Symmetry and Group Theory

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Lecture - 50
Generating SALC's using Projection Operators - Continued

Is more about SALC's. What is projection operator? How do we write it? P j right?

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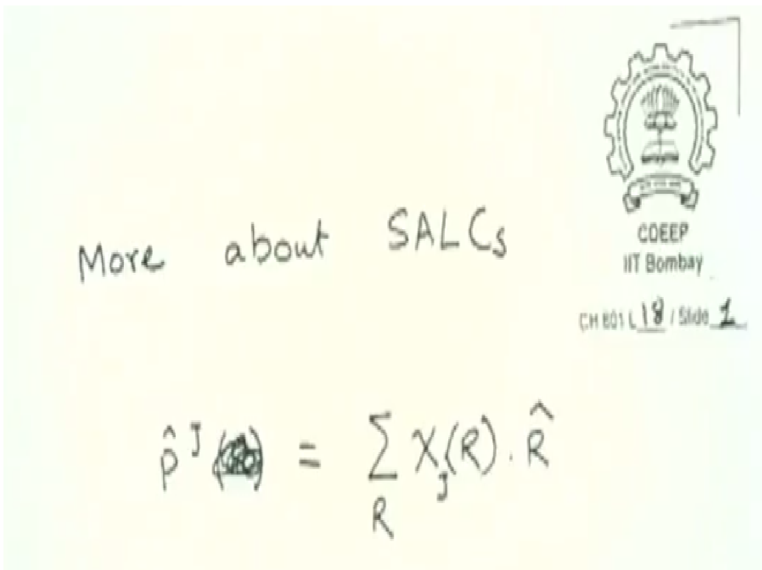

P j then R, is equal to what? Is it P j (R) or is it P j? P j, cannot be P j (R). What is P j? Sum over, sum over what? R. That is why it cannot be P j of R because they are summing over R. Sum over R then chi R. Should I write a j here or not, yes. Do I write it as a subscript or a superscript? Okay, chi j R multiplied by does not matter, you know what I am talking about, right? R. What is R, a symmetry operation, okay?

So to, in order to use a projection operator what you do is you take whatever basic element it is, make the R operate on it and multiply it by the character corresponding to that same symmetry operation R and you do this for each and every symmetry operation and sum over, right? The thing to remember is that we are summing over all symmetry operations, right? So summing over all symmetry operations means that suppose for C 3v what is it that we have?

What are the symmetry operations? E, 2C 3 and 3 sigma v. You should not forget the coefficients, right? Not only should we not forget the coefficients, do not forget we are actually using R. So what we get for C 3 operation is going to be different from what we get for the C 3 square operation, is it not? C 3 and C 3 square. So they are going to be different. Characters will be the same, but the effect of R is going to be different.

So please do not forget to use each and every symmetry operation. We are going to need that today. So today what we will do is we will just work out 3 or 4 more examples of SALC's. While doing so we will learn a useful technique of descending symmetry and use of group, sub-group relations, alright. So let us get ahead with it. We are going to talk about SALC's. Lecture 18 you said.

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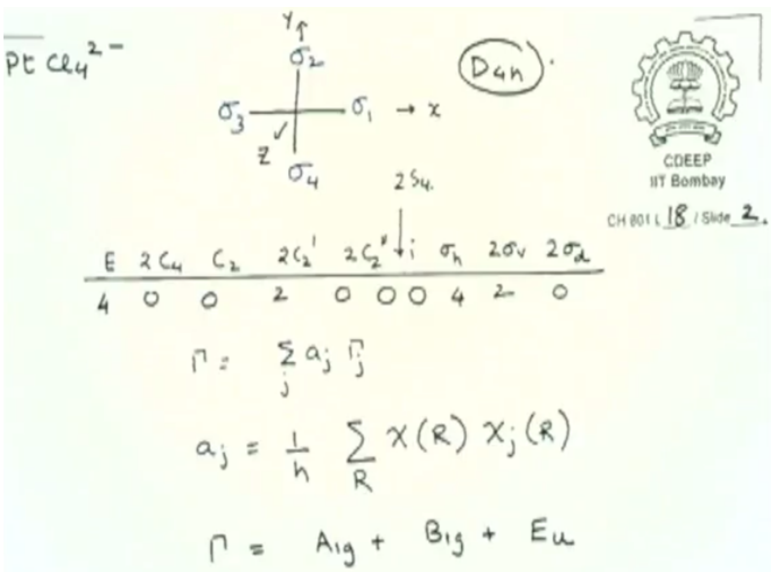

