Symmetry and Group Theory
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Lecture -42
Incomplete Projection Operator

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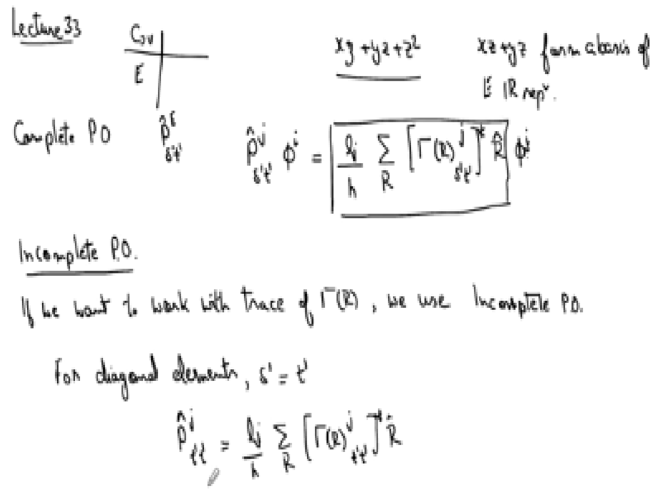

So, in the previous lecture what we saw that we can use projection operator to actually project a part of a function, which could be a random function with any given symmetry. So, for example we considered the case of C3v point group, so we used C3v point group and under that we saw that we projected a function with E representation with such that so we took a function xz + yz + z square.

And we use projection operator to project part of this function onto E so that part which is basically xz + yz forms a basis of E IR representation. This is what we saw, and in that case we considered complete projection operator. So, what was complete projection operator? Because we calculated the projection operator and we calculated for E representation and then we took out individual matrix elements.

So, for example 11 matrix element 22 and so on so this was the projection operator which we applied. So, in general if we write the complete projection operator the formulas stands like this.

So, you have P j or i any ith or jth irreducible representation. So, you have a typical matrix element and that when operated on to a given function, let us say phi i this gives you Lj over h times summation over all R.

And then you have the corresponding matrix element under the symmetry operation R, so the matrix element will be s prime t prime and for jth representation, and if it is a complex number then complex conjugate of that. And then the operators are applied on to and this part is called as complete projection operator this is the expression for projection operator. So, now let us see how we can obtain the similar result by handling using incomplete projection operator.

So, let us see what is incomplete projection operator. So, although it is incomplete but it gives you the similar result or same result with slight human intervention. So, now in this case if you notice that we are dealing with all the individual matrix elements of all these representations. So, for example, if for jth representation under any particular symmetry element we are always multiplying the corresponding matrix element with the effect of operation R onto a given function.

So, this thing requires the knowledge of full matrix for all symmetry operations, whereas if we want to work with traces, trace of this matrix, we use incomplete projection operator. Now let us see how do we get from here, from complete projection operator to incomplete. So, because, we want to work with traces so and traces deal with only diagonal elements, so we need to talk about only diagonal elements so this one deals with all elements.

So, for diagonal elements we can say, for diagonal only elements we can say that the index s prime is equal to t prime. So, I can substitute I can equate s prime to t prime and only worry about the diagonal elements. So, in that case the projection operator becomes p j t prime t prime and now I will only write about the right to expression of this and not the function form, not this phi functions Lj h summation over all R, and I have tau R so t prime t prime of jth representation and star and then I have R vector, this is the operator.

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For diagonal elements, $s' = t'$

$$\hat{P}^{j}_{t't'} = \frac{l_j}{h} \sum_R \left[\Gamma(R)^{j}_{t't'}\right]^{*} \hat{R}$$

Taking summation over all the values of t'

$$\sum_{t'} \hat{P}^{j}_{t't'} = \hat{P}^{j} = \sum_{t'} \frac{l_j}{h} \sum_R \left[\Gamma(R)^{j}_{t't'}\right]^{*} \hat{R}$$

$$= \frac{l_i}{h} \sum_R \left[\sum_{t'} \Gamma(R)^{j}_{t't'}\right]^{*} \hat{R}$$

$$\boxed{\hat{P}^{j} = \frac{l_i}{h} \sum_R \chi(R)^{j*} \hat{R}} \rightarrow \text{Incomplete P.O.}$$

