Symmetry and Group theory
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Lecture – 24
Properties of Great Orthogonality Theorem

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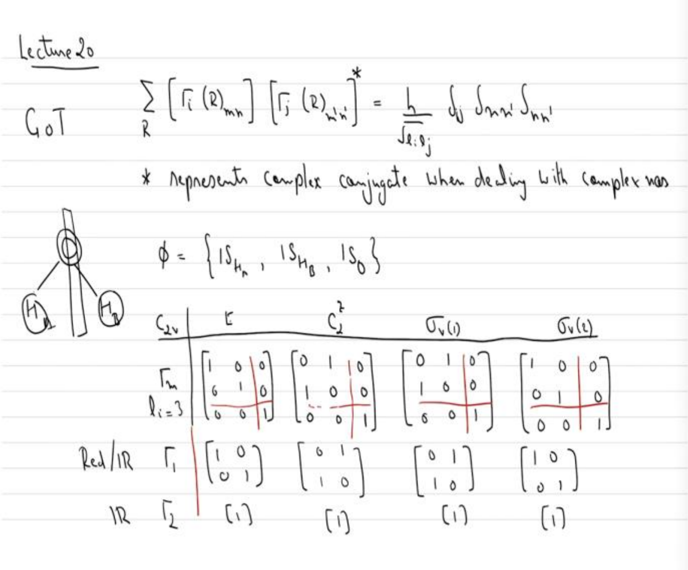

Welcome to lecture 20. So, in the last class we were discussing great orthogonality theorem and let me write down the expression for great orthogonality theorem again. So, this is a summation over all R, again where R is the symmetry operation in a particular point group, and then tau i is the ith irreducible representation and this represents the mth row and nth column matrix element under symmetry operation R for a ith representation.

So, that means, this particular is a matrix element and this is a second matrix element which is represented by jth under the same symmetry operation R with different mth and nth elements and this is given by h / li lj with Kroenecker delta of delta ij m m prime n n prime and of course, we did not discuss this in the last lecture, but one of the factors will be a complex conjugate if we are dealing with complex numbers here.

So, the matrix elements can take complex numbers we will see that when we will come to cyclic groups. So, in this when we are having complex numbers in matrix elements, we have to take complex conjugate for one of the factors here and the rest of the theorem remains same. So, let me see, it represents a complex conjugate when dealing with complex numbers.

So, now, let us see, how do we use great orthogonality theorem or GoT as we call it to actually identify whether a particular representation is reducible or irreducible.

So, sometimes it is difficult to find out by block factorization. So, we can easily use GoT rules in that case and we will see how. So, let us again, take the case of water molecule and let us develop a representation, we do not know whether it is reducible or irreducible, but let us take the basis set as this is my phi, which is the basis set as 1S orbital of HA. Let us call it as H A and this one is HB, 1S orbital of HB and 1S orbital of oxygen. This is my basis set. So, basis set is these 3 orbitals.

So, let us try to take these basis sets and developer representation. Again, we do not know whether it is a reducible or irreducible representation. So, the dimension of the matrix will be 3 cross 3, because number of basis is 3. So, point group is C2v. E and let us call it as tau m, because the dimension is 3 cross 3 E will be a unit matrix of order 3. So, this we have seen every time.

So, E will always be a unit matrix of a particular order, and the order will be defined by the number of basis sets in the basis set vector. Now, that means, the trace under E will define the order of the irreducible representation or the dimension of the irreducible representation which is defined by li. So, in this case, if we take the trace under representation E any matrix under E, the trace will come out to be 3, and that 3 will be the dimension of tau i. In this case li = 3 because trace of matrix under E will be 3.

So, this is just to highlight because we will be using this property later. So, C2z, now can you think what will be this thing? So, if I am taking HA will be replaced with HB that means this will be 0, 1, 1, 0 and z or 1SO remains same. So, this will be 1SO. Now for sigma-xy or we can call it as in this case sigma-V1 and then we have sigma-V2. So, let us see what is sigma-V1. So, let us say sigma-V1 is the one which is perpendicular to the plane.

