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5.111 Principles of Chemical Science, Fall 2008
Transcript – Lecture 8

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PROFESSOR: OK. As you're settling into your seats, why don't we take 10 more seconds on the clicker question here. All right, so this is a question that you saw on your problem-set, so this is how many electrons would we expect to see in a single atom in the 2 p state. So, let's see what you said here. Six. And the correct answer is, in fact, six. And most of you got that, about 75% of you got that right. So, let's consider some people got it wrong, however, and let's see where that wrong answer might have come from, or actually, more importantly, let's see how we can all get to the correct answer. So if we say that we have a 2 p orbital here, that means that we can have how many different complete orbitals have a 2 for an n, and a p as its l value? three.

So, we can have the 2 p x, 2 p y, and 2 p z orbitals. Each of these orbitals can have two electrons in them, so we get two electrons here, here, and here. So, we end up with a total of six electrons that are possible that have that 2 p orbital value.

So this is a question that, hopefully, if we see another one like this we'll get a 100% on, because you've already seen this in your problem-set as much as you're going to see it, and you're seen it in class as much as you're going to see it. So if you're still having trouble with this, this is something you want to bring up in your recitation. And the idea behind this, of course, is that we know that every electron has to have its own distinct set of four quantum numbers. So that means that if we have three orbitals, we can only have six electrons in those complete three orbitals.

All right, so today we're going to fully have our discussion focused on multi-electron atoms. We started talking about these on Wednesday, and what we're going to start with is considering specifically the wave functions for multi-electron atoms. So, the wave functions for multi-electron atoms. Then we'll move on to talking about the binding energies, and we'll specifically talk about how that differs from the binding energies we saw of hydrogen atoms. We talked about that quite in depth, but there are some differences now that we have more than one electron in the atom.

Then something that you probably have a lot of experience with is talking about electron configuration and writing out the electron configuration. But we'll go over that, particularly some exceptions, when we're filling in electron configurations, and how we would go about doing that for positive ions, which follow a little bit of a different procedure.

And if we have time today, we'll start in on the photo-electron spectroscopy, if not, that's where we'll start when we come back on Wednesday.

So, what we saw just on Wednesday, in particular, but also as we have been discussing the Schrodinger equation for the hydrogen atom, is that this equation can be used to correctly predict the atomic structure of hydrogen, and also all of the energy levels of the different orbitals in hydrogen, which matched up with what we observed, for example, when we looked at the hydrogen atom emission spectra. And what we can do is we can also use the Schrodinger equation to make these accurate predictions for any other atom that we want to talk about in the periodic table.

The one problem that we run into is as we go to more and more atoms on the table, as we add on electrons, the Schrodinger equation is going to get more complicated. So here I've written for the hydrogen atom that deceptively simple form of the Schrodinger equation, where we don't actually write out the Hamiltonian operator, but you remember that's a series of second derivatives, so we have a differential equation that were actually dealing with.

If you think about what happens when we go from hydrogen to helium, now instead of one electron, so three position variables, we have to describe two electrons, so now we have six position variables that we need to plug into our Schrodinger equation. So similarly, as we now move up only one more atom in the table, so to an atomic number of three or lithium, now we're going from six variables all the way to nine variables.

So you can see that we're starting to have a very complicated equation, and it turns out that it's mathematically impossible to even solve the exact Schrodinger equation as we move up to higher numbers of electrons.

So, what we say here is we need to take a step back here and come up with an approximation that's going to allow us to think about using the Schrodinger equation when we're not just talking about hydrogen or one electron, but when we have these multi-electron atoms.

The most straightforward way to do this is to make what's called a one electron orbital approximation, and when you do you get out what are called Hartree orbitals, and what this means is that instead of considering the wave function as a function, for example, for helium as six different variables, what we do is we break it up and treat each electron has a separate wave function and say that our assumption is that the total wave function is equal to the product of the two individual wave functions.

So, for example, for helium, we can break it up into wave function for it the r , θ , and ϕ value for electron one, and multiply that by the wave function for the r , θ , and ϕ value for electron number two. So essentially what we're saying is we have a wave function for electron one, and a wave function for electron two.

We know how to write that in terms of the state numbers, so it would be $1, 0, 0$, because we're talking about the ground state. We're always talking about the ground state unless we specify that we're talking about an excited state. And we have the spin quantum number as plus $1/2$ for electron one, and minus $1/2$ for the electron two. It's arbitrary which one I assigned to which, but we know that we have to have each of those two magnetic spin quantum numbers in order to have the distinct four letter description of an electron. We know that it's not enough just to describe the orbital by three quantum numbers, we need that fourth number to fully describe an electron.

