The following content is provided by MIT OpenCourseWare under a Creative Commons license. Additional information about our license and MIT OpenCourseWare in general is available at ocw.mit.edu. Last time, we saw that these electron configurations that you have been writing down are nothing other than a shorthand way of writing down the wave functions for each electron in a multi-electron atom within the one-electron wave approximation, where we let every electron in the system, or in the atom have its own wave function. And, as an approximation, we gave it a hydrogen atom wave function. But we also saw that at most, we gave two electrons a hydrogen atom wave function, the same hydrogen atom wave function. And, of course, you already know that the reason we did that is because of this quantum mechanical concept called spin, quantum mechanical phenomenon called spin. Spin is the intrinsic angular momentum. It is the angular momentum built into the particle. And that angular momentum comes in sort of two polarities, a spin up and a spin down, -- -- corresponding to the two possible values of the spin quantum number, m sub s, that we looked at last time. m sub s can have the value plus one-half, or it can have the value minus one-half. We are about to talk, now, about how spin was actually discovered. And it was discovered by these two gentlemen here, George Uhlenbeck and Sam Goudsmit. They were really very young scientists. They might have been post-docs at the time. What they were looking at was the emission spectra from sodium atoms. And this is 1925, and so they already knew enough about the electronic structure to anticipate at what frequency they ought to see emission from the sodium atoms. And so they got a discharge going, looked at the emission, disbursed it, and they thought that they would see some emission at this particular frequency. But instead, what they saw was some emission a little bit lower in frequency than they expected and a little bit higher in energy than what they expected. In spectroscopy, this kind of emission, here, is called the doublet. A little lower and a little higher. They looked at these results, thought about it and said I think we can understand those two lines, those emissions at the two frequencies there, if the electron, in particular that extra s electron in the sodium, existed in one of two spin states. This was a revolutionary idea. They were quite excited about it. They took the results of their experiment and their interpretation to the resident established scientist at the time that was closest to them, this guy, Wolfgang Pauli. Wolfgang Pauli was not a nice man. They showed him the data and said, this makes sense if the electron is in two different spin states. And Wolfgang Pauli said rubbish. You publish that and you will wreck your young scientific careers. Uhlenbeck and Goudsmit let dejectedly. No sooner than the door slammed shut, Pauli sits down and writes a paper on the presence of the fourth quantum number, m sub s. This is one of the best well-known travesties of science, now well-known. And it actually took, however, another three years and another gentleman, Dirac, who actually wrote down the relativistic Schrödinger equation and solved it. When you do that, out drops this fourth quantum number, m sub s. However, Pauli did contribute to this problem in the sense that he worked on the principles behind these problems with electrons being fermions, etc., which we won't go into. Out of that work came something called this, the Pauli Exclusion Principle. And the essence of that principle is that no two electrons in the same atom can have the same electron wave function and the same spin. Or, another way to say that, no two electrons can have the same set of four quantum numbers. For example, in our electron configuration here of neon, this electron has the quantum numbers 1, 0, 0, plus one-half for m sub s. This electron has the quantum numbers 1, 0, 0, minus one-half for m sub s. These two electrons don't have the same set of four quantum numbers, and that is why we could only put two electrons, here, in this 1s state. Likewise, this electron, here, has the quantum numbers 2, 1, minus 1, plus one-half. This electron has the quantum numbers 2, 1, minus 1, minus one-half. That is the Pauli Exclusion Principle, which prevents us from putting more than two electrons in each one of these states, 2s, 2s, 2px, 2pz, or 2py. Now, what I want to do is try to look at the wave functions and what they look like for the electrons in the multi-electron atom. And, to look at their shapes, what we are going to do is we're going to look at the radial probability distribution function. Remember what the radial probability distribution function tells us? It tells us the probability of finding the electron between r and r plus dr. I plotted those radial probability distribution functions versus r for each one of the electrons in the different states for this multi-electron atom, argon. And what we want to do is we