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5.112 Principles of Chemical Science, Fall 2005
Transcript – Lecture 28

We are back here for some stimulating discussion of chemistry.

And I want to begin today by just saying that I find it particularly ironic that on the day that I am all prepared to speak to you about the molecular orbital energy levels of polyatomic molecules for which I am using methane as an interesting example the boards are screwed up.

The reason for that apparently is that this screen came down and will not go back up. And one of the reasons that I have designed my presentation technique for you this semester so heavily around the use of the blackboard is that last year, when I taught the class, I had a lot of feedback from students about how the one day when we had audiovisual problems and I couldn't use my PowerPoint and instead gave an impromptu chalk talk that that was their favorite lecture.

Maybe next year we will entirely be back to PowerPoint.

I don't know. We will see. But, fortunately, I did write out my notes this morning in electronic format so I can make use of them on the side boards.

And, in addition, I want to display for you some molecular orbital shapes and properties. And I will do that by starting out --

Actually, I would like to start, if I could, with this one. I will go back to the document camera in a moment.

Starting out right where we left off last time, you will recall that we were looking at diatomic molecules.

We started out with a seven orbital problem two lectures ago. We looked at the planar BH3 molecule. We had a molecule where the MOs were mixing in two dimensions.

And then last time when we looked at homonuclear and heteronuclear diatomic molecules the MOs were, in fact, mixing in just along an axis in one dimension.

And so, when we left the situation last time, we arrived at some kind of an understanding of the energy levels in the carbon monoxide molecule. And these were being developed, especially with reference to CO being a poisonous molecule.

Whereas, N2, another ten valence electron diatomic molecule was very, very inert.

Why was that? It turns out that you have the very electronegative oxygen atom on one side of the diagram with its very low energetically lying orbitals mixing with the carbon orbitals that are higher in energy.

And the neat thing about this, for the carbon monoxide molecule, is that it results in an asymmetry of the molecular orbitals.

Because the coefficients are not the same on the carbon side as they are on the oxygen side as those atomic orbitals blend together into the four sigma and four pi molecular orbitals that we have.

We have a total of eight MOs and they distribute energetically as four energy levels in ascending energy that are sigma in symmetry. That is cylindrically symmetric about the internuclear axis. And then we had four that were pi.

Two energies, a pi bonding with four electrons and a pi antibonding with just virtual empty orbitals.

And because this highest occupied molecular orbital of carbon monoxide is so heavily concentrated on the carbon end of the molecule, you can essentially view this as a carbon-based lone pair.

It has this big lobe here through which the carbon can serve as a nucleophile or as a base and bind to something that has an empty orbital.

And that something that has an empty orbital also has a filled orbital that matches the symmetry of the LUMO of carbon monoxide then you get the possibility for multiple bonding between the carbon of the CO molecule and that other entity.

And we will see that that other entity may, in fact, be a d-block transition element such as iron.

And what I wanted to do was to go ahead and show you that the LUMO is an interesting and unsymmetrical one as well.

Let's take a look at that.

And so in this picture I have gone ahead and included a little ball and stick diagram underneath the representation of the orbital lobes. Here is the carbon and the oxygen is colored red.

And you can see that the lobes on the LUMO, the lowest unoccupied molecular orbital in this system are also large on carbon relative to oxygen.

The same as we had found for the highest occupied MO. What this means is that that carbon atom in the CO molecule is simultaneously a base in the sigma system. And because this is our lowest unoccupied molecular orbital our carbon atom is actually an acid in the pi system.

And that makes it electronically very complimentary to d-block elements, as we will see when we get into the chemistry of elements that do have valence d-orbitals in addition to S&P coming up in a couple of lectures.

And so what can happen is that let's say that a carbon monoxide molecule somehow erroneously finds its way into your blood stream, you have there hemoglobin, the iron atom at the center of which acts reversibly to bind the dioxygen molecule.

