Symmetry and Group Theory
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Lecture - 48
Projection Operators - Continued

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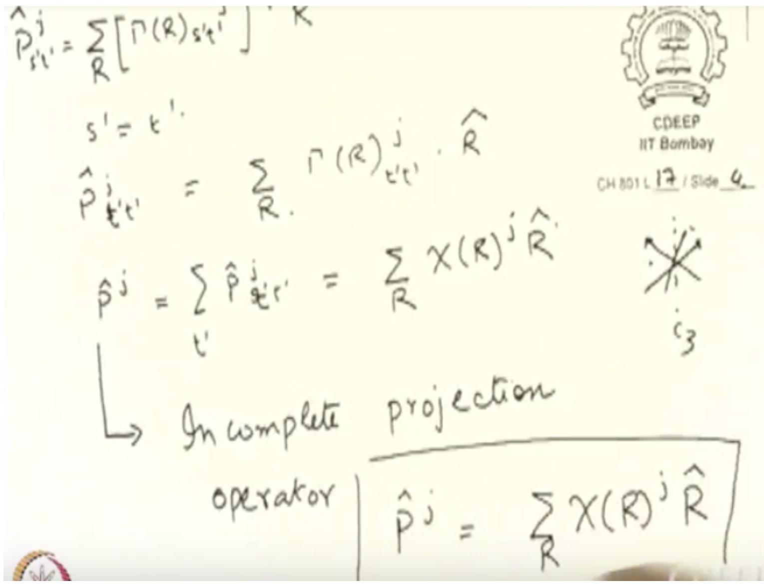

So what I am saying is, this is your complete projection operator, sum over R gamma R s dash t dashed j star R hat. Yes sir, yeah so that is C 3 operation. C 3, so let us see, let us say we are talking about the p x, p y, p z orbitals right and we are talking about a C 3 operation that is like this. P x, p y, p z and this is your C 3 operation. Then what will happen if you apply C 3, p x becomes p y, p y becomes p z, p z becomes p x.

So if you make this R hat operate on p x, the result you get is p y. This is only a matrix element and here what we do is you actually make the symmetry operation operate on it, see what is the transform function you get. That is what R does and then you simply multiply it by the symmetry operation. Then you sum it over all R. but let me take a special case. So this is your, what will I call it, I will call it P j s dash t dash, right?

So what happens when I write s dashed = t dashed. You get P j s dash t dashed is equal to sum over R gamma R, what should I write now? This is j. What will I write? Can I write t dash t dashed or not? And what I will do is I will not take the trouble of writing the star anymore. The star was just to emphasize that you might have to work with imaginary matrix elements as well, okay. For now let me just go with this, not write the star.

So consider that we are working only with real quantities multiplied by R hat. Looking at this, how do you think you can simplify this a little more. We will see the point in a minute. So this is s half set of that is it not? So right now what we have is we have the complete projection operator. The trouble of working with a complete projection operator is that you will have to work this out for every s dashed every t dashed, right?

Each and every matrix element and it is not as if it is not doable. So this is an example where they have done it.

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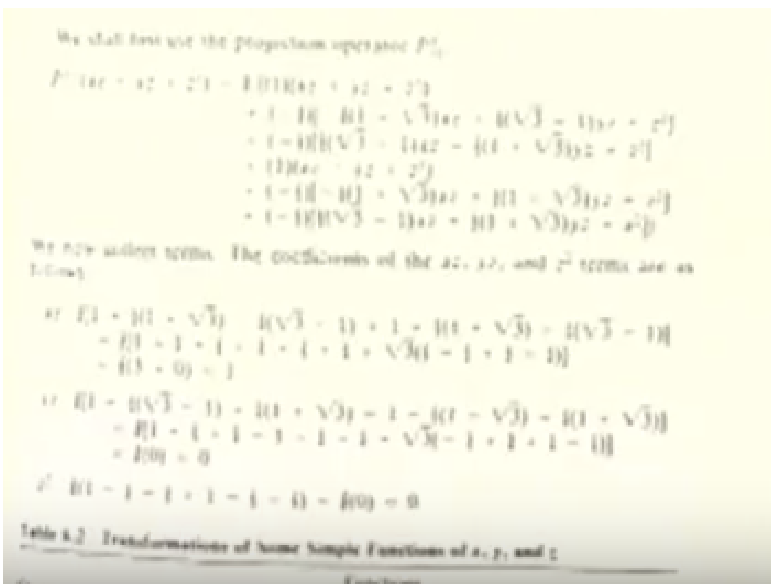

