Chemical Applications of Symmetry and Group Theory
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Lecture - 18

Hello and welcome to the day 3 of week 4 of this course. So, today we are going to deal with certain properties of irreducible presentation, which we mentioned that they are most important type of representations and particularly when we will deal with problems related to say valence theory or molecule orbital theory or spectroscopy there are this irreducible representations will be used a lot.

Now, before doing that let us quickly recap what are things that we learnt in the last three or four classes. So, we learnt to make the representation, matrix representations of the symmetry operations and they are by forming a set of matrices, which define the matrix representation of a group and we also learn that this representation may or may not be reducible.

So, when we get a presentation one can try to reduce it by doings similarity transformation and making the matrices block fatted and ultimately receive and irreducible a limit; now then we also looked at a table called character table, which we try to describe.

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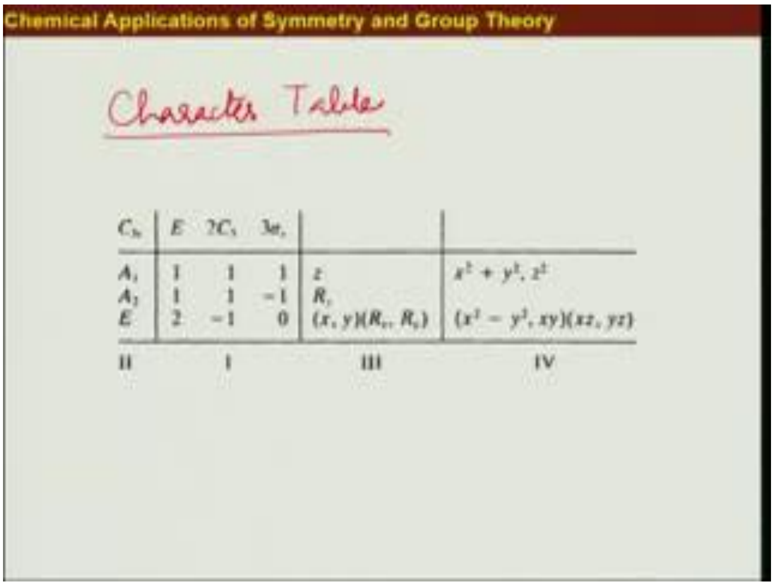

And we saw that took a this character table deals with the characters of irreducible representations and the number of irreducible presentation for a given point group is fixed; we dwelt with a point group C3 E in the last class and we try to divide the character table in four parts I, II, III and IV, and we described the different regions of those character tables and character the area a III and IV if you remember from the last class. We also showed that this area III and IV they provide some linear or none linear functions which can turns transform as one of the irreducible representation of that particular point group. Those particular functions will be extremely important when we go to the actual application part, which will come may be in another week or so.

Now, let us get in to today's class. So, were we will deal with, particular theorem. So, all the properties of a group representation and their characters which are important when we deal with all this problems in valence theory or molecule orbital theory or spectroscopy as I mentioned these properties can be derived from one particular theorem call the great Orthogonality theorem.

So, this basic theorem it concerns the elements of the matrices, which constitute the irreducible representation. So, this particular theorem you will not prove this theory; that will just mention this theorem and then explain that and we will try to utilize that theorem to achieve our goal. In a sense like finding out the properties of irreducible representations and this particular theorem will be extremely important not only to you know deal with all the properties of molecule, but also using this theorem one can actually form the character table; when in the last class I showed you a character table of C 3 v and then mention that these are the irreducible representation that are found that are possible for this particular point group.

Now if you ask me how I can get all this irreducible representation or other in other word how can I form the character table. So, this particular theorem will give you the ability to form the character table of any given point group. So, what this theorem says; it says the great Orthogonality theorem.

