Chemical Applications of Symmetry and Group Theory
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Lecture – 40

Hello and welcome. Today is the last day of this course. What we will do in today's class is, to summarize all those things that we have learnt so far. Hopefully in this course you have learnt about the introduction of quality description of molecular symmetry and also we have learned the way in which it can be used in both not only quality. Let us go through one by one, what are the things that we have learned over the past 8 weeks.

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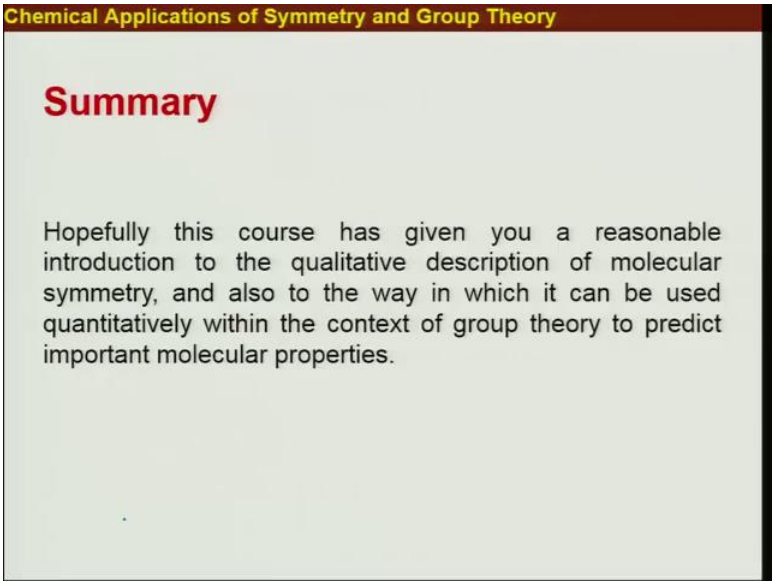

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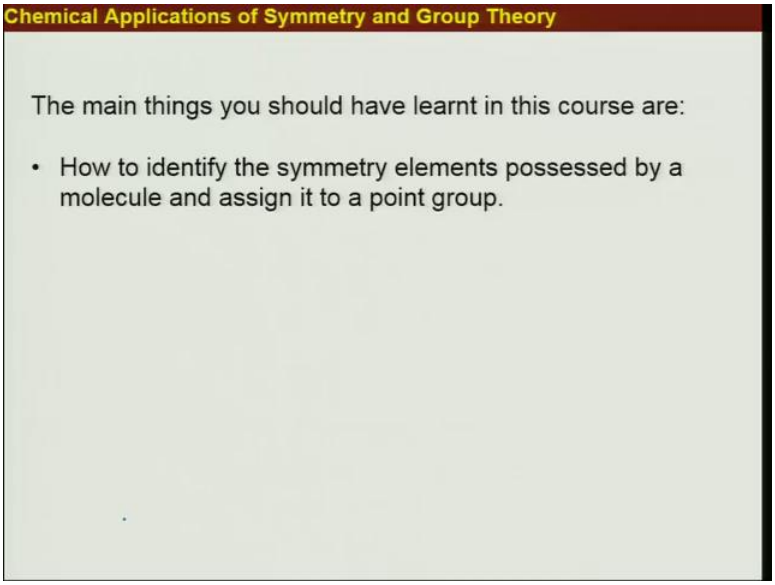

We started with giving you an idea about the symmetry and we said that this is something about the regularity or very much similarity or you know periodicity in certain way. When we know, started talking about molecule, we started talking about the symmetry elements present and we also talked about; how do we use those symmetry elements to generate the symmetry operations.

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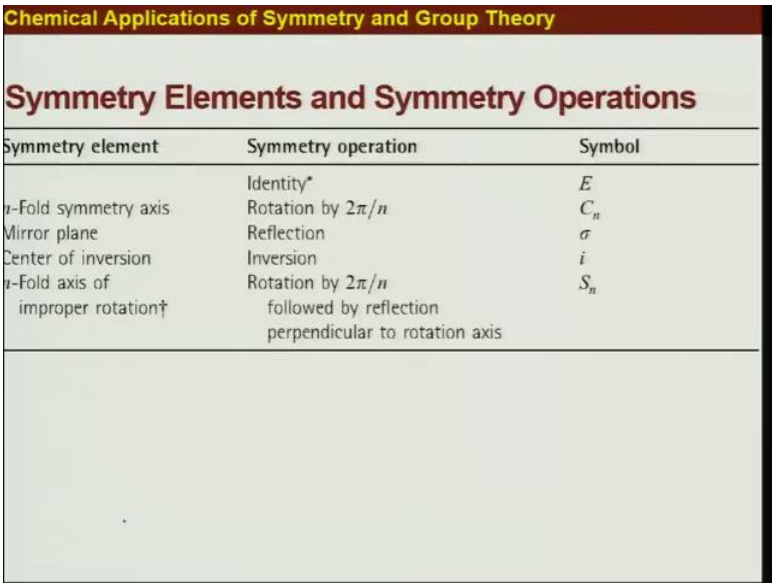

We identified that there are different symmetry elements. For example, identity which is present in almost every object in this, in every object of this universe and there are you know axis of symmetries namely proper axis of symmetry and improper axis of symmetry. Within the proper axis of symmetry, we learned about the principal axis of

rotation, that is the highest order of proper axis of rotation and that we learned about inversion symmetry, that is the element was center of inversion and we also learnt about the mirror planes.

We learnt about the symbols that are provided for each of this element as well as the operation. We had E for identity, C N for proper axis rotation of order, N S N for improper axis of rotation of order N we have I for inversion symmetry and sigma for the inflation planes and the symbols for symmetry elements were also used for the symmetry operation purposes. Only thing is that, in a number of 1 particular operation is being operated was denoted by that number in axis superscript. For example, C N operated 3 times, was written as C N 3 as A C N to the dot 3.

After learning about the symmetry elements and symmetry operations, when we started identifying those elements and also started understanding how to operate this symmetry operations on any given object primarily, the molecular structures then we looked at the possibility of expressing this you know symmetry operations using some mathematical framework. We introduced a concept of group theory first. We started with the mathematic abstract mathematical group theory.

Why we define what a group is, and what the conditions for a given set of any distinct object to form a group was discussed. So, we had four set of rules. So, existence of identity and you know satisfy this closer property and associability this had to be you know ensure before we can call set of any distinct object as a group when we define a particular binary apportioning and also we needed unique inverse for each and every element of the within the set, we needed unique inverse for each and every element of the set and apart from that we also learned that additionally.

