Symmetry and Group Theory

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Lecture -43
SALC Using Projection Operator

So, in the previous lecture we have seen how to calculate symmetry adapted linear combinations of 1s orbitals of hydrogen for water molecule. So, let us now take one more example. So, that the method is very very clear in our heads. So, let us start.

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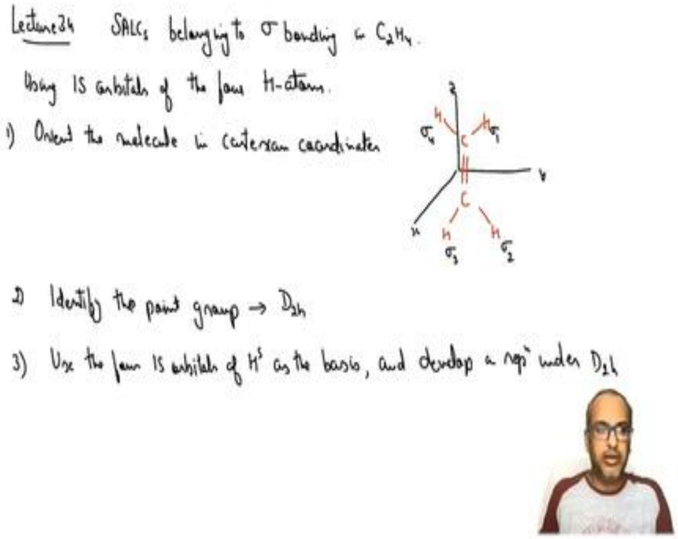

So, what we will do is, we will take another example to again develop SALCs using 1s orbitals only. And then we will go to more complex example, where we will be dealing with 2D representation. So, let us start with the SALCs belonging to sigma bonding in C2H4. So, what we will be doing here is, we will be calculating using 1s orbitals of the 4 hydrogen atoms. So, first and foremost thing is to orient the molecule in Cartesian coordinate system.

That way it will be easier to operate symmetry operations onto this. So, this is done. So, now how do we draw this? So, you have x, y and z and so, you have CC double bond which will be lying along the z axis and we will have four hydrogens like this. So, now if you do that, we can give 1s, each 1s orbital as some nomenclature. So, for example, let this be called as sigma 1, sigma 2, sigma 3, and sigma 4.

So, now the second step is identifying the point group. So, I am not going to go into all the details. I will just skip the steps which we have already learnt. So, identify the point group of this molecule, and to know the point group we should list down all the symmetry operations and find out the point group. So, you know all the steps here. So, I will just directly write the answer here. So, this will be D2h point group because there is one C2z and then two perpendicular C2s which is C2x and C2y.

So, this goes to D category and then there is a sigma h plane. Well in this case, it will not be called as sigma h, but it will be called as sigma x sigma y in sigma z. But there is one plane which is perpendicular to the principal axis, and hence it will be called as D2h point group. So, let us not go into those details. We have already discussed this molecule itself before. Now what we will do is use the four 1s orbitals of hydrogens as a basis, and develop a representation under D2h point group. So, when I say that what do I mean?

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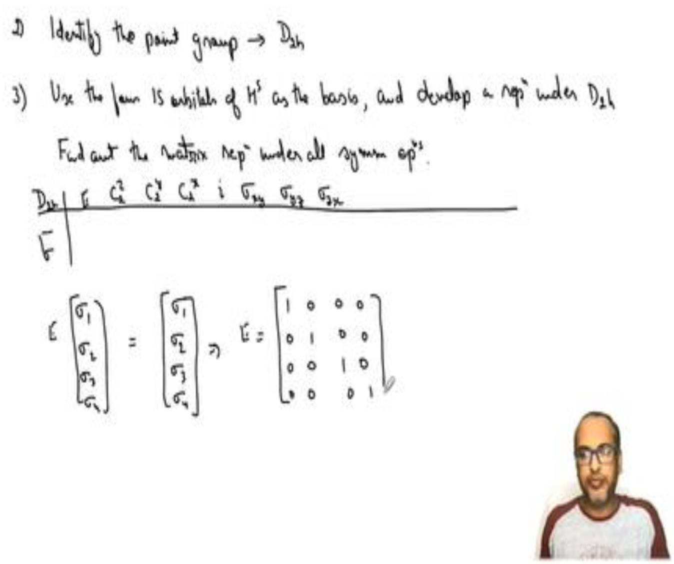

So, that means I am going to find out the matrix representation under all symmetry operations. So, now let us list down the symmetry operations we have. So, this is D2h and what we are trying to do is? We are trying to create tau sigma; sigma1, sigma 2, sigma 3, sigma 4. And the first is E then we have C2z then we are C2y, C2x then we have what else to be have here? We will have I think i will be there too.

