Concepts of Chemistry for Engineering
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Lecture No. 18
Molecular orbital theory 6: Polyatomic molecules

So far we have discussed diatomic molecules. That is a good beginning. And that is the only way to begin, because unless we talk about H_2^+, we would not get access to the molecular orbitals. But then having done that, we cannot stop there, can we, because if we have a chemistry course in which we only discussed diatomic molecules, then it is no fun. We do not want to stop there. We want to go beyond. And we want to, if possible, talk about molecules like this.

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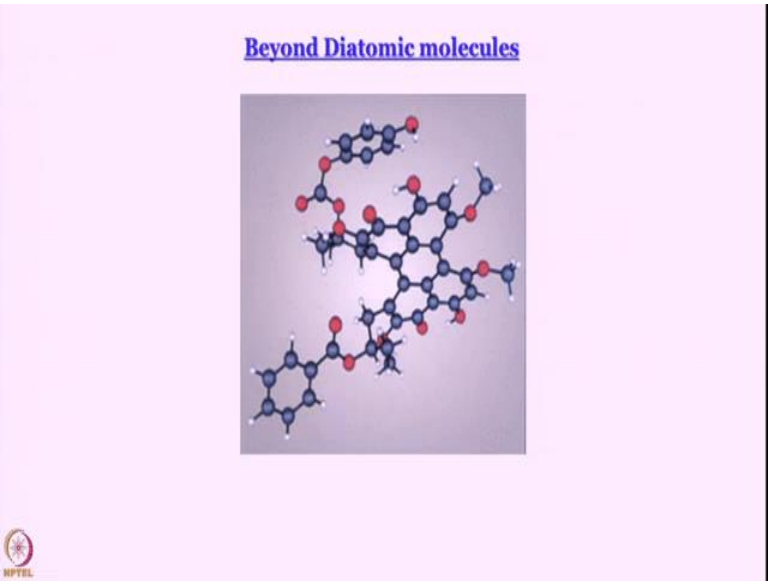

In this course, we will not reach here. This molecule, incidentally, is called Calphostin C. I had worked on this molecule. We did some experiment. And then our collaborators did a quantum chemical calculation. In those days, more than 20 years ago, in the best supercomputer that was available in that university, it took one year to get this optimized structure of Calphostin C, a definitely way beyond diatomic molecule.

We will not go this far. But we will at least try to talk about molecules that have some atoms, few atoms. And we will try to give you an idea of how one can start developing a molecular orbital theoretical treatment of molecules like this. Again, when we do that, we have to worry about σ

bonds and π bonds. We actually talked about π bonds a little bit when we discussed carbon monoxide. But we did not dwell upon it for too long.

So, what we will do is to start with, we are going to discuss a system which has exclusively sigma bonds. And then we will forget about sigma bonds completely and discuss a theory that is exclusively for π bonds. So, here goes. If I talk about polyatomic molecules, the first thing that comes to my mind is that polyatomic molecules have certain shapes. Diatomic molecules can only be linear. There are two atoms after all.

What happens if you have more than two atoms there, if you have three atoms? Well, the structure is determined by VSEPR, valence shell electron pair repulsion theory. And essentially, this is something that makes sure that the steric requirement of these so-called bond pairs and lone pairs are met. As we might have studied in classes 11 and 12, lone pair-lone pair repulsion is maximum followed by lone pair-bond pair repulsion followed by bond pair-bond pair repulsion.