If you have a communication relation valid for each and every element of that particular group, then it is an billion group and after learning this basic mathematical in a concept of the group we figured out that our symmetry operations also can form a group because all the conditions for calling a set, a group was satisfied by the symmetry operations of any particular molecule and this symmetry point groups are simply point groups, where you know were formed for any given particular molecule structure and we learned a systematic way to assign the point groups to any particular molecule.

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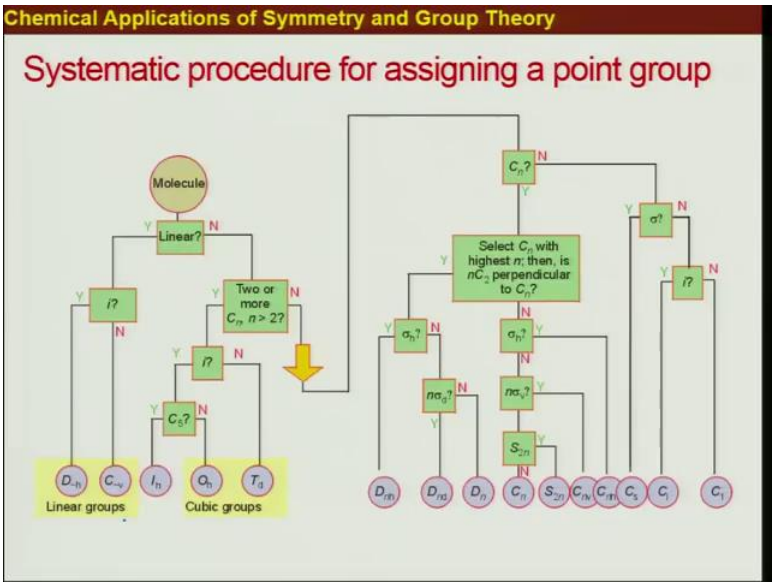

We learnt these steps, where we started with any given molecule, first what you have to do? You have to find out the structure and then you ask certain set of questions and then you have to step by step, find out to which particular point group our concerned molecule belong to. That is how we formed the table chart which will help us to assign the point group to a molecule very easily.

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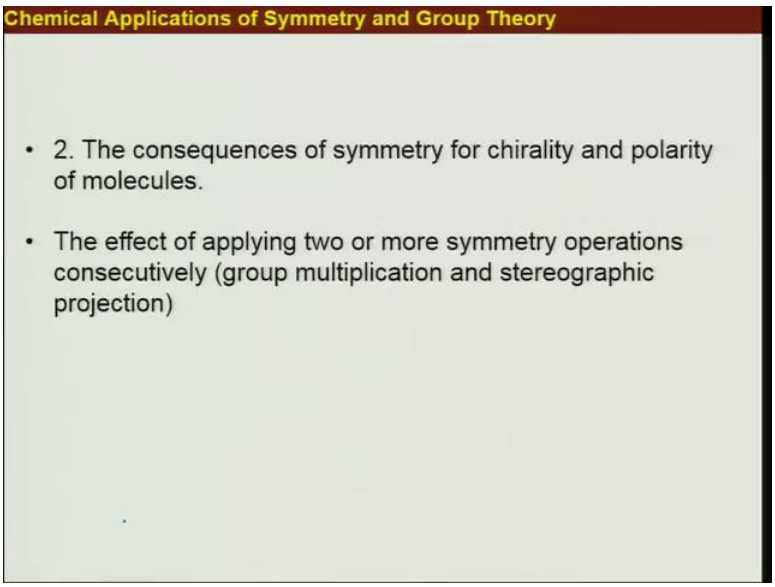

After you know we learnt about how to form the point groups. By the way we also know that this point groups where given certain symbols and this symbols known as so, implies

notation and after having gone through this part, we also learned that, the presence of certain symmetry elements are in a particular molecule, will also tell us about certain molecular properties namely Chirality and Polonity. We discussed in quite a bit of detail that how absence of the A C axis is strictly required in order for a molecule to show Chirality of the Chiral responses and those particular point groups, which does not have any sorts of ascent and when you say this ascent, we know that this N can be even this S 2. Any sorts of ascent and the same time S one is nothing, but the C 1.

We learned about the point groups which are intrinsically Chiral. For example, let us see one which is always Chiral and we also learned that point groups which can never be Chiral. That was one aspect and also we learned about the how to comment on the polarity of any given particular molecule because the polarity comes from a particular pictorial quantity called dipole moment and if there is something like sigma h are a perpendicular to this dipole moment or if you have inversion symmetry then the molecule cannot have a dipole moment because the effect of this dipole moment in a particular direction will be nullified by this symmetry elements.

We also learnt that how you know we can find out the effect of applied 2 or more symmetry operations successively. How did we do that? We learned 2 different things which helped us getting the answer of this question that is, what will happen if I operate 2 symmetry operations consecutively? 1 was group multiplication table, another was a geographic position.

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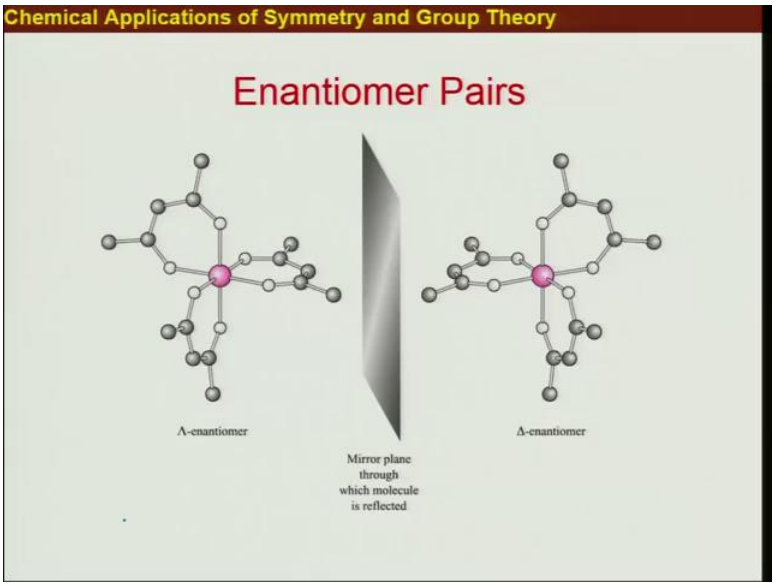

Here like we showed how this Enantiomer Pairs will look like, which are related by weird image relationships and this particular molecule was also mentioned earlier that this molecule belongs to D 3 symmetry, which does not have any kind of ascent and this mirror image of 1 particular structure of this molecule which is like COEN whole 3 type will have a non super impossible mirror image meaning that will constraint Chiral molecule structure.

