**Symmetry and Group theory**
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**Lecture – 23**
**Great Orthogonality Theorem**

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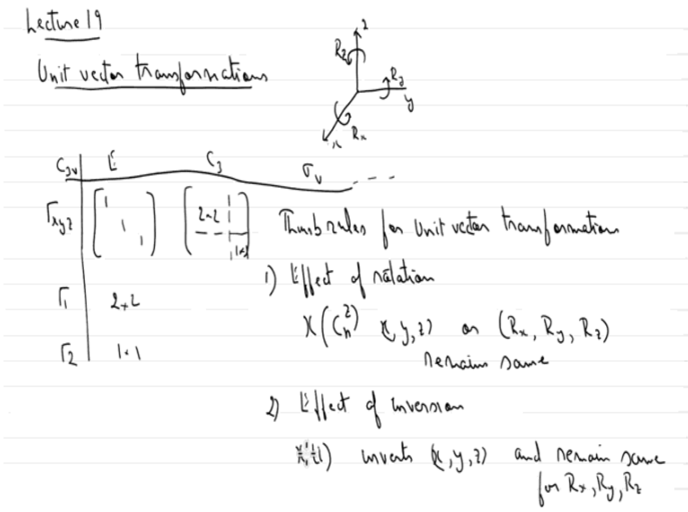

So, in the previous lecture, we have looked at different ways of writing irreducible representations. We have actually, we have just mentioned different ways of writing an irreducible representation and one of the ways was unit vector transformation. So, let us finish on that. So, the 2 types of unit vector we have seen was a linear set of vectors which are unit vectors along the x, y, and z axis.

And then the second set we have seen was the rotational vectors which are anti-clockwise rotation of x axis when visualized from positive side of the axis towards origin. Similarly, we have Ry and we had Rz. So, we can see that the effect of symmetry operations on to these vectors gives rise to irreducible representations. For example, we saw the case of C3v where we will not write all the elements but, so, for example, we saw let us say if we take tau-xyz where we are doing operations on to x y z basis.

We saw that we can form a 3 cross 3 matrix and then similarly, if we do it for C3v we saw again it can give us 3 cross 3 matrix and then this can be block-factored into 2 cross 2 and 1 cross 1 and similarly, for sigma-V and so, on we can observe. So, this upon blockfactorization gives you tau 1 which is of 2 cross 2 order and tau 2 which is of 1 cross 1 order and both are irreducible representations.

So, this we saw. So, now, let us see, so, although it is easy to visualize the effect of operations on to x, y, and z, but effect of operations on to Rx, Ry, Rz is little it is not as trivial as XYZ. So, let us see a certain thumb rules, which actually help you to see the effect of operations onto Rx, Ry, Rz. So, thumb rules for unit vector transformations. So, effect of rotation let us first look at effect of rotation.

So, character is represented by chi, character can also be called as if it is 1 cross 1 element, it is trace of the matrix element. But if it is more than 1 dimension, then it is strictly trace. Or we can say, a particular matrix element so, let us just call it as character of Cn^z. When Cn^z, that is operated upon x, y, z or Rx, Ry, Rz, this character remains same. So, that means, if you are operating Cn^z at on x and you are operating on Rx, result will remain same if x goes to positive x or negative x, Rx will also go to positive Rx or negative Rx.

So, if for example, if we are doing Cn^z on x it will go to - x. So, that means, the character will be -1and So, similarly, if we are doing Cn^z on Rx, it will go to -Rx. So, character again will be -1. So, the effect of rotation the character of Cn^z remains same whether you are doing it on x, y, z or Rx, Ry, Rz so, that is easy. Now, for effect of inversion; so, character under i inverts x, y, z and remains same for Rx, Ry, Rz.

What does it mean? So, if you are doing a inversion operation, so, x goes to -x, y goes to -y, z goes to -z. So, character inverts under x, y, z. So, that means you will get -1, -1, -1 as a character whereas character under i will remain same for Rx, Ry, Rz. So, that means Rx will remain same as Rx, Ry will remain same as Ry, Rz will remain same as Rz. So, that means the character will remain as + + +, so, +1, +1, +1. So, that means, the character under xyz is opposite to the character under Rx, Ry, Rz. So, that is easy.