What did we discuss last day? Where did we stop? So this is the disadvantage of not having slides. I also do not remember. C 2 H 4 is all that we did right? So right now we are following Cotton's book, almost page by page. Today we will digress a little bit into Cotton's book, okay? So what I am doing now is really solved problems that are there in Cotton's book. So let us go to the next problem. Something like Pt Cl 4 2-.

What is Pt Cl 4 2-? Is it tetrahedral or is it square planar? It is square planar complex, right? So this is what it would like. I am not drawing the atoms and you can figure out what I have drawn.

This point is platinum, then you have chlorine, chlorine, chlorine, chlorine right. What is the point group? Ya. D 4h every good. It is a D 4h point group. So let me write down the symmetry operations of D 4h. I hate the ugly lines I always draw. So I tried to get my son's ruler today but then he did not cooperate. So I got this, right. So the symmetry operations are E, this is large enough, ya? Large enough, right? Yes sir or no sir? 2 C 4.

What are the 2C 4 operations? C 4 and C 4 cube. What about C 4 square? C 4 square is C 2. This is C 2. So you know which C 2 I am talking about. And before going further maybe I will draw the axis. Let us say this is x, this is y, and then z will be pointing towards us, right? Okay, C 2. Next what would we have? Do we have more C 2s? Where are the C 2s? One along the bonds, that is one kind. How many of those C 2s are there, 2 and 2 will be between the bonds.

So those along the bonds are called C 2 dash. Those between the bonds are called C 2 double dash, okay. What else is there? Before going to sigma, is there a point of inversion, yes. And then I think everybody can see the horizontal plane, right? Xy plane is horizontal plane. It is sigma h and what else is there. So here we differentiate between sigma v's and sigma d's, right? These are the sigma v's, these are the sigma d's.

The ones that go through the bonds are called sigma v. Ones that go between the bonds are called sigma d, okay? I will show you the character table.

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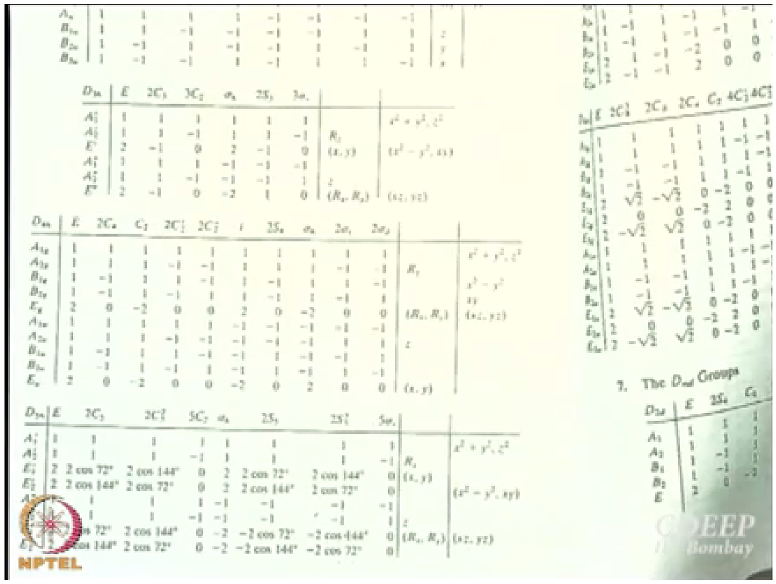

Okay, D 4h can you see? So E is 2C 4 C 2, 2C 2 dash, 2C 2 double dash, i, 2S 4 sigma h, 2 sigma v, 2 sigma d, alright and what was that? S 4 we have forgotten S 4. Now that is a mess. After drawing that line so carefully, I forgot. Where do I write 2S 4 now? I will write it somewhere here, 2S 4. So do not get confused with the characters, okay. Now I will, so right now we are focusing on sigma SALC's only. We are going to go on to pi SALC's today as well, okay?