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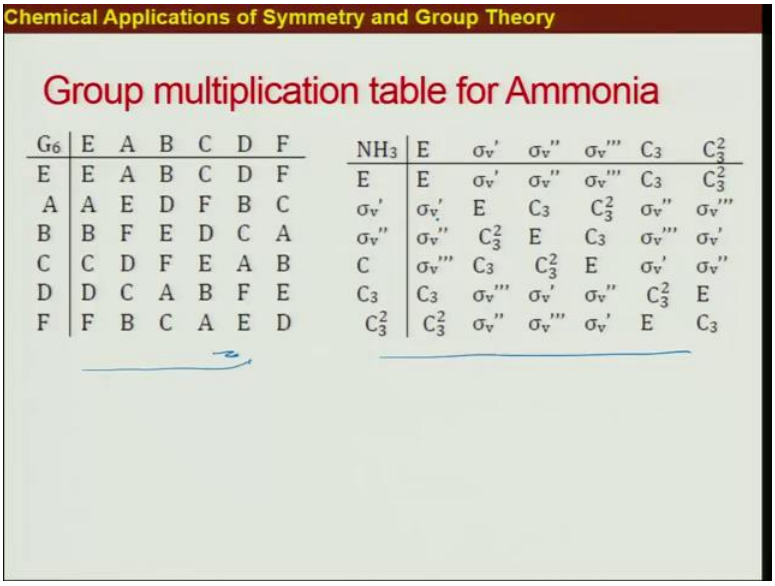

G_6	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

NH_3	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
E	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
σ_v'	σ_v'	E	C_3	C_3^2	σ_v''	σ_v'''
σ_v''	σ_v''	C_3^2	E	C_3	σ_v'''	σ_v'
C	σ_v'''	C_3	C_3^2	E	σ_v'	σ_v''
C_3	C_3	σ_v'''	σ_v'	σ_v''	C_3^2	E
C_3^2	C_3^2	σ_v''	σ_v'''	σ_v'	E	C_3

Now, we learnt about the group multiplication table, which were, we saw that all the symmetry operations because symmetry operations from the point group rate. For this symmetric point group, the contributing elements are the symmetry operations and you know we learnt how to be careful about using the terms symmetry elements and symmetry operations, what to use what. In the other context of group multiplication table we learned that we write down the symmetry operations for a particular group in this top as well as on the left side and then we have the we fill up the rows and columns to get that group multiplication table. Now an abstract way we learned how to get the group multiplication table and we also learn that there are certain numbers of multiplication tables, are possible for a particular order of group.

Like you know for group 3, group 4, group 5, group 6, we learnt a certain number of such a group multiplication tables are possible. Once we learnt this technique, how to form this group multiplication table, then if we encounter with any particular group of having any particular order, then it should have 1 to 1 correspondence with this particular abstract group. We took an example of this ammonia, which is having an order 6 and that should have 1 to 1 correspondence between this G 6 that was formed in an abstract way. We showed the similarity and in this way if I know about different G 1, G 2, G 3, G 6 and their various and possibilities then one can easily form the group multiplication table for a given molecule. Now this group multiplication table gives me actually results of operating 2 symmetry operation 1 of another. On another way, what I can see that group multiplication table gives me the products of two symmetry operations.

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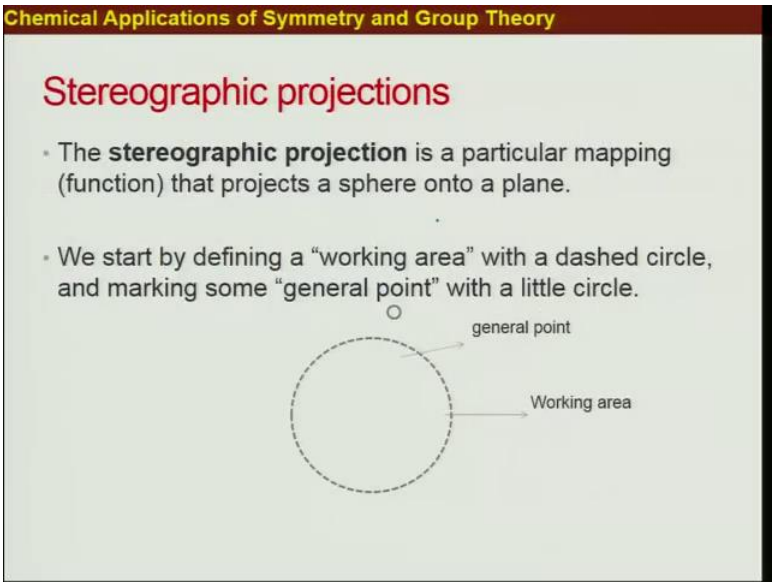

We also learnt another technique which was very useful for 2 reasons, 1 is, if I know about the point group then I should be able to you know, tell what are the symmetry operations existing in that particular point group. Symmetric stereographic projection was introduced as a tool for that and moreover after learning the stereographic projection, 1 should be very easily able to find out the result or effect of operating more than 1 symmetry operation consecutively. We define what stereographic projection is and we define how to, how to work on using this particular technique. We defined the working area; we defined all the particular symbols that are used in these cases.

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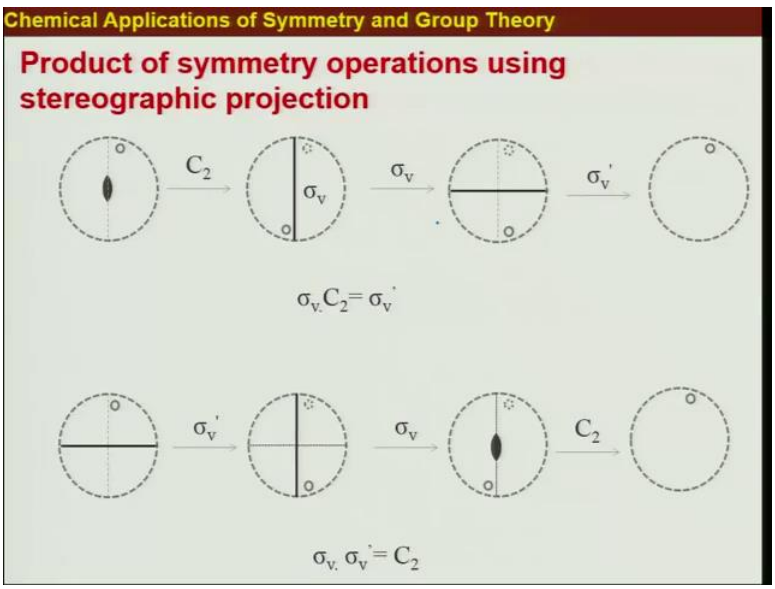

Then we took quite a number of examples. For example, here in this case, we showed as a preliminary example taking the point group C 2v and we use any general point and then operate it the C 2v on C 2 on that and then sigma v on that and then ultimately what we get is a result of the product of this 2 symmetry operations. Using group multiplication table and as well as the symmetry operation stereographic projection, we could find out the result of to search operations, operated on any molecule successively.

