Chemical Applications of Symmetry and Group Theory
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Lecture – 28

Hello everyone. Welcome to today's lecture. Today is day 3 for the 6th week. Let us see, what did we learn in the last 2 or 3 classes; we learned how to deal with so called projection operator which is used to form the symmetry adapted linear combinations or SALCs.

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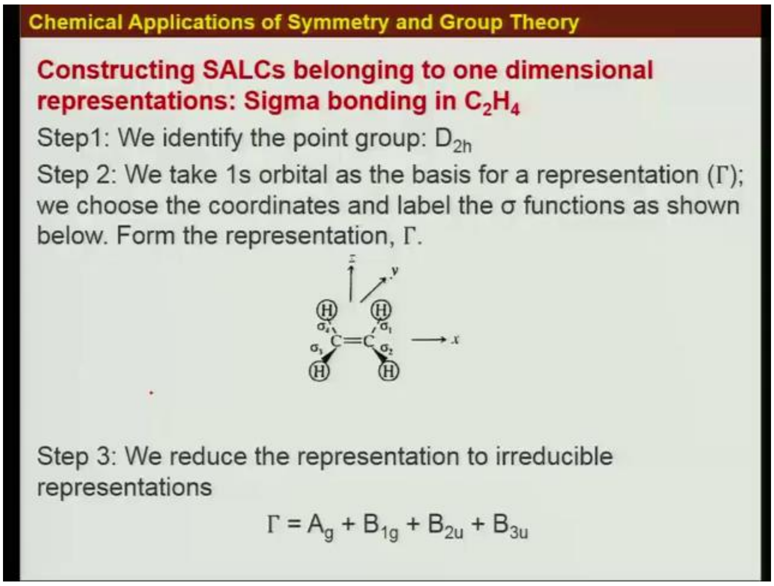

In the previous class, we particularly learned about one particular type of projection operator which we called as incomplete projection operator, which is formed by using the characters of the irreducible representations. Using that incomplete projection operator which is sufficient for our purpose, we could form the symmetry adapted linear combinations of 1 molecule that we discussed in the previous class that was ethylene. And we did that quite vigorously and we mentioned that there are certain steps involved. The first step, you have to identify the point group of the molecule and second you choose a right place. In that particular example we took the one is orbital's of the hydrogen atoms and we consider at the sigma bonds that is the C eighth sigma bonds.

All together 4 sigma bonds, we took this as basis functions and with that basis set, we formed a representation. That is the step 2, and in the next step we reduce that representation and find out what is the irreducible representation that it may contain.

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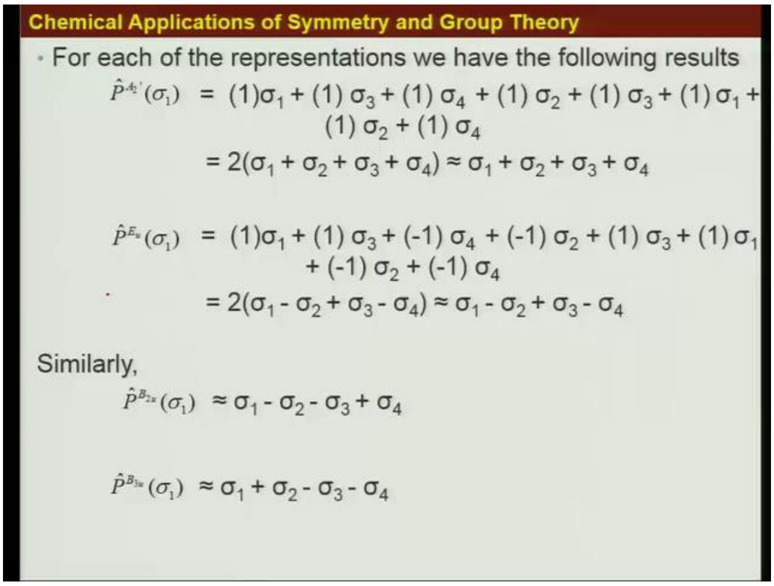

And, after that what we did? We carried out in the projection operators based on all those irreducible representation that we found by reducing the representation gamma that you formed earlier on each of this, you know basis functions. We started with only 1 basis function that was sigma 1 and we formed, you know operated the 4 projection operators corresponding to those irreducible representation that you got and ultimately we could get 4, you know sets of SALCs in terms of this, you know basis functions that is this sigma 1 sigma 2 sigma 3 sigma 4. This particular example was shown for 1 dimensional irreducible representation