Then you have sigma x sigma y sigma z. Anything else which I am missing? No, this will be sigma xy, yz, zx. So, now we need using sigma 1, sigma 2, sigma 3, sigma 4 as the basis that we need the matrix representation and all of these symmetry operations. So, to do that, we need to operate E onto let us say if we do that sigma 1, sigma 2, sigma 3, sigma 4 and what is the resultant of this?

Resultant is same sigma1, sigma 2, sigma 3, sigma 4. So, this would imply that my E is a unitary matrix of order 4.

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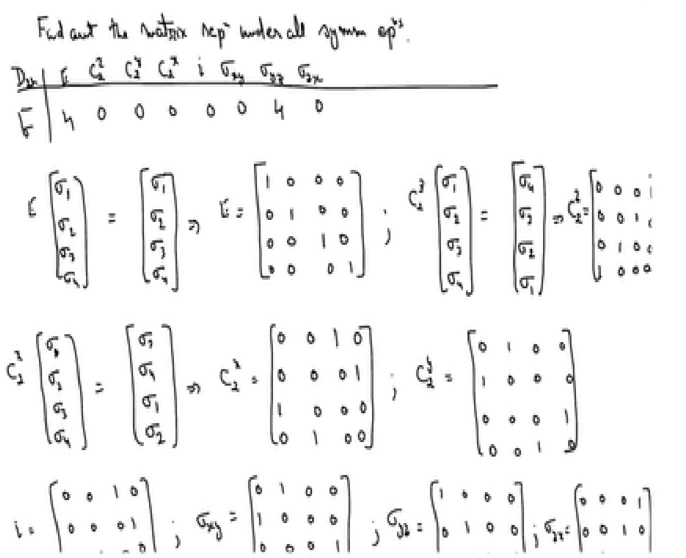

Let us do the same thing for next operation, which says C2z operation. So, if I do sigma 1, sigma 2, sigma 3, sigma 4 and if I do a C2z operation, what is the resultant which I am going to get here. So, C2z applied on sigma 1. That will give you sigma 4. So, I am rotating around this anti-clockwise so that means sigma 1 and sigma 4 will be replaced and sigma 2 and sigma 3 will be replaced.

So, sigma 2 will be replaced with sigma 3, so sigma 2 is going to sigma 3, sigma 3 is going to sigma 2, sigma 4 is going to sigma 1. So, this would imply that my C2z has a matrix representation which can be written as 0 0 0 1. Then you have 0 0 1 0. Then you have 0 1 0 0 and 1 0 0 0. So, now you can try yourself by doing this multiplication with this and see if you are getting this.

So, basically what I have done is I have placed 1 over where sigma 1 is going to its new position. So, sigma 1 is going to sigma 4, so I have placed 4 over here. Now sigma 2 that is the second-row sigma 2 is going to sigma 3, so I have placed 1 here. Similarly, sigma 3 is going to that is third row is going to second position so sigma 2. So, that is why the second column has placed 1 and, sigma 4 is going to sigma 1.

So, let us see that more carefully with other operations also. So, that it is very very clear. So, again, let us say if we are now applying C2x. So, you have sigma 1, sigma 2, sigma 3, sigma 4 what happens here if we do this? So, if we do this, let me go back to the molecule again. So, now we are rotating about this. So, that means now sigma 1 will go to sigma 3, sigma 2 will go to sigma 4.

So, sigma 1 is going to sigma 3, sigma 2 is going to sigma 4 and sigma 3 is going to sigma 1 and sigma 2. So, this implies that my C2x is so sigma 1 is going to sigma 3. So, that means I will put 1 at third position now sigma 2 is going to sigma 4, so I will put 1 at fourth position sigma 3 is going to sigma1 so, I will put 1 here. And sigma 4 is going to sigma 2. So, I will put 1 here.