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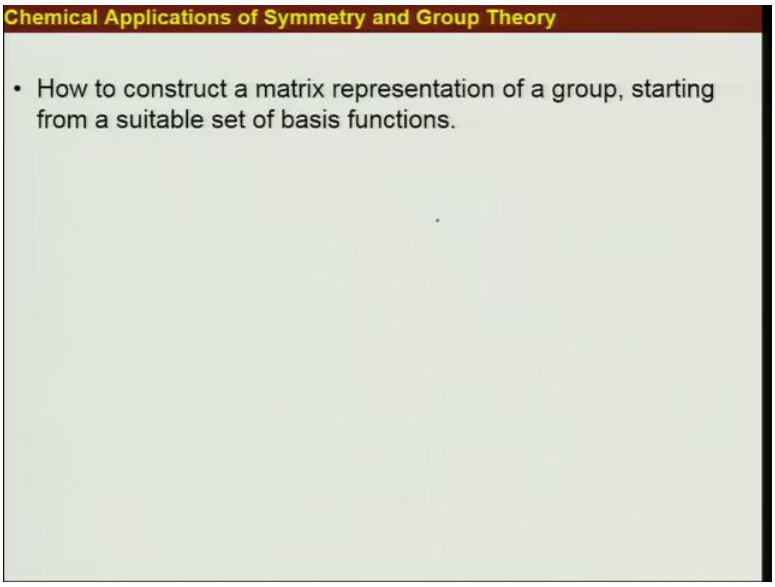

Then we learnt about the matrix representation. After learning all this symmetry and the point group symmetry point using the group theory, we wanted to have even updated mathematical way to have some sort of representation of this and you know these operations that we can constitute the representation of the group in a complete mathematical way.

This symmetry operations either 1 can draw or 1 can imagine and you know get the ultimate result, but in order to be able to use it for practical purpose 1 needs to have a mathematical way and we figured out that matrix is 1 of the best way to represent this symmetry operations because this matrices do the exact same thing as that of the symmetry operations when it is applied on a particular basis functions which is used to form the representation of any given molecule. In this particular section, what we learnt, that we have to first find out certain functions and form is say which is known as basis set and we have to apply each and every symmetry operation on this basis functions.

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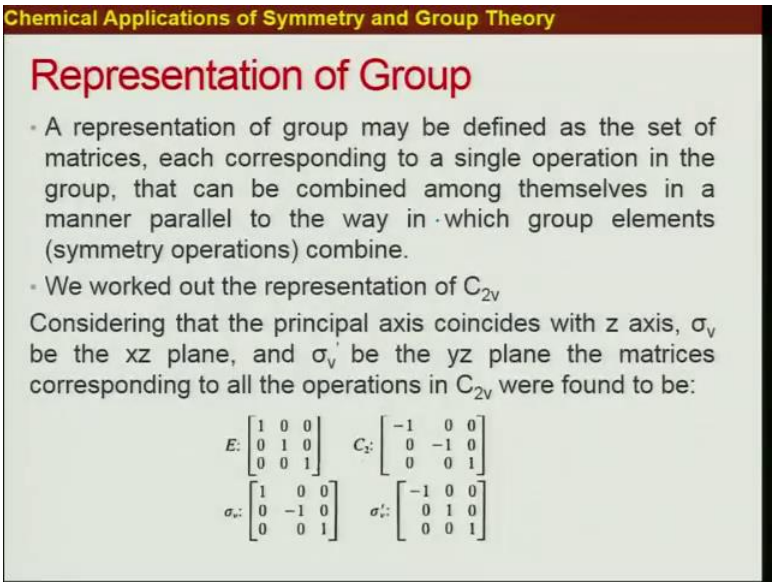

How did we get those matrices representation? We first selected certain basis functions forming a basis set and then you know based on this basis set, we found the matrices which are, which will represent the symmetry operations such that multiplication of this new matrix with the suppose we have column vector matrix representing the basis functions. Then the product of this new matrix and this matrix containing this basis functions, we give me the results that I could easily get using this symmetry operation itself. In that way, we took a simple example of C 2v point group and use the general point having present coordinates x, y, and z and thereby we formed the representation for identity C 2 sigma v and sigma v prime and we got 3 by 3 matrix for each 1 of them and you know once we find out all the matrices for all the symmetry operations then, we you know put this matrices in place of the symmetry operations and we call that as a representation of the point group.

And we also learned that these matrices are very useful and even more useful and handy thing is the trace of the matrices. We learned a lot of things about this matrix representations particularly matrices are which belong to class, that is a matrices which are conjured. This the trace of the matrix, we call that is actually called as character of the you know matrix representation because this traces bear, all the properties of the matrices in a very compact form and it is very easy to use because we can get the characters even without permission of the matrix that was showed the matrix part of this course.

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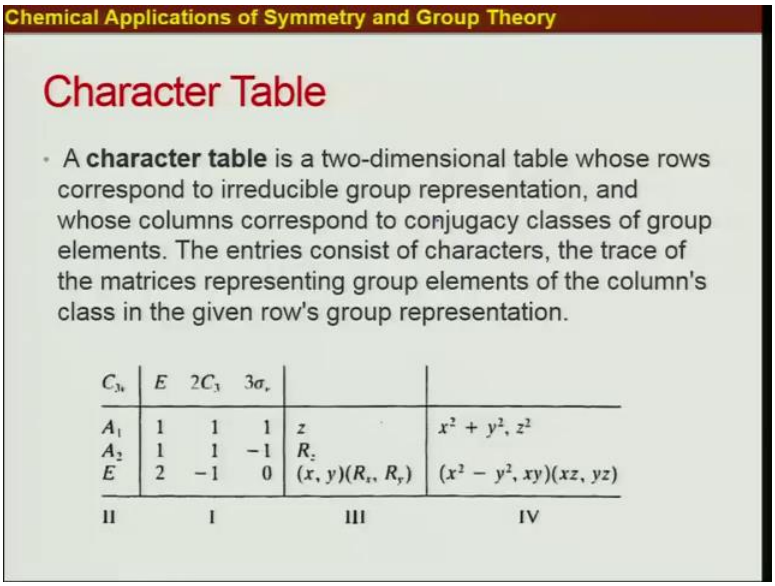

You know, we introduced the concept of the presentations which are reducible and which are irreducible. We also learnt about how to reduce representations into the irreducible representations. We also learnt about the table which is constructed for any given particular point group and we learned that 1 particular point group has a tab table called character table which contains the exhaustive list of irreducible representations that particular point of time have and we learnt in detail about the character table we learnt about each and every region of the character table and what their functions are.

