Symmetry and Group Theory
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Lecture – 45
SALC:CH4 Introduction

So what, what we will do is, we will now try to develop a treatment which is a little more involved and we are going to use character tables. Before that what is the symmetry point group of Dh2? **"Professor - student conversation starts"** D infinity. D infinity h. **"Professor - student conversation ends."** Have we discussed the D infinity h character table? I have forgotten. You have not? So let us do that.

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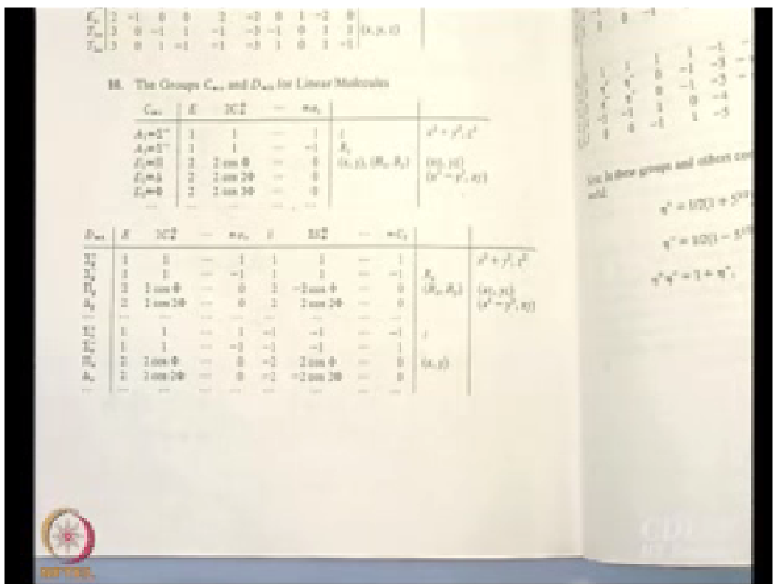

This is the D infinity h character table. Can you see? What was it that strikes you first? Yes it is complicated of course and also the names are different. Mulliken symbols are different. They are different to emphasize the fact that these are special kinds of groups. So instead of A B etc., you say sigma pi delta etc., okay. Let us see what we have here. What are the symmetry elements present in D infinity h?

First is C infinity axis, right. So now if I rotate it, if I rotate the molecule above the C infinity axis by say 0.0000000000001 degree, is there a symmetry operation? Think of a C3 axis. If I rotate by 10 degrees, is that a symmetry operation? No, but above C infinity axis, if I rotate by something that is as close to 0 that you can think of, even that is a symmetry operation, right. So which means that infinite number of symmetry operations will be associated with C infinity axis.

So that is why you have something like this. C infinity phi. What is the meaning of C infinity phi? Phi is any angle. **"Professor - student conversation starts"** Sir why it is 2. Because you can rotate this way or this way. **"Professor - student conversation ends."** Of course, it is kind of redundant because when you rotate this way, you can go all the way and reach there also. But this is a convenient way of writing it.

After all twice infinity is infinity. It is true to emphasize + and - rotation. **"Professor - student conversation starts"** When we take we take 2C because we can do 2 infinite operations. So we will get, there should be infinite C infinity operations because... There are infinite C infinity operations, that is right. But what we are showing here is that, this is C infinity to the power phi. So we want to write everything.

So, so +phi and -phi. Then you can write 2phi 3phi 4phi whatever phi you want. So that is why it gives you infinite number. That is what dot dot dot means. **"Professor - student conversation ends."** Then you have sigma v. Once again, why does we call it sigma v? Sigma v. Infinite number of sigma vs, where are the sigma v's? This, my palm here is sigma v, right, okay. Then what do you have?

Infinite number of centers with inversion. Then 1, 1 point of inversion. It cannot be infinite number of points of inversion, okay. The center, center of the 1 is the center of inversion, okay. Then once again like C infinity you can write S infinity also, same thing and finally you have infinite number of C2s. There are more than 1 ways of writing these D infinity h character table.

If you notice, one symmetry element that is missing very prominently is sigma h, right. So there are ways in which we could incorporate sigma h also. But it does not matter. You will follow any one convention, it will work. After all, you have infinite number of symmetry operations, okay. So C2, how many C2s are there? Once again infinite.

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This is a C2 and you can just turn it by whatever angle you want, infinite number of C2s, okay. So now the simplest case is of course, what will be the total number of irreducible representations? Infinite. So how many 1-dimensional representations? How many 2-dimensional representations? So what we do is, we only concern ourselves with a minimal description of the point group.