One dimensional irreducible representation using projection operator for 1 dimensional irreducible representation and forming the SALCs is, this very simple job because you have 1 operation and 1 function coming out of that and this 1 function means the linear combination of the basis function that you choose and that obvious always symmetry properties of that particular irreducible representation and I also asked you to find out whether this combination, that you are finding, do they really transform as that particular irreducible representation that we form the projection operator, we use in the projection operator for that particular irreducible representation meaning that this combination of all sigma's get getting sigma 1 sigma 2 sigma 3 and sigma 4 adding all of them whether this particular linear combination trans really transformed as this will be A G representation on mark. So this will be A G.

We will move to it high order irreducible representation; that means, with higher dimensions for example, 2 dimensional or 3 dimensional things will be little more harder and we will see right away, how to deal this 2 dimensional presentations or 3 dimensional presentations.

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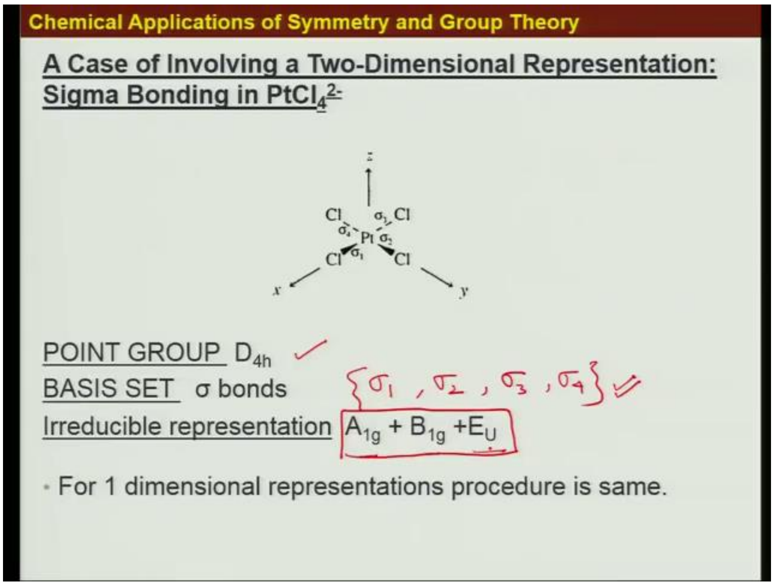

The next example that we will take is the case of square panel complex P T C L 4 having their user charts, which we will neglect for our purpose. The first step is to identify the point good selection. For square panel complex it is D 4 H, We should be able to readily find out the, or identify the point group of in a given molecule right now and then, we have to choose the basis function. Here also we will consider this 4 sigma bonds. This 4 sigma bonds taken to the sigma 1 sigma 2 sigma 3 and sigma 4 and we will use these as my basis functions. My sigma 1 sigma 2 sigma 3 and sigma 4 will constitute my basis sets alright. That was my step 2 and is still not complete.

Using this basis set, you have to form a representation. Well that representation most likely is going to be reducible because we are using this 4 basis functions and we will find out that it will be irreducible representation that, you will get and once you get this representation based on this basis set you consult the character table for the particular point D 4 H, which is given here.

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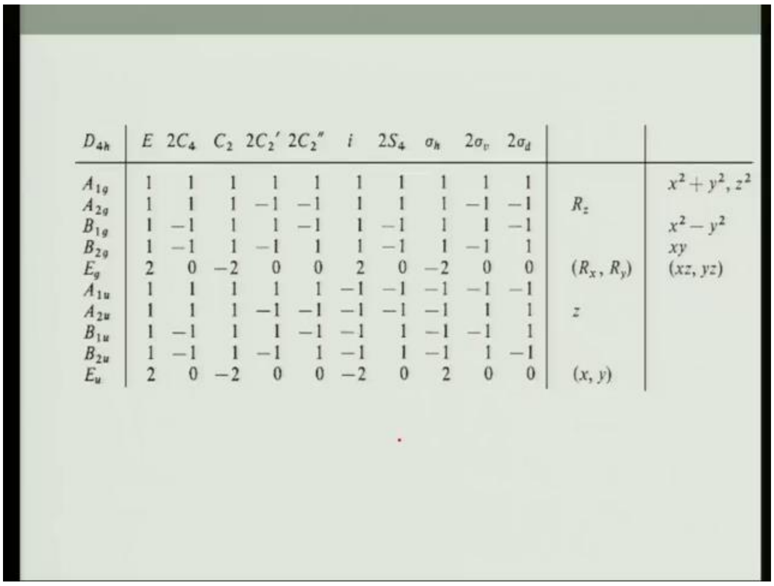

