Symmetry and Group Theory
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Lecture - 49
Generating SALC's using Projection Operators

So now what we will do is, we will not bother ourselves with lifeless quantities like xz, yx, z square right. We are going to talk about things that are more interesting to chemists. The question is how to use projection operators to get, that is over enthusiasm, to get SALC’s. How can one use projection operators to get SALC’s. Let us see.

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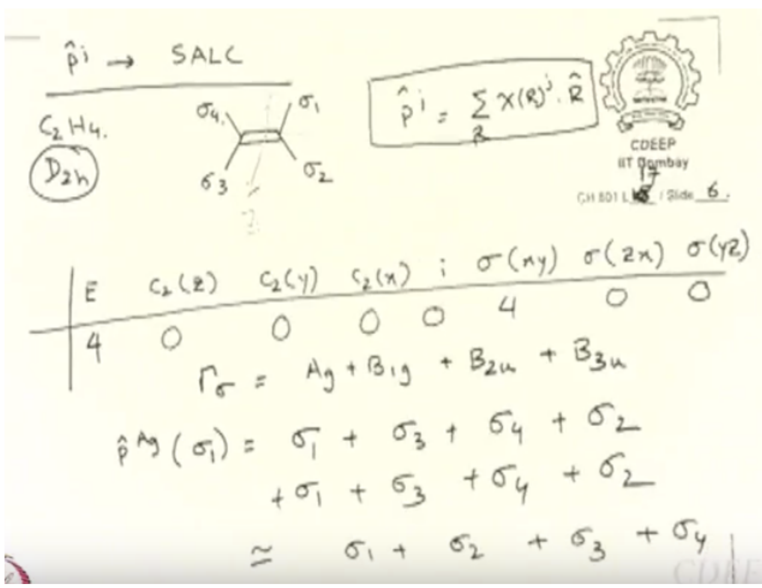

So let us take a simple example. Let us say C 2 H 4. What is the structure of C 2 H 4? And write like this, ethylene. What is the point group? D 2 h and this in case you have not known this is our exercise in symmetry point group. The only problem is that we are taking really very easy examples. So what I can say is I can call this s orbital on hydrogen atom sigma 1. I call this orbital of this hydrogen atom sigma 2. This is sigma 3. This is sigma 4, okay?

So first thing is already known to us. But before that let me define the axis. Otherwise, it can be pretty confusing. What is the principle axis of symmetry? How many C 2 axis are here, 3 right? But this is the unique axis. This is the principle axis of symmetry. This one. In this case, we call this the z axis, okay? C 2, C 2 (z). So this is x, this is y, okay? It does not matter because we are going to use x, y, z all the time, okay. Now, how many of us do not have character tables?

So henceforth kindly bring character tables so that we do not have to project. So what do we want to do? We want to use these sigma 1, sigma 2, sigma 3, sigma 4 and we want to generate a reducible representation. For that we do not need character tables. We just write down the symmetry operations. What will you have? You have E of course. Then you have C 2 (z), C 2 (y), C 2 (x), next is there a center of representation, i. What would else would be there?

Sigma xy, sigma zx, sigma yz. All are different classes. So now if I take sigma 1, sigma 2, sigma 3, sigma 4 as the basis what is the representation that I generate? What is the character of E? My basis is sigma 1, sigma 2, sigma 3, sigma 4. 4 or 6? Not 6? Sure? It is 4. Sigma 1, sigma 2, sigma 3, sigma 4. So there are 4, 4-dimensional basis. So E is 4. What about C 2? What is the character of C 2 (z)? C 2 (z) what is the character? 0 right because we are considering separate s orbitals for now, so 0. What about C 2 (y)?

C 2 (x), i; now this is getting boring, everything is 0. So to make more things a little more lively sigma xy. Do not forget what is x what is y; xy is the molecular plane, 4. Sigma zx 0, sigma yz 0. This is like the score of the Indian team in the disastrous match against England, right? 1, 2, 3, 4, 5, 6, 7, 8. The other 3 people scored maybe 10, 11, and that how we got that score, okay. If you break this down, I call it gamma sigma maybe.