We learnt about the properties of this irreducible representation, when we learnt about theory of called the great Orthogonality theorem.

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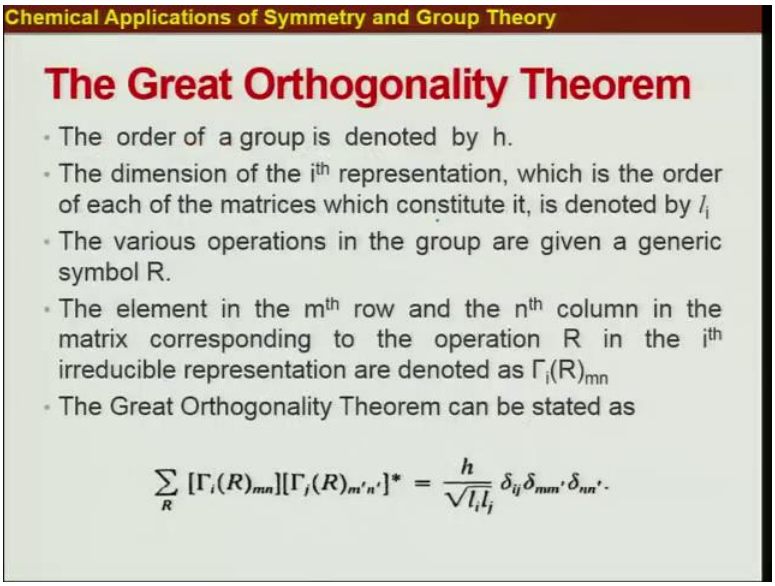

And we learnt about the consequences of this great Orthogonality theorem, we learnt about the properties of each and individual irreducible representations, what is the property of the dimensions, what are the properties of the characters and all, and you know as one of the consequence, we actually learned how to reduce up representation into the irreducible one.

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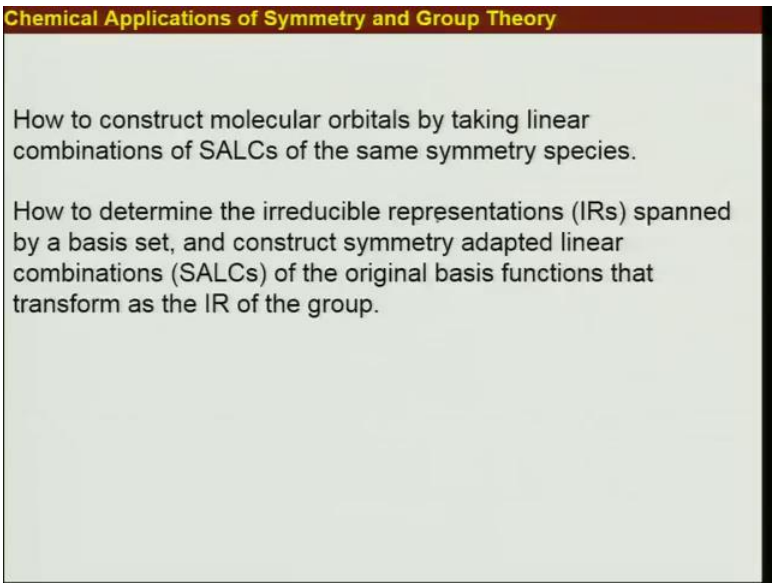

After your learning, this great Orthogonality theorem and also learning a little bit about the relation between the group theory and quantum mechanics, we started learning about

how to construct molecular orbitals by taking linear combinations of this you know atomic orbitals forming the SALCs symmetry adapted linear combinations. We constructed the symmetry adapted linear combinations for quite a few molecules.

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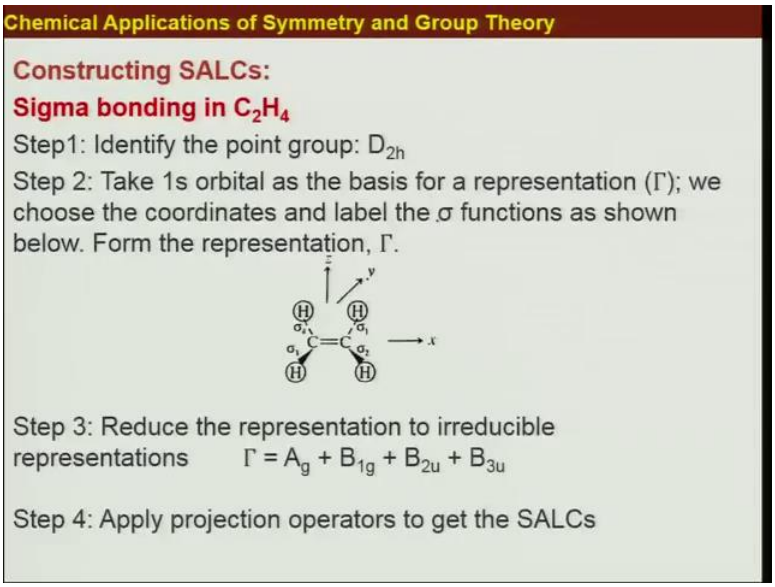

So that we you know get the essence of that. We described different steps involved in this particular process; for example, when we took the case of C 2 H 4, which we once again here. What we did there? We identified the point 2 first. we started with like finding all the structure using something like VSPR theory, something and find out the structure, finding the point group and in the next step we selected particular set of basis functions.

In this particular case we selected 1 is orbitals of the hydrogen as the basis set, basis functions and using those basis functions 1 has to form the representation. We did it for each and every molecule that we cared about and that representation was in the next step reduced to its irreducible representations and once we figured that irreducible representations then, we formed the projection operators for each and every irreducible representations, which is contained within our irreducible representations and then we applied this projection operators to find out in on this basis functions to find out what are the ultimate SALCs.

Once we found the required SALCs to start with we have 4 atomic and vital in this particular case of ethylene, so we should get a 4 symmetry adopted linear combinations

as why molecular orbital and this SALCs after we found those we also verified that they are in accordance with the symmetry properties of the final molecule. In this way, we found out all those symmetry adopted linear combinations like here.

