**Mathematics for Chemistry**
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**Lecture - 33**

We have seen the difference between reducible and irreducible representations. Now, we are going to prove, we are going to use the theorem called the great orthogonality theorem and this will help us construct what is known as the character table of the group. So, in order to introduce the great orthogonality theorem, I will start with a few notations.

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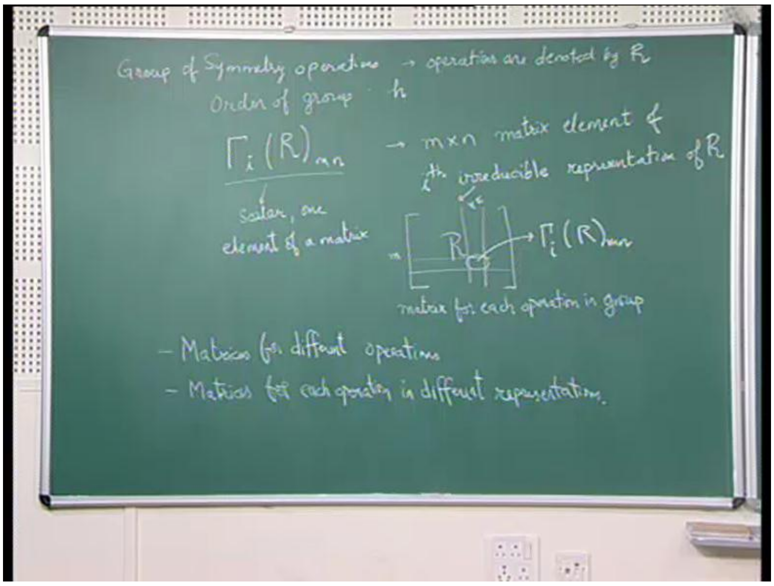


So, suppose you have a group, the order of the group, so you have a group of symmetry operations, the operations denoted by R. So, R can be any symmetry operation of the group, the order of the group will use h to denote the order of the group, so if it is a group of order 10, then h will be 10 if it is a group of order 3, h will be 3 we will use the symbol gamma i R m n.

So, this is the symbol that is used to this is the m cross n matrix m element of ith irreducible representation of R. So, this is the central object in the great orthogonality theorem, now gamma i of R m n represents the m cross nth matrix element of the ith irreducible representation of R. So, just to tell you what this means this let us look at the irreducible representation. So, irreducible representation corresponds to a matrix, so you have a matrix corresponding to an irreducible representation you have a matrix for every operation in the group.

So, irreducible at this is matrix, so matrix for each operation in group so for the ith irreducible representation you will have a matrix for R you have a matrix for all the element, for all the symmetry operations but you also have for R. So, now you look at the matrix for R, and you look at the m cross nth element so you look at the mth row and nth column and you look at this element, so this is gamma i R m n. So, this is one particular matrix element, so this whole thing is a scalar one element of a matrix, so it is just one particular element of a matrix.

Now, if you take a different irreducible representation I will have a different matrix gamma j R m n. And now the great orthogonality theorem is quite a remarkable theorem we will write down the theorem soon, but basically what it tells you is that these various matrices corresponding to different irreducible representations and corresponding to different elements; so they share some special properties. So, let us so you have matrices for different operations, you have matrices for different for each operation in different representations.

It will be a different matrix and I want to emphasize that all these representations need not have the same dimensionality. So, they might be one representation which is a 2 by 2 matrix another might be a 3 by 3 matrix or third might be a 1 by 1 matrix and all these matrices, so the great orthogonality theorem states.

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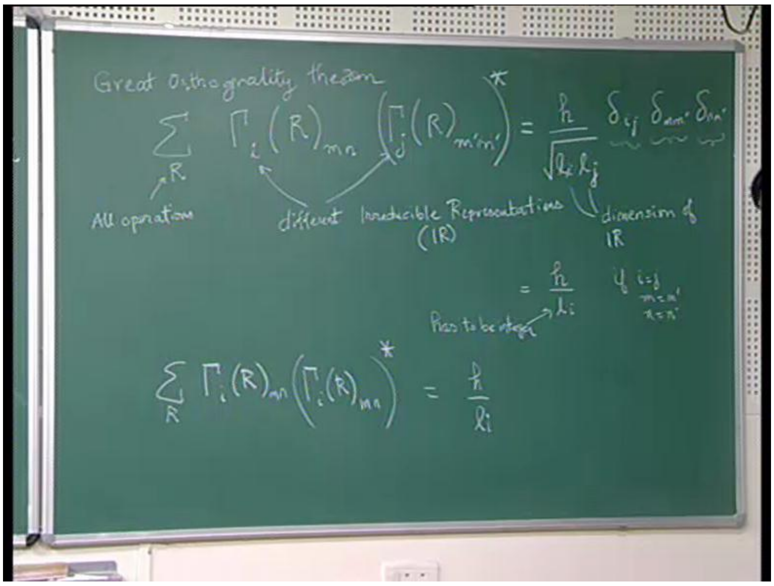


So, we will write it in the following form sum over R gamma i of r m n gamma j of r m prime, so you look at you look at the same matrix element in two different representations. So, i and j are different representations, so these are different irreducible representations. So, you look at the matrix corresponding to the same element in different irreducible representations and here you look at the m nth element here you look at the m prime n prime element.