We only discuss the iR's that usually show up and we usually use and these are those iR's, sigma g+, sigma g-, pi g is a 2-dimensional representation, delta g is a 2-dimensional representation. And then replace all the g's with use to more or less get another set of representations. You could go on writing. If you have time, you can go on writing all the different kinds of representations. But these are the 8 representations that we most commonly use.

So these are the ones that are usually written, okay. What is sigma g+? All characters are 1. So total is symmetric representation. What do we, what is the Mulliken name that we usually use for a totally symmetric representation? A1 or A1g or A1g- so on and so forth or Ag- depending on the molecular, depending on which molecule you use, depending on which character, which symmetry point group you use.

"Professor - student conversation starts" Sir. Yes, sir. Why not carry the + or - sign on the pi u or pi. Because it is not required. We only need to consider 1 pi g and 1 pi u, okay. You can actually write +- but as we had discussed earlier also, sometimes if you do not need the dash, you do not write it, right. So you are perfectly fine if you write +. No problem with that. But we do not need it.

That is why we write only what we need, okay. **“Professor - student conversation ends.”** So these are all, so this is something that you can see very easily, right. That these first 4 have all + characters of, with respect to i. So 1 1 and these are 2-dimensional representations, so these are 2. And u's are all -1 -1. Here it is 0. So there, it is a little more complicated, fine. So then what is the second sigma?

Sigma g-, sigma g- has a -1 for sigma v and -1 for C2. pi g and delta g are, the pi and delta are 2-dimensional representations. Now tell me this sigma pi delta, do they remind you of something? **“Professor - student conversation starts”** Sigma bond pi bond delta bond. **“Professor - student conversation ends.”** So the sigma bond pi bond delta bond has got their names from here.

Can we talk about sigma bonds from class 11? Right. So sigma bond pi bond delta bond actually get their names from here. Because they belong to these symmetric species, okay. So what we are now going to do is that we are going to work out the symmetric species of the molecular orbital and we will see that they are going to belong to some irreducible representation here or the other. Okay, fine. So the way to go about is this.

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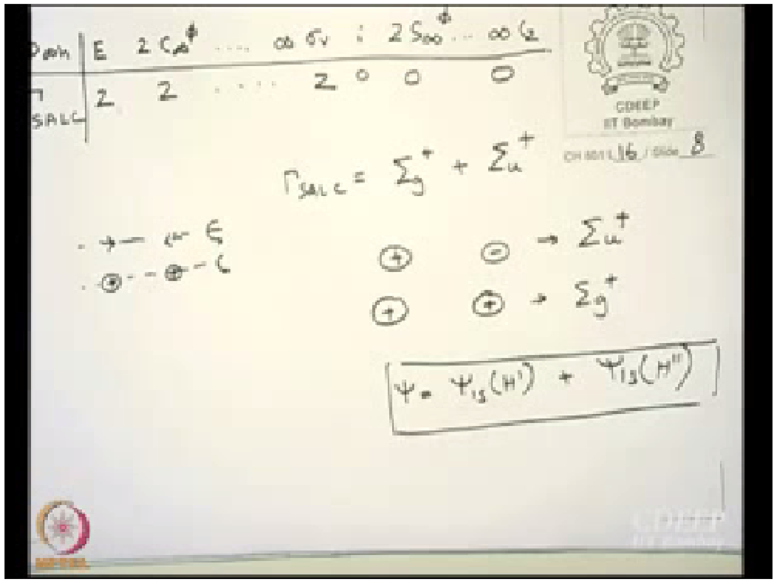

E 2C infinity phi, 2C infinity phi and dot dot dot, infinite number of sigma v's i 2S infinity phi dot dot dot infinite number of C2's. What we will do is? Now we will try to generate the reducible representation of the SALC's. Do not forget SALC's are generated by using atomic orbitals of the pendant atoms, hydrogens in this case, this case, okay. So the way, all our discussion today is from Carter's book.