But it irreversibly binds to the carbon monoxide molecule because the iron center, which is sitting at the center of a heme unit that I mentioned, and we will talk about the structure of hemoglobin and the way that it functions a little bit later.

But if CO gets in there, it binds to the iron through the HOMO acting as a base to the metal acting as a sigma acid. And also through d-electrons being able to act as a pi base from the metal binding with this LUMO of the carbon monoxide molecule.

And this LUMO is doubly degenerate.

That means there are two of them at the same energy. And we will come back to this issue of orbital degeneracy later in today's lecture, but that electronic asymmetry of carbon monoxide and the fact that the HOMO and LUMO are both centered on the carbon end of the

molecule are what make CO such an interesting molecule and such a reactive molecule and therefore a poison.

And so now let us please go back to the document camera.

What I have shown here are the five platonic solids.

Actually, I spent a lot of time over the weekend practicing drawing these on the chalkboard so that I would be able to do that very nicely for you.

And here it comes that we do not have that option today, so I will show them to you this way.

And the platonic solids are the five regular polyhedra. And that means that they are polyhedral that have, as their faces, regular polygons that are all identical. And the reason I am bringing this up today is that we had talked about issues of symmetry with reference to molecular orbital theory.

And these are all very highly symmetric shapes, as you can immediately recognize.

The buckyball that we looked at earlier is not here because it has both five-membered rings and six-membered rings on the faces.

And so it doesn't have all the faces identical. And those that do have all the faces identical are the platonic solids. And the complete list of those is shown here. With triangles, you can put four equilateral triangles together to make a tetrahedron.

There is actually a journal called Tetrahedron.

And there is another one called Tetrahedron Letters. And there is another one called Tetrahedron Reports. And the reason is that organic chemistry is carbon-based, and carbon so often gets involved in forming tetrahedra.

And so the tetrahedron is a very important symbol of organic chemistry. And we will get back to that. And with triangles, if instead of putting four of them together, you put eight of them together this way, you get the octahedron.

And the octahedron is equally important as a symbol for inorganic chemistry.

And the reason for that is that when we have metal ions in solution they often sit at the center of a coordination octahedron in which six ligands bind to that metal center. And we are going to get into how that was discovered pretty shortly by Alfred Werner, another Nobel laureate in chemistry.

And with triangles you can also make the icosahedron shown here, and this has 20 faces.

And the icosahedron is important in chemistry. And certain elements, for example, boron actually have structures in the solid state in which the boron atoms are arranged at the vertices of a regular icosahedron.

So, this is a chemically important shape as well.

And if you go from triangles to squares you can, of course, make a cube. And probably the most familiar of a platonic solid to us. And then, if we go up to pentagons and put those together, as you can see here, we can put 12 pentagons together in a regular way that gives rise to what we call the pentagonal dodecahedron.

And you can imagine that each of these vertices could be a CH unit, carbon-hydrogen.

And then each carbon would have its valence of four satisfied. And there would be all single bonds at the parameter of this round molecule.

And, in fact, that dodecahedron molecule was the objective of organic synthesis for quite a long time before it was finally successfully synthesized by Leo Paquette. You would be surprised the kinds of challenges maybe sometimes that do drive chemists to do what they do.

And that is the platonic solids.

I am going to be focusing our attention on methane. And, if I could have the side board go back to the computer for a moment, that would be great. These are the notes for today's lecture that I wrote up this morning that you will be able to download later today, or maybe you already can.

I don't know. In any event, when we approach the methane problem in molecular orbital theory, what we do is recognize that the tetrahedron can be conveniently inscribed into a cube by placing hydrogens at alternating corners of the cube, as shown here.

And then, when we do that, the carbon atom of the methane molecule lies at the very center of this cube.

And this way of arranging the system in space will help us to simplify the problem of the molecular orbital energy levels for the methane molecule.

And we are going to be ultimately working toward a comparison of the molecular orbital description of the methane molecule with that afforded by valance bond theory.

