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Let's get going, here. Remember where we were? We were trying to figure out the structure of the atom. At the beginning of the course, we saw classical physics, classical mechanics fail to describe how that electron in the nucleus hung together. Then we started talking about this wave-particle duality of light and matter. We saw that radiation and matter both can exhibit both wave-like properties and particle-like properties. And it was really important, this observation of Davisson and Germer, and George Thompson, this observation that electrons exhibited inference phenomena. That is when you took electrons and scattered them from a nickel single crystal. The electrons scattered back as if they were behaving as waves. There were diffraction phenomena or interference phenomena, bright, dark, bright, dark patterns of electrons. Actually, that Davisson and Germer paper is on our website. You are welcome to take a look at that. It was just that observation, coupled with de Broglie's insight into Schrödinger's relativistic equations of motion that led Schrödinger to say, well, maybe what I need to do is I need to treat the wave-like properties of that electron in a hydrogen atom. Maybe that is the key. In particular, maybe that is the key because the electron has a de Broglie wavelength that is on the order of the size of its environment. Maybe, in those cases, I need to treat the particle as a wave and not as a particle with classical mechanics. He wrote down this wave equation, an equation of motion for waves, this H Psi equals E Psi, where we said last time we are going to represent the electron, our particle, by this Psi, the wave. We are going to call it a wavef unction because we are going to put a functional form to it very soon. And there was some kind of operator, here, called the Hamiltonian operator, that operated on this wave function. And, when it did, you got back the same wave function times a constant E. And this constant, as we are going to see, is going to be the binding energy of the electron to the nucleus. But then, we took a little detour and I said, well, let's see if we can derive, in a sense, the Schrödinger equation. And that is what we started to do. And I am really doing this for fun, you are not responsible for it, but I am doing it because I want you to see just how easy this is. To illustrate this, I am just going to take a one-dimensional problem. I am going to let my electron be represented by this wave, one-dimension, Psi of x. 2 a cosine 2 pi x over lambda. And then I said, suppose I want an equation of motion, I want to know how that Psi changes with x. Well, you already know that if I take the derivative of Psi with x, that is going to tell me how Psi changes with x. And we did that last time. And then I said, well, I want to know the rate of change of Psi with x. I am going to take the derivative again. I have the second derivative of Psi of x. And that is what we got last time. And then, I noticed that in the second derivative, and you noticed, too, somebody said this was recursive, that we have our original wave function back in this expression. I can rewrite that whole second derivative here just as minus 2 pi squared, quantity squared, over lambda, psi of x. So far, this is just any old wave equation. Nothing special about this. This anybody could, and had, written down before. What is special is that Schrödinger realized, here, that if this is going to be a wave equation for a particle, then maybe this lambda here, maybe I ought to put in for lambda what de Broglie told me. And that is h over p. Maybe this lambda here is the wavelength of a matter wave, so let me write this expression in terms of the momentum of the particle, where the momentum has this mass m in it. And so when he did this, this became minus p squared over h bar squared, we said hbar is h over 2pi, times psi of x. Hey, this is getting good because now we have a Psi of x over here. But then what he said was, well, I want to write this momentum in terms of the total energy. Total energy is always kinetic plus potential. The kinetic energy, we said the other day, can be written in terms of the momentum. The kinetic energy is p squared over 2m-- plus the potential energy. And I am going to make this as a function of x, the potential energy. Now, I am just going to solve this for p squared. p squared is equal to 2m times the total energy minus this potential energy. Now, I am going to plug this into here right in there. And, when I do that, I am going to get the second derivative of Psi of x with respect to x equals minus 2m over h bar squared times E minus U of x times Psi of x. Just simple substitution for p squared there. Nothing else. Now, I am going to do some rearranging. And the rearranging, on the right-hand side, is I am going to have only E times Psi of x. E times Psi of x looks like the right-hand side of the Schrödinger as I wrote it down. That is good. When I rearrange this, I get minus hbar squared over 2m times the second derivative of Psi of x with respect to x plus U of x times Psi of x equals E times Psi of x. And now, I am going to pull out a Psi of x here, so that is minus hbar squared over 2m second derivative with respect to x plus U of