I hope you have not forgotten what SALC's are? Do you know what SALC's are? Symmetry adapted linear combination. So it is basically a linear combination of wave functions of orbitals that are of a certain symmetry, right? And what we do using projection operators is that we try to project out these symmetry adapted linear combinations using the atomic orbitals as the basis, okay, right. So the first step would be to name the orbitals.

Let me call them, the problem is you cannot even see the color I use. Still, let me call them sigma 1, sigma 2, sigma 3, and sigma 4. There is no sigma 5. There are 4 sigma bonds, right? So these are basically the atomic orbitals, you can say s orbitals that are being used by chlorine for the coordinate bonding or covalent bonding, whatever you want to call it. Do you see a difference in color between the line and the sigma's? I see it here, I do not see it there, okay no problem.

So now, the first thing to do is to construct the reducible representation using these 4 orbitals. Let us get ahead. The character of E is 4. What would be the character of C 4? Everything will change places, 0. C 2? C 2 is the same axis, z axis, 0. C 2 dash, which 2? Not any 2. Any 2 that are in the same line going through the central metal line ya. So 2. What was that? I am using this sigma 1, sigma 2, sigma 3, sigma 4. Let us say s orbitals of chlorine.

We are using them as the basis and we are constructing the reducible representation, okay fine. C 2 double dash? 0. You are all convinced right, C 2 double dash is 0 because this is where C 2 double dash is. Sigma 1 goes to sigma 2. Sigma 3 goes to sigma 4, right? So this is 0 and I have created enough space for writing the character of S 4 which is 0; i 0. Sigma h, 4. Sigma v, where is sigma v, here, right, is 2. Sigma d, 0. Very good, what is the next step?

Next step is to break this down into the constituent irreducible representations. What is the relationship we use? Gamma equal to sum over j, a j, gamma j and every time I forget whether I wrote i or j the previous day, it does not matter, right and what is a j? 1/h sum over R chi R, if it is a j it has to be chi j R, should not write chi i R okay. So now I will show you the character table. Please work out the a j's. So what I get is gamma = A 1g + B 1g + E u.

What do I do next? I have to use the P j operators corresponding to A 1g and B 1g and E you on sigma 1. It does not matter, you can use any one but conventionally we will start with sigma 1. So for that what I need to do is I need you to draw this diagram because you need to know what is what and then once again I will show you the character table and then you can work out right.

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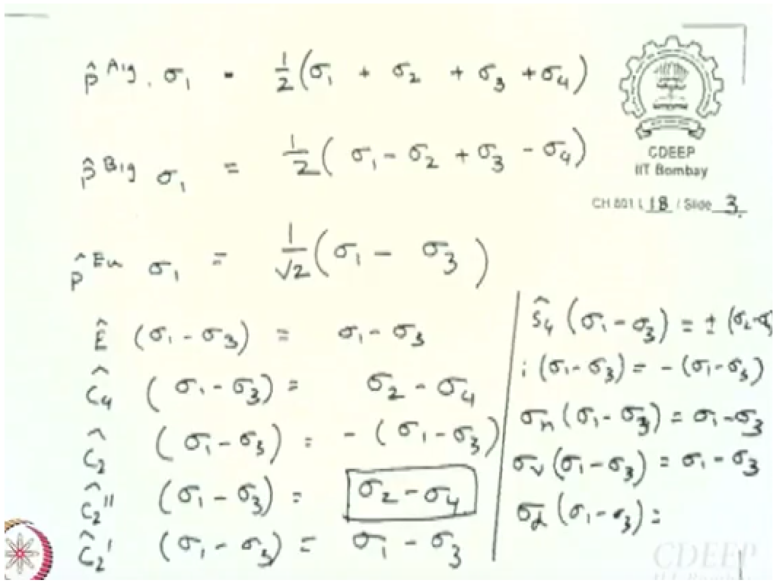

So what I want is I want you to tell me what is P A 1g operating on sigma 1 what do you get. What happens when you make P B 1g operate on sigma 1. What do you get when you make P E u operate on sigma 1 okay? Ready for the character table? B 3h right? What is the point group?