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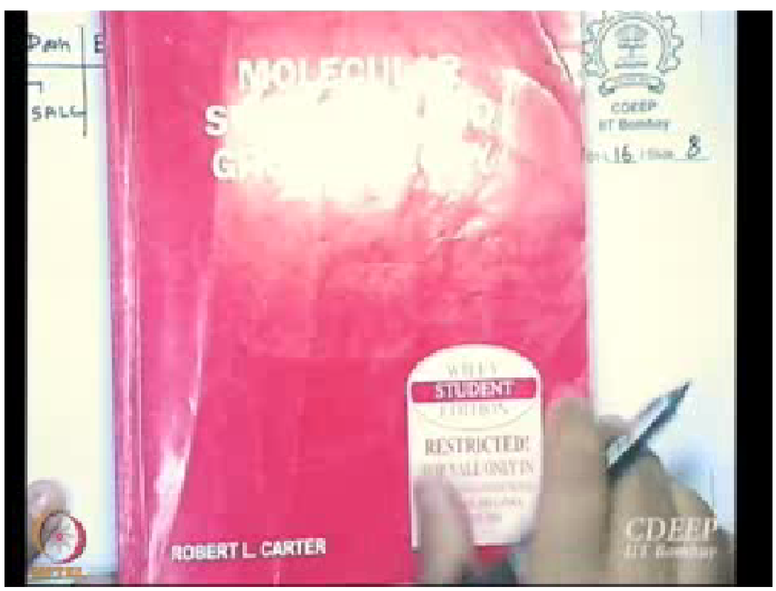

Cannot read, okay, Carter, it is there in the library. What Cotton has done is that he has gone on directly to something called projection operator. We will get there next day but before that I thought we will just develop a little less quantitative picture and then only we will go into the complicated one, okay. So gamma SALC, so what Carter has done is that he has represented these 1S orbitals as arrows.

After all this is how the bonds are going to form, okay. You take these vectors, use them as the basis 2-dimensional basis and construct a representation. You could also think that you take two 1S orbitals. Take two 1S orbitals separately, use them as a basis and construct gamma SALC, that I think we can do without much hassle. The character of E will be 2. What will be the character of C infinity?

Where is C infinity? Like this, right, like this and you are turning this way. You have an arrow, you turn it by whatever angle, what is the character for it? 1 for each arrow. Got it? So 2. What about sigma v? Sigma v what will be the character? 1 for this, 1 for this, right. 1 for this, 1 for this, 2. **"Professor - student conversation starts"** Which one? C. C infinity, these are the vectors, right. **"Professor - student conversation ends."**

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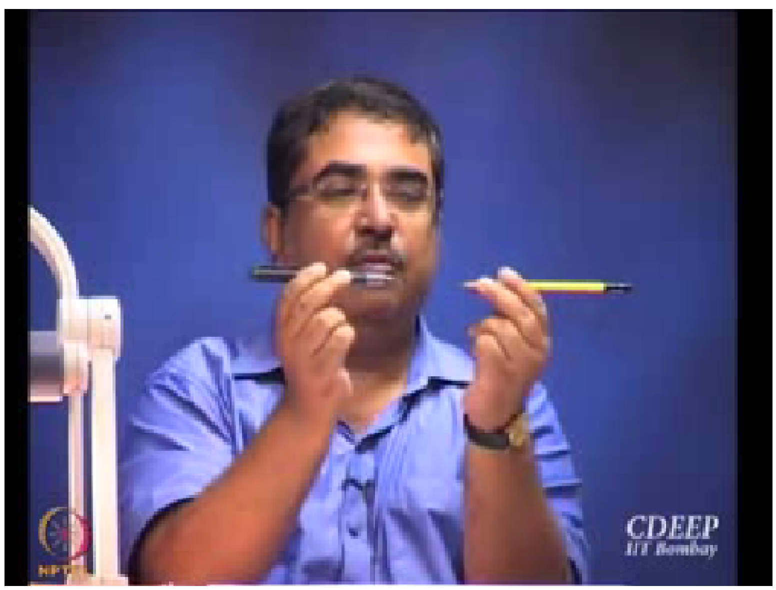

Where is C infinity? The line joining the 2? So you are turning like this. What will be the character, no matter what the angle is? 1 for this, 1 for this. Like, turn this way, 1 for this, 1 for this. Right. So E is 2, C infinity is 2, sigma v is 2. What about i? We are now considering them separately.