x, the quantity times Psi of x equals E times Psi of x. And guess what? We've got it. We got it because all of this is what we define as the Hamiltonian. All of this is h hat. H hat, operating on Psi of x, gives us E times Psi of x. This Hamiltonian, as you will learn later on, is a kinetic energy operator. This is the potential energy operator operating on psi. That is the Schrödinger equation. It is hardly a derivation. It is taking derivatives. It is a wave equation. The insight came right here, this substitution of the de Broglie wavelength in an ordinary wave equation. This is the insight, getting that momentum in there with the mass, making this, then, an equation for a matter wave. That is it. You just "derived the Schrödinger equation." Easy. Bottom line here is that the Schrödinger equation is to quantum mechanics like Newton's equations are to classical mechanics. When the wavelength of a particle is on the order of the size of its environment, the equation of motion that you have to use to describe that particle moving within some potential field U of x or U, you have to us this equation of motion and not Newton's equations. Newton's equations don't work to describe the motion of any particle whose wavelength is on the order of the size of the environment. It just does not work. Now, just as an aside, classical mechanics really is embedded in quantum mechanics. That is, if you took a problem and solved it quantum mechanically, and you solved the problem, a problem for which the wavelength of a particle was much, much greater than the size of the environment, which is the classical limit, quantum mechanics would give you the right answer. In other words, say you took some problem where the wavelength of the particle is larger than the size of the environment. That is, a problem where you would normally use classical mechanics. But if you use quantum mechanics, you would get the right answer, if you could solve the problem because the equations are very difficult. But, in principle, you would

right answer, if you could solve the problem because the equations are very difficult. But, in principle, you would get the right answer. However, if you took a quantum mechanical problem, that is, a problem where the wavelength of the particle is on the order of the size of the environment and you used classical mechanics, well, you won't get the right answer. Because classical mechanics is, in a sense, a subset. It is contained within quantum mechanics. It is a limit of quantum mechanics. We have to learn a new kind of mechanics, here, this mechanics for the motion of waves. Now, for a hydrogen atom, we have to think of the wave function in three dimensions instead of just one dimension, here. And so we are going to have to describe the particle in terms of three position coordinates. Usually you use Cartesian coordinates, x, y, and z. But this problem is solvable exactly if we use spherical coordinates. How many of you had spherical coordinates before and know what we are talking about? Not everybody. If I gave you an x, y and z for this electron in this atom, where the nucleus was pinned at the origin. If I gave you an x, y and z coordinate, you would know where that electron was. But, alternatively, I could tell you the position of this electron using spherical coordinates. That is, I could tell you what the distance is of the electron from the nucleus. I am going to call that r. That will be one of the variables. I could then also tell you this angle theta. Theta is the angle that r makes from the z-axis. That is the second coordinate. And then, finally, the third coordinate is phi. Phi is the angle made by the following. If I take the electron and drop it perpendicular to the x,y-plane and then I draw a line here, well, the angle between that line and the x-axis is the angle phi. Instead of giving you x, y, and z, I am just going to give you r, theta, and phi in spherical coordinates. And now, this wave function is also a function of time, and I will talk about that a little bit probably next time. So, that is the wave function that is in some way going to represent our electron. I haven't told you exactly yet how Psi represents the electron, and I won't tell you that for another few days. Question? No. I actually thought this was the way the book set it up. I may have it backwards. I think this is the way our book sets it up. It won't make a difference in any of the problems we solve here. But, in general, if you are given a problem to solve, you are going to have to look and see how they define their coordinate system. Actually, somebody else asked me that the other day. Now, what we have to do is actually set up the Hamiltonian for the hydrogen atom. That is, we have to set up the Hamiltonian specifically for the hydrogen atom. And we have to set it up in terms of spherical coordinates, r, theta, and phi. And when we do that, and we are not actually going to do that, that is what the Hamiltonian looks like. Actually, this is in three dimensions, and so if I were doing it in the x, y, z, what I would have here is a second derivative with respect to y, plus a second derivative with respect to z. That is what it would look like in three dimensions in Cartesian coordinates. But when I transform from Cartesian