And you sum this over all the operations, so these are sum over all operations of it and when you do this what you will find is quite a remarkable orthogonality. So, i will write this in a form and then so I will write it as h where h is the order of the group divided by square root of l i l j and I will explain what l i and l j are times delta i j delta m m prime n n prime. Now, l i and l j they refer to dimensionality, dimension of irreducible representation and I will use the symbol i R for irreducible representation.

So, l i is the dimensionality of the i th irreducible representation l j is the dimensionality of the jth irreducible representation. So, what it means is that corresponding to each irreducible representation you have a matrix and so the size of the matrix for the ith irreducible representation is l i, the size of the matrix for the jth irreducible representation is l j. And I have written it in this form, so it looks completely symmetric to changing i and j m and m prime n and n prime, so it is a completely symmetric result.

And notice that it says that so each one of these looks like an orthogonality relation, it says that that m has to be equal to m prime, n has to be equal to n prime, i has to be equal to j, if these conditions are not satisfied then the right hand side is 0. So, it is each of these looks like an orthogonality relation, so that is why this whole thing is called the great orthogonality relation, in fact, it is the product of these three orthogonality relations. So, this is zero unless i equal to j this is 0 unless m equal to m prime, this is 0 unless n equal to n prime all these three should be satisfied.

And this, so if i equal to j m and m prime are the same n and n prime are the same and this is just h over l i this is h i is is just equal to h over l i this is if i equal to j m equal to m prime n equal to n prime. Now, this is the matrix element so there is no restriction on this, this can be real, it can be integer, it can be a fraction, it can be complex, it can be negative, it can be anything. However, l i has to be an integer h is also h also, obviously has to be an integer since this is a dimension, this is the order of the group, so both of these have to be integers.

So, notice that this relation gives it looks very abstract and it does not look very practical but once we unfold this what we will do is, we will break this up into a series of relations. And then we will demonstrate the practicality of these relations. So we can we can write this in the following form we can say that suppose all these are the same i m n are equal to j m prime n prime. And we can write this as sum over r gamma i of R m n gamma i of R, this should be a complex conjugate gamma i R m n star this is equal to h by l i.

So, now you can see that you are taking the m nth element and you are just taking gamma i into gamma i star, so we are just squaring the matrix element for a particular operation and we are summing over all operations. So, essentially we are taking the same matrix element and we are squaring it over all particular operations and that gives you h divided by l i. So, we will keep this and then and then we will start trying to show how you can use this practically, before that I just want to tell you where we are trying to this, so why are we interested in the great orthogonality theorem and what is the significance.

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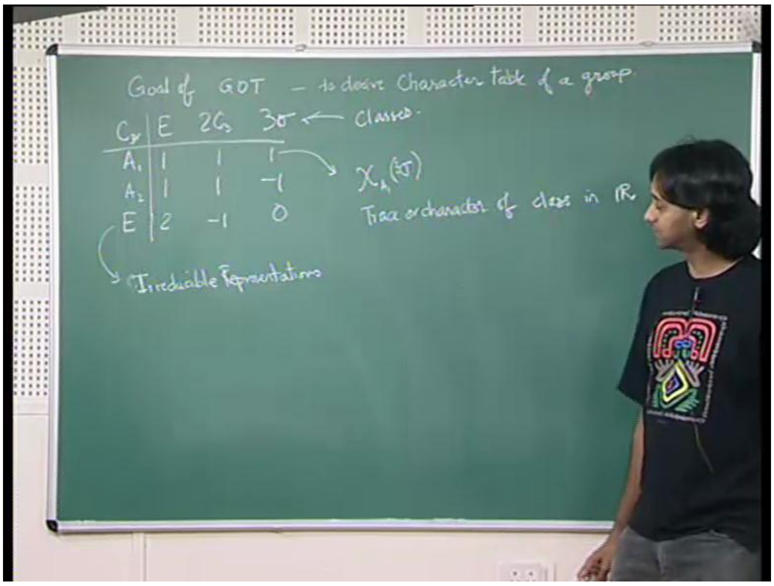


So, the goal of G O T is to derive character table of a group, so in other words we want to actually work out what the character table of any group is if you look at the character table of any group. For example, if you look at C 3 E now this has if you see the character table in any book you will see this as e that is 2 C 3 and 3 sigma. So, you will find something that is 3 sigma and then you will see something like this A 1, A 2 and E and what you will find I will show only part of the character table, so you will find one 1 1 minus 1 then you will find 2 minus 1 0.

So, what you find here in the character table these are the classes no, these are the irreducible representations and these are the classes. So, what we say is that C 3 has 3 classes the identity element is in a class, there are two elements in this class C 3 and there are 3 elements in class sigma, 3 elements belong to a class. And then what are these numbers, this number is nothing but the character now the character is also the trace. So, I will say trace or character of class in irreducible representation.

So, this refers to the character of sigma, so any element all these 3 elements since they belong to the same class they have the same character. So, this is the character of sigma in this A 1, so character of sigma which is the element of the class in A 1 or if you want you can write 3 sigma, since all these 3 sigma's have the same character. So, you just need to write the typical character of 1.

So, this is what the character table contains and now the kind of things you want to know is how many such irreducible representations are there, how many such irreducible representations can you have, what should be their characters, so these are the things that we want to find out. And we want to work them out and what you will find is that the great orthogonality theorem gives you a good to work out all these details. Now it turns out that the great orthogonality theorem in this form I already said that it is a great orthogonality theorem in the sense there are many orthogonality relations in it.