I spare your trouble of working it out and I will give you the answer. It is A g, B 1 g; A g + B 1g + B 2u + B 3u. Okay, you have to just believe me on that or you have to work it out. Now, let us see the character table. Yeah, I understand the confusion. We have only talked about 1 and 2 so far. But then if you have more than 2 B's what will you do? So you have to give preference to something else also. What is this, B 2h.

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6. The D_{nh} Groups

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

[illegible]	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2$

Too good is no good. If we give too large, you lose out on resolution. Ah, this is beautiful, okay. So see what we have here. 1, 2, 3, 4, 5, 6, 7, 8; 8 classes means 8. Irreducible representations. What are the dimensionalities? You can work that out I believe. So now you have A g okay. Only one A g kind of representation is there. So you do not have to call it A 1g, A g is enough. Now next the problem is you have and once again A u kind of representation also is only1, okay.

What is it that makes it B? What is it that makes it B? Character of, no first B, forget about everything else. Yeah. So z, C 2 (z) is negative, -1, -1, -1, -1. That is what make them B. But there are 4. So you can try to classify further using g right? So the problem that you get is that you get 2 g’s and 2 u's. Actually 3 g’s and 3 u's. Now let us focus on B 1g, B 2g, B 3g. Why have we called it B 1g? C 2 (y) is +. Here C 2 (y) is -. We should have a ruler.

I am getting paralyzed. This is B 3g right? Just let me draw the line. B 1g. This is -1, this is -1, this is -1. So now you go by this xz. Then you call it, according to that, I do not exactly know which one is used to make it 2 and 3 but then let us go by the character table. This is what you get. Now, what do you need to do now? We need to use the projection operators. Let us use the projection operator as A g. A g is one of this or not? Yeah, A g.

Projection operator of A g on sigma. Can you do that? Projection operator A g operating on sigma. What will happen? So what I want is I want projection operator of A g operating on sigma. What will I get? Characters are all 1, that is a good thing, is A g okay and the functions also remain unchanged under which operation? E. So to start, for E what will be the term? Sigma, right? Because R, what is P j hat? Hope you have not forgotten that.

It is sum over R chi R j multiplied by R hat. So basically what we have to do is we have to make R hat operate on that function and then multiply it by the appropriate character, right? So for the first one E, E operates on sigma, to give sigma, multiplied by 1 is 1 sigma. What happens when C 2 operates on sigma? When C 2 operates on sigma, C 2 (z) what do you get? What am I doing? Sorry. I completely forgot the 1.

Sigma 1, sigma 2, sigma 3, sigma 4. These are the 4 functions, right? I take the first one, sigma 1. You can take anyone, does not matter. You can take sigma 2, sigma 3, sigma 4 anything. But I want to take first things first. So I have taken sigma 1. I am operating the incomplete projection operator of A g on sigma 1 and I am trying to see what I get. So first one is R is E here. E operating on sigma 1 is sigma 1 multiplied by 1 is sigma 1.

What happens when C 2 (z) operates on sigma 1, what do you get? Sigma 3 multiplied by 1. That is sigma 3. What about C 2 (y)? y is here. Sigma 4, multiplied by 1, sigma 4. So you see what is happening? We are generating a linear combination. Plus what happens when x, C 2 (x) operates on it? Sigma 2. Then what happens when i operates on it, i sigma 3. What happens when sigma xy operates on it? What happens when sigma zx operates on it?

What happens when sigma yz operates on it? What do I get? I get a 2 which is outside but do not forget they are not even considered l i by j right? So essentially, if I forgot about the common coefficient, I get sigma 1 + sigma 2 + sigma 3 + sigma 4. So what is this? This is the A g SALC that I can generate using sigma 1, sigma 2, sigma 3, sigma 4, right? Understood? Now, if I want to normalize this what would be the normalization constant?