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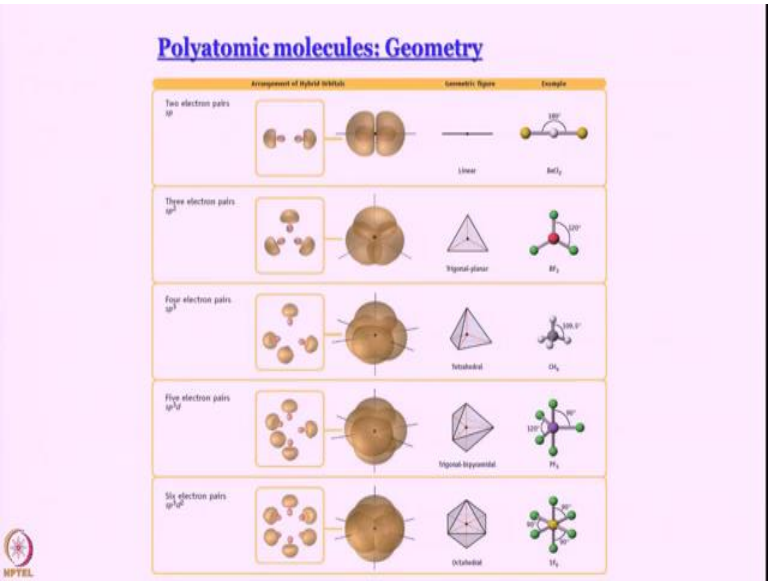

And that is why if you have two electron pairs, only two bond pairs, you get a linear molecule like you do in BH_2 or $BeCl_3$. If you have three, like in BF_3, it is a trigonal planar molecule. If you have four like in methane, we are going to talk about methane today, you are going to get a tetrahedral molecule, remember, tetrahedral not square planar, if it is just BH_4. And if you have more, if you have PF_5 kind of molecule, then the geometry is trigonal bipyramidal TBP. For SF_6 molecule, we

have an octahedral geometry. And all this is because the repulsion between pairs of electrons has to be minimized.

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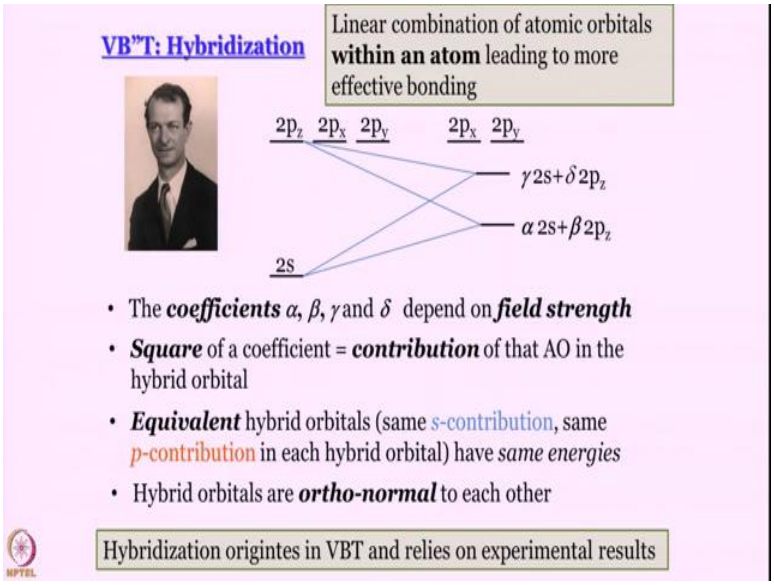

In valence bond theory, hybridization is used, as I said, to generate appropriately oriented orbitals. Hybridization provides directionality and that is its strength. Remember, in molecular orbital theory, the strength is delocalization and delocalization and directionality do not go hand in hand. So, in molecular orbital theory, it is possible to use hybrid orbitals, but that would give you a localized MOT, which we do not like so much.

Rather, we want to build a delocalized MO picture of the polyatomic molecules that we are going to discuss and the molecule that we want to discuss today is methane, delocalized molecular orbital theory picture of methane.