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

You get the character table using this 1 and utilizing the formula that you used to reduce irreducible representation into the irreducible. Once you get the irreducible presentations, if you do that you will find that your irreducible representation that you form out of this basis set, will give you A 1g B 1g and E U as the irreducible representation. Alright, here I have 2 1 dimensional irreducible representation A 1g and B 1g and 1 2 dimensional presentation.

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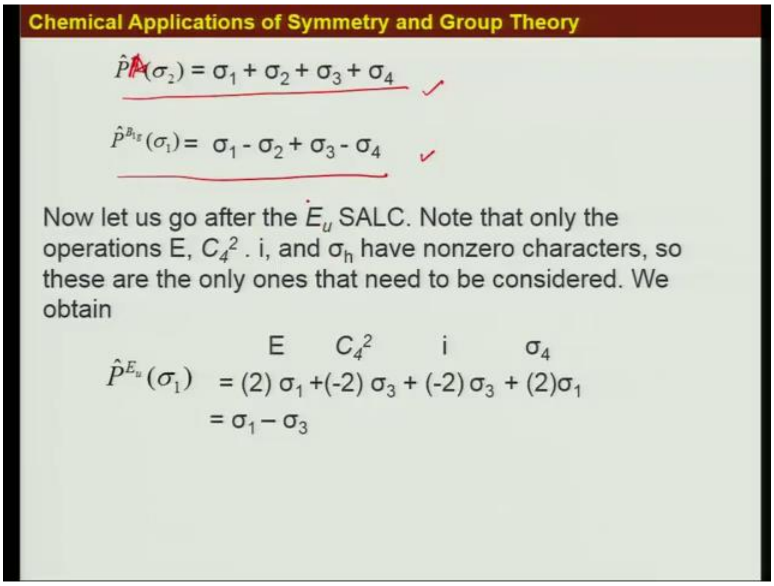

For 1 dimensional irreducible representation things are as usual that we have already discussed in case of ethylene. Here also you should be able to do that very easily. Here there is a mistake, this will be A 1. Specifically this will be A 1G. Now you can find out the, you know SALC for this 1 dimensional irreducible representation A 1 C and B 1 C using the respective projection operators, which is very straight forward and easy. Now next we will go after the two dimensional SALC. The 2 dimensional SALC is, we will transform as the E U irreducible representation corresponding to D 4 8 point group.

Here if you look at the character correspond to the E U representation for D 4 H point group, we will see that only the operations identity C 4 2 I means inversion and sigma H have non 0 characters. When you a find out the SALC. You operate a projection operator, you have to, you know look at the effect of all the symmetry operations on this particular function that you have all right. So, since we are dealing with the incomplete projection operator, where we deal with characters and if there are symmetry operations which give Z character as 0 then we really do not care about them. Take only the symmetry operations, which give non 0 characters. Here these 4 symmetry operations, we give us non 0 characters that you can find from the character table. That we consider and with that we formed the projection operator and operate on 1 of the basis function is the sigma 1 and then what we get? We get this sigma 1 minus sigma 3.

Here we jump to few steps. So, you can do everything thoroughly and you should be able to come up to this particular point. Let us see this symmetry adapted linear combination as sigma 1 minus sigma 3. Now I got one particular SALC, Now E U is a 2 dimensional irreducible representation therefore, for a 2 dimensional representation we need 2 orthogonal functions correct because all orthogonal functions will whether orthogonal functions, will be forming the basis for irreducible representations, and for 2 dimensional irreducible representations, I need 2 such orthogonal functions.