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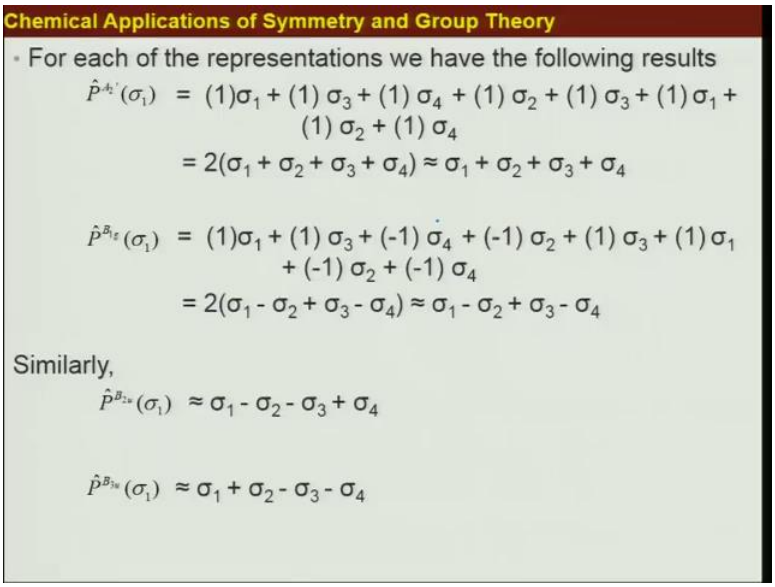

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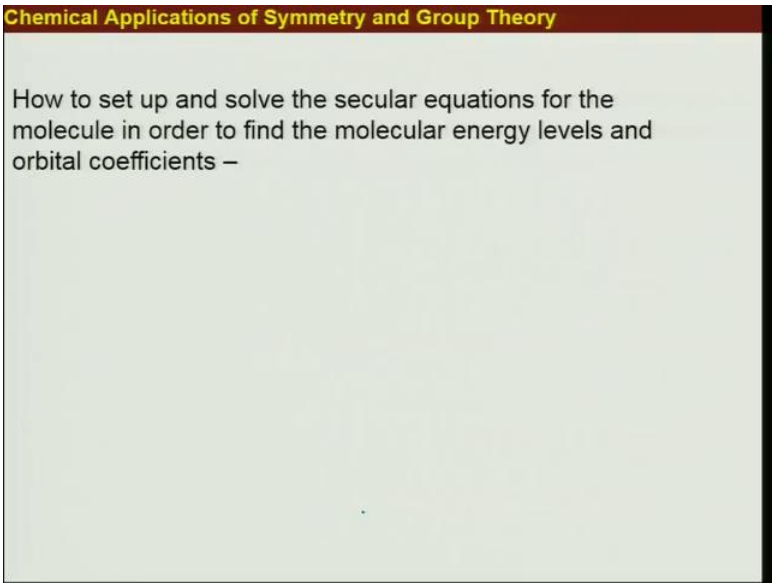

After learning about this symmetry adopted linear combination, our aim was to use these SALCs and you know which form the molecular orbitals and also assign the energies to them and later on to find out about the possibilities of you know electronic or you know transitions from 1 molecule orbital to another molecular orbital. In order to do that, we

learnt how to set up the secular equations and you know in the form of secular determinant and solve them, using certain approximations and which are known as Huckel's approximation and then we find energy levels and also we learnt about how to find out in orbital coefficients.

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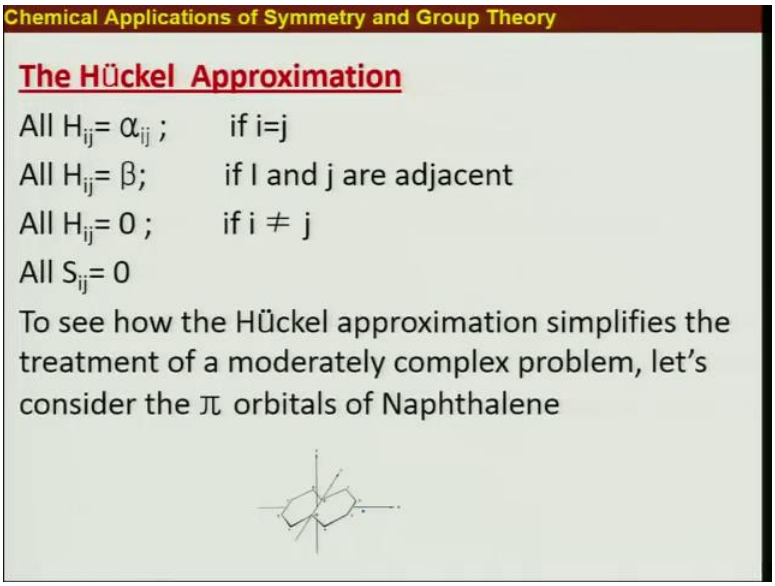

We learned about the Huckel approximation. You know though it is approximation, but it is quite good for you know the purposes that would like to serve. So, using the Huckel approximation, we try to set up the secular equations in form of secular determinants.

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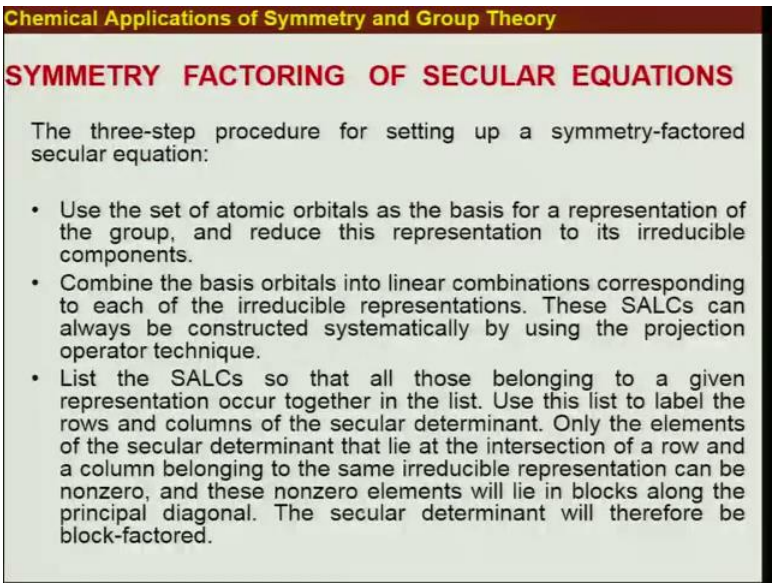

What are the steps that we followed here? We first took the atomic orbitals basis, is very similar to what we did in case of just formation of SALCs, those to start with you from the SALCs and find out the irreducible components to which they belong to and then you can, you use the projection operator to form this is SALCs and you know list all this SALCs. That is those belonging to a particular representation, all got together in the list and you know after getting the symmetric properties like to which particular irreducible representation, one is SALCs belongs to, you club them together that like for one particular SALCs suppose, one particular irreducible representation. I find 3 SALCs transformed as that particular irreducible representation then club them together and then from the secular determinant you solve it, apply the Huckel approximation and solve for the energies and once you find the energy, you get molecular orbitals as a function of energy.

we learned that and also you know after getting those molecular orbitals as a function of their energies in the end of the course when we are dealing with spectroscopy part, then we learned how to know whether one type of transition from 1 molecule orbitals and another molecule orbitals is allowed or disallowed and we also learned about that about the intensity is that I associated with one of such transitions.