So, again sigma-V1, 1SO orbital will remain as it is, so, it will be 1. S HA and HB will be reflected. So, we will have 0, 1, 1, 0. Now for sigma-V2 it will be the molecular plane. So, everything will remain at its own place. So, that means, this will be like a unit unitary with the identity matrix 1, 0, 0, 0, 1, 0, 0, 0, 1. So, now, let us say if we want to reduce this let us say if we it looks like as a reducible representation why it looks like the reducible representation because I can see that this can be easily block-factored in 2 cross 2 and 1 cross 1 matrix.

You cannot block factor into 1 cross 3, 1 cross 1 because this one is a square matrix of 2 cross 2 order. So, I can block factor it by 1 cross 2 and 1 cross 1 but can it be further reduced. So, let us say if I block-factor it and write it as tau 1 and tau 2 which is 1001 and 1 then I get 0110 and 1, 0110, 1, 1001 and 1. So, at this point, I know that this one is a irreducible representation, because this is already of the order 1 you cannot reduce this further. So, this is irreducible.

Now, whether this is a reducible or irreducible, I do not know, I can always say that, let us say like in the case of C3v, x and y are not separable. So, I can say that these 2 basis whatever is the basis set for this representation are not separable in this particular case and that is why it is giving me 2D representation 2 dimensional representation. So, this can be a irreducible representation, but this can also be a reducible representation.

If we manage to find matrix such that we can carry out a similarity transformation to convert into a diagonalized matrix and that is a tedious process. So, we do not know whether U prime exists such that a simulated transformation of this will convert into a block diagonalized matrix of 1 cross 1. So, in that case, we will be again able to reduce it further to 2 1 cross 1 matrices, but we do not know at this point whether it is possible or not.

So, let us try to apply the GoT properties to these 2 representation considering that it is an IR representation. So, this GoT applies only to IR representation that is irreducible representation. So, if these properties, which is defined by this particular equation, in this, this equation, if these properties are valid on these 2 representations, that means, both of them will be IR representation. If these properties are not valid, then we can say that this is not a IR representation this we already know that it is IR representation. So, let us try to find out how to do that.

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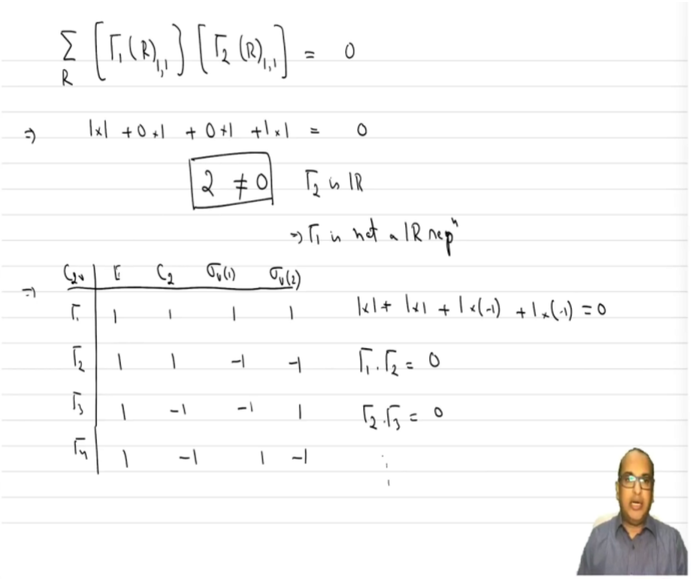

C_{2v}	E	C_2	$\sigma_v(1)$	$\sigma_v(2)$
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	-1	1
Γ_4	1	-1	1	-1

So, let us try to calculate summation over all R, tau 1 R 1,1 and tau 2 R 1,1. So, what should be the value of this, in 2 different representations, if we are taking the same corresponding matrix element, the product should come out to be 0. So, let us see for our case whether it comes out to be 0 or not. So, under all symmetry operations, we have to take the product of the corresponding matrix elements.