Now to obtain the trace here what we need is we need to carry out a summation over all t. So, now introduce so taking summation over all the values of t prime, which is nothing but different values of these phi functions, because phi functions vary from different values of t or s. So, if we do that, we have summation over all t prime P j, t prime t prime now this can be equated to we can write it as;

Now there is no matrix element because now this is the complete trace of what we are going to get. So, in complete projection operator, you will often see that there are indices written which indicates that it is a complete projection operator. If there are no indices written that means it is a trace and you are dealing with incomplete projection. So, now if we go there so we have summation over t prime Lj over h summation over all R tau R t prime t prime jth representation star operator R.

Now this summation t prime can be taken inside because this is the only term which is dependent on t prime, so hence we can take this summation inside and expand it, so what we will get is Li over h summation over all R summation over all t prime. And what I get is tau R t prime t prime j star R. Now if I do this summation what do I get so this is nothing but a matrix element with these summation over all diagonals.

So, I can say that if I take summation over all t this becomes the trace of this matrix, so all I have now is l i over h summation over all R so instead of tau R, now we have chi R. This is the trace under this operation a symmetry operator for jth representation and then you have R operator, and this is my expression for incomplete projection operator. So, this is incomplete projection operator, so now that is easy.

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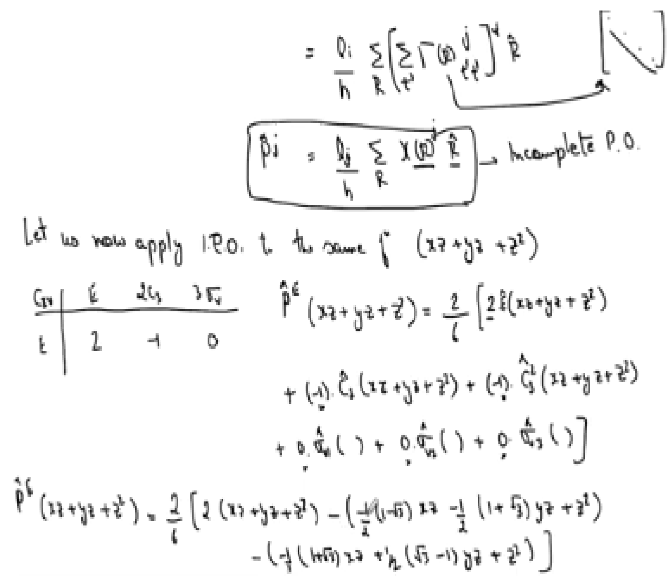

So, because now we do not have to worry about all the matrix elements that we were multiplying the saw in the last example, let us take the same example and see if we get the same result using incomplete projection operator or not. So, let us now apply incomplete projection operator to the same function, which was xz + yz + x square. So, even though we are taking incomplete projection operator, but the summation over all R still stands over all R and we cannot leave the class elements because effect of these symmetry operation difference symmetry operators are different even though they belong to same class, but their effect can still be different.

So, let us see that we have C3v example E representation E, 2C3, 3 sigma v even though we are writing the traces like this so it was 2, minus1, 0. I hope this is correct, yes. So, now let us try to calculate projection of projection of this function onto E representation which is represented like this. Projection of xz + yz + z square onto E representation, so now this should give you Li will be so this is i or j, Lj here is 2, order is 6 now effect of E so here we will be multiplying with the character which is chi r the character under E is 2.

And then what will be multiplying it with so let us write down effect of operator E onto x onto the function. So, let us do this completely, because we did not do that calculation completely so let us just do this one complete calculation, so we have minus 1 which is the character under C3 and effect of operation C3 onto xz + yz + z square. Again minus 1 which is now the character vendor C3 square.

So, we have C3 square operator onto xz + yz + z square. Similarly, we have sigma v 1 so the character under sigma v 1 is 0. This is 0 into sigma v 1 operator onto the function plus again, the character is see now look at that advantage here because when we were dealing with matrix element, we had to do with all four matrix elements of this but here now the trace is 0 so basically that does not contribute to the calculation at all. Sigma v 2, and the function plus 0 into sigma v 3 the function and the bracket this bracket is closed. So, now these functions these symmetry operators are coming because, you have R cap over here that means this R has to operate onto the function. This chi is coming as here that there are characters coming over here all these characters under the symmetry operation are and then you have Li and h.