Now, some of you approached me after lecture last time and say what happened to hybridization? And, if you wanted to talk about the methane molecule and the language of valence bond theory, you would say that this carbon atom is SP3 hybridized in order that it may form simultaneously for two electron bonds between the central carbon and the four peripheral hydrogens.

Well, where hybridization went is that it stayed with valence bond theory.

Let me reemphasize the distinction between the molecular orbital treatment of molecule electronic structure as contrasted with the valence bond theory in which hybridization plays a role. It does not play a role in the language of MO theory, so please keep those quite distinct.

Now we need to choose a coordinate system for our problem.

And I won't spend too much time discussing how we choose the coordinate system, but what we have done in the present case with methane is to choose the x, y and z axes each to come out of the faces of the cube.

And we do this because that choice of coordinate system will lead to the equivalence of the carbons 2px, 2py and 2pz orbitals in 3D space.

We could choose a different coordinate system, and that would make the problem more difficult. So, what we have done is chosen a convenient set of coordinates where the x, y and z axes each come out of the faces of our cube.

Now we recognize that the methane problem, like the homonuclear and heteronuclear diatomic molecule problems we talked about last time, is an eight orbital problem.

The diatomics N2 and CO each had ten electrons to go into their eight molecular orbitals. And here, with methane, we have eight electrons, four coming in as the valence orbitals from the carbon atom, valence electrons from the carbon atom rather, and four coming in as the four valence 1s electrons for the four hydrogens.

And our eight orbitals are the carbons 2s, 2px, 2py and 2pz orbitals.

And we have four more orbitals, the 1s from each of the four hydrogens. We know how may electrons are going to be able to go into our MO energy level diagram. We know how many MOs we are going to have because we know how many valance AOs we have.

And those numbers are equal at eight.

The choice of this problem is predicated on my desire to show you how things progress as we go from a planar system to a linear system to now a system that has molecular orbitals that stretch out in three-dimensional space.

Now we are going to take the following approach. We are going to say how can we generate linear combinations of the four hydrogen 1s orbitals that will be so constructed as to match the nodal properties of the carbon atomic orbitals that are the valence orbitals of that carbon?

OK.

So that is our goal and that is our strategy. And let me say also that in this tetrahedral symmetry you can recognize that you cannot distinguish any one of the four vertices of a tetrahedron from the other three.

And that is important.

And that is also true from the way that we have decided to situate the hydrogen nuclei on this cube relative to our coordinate system. In other words, none of these four hydrogens lie on any of the three Cartesian axes.

And their relationship to the coordinate system and to the shape of the cube each is indistinguishable from that of the other three hydrogens.

And that is an important aspect of the way that we set up the problem.

And why do I mention that? Because I mentioned that when constructing MOs in general, one of the first things you can do, if you are going to be able to take advantage of symmetry to help you solve the problem of these MO energy levels and how they are constructed from linear combinations of atomic orbitals is to identify symmetry-related sets of atoms in orbitals.

If you are keeping that in mind, you will realize that we are treating all four hydrogens together because they are indistinguishable from one another in the tetrahedral shape of the methane molecule.

So, that is important. If we had a more complicated molecule such as if we were looking at --

I get to use a little bit of board space today. Here is a slightly more complicated hydrocarbon molecule.

Here is a slightly more complicated hydrocarbon molecule. And in a molecule like this, this is cyclohexane drawn in a chair confirmation. Sir Derek Barton actually was the Nobel laureate who got his prize for discussing conformational aspects of hydrocarbons.

We would find that the hydrogens split up into two sets.

They are not all equivalent in the cyclohexane molecule in this frozen out chair confirmation, because we have one type that is equatorial and one type that is axial on each of these carbons as we go around this six-membered ring.

And so there are different sets that you would have to treat separately. But methane is more symmetrical. And all four hydrogens in the methane molecule are identical so we are going to treat them together in developing our linear combinations.