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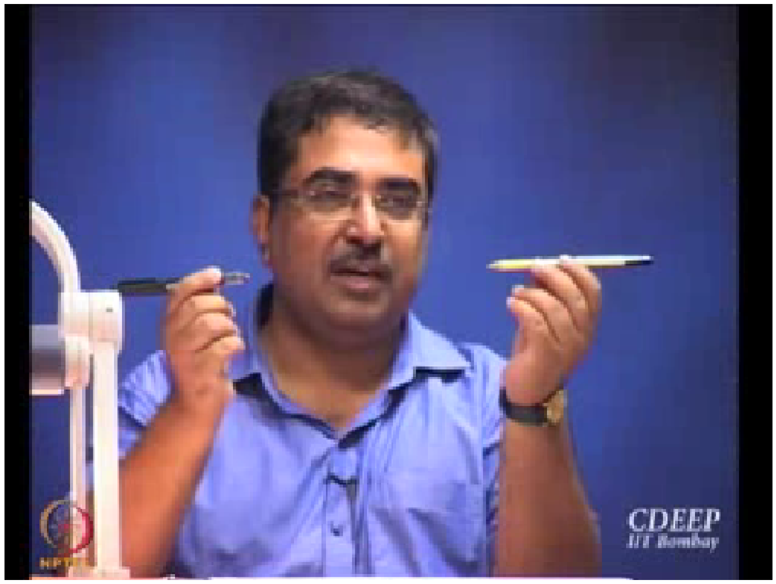

You perform I, what will happen?

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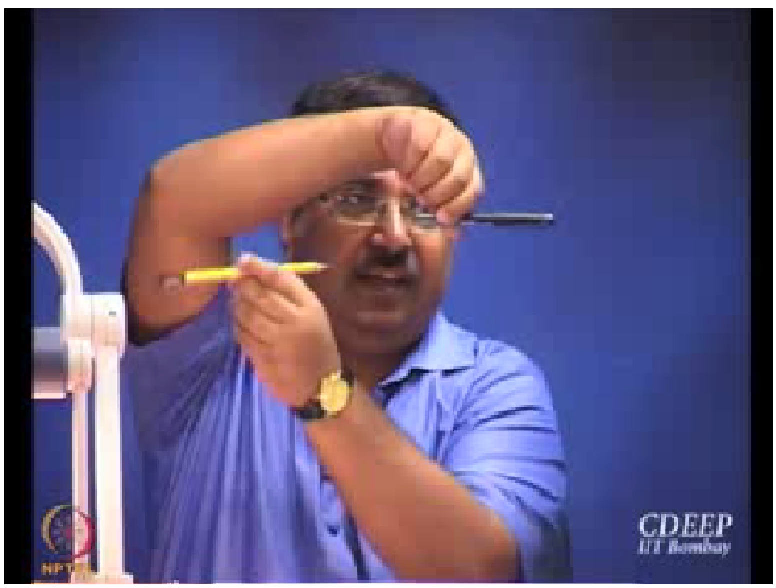

Like this, right. They will interchange. This and this will interchange. This will be here, this will come here. What will be the character? Are you all okay with this? Mayank, question? 0. S infinity?

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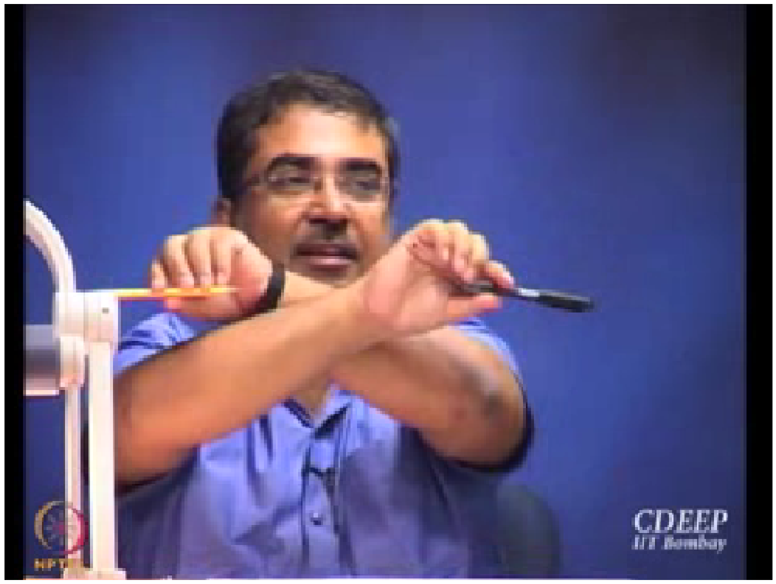

S infinity means you rotate by whatever angle and then deflect by the horizontal plane, deflect with respect to the horizontal plane. Once again change in place. So once again 0. Alright, okay, got it. C2? This is C2.

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This is C2 axis. How will I show I have a C2 axis in between otherwise? This is C2 axis. If you rotate with respect to it, what do I get? They interchange once again. So what is the character? 0. Nicely symmetric, right. 2 2 2 0 0 0. Now what is the next step? You have to break this thing down. This is reducible representation. You have to break into constituent irreducible representation.