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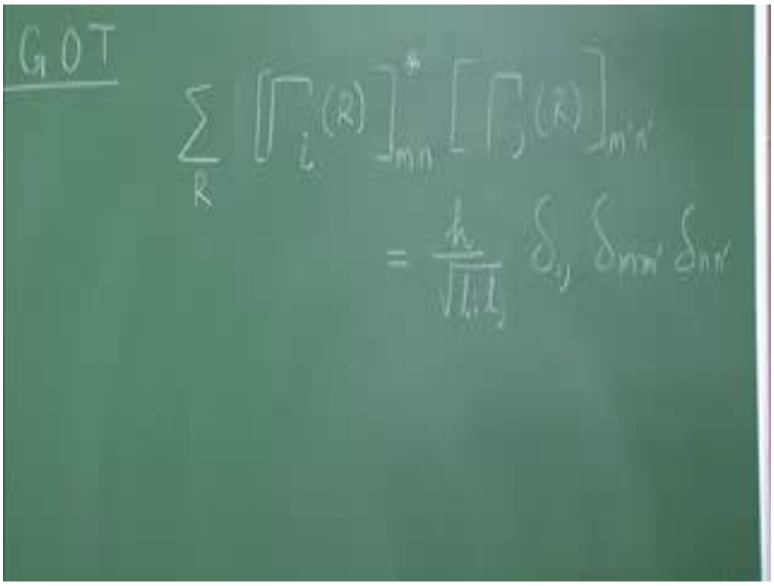

So, we will write it in short as G O T Great Orthogoanality Theorem. So, it is mathematical form is given as, I will explain this entire theorem. So, this is the mathematical representation of the great Orthogonality Theorem. So, this is an extra we do not need this one. So, let us first we talk about this terms that I have present here. So, h as we already know is that order of the group, this li or lj they are the dimension of the irreducible representation.

So, what is the dimension of any irreducible representation? So, for any given irreducible representation you have the matrix. So, the order of that matrices is the dimension of the representation or in other word I can say it is the character of the identity operation for any given IR any irreducible representation and R stands for symmetry operation. So, for any given symmetry operations R will change. like R is E, R can be CN, R can be SN all this things and this gamma of R is any particular irreducible representation and this mn stands for a particular element of that particular representation, which particular representation here it is i th representation and this is the j th representation. So, in the character table we have seen that there are several different i R stand for irreducible representation.

Now, for any given i R I have the matrices and I can choose any element from that matrix fine. So, if I choose one element for one particular matrix, corresponding to the one particular irreducible representation and then I can have another one from another irreducible presentation and these are the (Refer Time: 08:50) this relating i and j that is two different i r, m n prime; that means, two different elements then also n and prime two different elements.

So, now what does is this mathematical relation mean. So, this means that in the set of matrices constituting any one irreducible representation any set of corresponding matrix elements, one from each matrix behave as the component of a vector in h dimensional space, also it says that all this vectors are mutually orthogonal, that is given by my delta functions and more over such vectors are their links are normalized, I mean they are actually rather their squares are normalized to h by n pi. So, this is the interpretation of this theorem (Refer Time: 10:09).

So, what is says, if I repeat again is that if I take one particular element from the matrices corresponding to one particular irreducible representation and we keep picking the same type of element from each of the matrices in the set which from the representation of the group, then overall it behaves like a vector in a each dimensional of space because we have each number of elements in the group right. So, each number of elements in the group therefore, each number of matrices in the group and we are picking one element from each matrices and constituting a vector. So, there will be each dimensional vectors, and this vectors are all are mutually orthogonal and not only that, the square of the link of this vectors are equal to is h by l i.

Now, it will be clearer if we spelt this bid equation in compatibly a three shorted to be equation.

