Symmetry and Group Theory
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Lecture – 26
Irreducible Representation using GOT

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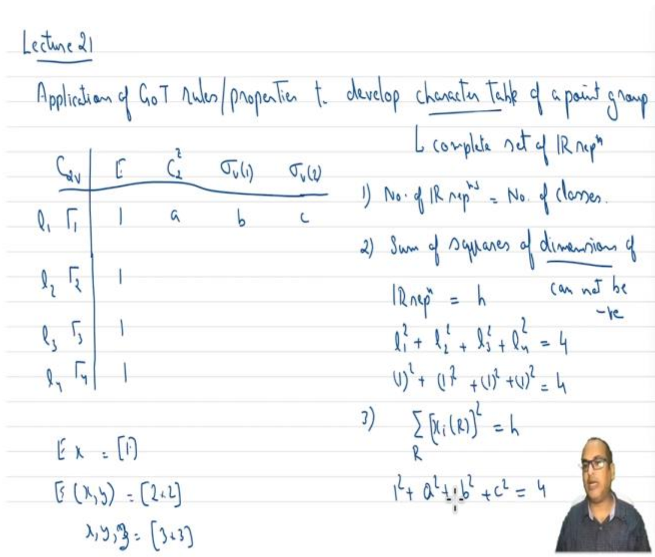

So, in the last class we have seen the 5 properties of great orthogonality theorem. Let us now try to see how to apply these properties. So, now we will see application of GOT rules or properties to develop character table. So, at this point I will mention that the character table is a complete set of irreducible representations of that particular point group and then many more things we will deal with that what all character table include but basic thing is that it should have the complete set of IR representations.

So, let us see by taking example how to use this great orthogonality theorem rules to actually develop all the IR representations, without doing any symmetry transformations or symmetry operations. So, let us take an example of our favorite molecule which is water because we have been dealing with that. So, we know all the irreducible representations already. So, C2z, sigma-V1, sigma-V2.

As I said, I will not even worry about what my basis sets are. So, I will just start from the basic rules. So; one of the properties says that the number of IR representations is equal to number of classes. So, this property tells me that there are 4 classes. So, this property tells me that there has to be 4 irreducible representations. So, I will just write tau 1, tau 2, tau 3, tau 4. So, at least I know that there has to be only 4, and not more not less, and it has to be only 4 irreducible representations. So, now we have to find out these 4 representations using this.

So, now another rule which is I think the property 1 which we said, which says the sum of squares of dimensions of IR representations is equal to h. So, what does it mean? So, we have 4 representations. So, that means each one has an associated dimension. Let us call these dimensions as l 1, l 2, l 3, 1 4. So, now sum of the squares of these dimension that is l 1 square + l 2 square + l 3 square + l 4 square = h, h is the order of the group which is 4 here.

Now what are the options or what are the possible solutions for this. So, the only possible solution for this particular equation so we have to use it hidden trial there are 4 variables and only one equation so there is no other possibility to solve but by doing hidden trial so what is the hidden trial say the only possible solution is if we do 1 square + 1 square + 1 square + 1 square. Now you can see that it can also take negative as the values.

So, it can take the negative values but because these are dimensions so dimensions cannot be negative. So, it has to take only positive values. So, dimensions cannot be negative. So, it has to take positive values only. And we also know that the character under E represents that dimension. Why do we say that? So, let us say if we are applying E on a unit vector then I will get a matrix for 1 cross 1 matrix.

If I am doing E operation on a basis set which has x and y I will get a 2 cross 2. So, in this case if I am getting 1 cross 1 the dimension is 1. If I am getting 2 cross 2 matrix that trace is 2 and that is the dimension. If I am having a basis set as x, y, z that is 3 basis set. So, I will get 3 cross 3, identity matrix for which the trace will be equal to 3 and the dimension will also be equal to 3. So that means that trace under the operation E represents the dimension.

So, now we know that all the dimensions are 1, 1, 1, 1. So, we can write the trace under E as 1, 1, 1, 1. So, from 16 unknown elements we have solved for 4 in one shot. So, I hope that is clear. So, again I am saying sum of squares of dimensions of an IR representation is equal to h which gives me l 1 square + l 2 squared + l 3 + square + l 4 square = 4. The only option the only solution is 1, 1, 1, 1. Because we cannot take negative values because these are dimensions and as we know that the dimensions are nothing but that trace of matrix under E.