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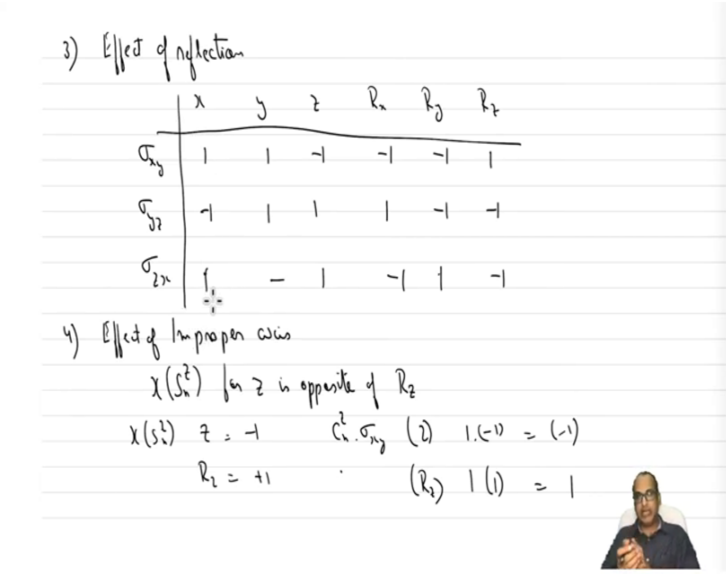


Now, let us look at the effect of reflection. So, let us say these are the basis sets Rx, Ry, Rz and these are the operators sigma-xy, sigma-yz, sigma-zx. So, again if we are talking about any other sigma which is not oriented along the axis, then you will have to calculate the new access system and then do all sorts of maths. But it is easy if you do only for sigma-xy, yz, zx. So, now let us see what happens here.

So, xy if you are doing x and y remains as x and y, so, the character will be +1, +1, z goes to negative and it is quite the opposite here. So, Rx and Ry will be reflected as negatives and z will remain positive and similarly for yz it is x which is negative 1, 1 and x which is positive -1, -1. So, you see that again it is opposite for reflection, zx will be positive for this and negative for this and then it will be positive for this -1 and -1 here. So effect of reflection is also easy. Now effect of improper axis.

So, character of Sn^z for z is opposite of Rz. So, typically, if you see that the character under Sn^z for z is equal to -1, but for Rx, it will be a +1. Why is that? So you can see that in essence, that is actually Cn^z into sigma-xy. So, if you are doing Cn^z operation on to z it will remain as z if we are doing sigma-xy on to z, so on to z. So this will be 1 into -1. So this will come out to be -1 whereas if you are doing on to Rz.

So Cn^z or Rz so if we are doing on Rz, so Cn^z on Rz will remain as same whereas sigma-xy on Rz, so sigma-xy, so we can read from here. So, if you see sigma-xy on Rz, it is positive one. So it is actually positive. So you will get product as positive, so, this will be opposite of the 2. So, character will be opposite for z and Rz. So that is easy. So, now also you can use this to generate irreducible representations, but we will see in different examples when you do it, it will not be generating the complete set of irreducible representations and hence we have to resort to something called his great orthogonality theorem.

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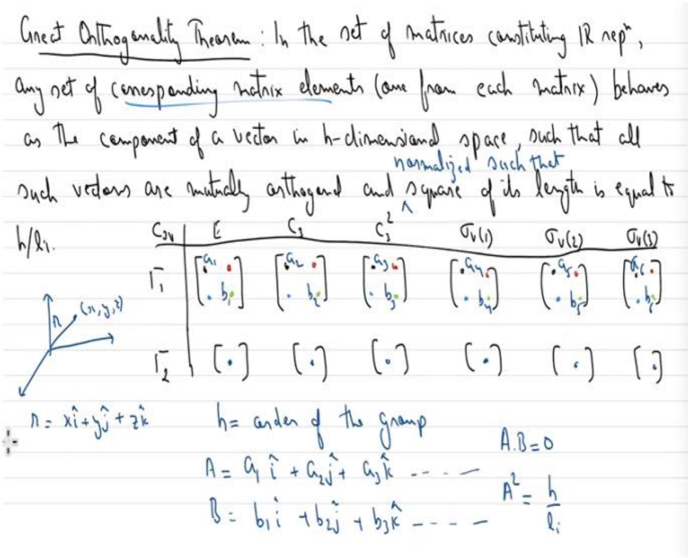


So, let us look at what that is. So great orthogonality theorem. So, let me first write down the complete statement and then I will try to explain what the theorem states. So, let us look at the definition. So in the set of matrices constituting IR representations, any set of corresponding matrix elements behaves as the component of a vector in h-dimensional space, such that all such vectors are mutually orthogonal and square of its length is equal to h / l i. So let us look at one by one, what does it mean actually?