So, suppose I fix m and n, then I can get an orthogonality relation that involves i and j. Suppose I fix i and j to some value, then I will get an orthogonality relation involving m and n. So, this gives you many different orthogonality relations and what we will do is to is to construct some very practical some relations that can be used in a very practical way using these using these orthogonality relations.

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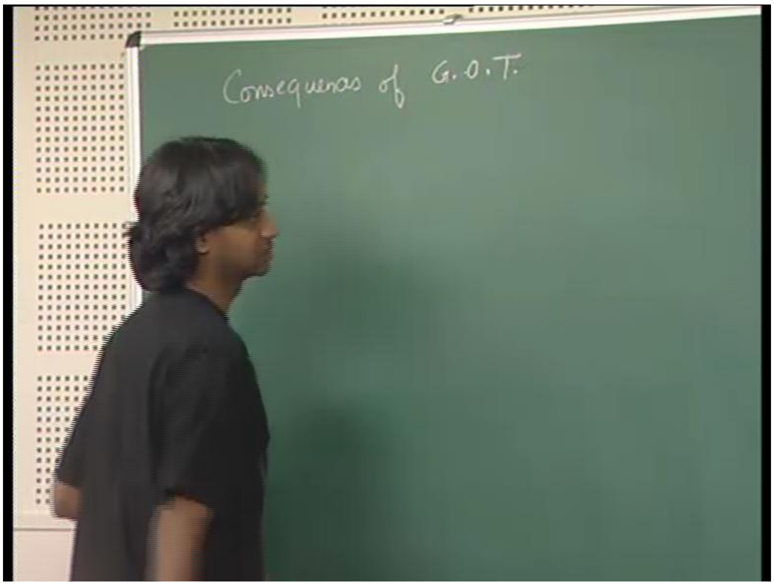


So, these are the consequences of great orthogonality theorem I will use the symbol G O T for this.

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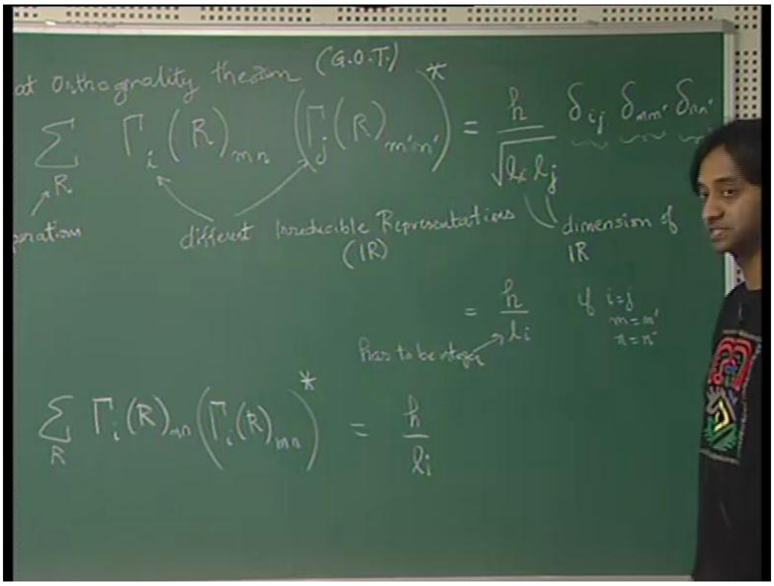


Now, let us look at this, this is the dimensionality of an irreducible representation, l i refers to the dimensionality of an irreducible representation.

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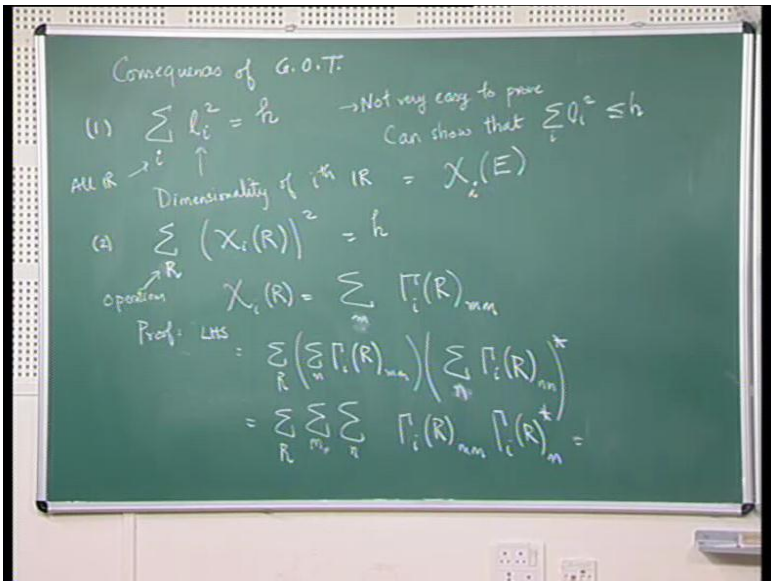


Now, you can you can easily see that if I sum over all irreducible representations and I sum over the dimensionalities of the irreducible representations, square dimensionalities of the irreducible representation. So, some of squares of the dimensionalities of the irreducible representation this is equal to h, so this is equal to h this is this is actually not so easy to prove this turns out to be not, so easy to prove. However you can easily show that this is relatively easier to show but to show this is slightly more difficult.