want to compare and contrast these wave functions for the individual electrons in this multi-electron atom to those of hydrogen. Well, first the similarities. If you look at the radial probability distribution for the 1s wave function here, what you see is that the radial probability distribution is zero at r equals zero, as all radial probability distributions. That is not a radial node. That probability distribution increases, goes to a maximum, and then decays exponentially with r. That is exactly what a 1s wave function looks like for a hydrogen atom. If you look at the 2s wave function, it starts at r equals zero, it goes up a bit and then goes to zero. Here is a radial node in the 2s wave function. And then goes back up. Here is the most probable value of r and then decays exponentially. Again, it has the same structure as the 2s wave function in the hydrogen atom. The similarity is that all of these wave functions have the same kind of basic structure as that in a hydrogen atom. They have the same number of nodes, the same number of radial nodes and the same number of angular nodes. The difference between these wave functions and those of the hydrogen atom is that all of these wave functions are closer in to the nucleus. For example, if you looked here at what the most probable value of r is for that 1s electron in argon, it is 0.1 a nought. What is the most probable value for r in the 1s state of hydrogen? a nought. This is ten times closer. This is much closer to the nucleus than it is in the hydrogen atom. And if we went and compared the most probable values for 2s, 2p for those of hydrogen and 3s, 3p for those of hydrogen, we would find that all of these are much closer into the nucleus. Why? Because the nucleus has a larger positive charge on it. The Coulomb interaction here is the charge on the electron times the charge on the nucleus. For argon, that charge is plus 18 times e. That greater attractive interaction holds those electrons in closer to the nucleus. That is the bottom line. That is how these differ. The structure is the same, node structure is the same, they are just all closer into the nucleus because of that greater attractive interaction. Now that I have this radial probability distribution function up here, I also want to use it to just illustrate a concept that I think you already know. That is this concept of a shell. You know about the n

equals 1 shell, n equals 2 shell, n equals 3 shell. And the word shell also denotes some kind of spatial information. I want to show you how the spatial information is depicted, here, on this graph. I want you to see that for the n equals 3 states, 3s and 3p, well, the most probable value is not exactly in the same place, but it is in the same place as when you compare it to the 2s and the 2p. You can see how well the n equals 3 shell is separated in space from the n equals 2 shell. Again, the most probable value for 2s and 2p are not exactly in the same place. We saw that 2p is actually a little closer than to 2s, but in terms of comparing it to where the most probable values are for 3s and 3p, that is much closer in. And so this graph, here, gives you an idea of the spatial information that is denoted when we talk about shells. The n equals 3 shell is further out, the n equals 2 shell closer in, and the n equals 1 shell even closer in. I think that is a concept that you mostly know. Here, you see it on the radial probability distribution. Now, we have taken a quick look at those wave functions. Now, it is time to actually look at the energies of the states. We have not done that yet. On the left here, I show an energy level diagram for the hydrogen atom. We saw this before. Here is the n equals 1 state. Here at n equals 2, we have four degenerate states. Here at n equals 3, we have 9 degenerate states. Here at n equals 4, we have 16 degenerate states. But the difference between the hydrogen atom and any other multi-electron atom, starting with helium, are two differences. One is that the energies of these states in the multi-electron atom are all lower than they are in the hydrogen atom. That is, the 1s state here is lower in energy than the 1s state in the hydrogen. The 2s is lower than the 2s state in hydrogen, the 3s is lower, the 2p is lower, the 3p is lower, etc. The energies of those states are all lower. Why? Because of the charge on the nucleus. That potential energy of interaction is greater because the charge on the nucleus is larger. That greater potential energy of interaction lowers the energy of the states. It makes those electrons more strongly bound. Starting with helium, all of these energies are lower than those in the hydrogen atom. That is the first difference. The second difference is, you can see, now, that the 2s state is lower in energy than the 2p state. The degeneracy between 2s and 2p in a hydrogen atom is lifted or is broken, as we say. Likewise, the 3s state is lower in energy than the 3p state, than the 3d state. The degeneracy in those states is