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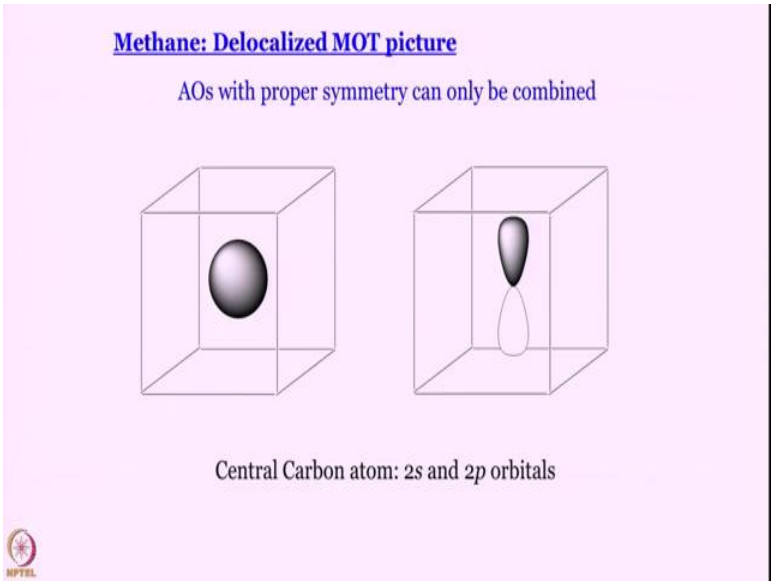

To do that, we will consider this picture that AOs, atomic orbitals with proper symmetry can only be combined. And what I mean by that will become clear as we go ahead in the discussion. First, let us think, in the central carbon atom which valence orbitals are there, 2s and 2p. This is 2s and this is 2p. So, we will try to do it like this for the hydrogen atoms that are there. The orbitals that will participate in bonding, they are the 1s orbitals.

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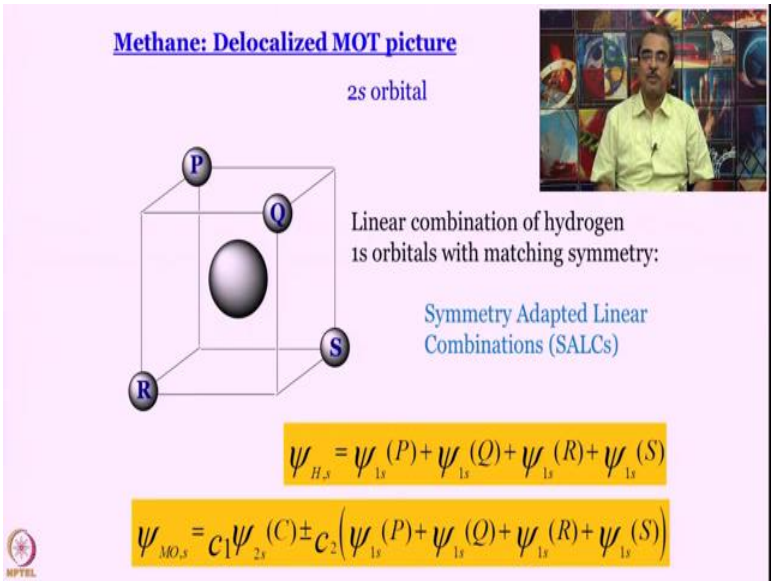

So, we will denote the hydrogen atoms as P, Q, R, and S. And we are going to take appropriate linear combinations of 1s orbitals of P, Q, R, and S. Very often I am just going to call these 1s

orbitals P, Q, R and S and we will try to generate linear combination which have the right symmetry to give a bonding and anti-bonding combination with the central 2s or 2p orbital of carbon atom. So, this idea of using linear combination of hydrogen 1s orbitals with matching symmetry generates what is called symmetry adapted linear combinations or SALCs or SALCs as many people pronounce them.

There is a more formal way of generating SALCs that is by using something called projection operators. I want something, some combination of P, Q, R and S that I will be able to add to or subtract from the 2s orbital. So, what is the matching symmetry that I am looking for? See, 2s is just plus, there is no node here. So, if it is all plus, then if I have plus sign of wave function of P and Q and R and S, that is good. Let us say all the four 1s orbitals on the hydrogen atoms have a plus sign on the wave function.

So, now, I can write them like this, $\psi_{H,S} = \psi_{1s}^{(P)} + \psi_{1s}^{(Q)} + \psi_{1s}^{(R)} + \psi_{1s}^{(S)}$. Could you write all minus, yes you could, does not matter. But the convention is to use plus wherever possible. Now, if I take linear combination of this combination, this combination here is the SALC, symmetry adapted linear combination, and this is the SALC of orbitals of the pendant atoms.

