelengths around the circular orbit. And that was telling you that it's stable because if it weren't an integer number of wavelengths, the electron would self annihilate. But that takes a valid point and moves it into something which is a little bit wrong. Because we're not trying to have a particle moving, we're having a distribution of probabilities. And there are still wavelengths and nodal structures. And the stable solutions do involve the particle not self annihilating.

And so, de Broglie scores another triple. I mean, he didn't come up with the Schrodinger equation. So that's the home run that says, OK, we have the material, now to explain everything.

The next lecture will be just introducing the mathematics of the wave equation and the crucial ideas. And that will lead into the following lecture, where we all talk about the Schrodinger equation. So I can stop now. Thanks.