For point group C 3v, what they have done is they have taken the total matrix element and they have worked out the complete projection operator and made it operate on some arbitrary function xz + yz + z square and they have shown what has happened. The trouble is that there are 2 way numbers here. So I want to make it a little simple. So let us see. So when you see something like this, gamma t dash t dash j. What is that you are inclined to do?

What is gamma t dash t dashed? Diagonal elements. What happens if I add all the diagonal elements? We get the character. What is the advantage of having the character? You can use the character table. It is as simple as that, okay? So what I will do is I will define P j = P j s dash t dashed sum over sorry what am I doing? Sum over t dashed P j t dash t dashed is equal to, I think you will allow me to write sum over R chi R of the jth irreducible representation multiplied by the symmetry operation.

And to satisfy Shantanu, we are going to name this the incomplete projection operator. It is incomplete because you are not considering the, not considering all the matrix elements, you are only considering the character, okay? But that is an advantage, not a disadvantage because so think of a 3 by 3 matrix, if you work with a complete projection operator then per matrix how many numbers would you have? 9, right?

Instead of that if you work with the character, how many numbers would you have per matrix? 1, only the character right? That is the advantage of using an incomplete projection operator and it does the same thing. So remember this is what is going to be very useful for us for the rest of our course, P j equal to sum over R chi R j R hat. If it is C 3v, for the first basis A 1, Z is a basis. For A 2 R z is the basis. So the fun here is this. See what they have done.

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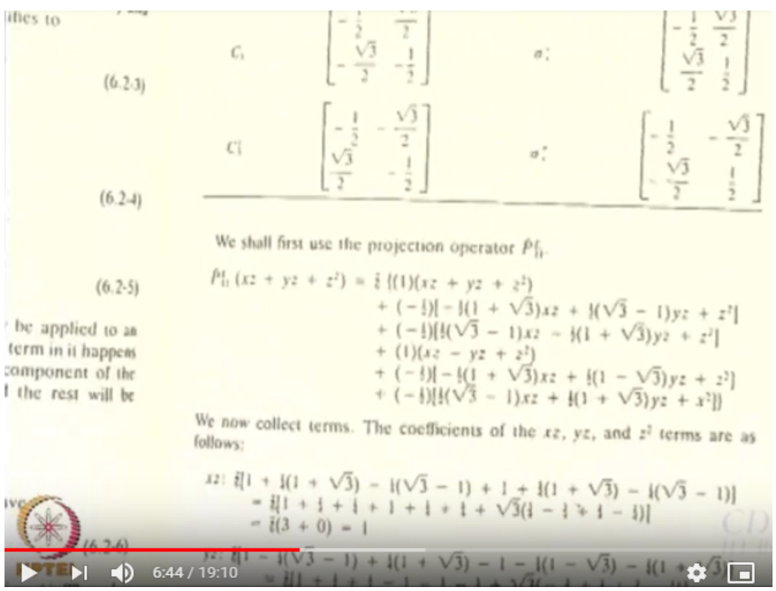

We will also work this out but using the reduced, can you read? Now? Now see what they have done is, they have worked with the complete projection operator. For that they need all the matrix elements, okay? With that, they are working with some arbitrary function xz + yz + zx. This is what I was saying, linear combination, okay? So roughly about this linear combination; xz + yz + z square. Let us quickly look at the character table and see where they belong.