So, actually this follows in quiet a straight forward way but to go from here to this relation is not as straight forward. Now, the dimensionality this is the dimensionality of ith irreducible representation and you are summing over all the possible irreducible representations, so sum over all irreducible representations. So, now the dimensionality of the ith irreducible representation is nothing but the character of the identity in the ith irreducible representation.

So, the identity element just has one along the diagonals, so the trace of the identity is nothing but the dimensionality of the representation so the trace of the identity is the dimensionality of the representation. So, this is one consequence of the great orthogonality theorem and once again I emphasize that I have not actually shown this, is not as easy to show, it is relatively easier to show something like this but doing this other part is not as easy to show.

Now, the second relation is a following, sum over all operations chi i of R square is equal to h, so this is another relation notice that out here we had one particular matrix element. So, gamma i corresponds to one element of the matrix whereas, chi refers to the trace of the same matrix, so chi gamma i m n is the m nth element, chi i is the trace of the matrix. So, chi i of R is nothing but sum over i, gamma i sum over j, I will say sum over n gamma i r m m, so sum over the diagonal elements, so chi i of R is nothing but this.

And so what this relation says is that if i take chi i star chi i that is like taking the complex conjugate of this and multiplying it by itself. And if you work it out you will get this is equal to h sorry this is sum over all the operations. So, this is and this actually directly follows from the great orthogonality theorem, so you can just substitute this value and you can, let us see what happens if we substitute this value.

So, left hand side, so proof is left hand side is equal to sum over R and you have sum over m gamma i of R m m that is chi i of R and chi i R square is nothing but chi i R into chi i R star sum over n; just to differentiate it from m this gamma i of R n n star. So, this is nothing but this and if you change the order you can say, you have sum over m sum over n, so you get sum over R sum over m and sum over n. So, I take the sum over n outside and what I will get is m and now I can switch the other I can put take the sum over R inside.

So, if I take the sum over R inside, then I use the G O T, so then I will get a delta m n and that will allow me to get rid of one of these sums.

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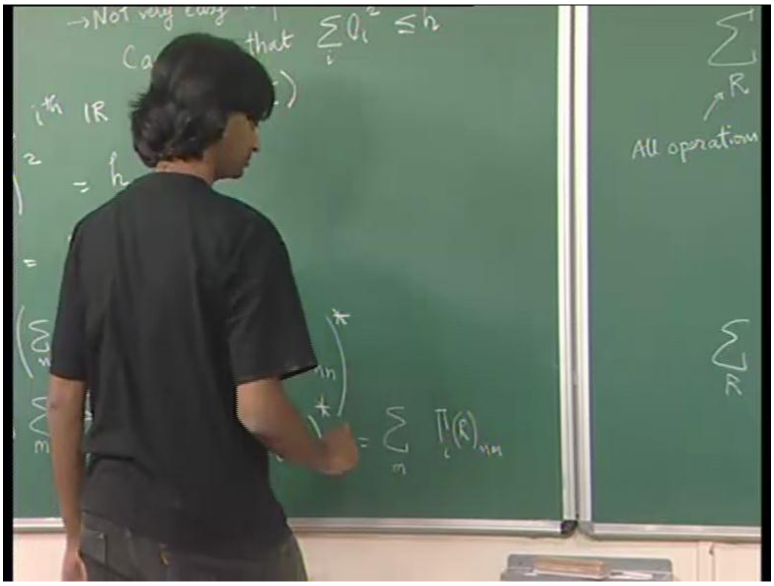


So, all I will be left with this sum over m and all I have is gamma i of R n m. So, if I use the great orthogonality theorem here.

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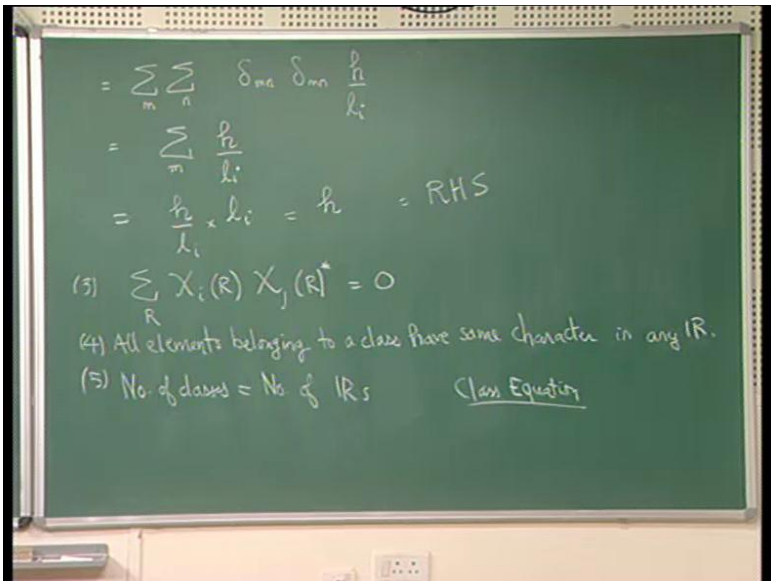

Then what I will get is sum over m sum over n, then I have the sum over R gamma i R gamma i R star. So, that will give me delta m n and delta m n into delta m n, so you will get it twice into h by l i, so that is what I have. So, now I can write this as, so h by l i and this is just equal to so if i do the sum over n it will just go away, so I will just get sum over m h by l i. And now sum over m and this is this is just a constant this is independent of m, so this is just, so sum over m will just give me a factor of l i because I am summing over all the rows of the matrix and the number of rows is equal to l i, so this is just equal to h.