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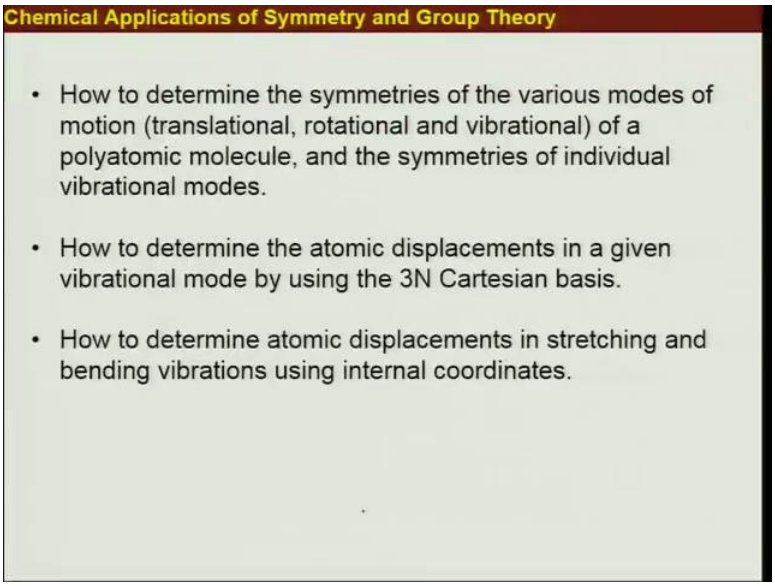

Then we learnt about the symmetry properties of various types of motions in the within the molecule. We talked about translational rotational and vibrational. Mostly we dealt

with the vibrational motion that is the motion of this internal coordinate where the center of mass elements stationary. We learned about the degrees of freedom, how to find them out, what the basis for finding this to use of them out and we learnt about how to determine the atomic displacements in a given vibrational mode by using 3 N Cartesian coordinate and also you know how to determine the atomic displacement, for example, in like stretching or bending vibration using the internal coordinates.

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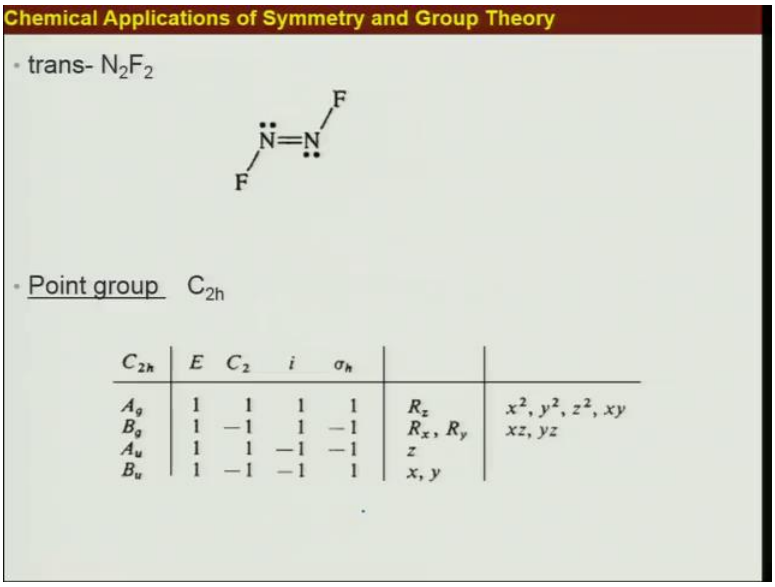

For example, we took the case of trans planner N 2 F 2 molecule and we systematically figured out, what are the normal modes? What are their symmetries and how the sum? You know normal modes look like. How did we do it? We first found out the point group, we opened the character table of that particular point group, kept it with pass because we needed to use it very similar to the case of you know SALCs.

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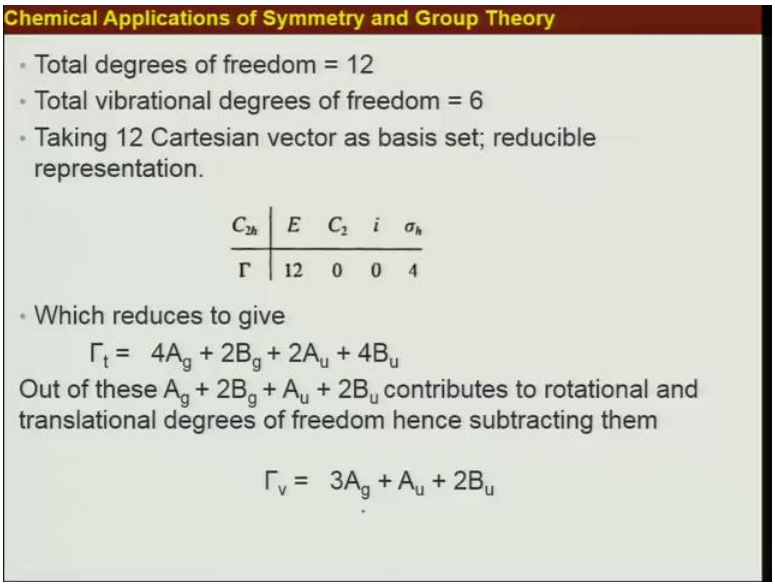

Then we figured out that, what you know first we took all the Cartesian coordinate on each and every atom as my basis function. There are 3 N number of basis function for any given molecule and we for this particular Nth molecule, we found that basis set of comparison 12 Cartesian vector and we found the representation and then in the next step we reduced it.

After reducing we eliminated the contributions coming from translational and rotational motion and we were left with only those irreducible representations that are you know related to the genuine Vibrational modes. So thereby we figured out that these are the symmetries of the possible normal modes for the particular molecule.

