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**CATHERINE
DRENNAN:**

We gotta move up to the next lowest energy orbital, which we'll also talk about today. All right. So that kind of completes our one electron systems, and now we're gonna talk about multi-electrons. But we're not going to move far away from the topics that we've discussed because with multi-electrons there are several things that are the same and some things that are different. But a lot of things are the same, so we're going to come back to radial probability distributions and energy levels and things like that. So we'll move on to today's handout.

So similarities and differences. Similarities. We have the same shapes of orbitals, whether we're talking about a one electron system or more. So again, we're gonna have our s orbital. So this is my version of an s orbital that you can hold in your hand, where you have it spherically symmetric and you have probability out in every direction of r that you might find an electron, except at our radial nodes.

And then we have our p orbitals, which can be in three different directions, where you have nodal planes. So it doesn't matter what you're talking about-- one electron system or more-- you still are going to have those same shapes of the wave functions. Other similarities again include the nodal structure, which I just mentioned. Whether s is always going to be spherically symmetrical. p is gonna have those nodal planes. The angular nodal planes. So that's the same. Differences, though, have to do with the energy levels. So orbitals in a multi-electron atoms are lower-- more negative-- in energy than their corresponding orbitals in the H atom.

So let's take a look at this and think about why this is true. So here we have our friend the hydrogen atom. It has a small Z. Z equals 1. Doesn't get smaller than that. We have our 1s. Then we have our n equals 2. And we talked about the fact that in a 1 electron system like hydrogen-- these are all degenerate in energy with respect to each other, so they're all equal in energy. And then we have our n equals 3. Again, degenerate energy levels and n equals 4 up here.

But when you go to a multi-electron system, the first thing that I'll point out is that the energy level is lower. So we have 1s over here. Now 1s is a more negative lower number. And we can

think about this in multi-electron systems-- you have a bigger Z . So you have more positive charge and it's kind of hauling all of those energy levels closer. So it's a lower energy for all of those.

So 1s, again, lower, and we have 2s. Again, that's lower in energy. And now importantly, 2s and 2p are no longer degenerate with respect to each other in energy. So now the 2p system is higher in energy than the 1s and so on. So we have 3s down here and then the 3p's.

So compared to hydrogen in a multi-electron atom, n is not the sole determinate of what the energy levels are. Now, instead of just n we have n and l .

So let's review. This is good. This is all getting ready for the test. Some equations that you've seen before. And again, equations will be on the equations sheet. You don't have to memorize them. And the equation sheet for the exam is handed out today, so you can take a look at it and see where things are. If I forgot anything you can ask me questions and maybe we'll add some more if I forgot any ones.

So for a one electron system, binding energy equals minus the ionization energy equals minus $Z^2 R_H$, the Rydberg constant, over N^2 . And so for hydrogens Z is 1, but there are other 1 electron at least ions and then you have to worry about Z .

What about a multi-electron system? Looks pretty much the same, but now instead of just having n we have n and l because l matters with a multi-electron system. So the binding energy for the electron is minus the ionization energy-- that's always going to be true. The binding energy is always going to be equal to minus the ionization energy, which is equal to minus Z . But now we have a different Z . We have Z effective, which is abbreviated Z_{eff} . So this is the effective charge, not the actual charge. And that's squared. And then we have Rydberg constant and n again. So $Z_{\text{effective}}$ is not the same as Z , and it's not the same Z because of shielding.

So we talked about shielding a little bit, and I made this point that you need to think about shielding a little differently. It's not just about the average size of the orbital. It's more about the likelihood-- the probability-- that they're going to be electrons close to the nucleus that will participate in-- that will be affected by shielding.

So let's look at some extreme cases now and think about what's happening in terms of this shielding. So extreme case one. Extreme shielding. Maximum shielding. So we have the case.

We have the helium nucleus. We have moved far in the periodic table. We've left hydrogen. And so what is the charge going to be on helium nucleus? Plus 2.