So, we showed this relation that this relation follows directly from the G O T, so the proof is complete, so this is equal to right hand side. So, the important step is right here that the sum over m of a constant, so the number of m goes from 1 to l i, so sum over m is just l i and this completes the proof. So, this is an extremely useful relation, because now this relates the characters of the operations and notice it is the characters of the operations that appear in the character table.

So, this is a very useful representation very useful relation of this and this will turn out to be two of the most useful relations, that we will use. And then we will mention two more things the third consequence is that sum over R chi i of R chi j of R equal to 0 this again follows directly from the great orthogonality theorem. Now obviously, all I said if 2 R's belong to the same class will have the same trace, in that particular representations. So, we will mention this all elements belonging to a class have same character in any irreducible representation.

So, you look at any irreducible representation and the elements belonging to the same class will have the same character, so the last useful thing is that the number of classes is equal to number of irreducible representations. So, the number of classes in a group is equal to the number of irreducible representation this is sometimes called the class equation in algebra. So, in abstract algebra this is sometimes called the class equation.

Now, this is again this you can immediately see that this is extremely useful and very practical relation, the number of classes is equal to number of irreducible representation. Notice it does not say that the dimensionality of the classes and the dimensionality of irreducible representations are the same. All it says is that the number of classes you have in any group should be equal to the number of irreducible representations. So, these

5 relations these 5 consequences of the great orthogonality theorem are extremely useful practically.

So, these are the ones, what we want to find out is, what are the dimensionalities of the irreducible representations and what are their characters; so we want to find out all the l i's and the chi i's, chi i of R. So, now what we are going to do is we will look at some examples where we use this information to derive the character table of various groups.

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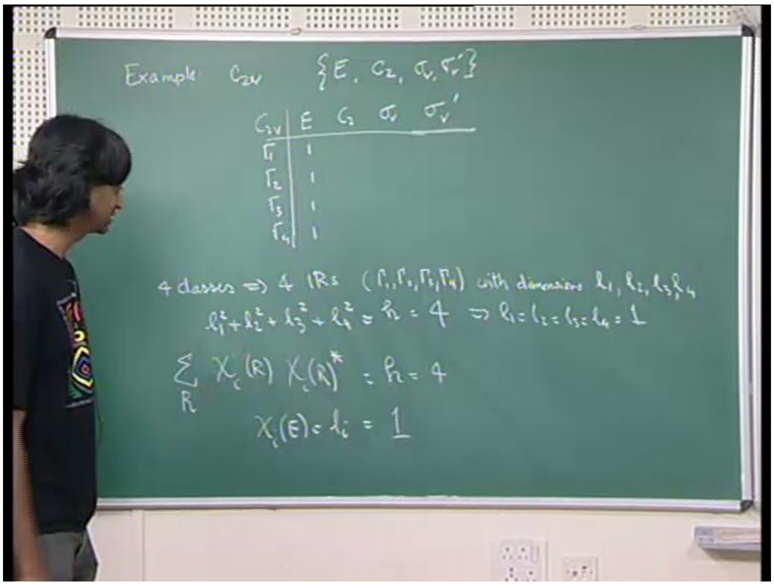


So, let us take an example I will take the group C 2 v, so let us take C 2 v. Now, C 2 v has the following has an identity it has a C 2 it has a sigma v and a sigma v prime so it has only four operations and each of these is in their own class. So, it has four classes so then C 2 v looks like this E C 2 sigma v sigma v prime, so there are four elements and there are four classes. So, we have to find the irreducible representation now you can immediately see that the number of, so I will just write down what are the various things we are using.

So, since 4 classes imply four irreducible representations and we will just call them gamma 1, gamma 2, gamma 3 gamma 4, so we denote as gamma 1. Now, we need to determine the dimensionality of each of these, so gamma 1 with dimensions l 1, l 2, l 3, l 4, so we just assume that they are you just denote them by l 1, l 2, l 3, l 4. Now, first thing you will say is that l 1 square plus l 2 square plus l 3 square plus l 4 square is equal to h and h is equal to 4.

Now, l 1, l 2, l 3 and l 4 have to be non zero positive integers, so this implies l 1 equal to l 2 equal to l 3 equal to l 4 equal to 1, so these have to be positive integers. So, immediately you can say that that is the only possibility, so therefore each of these are one dimensional representations. So, we conclude that each of these is a one dimensional representation, then we use the relation that sum overall operations chi i of R chi i of R star sum of the traces has to be equal to h, equal to 4.

So now what should be the character of identity in each of the representations that should just be equal to the dimensionality, so since we have chi i of E is equal to l i is equal to 1. So, you can immediately see that this should be 1 here and for each of the others so you can have each of so the squares of the remaining characters should add up to 3 and so squares of character of this, this and this should add up to 3.