Normally you will take care, a later first we have 2 orthogonal functions. These 2 orthogonal functions will transform together as they say, E U representation in this particular case. We have got 1 that is sigma 1 minus sigma 3 neglecting the normalization part. We need the count part. So, here we mention 1 thing that any member of a set of function that form the basis for a representation must be affected by the symmetry operations of the group in 1 of the 2 following ways.

What are those ways? First 1 that is the function wills, you know going to plus or minus 1 time, it is into itself. Upon the symmetry operations, it will either, you know gives by the same function or it will give, but the function with you know coefficient of minus 1 Second, it will go into another member of the set or a combination of the member of the set, that also we have learned earlier that it can act as you know the basis function, you know itself or it can if it is like if 1 forms linear combination of several basis sets then, also that can work as a basis for the irreducible presentation that is under consideration.

If you look at the effect of the operations that is E C 2, you know A 2 C 2 prime I and sigma H and 2 sigma B, we see that A, they give, you know this plus minus sigma 1 minus sigma 3. We take that SALC see that you got first that is sigma 1 minus sigma 3 and you know, here when we operate all these symmetry operations like identity C 2 C 2 primes I or sigma H and also sigma V, they give either the plus or minus 1of this all out already optics symmetry adapted linear combination. That is what surprising and, but at the same time this is not, you know informative it does not tell me anything new.

I need to find out what will be the other, you know function if you orthogonal to this existing sigma 1 minus sigma 3 and jointly form the basis for E U. We have to operate the revenue operations and A thereby we can find the other, you know functions. We take that, first SALC sigma 1 minus sigma 3 and operate the other the rest of the symmetry operations which does not give back this sigma 1 or sigma 1 minus sigma 3 either for plus 1 multiply by plus 1 or minus 1, but something else.

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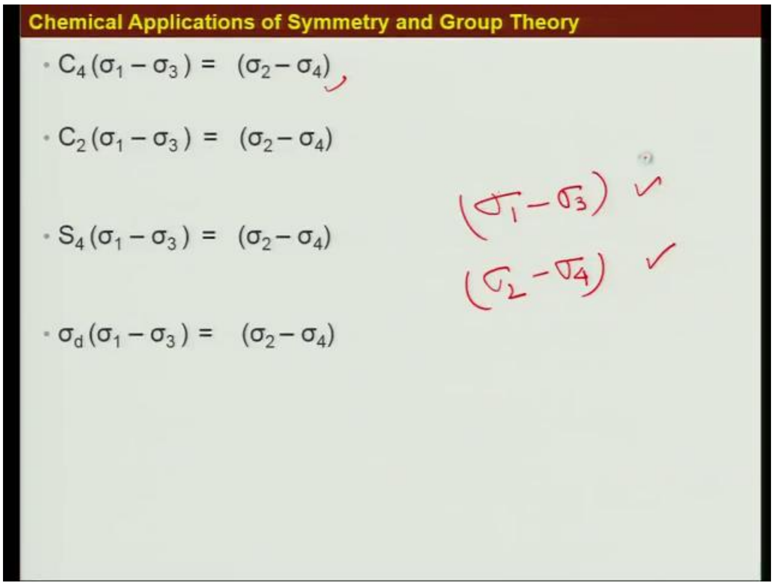

When I operate C 4 or sigma 1 minus sigma 3, I get sigma 2 minus sigma 4 and I get the same result. There is sigma 2 minus sigma 4 when I operate C 2 or S 4 or sigma D on that sigma 1 minus sigma 3 SALC. Therefore, I have got the other counterpart; that means this all together sigma 1 minus sigma 3 and sigma 2 minus sigma 4, this 2 set of you know, SALC will form the basis for E U. These are my right SALCs.

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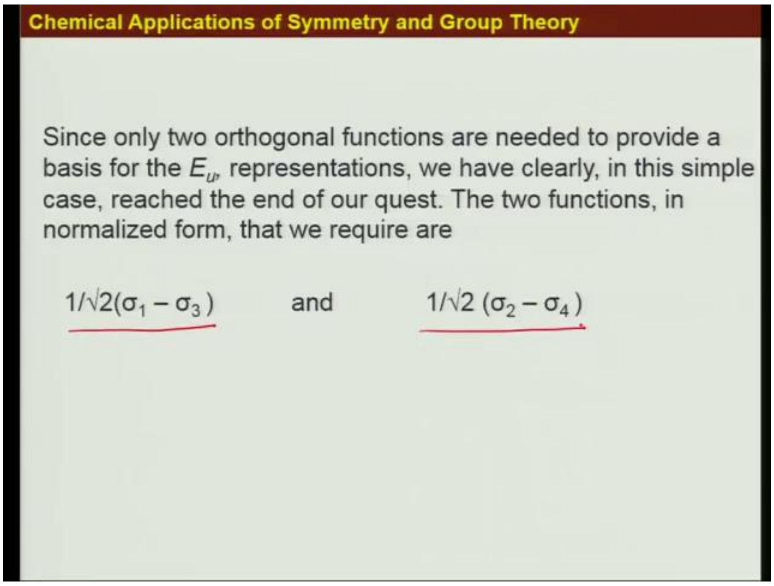