So, we can safely write 1, 1, 1, 1 here. So, you can write it as a matrix or as a trace now because it is a 1-dimensional representation so it does not matter whether you are writing it as a trace or a matrix but in this case, we are actually determining the trace. Now for our next property, so next property tells me which is the property 3 rules property 2 actually which tells me that summation over all R for chi i R and the square = h, that is the character the sum of square of character over all operations will be equal to h.

So, this again gives me a value, so let us call this as maybe we already know this so a, b, and c. So, this tells me that 1 square + a square + b square + c square = 4. Now you do not have a criteria that it cannot be negative. So, now a, b, c can be positive or negative. So, one we already know so now a, b, c can take all the positive values all 3 can be positive all 3 can be negative and so on or 2 can be positive or 1 can be positive or let us see what are the possible solutions here. So, let us say let us consider the first solution as a = b = c = 1 that is a valid solution. So, we can populate this table.

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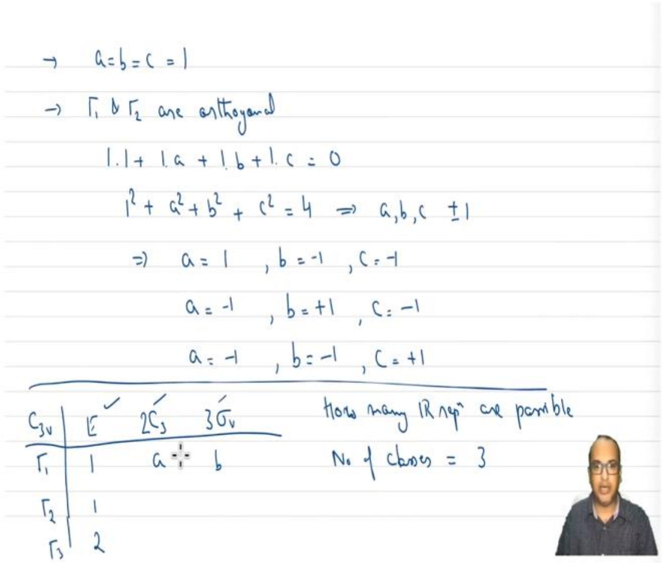

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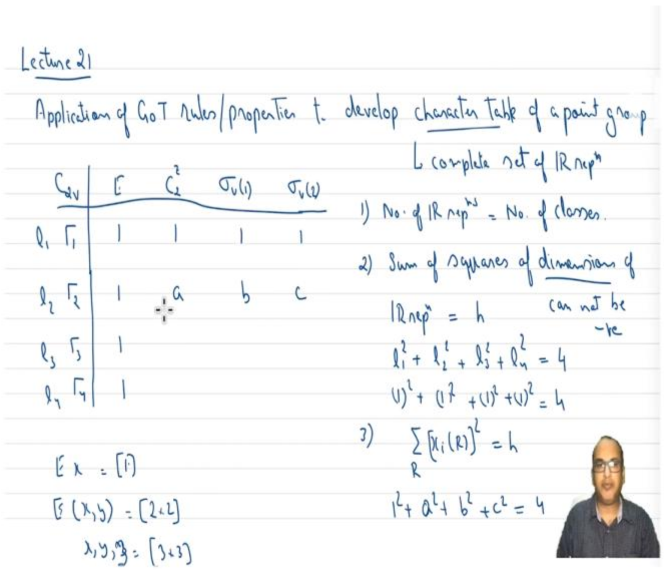

As so let me remove this and write down this as 1, 1, 1. Now let us say that let me write a, b, c over here now. So, now we need to solve for this. Now there is a condition which also tells me that tau 1 has to be tau 1 and tau 2 are orthogonal that means the product of these this product plus this product plus this product plus this product equal to 0. So, now we know that 1 into 1 + 1 into a + 1 into b + 1 into c = 0.

Now what are the options to solve this equation now again, and we know that 1 square plus a squared + b squared + c square also so now we have 3 unknowns and 2 equations a square plus b square this condition still holds. This is the orthogonality condition and this is the condition where I said that the sum of the square of characters should be equal to order of the group. So, solving this how do we solve this?