So, this is very very clear and you can again test it by multiplying this with this and then you should get the resultant matrix. So, similarly so let us not do this all over again, so I will just write down the matrices for C2y and just look the operand symmetry operations. So, I will have 0 1 0 0 then I have 1 0 0 0. Then I have 0 0 0 1 and I have 0 0 1 0. And then for i this will be so whatever is replaced with what.

So, you have 0 0 1 0 and you have 0 0 0 1 we have 1 0 0 0 we have 0 1 0 0. Similarly, you have for sigma xy which will be, so I suggest you all do this by yourself so that it is very very clear. Otherwise by just looking at it will not go into very deep. So, 0 1 0 0, 1 0 0 0. So, why we are writing these matrices I will tell you. We finally we need the trace of this. So, now that we are done writing all the matrix representations.

What we have to do is we have to find out the trace and put the trace here that will give us the reducible or irreducible representation. So, now let us write the trace. So, trace for E is going to be 4 trace for C 2 z is going to be 0 because all the diagonal elements are 0 here C 2 y also it is 0. C 2 x also it is 0 i will be 0, sigma xy will be 0, sigma yz will be 4 and sigma zx will be 0. So, this is what we are got as the reducible representation.

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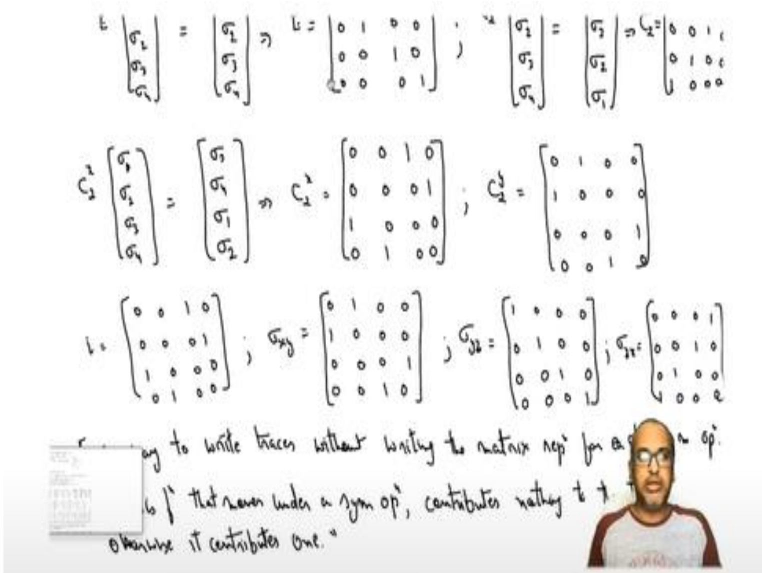

So, before we actually go to 4 steps, let me give you a way of writing directly the traces without having to write all the matrices. So, easier way to write traces without but you should know how to write the matrix. So, that if it comes to that you should be able to do that but there is actually no need to write the full matrix and then find out the trace. There is a much easier way you can just look at it and write it.

I will just tell you without writing the matrix representation for each symmetry operation. So, the method is basically it is a thumb rule. So, I will just quote that. Any basis functions that moves under symmetry operation contributes nothing to the trace or character, otherwise it contributes one. So, let us see that again. What do I mean by that so when I apply E on the basis function none of the basic functions move.

That means all of them will contribute 1 for the trace that will give you trace 4. If I do C2z, all 4 will move that means they will not contribute anything towards the base towards the character or trace. So, the trace will be 0. Again, everything will move here, everything will move here everything will move here, everything will move here. Now sigma yz if you carefully look sigma yz is the plane which is the molecular plane here.

So, if we do sigma yz sigma 1 stays where it was sigma 4 stays where it was sigma 3 and sigma 2 stays where they were. So, that means none of this move, so that is they contribute 1 towards the trace. So, the character on the sigma yz will be 4 interest everything will be zero, except E. So, this is much easier way.