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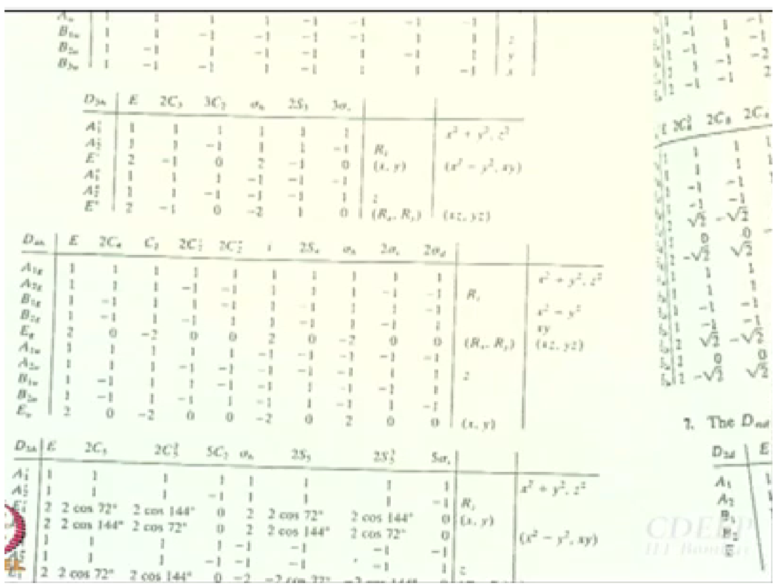

So can you work out? What happens when you make the projection operator of A 1g operate on sigma 1? Okay, let us see. Let us work it out. You write I speak okay. What happens when E operates on, see the chi R is very easy here right? A 1g chi R is all 1 right. So E operating on sigma 1 what you get. Sigma 1 multiplied by 1, write that. Plus C 4 operating on sigma 1. What do you get? No, be careful now. C 4 operating on sigma 1 what is it? One wave it is sigma 4.

The other wave it is sigma 2. So you have to write sigma 2 + sigma 4 is it not? Plus minus. So you get sigma 2 + sigma 4. There are 2 operations. What about C 2? Sigma 3. So, so far what have you got? Sigma 1 + sigma 2 + sigma 3 + sigma 4. Now, what is next C 2 dash, 2C 2 dash once again. What is C 2 dash? The one going through the bonds, right? So first C 2 dash what do you get? Sigma 1. Second C 2 dash, sigma 3. So write sigma 1 + sigma 3.

So far I have 2 sigma 1 + sigma 2 + 2 sigma 3 + sigma 4 is it not? Then what about i? No what about C 2 double dash? Sigma 2 and sigma 4. So write + sigma 2 + sigma 4. It is very easy. It is like a back to class 2 class 4 days okay. How far have you gone? 2C 2 double dash right? Then i, what about i, you do not want i? sigma 3. Then S 4, sigma 2 and sigma 4. Sigma h sigma 1. Sigma v, again there are 2 sigma v's. And 2 sigma d.

So finally you get something multiplied by sigma 1 + sigma 2 + sigma 3 + sigma 4. But that 4 is not relevant is it not? The relevant part is ya and normalization is something that we can now do as a mental arithmetic. Sigma 1 + sigma 2 + sigma 3 + sigma 4. If it is to be normalized what should be the coefficient? Multiplied by itself what do you get? Suppose this is n, what do you get? Do you not get n square multiplied by 4 = 1? Why 1/2? N square right?

N square multiplied by 4 is equal to? So n is 1/2. That is what you are saying. Okay, that is what you are saying is equal to 1/2, okay fine. So is equal to 1/2. That was easy. Next is B 1g. In B 1g we have to be careful because signs will also change, is it not? Because all characters are not +1. Do not forget, it is character multiplied by symmetry operation.