lifted, or it is broken. That is now what we have to talk about, why that is the case. Why is 2s, for example, lower in energy than 2p? And the reason for this has to do with the phenomenon called shielding. We have to talk about this phenomenon, shielding, and we have to talk about how that leads to a concept called effective charge. But to do that, I am going to do the following. I am going to realize that each one of these energies here, E sub nl, so now these energies are labeled by both the principle quantum number and the angular momentum quantum number. I am going to realize that these energies here physically are minus the ionization energy because these energies are minus the energy it is going to require to rip the electron off from that particular state. And I am going to set those binding energies equal to a hydrogen atom like energy level here. And now I am going to use the board and explain that just a little bit more. I said these energies, which are now a function of n and l, they are minus the ionization energy from that nl state. And I am going to approximate that as a hydrogen atom kind of an energy scheme. That is, I am going to set this equal to R sub H, the Rydberg constant over n squared. Out here, there is going to be a Z, but this Z is going to be Z effective, Zeff. And it is going to be squared, of course. And that Z is going to depend on that particular nl state that you are in. This Z effective, here, is the effective nuclear charge. It is not the nuclear charge. It is the effective nuclear charge. Why? Well, because of shielding. Let's try to explain that. Let's take helium. Z is equal to plus 2e. We have plus 2e here, and let's do a thought experiment in that we are going to take electron number two, here, and place it kind of close to this plus 2 charged nucleus. And then we are going to have electron number one way out here. In this case, with electron number one way out here, the nuclear charge that electron number one experiences, because it is so far out, kind of looks like a plus one charge. Because this electron, on the average, is canceling one of the positive charges on the nucleus. So, the effective charge here for this electron way out there, we are going to say, is plus one. If that is the case, well, then the binding energy of that electron is one squared times R sub H over n squared. We are going to consider n equal one because we are going to talk about the ground state of the helium atom, here. But you know what this value is going to turn out to be. It is going to turn out to be minus 2.180×10^{-18} joules. That is the binding energy of an electron in a hydrogen atom. This is a thought experiment, now. This is helium, this is just one electron way out here, and it cannot discriminate too well between the nucleus and this electron, so the overall effective charge it sees is plus one. But now, we take the other case. The other extreme case is we are going to bring in electron one really close to the nucleus. And electron two is way out here such that it does not do anything as far as this electron is concerned. And so this electron, in this case, is experiencing the total nuclear charge on the nucleus. And so we say in this thought case here, with this electron really close, that the effective charge is equal to plus 2e for this electron. Well, if that is the case, we can calculate the binding energy of this electron. And that is going to be 2 squared R sub H over one squared. We can plug in R sub H. And we are going to get minus 8.72×10^{-18} joules. What this is is the binding energy of an electron in helium plus. And so, in this extreme case, with the electron really close, that is the binding energy. With this extreme case, with the electron way far out, this is the binding energy. This is total shielding. This case is no shielding. The electron is much more strongly bound. The reality is that the binding energy of an electron in helium is somewhere in between. That is, the ionization energy for helium, for an electron in now neutral helium here, is 3.94×10^{-18} joules. Somewhere in between this extreme case of total shielding and this extreme case of no shielding at all. And that is because, on the average, there is another electron in between that electron and the nucleus. And we can calculate the effective charge, then, from the experimental binding energies by just taking this expression and rearranging it. I am going to solve that expression for the effective charge, Zeff. And, when I do that that, add, of course, this n squared times the ionization energy over the Rydberg constant. n squared is going to be one because we are talking about the ground state. The ionization energy, I said, was 3.94×10^{-18} joules. The Rydberg constant is 2.180×10^{-18} joules. In the end, I find an effective charge here of plus 1.34. Again, why is that the case? Well, that is the case because here is my electron, here is my helium nucleus and, just on the average, between this electron and the nucleus there is always another electron around. This electron kind of partially shields this nuclear charge. It partially