And, coming back to this, what we are going to do, once again, to generate these things, is to imagine the central atom atomic orbital as growing out in space out to where the hydrogen nuclei are.

And then we are going to take the sign of the wavefunction that we find out there and apply it to those hydrogens that are out there in space in order to see what our linear combination must look like.

If you imagine the carbon 2s orbital, which has the same sign positive everywhere, and imagine it growing out to where the hydrogens are, and we are labeling the hydrogen A, B, C and D, as shown here.

And we will keep that same labeling scheme throughout the development of this problem. You would see that the carbon 2s positive wavefunction, as we imagine it growing out to where the hydrogens are, would touch each of these hydrogens at the same time.

And, thus, we confer the sign positive on all four of the contributors to this first of our linear combinations.

And what that will represent is simultaneous bonding of the carbon 2s orbital with all four hydrogens and with the same sign everywhere.

And so we can write down one-half A plus B plus C plus D, where I am using A here to represent the hydrogen 1s orbital associated with hydrogen labeled A.

So I have just abbreviated that in A. And, similarly, B is the hydrogen 1s orbital associated with hydrogen B and so on.

So, this is a linear combination of these four hydrogen orbitals. And it is normalized with a half here. And we have the same coefficient on each of the four hydrogens, so the size of the lobe that you would draw at each four of these positions would be the same.

That is number one.

We have built a linear combination based on the nodal properties of the carbon 2s atomic orbital. And now let's do two more. And we are going to base these on the nodal properties of the central carbon 2px orbital and the central carbon 2py orbital.

I am using the same coordinate system as I started with, namely that the positive x-axis comes out of the face of the cube and comes toward us and the positive y-axis comes out of this face of the cube and goes that way.

And we will look at z in a moment.

That one is going straight up out of the top face of the cube for positive z. What you can see is that if you imagine the carbon 2px atomic orbital as just growing out to where the four hydrogens are, we will see that the hydrogens in positions A and B will experience the positive lobe of the carbon 2px orbital at the same moment as the two hydrogens in back labeled C and D experience the negative lobe of the carbon 2px orbital.

And so we give positive phase to A and B and negative phase to C and D.

And we give them the same coefficient everywhere such that this linear combination is normalized as one-half A plus B minus C minus D.

That is our second linear combination of hydrogen orbitals. And this one has been so generated as to match the nodal property of the carbon 2px orbital, the key feature of which is that it is everywhere positive along positive x and everywhere along negative x it is negative.

And the 2py orbital of carbon has the property that everywhere in the plus y region of space it is positive so that C and B will be associated with a positive sign for this linear combination.

And the 2py orbital is negative everywhere along negative y back here.

And that is where hydrogens A and D are located. So, A and D will carry a negative sign for this new linear combination, which is one-half of minus A plus B plus C minus D. This is just one way of writing down the picture that we see here.

And there is only one left to be generated from the nodal properties of the carbon 2pz orbital which has its positive node oriented along positive z and its negative lobe oriented along negative z, and it has the xy plane as a nodal surface.

And so, therefore, hydrogens A and C will carry a positive sign because they are oriented and located in the plus z region of space.

Whereas, hydrogens B and D are located in the negative z region of space so they will carry a negative sign.

And that one can be normalized also with a normalization coefficient of one-half. And so it is A minus B plus C minus D. And just don't forget that these letters refer to the 1s orbitals associated with the hydrogens that are so labeled.

And we started with identifying the fact that the four hydrogens in this problem are all equivalent.

And, thus, their 1s orbitals are all equivalent, indistinguishable from each other with respect to their spatial orientation. And so we took four atomic orbitals, and we are constructing from them four linear combinations of those four atomic orbitals.

I want to emphasize what I have written here, which is that with the coordination system we have chosen and in this high tetrahedral symmetry the carbons 2px, y and z orbitals are identical.