So, now let us try to solve this and see what do we get so we have P E xz + yz + z square and you have 2 by 6, 2 into xz + yz + z square minus 1 minus of now effect of E on to this remains same, now effect of C 3 on to this we had calculated in the last lecture so I am just going to note down what do we get here so effect of C3 will be minus half 1 minus root 3 xz minus half 1 plus root 3 yz + z square.

And similarly, we will get the negative sign and then effect of C3 square onto this. So effect of C3 square is minus half 1 plus root 3 xz and we will have plus half root 3 minus 1 yz + z square and then you have big bracket closed. So, now if you solve this; what do you get? So, if we solve this, we will see that there are 2 xz over here and what other except as are coming, so you have minus half minus half and then you have minus root 3.

So, plus root 3 minus root 3 and plus root 3 will be cancelled so you will have minus half coming from here and minus half coming from here so they will be adding up so you will have 2 xz from here and minus xz from here, so 1 xz will come.

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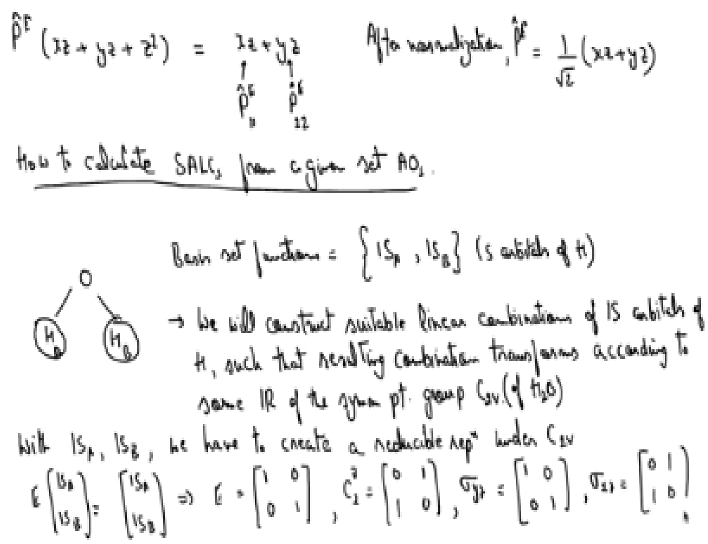

So, in the same way if you keep on doing this you are going to notice. So, let us not spend time on this calculation because now it is just this simple algebra. So, if we see that p E xz + yz + z square gives you xz plus yz, which was what we obtained from if you remember that we obtained this from P E 11 and P E 22. So, we obtained this one and this one or vice versa. So, one of them gave you xz and one of them give you yz which one gave, yeah 11 gave you xz.

And 22 gave you yz, so now if you want to normalize so this is not yet normalized. So, upon after normalization you have P E is equal to 1 over root 2 xz + yz. So, now this is the normalized set of function which has symmetry which transforms as E representation of C3v point. So, all we have done is we have applied incomplete projection operator only once and that has simplified the calculation, a lot as compared to what we were doing, when we are doing complete projection operator.

So, now that we are well versed how projection operator calculation works, so, we will see how to calculate SALCs from a given set of atomic orbitals. So, remember we discussed that there are a set of atomic orbitals. Which upon linear combination gives you a set of functions which; will form basis for irreducible representation, if we combine them in an appropriate manner.

So, that process can be done by projection operator. Why do we need to do that process? Because such combined atomic orbitals will form the acceptable solutions for the Hamiltonian equation or the Hamiltonian operator the energy equation. So, let us see how to do this thing so by taking an example, so let us take a different example than C3v now. Let us take water that also is easy and we have been working on that.

So, now in this case let us take basis set function as 1SA and 1SB, which is nothing but S orbitals of hydrogen, so we are taking S orbitals of let us say this is A this is B, and now we are taking S orbitals of this hydrogen, which are oriented something like this because these are spherical in nature these are now taken as basic set. And now we will try to combine them in an appropriate linear combination and see that if we can obtain using projection operator.