We have got this as orthogonal; you know function. 1 thing is remaining that is we have to find ortho normal function. The requirement of normalization will give us the normalized SALCs which is given as 1 upon root 2 into sigma 1 minus sigma 3 and 1 of upon root 2 sigma 2 minus sigma 4. This is pretty straight forward to normalize these functions. That is how we got the SALCs that we can form by using projection operator for 2 dimensional irreducible representations.

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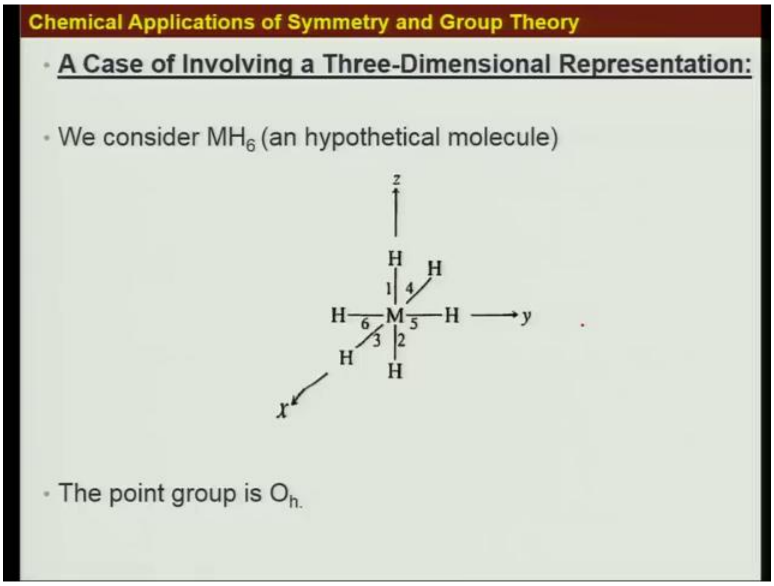

Next we will move toward even little higher case fact, little bit, you know complication limit is little bit higher. We will look for a case which involves a 3 dimensional irreducible representation and we would try to find the SALC for that particular 3 dimensional representation. We will consider molecule A hypothetical molecule, say image 6. Here this image 6 has octahedral geometry and all the image bonds are equal equivalent. This surely belong to the which point group. While dealing with this problem you must have the character table for which point group with you.

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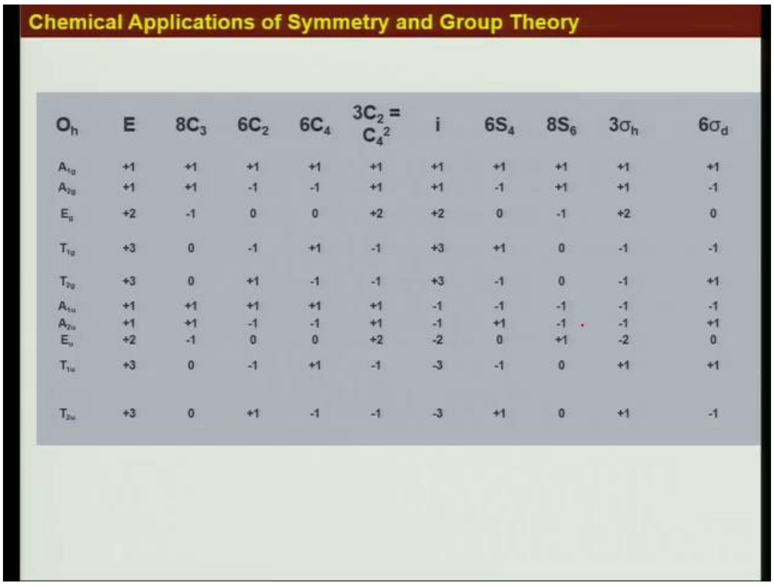
Chemical Applications of Symmetry and Group Theory