And when we describe this in terms of talking about chemistry terminology, we would call the first one the $1s$, and 1 is in parentheses because we're talking about the first electron there, and we would multiply it by the wave function for the second one, which is also $1s$, but now we are talking about that second electron.

We can do the exact same thing when we talk about lithium, but now instead of breaking it up into two wave functions, we're breaking it up into three wave functions because we have three electrons.

So, the first again is the $1s$ 1 electron. We then have the $1s$ 2 electron, and what is our third electron going to be? Yeah. So it's going to be the $2s$ 1 electron. So we can do this essentially for any atom we want, we just have more and more wave functions that we're breaking it up to as we get to more and more electrons.

And we can also write this in an even simpler form, which is what's called electron configuration, and this is just a shorthand notation for these electron wave functions. So, for example, again we see hydrogen is $1s$ 1 , helium we say is $1s$ 2 , or $1s$ squared, so instead of writing out the $1s$ 1 and the $1s$ 2 , we just combine it as $1s$ squared, lithium is $1s$ 2 , $2s$ 1 .

So writing out electron configurations I realize is something that a lot of you had experience with in high school, you're probably -- many of you are very comfortable doing it, especially for the more straightforward atoms. But what's neat to kind of think about is if you think about what a question might have been in high school, which is please write the electron configuration for lithium, now we can also answer what sounds like a much more impressive, and a much more complicated question, which would be write the shorthand notation for the one electron orbital approximation to solve the Schrodinger equation for lithium.

So essentially, that is the exact same thing. The electronic configuration, all it is is the shorthand notation for that one electron approximation for the Schrodinger equation for lithium. So, if you're at hanging your exam from high school on the fridge and you want to make it look more impressive, you could just rewrite the question as that, and essentially you're answering the same thing. But now, hopefully, we understand where that comes from, why it is that we use the shorthand notation.

So, let's write this one electron orbital approximation for beryllium, that sounds like a pretty complicated question, but hopefully we know that it's not at all, it's just $1s$ 2 , and then $2s$ 2 . And we can go on and on down the table. So, for example, for boron, now we're dealing with $1s$ 2 , then $2s$ 2 , and now we have to move into the p orbital so we go to $2p$ 1 .

So that's a little bit of an introduction into electron configuration. We'll get into some spots where it gets a little trickier, a little bit more complicated later in class. But that's an idea of what it actually means to talk about electron configuration.

So now that we can do this, we can compare and think about, we know how to consider wave functions for individual electrons in multi-electron atoms using those Hartree orbitals or the one electron wave approximations. So let's compare what some of the similarities and differences are between hydrogen atom orbitals, which we spent a lot of time studying, and now these one electron orbital approximations for these multi-electron atoms.

So, as an example, let's take argon, I've written up the electron configuration here, and let's think about what some of the similarities might be between wave functions in argon and wave functions for hydrogen. So the first is that the orbitals are similar in shape. So for example, if you know how to draw an s orbital for a hydrogen atom, then you already know how to draw the shape of an s orbital or a p orbital for argon.

Similarly, if we were to look at the radial probability distributions, what we would find is that there's an identical nodal structure. So, for example, if we look at the 2 s orbital of argon, it's going to have the same amount of nodes and the same type of nodes that the 2 s orbital for hydrogen has. So how many nodes does the 2 s orbital for hydrogen have? It has one node, right, because if we're talking about nodes it's just $n - 1$ is total nodes, so you would just say $2 - 1 = 1$ node for the 2 s orbital. And how many of those nodes are angular nodes? zero. $l = 0$, so we have zero angular nodes, that means that they're all radial nodes. So what we end up with is one radial node for the 2 s orbital of hydrogen, and we can apply that for argon or any other multi-electron atom here, we also have one radial node for the 2 s orbital of argon.

But there's also some differences that we need to keep in mind, and that will be the focus of a lot of the lecture today. One of the main difference is that when you're talking about multi-electron orbitals, they're actually smaller than the corresponding orbital for the hydrogen atom.

We can think about why that would be. Let's consider again an s orbital for argon, so let's say we're looking at the 1 s orbital for argon. What is the pull from the nucleus from argon going to be equal to? What is the charge of the nucleus? Does anyone know, it's a quick addition problem here. Yeah, so it's 18. So $Z = 18$, so the nucleus is going to be pulling at the electron with a Coulombic attraction that has a charge of plus 18, if we're talking about the 1 s electron or the 1 s orbital in argon. It turns out, and we're going to get the idea of shielding, so it's not going to actually feel that full plus 18, but it'll feel a whole lot more than it will just feel in terms of a hydrogen atom where we only have a nuclear charge of one.

