Chemical Applications of Symmetry and Group Theory
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Lecture - 19

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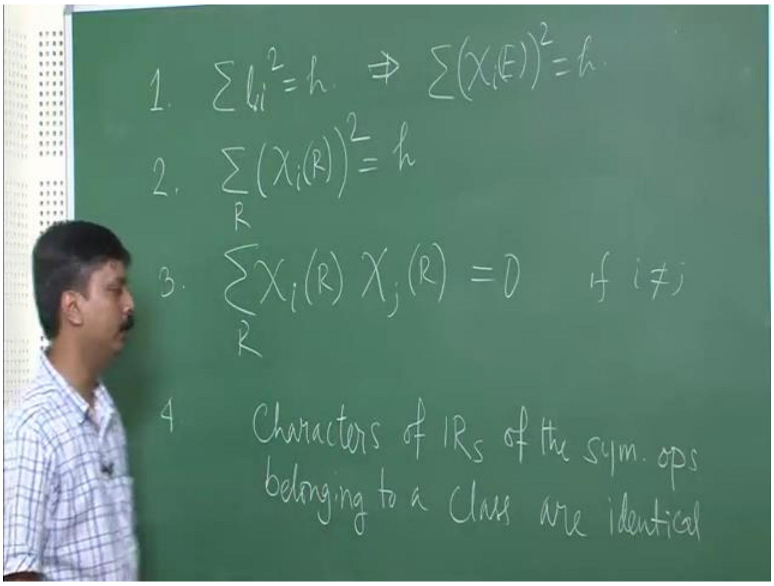

Welcome back. So, we were discussing the consequences of the greater (Refer Time: 00:19) theorem. So, as consequence we say that there are certain rules. So, what did we find in the last class that rule 1 is the sum of the dimension square of any given representation ith representation is equals to the order of the group. From there, we also found that sum over characters corresponding to identity operation is equals to h. And as a rule 2, we found that sum over all the symmetry operation, if we take the characters corresponding to any particular given representation, and then sum it over all the symmetry operations and square it and sum it over all the operation then that is equals to the order of the group.

As a third rule, we found that into irreducible representation will be of octagonal to each other meaning that if I choose ith representation and jth representation then they will be orthogonal if i naught equals to j. And as a fourth rule we said that the character, so characters of irreducible representations of the symmetry operations belonging to a particular class is identical. And as a proof we said that basically we have proved this one because the elements of the class are conjugate to each other. And the matrixes that represent those element in our case (Refer Time: 03:13) that belong that forms class will also be conjugate to each other, and we have proven that conjugate matrixes have identical characters. So, this is already proven.

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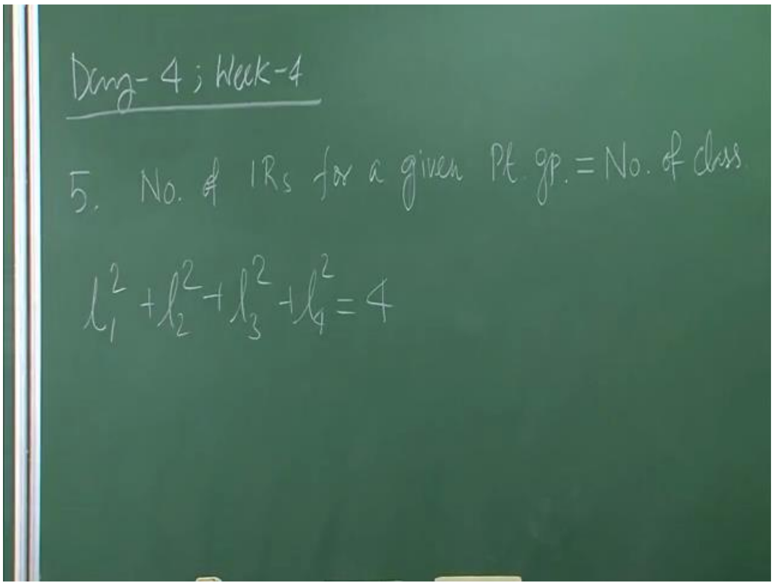

Now, the fifth rule, which is another very important one says that the number of irreducible representation number of irreducible representation for any point of group, say for a given point group is equal to the number of classes that is present in the point group. So, this is very important one, and we can quickly cross check that one. So, if you again go back and look at the character table of ammonia, what you will see that there are three classes E, the classes of C 3 and class of sigma B and the number of irreducible representation also three. So, you can pick up the character you know character table of any point group and you can verify this one.

So, we are also not going to give you the proof because it is pretty lengthy. However, if you consult book, say for example, by if you gotten then you will see that they do not give a direct proof, but at least they will tell you that then you know this relation that is number of IR is equal to the number of class. It can be proven in the indirect way that is that number of irreducible representation has upper bound which is given by the number of class. So, let us try to illustrate all this 5 rules that we have got from get of it theorem. And this will help us a lot because in this process while you know doing this illustration, will be able to see how one can form a character table for a particular point group, so let us try to do that.