coordinates to spherical coordinates, an exercise that takes five pages, and everybody should have that experience once in their life, but maybe now is not the right time for that experience, you do get this. And essentially, the Hamiltonian is a sum of second derivatives with respect to each one of the coordinates, because essentially this term is a second derivative with respect to r. This term is a second derivative with respect to theta. This term is a second derivative with respect to phi. That is the specific Hamiltonian. These are all kinetic energy operators, as you will learn later on. And then there is this term here, U of r. This U of r, what is that? What is $U(r)$? Potential energy. It is the Coulomb potential energy of interaction. It is isotropic, meaning it is the same at all angles. The only thing it depends on is the distance of the electron from the nucleus. It only depends on r. It doesn't depend on theta and phi. So, that is the Schrödinger equation for the hydrogen atom. It is a differential equation, second-order ordinary differential equation. In 18.03, you are going to learn how to solve that. In 5.61, or 8.04 I think it is, in physics, in quantum mechanics, you are going to solve that. You can do that. It is not hard. But what do I mean when I say solve? What I mean is that we are going to calculate these Es, these binding energies, this constant in front of the psi. That is called an eigenvalue, for those of you who might know something already about these kinds of differential equations. This E is the binding energy of the electron to the nucleus. We are going to look at those results in just a moment. And the other quantity we are going to solve for, here, is psi. What we are going to want to find is the actual functional form for the wave functions. That, we can get out of solving this differential equation. The actual functional form for psi. The functional form is going to be more complicated than what I wrote here, but we can get that. We will look at that in a few days from now. And do you know what those wave functions are? They are what you studied in high school as orbitals. You talked about an s-orbital, p-orbital, d-orbital. Orbitals are wave functions. That where they come from, orbitals, from solving the Schrödinger equation. Now, specifically, orbitals are the spatial part of a wave function. There is also a spin part to the wave function, but for all intents and purposes, we are going to use the term orbital and wave function interchangeably because they are the same thing. Question? We are going to get to that in just a moment, and if you think I don't answer it then we will go back to it. We are going to solve this. And this equation is going to predict binding energies, and it is going to predict these wave functions in agreement with our observations, and it is going to predict that the hydrogen atom is stable. Remember when we tried to predict the hydrogen atom using classical ideas? We found it lived a whole whopping 10^-10 seconds. Not so when we treat the hydrogen atom with the quantum mechanical equations of motion. Let's write down the results for solving the Schrödinger equation. And the part I am going to concentrate on today is these binding energies. And, on Friday, we will talk about the wave function, solving the Schrödinger equation for those wave functions. What does the binding energy look like? Well, the binding energies, here, coming out of the Schrödinger equation look like this, minus 1 over n squared times m e to the 4 over 8 epsilon nought squared time h squared. m is the mass of the electron. e is the charge on the electron. Epsilon nought is this permittivity of vacuum we talked about before. This is a conversion between ESU units and SI units. h is Planck's constant. Planck's constant is ubiquitous. It is everywhere. What we typically do is we lump these constants together. And we call those constants a new constant, the Rydberg constant, R sub H. And so our expression is equal to minus R sub H over n squared. The value of R sub H is equal to 2.17987x10^-18 joules. That is a number that you are going to use a lot in the next few days. But what you also see, here, is an n. What is n? Well, n is what we call the principle quantum number. And its allowed values are integers, where the integers start with 1, 2, 3, all the way up to n is equal to infinity. Well, let's try to understand this a little bit more by looking at an energy level diagram again. I am just plotting here energy. Here is the zero of energy. Here is the