shields it so that we calculated, from using this scheme and using the experimental ionization energies, an effective charge of 1.34. So now, we sort of understand shielding and effective charge. That is a square root, thank you. All right. Now, we have to use this idea of effective charge and shielding to understand why the 2s state is lower in energy than the 2p state. And here comes that. Let's think about the lithium atom. The electron confirmation of lithium is 1s 2 2s 1. The electron configuration of lithium is not 1s 2 2p 1. Why? Because 2s is lower in energy than 2p. But why is that the case? Well, to look at that, we have to look at the radial probability distribution functions for 2s and 2p. Here is a radial probability distribution function for 2s. Here is the radial probability distribution function for 2p. Now, you have to do a thought experiment, here. In this 2s radial probability distribution function, what you see is that there is some finite probability of the electron in the 2s state being really close to the nucleus. For the sake of the argument, here, I am going to say that for this part of the probability distribution function, the effective charge Zeff is going to be plus 3e. I mean, that is an exaggeration because obviously we have some s electrons. But for the sake of this argument, I am going to say the effective charge for this part of the probability distribution function is plus 3e. For this part of the probability distribution function for 2s that is much further out. And I have those 1s electrons closer in. So, for the sake of this argument, I am going to say that these s electrons completely shield the nuclear charge. And so, the effective charge for this part of the distribution is plus 1e. Now, what about 2p? Well, in the case of 2p, you can see that this 2p wave function, although it is a little bit closer in, for the most part it is about in the same place as the second lobe here of the 2s wave function. We are going to say that this effective charge is plus 1e, just like this lobe of the 2s wave function. But now, to get the kind of total effective charge, I am going to have to take the effective charge and average it over this probability distribution function. And so, since in the 2s function I am going to average over a part that has a plus 3 effective charge and a part that has a plus 1 effective charge. Well, if I average over that, that is going to be larger than the effective charge of this 2p wave function because the 2p everywhere is plus one. The effective charge here for the 2s is going to be greater, on the average, than for the 2p. Because of this part of the probability distribution function, this part that is really close to the nucleus, where the electrons can feel more of the nuclear charge or experience more of the nuclear charge than they could if they were a 2p electron. Therefore, since that 2s electron has a greater effective charge, here, what that is going to mean is that the binding energy of the 2s state is going to be lower in energy. It is going to be more negative than the binding energy of the 2p state. The same thing for 3s and 3p. The same reasoning there. And it is all because of this little part of the probability distribution function. Now we can understand why the 2s is, in fact, lower in energy than the 2p. Yeah? Because the 3s, although it does, in fact, have this, it is a little bit further out here, enough to make for this to compensate. But, again, 3s is lower than 3p. We are just going to compare 3s and 3p within the same shell. Yes, it does have to do with the net area underneath. If the probability was much higher, and it is not that much higher, but if it were then you are right, it could cancel it out. Now, therefore, we are ready to write the electron configurations of all the atoms on the Periodic Table. And you already know that we use the Aufbau Principle to do that. Aufbau means building up. What do you do? You take all the allowed states and order them according to their energy. Most strongly bound or most negative energy goes on the bottom, and next most negative energy, on and on. And we will talk about a pneumonic for remembering those energies in a moment. We use the Aufbau principle. We start with the lowest energy state and we put an electron in for hydrogen. There it is, the 1s state. For helium, well, we also put that into the 1s state. Except, as we fill these states, we have to heed the Pauli Exclusion Principle. This electron, here, goes in with the opposite spin. Next lithium, 2s electron. For beryllium, another 2s electron, opposite spin. And then for nitrogen, electron, here, has to go into the 2p state. Now, it does not matter whether you put it in 2px, 2py or 2pz. They are all the same energy. The next electron, carbon, what are we going to do here? Well, here we have to obey something called Hund's Rule. And Hund's Rule says that when