So, this particular tells me that a, b, c can take the values as +-1, nothing else is possible but this one restricts the values how does it restrict that 2 of the summations or 2 have the products have to be positive 2 of them have to be negative so that the product is equal to zero. So, sorry this one is not zero. This one is four. So, this tells me this implies that if a is positive b will be negative and c will be negative.

I can say that a is negative then b is positive + 1 and c -1. I can say that these are the possible 3 solutions b is negative and c is positive no other solution is possible to even try this out which will satisfy all these 3 solutions will satisfy these 2 equations. So, this implies that.

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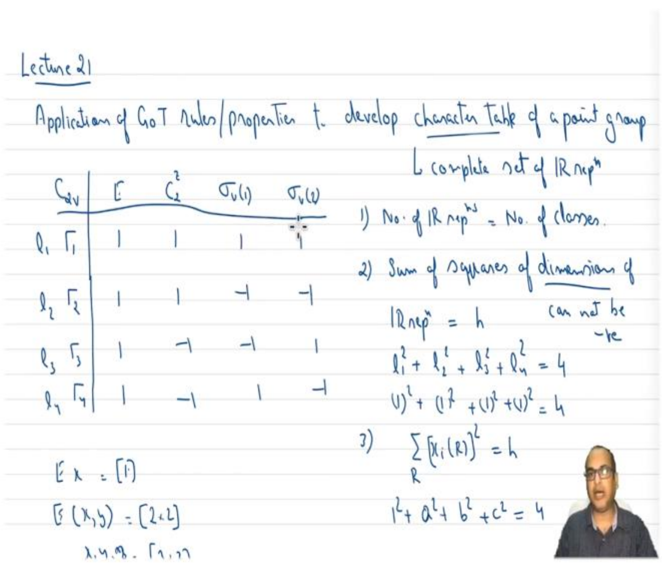

I can populate this table as 1, -1, -1, -1, -1, 1, -1, 1, -1 and now you must appreciate this fact that when we did unit vector transformations, we got this particular character table while doing symmetry operations and looking at its effect onto x, y, z and Rx, Ry, Rz. So, here we have not done any of these operations or we have not considered the basis set we have not considered the molecule also we have just worried about the solutions of this using the rules or properties of great orthogonality theorem.

So, I hope this is clear so now let us take another example. So that it goes into heads nicely. Consider C3v weeks we have seen this example also. So, C3v has E, C3 and sigma-V. So, now that we are dealing with trace so we will only use one of the class elements and will not bother about rest of the class elements because the traces are seen. So, now first of all; how many IR representations are possible here? So, number of classes are 3. So that means number of irreducible representations are also 3, that is defined by the number of classes because you have 1, 2 and 3 classes. So that means you have tau 1, tau 2, tau 3.

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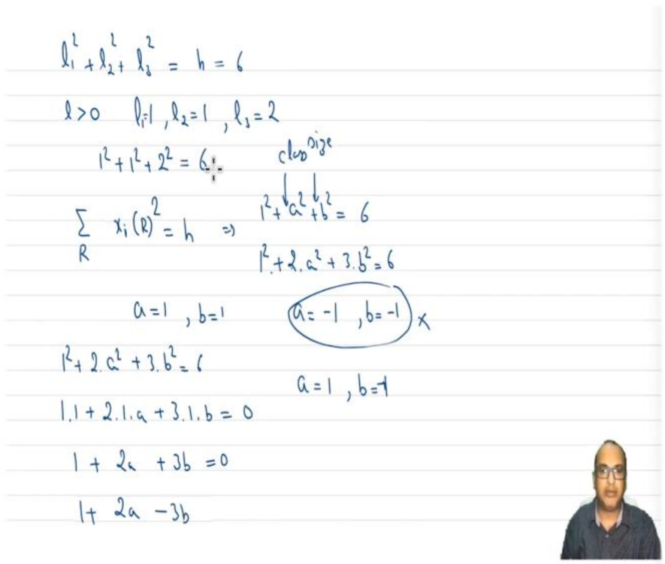

Now let us go to the first rule which says that l 1 square + l 2 square + l 3 square the sum of square of dimensions = h. What is h here? The order of the group is 6. So, now what are the options? l has to be positive, it cannot go negative. So that is one of the conditions so now by using hidden trial again we have to resort to hidden trial because we have 3 variables and only one equation to solve.