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0
T_{1g}	+3	0	-1	+1	-1	+3	+1	0	-1	-1
T_{2g}	+3	0	+1	-1	-1	+3	-1	0	-1	+1
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1
E_u	+2	-1	0	0	+2	-2	0	+1	-2	0
T_{1u}	+3	0	-1	+1	-1	-3	-1	0	+1	+1
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1

Here which point group, you know character table for various point group has been given. You notice how many total number of switch operations are there. You have like a 9, 6, 15, 21, 24, 25 and 31, 39, 42 and 48. All together they are 48 symmetry operations.

Things can, you know things may seem to be pretty complicated of the beginning, but as we will, you know go ahead you will see that things are not so complicated and as it is seems initially. After finding the point group to be octahedral or O H what we need to do will to form the, you know a presentation.

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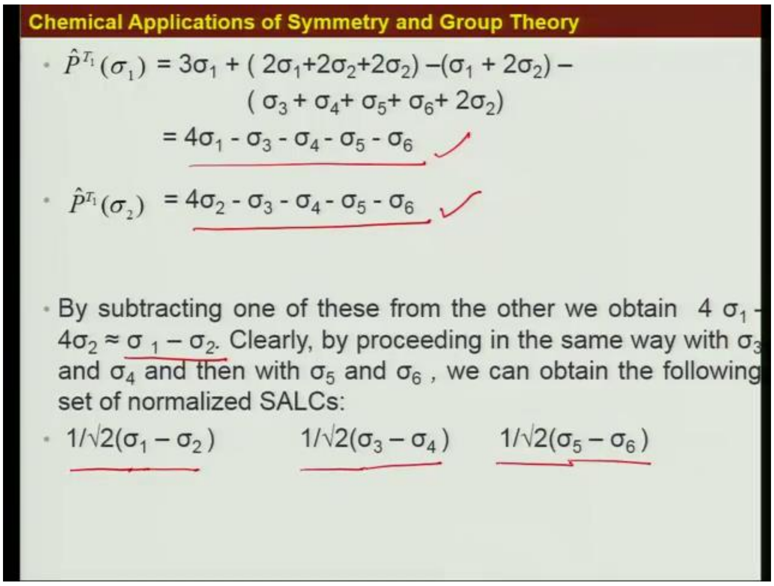

But after you get the representation you reduce them and here A 1 thing is, you know important to note that you do not need to really consider all the, you know all the operations that is like 48 operations, that are involved, but you can actually select the particular sub group of which is which comes out as O from which you can get a sub group of O. You use the symmetry operations corresponding to that particular group O and your job will be done.

Here solving this particular problem, we have used that particular approach and you form the position operator and then apply on the basis functions alright. What we have got. So far we have like if you look at the character table for O H, here we will see there are you know there (Refer Time: 18:22) representations. So, it is like T 1 and T W and both A and U. You get the symmetry adapted linear combinations for T 1 irreducible representation when you operate on any of this function. You first operate on sigma 1 which is one of the sigma bonds N S bonds and you get this to start with and many operator sigma 2 you get another 1.

If you subtract, 1 from another, what you get? You get sigma 1 minus sigma 2, if you keep going in the same direction. You can, you know operate you know projection operator on sigma 3 sigma 4 sigma 5 and sigma 6 and ultimately you can get the you know SALCs and then normalized. You get the orthogonal functions. You get the ultimate orthogonal function because see this and this ultimately should be orthogonal. Until and unless you get the orthogonal functions, you have to try orthogonal lives and thereby you here, you use this you know subtraction.

Where you subtracted this first combination and for second combination from the first 1 and you got this function sigma 1 and minus sigma 2 and in this way, you form the whole thing, the whole state of combination by operating projection operator for T 1 on all the basis functions and you get several combinations and then you perform the orthogonalization and you ultimately get, you know in terms of Sigma 1 minus sigma 2 or sigma 3 minus sigma 4 and sigma 5 minus sigma 6 and when you know incorporate the normalizing condition, you get the overall normalized orthogonal functions that will form the basis, that we together from the basis for the 3 dimensional representation which we are considering here alright.