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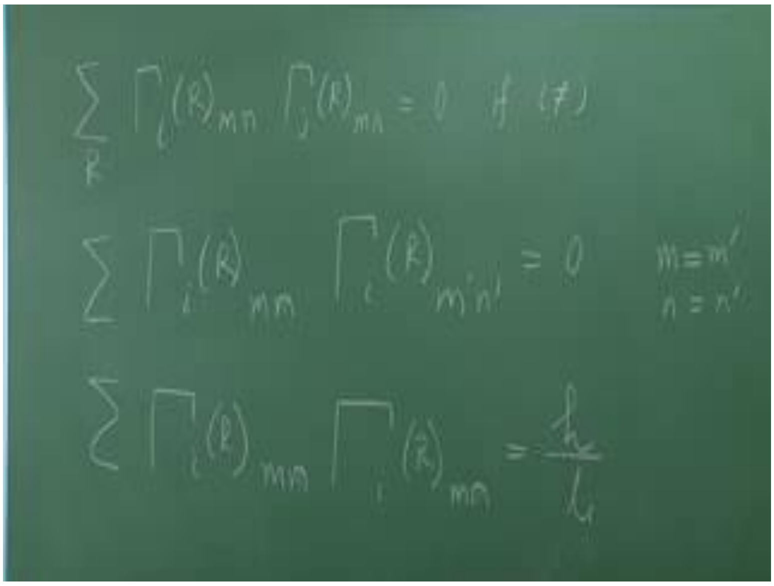

So, let us first we can write in this way, by the way one thing I missed out here, what is this star. So, star corresponds to the complex conjugate. So, this representation can have in the complex quantities. So, therefore, one of the matrix elements we should take the conjugate of that matrix element. Now we will remember that we always have to put this conjugate, but for convenience we are removing this star here, but we will keep that in mind.

So, I can skip this part. So, I can see directly at this will be 0, if I not equals to j. So, this can be verified from here. So, instead of choosing different elements, we are choosing the same particular element from each matrix; now we are choosing from two different irreducible representations correspond to i and j. So, i th and j th is irreducible representation. So, this product and the some over all the symmetry operations will give me 0 until or unless i is equal to j. What does that mean that is if the elements do not belong to the same irreducible representation then they are Orthogonal; so, what we can see if I look at any character table. So, I have two different irreducible representations.

So, now if I want to multiply two different irreducible representations, then the character of the irreducible representation then they will give me 0, but if I do it with itself like choose one particular representation and multiply with itself then that will not be 0; and if I choose same irreducible representation, but if I do not choose the same element then what will happen. So, if I choose same irreducible representation, so then this will be 0, until unless m equals to m prime and m equals to n prime if this does not hold then this part will be 0.

And thirdly gamma i R this will give me the value of h by l i. So, this three are actually the simplified version of this mathematical (Refer Time: 16:22) mark of this great orthogonally theorem and we can see here that if I take the irreducible representation and if I choose the same irreducible representation and same element of the matrix and if we multiply them and then ultimately some over all the symmetry operations, then essentially I get the square of the link of the vector, if I think that taking all this elements one each from each matrices from the set of matrices which gives me the representation of the group, then they behave like a vector.

So, essentially this part is the square of the length of the vector and that is equals to h by l i where l i is the dimension of the present representation and h is the order of the group. So, this three equations will be very much useful for us; now we will deal with certain rules that results from this great orthogonally theorem.

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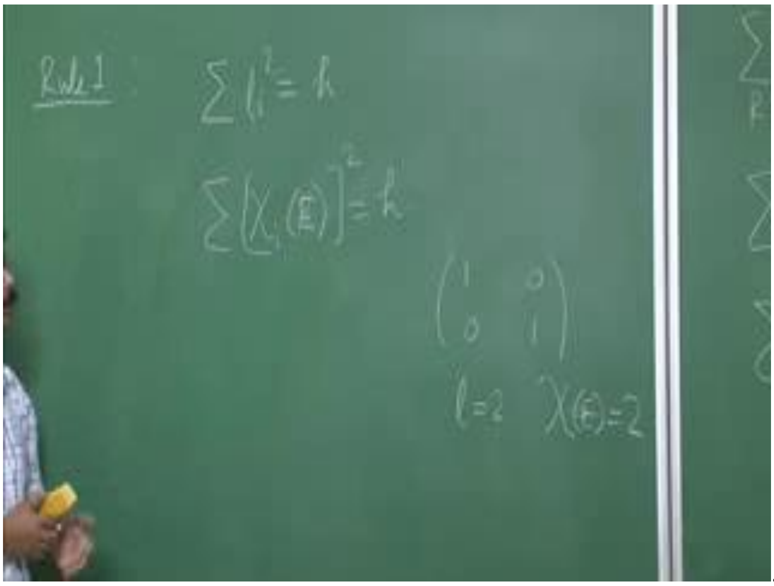