So it is a complicated statement. But let us see. Let us take an example and see what does it mean. So in the set of matrices constituting IR representations, so let us take the case of C3v because we have seen the matrices there. So let me write down all the class elements expanded, because here we are dealing with the matrices. So, matrix for different even if the trace of the class elements are same, the matrices are different.

So I am not going to write the complete matrices, I will just mention, I am mentioning this point because it is important for this theorem. Now let us write down first irreducible representation, which is of 2 cross 2 matrix. So I will just write down all the matrices and I will mention that these are the corresponding elements of the matrices of a given irreducible representation. So, for example, in a 2 cross 2 matrix, you will have 4 elements.

So I am just giving a colour code to all the corresponding matrix elements, because it talks about the corresponding matrix elements here and then let us choose one more colour. So you have and then let us also write one more irreducible representation for 1 cross 1 matrix. So, in this case, the matrix element is only 1. So, if we are talking about corresponding matrix elements, it means only 1 element basically, which is given by this colour over here. So, we have seen, so, set of matrices constituting IR representations.

So, these are the set of matrices which are constituting IR representation, this is one set this is another set. So and we have also seen what is the corresponding matrix elements, so, these are the corresponding matrix elements for one particular set of behaviour behaves as the components of a vector in h-dimensional space. So, now, what are the components of a vector in h-dimensional space, what does it mean? So, let us start with a simple case of 3 dimensional vector.

So, 3 dimensional vector is represented by let us say, x, y, z is the coordinate of that vector and if the vector length is r, so, you can write this as x i + y j + z k right, where i, j, k are unit vectors along x, y, and z dimension. So, x, y, z are the components of a vector in 3 dimensional space, this is a 3 dimensional space where x, y, z are mutually orthogonal to each other. Now, here we are talking about h-dimensional space.

So, what is h-dimension here, h-dimension is nothing but order of this group and we are saying that the corresponding matrix elements, so let us say if you are talking about these matrix elements, a1, a2, a3, a4, a5, a6, so, these form a vector, let us call that vector as A a1i + a2j + a3k and so on. So, here he is the order of the group, so, order of the group is 6 here. So, in this case it is in 6 dimensional spaces, these are the components of the vector.

So, all these matrix elements form components of a vector in h-dimension space such that all the vectors are mutually orthogonal. So, when I say mutually orthogonal what do I mean, if I take another vector as a B vector, let us say I call it as b1, b2, b3, b4, b5, b6, then my B is nothing but b1i + b2j + b3k and so on because it is a vector. So I am just writing caps where caps are unit vectors along these dimensions, E, C3, and now when I say that these vectors are mutually orthogonal, that means my A dot B = 0.

That is the definition of orthogonal vectors. So, if these 2 vectors are mutually orthogonal the product of these 2 components and the summation over all operations will go to 0 and then square of its length if I talk about square of its length then the square of the length of this vector is nothing but a 1 square + a 2 square + a 3 square and so on will be equal to h / l i. So, if I write mod of A, it will be h / l i, what is li here li is the dimension of the given irreducible representation we are talking about and then h is the order of the group.

So, in this case, let us say we are talking about tau 1. So, for tau 1, h will be 6, h will be 6 for any tau here, but li will be equal to 2 for this tau 1. So, that makes sense. So, now, this orthogonality theorem does make sense that any component of this corresponding matrix elements form the components of a vector in h-dimensional space and these vectors are mutually orthogonal and they are normalized, we can write here normalized, such that square of its length is equal to h/li. So, now, let us look at now that we have understood the meaning of this theorem.

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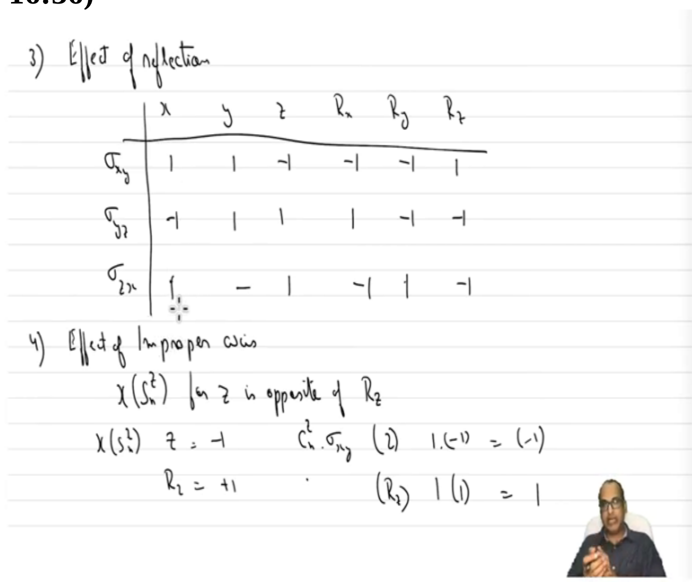