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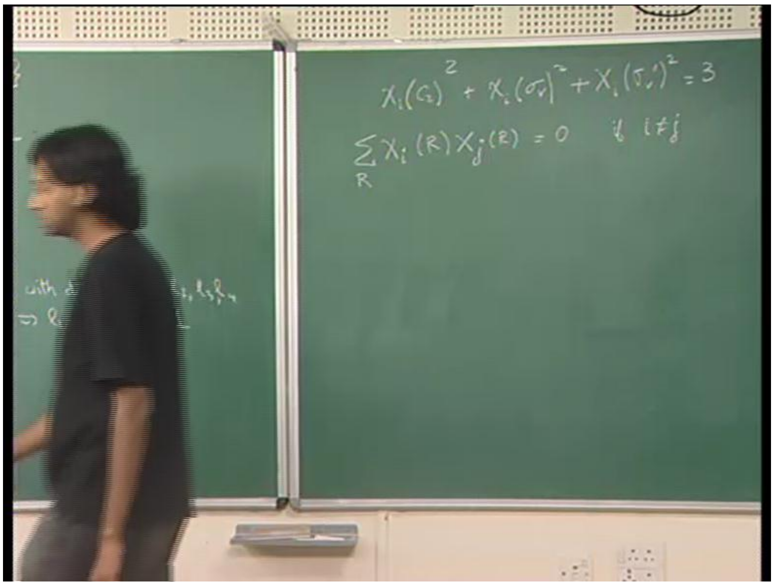


So suppose you choose chi i of C 2 square plus chi i of sigma v square plus chi i of sigma v prime square equal to 3. And the additional relation is your orthogonality relation the other, which says that chi i of R, chi j of R sum over R is equal to 0, if i not equal to j so for two different representations they should be orthogonal to each other. So, now you can clearly see, how I mean this will end up giving you sufficient conditions to derive all the characters.

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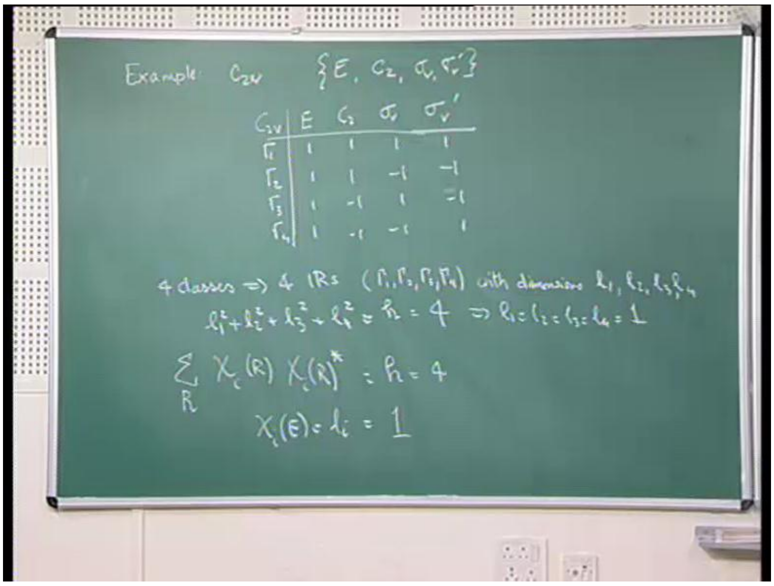


You can see that one will be what is called the trivial representation, so we are already seen that each of these can be represented by one and the products are reserved. Now, the other representations should be such that if I multiply these two, these two and these two add all of them up I should get 0. So, I already have one here, so if I multiply these two these two and these two I should get add them up I should get minus 1. So, one way to satisfy this is to put two of them to be minus 1 and one to be 1, so suppose I put 1 here minus 1 minus 1 then or else I can do minus 1 1 minus 1 or I can do minus 1 minus 1 1.

So, you now clearly see that if I multiply these two if I take a dot product of these two vectors, which is essentially this condition. So, if I take chi i if I have to sum over R, so sum over all these so it is this into this plus this into this plus this into this plus this into this, clearly it gives me 0. Similarly, if I take these two I will get 0, if I take these two I will get 0, now what about what about these two, suppose I take these two what do I get 1 into 1 is 1, minus 1 into minus 1 is 1, 1 into minus 1 is minus 1, 1 into minus 1 is minus 1, so I get plus 2 and minus 2 it get cancel I get 0.

So, basically these 4 gammas looked at as vectors are mutually orthogonal. So, this turns out to be the character table of this group, so you need, so we use both these results in the following way; now you can also show that these are the only possible representations it is not hard to show that these are the only possible representations. And in fact, that is not a very difficult exercise to shows. So, over all I think this illustrates the power of this method the power of the great orthogonality theorem. Now, I just want to make a connection with the multiplication table.

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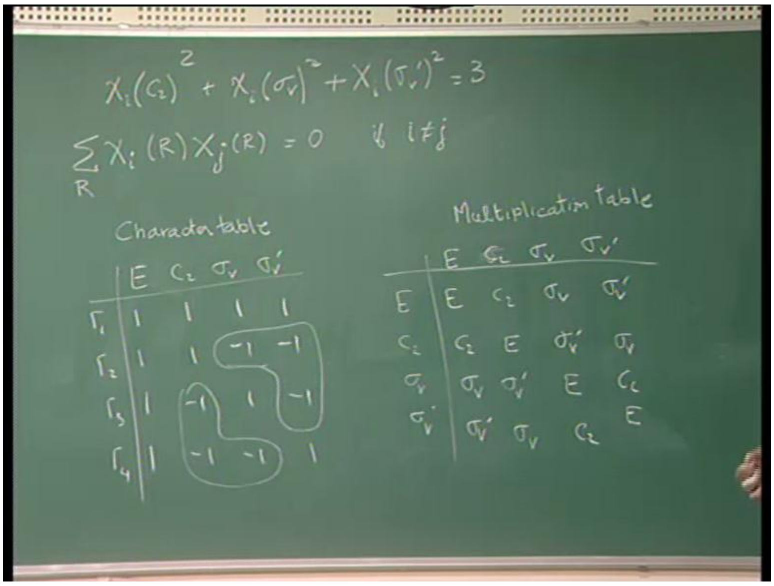