So rule one what is says, it says that the some of the square of the dimensions of the irreducible representation, of a group is equal to the order of the group. So, mathematically if I want to say that, that is equals to this. So, li represents the dimensions. So, it says the sum of square of the dimension of all the irreducible representation of the group is equal to the order of the group.

So, one can proof this particular rule, but that is pretty tedious and do you will not try to prove this one, but one thing that we can figure out from this particular expression is this that li, if I have find out the li from the character table of any particular point group and l i means the dimension of i th irreducible representation. So, how do I know that? So, if you look at the character of the identity of operation because identity operation will have all whatever the order of matrix, it will have one as its diagonal elements. So, therefore, the some over all the diagonal elements will tell me what is the order of the matrix? That means, what is the dimension of this representation.

So, for example, like if I have a two dimensional representation. So, identity matrix will give me this one right. So, this representation is a two dimensional representation; that means, l equals to 2 here. So now, if I look at the character under the identity operation; so, what will be the character here? So, Xi of E here, E is equals 2 because 1 plus 1 equals to 2. So, therefore, if we want to figure out what is the dimension of any given irreducible representation, then all I should do is to look at the character of the identity operation for that representation. Since this is the relation between the dimension of the representation and the character of the identity operation, for that particular presentation; then I can rewrite this one like this, Xi of identity square equals to the order of the group; this is useful relation. So, this comes from this rule 1.

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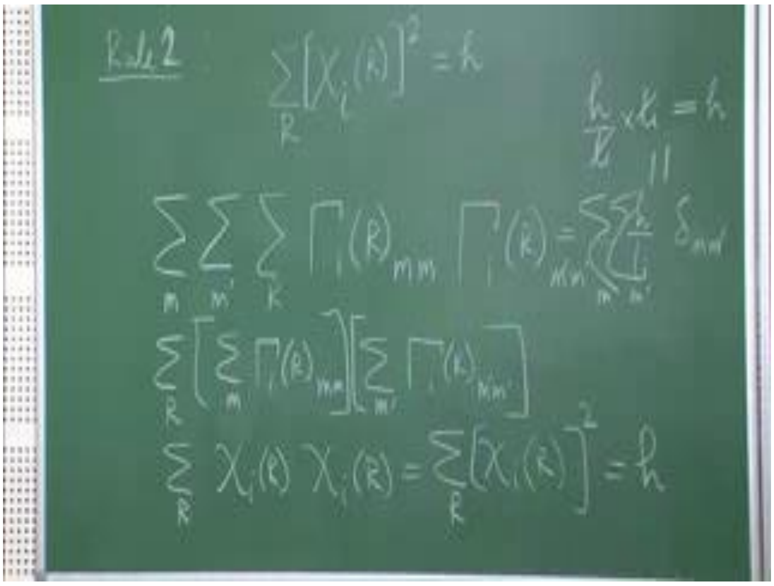

Now, we can have another four different rules. So, let us look at rule 2. So, rule 2 says that, the summation of the square of the characters for any given irreducible representation is equal to h the order of the group. So, mathematically what we can say is this character of any given irreducible representation, see for example, i th representation for any operation is given by (Refer Time: 21:55) i of R and if I take the square of that and sum it over all the symmetry operation, then that will be equals to the order of the group. So, we can easily proof this one. How we can take from this expression itself and we can write some over R if I take any particular i th representation, for any given operation, so this should be equals to h by li delta m m prime, because I have chosen the same irreducible representation that is i th representation. So, delta i j in the original form of orthogonal theorem, gives me unity; we are left will two delta m m prime.