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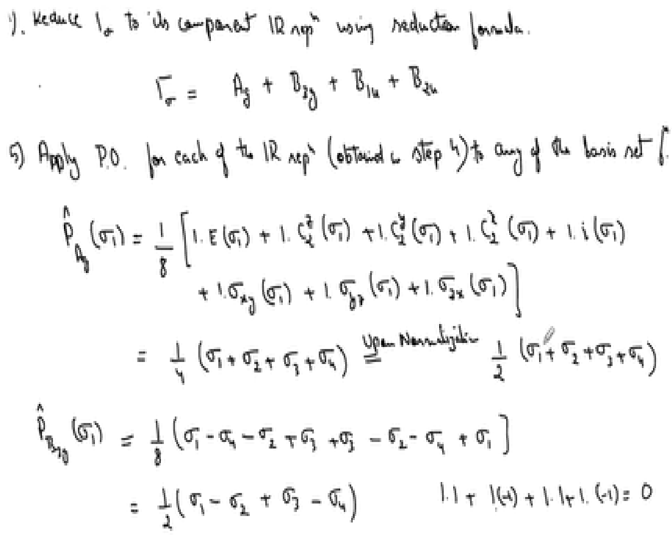

So, now next is to calculate the irreducible representation. So, step number four is reduce tau sigma to its component irreducible representations using reduction formula. So, at this point, I do not think I need to remind you what is the reduction formula? You should be well aware of this. So, by reduction formula and I am not going to do this that calculation either. So, look back the previous notes and see what is the reduction formula.

And how do I use that to reduce sigma tau sigma into the following. So, if I do that, I will get Ag + B3g + B1u + B2u. So, I have got 4 representations, there were 4 basis sets. So, 4 1-d representations will you will get. And so, the linear combination of this will be tau sigma to which the four sigmas are forming basis of. So, now fifth step is to apply projection operator. So, aim is to find out the linear combination which will have these four symmetries.

So, apply Projection operator for each of the IR representation obtained in step four. So, you do not have to consider all the IR representations of D2h point group, you have to consider only those which are coming as a result of reducing this reducible representation, which was in turn formed using four sigma's as the basis. So, only those representations you have to consider. Other representations even if you consider they will turn out to be 0.

So, there would not be any contribution coming from other representations. We can test it out if you want to. So, each of the representation to any of the basis set function. So, what do I mean? So, let us say if I want to find out what is the linear combination of the basis, which has symmetry as Ag. So, I will apply projection operator corresponding to Ag onto sigma 1. So, you can choose any of these basis function, they will give you all the same result.

So, it does not matter if you start with sigma 1 or sigma 2 or sigma 3 or sigma 4. So, now what do I have here? So, remember that the formula is L by h. So, L is the dimension of this representation, which is 1 and h is 8 here. That is the order of the group. Then what we have to do is? You have to take out from the character table. What is the character under Ag representation?

That is 1 into E symmetry operation effect of E onto sigma. Similarly, 1 into C2z sigma 1, plus so Ag is a totally symmetric representation so all the characters are going to be 1. So, that is why I do not have to look at the character table here. But for other symmetry operations other IR representations you will have to look at the character table. C2y applied on sigma 1 + 1 into C2x applied on sigma 1 + 1 into i applied on sigma 1 + 1 into sigma xy applied on sigma 1 + 1 into sigma yz applied on sigma 1 and so on, sigma zx applied on sigma 1.

So, again, it is not required for me to do this complete calculation for you. So, you can I will just give you a couple of solutions. So, if you do apply E on sigma 1, you will get sigma 1. If you apply C 2 z on sigma 1, so let us again look back. So, if you apply C2z on sigma 1, you will get sigma 4. Similarly, if you apply C2x on sigma 1 will get sigma 3. If you apply C2y on sigma 1, you will get sigma 2 and so on.

So, the resultant of this is going to be 1 over 4 sigma 1 + sigma 2 + sigma 3 + sigma 4 and this upon normalization. You can write this as 1 by 2 sigma 1 + sigma 2 remember we need to develop orthonormal sets, so this has to be normalized; sigma 3 + sigma 4. So, this linear combination would form basis for Ag representation and this is going to be normalized. Now let us calculate for rest of these. So, what you have to do is? You to do this exact same thing; so for B3g applied on sigma 1 again, you can choose any of the basis function over here.