at an energy level diagram again I am just plotting here energy. Here is the zero of energy. Here is the expression for the energy levels that come out of the Schrödinger equation. When n is equal to one, that is the lowest allowed value for n, binding energy is essentially equal to minus the Rydberg constant. **E = -(R)H** But our equation says the binding energy of the electron can also be this value because when n is equal to 2, well, the binding energy now is only a quarter of the Rydberg constant. It is higher in energy. When n is equal to 3, well, the binding energy of that electron to the nucleus is a ninth to the Rydberg constant. When it is equal to 4, it is a sixteenth. When it is equal to 5, it is a twenty-fifth. When it is equal to six, it is a thirty-sixth. So on, so on, and so on until it gets n equal to infinity. When n is equal to infinity, then the binding energy is zero. When n is equal to infinity, the electron and the nucleus are no longer bound. They are separated from each other. They don't hang together when n is equal to infinity. Now, this is rather peculiar. This is saying that the binding energy of the electron to the nucleus can have essentially an infinite number of values, except it is a discrete number of infinite numbers of values. In the sense that the binding energy can be this or this or this, but it cannot be something in between, here or here or here. This is the quantum nature of the hydrogen atom. There are allowed energy levels. Where did this quantization come from? It came from solving the Schrödinger equation. When you solve a differential equation, as you will learn, and that differential equation applies to some physical problem, in order to make that differential equation specific to your physical problem, you often have to apply something called boundary conditions to the problem. When you do that, that is when this quantization comes out. It drops out of solving the differential equation. What are boundary conditions? Well, remember I told you in the spherical coordinate system, r, theta, phi? Well, phi sweeps from zero to 360 degrees. Well, if you just went 90 degrees further, so if you went to 450 degrees, you really have the same situation as you had when phi was equal to 90 degrees. What you have to do in a differential equation, which usually has a series as a solution, is that you have to cut it off. You have to apply boundary conditions. You have to cut it off at degrees. Because otherwise you just have the same problem that you had before. This is a cyclical boundary condition. And it is that cutting it off to make the equation be really pertinent or apply to your physical problem, that is what leads to these boundary conditions, mathematically. That is where it comes from. That is where all the quantization comes from. Now, let's talk a little bit about the significance here of these binding energies because somebody asked me about it already. When the electron is bound to the nucleus with this much energy, we say that the electron is in the n equals 1 state, or equivalently, we say that the hydrogen atom is in the n equals 1 state. We use both kinds of expressions equivalently. When the hydrogen atom or the electron is in the n equals 1 state, we call that the ground state. The ground state is the lowest energy state. The electron is most strongly bound there. The binding energy is most negative. And the physical significance of that binding energy is that it is minus the ionization energy. Or, alternatively, the ionization energy is minus the binding energy. It is going to require this much energy, from here to here, to rip the electron off of the nucleus. The binding energy here is minus the ionization energy. That is the physical significance of it. Now, did you ask me about the work function? Okay. The work function is the ionization energy when we talk about a solid. That is just a terminology, that is historical. When we talk about ripping and electron off of a solid, we call it the work function. When we talk about ripping it off of an atom or a molecule, we call it the ionization energy. And the other important thing to know here is that when we talk about ionization energy, we are usually talking about the energy required to pull the electron off when the molecule or the atom is in the lowest energy state, the ground state. That is also important. But our equations tell us we also can have a hydrogen atom in the n equals 2 state. If the hydrogen atom is in the n equals 2 state, it is in an excited state. Actually, it is the first excited state. The electron is bound less strongly. It is bound less strongly, and consequently, the ionization energy from an excited state hydrogen atom is less because the electron is not bound so strongly. And, of course, we could have a hydrogen at n equals 3, n equals 4 and n equals 5, any of these allowed energy levels. Not all at the same time, but, at any given time, if you had a lot of hydrogen atoms, you could have hydrogen atoms in all of these different states. Now, the other point that I want to make is that this Schrödinger result, here, for the energy levels predicts the energy levels of all one electron atoms. What is a one electron atom? Well, helium plus, that is a one electron atom or a one electron ion. Helium usually has two electrons, but if we pull one off it only has one left, so it is a one electron atom. Lithium double plus is a one electron atom because we pulled two of its three electrons off. One electron is left, and that is a one electron atom or an ion. Uranium plus 91 is a one electron atom. We pulled 91 electrons off, we have one left, and that is a one electron atom. The Schrödinger equation will predict what those energy levels are, as long as you remember the Z squared up here. For hydrogen, Z is 1, and so it doesn't appear. But Z is not one for all of these other one electron atoms. Where does the Z come from? It comes from the Coulomb interaction. That potential energy of interaction is the charge on