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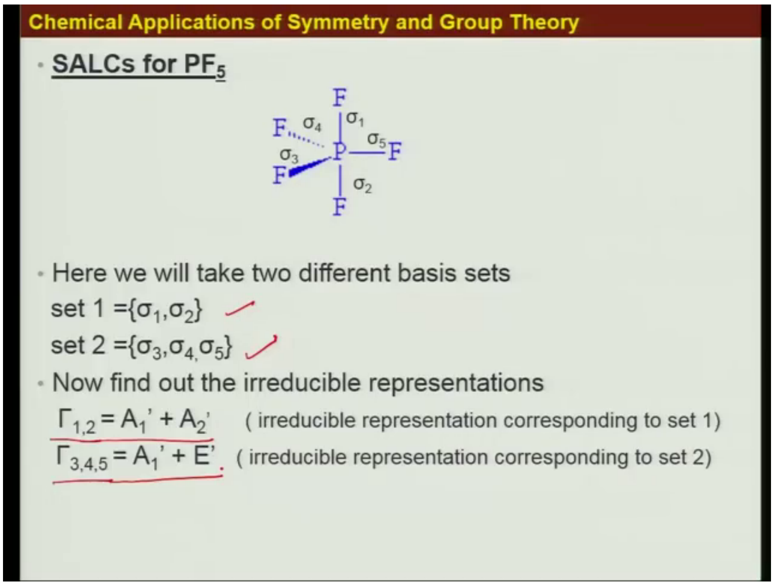

Now we will go to some, you know some other molecule general where you remain counter 1 dimensional 2 dimensional 3 dimensional and here we are going to consider one particular molecule which is P F 3. Now in the last class, we mentioned that we may actually have some problem particularly when you have equivalent atoms and A, that is because that each of the, you know atoms or the basis functions will contribute to the emotion, in case of A P F, 3 when we set out to form SALCs. First we have to choose the basis functions. Now here you see that the 2 axial P F bonds are equivalent while other 3 equatorial P F bonds are equivalent.

Now, this axial and equatorial PF bonds they are not equivalent. I have to take them separately. Here actually you know with this, so many examples where you have to be careful when you want to choose the basis set and then do the rest of the word. Here we would take the sigma bonds as my basis functions true, but all together 2 will what form the basis set as sigma 1 to sigma 5 rather what I will do, this sigma 1 and sigma 2 which corresponds to this axial bonds at circulate bond, I will forward this basis set out of these 2 while the rest 3 sigma bonds in the equatorial plain I will use, you know I will form separate plain and use them as another basis set.

I got set 1 and set 2. Next step I have to form the, you know irreducible representation and then in the next step into irreducible. I have to do it for both the basis sets. I do it for set 1 and as well as set 2. Here we get the representations which we have, we writing as gamma 1 2 meaning that this gamma is formed by a taking sigma 1 and sigma 2 as basis functions while the other representation, we are writing as gamma 3 4 5 meaning that linear combination representation using that basis set comprising of sigma 3 sigma 4 sigma 5. Upon reducing gamma 1 2, we get it as A 1 prime plus A 2 prime and from gamma 3 4 5 we get A 1 prime plus E prime, alright.

Here we have 1dimensional as we as 2 dimensional irreducible representation now first we have to get A SALCs for 1 dimensional representations.

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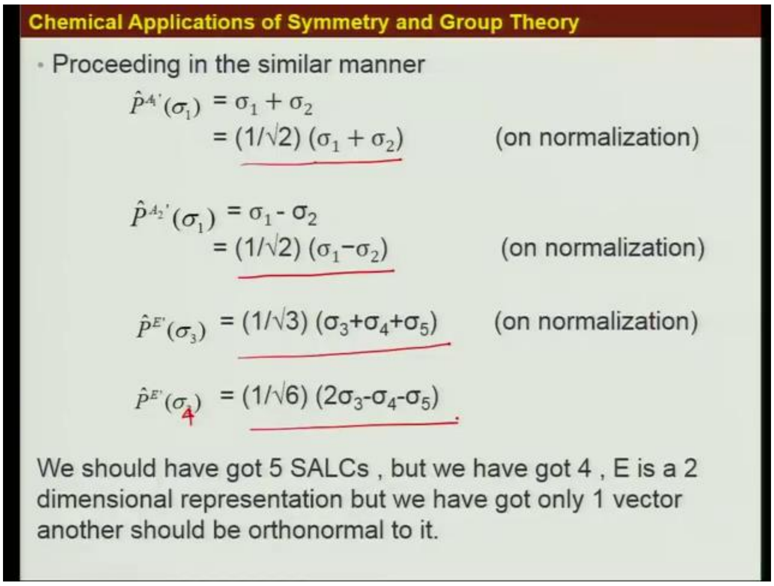