So, what you have is, you have the character table and you have the multiplication table, so you have E C 2 sigma v sigma v prime and you have E prime. So, if I take these 2 E times E is E prime v prime sigma v C 2 sigma v prime sigma v C 2 so this is the multiplication table. And now let us look at the character table, so you have E C 2 sigma v sigma v prime. Now, you have gamma 1 gamma 2 gamma 3 gamma 4, so the trivial representation is 1 1 1 1 then you have 1 1 minus 1 minus 1 1 minus 1 1 minus 1 and 1 minus 1 minus 1 1.

So, I deliberately wrote it in this order, so I have ones along the diagonals that just looks like I have identity along the diagonals then I have this so I have minus ones here and I have minus ones here, I have minus ones in this region. Now, notice that that what you have is C 2 is same as here, so it is like minus 1 that is here sigma v is same as here sigma v prime is here. So, you can see that this sort of anti symmetry is built in this also. So, basically the product of operation, suppose I take C 2 times sigma v then I get sigma v prime. Now, if I take any representation, so let us say I take this representation, I multiply the character of C 2 multiply the character of sigma v, I should get the character of sigma v prime.

And indeed this is 2 I multiply minus 1 by 1 I get minus 1 1 times minus 1 I get minus 1 1 times 1, I get 1 minus 1 times minus 1 I get 1. So, this multiplicative property of the groups is preserved in the character table, so the character table basically gives you all this information, so the same information is given here. Now, in this case the character table since each of the representations was one dimensional and each of the classes just had one elements. So, the character table looks just like a multiplication table so the character table and multiplication table look identical. Next, we will look at an example where the character table and multiplication table look a little different.

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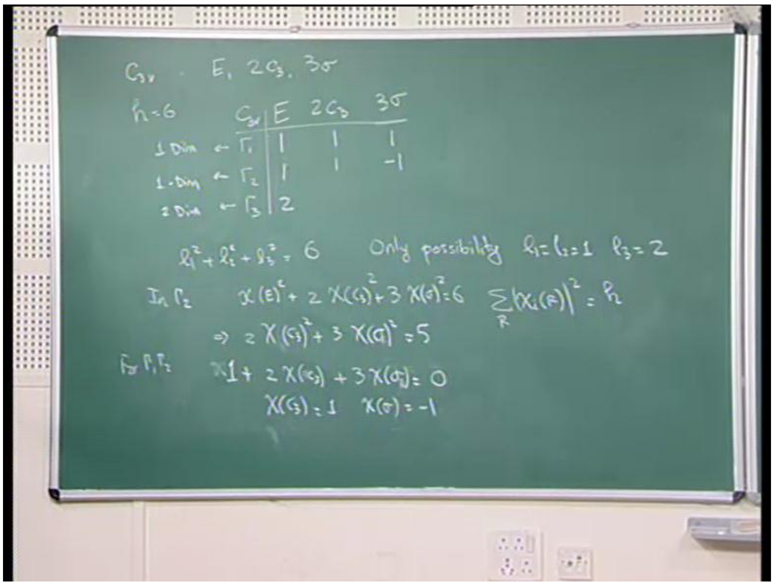


So, let us take the group C 3 v this has, the order of this group is 6 so h equal to 6 it has three classes it has E 2 C 3 and 3 C sigma, so it has 3 classes and now we have to work out the character table of this group. So, the character table will look like this E 2 C 3 3 sigma, now the number of irreducible representations has to be 3. So, we can just say gamma 1 gamma 2 gamma 3 now you can say that l 1 square plus l 2 square plus l 3 square equal to 6, so this is the condition that has to be satisfied.

So, if l 1, so this is at only possibility l 1 equal to l 2 equal to 1 l 3 equal to 2 and actually you can always switch the numbers but basically two of them have to be 1 and 1 has to be 2, so the 2 that are 1 you call l 1 and l 2 the 1 that is 2 you call it l 3. So, that is the possibility, so you have a one dimensional representation, this is also a one dimensional representation and this is a two dimensional representation. Now, you can work out the character of identity will be 1 1 and 2 so the character of identity is this, now you will always have what is called the trivial representation, so where both these will be 1.

So, this is called the trivial representation and this will always be one of the possible representations, so where the character of everything is 1, because then the multiplication and all the products are preserved. So, now what you want is to two other representations so let us try to determine them we will use the, so let us look at this representation. So, in gamma 2 chi of E square plus, now there are two operations in C 3, so we are using sum over r chi i of r square equal to h.

So, chi of E square plus 2, so there are two operations in C 3 each of them have, in class C 3 each of them have the same character plus 3 chi i of sigma square this is equal to 6. Now, chi E square is just 1, so this implies 2 chi 3 or chi C 3 square plus 3 chi C 2 square is equal to 5. Now, the squares have to be positive they cannot be negative and more over more over you have the property this should be orthogonal to this, so also we have, so use of r gamma 1 gamma 2, so for gamma 1 and gamma 2 we have chi.