So because we're feeling a stronger attractive force from the nucleus, we're actually pulling that electron in closer, which means that the probability squared of where the electron is going to be is actually a smaller radius. So when we talk about the size of multi-electron orbitals, they're actually going to be smaller because they're being pulled in closer to the nucleus because of that stronger attraction because of the higher charge of the nucleus in a multi-electron atom compared to a hydrogen atom.

The other main difference that we're really going to get to today is that in multi-electron atoms, orbital energies depend not just on the shell, which is what we saw before, not just on the value of n , but also on the angular momentum quantum number. So they also depend on the sub-shell or l . And we'll really get to see a picture of that, and I'll be repeating that again and again today, because this is something I really want everyone to get firmly into their heads.

So, let's now take a look at the energies. We looked at the wave functions, we know the other part of solving the Schrodinger equation is to solve for the binding energy of electrons to the nucleus, so let's take a look at those. And there again is another difference between multi-electron atom and the hydrogen atoms. So when we talk about orbitals in multi-electron atoms, they're actually lower in energy than the

corresponding h atom orbitals. And when we say lower in energy, of course, what we mean is more negative. Right, because when we think of an energy diagram, that lowest spot there is going to have the lowest value of the binding energy or the most negative value of binding.

So, let's take a look here at an example of an energy diagram for the hydrogen atom, and we can also look at a energy diagram for a multi-electron atom, and this is just a generic one here, so I haven't actually listed energy numbers, but I want you to see the trend. So for example, if you look at the 1 s orbital here, you can see that actually it is lower in the case of the multi-electron atom than it is for the hydrogen atom.

You see the same thing regardless of which orbital you're looking at. For example, for the 2 s, again what you see is that the multi-electron atom, its 2 s orbital is lower in energy than it is for the hydrogen. The same thing we see for the 2 p. Again the 2 p orbitals for the multi-electron atom, lower in energy than for the hydrogen atom.

But there's something you'll note here also when I point out the case of the 2 s versus the 2 p, which is what I mentioned that I would be saying again and again, which is when we look at the hydrogen atom, the energy of all of the n equals 2 orbitals are exactly the same. That's what we call degenerate orbitals, they're the same energy. But when we get to the multi-electron atoms, we see that actually the p orbitals are higher in energy than the s orbitals. So we'll see specifically why it is that the s orbitals are lower in energy. We'll get to discussing that, but what I want to point out here again is the fact that instead of just being dependent on n, the energy level is dependent on both n and l. And is no longer that sole determining factor for energy, energy also depends both on n and on l.

And we can look at precisely why that is by looking at the equations for the energy levels for a hydrogen atom versus the multi-electron atom. So, for a hydrogen atom, and actually for any one electron atom at all, this is our energy or our binding energy. This is what came out of solving the Schrodinger equation, we've seen this several times before that the energy is equal to negative z squared times the Rydberg constant over n squared. Remember the z squared, that's just the atomic number or the charge on the nucleus, and we can figure that out for any one electron atom at all. And an important thing to note is in terms of what that physically means, so physically the binding energy is just the negative of the ionization energy. So if we can figure out the binding energy, we can also figure out how much energy we have to put into our atom in order to a eject or ionize an electron.

We can also look at the energy equation now for a multi-electron atom. And the big difference is right here in this term. So instead of being equal to negative z squared, now we're equal to negative z effective squared times r h all over n squared.

So when we say z effective, what we're talking about is instead of z, the charge on the nucleus, we're talking about the effective charge on a nucleus. So for an example, even if a nucleus has a charge of 7, but the electron we're interested in only feels the charge as if it were a 5, then what we would say is that the z effective for the nucleus is 5 for that electron. And we'll talk about this more, so if this is not completely intuitive, we'll see why in a second.

So the main idea here is z effective is not z , so don't try to plug one in for the other, they're absolutely different quantities in any case when we're not talking about a 1 electron atom. And the point that I also want to make is the way that they differ, z effective actually differs from the total charge in the nucleus due to an idea called shielding. So, shielding happens when you have more than one electron in an atom, and the reason that it's happening is because you're actually canceling out some of that positive charge from the nucleus or that attractive force with a repulsive force between two electrons. So if you have some charge in the nucleus, but you also have repulsion with another electron, the net attractive charge that a given electron going to feel is actually less than that total charge in the nucleus.