So now we have this electron one. We're interested in how much this electron is shielded by electron two because we've got two electrons. Now say electron two is close to the nucleus and it's maximally shielding electron one from this positive charge down here.

So think about this electron. I like to think about this electron two as kind of the elasti-girl of electrons. So elasti-girl electron is shielding everywhere, stretching everywhere around that nucleus. Just completely shielding it from electron one, using the full negative charge to really shield. So in that kind of exaggerated case, the Z effective is not 2. It's 1. So this electron basically cancels the whole positive charge of this nucleus. Really shields that away. And so this is the effective charge with total shielding. Maximal shielding that you can get.

So now we can calculate what the binding energy-- or if we wanted, what the ionization energy would be for this case, given that particular effective charge. So again, the binding energy of electron one is equal to minus its ionization energy equal to minus the Z effective squared R_H over n squared.

And we can plug in those numbers. Don't forget the minus. We can have Z effective 1 over 1 and we calculate this value, which is, of course, just the Rydberg constant or minus the Rydberg constant minus 2.18 times 10 to the minus 18th joules.

So this is just like it was a hydrogen atom. A one electron system. So it had two electrons but one of the electron shielded so completely it was like a one electron system. Again, this is an exaggerated case of total shielding.

So now let's go to the other extreme and consider zero shielding. No shielding at all. So here we have the helium nucleus. We have electron one is now close and electron two is pretty far away. So again, we're asking, how much is this electron one going to shielded by electron two?

And in this extreme scenario, electron two is not participating in shielding at all. It's far away. I'm not sure what it's doing. Maybe it lost its super suit and can't find it. It might be at the dry cleaner's. We don't know what's going on. In any case, it is out of the game. It is not involved. It is not shielding at all.

So in this extreme case, electron one feels that full force of the nucleus. So its effective charge

is the full complete plus 2. So we can plug that in now and calculate what the binding energy is going to be. Again, binding energy for electron one equals minus the ionization energy for this electron. Same equation. We put this in but now the Z effective is 2 and we can calculate that. And now we get a value of minus 8.72 times 10 to the minus 18th joules. And this is actually the same as you would get for the scenario of helium plus, which is a one electron system. Then, in a one electron system you can use a formula of just Z where Z is 2 and get your value.

So here are the two extreme cases for helium. One it's like a hydrogen atom one electron system, and one it's like helium plus. And one case is like it just has one electron, and in the other case you have zero shielding.

So extreme case one the Z effective is 1, and we have the binding energy that's very similar to hydrogen. And so this is a total shielding case. It's shields so much it's like a one electron case. Extreme case two you have the full force. So there's zero shielding. No shielding at all. And then, this is like helium plus case where you've actually lost that other electron. It's not shielding. It's not even there. So no shielding.

And the reality in most cases is that you're in between, and you can determine this experimentally. You can measure ionization energies. So if we measured the ionization energy for helium we would find that it's 3.94 times 10 to the minus 18th. So it's greater than the 2.18 and less than the 8.72. So it's in between, and that's what you find most of the time. The Z effective is in between zero shielding and total shielding.

So we can calculate what the Z effective is actually in this case if we know the ionization energy. So if you know the ionization energy you can calculate the Z effective, or if you're given a Z effective you can calculate what the ionization energy should be for that case.

And so I told you that it was measured at 3.94 times 10 to the minus 18th. And so in that case the Z effective, if you plug the numbers in would be 1.34. And so this number is in fact in between the two cases.

With total shielding you would have a Z effective of 1 and with no shielding you have a Z effective of 2. And so in reality, we're somewhere in between in this case.

So thinking about this now, let's try your hand at a clicker question and see if you can tell me which of these is a possible Z effective for an element with a Z equals 3. I'm doing good time

wise. OK. 10 more seconds.

So does someone want to say why the other ones are not correct? Why don't you run up there and you can give them this pen? American Chemical Society pen. Hand up there.

AUDIENCE: Who had their hand up?