So, that means, this, this, this, this into this, this this this, so, 1 into 1, 0 into 1, 0 into 1 1 into 1. So, that means 1 into 1 + 0 into 1 + 0 into 1 + 1 to 1, this should turn out to be 0. However, we are getting this as 2 which is not equal to 0. So, this tells us that since this product is not going to 0 that means the GoT property is not valid and we know that tau 2 is irreducible representation, this implies that tau 1 is not an irreducible representation and can be reduced further.

So, let us also consider the case we already know that we have seen for water, the set of irreducible representations are obtained by unit vector transformations. So, we got 4 such representations, which was 1, 1, 1, 1, 1, 1, -1, -1, 1 -1, -1, 1, 1 -1, 1, -1. So, now, if we apply the same property, so, let us take the product of any 2 matrix elements and take the sum, this will always come up to be 0.

So, let us do this 1 into 1 + 1 into 1 + 1 into -1 +1 into -1 this will be 0. So, you can test any of these 2, all 4 tau 1 tau 2 tau 3 tau 4 will be orthogonal to each other, which satisfies the rule of GoT. So, I can say that tau 1 dot tau 2 = 0, tau 2 tau 3 = 0 any 2 products you can take in this case everything will be equal to 0. So, that tells us that the rules of GoT are valid in this case. So, this is how you can test any given representation for whether it is a reducible or irreducible representation.

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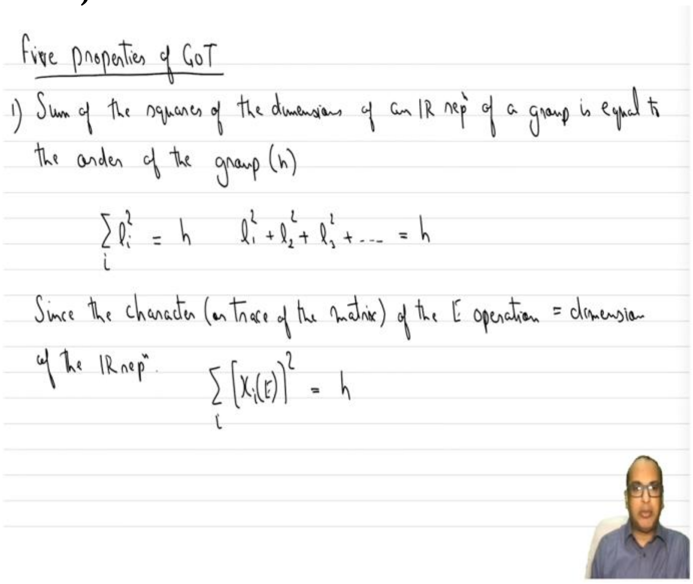

So, that is one very nice application and let us now look at the 5 properties which we will be using to develop IR representations for a given point group, so 5 properties of GoT. So, the first property is the sum of the squares of the dimensions of an IR presentation of a point group is equal to the order of the group. Order the group is h, so, what does it say that sum of the squares of dimension of an IR representation.

So, dimension of the IR representation is denoted by l i. So, that is li square for various i = h. In other words, we can say that l1 square + l2 square + l3 square = h or we can also say since character or trace of the E operation is equal to dimension of the IR representation. Now, we know that the character or trace of the matrix for E operation is equal to dimension of the IR representation.

So, we can always say character of E square summation over all i = h this will be summation over all i. So, this is our first property. So, we will see the use of different properties and we will not provide proof of all the properties because that is not in the scope, but, for a couple of properties I will provide which for which the proofs are straightforward rest of the proofs you can actually find in different mathematical group theory books, but, these proofs do not concern in the applications of group theory to chemical applications. So, that is why we are not including here.