And shielding is a little bit of a misnomer because it's not actually that's the electron's blocking the charge from another electron, it's more like you're canceling out a positive attractive force with a negative repulsive force. But shielding is a good way to think about it, and actually, that's what we'll use in this class to sort of visualize what's happening when we have many electrons in an atom and they're shielding each other. Shielding is the term that's used, it brings up a certain image in our mind, and even though that's not precisely what's going on, it's a very good way to visualize what we're trying to think about here.

So let's take two cases of shielding if we're talking about, for example, the helium, a helium nucleus or a helium atom. So what is the charge on a helium nucleus? What is z ? Yup, so it's plus 2. So the charge is actually just equal to z , we can write plus 2, or you can write plus 2 e , e just means the absolute value of the charge on an electron. When we plug it into equations we just use the number, the e is assumed there.

So, let's think of what we could have if we have two electrons in a helium atom that are shielded in two extreme ways. So, in the first extreme way, let's consider that our first electron is at some distance very far away from the nucleus, we'll call this electron one, and our second electron is, in fact, much, much closer to the nucleus, and let's think of the idea of shielding in more of the classical sense where we're actually blocking some of that positive charge. So if we have total and complete shielding where that can actually negate a full positive charge, because remember our nucleus is plus 2, one of the electrons is minus 1, so if it totally blocks it, all we would have left from the nucleus is an effective charge of plus 1.

So in our first case, our first extreme case, would be that the z effective that is felt by electron number 1, is going to be plus 1.

So, what we can do is figure out what we would expect the binding energy of that electron to be in the case of this total shielding. And remember again, the binding energy physically is the negative of the ionization energy, and that's actually how you can experimentally check to see if this is actually correct. And that's going to be equal to negative z effective squared times r_h over n squared.

So, let's plug in these values and see what we would expect to see for the energy. So it would be negative 1 squared times r_h all over 1 squared, since our z effective we're saying is 1, and n is also equal to 1, because we're in the ground state here so we're talking about a 1 s orbital.

So if we have a look at what the answer would be, this looks very familiar. We would expect our binding energy to be a negative 2.18×10^{-18}

joules. This is actually what the binding energy is for hydrogen atom, and in fact, that makes sense because in our extreme case where we have total shielding by the second electron of the electron of interest, it's essentially seeing the same nuclear force that an electron in a hydrogen atom would see.

All right. Let's consider now the second extreme case, or extreme case b, for our helium atom. Again we have the charge of the nucleus on plus 2, but let's say this time the electron now is going to be very, very close to the nucleus. And let's say our second electron now is really far away, such that it's actually not going to shield any of the nuclear charge at all from that first electron. So what we end up saying is that the z effective or the effective charge that that first electron feels is now going to be plus 2.

Again, we can just plug this into our equation, so if we write in our numbers now saying that z effective is equal to 2, we find that we get negative 2 squared $r h$, all divided again by 1 squared -- we're still talking about a 1 s orbital here. And if we do that calculation, what we find out is that the binding energy, in this case where we have no shielding, is negative 8.72×10^{-18} joules.

So, let's compare what we've just seen as our two extremes. So in extreme case a, we saw that z effective was 1. This is what we call total shielding. The electron completely canceled out it's equivalent of charge from the nucleus, such that we only saw in a z effective of 1. In an extreme case b, we had a z effective of 2, so essentially what we had was no shielding at all. We said that that second electron was so far out of the picture, that it had absolutely no affect on what the charge was felt by that first electron.

So, we can actually think about now, we know the extreme cases, but what is the reality, and the reality is if we think about the ionization energy, and we measure it experimentally, we find that it's 3.94×10^{-18} joules, and what you can see is that falls right in the middle between the two ionization energies that we would expect for the extreme cases. And this is absolutely confirming that what is happening is what we would expect to happen, because we would expect the case of reality is that, in fact, some shielding is going on, but it's not going to be total shielding, but at the same time it's not going to be no shielding at all.

And if we experimentally know what the ionization energy is, we actually have a way to find out what the z effective will be equal to. And we can use this equation here, this is just the equation for the ionization energy, which is the same thing as saying the negative of the binding energy that's equal to z effective squared $r h$ over n squared.

So, what we can do instead of talking about the ionization energy, because that's one of our known quantities, is we can instead solve so that we can find z effective. So, if we just rearrange this equation, what we find is that z effective is equal to n squared times the ionization energy, all over the Rydberg constant and the square root of this. So the square root of n squared $r e$ over $r h$.

So what's our value for n here? one. Yup, that's right. And then what's our value for ionization energy? Yup. So it's just that ionization energy that we have experimentally measured, 3.94×10^{-18} joules. We put all of this over the Rydberg constant, which is 2.18×10^{-18} joules,

and we want to raise this all to the $1/2$. So what we end up seeing is that the z effective is equal to positive 1.34 .