See, the molecule is such that there is a central atom carbon and there are pendant atoms. Pendant means something that is hanging or projecting. So, these hanging atoms here are hydrogen atom. So, we take symmetry adapted linear combination of orbitals of the pendant atoms, P, Q, R, and S in this case. So, if I now take a linear combination of this SALC with the 2s orbital, I can combine in two ways, plus and minus.

So, I can write like this C_1, a coefficient, multiplied by $\psi_{MO,S} = C_1\psi_{2s}^{(C)} \pm C_2(\psi_{1s}^{(P)} + \psi_{1s}^{(Q)} + \psi_{1s}^{(R)} + \psi_{1s}^{(S)})$. That is one of the molecular orbitals that I get involving the 2s orbital and a particular SALC of the hydrogen atom 1s wave functions. Where is this wave function? I hope we all see that this wave function that I have written here $\psi_{MO,s}$ is actually delocalized over the entire molecule. It is not only between carbon and P, it is not only between carbon and Q, it is delocalized all over.

So, the orbital is all over, recognizing the fact that when an electron moves in the joint field, it can be anywhere in the molecule. It does not have to be in one particular place. It cannot be in one particular place. Probability of finding it is distributed all over the molecule and that is what automatically takes us to electron density distributed over different centers and that takes us to sort

of multi-center bonds, you can call it. But is this a bond, is a molecular orbital a bond, we will come to that discussion later on.

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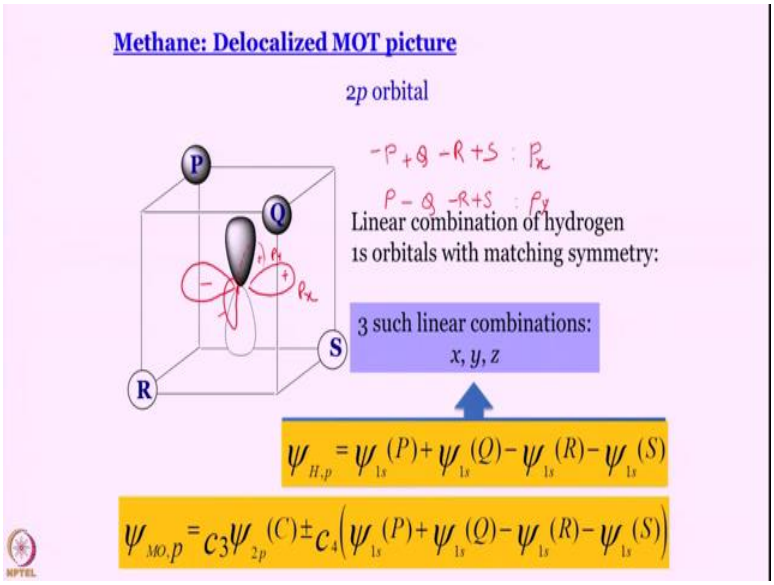

Now, that being said, let us think of the 2p orbital. The 2p orbital, the two lobes have different signs. So, if I take P+Q+R+S, then what will happen, then that does not have the right symmetry, because P plus Q will give you a constructive interference you can say with the upper lobe of the 2p orbital, R plus S will actually give you a destructive interference. So, I can say P and Q will give bonding interaction, R+S will give you anti-bonding interaction. Overall, you have a non-bonding interaction that means the MO is not formed.

So, P+Q+R+S is not the right SALC for forming MO with the 2p orbital of carbon. Then what would be an appropriate geometry? If I take P+Q-R-S that works, does not it?

$$\psi_{H,p} = \psi_{1s}^{(P)} + \psi_{1s}^{(Q)} - \psi_{1s}^{(R)} - \psi_{1s}^{(S)}$$

We can write this. This is a different SALC from the one that I had written earlier, but this SALC

$$\psi_{MO,p} = C_3\psi_{2p}^{(C)} \pm C_4(\psi_{1s}^{(P)} + \psi_{1s}^{(Q)} - \psi_{1s}^{(R)} - \psi_{1s}^{(S)})$$

has the right symmetry to give bonding and anti-bonding combinations with the central 2p atom on carbon, on the central 2p orbital on the carbon atom, on the 2p orbital of the central carbon atom. So, we have to use different SALCs of the pendant atom for different orbitals of the central atom.