So this is your normalized SALC which has A g symmetry. So what I am saying is the example that we took earlier, xz + yz + z square. What we did is we made this the projection operator operate on it and we projected out the components that had the right symmetry. Now what I am saying is the reverse is also true. You take one of the components and make the projection operator operate on it.

Of course, you have cheated a little bit because you have not taken the complex conjugate. The complex conjugate here is the same. So what we are doing is, we are making the projection operator, so when you make the projection operator operate on a linear combination then you get the components. When you use the projection operator on the components you get the linear combination okay. But life may not be all that simple as we get to see eventually, okay. What is the, what about the next one.

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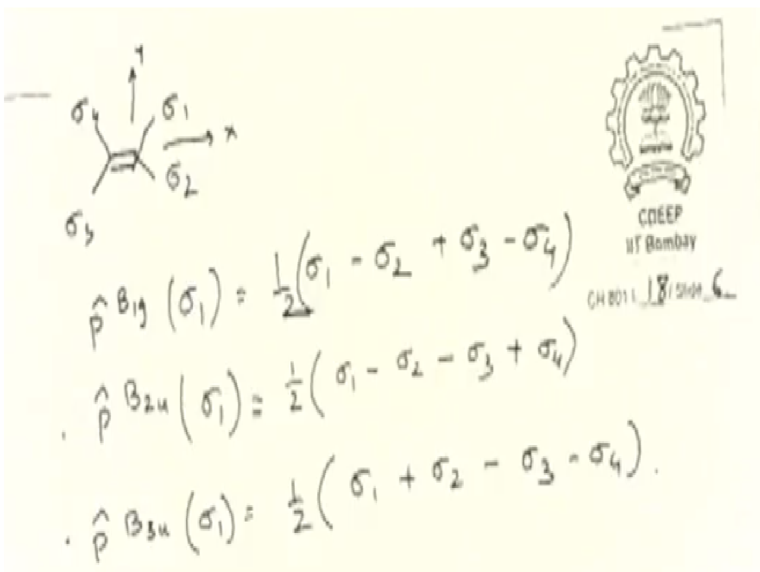

Character table is required. I hope you have not forgotten that this is x, this is y, z is pointing towards us and what I want next is projection operator, incomplete projection operator of B 1g operating on sigma 1. What I will do is I will just read the characters to you. B 1g right? The characters are 1, 1, -1. Sorry I repeated what I said. So 1, 1, -1 those are the first 3. Then fourth one is -1, fifth is +1, sixth is +1, last two are -1, -1. I will read again. 1, 1, -1, -1, 1, 1, -1, -1.

That would have been the easiest thing to say in the first place. 1, 1, -1, -1, 1, 1, -1, -1, 1, 1, -1, -1. Sounds like a mantra. So knowing the characters to be 1, 1, -1, -1, 1, 1, -1, -1 can you tell me what you get by making the partial projection, the incomplete projection operator corresponding to B 1g operate on sigma 1. Sigma 1 then sigma 3 very good. Normalization constant will be the same. Now, what is the next one? Next one is B 2u.

So projection operator of B 2u operating on sigma 1. Projection operator of B 2u. So I will tell you, what is this B 2u right? B 2u is 1, -1, 1, -1, -1, 1, -1, 1. I repeat 1, -1, 1, -1, -1, 1, -1, 1. Make it operate on sigma 1 and tell me what you get. I will write the half outside for you. Sigma 1 - sigma 2 - sigma 3 and what happens when projection operator of B 3u operates on it? Now you are guessing.

I have not even told you the characters. B 3u is 1, -1, -1, 1, -1, 1, 1, -1. 1, -1, -1, 1, -1, 1, 1, -1. I might as well write the answer. Sigma 1 + sigma 2 - sigma 3 - sigma 4. Now can you just tell me whether I say this SALC is normal to this SALC or not? So these are negative, right? Sigma 1 minus sigma 2. I know about character coefficient, Character is of course, negative character, negative -1, +1 are there. Which one, you are talking about character of i?

Character of i of B 3u is -1 and character of i of B 2u is also -1 unless I read it incorrectly. (()) (19:17) of course is -1. So this is how you generate SALC's.