electrons are added to states of the same energy, and that is what we are doing here in the 2p, a single electron enters each state before a second electron enters any state. And, those single electrons have to go in so that the resulting spins are parallel. That is, they have the same spin. Do we put in an electron like this? No. Do we put it in like that? No. Do we put it in like this? Yeah, according to Hund's Rule. And then the next electron has to go into that other empty p state before any of these states double up. Then we keep doubling them up. The next electron has to go into the next state 3s. Again, we double them up. Now we are to the 3p state again. One electron goes into 2px. The next electron will go into either 2py or 2pz, according to Hund's Rule, and the spins remain parallel to get the lowest energy configuration. And then the next electron 2pz. And then we start doubling up. And we keep going. You keep going in that way so that you write the electron configuration of all the atoms in the Periodic Table. Let's look at these electron configurations kind of quickly here. Let's start with the third period, the third row here, sodium going across here to argon. Here is the electron configuration for sodium. Notice here that I don't mind if you write that electron configuration as 2p 6 instead of 2px, 2py, 2pz. Because you cannot tell the difference between x, y, and z, anyway, if you are not in a magnetic field. These electrons here in sodium that make up the inert gas configuration of argon, of course, are the core electrons. When we talk about core electrons, we are talking about the electrons that make up the nearest rare gas configuration. And then the valance electron, well, is the electrons that are beyond the nearest but lowest inert gas configurations. And also, when you are writing these electron configurations, say, for sodium, you can write it as the neon configuration and then just show the valence electron, 3s 1. As we go across that third period here everything is very normal. 3s fills up first and then the 3p's fill up. Now we get to the fourth period, from potassium to krypton. Fourth period, what happens here is that those first two electrons go into the s states. They do not go into the 3d states. They don't because those s states are lower in energy than the 3d states. And so these electron configurations are argon 4s 1, argon 4s 2 **[Ar]4s^2**. And then, once we fill those 4s states, we start filling the 3d states. Here is scandium, here is titanium, here is vanadium, everything is normal, 3d 1, 3d 2, 3d 3, and then we get to chromium. We have an exception here, chromium. Chromium is not what you would expect. It is not 4s 2 3d 4. Chromium is 4s 1 3d 5. There is no way for you to know that a priori, unless you do a very sophisticated calculation, but this is

experimentally observed that this is the configuration. Why? Because it is lower in total energy than this configuration. It turns out that there is some extra stability in having a half filled 4s shell and a half filled 3d sub-shell compared to having a filled 4s shell and a less than half filled 3d shell. This is an exception that you do have to know. But after chromium, here, manganese behaves well. Iron behaves well. Cobalt okay. Nickel okay. And now we get to copper, and we have a problem. It is not what you would expect. It is not 4s 2 3d 9. Instead, it is 4s 1 3d 10. *Again, this configuration is something you could not have predicted a priori. If you do a sophisticated calculation you can see it, but this is also experimentally observed. We know this to be the configuration. This is not the configuration. This is the lower energy configuration. Here is another exception that you have to know, copper. And then after copper here, zinc, things follow a pattern again. The next electron, then, just fills up the 4s 2 3d Now, at gallium, all of those are filled. We start filling up the 4p states. Everything is fine until we get to krypton. So, you have to know chromium and copper. Now, the fifth row here, starting with rubidium, strontium, ytterbium, zirconium, etc. all the way across here. Starting with rubidium, again, the electrons go into the 5s shell. They do not go into the 4d. That is because with rubidium and strontium, 5s is actually lower than 4d. And it is only once you fill up the 5s states that you start filling up the 4d states right here. Now, there are exceptions along this fifth row. The two exceptions, molybdenum and silver, are the same kind of exceptions as chromium and copper. You have to know the exceptions for silver and copper and molybdenum and chromium. The same identical kind of exception as in the fourth row here. There are other exceptions along this fifth row. You do not have to know those. There is really no way, a priori, for you to know that. Again, it is an experimental observation. A sophisticated hard calculation will also show that. And then, once you are done with cadmium, well, then the 5p's start filling and everything