I hope it is not difficult to understand that here let us say I had drawn the p_z orbital. I can generate a similar SALC for px orbital. Where is px orbital? Here. So, p_x orbital would be, let us say, here. This is plus, this is minus. If this is the case, then what will be the right SALC for the p_x orbital. The right SALC would be, see this has to be plus Q, S has to be plus, P has to be minus, R has to be minus. So, I can write like this -P+Q-R+S. So, this gives us the SALC that can give you bonding and anti-bonding MOs with the p_x orbital of your carbon atom.

What about p_y? I can draw like this, let us say, this thing is pointing towards us, let us say, that is minus and the one that is behind us that is plus. This is your py. For py what is the right combination that is required? P and S must have plus sign. Q and R minus, must have minus sign. So, P-Q-R+S this is the SALC that gives us the right symmetry for forming the bonding and anti-bonding MOs with p_y orbital of the central carbon atom. Three such linear combinations are there.

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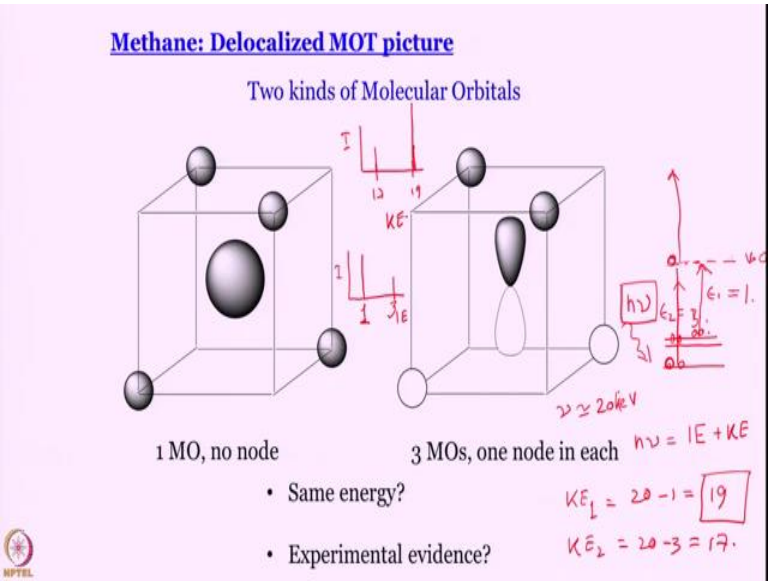

So, now, see, we have two kinds of MOs; one that involves the 2s orbital and the other that involves the 2p orbital. What is the difference between the two? One is that involves the 2s orbital, there is only one possible MO. And there are three MOs that are possible involving the $2p_x$, $2p_y$, $2p_z$ atoms, atomic orbitals. That is point number 1. Point number 2 is there is no node in the first MO. There is a node in the second MO. This node is the one that is already there in that particular p orbital.

So, we have two kinds of MOs. Should they have the same energy? From our elementary knowledge of chemistry, we can expect that they will have different energy, because the first one

has no node, second one has one node and generally energy goes up with the number of nodes. But then, what is the experimental evidence to tell us that there are indeed two kinds of MO orbitals. The experimental evidence comes in the form of photoionization.

What is photoelectron spectroscopy? We are familiar with ionization energy, I think. Ionization energy would mean suppose this is an atomic orbital or a molecular orbital, provide ionization energy, the electron is promoted from here to an infinitely high level. Infinitely high level means it does not feel the attraction of the nucleus anymore. It is not in the orbital you can think. That is your ionization energy.

Now, let us say I have two different MOs in some atom or some molecule. I can expect two different first ionization energies, I am talking about first ionization energy here, electron can go from the lower level, electron can go from the higher level, I will call this ε_1. I will call this ε_2. Even though I actually drew them in the reverse order, it does not really matter. Now, see, so this is v=0 kind of limit.