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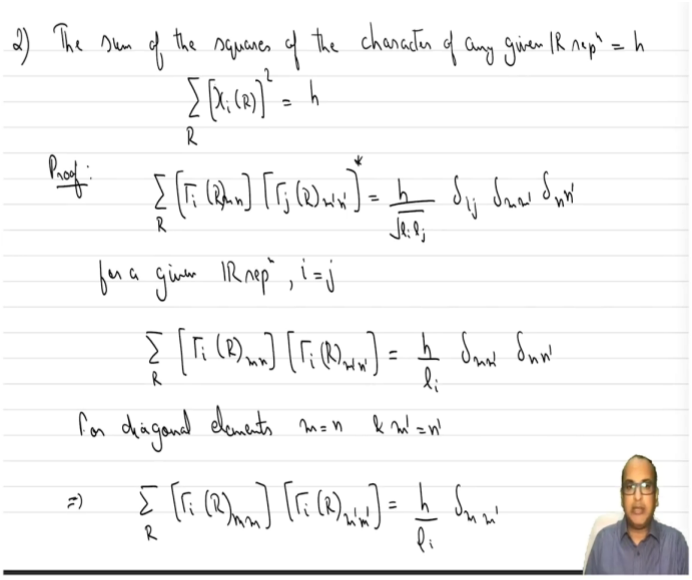

So, let us look at the second property the second property says the sum of the squares have the character of any given IR representation is equal to h, mathematically speaking sum of the squares that is character of under any operation and square of that under all operations is equal to h. So, if you are taking trace of a matrix under a particular symmetry operations and we square it and take the sum over all symmetry operations, what we will get is h. So, let us try to prove this one because the proof is straightforward.

So, let us do this. So, let us start with GoT, which is summation over all R tau i R mm tau j m prime n prime = h / l I lj delta ij delta m m prime delta n n prime. So, I am not putting the complex conjugate or you can actually put complex conjugate also here, so, that does not matter. For a given IR representation, we can say that i = j, because it says for any given IR representation, so, we are not taking product of two different IR representations we are just considering here single representation that means i = j here.

So, let us do that. So, what we will get is summation over all R tau i R mn tau i R m prime n prime and so let us drop the star yet because we are not considering any complex conjugate if there is a complex conjugate you can consider star does not matter here. So, delta ij term is gone because that will be equal to 1 and li and lj will become li square so, this square square root will cancel so, you will have h / li and delta m, m prime delta n, n prime.

Now because we are interested in trace, so, we have to consider only the diagonal elements. So, for diagonal elements what will be the condition m will be equal to n and m prime will be equal to m prime. So, that means, we are getting rid of one set of indices here. So, this implies summation over all R tau i R so, put m = n, so, you have m m and tau i R m prime = n prime, so, you will have m prime m prime.

So, now you do not have that index, so, there is no point writing the Kronecker delta for this m m prime. So, that goes. So, equation is reduced for diagonal elements, we have this now from diagonal elements, if you have to go to trace, then we have to sum over all m, we will get trace of this matrix. If we sum over all m prime, we will get sum of this matrix.

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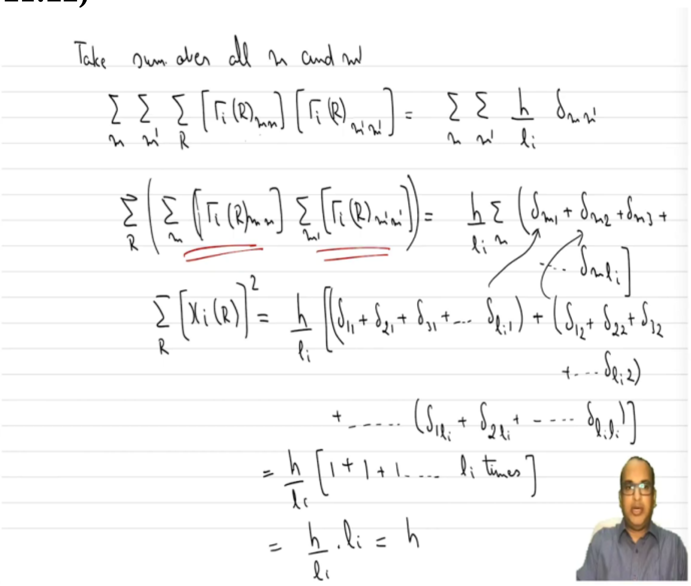

So, what we will do is we will take summation on both sides, we will take summation over all m and some which are all R all m prime, and we already had summation over all R. So, what do we have tau i R mm tau i R m prime m prime, and this will be equal to summation m summation m prime h/li delta m, m prime. Now, this summation only applies to first term because the indexes m indexes only over here, m prime will apply only to this.