So, this is what we find the actual z effective is for an electron in the helium atom. Does this seem like a reasonable number? Yeah? Who says yes, raise your hand if this seems reasonable. Does anyone think this seems not reasonable? OK. How can we check, for example, if it does or if it doesn't seem reasonable. Well, the reason, the way that we can check it is just to see if it's in between our two extreme cases. We know that it has to be more than 1, because even if we had total shielding, we would at least feel is the effective of 1. We know that it has to be equal to less than 2, because even if we had absolutely no shielding at all, the highest z effective we could have is 2, so it makes perfect sense that we have a z effective that falls somewhere in the middle of those two.

So, let's look at another example of thinking about whether we get an answer out that's reasonable. So we should be able to calculate a z effective for any atom that we want to talk about, as long as we know what that ionization energy is. And I'm not expecting you to do that calculation here, because it involves the calculator, among maybe a piece of paper as well. But what you should be able to do is take a look at a list of answers for what we're saying z effective might be, and determining which ones are possible versus which ones are not possible.

So, why don't you take a look at this and tell me which are possible for a 2 s electron in a lithium atom where z is going to be equal to three? Let's do 10 more seconds on that.

OK, great. So, the majority of you got it right. There are some people that are a little bit confused still on where this make sense, so, let's just think about this a little bit more. So now we're saying that z is equal to 3, so if, for example, we had total shielding by the other two electrons, if they totally canceled out one unit of positive charge each in the nucleus, what we would end up with is we started with 3 and then we would subtract a charge of 2, so we would end up with a plus 1 z effective from the nucleus. So our minimum that we're going to see is that the smallest we can have for a z effective is going to be equal to 1. So any of the answers that said a z effective of $.39$ or $.87$ are possible, they actually aren't possible because even if we saw a total shielding, the minimum z effective we would see is 1. And then I think it looks like most people understood that four was not a possibility. Of course, if we saw no shielding at all what we would end up with is a z effective of 3.

So again, when we check these, what we want to see is that our z effective falls in between the two extreme cases that we could envision for shielding. And again, just go back and look at this and think about this, this should make sense if you kind of look at those two extreme examples, so even if it doesn't make entire sense in the 10 seconds you have to answer a clicker question right now, make sure this weekend you can go over it and be able to predict if you saw a list of answers or if you calculate your own answer on the p-set, whether or not it's right or it's wrong, you should be able to qualitatively confirm whether you have a reasonable or a not reasonable answer after you do the calculation part.

All right. So now that we have a general idea of what we're talking about with shielding, we can now go back and think about why it is that the orbitals are ordered in the order that they are. We know that the orbitals for multi-electron atoms depend both on n and on l . But we haven't yet addressed why, for example, a 2 s orbital is

lower in energy than the 2 p orbital, or why, for example, a 3 s orbital is lower in energy than a 3 p, which in turn is lower than a 3 d orbital.

So let's think about shielding in trying to answer why, in fact, it's those s orbitals that are the lowest in energy. And when we make these comparisons, one thing I want to point out is that we need to keep the constant principle quantum number constant, so we're talking about a certain state, so we could talk about the n equals 2 state, or the n equals 3 state. And when we're talking about orbitals in the same state, what we find is that orbitals that have lower values of l can actually penetrate closer to the nucleus.

This is an idea we introduced on Wednesday when we were looking at the radial probability distributions of p orbitals versus s orbitals versus d orbitals. But now it's going to make more sense because in that case we were just talking about single electron atoms, and now we're talking about a case where we actually can see shielding. So what is actually going to matter is how closely that electron can penetrate to the nucleus, and what I mean by penetrate to the nucleus is is there probability density a decent amount that's very close to the nucleus.

So, if we superimpose, for example, the 2 s radial probability distribution over the 2 p, what we see is there's this little bit of probability density in the 2 s, but it is significant, and that's closer to the nucleus than it is for the 2 p. And remember, this is in complete opposition to what we call the size of the orbitals, because we know that the 2 p is actually a smaller orbital. For example, when we're talking about radial probability distributions, the most probable radius is closer into the nucleus than it is for the s orbital.

But what's important is not where that most probable radius is when we're talking about the z effective it feels, what's more important is how close the electron actually can get to the nucleus. And for the s electron, since it can get closer, what we're going to see is that s electrons are actually less shielded than the corresponding p electrons. They're less shielded because they're closer to the nucleus, they feel a greater z effective.