Now if I do that what I get here is again, I am not going to repeat all of this. But here you have to read out the characters from character table. So, if I do this, I will get sigma 1 - sigma 4 - sigma 2 + sigma 3 + sigma 3 - sigma 2 - sigma 4 + sigma 1. So, again after normalization and cancellation what you will get is 1 by 2 sigma 1 - sigma 2 + sigma 3 - sigma 4. So, now this one is also normalized and this linear combination, although it is coming from the same s orbitals of hydrogen but the linear combination will have symmetry as of B3g. So, this will transform as B3g this linear combination will transform as Ag and these two sets will be orthonormal to each other, which is we know that the irreducible representations are orthogonal to each other. So, similarly because these are forming basis for two different IR representations so they will have to be orthogonal to each other.

We can also test the normality or orthogonality condition which is if you take the coefficients of these four sigma's and then multiply with each other. And take the sum over all coefficients, you will you should get 0. So, that is if I take 1 into 1 + 1 into - 1 + 1 into 1 + 1 into – 1. So, the summation of the product is going to be 0. That means these two representations or these two linear combinations are orthogonal to each other they are also normalized.

So, we have what we have got is orthonormal sets of linear combination, so that is why it is called as symmetry adapted linear combinations. Because we now we know the symmetry of these linear combinations.

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$$= \frac{1}{4}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \overset{\text{Upon Normalization}}{=} \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

$$\hat{P}_{B_{3g}}(\sigma_1) = \frac{1}{8}(\sigma_1 - \sigma_4 - \sigma_2 + \sigma_3 + \sigma_3 - \sigma_2 - \sigma_4 + \sigma_1]$$

$$= \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \qquad 1.1 + 1(-1) + 1.1 + 1.(-1) = 0$$

$$\hat{P}_{B_{1u}}(\sigma_1) = \frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4) \; ; \; \hat{P}_{B_{2u}}(\sigma_1) = \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$$

So, let us finish this quickly. I am just going to write the answers and I expect that you go back and complete this yourself. So, far P B1u applied on sigma 1 what you will get is 1 by 2 Sigma 1 - sigma 2 - sigma 3 + sigma 4. Now this will be orthogonal to the first one as well as the second. And similarly, if I do the P of B2u on to sigma 1 what you will get is half sigma 1 + sigma 2 - sigma 3 - sigma 4.

So, you started with 4 basis functions and you have got 4 linear combinations of those basis functions, which are now defined by a particular symmetry. This is what our aim was and we will see that this is very very useful when we go to the next topic which is chemical bonding. So, far what we have been doing is we have been looking at representations which are only one-dimensional representations. So, let us also see how to develop SALCs where 2D representations are involved.

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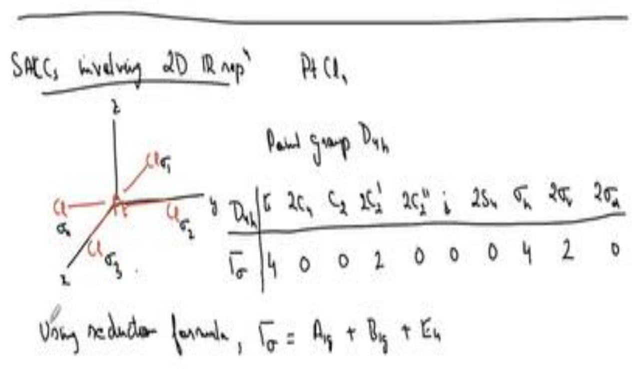

So, let us take an example, so, I will say I just put a line here. So, SALCs involving 2D IR representation. And the example I am taking here is PtCl4. Now the first step is to orient the molecule about the axis in the Cartesian axis. So, we have central atom which is at the axis and then you have Cl here, Cl here and you have Cl here, and Cl here. Now the next step is to know the, to identify the point group.

So, point group here is D4h. That is very simple to see, also let us list down the symmetry operations of deference. So, you have E we have 2C4, then we have C2, 2C2 prime and 2C2 double prime, we have i, 2S4 then we have sigma h. And we have 2 sigma v, then we have 2 sigma d. So, now let us quickly write down the reducible representation using the sigmas four sigmas of chloride atom as the basis.

So, this is D4h and this is my tau sigma. I will label it as sigma 1 sigma 2, sigma 3, sigma 4. Now if I apply E all four sigmas will remain at their position. So, that means the character will be 4. If I apply C4 all 4 will change their position. So, the character will be 0 if I apply C 2 here again all 4 will change this C2 is collinear with C4, so sigma 1 goes to sigma 3 and sigma 2 goes to sigma 4 and so on.