So, the only option this equation will give you four positive numbers that l 1 = 1, l 2 = 1 and l 3 = 2. So, 1 square + 1 square + 2 square will give you 6. So, now let us go back and fill this up. So, 1, 1 and 2. Now let us write this as a and b and see how do we solve this. So, now we also know that summation over all R, sum of squares of characters over all R is equal to h which tells me that 1 square + a square + b square = 6.

So, we already know this is 1 so the important thing which is not to be missed is that you also have to multiply here because we are only dealing with traces here. So, you also have to multiply with the class size here so class size goes here. So, what is the class size here class size is 2 here and 3 here. So, we are multiplying with class size because we have to take summation over all R and if you are doing only 1 square + a square + b square we are doing this is under E This is under C3 this is under sigma-V1.

So, we have not considered for C3 square and sigma-V2 and sigma-V3. So, we have to multiply this so 1 square + 2 into a square + 3 into b square will be equal to 6. Now again what are the possible solutions a and b can be positive or negative let us consider the first solution where a = 1 and b = 1. So, this satisfies the condition so you have 1 + 2 + 3 = 6. So that means we can fill over here.

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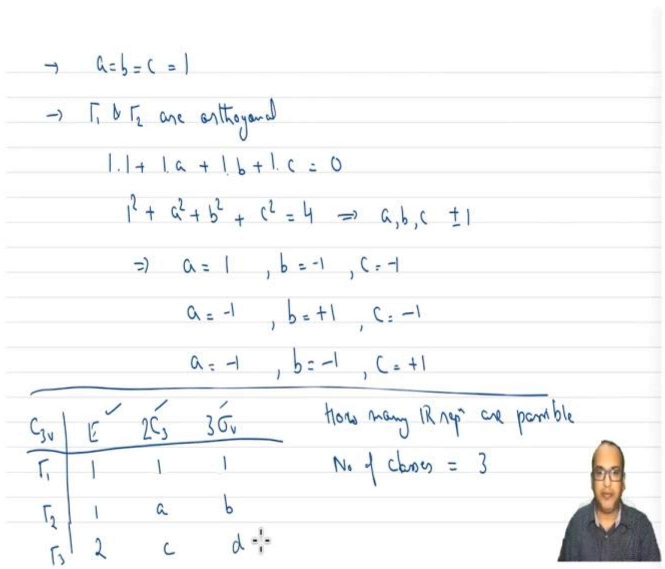

Fill the table as 1 and 1, so that is easy. So, now let us write down a, b and c, d again and apply the same conditions again. Now if we do so 1 square + 2 a square, so again multiplying with the class size, + 3 b square is equal to 6 and the second equation is 1 dot 1 + 2 into 1 dot a + 3 into 1 dot b = 0. Now this is the orthogonal condition. So, what is the solution for this if I do this what will be my solution.

So, if I have this I get 2a, 1 + 2a + 3b = 0. So, now I have to find out which number which digit a and b both can take +1 and -1 we have seen that earlier in this case like if you put +1 one also it will take the values but +1 values are already taken for tau 1. Now the negative one values can it take both a and b can be negative or not. So, let us test that let us say a is -1 and b is also -1 does it follow this equation also.

So that will give you 1 - 2 - 3 which is not equal to 0. So that means this is not a solution. So, again we are doing hidden trial because we actually we do not need to do hidden trial here. So, we can actually solve it properly because there are 2 variables and 2 equations. So, now if we do a = 1, b = -1, it does solve this. So, you can see that this becomes + 1 one and now this becomes 1 + 2a – 3b.

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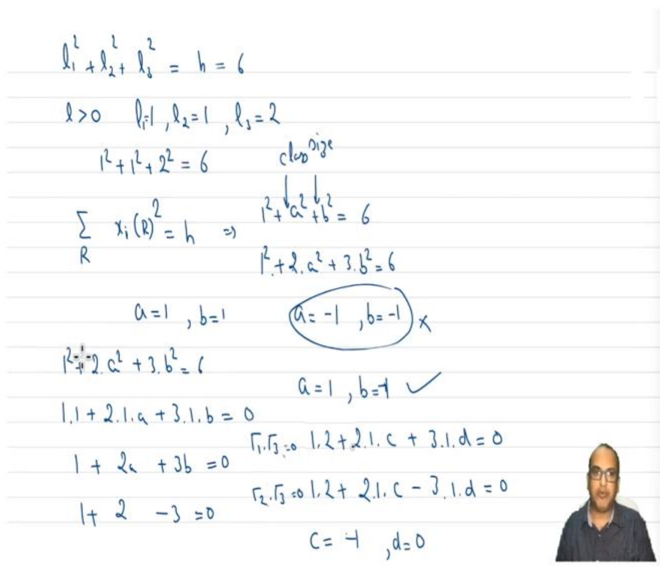

