Symmetry and Group Theory
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Lecture - 52
Group-Subgroup Relation

We are going to take advantage of this group-subgroup relation and we are going to work with the subgroup O, okay? So you look it up yourself what is T 1u in octahedral O h point group becomes a T 1 group in the O point group.

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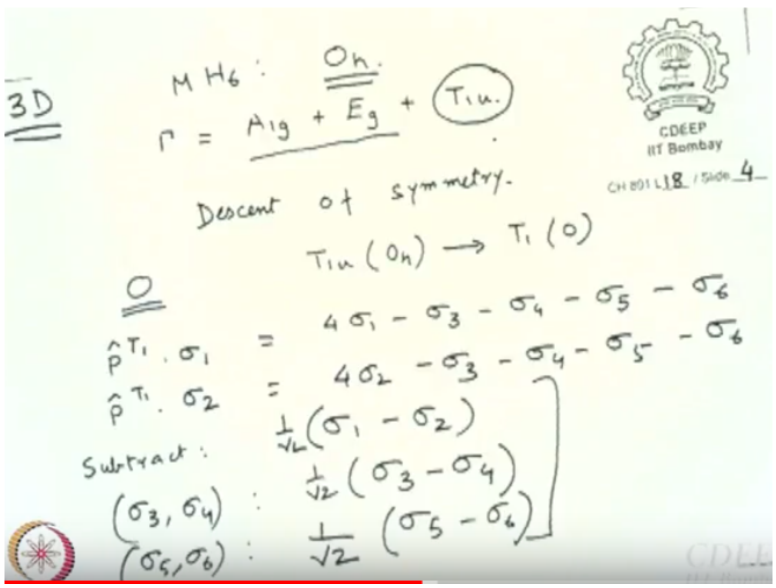

So what I need to do is, I need to make the projection operator of T 1 operate on say sigma 1. Projection operator of T 1 to be operated on sigma 1, okay? I hope you have drawn the diagram?

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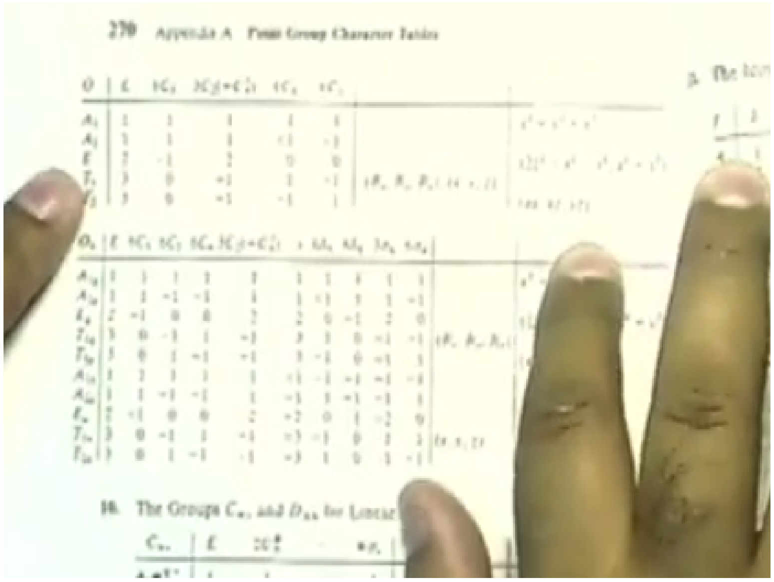

This is the point group O, okay? But I had promised that I will not make you work out the projection operators for anything after the first problem, right? So I will just give you the answer. But I strongly suggest that you please work it out yourself later on. Otherwise you will not get the practice. So I will just tell you that when the projection operator of T 1 operates on sigma 1 then you get 4 sigma 1 – sigma 3 – sigma 4 – sigma 5 – sigma 6 okay.

So that seems to be one of the SALC's. It could be one of the SALC's or it could be a linear sum of some SALC's okay? How many SALC's would be there? 3. Why 6? T group right. T is 3-dimensional, T 1. I am only talking about T 1u. I am not really talking about A 1g and E g anymore. I am focusing on T 1u only. So you should have 3 SALC's of T 1u symmetry and this kind of looks too big, T 1u symmetry but we will see.

Now, I will tell you that when P T 1 operates, of course I only have 1 right I have to find the others. So what I will do is I will make this projection operator operate on sigma 2 now and the answer I get is 4 sigma 2 – sigma 3 – sigma 4 – sigma 5 – sigma 6. So now tell me are they orthogonal to each other? Minus multiplied by minus fortunately or unfortunately is plus. So - sigma 3 * - sigma 3 is + sigma 3 square which is 1, right?

Sigma 3 etc. is all normalized. Sigma 4 * sigma 4 is +1. - sigma 5 – sigma 5 is +1. - sigma 6 * – sigma 6 is +1. And all other terms are 0 right. Because sigma 1 is orthogonal to sigma 2, sigma 3 so on so forth right. So the only terms that survive are sigma 3 square + sigma 4 square + sigma 5 square + sigma 6 square which is equal to 4, not 0 is it not? So these cannot be the SALC's.