So, C2 under C2, also, it is going to be 0 so 2C2 prime now this C2 prime is 1 along x axis and along y axis. So, in one of the C2 primes at least 2 chloride atoms will not move so that means it is going to contribute to 2 towards the trace or character. For the other C2 prime also is going to be 2 so the trace is going to be 2 for both of them. The matrix will be different for the 2C2 primes.

Now for 2C2 double primes now these C2 double primes are running in between x and y axis. So, the trace is going to be 0, i the traces going to be 0, S4 again, it is going to be 0, sigma h, it is going to be 4 because nothing will change 2, sigma v's going to be 2, 2 sigma d's is going to be 0. So, without having to write the full matrices full matrix representation for each of the symmetry operation.

What we have done is we have very quickly written by just looking at what s orbital moves under what symmetry operation and so on so forth. So, now again using reduction formula we will reduce this to component IRs using reduction formula we get tau sigma is equal to we will see A1g + B1g + Eu. Now you see that these two are 1D representations, so the solution using this next we have to apply projection operator.

Using this onto any of the sigmas, which we have seen already and it is very easy to do. But now we will see how to be get this when we apply projection using Eu. So, let us go step by step.

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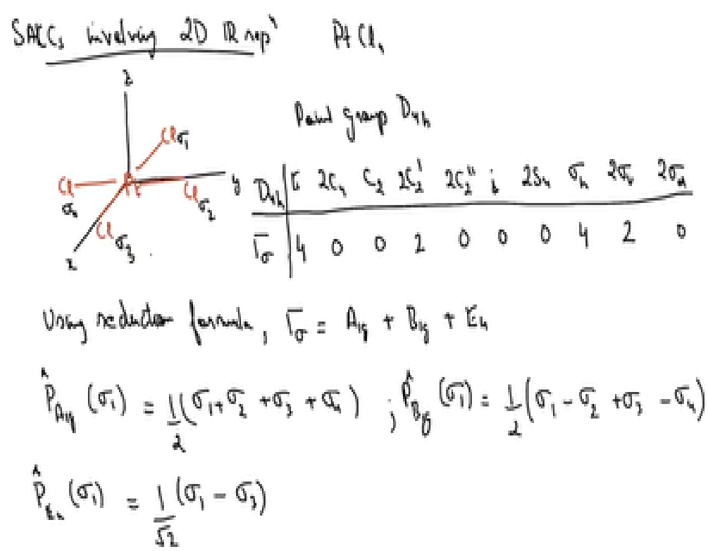

I will not be solving the complete thing. I will just write down the answers and I expect that you will go back and solve it. A1g so I apply A1g onto sigma 1 and the result is sigma 1 + sigma 2 + sigma 3 + sigma 4. And of course, you can normalize it to get half over here. Similarly, for B1g on to sigma 1, what do you get is half of which is the normalization constant and you will get sigma 1 - sigma 2 + sigma 3 - sigma 4.

So, because these; are 1D representations, 1-dimensional IR representations. So, projection operator will give you only 1 linear combination, whereas if you use this for projection operator, you should get 2 linear combinations because this is 2-dimensional representation. So, now if I do this P Eu, I apply projection operator onto sigma 1. What do I get? I will get and again I expect you to do this yourself.

So, you will get sigma 1 - sigma 3. So, do this complete calculation, which you know, the formula and the normalization constant will be 1 by root 2. So, sigma 1 - sigma 3. Now how do we get the second linear combination which will also have the same symmetry as Eu. So, there are different methods for this but there is no unique method to solve this.

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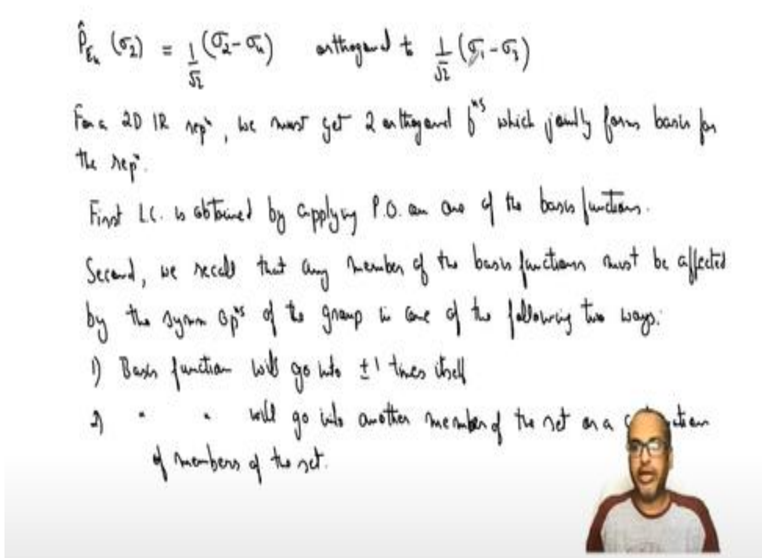