So, we can write take this summation inside so, we will have summation R, summation m you can write this as tau i R mm, and summation m prime tau i R m prime m prime. Now let us expand one of these summations. So, if we open this summation, so, let us say h/li summation m. So, this becomes delta m1. So, I am expanding m prime from 1 to l i, + delta m2 delta m3 and so, on this goes up to delta mli and because that is the dimension of the matrix, dimension of the IR representation that means dimension of the matrix.

So, m prime varies from 1 to li. So, this is 1. Now, let us see, this particular term is equal to this is equal to trace this is also equal to trace. So, we have got what we wanted on the left hand side. So, what we have here is a summation over all i, trace of ith representation under the operation R and this is also trace of ith representation under operation R. So, this becomes square and we wanted this to prove, at the left hand side it was this. Now, let us see h out of this. h upon li, now let us try to expand summation m over here.

So, let us take the delta m1 the first term here and expand. So, this will be delta 11 + delta 21 + delta 31 and so on delta li1. That is my first term. This comes as a result of expansion of this one. Similarly, for delta m2 we will have delta 12 + delta 22 + delta 32 + delta li2. So, this comes as an expansion of this one. Similarly, we can keep on going and then for last one we will have delta 1li + delta 2li + delta lili.

Now, if you notice, each of the terms will go to 0 except where the indices are same. So, delta 11 will remain as 1 and rest all will go to 0. So, that means out of each bracket I will get 1. So, h/li, I get 1 from here, I get 1 from here, because again 12 will be 32 will be 0 and so, is li2 only delta 22 will survive similarly, from the next one delta 33 is survive and then here delta l i l i will survive.

So, I will keep on getting 1 up to l i times because the dimension of this was l i. So, originally it was l i, so, we will get li times 1, this implies that we will get li over here, h/li into li, which is equal to h, that is the square of the trace under any symmetry operation over all symmetry operations is equal to h. So, that was easy to show.

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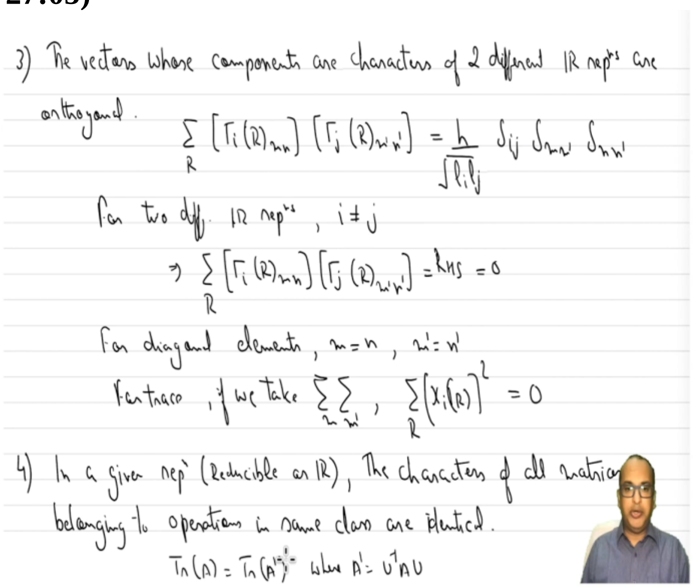

Now, let us look at third property. So, we will quickly see the third, fourth and fifth property and then we will do illustrations of these properties in the next class. So, now, it is saying that the vectors whose components are characters of 2 different IR representations are orthogonal. So, again let us start with the statement of GoT and then we will keep on simplifying that mn and tau j m prime n prime = h over again, I am dropping star over here, explicitly, I am not writing all the time, but I mean it is there if we are using any complex number.