the electron times the charge on the nucleus, which is Z times e. That is where the Z squared comes from. We have to remember that. Now, how do we know that the Schrödinger's predictions for these energy levels are correct, are accurate? Well, we have to do an experiment. The experiment we are going to do is we are going to take a bulb here, pump it out, and then we are going to fill it up with molecular hydrogen. And then in this bulb, there is a negative and a positive electrode. What we are going to do is crank up the potential energy difference between those two so high until finally that gas is going to ignite, just like that. And we are going to look at the light coming out. And what we are going to do is we are going to disperse that light. We are going to send it through a diffraction grating, essentially. And that is like an array of slits. What you are going to see are points of constructive and destructive interference. But in the constructive interference, you are going to see the color separated. There is going to be purple, blue, green, etc. The reason is that the different radiation, the different colors have different wavelengths. They have different wavelengths, then they have slightly different points in space at which constructive interference occurs, and so the light is dispersed in space. We are going to analyze what the wavelengths of the light that are being emitted from these hydrogen atoms are. See, the discharge pulls apart the H two and makes hydrogen atoms. We have to do this by taking a diffraction grating. The TAs are going to give you a pair of diffraction grating glasses. You are supposed to come and look at the discharge here. You can see it. I will turn it a little bit for those of you on the sides here. And we will see what we

discharge here. You can see it. I will turn it a little bit for those of you on the class here. And he will see what we see. If you cannot see the lamp, you are welcome to get up and move around so that you can see it. Can you do this light, too? This one over here, sir. Can you move this one away? If you look up at the lights in the room, you can see the whole spectrum, because that is white light. I am going to turn the lamp over here so that you can see this a little better. The spectrum that you should see is what is shown on the board. If you look to the right of the lamp, here, you should see a purple line. The purple line is actually very light, so only if you are up close are you going to see the purple line. You can see the blue line very well. That is very intense. The green line is also very diffuse. Again, only if you are close are you going to be able to see the green line. And then, the red line is very bright. And now I am going to move this over here so you have the opportunity to see it. Again, you are welcome to get out of your seats and move around so that you can, in fact, see it. What you should be seeing, hey, interference phenomena works. Useful pointer. What you should see, depending on which one of the constructive interference patterns you are looking at, there should be a purple line, there should be a blue line, very intense, purple is weak, green is rather week, and the red is very intense. What is happening, here? Well, what is happening is that in this discharge, there is enough energy to put some of the hydrogen atoms in a high energy state. And we will call that state E sub i, the energy of the initial state. Actually, that is an unstable situation. That hydrogen atom wants to relax. It wants to be in the lower energy state. And what happens is that it does relax. It relaxes. The electron falls into the lower energy state, but, because it is lower energy, it has to give up a photon. And so the photon that is emitted, the energy of that photon has to be exactly the difference in energy between the energy of the initial state and the final state. That is the quantum nature of the hydrogen atom. The photon that comes out has to have that energy difference exactly. And, therefore, the frequency, here, of the radiation coming out is going to correspond to that exact energy difference. And, for the different energies, for the different transitions, you are going to have very specific values of the frequency of the radiation or the wavelength of the radiation. For example, some of those hydrogen atoms in this discharge have been excited to this excited state, which we will call B. The energy difference between B and this ground state here is small. Therefore, we are going to have some radiation that is low frequency because delta E, the difference in the energy between the two states is small. And then there are going to be some hydrogen atoms that are going to be excited to this state, the A state. And, relatively speaking, that energy difference is large. There are going to be some hydrogen atoms that are going to be relaxing to this ground state. And when they do, since that energy difference is large, the frequency of the radiation coming off is going to be high. Or, correspondingly, the wavelength of the radiation coming off is going to be low because the wavelength is inversely proportional to the frequency. And, likewise, for this transition we are going to have some long wavelength radiation emitted. Well, let's see if we