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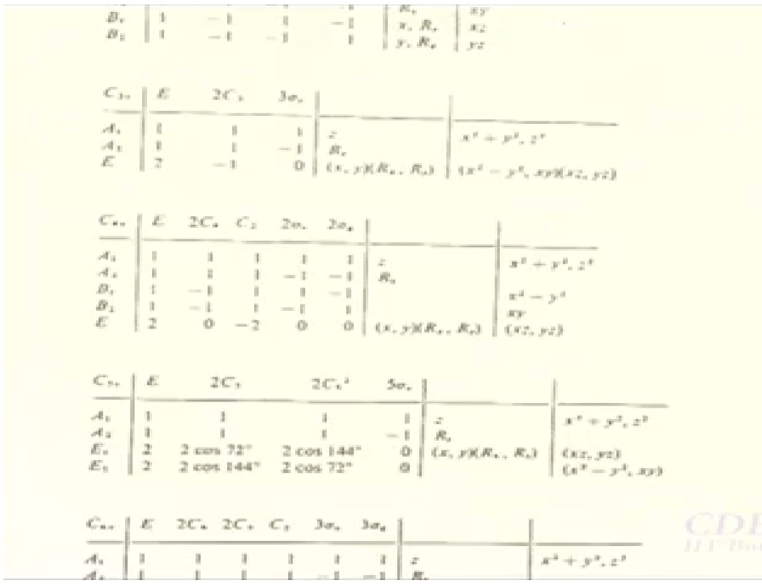

Where does xz belong? Xz and yz belong to E. Can you see or not? Xz and yz jointly form the basis for E, right? So xz has E symmetry, yz also had E symmetry. What about z square? Z square is A1, okay.

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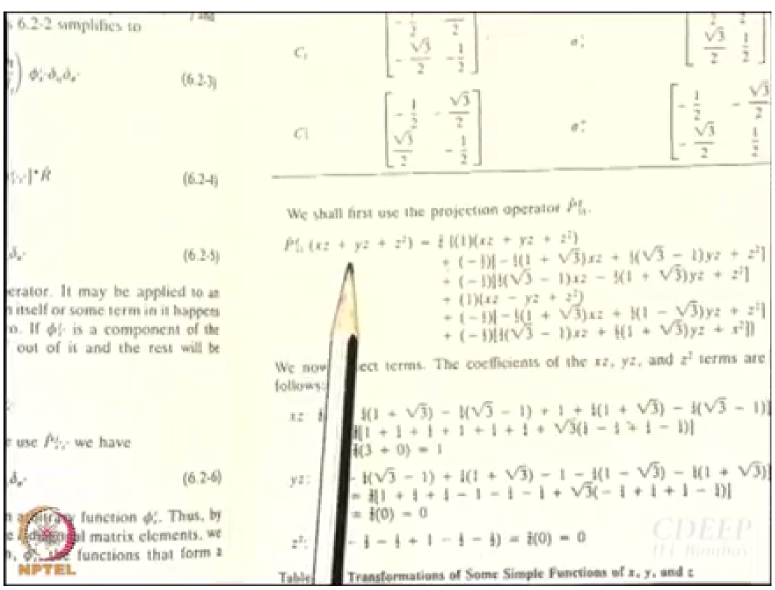

So I am taking, they have taken a sum of linear combinations of 3 terms, 2 of which have E symmetry and z square has A1 symmetry. And they have made this projection operator operate on it, okay? And then, since they have worked with whole matrices, they have a lot of numbers. We will have a little less numbers. They have done that and see what they had got. Also, what they have done is they have used P 1 1 E. So I have to do it for every matrix element is it not?

So this is P 1 1 E. they have used that and they have got the coefficient of xz to be 1, coefficient of yz to be 0, coefficient of z square to be 0. So, so on and so forth they have done all this and finally they see that the coefficients of xz and yz are nonzero whereas the coefficient of z square is 0. But the problem is that it is a longish route, okay? Let us use the incomplete projection operator on the same thing. Let us see the least one. There it is throughout 0 yes, okay. Let us take this now.