If you can obtain linear combinations which are symmetry adapted. What do I mean by symmetry adapted that they are basis of a certain irreducible representation of C2v point group which is the water point group. So, what we are going to do is aim is we will construct suitable so this is a very simple example, we will see we will take more complex examples later. This is a very simple one to see. Linear combinations of 1S orbitals of hydrogen, such that resulting combination transforms according to some IR.

So we do not care about which IR but some IR of the symmetry point group C2v of water. So, now first what we have to do is with 1SA, 1SB we have to create a reducible representation under C2v. How do we do that? That is very simple and we have seen that so if we apply E onto 1SA, 1SB what do we get? We get the same matrix back this implies that E can be written as 2 cross 2 matrix of 2 cross 2 unit matrix, similarly we can say that C2Z can be written as we have done that earlier.

So, I am not going to write do this for all the operations 0 1 1 0, because 1S A and 1S B are now replaced with each other, sigma let us call it as yz and that will be 1 0 0 1, and sigma xz the matrix come out to be 0 1 1 0.

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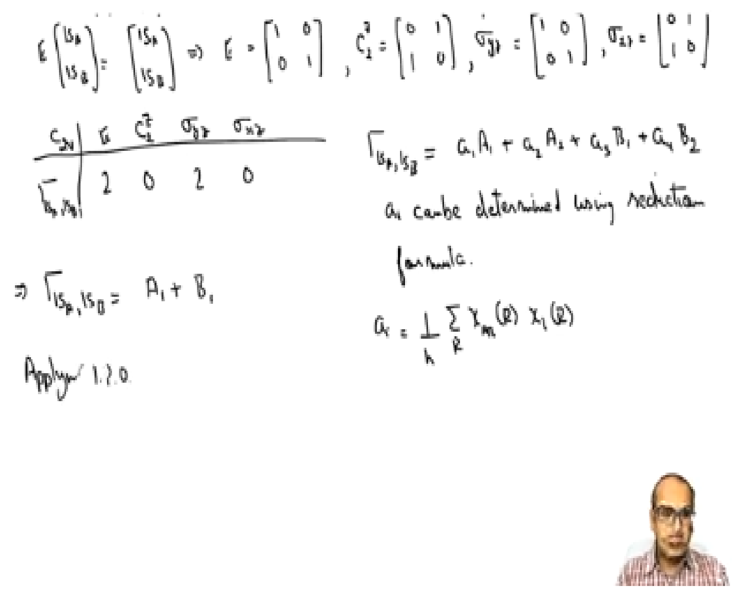

So, once we have obtained the irreducible representation using the basis set of functions, we have to reduce this to component IRs. So, this means what we can say is C2v let us write the E, character table, C2z, sigma yz, sigma xz and this is our tau 1SA, 1SB and the traces are now this is 2 this is 0. So, now we can say that tau 1SA, 1SB can be reduced into a1 times A1 + a2 times A2 + a3 times B1 + a4 times B2.

What are these A1, A2, B1, B2? These are the Mulliken symbols for the irreducible representations of C 2v point group. So, I am not going to write the character table of C2v point 2, but we can see that these are the 4 irreducible representations C2v has. So this particular tau which is the reducible representation would be a linear combination of these irreducible representations.

Where a1, a2, a3, a4 can be determined using ai can be determined using reduction formula. So, go back and see what is reduction formula. This was, 1 over h and let us just write it down, so you have ai 1 over h and summation over all R chi AB of R and chi of R. This is the trace of reducible representation, this is the trace of irreducible representation you multiply the 2 and then take summation over all R divide by the order of the group and you will get ai.

So, if you do this for this particular tau what we get 1SB what we get is A1 + B1. So, we see that the small a1 is equal to 1 and this a3 is equal to 1 a2 and a 4 goes to 0, so that is where there is no contribution of a2 and b2 towards this one. So, what we get here is only A1 + B1. Now let us see what happens if we apply projection operator and we will use only incomplete projection operator because we have the traces only.

I mean we do have matrices but we are not going to do the complete because it takes more time and gives you the same thing. Applying incomplete projection operators so let us see how do you do that.