Suppose, I have excited this molecule with some radiation x-ray typically, which has a frequency υ. What is the energy of a photon, h υ. And let us say υ is very high something like 20 eV or something like that, 20 keV or something like that. So, what will happen? The molecule is going to, the electron is going to promote it beyond ionization limit. This here is the ionization limit. So, if it goes beyond ionization limit, what will, what does that mean?

The energy that you provide h υ, it will be too much actually. It will be in excess. So, you can write it as $h\upsilon = IE + KE$ of the free electron. So, if I now use the same h υ, so typically what you would have is you would have your sample that would be irradiated with this very high energy photons with energy h υ and your detector is going to record what is the kinetic energy of the electrons that are set free. So, see let us put some values.

Let us say this $\upsilon \approx 20$ keV, let us say ε_1 is something like 1, and ε_2 is something like 1, well, 1 will be the same thing, is something like 3. So, what will be the kinetic energy in the first case? $KE_1 = 20 - 1 = 19$, $KE_2 = 20 - 3 = 17$. So, you get two values. So, if I try to plot the spectrum of kinetic energies, then I will get one line at 17, one line at 19. Actually, I should write like this, x axis is kinetic energy. And what is y axis? Y-axis is intensity.

In the way I have drawn it here, I should get equal intensity for both the lines. And so, I should get two lines like this. Let us say for whatever reason, this one is doubly degenerate. That means, there

are two MOs with the same energy, same ionization energy of 1. Now, what will happen? They will be actually twice the probability of a transition occurring from here than from here. So, then, and these have to be all occupied energy levels remember, otherwise will not see anything.

So, now, what will happen is that, this KE_1, this line is going to be twice as intense. Why, because number of transitions from there is double. We are assuming that both are all levels that we are talking about our occupied. The population of electrons in this higher energy level is going to be double the population of the lower energy level. That is why that corresponding kinetic energy will be twice as much.

Of course, I do not have to plot kinetic energy in the x-axis, I might as well plot ionization energy, then what will the plot look like? Now, it will be just the other way around. So, for ionization energy of 1, the line will be twice as intense as that for IE_3. This is photoelectron spectrum in a nutshell for you. And this is what is going to be used to establish that indeed there are two different kinds of MOs.

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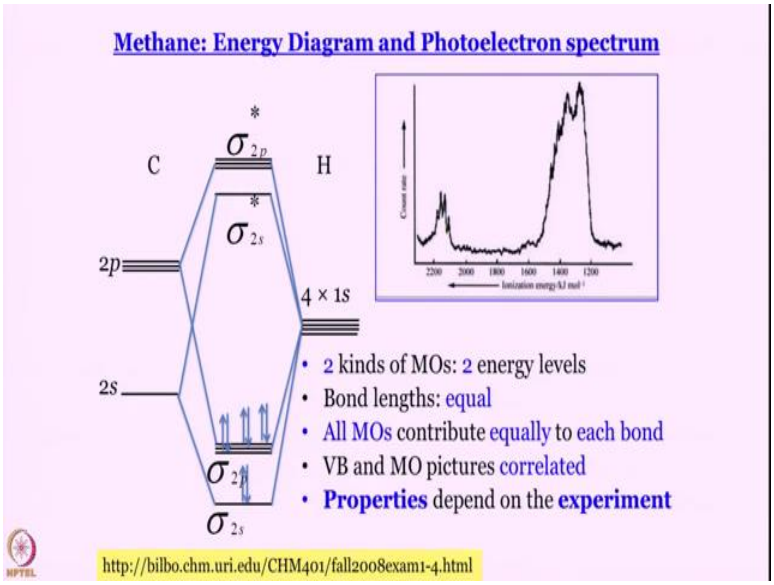

So, let us draw the energy level diagram now. So, here briefly discussed HF and all, so we know that depending on which atom you are talking about, energies of 1s orbitals are going to be different from each other. So, this is roughly to scale where the energies of the 1s orbitals of hydrogen atom and I have drawn four of them, because for hydrogen atoms are participating in bonding, they are somewhere between the energies of 2s and 2p orbitals of the central carbon atom.