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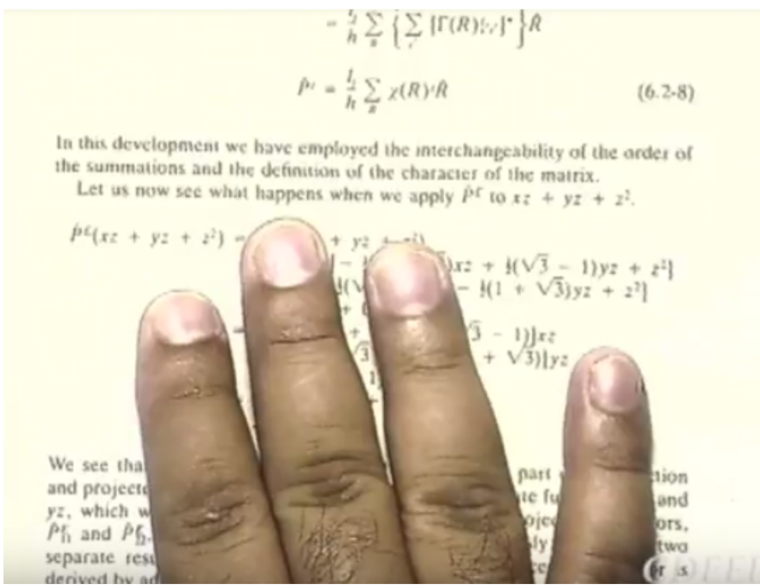

$$\hat{P}^{i} = \frac{l_i}{h} \sum_R \chi(R)^* \hat{R} \qquad (6.2\text{-}8)$$

In this development we have employed the interchangeability of the order of the summations and the definition of the character of the matrix.

Let us now see what happens when we apply $\hat{P}^E$ to $xz + yz + z^2$.

So this is the expression of the incomplete projection of character. It is, the only difference is that they want to give l i and l i h and I am not interested. Sum over R chi R j R right? Now, I want to use this on xz + yz + z square. Want to work this out?

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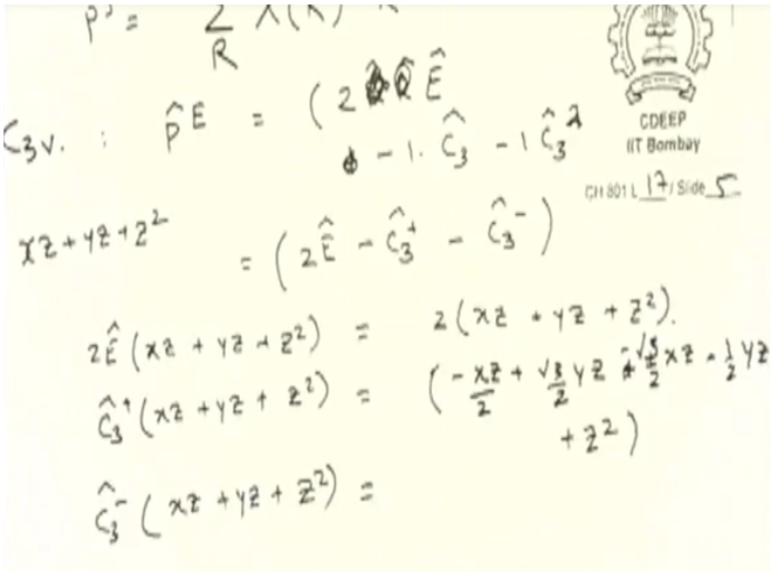

P superscript j hat is equal to sum over R chi R j R hat. So what I want to do is for C 3v I want to use P E. You understand what is the meaning of P E? Projection operator corresponding to the E symmetry species, E i R. E irreducible representation the third one, the 2-dimensional one okay got it? So what will that be equal to? 2 R hat what is the character of E? What is the character of identity in the E representation? Character of E and E would be confusing.

Identity in E representation? 2. So instead of chi E in the E representation I have written 2 right? In fact, I can take the R out also maybe. No I cannot. 2 R plus what is the character of the second one, what is the second one? C 3 what is that? So I will write E, 2 E something like this instead of R. I should also, otherwise you will get confused, E. What is the second one? C 3 - 1 right? So - 1 * C 3. What will be the next one? No.

It will be -1 into C 3 inverse or C 3 square. Do not forget 2 C 3 means C 3 and C 3 square. They belong to the same class. That is why they have the same character. So they are hidden together in the character table. But in applications like these, you have to consider C 3 as well as C 3 square understood. Yes, of course. See, think of x once again. X you rotate by 120 degrees, you will get some x intercept some y intercept.