So, this one that is kai of R this equals to let me start from the other round. So, that will be helpful for you. So, If I some it over m and m prime separately on both the side, then see what happen. So, if I see some it over m and m prime on this side as well as on then let us figure out what do you get. So, the order of summation is m material. So, what we can do, we can reanalyze this one and we can have some over m gamma i R mm and some over m prime, gamma i of R, m prime m prime. So, what does this give me because gamma i of R, m m mean the diagonal element and I am summing it to oven m; that means, it will give me the, tress of the matrices that is character of the representation?

So, this is nothing, but the character of i th of the symmetry operation are for the i th irreducible representation correct and same thing is here. So, summing over m prime and I have the m elements as the diagonal elements m prime m prime. So, this will also give be the character of the operation art for i th representation i th irreducible representation. So, this is nothing but a square of this Xi of R. So, this is equal to some over R Xi i of R square, now let us look at this part. So, if I take out this h by l i outside the summation. So, this summation this one this will give me h by l I and then two summations over m and m prime of delta m m prime. So, that is going to ultimately give me l i because this m runs from one two l i correct because that l i is the dimension. So, ultimately I will get l i correct. So, this is going to give me h.

So, there why this part equals to h and that is what this rule is. So, this is the way you can prove it. So, what does it mean, if you if you quickly look at the character table for C3v which is on your screen and take any representation; so, you have let us choose A1. So, if I take these squares. So, what will happen? So, of course, here one thing you should notice that, all the symmetry operation belong the particular class is club together and their characters are same that we have already proved earlier. So, when you want to some over all the R.

So, you have to keep in mind that, say for example, C3 has two different symmetry operation, sigma v in that class we have three different symmetry operations. So, ultimately, if I look at the irreducibly representation A1 what I have, if I want to some over all the symmetry operations and we get 1 plus 2 into 1 plus 3 in to 1 equals to 6 and order of the group is also 6 which use another one let us choose the representation E. So, here E will give me 2 squares minus 2 into 1 plus 3 into 0. So, what is the ultimate value here; so, we get the again the order of the group. So, that is the rule 2.

So, now let us go to rule three, so, rule three this is the vectors whose component belong to two different irreducible representations are orthogonal.

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So, what does it say, it says if I have if i not equals to j. So, this are the characters for a given particular irreducible representation, now if we have the irreducible characters for any given symmetry operation or if we multiply that with another same character for another irreducible representation j and then sum it over all the symmetry operations I will get 0, remaining this and this are orthogonal.

So, how do I prove that; we can choose here this particular part and you can slightly modify that; so, if I look at the first equation what we can write. Here I am using only m equals to n rest of the things are same. So, what it should give me it should give me 0. So, this one if I rewrite, this is equal to, if you think carefully if I sum it over m then I get Xi of R. So, if I write that kai over m gamma i R m m. So, this is my part Xi of R and if I again sum it over m for j, I get the character form j th irreducible representation. So, this part I have already seen. So, this is since you are summing over the same m. So, instead of writing this I can club it all together, now this I have already got as 0 correct this is exactly written here.

So, this part is also 0, only in case i is equal to j this will b tone 0. So, in that case that will give me the value of the square of the length of the vector that is the irreducible representation here. So, that is rule Three and the rule Four says that, in a given representation B3 reducible and irreducible; the characters belong to the matrices which form a class or identical, which we have already seen in one of the previous classes that So, I think at different way that the conjugate matrices have identical characters.

Now, we think about it that is in a class all the elements are conjugate to themselves if they are conjugate then they are corresponding matrix representations, does not matter whether it is reducible or irreducible; they will also be conjugate each other so; that means, they are related through a stimulatory transformation. So, therefore, their characters will be identical which we have already proven and then so this was ruled three and the characters for all the symmetry operations belonging to particular belonging to particular class are identical.

So, this we will stop here and we will continue with the other rules that are you know are (Refer Time: 35:02) from the great orthogonally theorem in the next class.

Thank you.