And, just like in a carbon atom floating free in space, they are degenerate. That means they have the same energy. And so we will talk about orbitals in atoms being degenerate in a moment.

But we find that the 2px, y and z orbitals on that carbon are going to have the same energy and they are degenerate.

And the molecular orbitals constructed from them in this tetrahedral system will have the same property. They will be degenerate. So, something that is occasionally associated with high symmetry is multiple MO degeneracy.

Next, knowing what our carbon atom atomic orbitals are and knowing also what our four linear combinations are of the hydrogen 1s orbitals, we can now allow them to interact in ways that are either bonding or antibonding.

And they interact, of course, according to their nodal properties. Those linear combinations that have the same nodal properties as a

particular carbon atom atomic orbital will lead to a bonding interaction and an antibonding interaction.

And we have an eight orbital problem, so we better see eight energy levels appearing in our molecular orbital energy level diagram for this methane molecule.

And, when we go down here, starting at the lowest energy molecular orbital, we find that it can be constructed by adding to the carbon 2s orbital, which is, once again, spherically symmetric, this linear combination that is A plus B plus C plus D.

And we can draw this with a surface like this, which envelopes all five of our nuclei which has the same sign everywhere.

And so our lowest lying molecular orbital, our most bonding molecular orbital, our most stabilized MO, which can house a pair of electrons because it is singly degenerate, is one that will look something like this.

It envelopes all five of our nuclei. And, effectively, the pair of electrons is associated simultaneously with all five nuclei.

And the wavefunction has the same sign everywhere, just like the carbon 2s orbital from which this is partially constructed does.

And then next we have three molecular orbitals that are each built by forming bonding interactions with the carbon's p-orbitals, px, py and pz with the linear combination that matches that carbon orbital in terms of the nodal properties.

And we built them that way so that becomes particularly straightforward.

This one here is coming out, the face that points to the right. And so you can see that this one is based on the carbon 2py orbital.

And, if that carbon 2py orbital makes a bonding interaction with the linear combination denoted as minus A plus B plus C minus D, the bonding interaction here is signified by this plus sign. So, we have a plus sign here and a plus sign here.

And, thus, we have a molecular orbital that has the same nodal properties as a carbon 2py orbital does, which means that the xz plane is a nodal surface for this molecular orbital.

And what it looks like is kind of a two-bladed propeller. You have a plus phase that is distributed enveloping the two hydrogens that we labeled B and C, along with that positive lobe of the carbon 2py orbital.

So that you have that forming one blade of our two-bladed propeller.

And the blade with the other sign is rotated relative to the first by 45 degrees. Sorry, by 90 degrees, in fact. And will involve the distribution of bonding character over carbon's negative 2py lobe interacting with these two hydrogens back here, which are hydrogens A and D.

And so we will visualize these in a moment to make that more clear.

But these three bonds, one oriented along x, one oriented along y and one oriented along z all look exactly like this. They are just rotated 90 degrees to each other in space, just like the x, y and z Cartesian axes are.

I have only drawn one of them, but we have three of them because there is a three-fold orbital degeneracy in this molecular orbital.

So, singly degenerate and then triply degenerate. And then, as we go up in energy, we will find that our lowest unoccupied molecular orbital is constructed by subtracting.

It is the same as I have written here but with a minus sign, the C2s subtracting A plus B plus C plus D. A, B, C and D hydrogens all have the same sign to their wavefunction as each other, but they have the opposite sign as the contribution from the carbon 2s orbital to this molecular orbital.

And what that results in, as I have tried to indicate with some red dashes here, is that you generate a nodal surface in between the carbon and hydrogen nuclei that will go completely around and will intersect perpendicular to each of these carbon-hydrogen inter-nuclear vectors.

You have a change of sign as you are traversing the path from carbon to any one of the four hydrogen nuclei.

And that is what we get by just reversing the sign relative to the bonding counterpart of that orbital.