So, character of identity in this multiplied by character of identity in this, so that is 1 plus character of C 3 in this, so we have twice chi C 3 character of C 3 in this is just 1 plus 3 chi sigma equal to 0. So, this should be satisfied and you can immediately see that there are two ways of satisfying both these relations so the squares of you can the, this plus this can be equal to minus of this. So, you can have, so chic 3 equal to equal to 1 chi sigma equal to minus 1 so this satisfies both these relations, because their squares will automatically this square is equal to 1, this square is equal to 1, so the sum of 2 times this square 3 times this square is 5.

Similarly, this is equal to 1, so 1 plus 2 is 3 and this is minus 3, so you get 0. So, this is one method that works, now and you can easily show that, you know based on this orthogonality this is the only thing that can work.

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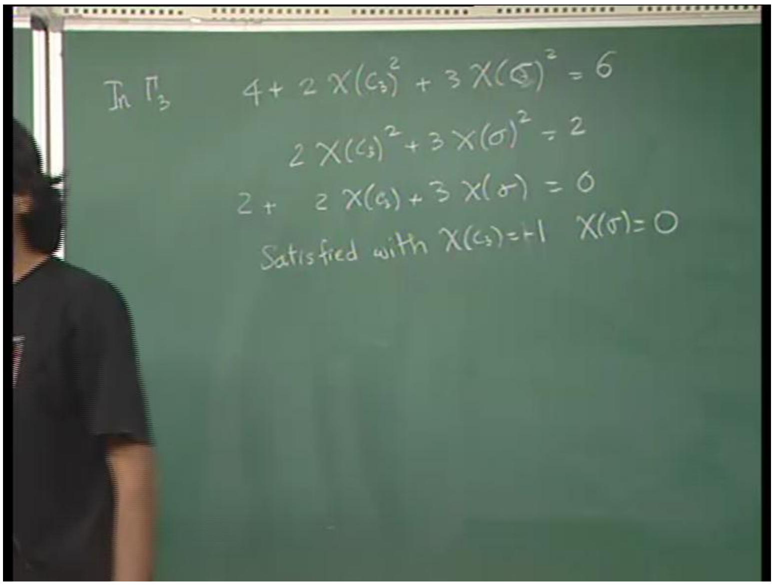


What about this condition, so how do you determine these two, so let us look it. So, in gamma 3, so in gamma 3 we have chi of E square is 4 plus 2 chi of C 3 square plus 3 chi C 2 power sigma square is equal to 6. So, this implies twice chi C 3 square plus thrice chi sigma square equal to 2 and the other condition the orthogonality condition will say that this is 2. So, 2 plus twice chi C 3 plus thrice chi sigma equal to 0 so twice this plus 3 times this should be minus 2 whereas, twice square of this plus thrice square of this should be equal to 2.

And you can easily see that this has satisfied with chi C 3 equal to 1 chi sigma equal to 0, so clearly this is that chi C 3 equal to 1 and chi sigma equal to 0. So, chi C 3 equal to minus 1 sorry minus 1. So, if this is minus 1 this minus this will this 2 plus minus 2 gives 0 and this is 0, so it does not affect.

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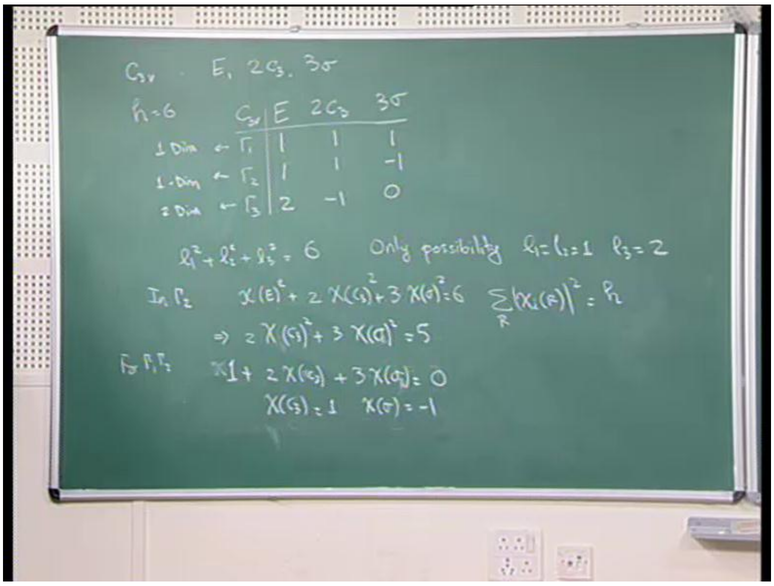

So, what we conclude is that this should be minus 1 and this should be 0 and these are the three irreducible representations and these are the characters of the representations. So, we constructed the character table of a group that is non-trivial and these are, in fact, all the irreducible representations that you can do these are the, whatever if you generate a two dimensional irreducible representation, these will be the characters. And if you generate the one dimensional irreducible representation the characters can be this or this.

So, now we have seen how to construct the basic character table, what we will do next is to is two things; one is how to go from how to express a reducible representation in terms of irreducible representations, and then we will go to the actual character table that is seen in most of your books.