We can see the same thing when we compare p electrons to d electrons, or p and d orbitals. I've drawn the 3 p and the 3 d orbital here, and again, what you can see is that the p electron are going to be able to penetrate closer to the nucleus because of the fact that there's this bit of probability density that's in significantly closer to the nucleus than it is for the 3 d orbital.

And if we go ahead and superimpose the 3 s on top of the 3 p, you can see that the 3 s actually has some bit of probability density that gets even closer to the nucleus than the 3 p did. So that's where that trend comes from where the s orbital is lower than the d orbital, which is lower than the d orbital.

So now that we have this idea of shielding and we can talk about the differences in the radial probability distributions, we can consider more completely why, for example, if we're talking about lithium, we write the electron configuration as 1 s 2, 2 s 1, and we don't instead jump from the 1 s 2 all the way to a p orbital. So the most basic answer that doesn't explain why is just to say well, the s orbital is lower in energy than the p orbital, but we now have a more complete answer, so we can actually describe why that is. And what we're actually talking about again is the z

effective. So that z effective felt by the 2 p is going to be less than the z effective felt by the 2 s.

And another way to say this, I think it's easiest to look at just the fact that there's some probability density very close to the nucleus, but what we can actually do is average the z effective over this entire radial probability distribution, and when we find that, we find that it does turn out that the average of the z effective over the 2 p is going to be less than that of the 2 s.

So we know that we can relate to z effective to the actual energy level of each of those orbitals, and we can do that using this equation here where it's $-\frac{Z_{\text{effective}}^2}{n^2}$, we're going to see that again and again. And it turns out that if we have a, for example, for s, a very large z effective or larger z effective than for 2 p, and we plug in a large value here in the numerator, that means we're going to end up with a very large negative number. So in other words a very low energy is what we're going to have when we talk about the orbitals -- the energy of the 2 s orbital is going to be less than the energy of the 2 p orbital.

Another way to say that it's going to be less, so you don't get confused with that the fact this is in the numerator here, there is that negative sign so it's less energy but it's a bigger negative number that gives us that less energy there.

All right, so let's go back to electron configurations now that we have an idea of why the orbitals are listed in the energy that they are listed under, why, for example, the 2 s is lower than the 2 p. So now we can go back and think about filling in these electron configurations for any atom.

I think most and you are familiar with the Aufbau or the building up principle, you probably have seen it quite a bit in high school, and this is the idea that we're filling up our energy states, again, which depend on both n and l , one electron at a time starting with that lowest energy and then working our way up into higher and higher orbitals.

And when we follow the Aufbau principle, we have to follow two other rules. One is the Pauli exclusion principle, we discussed this on Wednesday. So this is just the idea that the most electrons that you can have in a single orbital is two electrons. That makes sense because we know that every single electron has to have its own distinct set of four quantum numbers, the only way that we can do that is to have a maximum of two spins in any single orbital or two electrons per orbital.

We also need to follow Hund's rule, this is that a single electron enters each state before it enters a second state. And by state we just mean orbital, so if we're looking at the p orbitals here, that means that a single electron goes in x, and then it will go in the z orbital before a second one goes in the x orbital. This intuitively should make a lot of sense, because we know we're trying to minimize electron repulsions to keep things in as low an energy state as possible, so it makes sense that we would put one electron in each orbital first before we double up in any orbital.

And the third fact that we need to keep in mind is that spins remain parallel prior to adding a second electron in any of the orbitals. So by parallel we mean they're either both spin up or they're both spin down -- remember that's our spin quantum number, that fourth quantum number. And the reason for this comes out of solving the relativistic version of the Schrodinger equation, so unfortunately it's not as

intuitive as knowing that we want to fill separate before we double up a degenerate orbital, but you just need to keep this in mind and you need to just memorize the fact that you need to be parallel before you double up in the orbital.

So, we'll see how this works in a second. So let's do this considering, for example, what it would look like if we were to write out the electron configuration for oxygen where z is going to be equal to 8. So what we're doing is filling in those eight electrons following the Aufbau principle, so our first electron is going to go in the 1 s , and then we have no other options for other orbitals that are at that same energy, so we put the second electron in the 1 s as well. Then we go up to the 2 s , and we have two electrons that we can fill in the 2 s . And now we get the p orbitals, remember we want to fill up 1 orbital at a time before we double up, so we'll put one in the 2 p_x , then one in the 2 p_z , and then one in the 2 p_y .

At this point, we have no other choice but to double up before going to the next energy level, so we'll put a second one in the 2 p_x . And I arbitrarily chose to put it in the 2 p_x , we also could have put it in the 2 p_y or the 2 p_z , it doesn't matter where you double up, they're all the same energy.