is normal and you get to the xenon inner gas configuration. How do you remember what the ordering is of these states, the energy ordering? Well, here is a pneumonic that maybe some of you have seen before. Start out and write 1s, then write 2s right below it and then 2p to the side of it. And then write 3s, 3p, 3d. And then write 4s, 4p, 4d, 4f. And then write 5s, 5p, 5d, 5f, and 6s, 6p, 6d, and 7s, 7p. And now, to get the energy ordering we are going to draw diagonals. Well, first of all, the 1s is the lowest energy state, and then the next highest energy state is the 2s state, and then the next highest energy state is the 2p. We are going to draw a diagonal. The next state to fill is 2p. The next one is 3s. Now we are going to draw a diagonal again. The next one to fill is 3p. The next one to fill is 4s. Draw another diagonal. The next one to fill is 3d, 4p, 5s. 4d, 5p, 6s. 4f, 5d, 6p, 7s. 5s, 6d, 7p, and that is all that is going to be important. That is one way to remember the relative energy orderings here. And you do have to be able to write this down on an exam. You will have a Periodic Table, but it won't have the electron configurations on it. Now, I am going to tell you something that sometimes people find a little bit confusing. That is, the electron configuration of ions. What I am about to say has no effect on what I just said about how to write the electron configuration for neutrals. This does not affect anything in your writing down the electron configuration for neutrals. This is for ions. The point I want to make is that if you actually look at the energies of the individual 3d states and 4s states across that fourth row, this is what they look like. For example, at potassium, that 4s state is lower in energy than the 3d state. That is why we put the electron in the 4s state when we wrote the neutral. The same thing for calcium. That is why we put that electron into the 4s state and not the 3s state. Lo and behold, right here at scandium, Z equals 21. What happens is that the 3d state actually drops below in energy than the 4s state. These are the energies of the individual state now, and that continues all the way across the Periodic Table. However, that does not affect how you write the electron configuration of the neutrals. For example, if you are writing the electron configuration for titanium, here it is. It is the argon core, 4s 2 3d 2. And, by the way, I don't care whether you write 3d 2 4s 2 or 4s 2 3d 2. You can write them in either order. Now, you might say, well, why is this the electron configuration if at this value for Z, Z equals 22, titanium, the 3d state is lower than the 4s state? Why don't these 4s electrons just hop into the 3d states? Well, they don't do that because this electron configuration actually minimizes the electron repulsions. If these four electrons were in the 3d state, well, then the repulsive interactions would be greater. Because they are in the same state now. And, therefore, the entire energy of the atom will be larger. And it is the entire energy, the total energy of the atom that is important when we look at the electron configurations. In this particular case, if we look at the individual d states and the 4s states, yeah, the d states are lower in energy. But what is important is when we sum up all of the energies of the interactions, what is lower? What I am saying to you is that when we do that, when we sum up all of the interaction energies, this still is the lower energy configuration, even though the 3d electrons at this value of Z, those 3d states are lower in energy than the 4s states. That is why we do not have this hoping over into the 3d states for the neutral. Now, here comes the ion configuration. If you have this configuration for the neutral, and now you ionize titanium to make titanium plus, the electron configuration is argon 3d 2. That is, it is the 4s electrons that come off, that are plucked out. They are plucked out because they are the higher energy electrons now. This is the electron configuration for titanium plus We are going to pull out those higher energy electrons, which are the 4s electrons. Again, this affects only the ion configuration. The same thing happens here on the fifth row. The fifth row starting here with rubidium and strontium, 5s is lower in energy than 4d. That is why that rubidium electron went in the 5s state. The same thing with the strontium electron, it went in the 5s state. But right here at ytterbium, the 4d state goes below in energy the 5s state. Again, that does not affect how you write the electron configuration of a neutral. For example, silver, which is way out here and is one of those exceptions, if you ionize it, if you pluck off an electron, which electron is going to go? 5s. And so the silver plus one configuration is the krypton core, 4d 10. It is that 5s electron that is going to disappear. This is important. Do not let it confuse you with the writing the electron configurations of the neutrals. Okie-dokie. See you Friday.