So, what you can do is you can either apply P Eu onto sigma 2 and see what you get sometimes you may get a second linear combination, sometimes you may not get the second linear combination. And what you will get is simply the previous, the first linear combination which you got, when you applied this on sigma 1. So, when I do this, I do get a linear combination, which is sigma 2 - sigma 4.

And I know that this is going to be orthogonal to the previous one; sigma 1 - sigma 3. So, I do get this and both of them will have same symmetry as Eu. And but in certain cases you do not get two unique linear combinations and in those cases what you have to do is? So, I will just write down for a 2D IR representation we must get 2 orthogonal, you can of course normalize them, so that is why it is orthonormal, orthogonal functions which jointly form basis for the representation.

So, these two together will jointly form the basis for Eu representation. Now first is as usual, so first is applied first is obtained by, first linear combination is obtained by applying projection operator on one of the basis functions. Now for second, there is no unique way of doing that, in different point groups, you will see that you will have to adopt different methods.

But we recall that any member of the basis functions or you can say basis set like sigma 1, sigma 2, sigma 3, sigma 4 all forms function must be affected by the symmetry operations of the group in one of the following two ways. The first is the basis function will go into plus minus 1 times itself. That means if you apply the symmetry operations on to this 1 sigma 1, you will get either plus sigma 1 or minus sigma, that is one of the ways.

And the second way is the basis function will go into another member of the set or a combination of members. So, what do I mean, let us say if I apply any symmetry operation on sigma 1, it will either turn into plus 1 plus sigma 1 or minus sigma 1 or it will go into any linear combination of rest of the members, including sigma 1.

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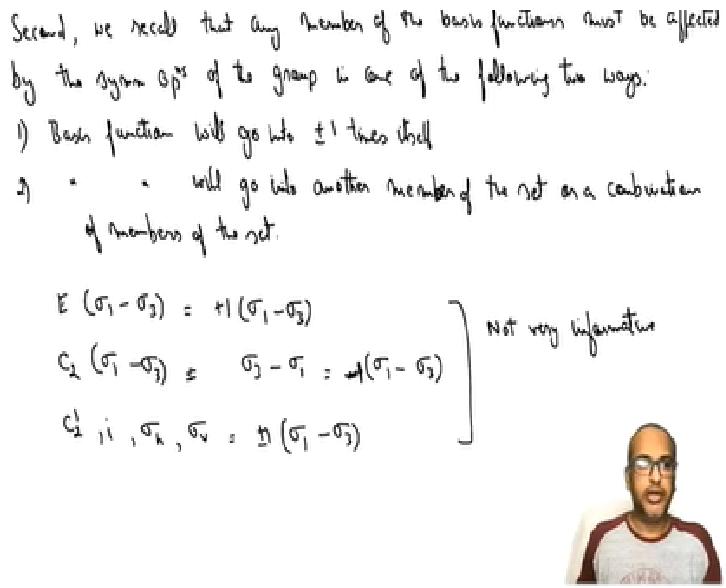

So, let us see an example for this one. Let us see if I am applying E onto sigma 1 - sigma 3, it gives me + 1 times sigma 1 - sigma 3. If I apply C2 on sigma 1- sigma 3, I will still get, so let us say this if I do C2, then sigma 1 will be replaced with sigma 3 and sigma 3 will be replaced with sigma 1. So, that means it is minus 1 times sigma 1 - sigma 3. So, minus 1 times. So, that is plus minus 1 times.