can understand specifically the spectrum, here, in the visible range for the hydrogen atom. What I have done is to draw an energy level diagram again. Here is the energy of n equals 1, n equals 2, n equals 3, etc. Here is the n equals infinity, up here. It turns out that this purple line is a transition from a hydrogen atom in the n equals 6 state to the n equals 2 state. That blue line is a transition from n equals 5 to n equals 2, the green line is a transition from n equals 4 to n equals 2 and the red line from n equals 3 to n equals 2. Notice that since this energy difference here is small, this line has a long wavelength. Since this energy difference is larger, this line has a shorter wavelength. All of these transitions that you are seeing in the visible range have the final state of n equals 2. Now, how do we know that the Schrödinger equation is making predictions that are consistent with the frequencies or the wavelengths of the radiation that we observe here? Well, we have got to do a plug here. This is the frequency that we would expect. It is the energy difference between two states over H. Here is the initial energy. Here is the final energy. We said that the Schrödinger equation tells us that the energies of the state are minus R sub H over n. For the initial energy level, it is minus R sub H over n sub i squared. We plug that in. For the final energy level, well, it is minus R sub H over n sub f, the final quantum number squared. We plug that in. We rearrange some things. And then this is the prediction for the frequency. I said that this level right here is the n equals 2 level, so we will plug in the two for the final quantum state. And so this is then the prediction for the frequencies of the radiation to the n equals 2 level. You just plug in n equals 6, n equals 5, n equals 4, n equals 3. And you know what? The frequencies that are predicted match what we observe to one part in 10^8. There really is precise agreement between the results of the Schrödinger equation and what we actually observe in nature, therefore, we think it is correct. And there are no experiments that cast any doubt, so far, on the Schrödinger equation. Now, the set of transitions that we just looked at are these transitions. Plotted here is another energy-level diagram for the hydrogen atom. Here is the n equals 1 state, n equals 2, n equals 3, n equals 4. And we looked at all the transitions that end up in the n equals 2 state. This set of transitions. It is called the Balmer series. Now, the n equals 2 state is not the ground state. There is a transition from n equals 6 to n equals 1, the ground state. It is this one right here. But, you see, that is a very high energy transition. Actually, this transition, from n equals 6 to n equals 1, is in the ultraviolet range of the electromagnetic spectrum. And so you cannot see it with the experiment that we did, but it is there. And then, of course, the hydrogen atoms that relaxed to n equals 2, well, they actually eventually relax to n equals 1. And there is a transition there, it is over here, n equals 2 to n equals 1. But, again, that is a high energy transition. It is also in the ultraviolet range of the electromagnetic spectrum. And so all of these transitions that end up in n equals 1 are in the UV range. They are called the Lyman series. All the transitions that end up in n equals 2 are in the visible. They are called the Balmer. n equals 3, the Paschen, is in the infrared. Brackett is in the infrared. Pfund is in the infrared. And so we cannot see these easily. Now, these are named for the different discoverers. The reason there are so many discovers is because these are all different frequency ranges. Different frequencies of radiation require different kinds of detectors. And so, depending on exactly what kind of detector the experimentalist had, that will dictate then which one of these sets of transitions he was able to discover. But not only does this work for emission, but this also works for absorption. That is, we can have a hydrogen atom in the ground state, a low energy state. And if there is a photon around that is exactly the energy difference between these two states, well, that photon can be absorbed. If that photon is a little bit higher in energy, it won't be absorbed. If it is a little lower, it won't be absorbed. It has to be exactly the difference in the

energy, it won't be absorbed. If it is a little lower, it won't be absorbed. It has to be exactly the difference in the energies between these two states. Again, that is the quantum nature of the hydrogen atom. And now, if you are calculating the frequency for absorption, what I have done here is I have reversed n sub i and n sub f. This is 1 over n sub i squared instead of 1 over n sub f squared, which was the case in emission. And I have reversed this so that you get a positive value for the frequency of the radiation absorbed. We will have two different equations for absorption and for emission. So, those are the SchrÃ¶dinger equation results. I forgot to announce that there is a forum this evening from 5:00 to 6:00. You should have signed up in recitation. If you didn't, and still want to come, send us an email and come. And we need the diffraction glasses back as you are exiting. See you Friday.