CATHERINE I think it's on.

DRENNAN:

AUDIENCE: So in the case of no shielding the charge should be 3, and in the case of maximum shielding there's only two electrons in the 1s so it would be 1. So anything below 1 would be beyond maximum shielding, so it's gotta be between 1 and 3.

CATHERINE Yeah, that's right. So now we're going to talk more about why shielding is important. And
DRENNAN: shielding really has to do with this order of orbital energy that we all know and are very fond of.

So when I show you this we want to ask the question, why is 2s lower than 2p or 3s lower than 3p? So let's take a look at this, and we're going to go back to our radial probability distribution. I told you I wasn't going to leave it for very long and we're back again.

So here, again, if we're considering 2s and 2p-- so we'll consider this case here-- the maximum probable radius is longer. It's greater for 2s than for 2p. But what we really care about when we're talking about shielding is this part right here.

And so there are different ways you can express this. You can say that the electrons in the orbital with lower values of l , like 2s is lower than 2p-- those electrons penetrate closer to the nucleus, even though we have this trend where the radius decreases with increasing l . So despite this size difference, when you compare this dotted line with this line here, there's more probability that they're going to be electrons near the nucleus with 2s. And that results in this lower energy. So there's less shielding for the s orbitals than for the p orbitals. And as a result of that, with less shielding because their probability is that they're closer, that they're bound more tightly, you have this lower energy. So that explains this energy difference.

So we can look at this now for the three system again for n equals 3. And here we see that p electrons are also less shielded than the d electrons, despite the fact if you look that the most probable radius over here is longer for p than for d. But now, if we look near the nucleus at the probability that they're going to be electrons near the nucleus, there's a higher probability that

they'll be electrons near the nucleus with p than with d. So these are going to be less shielded and lower in energy.

And if I throw s on there now we see s has the most probability here of being closer. Then p then d. So for a multi-electron atom, the order of energy-- we have s lower than p, p lower than d, d lower than f due to this shielding.

So again, we want to be able to draw some version of these diagrams with appropriate features to explain answers. And this all leads into what we're doing next, which is electron configurations. So we're going to think about how we're going to write the electron configurations and this indicates how you build up in energy.

So electron configurations. So first, we're going to fill our electrons in to the energy states that are our lowest. Nature doesn't want to do a lot of work, so it's going to put them in the lower states. And again, where those energy levels are depends on, for multi-electron atoms, both n and l. And we're going to put them in one electron at a time, starting with the lowest energy state and heading the following rules.

So there are some rules in doing this, and most of you have probably heard some of these before. And if you haven't I'm sure you'll like them. I know you heard this because I already just told you about that a few minutes ago. We have Pauli's Exclusion Principle, which says that you can't have the same four quantum numbers. So if you put one electron in and it's spin up the next one has to be spin down.

And Hund's Rule, which is one of my favorite rules in chemistry, and that is when you're adding electrons to the same state you're going to put them in singly, when there's degenerate energy orbitals, before a second one enters the same orbital. And the spins remain parallel as you're adding them across. So let's consider these and put some electrons into these. And we'll do this for oxygen, which is a Z equals 8 system.

So first, I want to put them in the lowest energy state. So that's 1s. So I'll put one electron in there. And then I'm going to put the second electron in there because it's the lowest energy state, so I'm going to fill it up. But I'm going to pay attention to Pauli's Exclusion Principle and put it in spin down. One electron spin up. One electron spin down. I can't put them both spin up because they would have the same four quantum numbers, and that would violate Pauli's Exclusion Principle.

So next I'm going to put electrons in 2s because that's the next lowest energy state. I'll put one in spin up. And then, because of Pauli, I'll put the other one in spin down. Next, we come to the 2p system. And I'm going to put the first electron in, but I'm not going to pair the second one. I'm going to put electron in the second orbital, both being spin up. And then I'm going to do that again.