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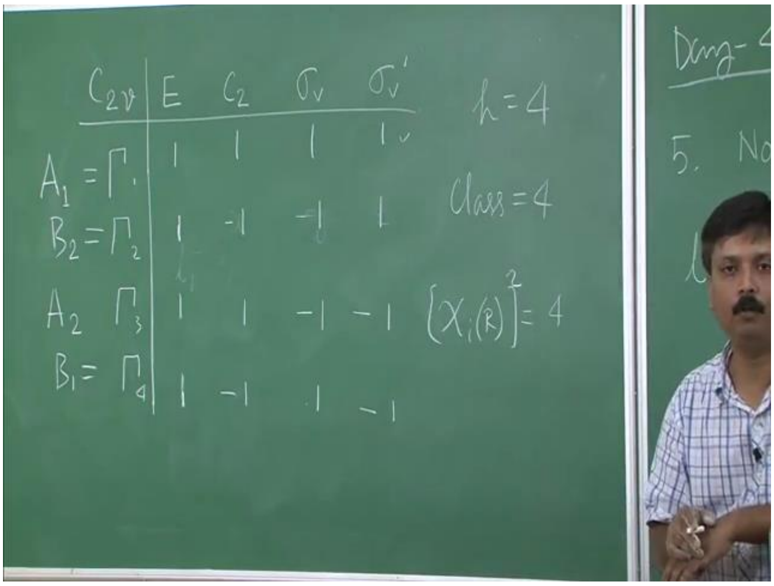

So, let us take a particular point group. So, because take a point group C 2 v, we are all familiar with C 2 v point group. What are the symmetry elements that it has identity, it has C 2, it has sigma v, and it has sigma v prime. So, what we will do, we will try to form the character table. So, to start with I do not know how it is going to be. And what we will do exactly is a self, we will start from rule 1, and we will go all away to rule 5. And then ultimately you will form the character table. And remember this character table that we are going to form that is going to give you the characters of irreducible representation, we have learnt earlier that we can form any representation that may be reducible or may not be reducible. But we are going to do now is that we are going to forms the irreducible representation which are possible for this particular point group, and thereby forming the overall character table.

So, what is our first rule first rule says that sum over n square is equal to the order of group. So, here I have four symmetry operations and all of them form a class by themselves that we have seen quite some time back. So, the order of the group is the number of total symmetry operations. So, order group is 4, now, as per rule 1, what I have that sum over l i square equals to 8. So, I have l 1 square plus, now, before even going here I can take the help of this particular rule that will really help me, how, I will know what is the number of irreducible representation that is possible. So, now, here I have four different classes. So, number of class is equals to also 4. So, therefore, I can have four different irreducible representations. So, let us just give them the name gamma 1, gamma 2, gamma 3, gamma 4 in one of the previous classes I mentioned that in general we try to use this gamma to for any given representation.

So, later on we will try to figure out what this gamma 1, gamma 2, gamma 3, gamma 4 actually stands in terms of the (Refer Time: 09:08). Now, I know that there are four irreducible representations with of there are four classes. So, now, come back to rule 1 which says that sum way sum over l i square equals to h. So, sum over l i equals to 4 in our case, precisely what I can say that l 1 square plus l 2 square plus l 3 square at l 4 square equals to 4 got it. Now, since I will have four irreducible representations, none of this representation can have dimension zero, the minimum dimension that is possible is one.

So, if I keep that in mind then only one way I can solve this that is all of this l 1, l 2, l 3, l 4 are 1. Therefore, it means that their dimensions are all unique. So, dimension of any representations can be found from the characters of that representation and the character correspond to identity operations. So, therefore, what I can write is this is one, this is one, this is one, and this is also one. So, we got four numbers here correspond to four irreducible representation. And all of them are one-dimensional representation. Now one-dimensional representation means only one number in the matrix. So, you can easily figure out that there is no possibility of having any other number other than one. So, either that will be plus 1 or minus 1.

Now, the first irreducible representation, we can try to find out in a way. If I go to rule 2 which says chi of i in R and if I take square is equals to in our case four. And suppose this i is my gamma 1. Therefore, what I have in chi of E plus square plus chi of C 2 square plus chi of sigma v square of plus chi of sigma v prime square is equal to 4. Now, again already I said that all this characters can be plus or minus 1 by its definition because is one-dimensional matrix this representation essentially. So, therefore, I can have all these character as 1 mean plus 1. So, if I do that I get this you can verify this one, 1 square plus 1 square 1 square 1 square is equals to 4. So, this rule 2 is verified for this particular representation. So, I got my first irreducible representation here.