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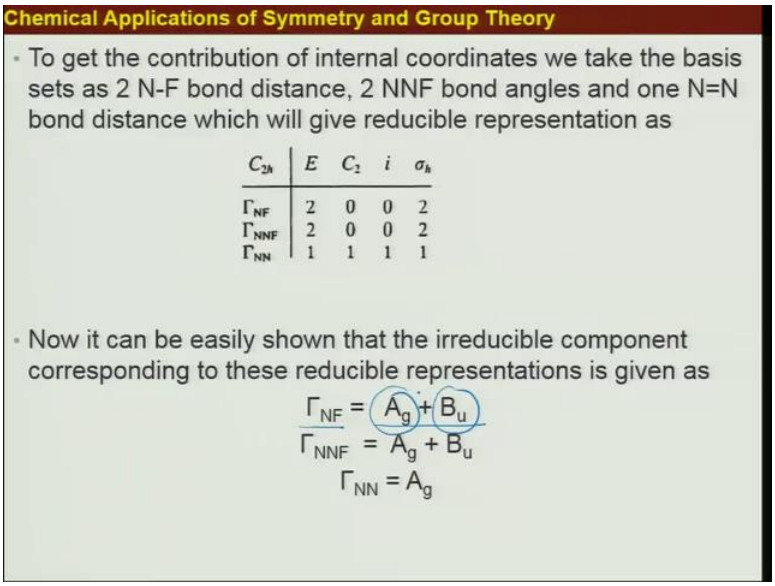

Once we have figured it out then, what we did? We use the internal coordinate. We could select any particular integral coordinate such as the bond distances or the bond angle. We used for this particular case the Nth NN bond distances and N NF bond angles to figure out which particular, we found out that we have normal mode which deals with the motion of this NF bond and they belong to this and this symmetries.

Looking at these symmetries, we could easily figure out what will be the nature of each 1 of these normal modes. For example, when we found the representation based on this in NF bond distance we figured out that there are 2 irreducible representations according to which these particular N F bonds distance, they can transform as. We had at least figured out there are 2 normal modes, which involves this motion of this NF bonds.

Now whichever way that was given by this symmetries like Ag or Bu symmetries knowing the property of this Ag and Bu we could very easily tell that 1 of this motion of NF bond in 1 normal mode is purely a symmetric in nature. It is symmetry starching on the other hand, other mode is of asymmetric nature. It was in asymmetric stretching. In that way we could exactly figure out, what are the exact normal modes for this molecule, what are their symmetries and figure out what in which particular way that atom in that particular normal mode shows the displacement.

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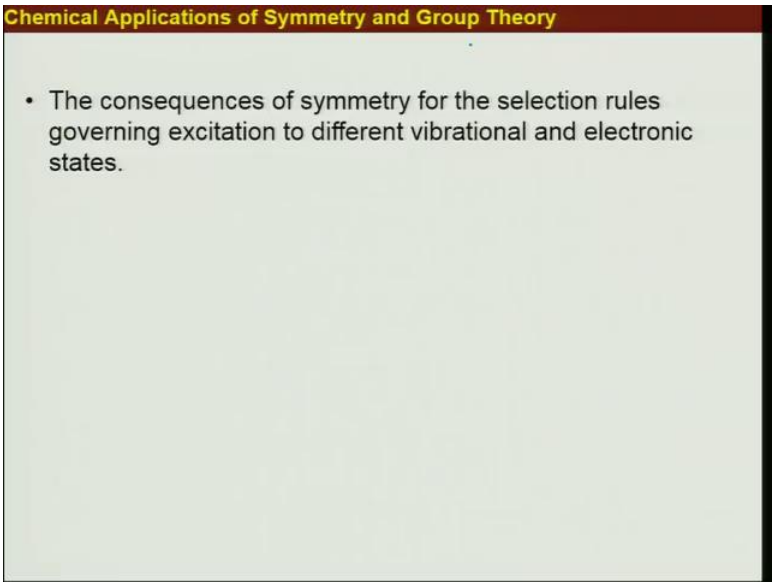

We learnt about also how to find out the rules that control the excitation of different Vibrational as well as electronic states. The main thing here we learned is the application of direct product. We ultimately have situation where 2 states are connected by an operator which is either a dipole moment operator or is the Polarizability operator and depending on the case that we are studying. We constructed a transition moment integral involving this initial and final states the Vibrational or electronic and where NN operator. We look, we learnt from the relation between good theory and quantum mechanics that each of this wave functions they form the basis of 1 of the irreducible representation for that particular molecule point group. If we know the states, we know the symmetries. Once we know the symmetries, we can have a sincerely the direct product between the functions and operators.

If the direct product contained the totally symmetry irreducible representation then this transition moment integral will survive, otherwise it will vanish meaning if the direct product contained the totally symmetry irreducible representation of the molecule point group, then the transition will be allowed, otherwise the transition will be forbidden. We took certain cases and in case of molecular electronic transition, what we did is we used the same set of molecular orbitals that was formed by forming the SALCs for natural molecule. In 1 of the classes, we took the same example. We got a series of molecular orbitals, we you know took 1 electron out from 1 orbital and then put it in their higher

energy already and knowing the symmetries of these SALCs, we could find the symmetry of the overall electronic state.

We learnt how to find the symmetry of the overall state from the symmetries of the orbitals and using those states, we found out with the 1 particular transition was allowed or not. You know in this way kind of completed this particular lecture series. The basic aim of this course was to give your introduction about the symmetry and group theory and you know take you through several relations that you know you were able to utilize those techniques to solve certain chemical problems. For example, like finding out with that you know certain particular orbitals will take part in the molecule orbital formation, whether certain you know whether we can figure out, what is the symmetry of a given normal mode, how will be the normal mode and you know also how to find out whether the transition will be allowed or not, how to find out this symmetry of the electronic state and so on.

Using this basic knowledge, 1 can go to the advanced level where 1 can actually use it for the problems which are encountered in 1 side this is slide. For example, someone works in the field of inorganic chemistry. All the time dealing with mechanical bonding, 1 can use actually use the knowledge of this how to form the symmetry adapted linear combinations and then how to get the energies of this particular molecules states can be applied on those kind of systems, 1 someone who is working in the field of Vibrational spectroscopy or Raman spectroscopy. The basic knowledge that we start we tried to you know get through this course will be extremely valuable 1, when 1 you know tries to find out or do some normal mode analysis for a molecule having a larger size and you know find out the possibilities or various different type of transition involving the Vibrational states within that molecule.

I hope that all of you have enjoyed this course and I also I am extremely hopeful that you know you learned certain basic stuff which will be extremely helpful for you in the near future. Thank you for your attention throughout this course and I wish you all the best.

Thank you very much.