Most people kind of refer to the Hund's Rule as kind of the rule of seating on a bus, where it always seems that one person goes in-- and even though there are two seats, one person takes it. The next person gets on the bus. Doesn't sit next to the person who's already there. They take another empty seat and so on and so on.

And so you fill up the bus with one person per bench before all those seats are taken. Then the next person comes on. Sadly has to sit with someone else. So if you think about that, that's the Hund's Rule. You'll always remember to do that. And once you put one in each, then the next person on the bus has to sit next to someone and they're going to do that spin down. Because if it was spin up again you'd have the same four quantum numbers. So these are the rules that you need to know to put these in. And then, after you do that you can write an electron configuration that says what you did.

So here we can write it this way. We'll say we have 1s two. There are two electrons in the 1s. 2s two. Two electrons in 2s. And 2p four. We have four electrons in the 2p orbitals. And if for some reason the question asks you to specify m sub l, you can do that too.

So then instead of just saying 2p⁴ then you would say 2p_x². So there were two electrons in p_x. And then to 2p_z¹ and 2p_y¹. And if you don't write 1, 1 is implied. So you will see this both ways.

You will see the 1 indicated and then you'll see the orbital just listed with nothing. If you do that you are implying there is one electron in there. If you don't mean to imply there is one electron in there don't write it that way because that's what is implied if that's the way it is.

So now let's do a clicker question. OK. 10 more seconds. I think we can get at least 93% on this one. That's not bad. 90. That was a decent guess. That was a decent guess.

So I think the trick here was just counting. So the bottom one that some people liked-- there are only six electrons and that has more.

AUDIENCE: Question.

CATHERINE

Yep.

DRENNAN:

AUDIENCE:

Are the p and sub l notations always filled in with order x, z, y or can it be x, y, z, or [INAUDIBLE]?

CATHERINE

Yeah, you don't have to worry about that. That's kind of arbitrary what you put for that. So if it is indicated then that's fine, but we didn't give you an option that would be different.

DRENNAN:

So now you can imagine that if you were writing these electron configurations and you were asked to write an electron configuration for something way down on the periodic table you would be writing for a very, very, very long time. So you can use information about core electrons and valence electrons to make your life easier.

Now, sometimes you will be asked to write the full electron configuration. It will say don't use the noble gas short hand, then that's what you have to do. Very important on the exam. Read questions carefully.

So let's introduce this concept of core electrons and valence electrons. So if we look at the periodic table we have our 1s¹, 1s², and then we come down. We have our 2s's and our 2p's, and then we have a noble gas, and then we come down and we have our first 3s¹. And so if we're talking about sodium, we have core electrons, which are the electrons that make up the noble gas element that's on the row before. And then, those are usually not very reactive. They're held pretty tight.

And the valence electrons-- the valence electrons are the electrons that do all the exciting chemistry-- lose and gain valence electrons. They're the fun ones. And so those are going to be beyond that noble gas configuration. Those core electrons. And so here sodium has one 3s¹.

So we can also write sodium then as bracket neon, indicating the noble gas before, and then just put the valence electrons. The 3s¹. And unless it's clearly specified you're not supposed to do that this will be acceptable. So we can go on in that row of the periodic table in the third period. And so the next one we would have 3s², and then we jump over here to the 3p's and so on and so on until we get to our next noble gas.

So this is pretty straightforward. There are no exceptions on the third period. But when we get

to the fourth period of the periodic table we start to have a couple of exceptions that you will be responsible for. So it's looking good up here in the beginning. We have now our noble gas, and then we have our valence electrons $4s^1$, $4s^2$, and then we start down in the $3d$'s over here. And when we get halfway through we have an exception.

So you have exceptions halfway through and also when you're almost at the end. So instead of having $4s^2 3d^4$, it really wants to have 5 electrons. And in this case, instead of $4s^2 3d^9$ it wants 10. So it like things being half full or totally full, and so you have these exceptions there. So you don't have a d^4 and you don't have d^9 . And you're responsible for these two, and then in the period right below same position same exception.