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B 1g. First one is 1, second one is -1. So again, so from here we get sigma 1 then from here we get minus sigma 2, minus sigma 4, right? If there is a question please ask. This is symbol, but it is also very easy to get confused. Anup? Then C 2, sigma 3, + sigma 3. Then C 2 dash, right. I hope you are writing? Then there is a -1 and the operation is 2C 2 double dash. **"Professor - student conversation starts"** We are honored by your presence, but there was a lab I remember. Sir, we thought it is 5:45. Okay, not a problem. **"Professor - student conversation ends"**.

C 2 double dash. B 1g. Then i, + sigma 3. S 4 - sigma 2, - sigma 4. Sigma h, + sigma 1. Sigma v, yes and 2 sigma d, - sigma 2, - sigma 4. You add that all up. Now you do not have to write, you can see. What do I get? I get sigma 1 – sigma 2 + sigma 3 – sigma 4 and Mehak knows what the normalization constant is. So this is what we are discussing today, more about SALC's. I hope you have not forgotten what the projection operators are, right?

So basically today what we will do is we will ensure that we get bored of projection operators. We will operate the projection operators so many times, okay? And the system that we are working on is Pt Cl 4 2- which is of D 4h point group okay and the wave we have drawn it is this is your platinum. This sigma 1, sigma 2, sigma 3, sigma 4 are 4 s orbitals that chlorine atoms use for sigma bonding or (()) (22:16) bonding whatever you might want to call it, right?

This is the x direction, this is the y direction, z direction is pointing towards you and saying you are late, okay. So what we did is we use this 4 sigma orbitals and we constructed a reducible representation and I am particularly proud about this nice straight line that I have drawn. So this is the reducible representation that we got and while you were away we reduced this reducible representation into its constituent irreducible representation and with a great difficulty we figured out that it is A 1g + B 1g + E u.

So what we are trying to do now is we are trying to generate the A 1g and B 1g and E u SALC's, right? These are all sigma SALC's okay. And we have already worked out 2 of these SALC's without your help. So you better help us work out the last one. One thing that should not be forgotten is that when you have a situation like this 2C 4, 2C 2 dash and so on and so forth do not forget that they are actually different symmetry operations.

It is just that they belong to the same class. So character is the same, but the effect will be different. So for example 2C 4 means one is C 4 this wave, the other is C 4 that wave. Or you can think one is C 4 the other is C 4, C 4 square, C 4 cube, right? So see if you start with sigma 1, the first C 4 will take it to sigma 2, the second C 4 will take it to sigma 4 okay. That is what you should not forget when you work out the projection operators.

So are we ready for the last one, projection operator of E u? Shall we do it? And see in this case even u is easy because there are so many 0s. So we do not have to work with everything. I only have to work with E and C 2 and i and sigma h and that is it, is it not? What was that? Okay, very good. Sigma 1 minus what? Okay, I heard sigma 2. So if you make the projection operator of E u operate on sigma 1 then you get sigma 1 – sigma 3.

What is the normalization constant? 1 by root 2, okay? So you have generated 3 SALC's. How many SALC's should we generate, 4. And how do I generate the fourth SALC? Do not forget the fourth SALC also has E u symmetry. Which means that, that SALC along with sigma 1 – sigma 3, wait do not jump wait. It is not sigma 1 + sigma 3. That along with sigma 1 – sigma 3 is going to form a basis for the E u representation. Because E u is a 2-dimensional representation, right?

There are 2 one-dimensional representations A 1g and B 1g. we have already worked out the SALC's for them. Now what is left is one of the SALC's for E u because E u must have 2 SALC's. There must be 2 SALC's with E u symmetry, is it not? So what you did I think, correct me if I am wrong is that we just worked out what is going to be orthogonal to this is it not? But see there are several functions that can be orthogonal to this.

You are looking for the specific function that will also belong to E u symmetry along with E u. So how do we do that? Now suppose I make the symmetry operations operate on this wave function sigma 1 – sigma 3, this SALC. Then what will happen? What happens in a 2-dimensional basis when you apply the symmetry operations? Think of that x and y in C 3v. What happened there? When I applied C 3, x and y mixed is it not? X and y mixed.