So, for two different representations, we know that i is not equal to j, this implies that our right hand side goes to 0, we already know that because i is not equal to j, delta ij will be equal to 0 turning everything else equal to 0, we do not care about now what happens here. Now, for the left hand side, if i is not equal to j, we can write it as. Now, again for diagonal elements, what you do is equate m = n and m prime = n prime, we can do that because we are only choosing diagonal elements out of this.

So, once we do that and then we take for trace, if we take summation over all m and summation over all m prime, we will get trace like in the last property we saw that this is equal to nothing but square of trace under the representation under ith representation for a particular symmetry operation and square of this and right hand side we have already seen that it is equal to 0.

So, this was very simple to prove basically, left hand side was very similar to the second property 2 and right hand side is very simple to show that it is equal to 0 because delta ij, i is not equal to j, so everything goes to 0. So, let us look at the fourth property again fourth property we have already shown before. In a given representation, now, this can be reducible or irreducible.

So, that is why it says in a given representation of the characters of all matrices belong to operations in same class are identical. So, what I am saying is in a given representation, the characters of all matrices belong to operations in same class are identical, we have already seen that operations under same class are related to each other by similarity transformation and similarity transformation does not change the trace.

So, that means the character or the trace of the matrix will not change. So, there is nothing to prove here, we have already shown this by showing that the trace of A is equal to trace of A prime where A prime is equal to, this we have shown a trace of A is equal to trace of A prime which is, trace is called as character here, where A prime is nothing but U inverse A and U. So, there is nothing to prove here, but this can also be shown as a proof from GoT, we have shown it using non GoT, but GoT can also be used to show this, again we are not going to discuss this.

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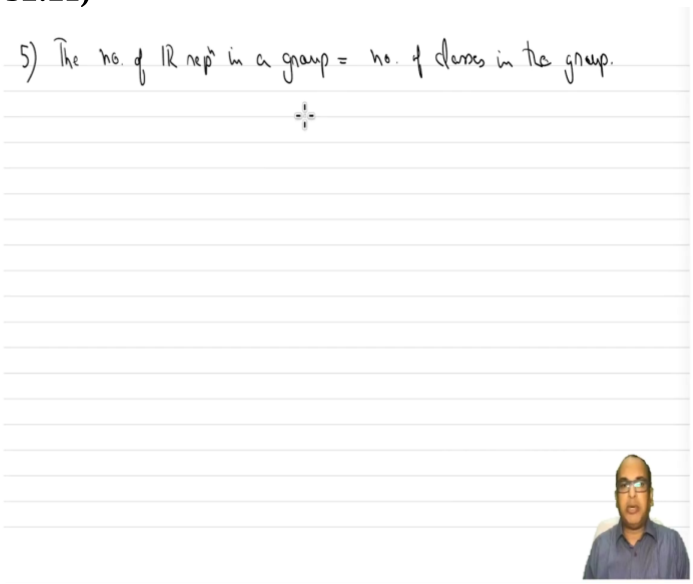

And the fifth property which is derived from GoT is that the number of IR representations in a group is equal to the number of classes, this also we have seen. So, these are the 5 properties of great orthogonality theorem and we have seen couple of proofs, but rest of them we are just using the properties as is. So, now we should be well aware of what each property is saying what is the meaning of each property.

So, please go through it nicely and then in next class, we will be dealing with some examples of how to use these properties to write character table or in other words, write the irreducible representations, all the irreducible representations of a particular point look, without actually worrying about what is the basis set, what are the symmetry operations, what are the effects of symmetry operations, nothing we are going to do we are just going to write directly the character table or that trace or the irreducible representations directly.

So, this theorem is very, very important. So, try to go through it once again all the properties and let us discuss again the next class, how to implement these properties to write down various irreducible representations. Thank you.