And that makes this one anti-bonding. We will give it an asterisk here to denote antibonding character to this molecular orbital. And now ascending in energy we will find that for each one of these orbitals that is bonded and oriented with respect to x, y or z in Cartesian space, we find that there is an antibonding counterpart.

Again, what we are doing is taking, for example, carbons 2py and subtracting the linear combination that corresponds to carbon 2py in terms of its nodal symmetry properties.

We are subtracting minus A plus B plus C minus D. The carbon 2py has the same plus its positive lobe is oriented along positive y, just as it is down here, but now we have reversed the sign of the four hydrogens.

And what this introduces will be antibonding nodal surfaces in between the carbon and the hydrogens.

And they are strong antibonding interactions because of the good directional overlap of, say, the positive lobe of carbon's 2py with these s-orbital contributions in the negative from hydrogens C and B here.

And back here A and D rotated, of course, by 90 degrees.

One of the points that I was illustrating last time and really trying to emphasize in the context of MO theory is that, in general, we expect orbitals to be higher in energy if they have more internuclear nodes.

And the energy of the orbitals is also affected by which atomic orbitals are close to the MO in energy and also by factors of overlap.

And normally, for example, a sigma bond is typically associated with greater overlap than a pi bond because of the directionality of the overlap.

And here you have an interesting case where this p-orbital is not directed right at the hydrogen. And it is not a pi bond either. It is something in between sort of sigma and a pi type of orientation.

It is an oblique interaction of the hydrogen 1s wavefunction with that lobe of the p-orbital. But, still, it gives rise to very good overlap down here and consequently a very strong antibonding character up here in the counterpart.

And, from calculation, this is the order of the energy levels that come out of that. And so we have only four energy levels, two of which are triply degenerate, so we indeed have eight wavefunctions that correspond to the molecular orbitals of this system.

Question down here?

[STUDENT]

Why did this not have the one-half? The one-half is missing there because I forgot to put it there.

Yes, to be normalized it should have a one-half there.

That is right. But then there is a further point that that brings up, which is the following. What I am implying here is that there are equal amounts of carbon 2s in the bonding orbital and as in the antibonding counterpart.

But that need not be the case. It could be that this is 0.6 here and that this 0.4 up here.

And that is a greater level of detail than I am really interested in going into for the purposes of this problem.

But your point, with respect to the coefficient, is well taken. Thanks. Christine, maybe we can fix that on the one that gets posted on the Web. Let's now look at these things using our VMD program.

Starting from the lowest energy and we will work our way up.

Which orbital is this? This is a molecular orbital of the methane molecule.

One way you can identify orbitals is where they are with reference to the HOMO or the LUMO.

In this case, the HOMO is triply degenerate. And there is one orbital lower in energy than the HOMO. This would be then the HOMO minus

one because it is one below the HOMO in energy. That is the one which is the carbon 2s plus A plus B plus C plus D.

That is that MO there.

Actually, let's go ahead and take that one away.

Sorry about that.

Let's see if you can figure out which one this is.

In order to figure out which one it is, you need to be able to realize where the nuclei are and where your internuclear nodes are, if any.

And, if so, how many. This is one of our hydrogen contributions.

Here is a hydrogen contribution with opposite sign. And there is a piece of our carbon 2p orbital in the center. Now, this is just one of three identical counterparts that are rotated 90 degrees with respect to each other in space so I am not going to show you all three of them.

They all look exactly the same. Is this one bonding or antibonding? Yeah, this one is antibonding.

And it does not have the same sign on all the hydrogens, so it has to be part of our LUMO which is triply degenerate and involves bonding or, in this case, the antibonding between a carbon 2p orbital with a linear combination of four hydrogens.

You can see that when you have an antibonding orbital you are depleting the electron density in the space between the nuclei rather than increasing it as you do in a bonding orbital.

Let's go ahead and look at the bonding counterpart of this one.