These have to be linear sums of SALC's right? So now see if I have generated these expression by linear sums of SALC's then some kind of a linear sum of these should give me back the SALC, right or wrong? Let us say x = a * A + b * B okay. Y equal to now I am at a loss. What will I write? Small a dashed capital A + small b dashed capital B okay? So then x and y are linear sums of A and B.

Can you not write linear sums of x and y so that you will get A or B? Understand what I am saying? What I am saying is this. We will use another paper.

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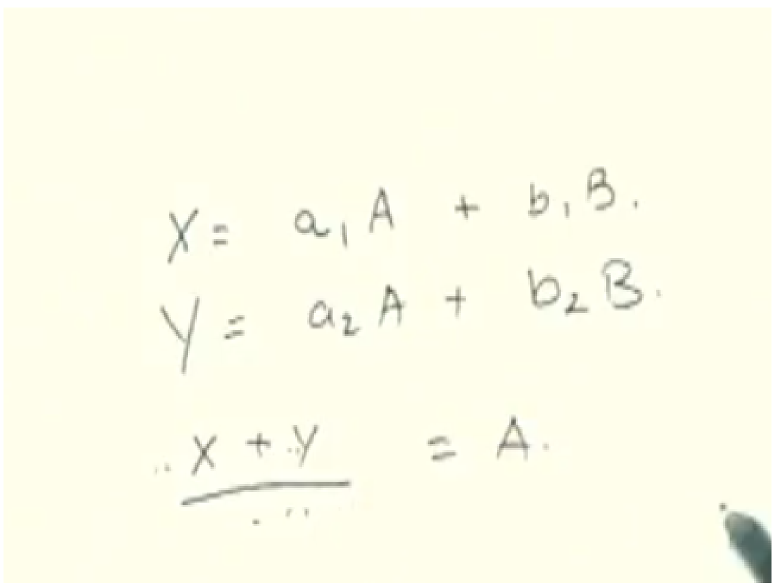

If x equal to and now that I am a little wiser a 1A + b 1B and y = a 2A + b 2B. Can I not write x + y something into x plus something into y divided by something and get A? And then something into x minus something into y divided by something equal to B. That is what I will try to do. And looking at this what I am inclined to do is subtract one from the other. You subtract it because if I subtract one from the other then I am left with only 2 terms.

Minimum energy pathway. Let us subtract one from the other and let us see what happens. What do I get if I subtract one from the other? I get sigma 1 – sigma 2. What would be the normalization constant 1 by root 2. Now, you try doing this same operation with sigma 3 and sigma 4. What you will get? What is left? Sigma 5, sigma 6. If you try to do it with sigma 5 and sigma 6, satisfy yourselves because if I try to work this out I will definitely dissatisfy yourself at quarter to seven you get sigma 5 – sigma 6 okay. So maybe these are my SALC's.

Let me check. What is the first condition? They should be orthogonal to each other. Are they orthogonal to each other? Of course they are. What would be the second condition? They should conform to T 1 symmetry or I might even want to go back to the original group and say that they should conform to T 1u symmetry. Understand what I am saying? I am saying that they should conform to T 1 symmetry in O point group that is T 1u symmetry in O h point group. So we can check whether that happens or not?

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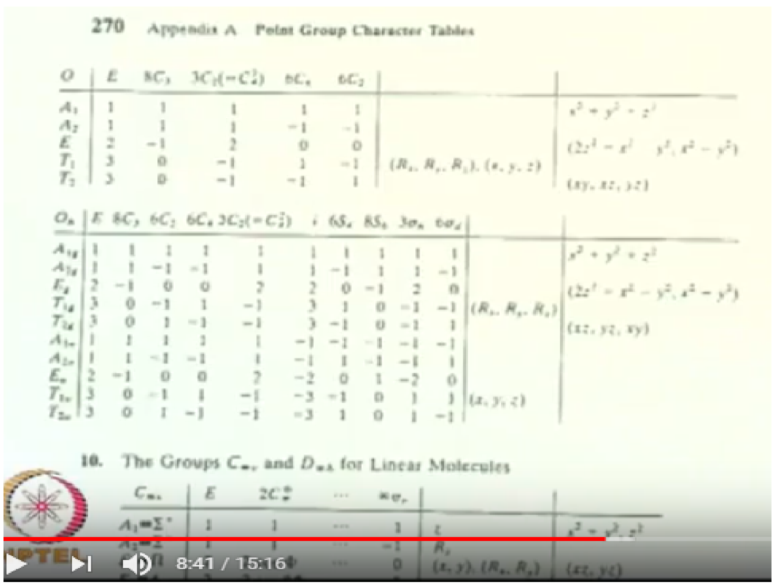
270 Appendix A Point Group Character Tables