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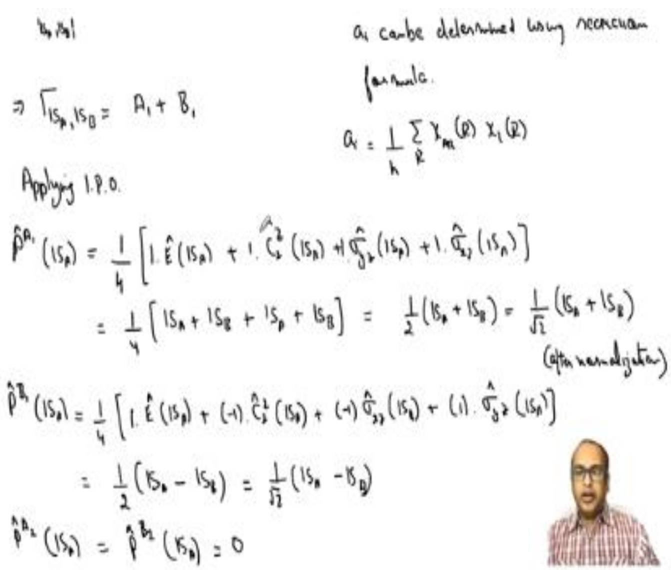

So, we have a what we can do is we can either apply projection onto A1 or on to B1 because both of them contribute to this. So, basically what we will get is we will get one linear combination corresponding to A1 another corresponding to B1. Now this can be applied on to either 1SA or it can also be applied to 1SB. So, we are going to apply 1SA onto A1, what do we get?

So, L is 1, h is 4, and the corresponding matrix element for A1 for all of them will be 1 now E operator on to 1SA + 1 into this is the trace C2z operator on to 1SA + sigma yz operator on to 1SA. This is of course 1 into plus 1 into sigma xz operator onto 1SA. Now this gives me 1 by 4 1SA, C2z will replace this thing so we will get 1SB. Sigma yz will also replace so we will see what happened here.

Sigma yz, now sigma yz will remain same. So, we will get 1SA sigma xz will replace so we will get 1SB. Now this can be written as 1 by 2, 1SA + 1SB and upon normalization we can say that this can be 1 by root 2, 1SA + 1SB this is after normalization. So, these are now normalized. Now this linear combination of 1SA and 1SB transforms as A1 representation of C2v point group.

That means they will form basis for A1 representation. So, now we know the symmetry of this that this is, what is the symmetry of this under C2v point group. Now let us do the same thing for B1 representation, so P B1 will on 1SA, so you can choose either of this either one of the functions fine. It does not matter which function you choose, you will get the same result. So, again 1 over 4 you should know what are the traces for B 1, B1 representation.

So, we will write that so under E it will be 1 and then you have E on 1SA, then for C 2 it will be minus 1 character and C2Z on 1SA then you have sigma yz so character under sigma, yz is again minus 1. So, in one of the cases it will be yz the one of the cases it will be plus 1. So, idea is that you will get linear combination will see what in combination so you will have yz, this will be xz. So, sigma xz 1SA plus 1 sigma yz 1SA.

Now this if you do it you will see that what you are going to get is 1SA minus 1S B. So, you can see the effect of this. And do this and this upon normalization will get 1 over root 2 1SA – 1SB. So, these are the two linear combinations which you will get using projection operator. And now you will know the symmetry of these linear combinations.

So, if you randomly combine any two atomic orbitals, you will not know what is the symmetry of this how will they transform under C2v point. But here you know the symmetry so that is why projection operator technique is very, very useful. So, now as a proof if you let us say if you do projection on to the irreducible components which are not present in this reducible part. So, let us say if you do it for A2 onto 1SA or projection of 1SA onto B2.

Now A2 and B2 are not forming not contributing to this tau, this reducible which we obtained using the atomic orbitals as the basis set. So, if you do that you will see that the answer which you will get here is actually 0. So, that means any combination of SA and SB will not transform as A2 and B2 and so you cannot combine this in any forms so that it will transform as A2 and B2.

Because A2 and B2 do not contribute to this reducible representation, so in next class we will see we will take up more examples of obtaining SALCs. So, that we are through with this, thorough with this calculation and we know in our heads and that how to carry out this before we actually go towards chemical bonding. I think that is all for this class, thank you very much.