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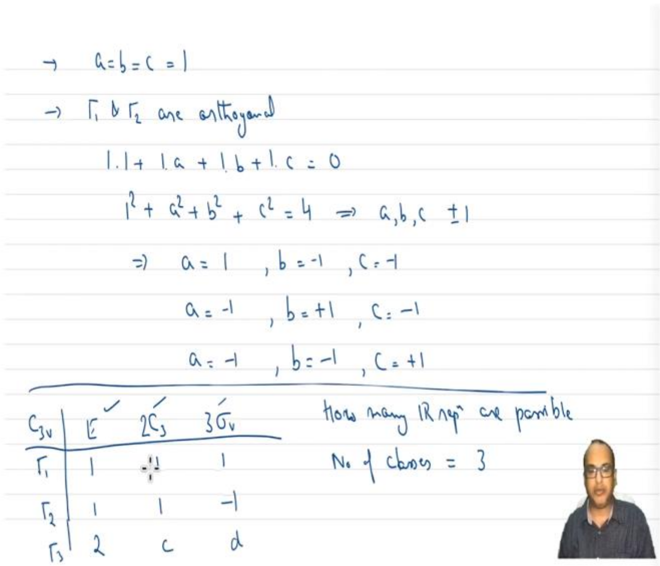

1 + 2 – 3 = 0. So, now we have found 1 more solution. So, let us go back and fill this up. So, 1 and – 1, so now we have 2 variables and we can easily get 2 equations from 2 orthogonality condition. So, let us do that so 1 into 2 + 2 into 1 into c + 3 into 1 into d should be equal to 0 then 1 into 2 + 2 into 1 into c - 3 into 1 into d = 0. So, here I have exploited tau 1 dot tau 3 = 0 and here I have exploited tau 2 dot tau 3 = 0. So, now if you have 2 equations 2 variables you can easily solve it and you can see that c will come out to be -1 and b will come out to be 0 for this.

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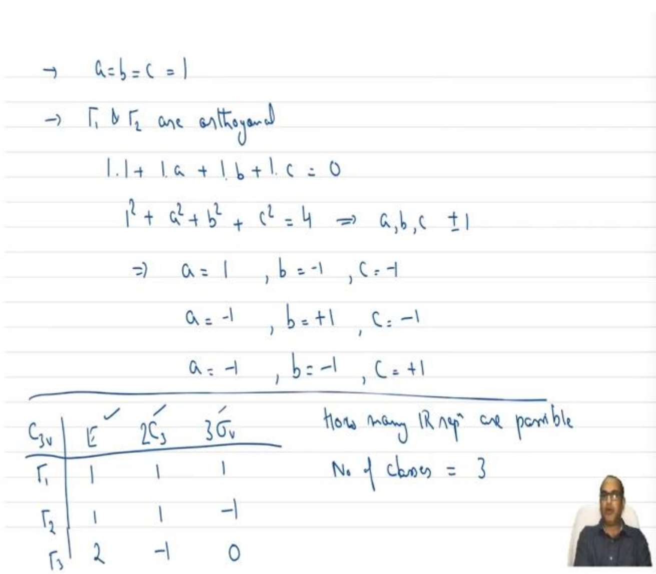

So, that means we have got this trace also. Remember we are now getting the trace not even the matrix elements directly trace. So, this is the complete character table, not complete partial character table which has complete set of IR representations why I am not saying it is a complete because we still do not know what are the basis, sets for this. We will work it out later but let us first see how to write down IR representation.

So, we have successfully written down IR representations for C2v, C3v point groups without having to worry about what are the basis sets, what is the molecule, how do you operate C3 or how do you operate sigma-V onto different operations but by just following mathematical rules we are able to write down the characters under irreducible representations. So, in the next class we will see how to go from reducible representation to irreducible representation.

So, for what we have done is we have used GOT to identify how to write irreducible representations alone. Now we will do reducible we will go from reducible representation to irreducible representation which is also important. So, we will discuss that in next class. Thank you.