You know the formula, do it quickly. Do it, do it using the formula. 1/h sum over R XR XiR. h is infinity, so the formula will not work. That is why I wanted to, you to use it. If you do not even try, how will you know that it will not work. It will not work, right. So our old faithful relationship does not work for an infinite row because h is infinity, multiplied by 1/h, everything becomes 0 anyway, that is not going to work.

Does that mean you cannot break this down? That is not right. You can break it down. It is just that you have to do it the hard way. By inspection, okay. So what we need to do is, we need to take a look at the character table, right and we see what is it that gives us 2 2 2 0 0 0 when you are added up and that is the answer you were giving.

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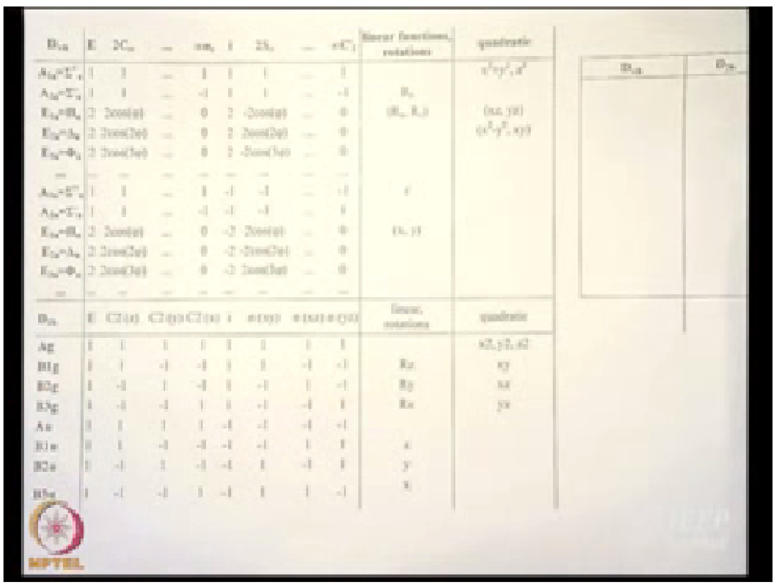

There is a reason why I have written D2h in the bottom. Do not look at it now. What will give me 2 2 2 and 0 0 0? Which 2 representations added together? **“Professor - student conversation starts”** A1g sigma +g and sigma. Do not say A1g, forget about this. This is just that what this guy has written to make things complicated in a simple matter, manner. **“Professor - student conversation ends.”**

So sigma g+ +sigma u+. Is not it? Sigma g+ + sigma u+. If you do it by inspection, there is no other way. Right or wrong? So what you get is, you get gamma SALC=sigma g+ + sigma u+. Now what we can do is, we can try to see what are the combinations that are there. Now you already know the combinations here. When I take it as a combination. Okay I have already combined them, what will be the symmetry of this?

It will be sigma g+ right. Do not get confused. Here it is 2, but in version, this and this will interchange places. But I have already combined them. So it is now not a 2-dimensional representation, it is a 1-dimensional representation. It does not matter if this + go to that +, character is still 1. Do you agree that this is going to be your sigma g+ combination? Agree or not agree? Agree.

"Professor - student conversation starts" No. It is going to be 1. Yes. But in case of inversion, this will interchange and you are taking... Right in that case, what we did is, we took them as 2 separate vectors. We have not performed the linear combination yet, right. We took them in their unmixed form. So there are 2 vectors, right. 2 vectors, 2 atomic orbitals, separate. So the basis is 2-dimensional.

When we invert, one goes here, this, second goes there, that is why the character was 0. Now I am taking their linear combinations, right. So I can write this like psi=psi1sH-+psi1sH--. If I take this, they are in any case separated by some distance, right. Beryllium has to come in between. So If I take this, what is the dimensionality of the representation now? 1. These have already performed the mathematical combination.

So when it is 1, then it does not really matter if these 2 change places, okay. Now they are not being considered separately, they are 1, okay. That is why character is 1, alright. Can I go ahead now. Fine. **"Professor - student conversation ends."** So this is sigma g+ and what is, what is the other one? Sigma u+. Sigma u+ means what? Sigma u+ is 1 1 1. With respect to i, it should be -1.

With respect to C2- also, it should be -1. So without much ado, I can write the other combination as + and -, this is your sigma u+, okay. So I have got this. Now what I do is, I combine suitably with the atomic orbitals of the central atom and we generate the molecular orbitals, alright. So we have done 2 things so far. First is, we have done the entire exercise even without using character tables and then we have done the same thing using character tables which is not really necessary here.