So if we think about what we would do to actually write out this configuration, we just write the energy levels that we see here or the orbital approximations. So if we're talking about oxygen, we would say that it's 1 s^2 , then we have 2 s^2 , and then we have 2 p , and our total number of electrons in the p orbitals are four.

So it's OK to not specify. I want to point out, whether you're in the p_x , the p_y , or the p_z , unless a question specifically asks you to specify the $m_{sub} l$, which occasionally will happen, but if it doesn't happen you just write it like this. But if, in fact, you are asked to specify the $m_{sub} l$'s, then we would have to write it out more completely, which would be the 1 s^2 , the 2 s^2 , and then we would say 2 p_x^2 , 2 p_z^1 , and 2 p_y^1 .

So again, in general, just go ahead and write it out like this, but if we do ask you to specify you should be able to know that the p orbital separates into these three -- the p sub-shell separates into these three orbitals.

So let's do a clicker question on assigning electron configurations using the Aufbau principle. So why don't you go ahead and identify the correct electron configuration for carbon, and I'll tell you that z is equal to 6 here. And in terms of doing this for your homework, I actually want to mention that in the back page of your notes I attached a periodic table that does not have electron configurations on them. It's better to practice doing electron configurations when you cannot actually see the electron configurations. And this is the same periodic table that you're going to get in your exams, so it's good to practice doing your problem-sets with that periodic table so you're not relying on having the double check right there of seeing what the electron configuration is. So, let's do 10 seconds on this problem here.

OK, great. So this might be our best clicker question yet. Most people were able to identify the correct electron configuration here. Some people, the next most popular answer with 5%, which is a nice low number, wanted to put two in the 2 p_x before they moved on. Remember we have to put one in each degenerate orbital before we double up on any orbital, so just keep that rule in mind that we would fill one in each p orbital before we go to the second one. But it looks like you guys are all experts here on doing these electron configurations.

So, let's move on to some more complicated electron configurations. So, for example, we can move to the next periods in the periodic table. When we talk about a period, we're just talking about that principle quantum number, so period 2 means that we're talking about starting with the 2 s orbitals, period 3 starts with, what we're now filling into the 3 s orbitals here. So if we're talking about the third period, that starts with sodium and it goes all the way up to argon.

So if we write the electron configuration for sodium, which you can try later -- hopefully you would all get it correctly -- you see that this is the electron configuration here, $1s^2, 2s^2, 2p^6$, and now we're going into that third shell, $3s^1$.

And I want to point out the difference between core electrons and valence electrons here. If we look at this configuration, what we say is all of the electrons in these inner shells are what we call core electrons. The core electrons tend not to be involved in much chemistry in bonding or in reactions. They're very deep and held very tightly to the nucleus, so we can often lump them together, and instead of writing them all out separately, we can just write the equivalent noble gas that has that configuration. So, for example, for sodium, we can instead write neon and then $3s^1$.

So the $3s^1$, or any of the other electrons that are in the outer-most shell, those are what we call our valence electrons, and those are where all the excitement happens. That's what we see are involved in bonding. It makes sense, right, because they're the furthest away from the nucleus, they're the ones that are most willing to be involved in some chemistry or in some bonding, or those are the orbitals that are most likely to accept an electron from another atom, for example. So the valence electrons, those are the exciting ones. We want to make sure we have a full picture of what's going on there.

So, no matter whether or not you write out the full form here, or the noble gas configuration where you write ne first or whatever the corresponding noble gas is to the core electrons, we always write out the valence electrons here. So for sodium, again, we can write ne and then $3s^1$. We can go all the way down, magnesium, aluminum, all the way to this noble gas, argon, which would be ne and then $3s^2, 3p^6$.

Now we can think about the fourth period, and the fourth period is where we start to run into some exceptions, so this is where things get a teeny bit more complicated, but you just need to remember the exceptions and then you should be OK, no matter what you're asked to write. So for the fourth period, now we're into the $4s^1$ for potassium here. And what we notice when we get to the third element in and the fourth period is that we go $4s^2$ and then we're back to the 3 d's.

So if you look at the energy diagram, what we see is that the 4 s orbitals are actually just a teeny bit lower in energy -- they're just ever so slightly lower in energy than the 3 d orbitals. You can see that as you fill up your periodic table, it's very clear. But also we'll tell you a mnemonic device to keep that in mind, so you always remember and get the orbital energy straight. But it just turns out that the 4 s is so low in energy that it actually surpasses the 3 d, because we know the 3 d is going to be pretty high in terms of the three shell, and the 4 s is going to be the lowest in

terms of the 4 shell, and it turns out that we need to fill up the 4 s before we fill in the 3 d.