Now, let us take the help of rule 3, which says let any two irreducible representation are orthogonal to each other. Meaning that if I have another irreducible representation here, suppose if I write like x y z some arbitrary numbers I know of course, that this x, y, z can be either plus 1 or minus 1 nothing else. Now, in that case, this and this if I multiply I should get 0 because they are orthogonal mutually orthogonal and that is true for any two ir belong belonging to this particular group, so that is possible if two of them are minus 1 right because here all are positive plus 1. So, if I have 2 plus 1 here out of this four characters in a representation say gamma 2 then two of the character if it is plus 1 or other two are minus 1 then if I multiply with this one, 1 to 1, I will get 0. So, the orthogonality will hold.

So, without worrying about anything else, I can just arbitrarily first put I put minus 1 here, minus 1 here plus 1 here and then say 1 into 1, 1 minus 1, 1 minus 1 and 1 1. So, I get orthogonality verified. So, now, I have to find out the other two. So, what I have to do whatever the irreducible representation that I will forms here in terms of plus or minus 1 that should be an unique one that should not repeat one of the ir's and at the same time that should be orthogonal to any other ir's. So, I can do that quite carefully.

So, now, I make it plus 1 and this one if I make it again plus 1. So, I have made this one minus 1, therefore I can make this one as minus 1, and this one as minus 1. Now, we can verify whether this orthogonality holds. So, here minus 1, 1 will give you minus 1 and here minus 1 into plus 1 will give you minus 1, and this combination and this combination will give the plus 1. So, overall this multiplication will be 0. Again if I check with this gamma 1 then obliviously I can see that there are 2 plus 1's and 2 minus 1's combining with this ir have a all plus 1's will give me 0. So, I am left with the plus one that I can fill up in this way that I can make this one as minus 1 and this one as minus 1 and this one as plus 1. So, you can easily verify that this is also orthogonal to any one of them.

So, if you see how easily input formed this character table. Now we are just left with assigning this (Refer Time: 15:55). These also, let us do it right away. Now, what we know that all the one-dimensional irreducible presentation are given terms as A or B. So, I do not have any scope of having E or T. So, this will be either A or B. How I decide about whether it is A or B, we look at the symmetry of the character correspond to the principal access of rotation that is here it is C 2. So, this one is positive. So, therefore, this type is definitely it belongs to a type. Similarly, this one also is symmetric with respect to C 2. So, this also will be A type. And gamma 2 and gamma 4 they are anti symmetric with aspect to C 2, therefore, this chi will be of B type and this chi will also be of B type, gamma 2 and gamma 4 will be B type.

Now we have to differentiate between 2 A’s and 2 B’s, so that can be done by putting some subscript one and two how do we put the subscript we look at the perpendicular C 2’s or in case perpendicular C 2’s are not present we look at the sigma v’s. So, if I look at this sigma v then this is or for A this sigma v is symmetric, the character with respect to sigma v is symmetric, so I put it as 1. And then another A, if I look at this is anti symmetric with respect to sigma v, so let us put 2. And now this B is symmetric this character symmetry with respect to sigma v, so I give this one as B 1 then I am left with this one it will be B 2, let us verify this one yes this under symmetry with respect to sigma v. So, got my main character table, so this is what we need.

Now, about area two and area three that also one can easily verify, so all you have to do you have to take these functions say x, y and z or rx, ry, rz or on the other side you know xy, xz x square all these individually operate all the symmetry operations belong in to C 2 v, and you generate the representation. If you form representation which is irreducible you can immediately find out that which irreducible representations that is, suppose you are choosing z as your basis function. So, your basis comparison is only z then if you form a representation you will find that this is the irreducible representation that it belongs to. So, therefore, you will be able to say that you know you know if you go to area three then you can write z against A 1. Similarly, y or x or rx ry other binary combinations of this continuous coordinate you can fill up the area three and area four, and that kind of exercises we will need to do when we will particularly do the normal mode analysis that we coming probably in the seventh week of this lecture 6.

So, this is a you know very nice illustration of all those rules that we talked about we obtained from (Refer Time: 20:07) theorem that using those five rules we can very easily form the character table of in particular point group. So, we took C 2 v as an example and we proved it. So, what we will do, we will try to illustrate this with the help of another example, which is little bit more complicated than this simple point group. So, what we will do, we will choose C 3 v instead of C 2 v now.

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So we have already seen the character table of C 3 v. Now, we will see how do we form the character table. So, how many symmetry operations C 3 v has, it has total 6 symmetry operations 2 C 3 and 3 sigma v, and of course identity is there. Now, when you write the character table, you write in terms of the class, because any symmetry operations belonging to a class will give you identical character. So, there is no point in writing with you know very much explicitly. So, what is meant here is that I have C 3 and C 3 square two operations both of them will have same character corresponding to three particular irreducible representations. So, C 3 v, C 3 v square belongs to a class. Therefore, what we write instead is 2 C 3, so that I know that there are two operations, but both of them will have the same character and same is the fate for the sigma v's, 3 sigma v form the class. So, I write in this way. And with this we can, we will start forming the representation.

So, we will stop here today, and we will come back tomorrow with that when we will form the character table of C 3 v point group.

Thank you very much for your attention.