We start, you know applying the projection operators for the particular irreducible representation that is A 1 prime or A 2 prime, on the basis function is sigma 1. When I operate this projection operator for a 1 prime on sigma 1, I get this sigma 1 plus sigma 2 and when you normalize then you will get the corresponding normalization factor easy. Something is applicable on this projection operator for a 2 prime and we get the corresponding normalized SALC.

Now when we apply it on sigma 3, we form a basis for E prime sorry (Refer Time: 24:30) projection operator how v prime and then we get the function orthogonal function and we normalized this and get another SALCs and a when we operate on sigma 4, we get another SALCs, now this P X L P projection operator for e prime that should ultimately give me 2 functions. Now all together I have got so far 4, but I should get all together 5 SALCs correct because it has, you know 5 basis functions. I should have five

SALCs, we should get another basis function which will be orthogonal to the one that we are getting here or here.

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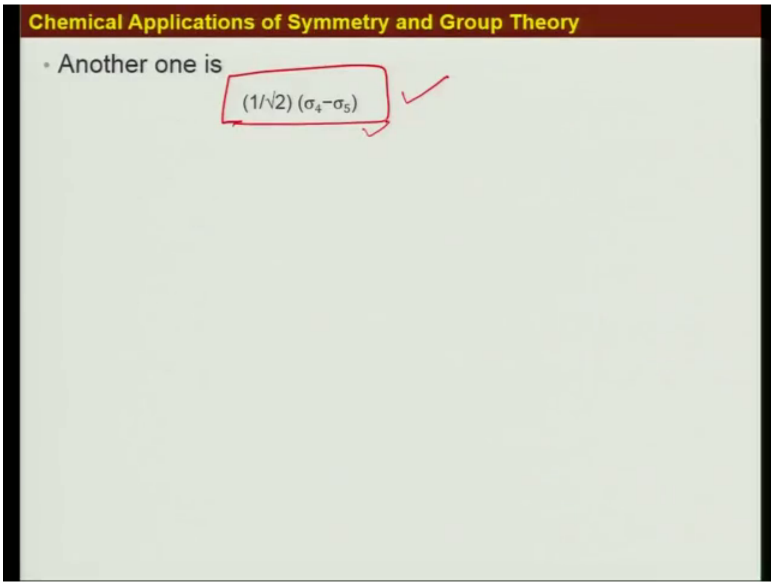

If we find that out we should get another SALCs like this 1, this 1 I am leaving after you to how to find that out how to orthogonalize and then ultimately find out this fit SALCs. I request you to try this 1 out, you know later. What did we learned to the overall?

We used projection operator to find out the SALCs corresponding to 1 dimensional, 2 dimensional, 3dimensional representation and also we looked at molecule which has a 2 different sets of, you know bonds and which suggested us that we should consider 2 different basis sets. instead of forming only 1 representation we formed 2 representations reduce them individual and then form the projection operators use the projection operators on those individual basis functions and got the symmetry adapted linear combinations and ultimately we saw that, we could get 4, but then we said that using the concept of orthogonalization, we can find out the fifth one which has to be there because the number of basis function and the number of SALCs should be equal.

With this, I will stop here today and in the following class we will come back with some of the applications of this SALCs because see we are forming this SALCs because there is a definite reason at the beginning, we said that whenever we consider a bond formation, we have to find out the second orbitals which will combine and it will keep rise 2 molecular orbital which will maintain the symmetry of the forming molecule.

After when this SALCs, we should be able to get some other information, say for example, the energy levels of the molecules and the orbitals and how this orbitals are occupied in the molecule.

We will try to learn those things in the following class. Till then, I thanking for your attention and have a good day.