So, this is not very informative because you are getting the same function back and similarly if you keep on doing this so you see C2 prime, i, sigma h, sigma v all of this will give you either + 1 of sigma 1 - sigma 3 or - 1 of sigma 1 - 3, sigma 3, so it will give you plus minus 1 times sigma 1 - sigma 3. So, not very informative, this is not very informative. Now let us see that quickly.

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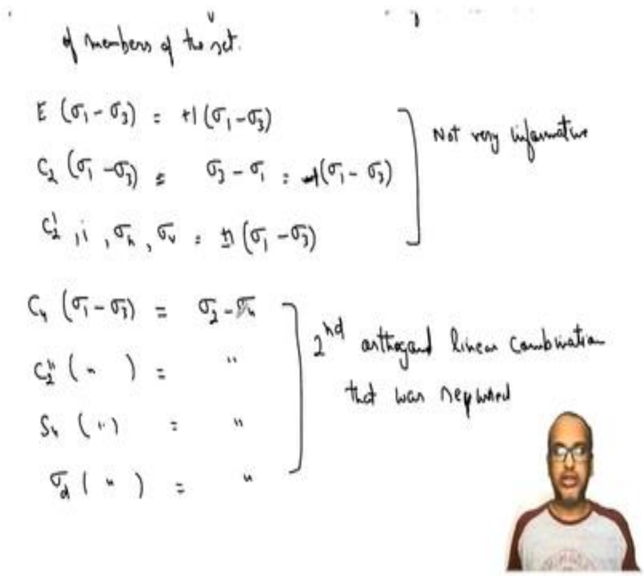

If we apply however if you apply C4 on to sigma 1 - sigma 3, what do we get? We will get sigma 2 - sigma 4. Similarly, if you apply C2 double prime on to this you will get sigma 2 - sigma 4. Similarly, S4 onto this you will get again the same thing. And sigma d onto this you will get the same thing. So, this is the second orthogonal linear combination that was required. So, all it has to do is, it has to fulfill the orthonormality condition with the first one.

So, the first one is obtained directly by applying projection operator. Second one can be obtained by applying projection operator onto an alternate basis function out of that set only. Or what you can do is you can apply different symmetry operations on to the first function which is first linear combination, which is obtained and see if you get a second linear combination or not. So, this way there is no unique way of doing it.

Because the; number of equations are less and the unknowns are more. So, that is why we need to go for hit and trial and this is how it is done. So, as and when we come into this kind of trouble, we will see that there can be more unique ways of finding degenerate linear combinations. So, these are two degenerates linear combination because they form jointly basis for Eu representation. So, here we wanted to have two representations two linear combinations and we have got two. So, there is no need to go for further calculations here.

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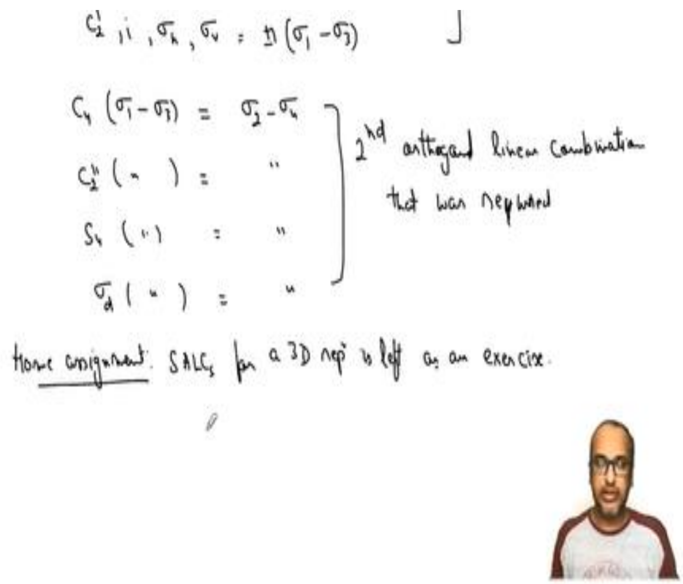

And I would suggest you to take a molecule. Take this as a home assignment SALCs where you will develop SLCs for a 3D representation, where you should get a 3D representation try to pick up some molecule which has tetrahedral or orthogonal octahedral symmetry. And see if you find a 3D representation. And you can get three linear combinations which will jointly form basis for a 3D representation is left as an exercise. So, that is all for today. And next class onwards will be discussing chemical bonding, alright, thank you very much.