And when I applied sigma d then what happened? In C 3v if you applied sigma d then what happens? Then what happens if I apply sigma d in C 3v. I am talking about x and y in C 3. Sigma v not sigma d. What happens when I apply sigma v? x and y interchange is it not, x and y interchange. So this is what happens in multidimensional basis. Some symmetry operations cause a mixing of the basis elements and some symmetry operations cause an interchange.

An interchange of course if you think a little deeper, a interchange is really a very drastic case of fixing is it not? A interchange is just mixing in such a way that one of the coefficients has become 1 and the other coefficient has become 0. So interchange is really a special case of mixing. So essentially what happens in multidimensional basis and this is a theme that we keep coming back to again and again.

And it is very important to understand is that in a multidimensional basis a mixing of the basis elements takes place upon the symmetry operations. So now see if I now apply the symmetry operations on sigma 1 – sigma 3 what should I get? I should get the other SALC of the same symmetry or I should get a linear sum of sigma 1 – sigma 3 and the other function is it not? Because once again think of x and y in C 3v. When I apply C 3 then what happens?

There is a mixing of x and y. When I apply sigma v then what happens? There is an interchange of x and y. When I apply E then what happens? X remains x y remains y. These are the only 3 things that can happen. So if I apply, go on applying the symmetry operations one by one then I should be able to generate in some case the other SALC from this one.

"Professor - student conversation starts" Last time you were talking about only a particular symmetry operation. Yes, I tried out all. **"Professor - student conversation ends"**. To start with I am going to try out everything. What are the symmetry operations here? E, C 4, then C 2 etc. To start with we will try out all and then later we will think if we can make the problem a little simpler, okay? So let us try out all. What happens when E operates on sigma 1 – sigma 3.

I do not care about that 1 by root 2 at the moment. What do you get? You get the same thing. What is the next symmetry operation? C 4 and C 4 operates on sigma 1 – sigma 3. What do you get? Sigma 2 – sigma 4. And Rahul are they orthonormal or not? Sigma 1 – sigma 3 and sigma 2 – sigma 4 are they orthonormal or not? So this could be our SALC.

"Professor - student conversation starts" Sir, what was C 4 negative of this. Yes. How do I account for that? I does not matter. It is just negative. It is just +x and –x. It is up to you, okay. **"Professor - student conversation ends"**. What is next after C 4. C 2. C 2 operating on sigma 1 – sigma 3 what will you get? Same thing right, sigma 3 – sigma 1 which is – sigma 1 – sigma 3. See it is unfolding in front of our eyes is it not, what is going to happen.

Then what about what is next? C 2 dashed operating on sigma 1 – sigma 3. What do we get? Sigma 2 – sigma 4 once again. So now the suspicion is getting stronger and stronger. That sigma 2 – sigma 4 seems to be the other wave function, other SALC rather. C 2 double dash C 2 dash. Which one is C 2 dash, this. So C 2 dash should give me what? This is one C 2 dash. That will give me sigma 1 – sigma 3. What about this C 2 dash? Sigma 1 – sigma 3.

So and what about C 2 double dash? Sigma 2 – sigma 4. So it is very convenient, add a dash. I am really getting on the nerves of some of us. And then C 2 dash operating on sigma 1 – sigma 3 gives us sigma 1 – sigma 3. Okay, what is left? S 4. What do we get? Sigma 2 – sigma 4 or sigma

4 – sigma 2? Depending on which direction you turn, right. But it does not matter, it is just plus minus. Sigma 2 – sigma 4. Then i. Then sigma h that is too simple. I will not insult your intelligence by asking you this.

Sigma v, okay you do not want your intelligence to be insulted, so I will write it. Sigma d, plus minus right plus minus fine. Sigma d, sigma 1 – sigma 3 once again ya. So then sigma 2 – sigma 4 is the fourth what is it called SALC and it is the second SALC which has the E u symmetry, okay, right? What is the property that has to be satisfied for it to have E u symmetry? You take sigma 1 – sigma 3 and you take sigma 2 – sigma 4.

We just worked out all the symmetry operations. So what we see is that they either interchange or they remain what they were. That means they are jointly forming a basis of E u. They are not forming the basis for any one-dimensional representation because they are interchanging within each other, right? So they jointly form the basis for this 2-dimensional representation, okay Debindu? Fine. That was very easy.