So you can think about this-- I don't know if it's four exceptions or really just two in two places, but these are the exceptions you need to know. So in the fifth it's the ones right below are the same. You're not going to have d^4 or a d^9 here. So you bump one up because it's just happier when it has 5 or 10 electrons in the d orbitals.

You're also responsible for knowing the orders. We have a question way up there. Who wants to run? Get some exercise. I don't always see questions so yell out my name if I don't see people. I am wearing my glasses. That's good. Yeah?

AUDIENCE: So what happens when we have an ion? Like a titanium [INAUDIBLE]--

CATHERINE DRENNAN: Good question. I'm getting to that.

DRENNAN:

AUDIENCE: All right. Cool. Thanks.

CATHERINE DRENNAN: Hold on a minute. Yes. We're getting to ions. They're right at the end. So first, let's consider what happens when we're not doing an ion. And there are a couple different ways that we can look at this. This is one way to remember. So you just write out $1s$, $2s$, $2p$, threes, your fours, your fives, your six, your sevens, and then draw a line. First you fill $1s$, then $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, et cetera, et cetera, et cetera. That works. That's one way to do it. It's kind of time consuming. Not sure that's the easiest way.

The other way that you can do-- this is the periodic table you'll be getting on the exam, and you can just remember what's happening at these different cases. So over here we're filling up our s 's. Over here we're filling up our p 's, except for helium. Over here we're doing our d 's in

the transition metals. Over here we have f.

And then in terms of the period numbers-- so we have one over here. So we do $1s^2$, $2s^2$, or $1s^1$, $1s^3$, $2s$. Then we come over here. We have the two p's, three s's, three p's, four s's. Then we have four d's and go to four p's, five s's, four d's, five p's, and then we can't forget when we get down here that we have f.

What number goes here? Four. So when you get to principal quantum number four is when you start having f orbitals. So if you just remember this, it's going to help you think about what the energy levels-- how you're going to write those configurations.

So maybe I'll leave this up and we'll do a clicker question now on this. And you have your periodic table available to look at. And then we'll get to ions. This should be 93%. Yeah. OK. 10 seconds. Well, 85. That's still pretty good.

So this one was one of our exceptions over here. And we wanted to have no d^9 . So it just is happier as d^{10} system, so that's our exception. One of the four that you need to know for this.

So now we have our two methods of remembering this. And we did the clicker question, and so I'm going to jump to ions. There's one question on problem sets and people have been asking about ions.

So when we're just here filling up our 4s ones. 4s we're putting in first and then we're going to our 3d, which is what we just learned about. But what actually happens when you start putting electrons in your d orbitals is that the orbital energy of the d orbitals drops below the 4s. So once they start becoming filled you have this change that happens.

And this is really only important when you're talking about ions. So if we were asking here about this one-- so we would normally say, OK, we put our two 4s in and then we have two 3d electrons. But now, because we've started to fill the 3d, if we're going to really do this in terms of energy level we could reverse the order. And we would accept both of these for the neutral ion. You could do either here.

But importantly, if you start ionizing it and losing electrons, you need to think where are those electrons coming from? Which are the electrons that are easiest to remove? And what happens is that you end up losing the $4s^2$ electrons. And so the configuration for titanium plus 2 is just $3d^2$. And so this is different. Ions behave differently, and now you can go run and finish problem set two. That last question. And this is because now we're at the end of exam

one material.

So one thing I didn't get to-- it said in the beginning. Number 12 on the problem set we're not going to get to until next week. So if you've done number 12 already you can turn it in. It won't be graded and you can turn it in again on problem set 3 so you won't have wasted time. But that won't be on exam one material.

So this is the end of exam one material. And read your instructions for the exams very carefully. And there's a couple questions, but I think it's too noisy to answer them. Note that not everyone is taking the exam in this room, and you need to go to the appropriate place. So please look at the instructions.

All right. And who won the clicker competition for today? Recitation 12.