And we will do that. And let's delete it. One thing that you will get, if you haven't already gotten it, is you are going to get a link to be able to download all the files that I used to show you molecular orbitals with in class.

Because this program I am using, this VMD program is available on Athena.

And you can also download it yourself for free onto your own computer if you want to. And so this is going to give you the opportunity to study these orbitals and rotate them around at your leisure on your desktop.

And now let's look at the bonding counterpart to that antibonding orbital that we just looked at. This one is the two-bladed propeller to which I referred.

And you can see that this orbital has the same symmetry with respect to its nodal properties as a carbon 2p orbital because it has a single nodal plane.

And one side all the signs are positive and on the other side all the signs are reversed. And we have a nice piece of bonding going on there and there when we have this oblique interaction of one of the lobes of a p-orbital simultaneously with two of the hydrogens that it sits directly between in space.

There is one of our triply degenerate components of our highest occupied molecular orbital.

And then there is just one left to visualize.

All right. We will delete that one.

We looked at our most symmetric and most bonding molecular orbital. And now we are going to go ahead and look at the antibonding counterpart of that one.

And so this is clearly a molecular orbital that is formed using some piece of the carbon 2s orbital.

And you see that you get a change in sign as you go from carbon to each of the hydrogens that accordingly the electron density is depleted in the region of space between the nuclei.

And that is a characteristic of an antibonding orbital.

And this one, according to our diagram, in fact, is the LUMO. So, as you will see over here, that was what we predicted our lowest unoccupied molecular orbital would look like. And then up here we had our triply degenerate LUMO plus one based on the carbon 2p orbital interactions.

Now you can see what these four types of molecular orbital would look like.

And now you wonder just what kind of prediction does this make regarding experimental observables. And so let's look at this picture.

This diagram contains a number of interesting features.

It is a diagram that plots ionization energy here on the x-axis against a number of different molecules on the y-axis.

At the top you have simply a neon atom. Neon is our noble gas atom that lies just immediately to the right of fluorine in the Periodic Table. If anything is more electronegative than fluorine it would actually be neon.

This inert gas that is extremely difficult to ionize because it holds so tightly onto all eight of its electrons.

Does it hold equally tightly onto all eight of its electrons? The answer is no because, as you scroll across here in ionization energy, you see that its 2p electrons ionize here and its 2s electrons ionize way over here.

The type of diagram I showed you last time where the 2s orbital, as you go across the Periodic Table, decreases in energy faster than does the set of 2p orbitals associated with an atom is expressed in this diagram here because we have neon.

And then we are going across the Periodic Table. This next molecule is HF, an eight electron species, and H_2O, an eight electron species, and then NH_3 ammonia, the other eight electron species.

And then over here we get to CH_4, the molecule that we have just discussed today.

And what is very interesting here is that the ionization energies of the molecular orbitals, in the case of the molecules, and of the atom in the case of neon track very nicely. Here is the molecular orbital that has 2s character of HF, of H_2O, of NH_3 and of CH_4.

And it is rising in energy as we go from right to left across the Periodic Table.

And that is because the carbon 2s orbital is much higher than the neon 2s orbital is, for example. And the carbon 2s orbital is contributing to that most bonding of molecular orbitals of the methane molecule.

And then there is this manifold here that corresponds to ionizing an electron out of the HOMO of methane.

And it is a broadened peak distribution here because of the different vibrational states that the methane can be found in when, in fact, it experiences an incoming high energy photon that is capable of knocking the electron out of the methane molecule and ionizing it.

This is called photoelectron spectroscopy. And you will be reading about it also in the context of your problem set because we have a problem that deals with this.

And I point you to a piece of your text that covers photoelectron spectroscopy.

But the key point here is that if you had all your eight electrons at one energy, as valance bond theory might suggest for a molecule like this, you might think you should only see one peak in the PES of methane.

But you see two because methane the molecule has two molecular orbital energy levels. One of them being triply degenerate. See you on Wednesday.