Now, what happens? We said that there are two kinds of MOs; one involves 2s orbital and that is associated with lower energy. Let us put it in. This is a sigma bonding orbital, σ_{2s} and you are going to have an anti-bonding orbital involving 2s also. And for the remaining 3p orbitals they will participate to form σ_{2p} and σ^*_{2p} well. And these are going to be triply degenerate as we have discussed.

Next, let us fill in the electrons. How many electrons are there, 2, 4, 6, 8. 4 from hydrogen, 4 from the valance shell of carbon. So, you see both the bonding MOs actually are occupied. So, now if I do photoionization, then what kind of spectrum do I expect? I expect a spectrum with two bands, is not it or two lines. Actually, you will never get lines. All spectra have some finite line width for different reasons.

So, what kind of ionization energies do I expect? I expect two kinds of ionization energies and this one is lower. So, the higher ionization energy should have, should be associated with a smaller band in the photoelectron spectrum. The lower ionization energy band should be thrice as intense

as the one with the higher ionization energy band. And this is the spectrum for you. It is taken from the net. It is drawn in the opposite direction. But as you see, for lower ionization energy, the band is much more intense compared to the band for higher ionization energy.

And from here, you can experimentally determine the, what is separation between these levels also. So, our model stands validated. Also, often, we asked, we get the question, what is the meaning of all this structure? There is some structure here. There is some structure. Is it 1 or is it 2. Actually, all this is vibronic structure, molecules vibrate as well.

Using Born-Oppenheimer approximation, you can think that they are separated from electronic transitions, they are not always. They can couple. So, this is something called vibronic structure. Again, something we are not going to go into in any detail in this course, at least. What is, what matters to us is the area under the bands. The area under this band is thrice the area under this one. So, this band is associated with lower ionization energy. This is associated with higher ionization energy. And this is exactly in line with the MO energy levels, energy level picture that we had drawn. The model stands indicated.

What have we learned? We learned that you can have two kinds of MOs in molecules like this, and they are going to be associated with two energy levels. However, we know that the bond lengths are equal. Otherwise, the model itself would have not been sustainable. So, do we have a contradiction here? We are saying there are two kinds of MOs. And we are saying that all bonds are equivalent. So, is there a problem? Actually, there is not, because it is important to realize that MOs are not bonds. MOs are wave functions.

Using wave function, you can figure out the electron density, you can figure out the probability distribution of electrons over the molecule. And actually, each MO contributes equally to each bond. That is why , end of the day, you get a uniform distribution of electrons all over the molecule. It is completely delocalized. So, if you think of the valence bond picture that most of us would know, using sp^3 hybrid orbitals, there is no contradiction, to be honest. Valence bond picture focuses on the bond. A bond means electron density between two atoms.

Molecular orbital talks about the wave function delocalized over the atom from there and this is something that we are going to learn in a little more detail when we talk about pi electronic systems. We can actually figure out what is the electron density between two particular atoms also.

The pictures are correlated. Same story being told in two different ways. There is no contradiction. And it also brings us to this very important realization that which property of the molecule you see is determined by which experiment you do.

Remember, wave function collapse, before you make a measurement, the molecule is in an entangled state. Make a measurement there is wave function collapse and you get to see some property of the molecule. How do you bring about that wave function collapse in real life, you perform some experiments. So, you perform photoelectron spectroscopy. The idea you get is about molecular orbitals. You do rotational spectroscopy. We will talk about rotational spectroscopy later. You can get an idea about the bond length.

So, you do some other kind of experiment. If it is possible to crystallize from crystals, you can tell what the bond lengths are and what is the shape of the molecule. So, which experiment to perform will reveal different aspects of the molecule to you. So, from this discussion today we have learned so many different important points about polyatomic molecules. And now that we have discussed the molecule with sigma bonds only, we will go over to other molecules where pi bonds are involved.