And we can do that just going along, 3 d 1, 2 3, and the problem comes when we get to chromium here, which is instead of what we would expect, we might expect to see 4 s 2, 3 d 4. What we see is that instead it's 4 s 1, and 3 d 5. So this is the first exception that you need to the Aufbau principle. The reason this an exception is because it turns out that half filled d orbitals are more stable than we could even predict. You wouldn't be expected to be able to guess that this would happen, because using any kind of simple theory, we would, in fact, predict that this would not be the case, but what we find experimentally is that it's more stable to have half filled d orbital than to have a 4 s 2, and a 3 d 4.

So you're going to need to remember, so this is an exception, you have to memorize. Another exception in the fourth period is in copper here, we see that again, we have 4 s 1 instead of 4 s 2. This is 4 s 1, 3 d 10, we might expect 4 s 2, 3 d 9, but again, this exception comes out of experimental observation, which is the fact that full d orbitals also are lower in energy than we could theoretically predict using simple calculations.

So again, you need to memorize these two exceptions, and the exception in general is that filled d 10, or half-filled d 5 orbitals are lower in energy than would be expected, so we got this flip-flip where if we can get to that half filled orbital by only removing one s electron, then we're going to do it, and the same with the filled d orbital.

And actually, when we get to the fifth period of the periodic table, that again takes place, so when you get to a half filled, or a filled d orbital, again you want to do it, so those exceptions would be with molybdenum and silver would be the corresponding elements in the fifth period where you're going to see the same case here where it's lower in energy to have the half filled or the filled d orbitals.

So here's the mnemonic I mentioned for writing the electron configuration and getting those orbital energies in the right order. All you do is just write out all the orbitals, the 1 s, then the 2 s 2 p 3, 3 s 3 p d, just write them in a straight line like this, and then if you draw diagonals down them, what you'll get is the correct order in terms of orbital energies. So if we go down the diagonal, we start with 1 s, then we get 2 s, then 2 p and 3 s, then 3 p, and 4 s, and then that's how we see here that 4 s is actually lower in energy than 3 d, then 4 p, 5 s and so on.

So if you want to on an exam, you can just write this down quickly at the beginning and refer to it as you're filling up your electron configurations, but also if you look at the periodic table it's very clear as you try to fill it up that way that the same order comes out of that. So, whichever works best for you can do in terms of figuring out electron configurations.

So the last thing I want to mention today is how we can think about electron configurations for ions. It turns out that it's going to be a little bit different when we're talking about positive ions here. We need to change our rules just slightly. So what we know is that these 3 d orbitals are higher in energy than 4 s orbitals, so I've written the energy of the orbital here for potassium and for calcium. But what happens is that once a d orbital is filled, I said the two are very close in energy, and once a d orbital is filled, it actually drops to become lower in energy than the 4 s

orbital. So once we move past, we fill the 4 s first, but once we fill in the d orbital, now that's going to be lower in energy.

So that doesn't make a difference for us when we're talking about neutral atoms, because we would fill up the 4 s first, because that's lower in energy until we fill it, and then we just keep going with the d orbitals. So, for example, if we needed to figure out the electron configuration for titanium, it would just be argon then 4 s 2, and then we would fill in the 3 d 2.

So, actually we don't have to worry about this fact any time we're dealing with neutrals. The problem comes when instead we're dealing with ions. So what I want to point out is what we said now is that the 3 d 2 is actually lower in energy, so if we were to rewrite this in terms of what the actual energy order is, we should instead write it 3 d 2, 4 s 2.

So you might ask in terms of when you're writing electron configurations, which way should you write it. And we'll absolutely accept both answers for a neutral atom. They're both correct. In one case you decided to order in terms of energy and in one case you decided to order in terms of how it fills up. I don't care how you do it on exams or on problem sets, but you do need to be aware that the 3 d once filled is lower in energy than the 4 s, and the reason you need to be aware of that is if you're asked for the electron configuration now of the titanium ion. So, let's say we're asked for the plus two ion. So a plus two ion means that we're removing two electrons from the atom and the electrons that we're going to remove are always going to be the highest energy electrons. So it's good to write it like this because this illustrates the fact that in fact the 4 s electrons are the ones that are higher in energy. So the correct answer for titanium plus two is going to be argon 3 d 2, whereas if we did not rearrange our order here we might have been tempted to write as 4 s 2 so keep that in mind when you're doing the positive ions of corresponding atoms. Alright, so we'll pick up with photoelectron spectroscopy on Wednesday. Have a great weekend.