If you rotate by 120 degrees more the x intercept, y intercept not intercept x component y component will be different no? So it is definitely going to be different. So let me write it in a little less untidy manner. 2 E hat - C 3 + hat - C 3 - hat. Or I could have just written C 3 and C 3 square. This is what I have to operate on xz + yz + z square, okay? Can you do this and tell me what you get? Let us see.

2 E operating on xz + yz + z square is equal to what? 2 * xz + yz + z square. C 3 plus operating on xz + yz + z square. What will it be? C 3 plus operating on z is z. C 3 plus operating on z square is z square, right? Because C 3 is along z direction. So all you have to consider is how this x and y transform is it not? So what will it be? C 3 plus operating on x what will you get? -1/2 * x + root 3/2 y. I will just write the z's, okay?

Then, so xz is taken care of. Then what about yz? How does y transform? +1/2 xz then +1/2 xz y. How does y transform? Y. Y has that root 3 by 2 x is it not? Okay I am not very good at remembering these things. So you need to help me here. Minus root 3/2 xz then -1/2 yz. What I remember is the character is -1 okay. So diagonal elements have to be -1/2 and -1/2 and then where it is plus root 3/2, where it is minus root 3/2, I have to work out, okay? So this is done and then z square? I will leave it as z square, fine?

And then C 3 minus operating on xz + yz + z square. You can work that out. Can you work that out or not? So just work it out and satisfy yourself that this is what you are getting.

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In this development we have employed the interchangeability of the order of the summations and the definition of the character of the matrix.

Let us now see what happens when we apply $\hat{P}^E$ to $xz + yz + z^2$.

$$\begin{aligned}\hat{P}^E(xz + yz + z^2) &= \tfrac{1}{3}\{(2)(xz + yz + z^2) \\ &\quad + (-1)[-\tfrac{1}{2}(1 + \sqrt{3})xz + \tfrac{1}{2}(\sqrt{3} - 1)yz + z^2] \\ &\quad + (-1)[\tfrac{1}{2}(\sqrt{3} - 1)xz - \tfrac{1}{2}(1 + \sqrt{3})yz + z^2] \\ &\quad + 0 + 0 + 0\} \\ &= \tfrac{1}{3}\{[2 + \tfrac{1}{2}(1 + \sqrt{3}) - \tfrac{1}{2}(\sqrt{3} - 1)]xz \\ &\quad + [2 - \tfrac{1}{2}(\sqrt{3} - 1) + \tfrac{1}{2}(1 + \sqrt{3})]yz \\ &\quad + (2 - 1 - 1)z^2\} \\ &= \tfrac{1}{3}(3xz + 3yz + 0z^2) \\ &= xz + yz\end{aligned}$$

See they worked it out here. See what is the advantage? Well we will come to the advantage. Once you work this out, finally this is what you get xz + yz. All the terms in z square cancel off, okay? So what I have done essentially? I have taken a linear sum of 3 terms, 2 of which have E symmetry and the third of which does not have E symmetry.

When this incomplete projection operator corresponding to E symmetry operates on this linear sum what it does is that it annihilates the term that does not belong to that symmetry species and it retains the term that belongs to that symmetry species. So it projects the terms with the desired symmetry. That is why it is called the projection operator. No, it depends on what we need. If you need them to be normalized like what we need our SALCs to be then you work out the coefficients. And it could have been 2 xz + yz or 2 xz – yz also.

But that let us not get into that. We will get the crux of the matter. That I have taken a mixture of terms belonging to 2 different symmetries and when I have used the projection operator corresponding to PE then the term that is not PE, not, that does not have E symmetry gets annihilated and the terms that have E symmetry survive. So that is the magic of projection operators.

"Professor - student conversation starts" Sir, if I have to take xy and if the coordinates gets transformed can we take it as a product of the 2 transforms. Yeah, yes. That we worked out right once, direct products. When we talked about direct products that is what we did. **"Professor - student conversation ends"**.

Alright, are you all okay with this? So now you have got Aladdin's genie. Now you can do whatever you want.