So, let us see how to write this theorem in mathematical form. So, let us see how to write it up. So, if I have summation over all R, because we are summing over all the symmetry operations, so R here is the symmetry operation. So, we are taking summation over all R and we are talking about tau i R mn and tau j R m prime n prime and then we have to take complex conjugate of this if we are dealing with complex numbers.

If you are dealing with complex numbers, then one of the factors here in the product will be complex conjugate you can take complex conjugate of any of these it does not matter. So, this is equal to h / l i l j and this will be delta ij delta m, m prime, delta n, n prime. So, let us look at the meaning of all of this. So, R is symmetry operation. So, we have seen, so, this is summation over all symmetry operations, m and n are indices of various matrices.

So, mn represent basically mth row and nth column have a particular matrix, and then tau i is ith irreducible representation. So, tau j is jth irreducible representation and so on, h is order of the group we all know that, and li is a dimension of ith IR representation or we can say a dimension of tau i. What do you mean by dimension? Dimension means the size of the matrix if the matrix is 1 cross 1, li is 1, if the matrix is 2 cross 2, li is 2 and so on.

Now, delta is Kronecker delta, we all know what this means, it takes the value as 0 if i is not equal to j, takes the value as 1 if i = j, and same is for m, m prime and n, n prime. So now let us quickly get the orthogonality condition and the normalization condition.

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If the vectors are chosen from matrices of diff IR rep, they are orthogonal $\Rightarrow i \neq j$

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = 0$$

If the vectors are chosen from matrices of same IR rep, they are orthogonal $m \neq m'$, $n \neq n'$

$i = j$ $m = m'$ $n = n'$

$$\Rightarrow \sum_R [\Gamma_i(R)_{mn}]^2 = \frac{h}{l_i}$$

If the vectors are chosen so, we know what vectors we are talking about now, if the vectors are chosen from matrices of different IR representations. So, that means then we say that they are orthogonal. So, we saw the example of a different IR representation that is tau 1 and tau 2 if we are taking the matrices vectors which are formed by components from different IR representations then these will be orthogonal.

So, that means my, this implies that i is not equal to j the moment you say that i is not equal to j the right hand side goes to 0 and what happens to the left hand side. The left hand side remains same. There is no change. So, what we had will remain same. So, tau i R mn tau j R n prime n prime. Now, let us see if the vectors are chosen from same IR representation, if the vectors are chosen from matrices of same IR representation, they are still orthogonal.

So, in this case we are talking about m is not equal to m prime, n is not equal to n prime. So, that means, we are talking about the product of which 2 matrices, matrices which are found by this vector and this vector for example. So, this set of vectors and this set of vectors or this and this set of vectors. So, in this case your m and m prime, and n and n prime will not be equal.

So, again due to delta m m prime and delta n n prime, you will again see that the right hand side will be equal to 0 and the left hand side will remain as same. Now, the normalization condition, so, for normalization what we had i = j we have to take from the same product. So, normalization condition means that you are taking a product of a1 with a1. So, i = j, m = m prime, n = n prime because we are multiplying the same vector twice.

So, this means that you have i = j, m = m prime, and n = n prime. So, this implies that you have summation over all R tau i R mn this is my first and then the second is also same, so, this goes as square and then this becomes h upon l i. So, this is the mathematical meaning of what we just explained using the C3v point group example and we saw that how these vectors are orthogonal and normalized.

So, in the next class we will see the different properties of this GOT that is great orthogonality theorem and then how these properties are actually used to deduce irreducible representation without having to worry about what is the basis set, what is the effect of symmetry operation on to the basis set or on to the molecule also. So, we will not worry about all of this.

We will just take a point group, pick up a point group and then write down the irreducible representation by doing the maths defined by great orthogonality theorem properties. So, that is all for today. So see you in next class.