O	E	$8C_3$	$3C_2(=C_4^2)$	$6C_4$	$6C_2$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	$(R_x, R_y, R_z), (x, y, z)$	
T_2	3	0	−1	−1	1		(xy, xz, yz)

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		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
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	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

10. The Groups $C_{\infty v}$ and $D_{\infty h}$ for Linear Molecules

$C_{\infty v}$	E	$2C_\infty^\Phi$	···	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	···	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	···	−1	R_z	
[illegible]	[illegible]	[illegible]	···	0	$(x, y), (R_x, R_y)$	(xz, yz)

You can read could you not? Let us work in the O point group. What is it T 1 is it not? T 1. So remember what they are, sigma 1 – sigma 2, sigma 3 – sigma 4, and sigma 5 – sigma 6. The character of E of course is 3. There is no issue with that. What is the character of C 3? That also is very easy to see. If you apply C 3 then what happens? Then what happens, sigma 1 becomes, no matter which C 3 you apply, all will change places, right?

So sigma 1 – sigma 3 will not remain sigma 1 – sigma 3. It will be something else minus something else. So they change places. Character is going to be 0, right? Then what is next C 2.

What happens when you apply C 2? Sigma 1 and sigma 3 interchange. Sigma 2 and sigma 4 interchange. What do you get? But what does not interchange? 5 and 6 do not interchange. So what is it that you get? Sigma 1 becomes sigma 3, right?

So sigma 1 – sigma 3 becomes what? Sigma 3 – sigma 1, right? No, what am I saying? So sigma 1 sigma 3 remain the same, right? So what will be the character, 1? Right. So sigma 1 remains what it is. What about sigma 3? Changes and becomes what? And then? So can you work that out, work out that matrix and see what the character will be?

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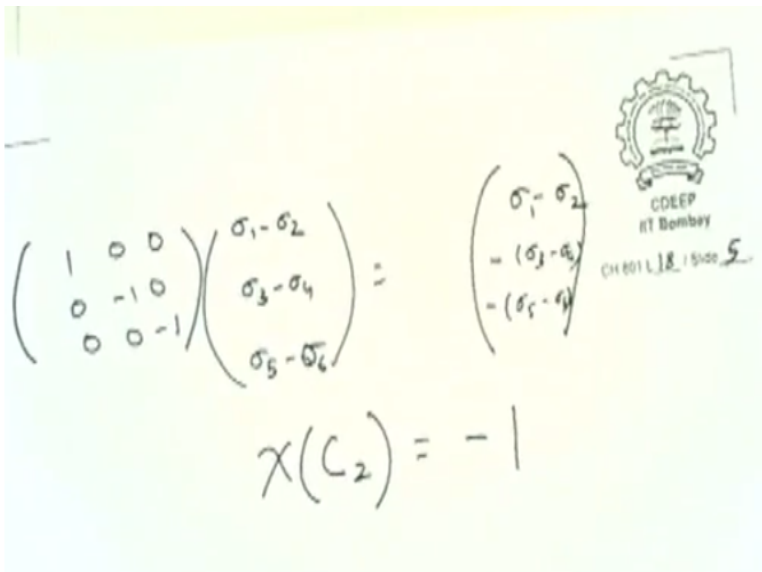

That becomes what? What are we applying? You are applying C 3, C 2. If you apply C 2 then what happens? Sigma 1 – sigma 2 remains sigma 1 – sigma 2. What about sigma 3 and sigma 4? What does it become? Sigma 4 – sigma 3 which is – sigma 3 – sigma 4. Sigma 5 – sigma 6 becomes – sigma 5 – sigma 6. So what is the transformation matrix? 1, 0, 0; 0, -1, 0; 0, 0, -1. What is the character? This is what, chi C 2 is -1, right? Now see, oh you should have told me.

So this is what I have written, alright. The character is -1. This is like Gulliver going from the land of Lilliput to the land of Gargantuan or whatever the name was. Gulliver's Travels, has 2 right? So see we got -1. What happens when you apply C 4? You work it out you will get character of 1. When you apply C 2 you will get character of -1 okay? So you can satisfy yourself that these 3 actually belong to T 1, okay?

So what we have learnt then is that we have learnt how to use, how to generate SALC's for irreducible representations of a higher dimensionality and while doing that we have learnt how to use the group subgroup relationship. Tomorrow we come back and so far we have kind of been not so ambitious. We have restricted ourselves to discussion of sigma bonds. So tomorrow we make up for that and we discuss only about pi bonds.

And the homework problem that you have, self-study problem that you have is actually sigma + pi both I think, okay? So we discuss pi bonds tomorrow and after that, are we all familiar with Huckel's theory? Huckel MO, okay. Maybe what we will do is we will recapitulate very briefly and let us see if we can discuss naphthalene tomorrow.

Let us come at 10:30. Tomorrow, our agenda, the thing is I want to discuss as much of naphthalene in 1 day as possible. Otherwise it is no fun, okay? Please go through Huckel theory if you can tonight from some simple book, McQuarrie and Simon or some such place.