But the reason why we do it is to show how character tables can be used to generate such combinations. Now let us take a little more difficult example. How can we make it more difficult? One is by adding pi bonds, the other is by taking your, adding more atoms. But before that, let me just show you the molecular orbitals that are generated once. Because there is one more thing that I wanted to say.

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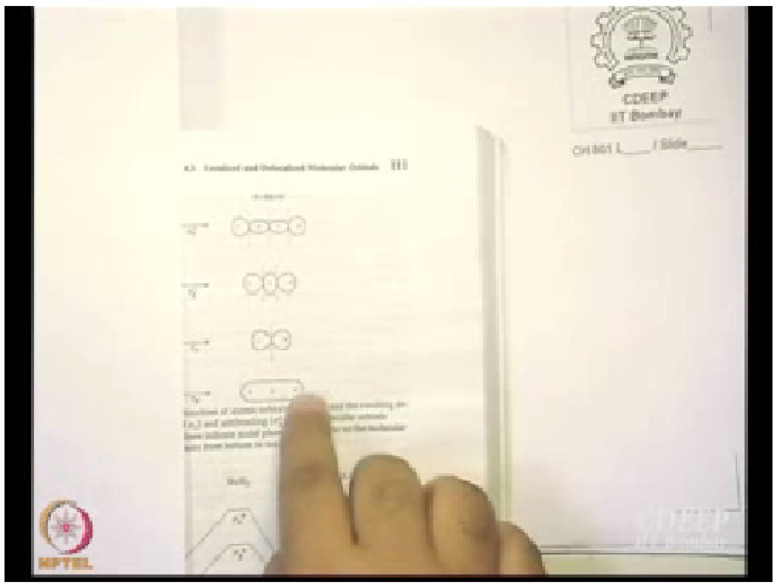

These are the MO that are generated. Look at this. Is it not the sigma g+ orbital? Sigma g+ symmetric? Right. What about this? What is the symmetry of this? Sigma u+, is not it? Right or wrong? Now I am using these as the basis and trying to see whether I can identify the symmetric species to where these belong. Earlier we have seen that vibrations belong to sound symmetric species or the other.

Now we are showing you that even these orbitals belong to some symmetric species or the other, okay. So see this is sigma g+. This is sigma u+. What about this? What is this? The third one? **"Professor - student conversation starts"** Sigma g. Sigma? g. sigma g+, you understand that right. What will be the character for i here? The reason why I am saying this again is because when you see + and -, you tend to think it is u, it is not.

Even here you start from a -, go through the center, equal distance on the other side, you still get -, right. It is g. It is once again sigma g+. And what is this? This is sigma u+, okay. **“Professor - student conversation ends.”** So what we have done is, you have done a symmetry classification of molecular orbitals as well. These are all sigma orbitals, right and these are all sigma bonds. So sigma bonds derive their names from the symmetric species where they belong.

It is usually customary to write small sigma instead of capital sigma when you are talking about molecular orbitals. **“Professor - student conversation starts”** Sir. Yes, sir. If you combine the (()) (21:21) reducible representation with the molecular… Yes. Can you combine 2 atoms with central atom in a 2-dimensionality. Yes. We can get 3 atomic orbitals or molecular orbitals. Okay and.

Getting 4, we have to take these sigma g+ and sigma u+ separately. Yes. Then combine. So what we do is we want to combine reducible representation with reducible representation. That is the most fundamental. Otherwise, if you combine irreducible representation with the reducible representation, then more often than not you end up with that same problem of redundant coordinates or coordinates that appear in more than 1 kind of thing.

Because you are taking an incomplete description many times. Sir but that is okay if you get something redundant. Here we are missing something with that possible. We are not missing something out. We are getting something extra which would come in the other representation also. If you want to take the SALC similar 2-dimensional one, I think the third one is 1-dimensional from the, I think, orbital is in the central. Okay. Alright.

So if you do that, then what you are doing is you are only taking 1 atomic orbital, right. Is that not an incomplete picture? Because S as well as P, both can contribute. So in that case also you should take both. Right. So that is why it is a little dangerous to work with reducible representations because you can end up describing your basis as something that is not complete like in this case.

That is why we always want to work with reducible representations. **"Professor - student conversation ends."** And also only when we work with reducible representations, do we get to use the character tables easily. Fine. So next what we will do is, we will just increase this, we will talk about pi bonds next day.