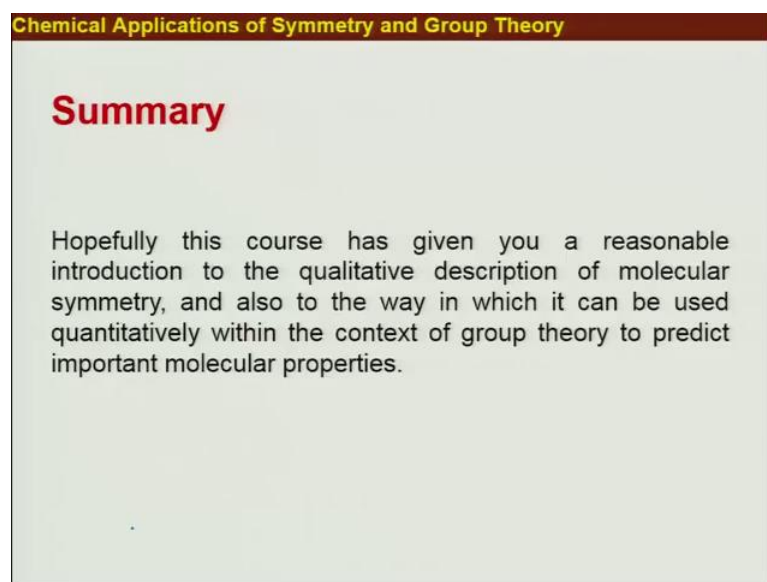


Chemical Applications of Symmetry and Group Theory
Prof. Manabendra Chandra
Department of Chemistry
Indian Institute of Technology, Kanpur

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 qualitative description of molecular symmetry and also we have learned the way in which it can be used in both not only qualitative. Let us go through one by one, what are the things that we have learned over the past 8 weeks.

(Refer Slide Time: 00:40)



Chemical Applications of Symmetry and Group Theory

Summary

Hopefully this course has given you a reasonable introduction to the qualitative description of molecular symmetry, and also to the way in which it can be used quantitatively within the context of group theory to predict important molecular properties.

(Refer Slide Time: 01:13)

Chemical Applications of Symmetry and Group Theory

The main things you should have learnt in this course are:

- How to identify the symmetry elements possessed by a molecule and assign it to a point group.

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.

(Refer Slide Time: 01:50)

Chemical Applications of Symmetry and Group Theory

Symmetry Elements and Symmetry Operations

Symmetry element	Symmetry operation	Symbol
	Identity*	E
n -Fold symmetry axis	Rotation by $2\pi/n$	C_n
Mirror plane	Reflection	σ
Center of inversion	Inversion	i
n -Fold axis of improper rotation†	Rotation by $2\pi/n$ followed by reflection perpendicular to rotation axis	S_n

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.

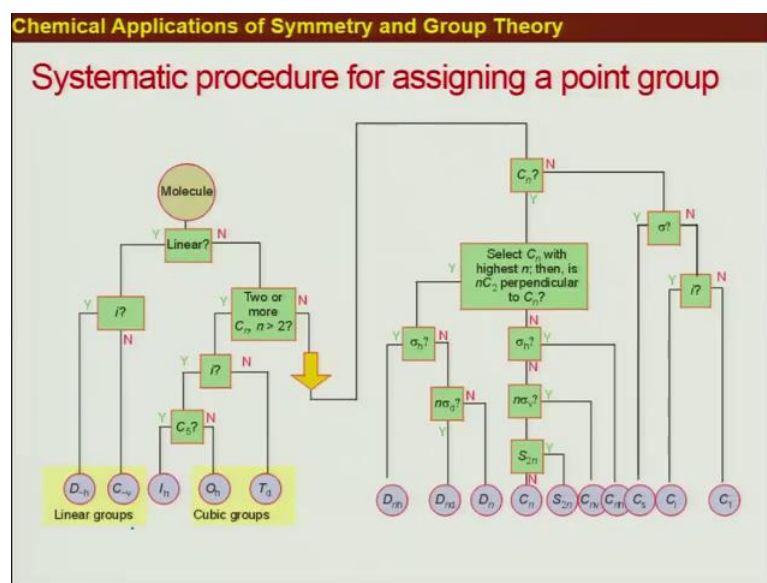
We learnt about the symbols that are provided for each of this element as well as the operation. We had E for identity, C_N for proper axis rotation of order N, S_N for improper axis of rotation of order N we have I for inversion symmetry and sigma for the reflection planes and the symbols for symmetry 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_N³ 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 closure 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 operation 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 Abelian 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.

(Refer Slide Time: 06:07)



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.

(Refer Slide Time: 06:44)

- Chemical Applications of Symmetry and Group Theory**
- 2. The consequences of symmetry for chirality and polarity of molecules.
 - The effect of applying two or more symmetry operations consecutively (group multiplication and stereographic projection)

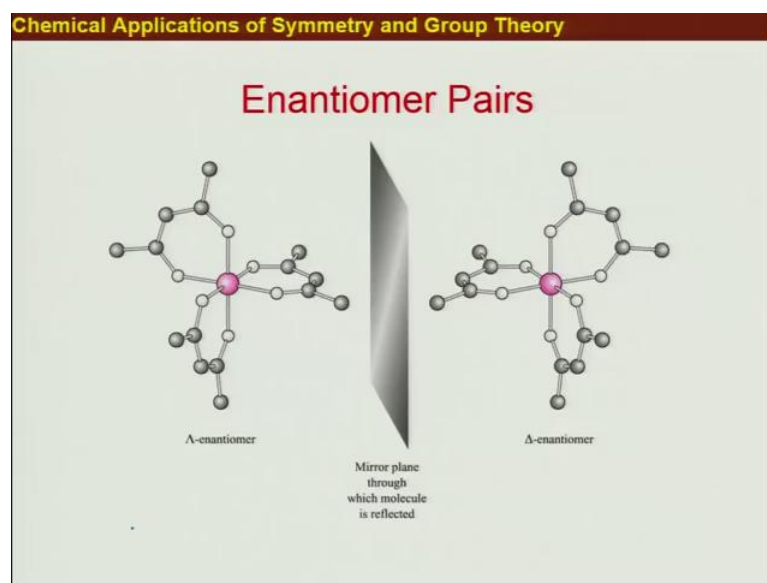
After you know we learnt about how to form the point groups. By the way we also know that this point groups were given certain symbols and this symbols known as so, implies

notation and after having gone through this part, we also learned that, the presence of certain symmetry elements in a particular molecule, will also tell us about certain molecular properties namely Chirality and Polarity. We discussed in quite a bit of detail that how absence of the σ_h 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 sort of σ_h and when you say this σ_h , we know that this N can be even this S_2 . Any sort of σ_h and the same time S_1 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 σ_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.

(Refer Slide Time: 09:39)



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.

(Refer Slide Time: 10:18)

Chemical Applications of Symmetry and Group Theory

Group multiplication table for Ammonia

G_6	E	A	B	C	D	F	NH_3	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
E	E	A	B	C	D	F	E	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
A	A	E	D	F	B	C	σ_v'	σ_v'	E	C_3	C_3^2	σ_v''	σ_v'''
B	B	F	E	D	C	A	σ_v''	σ_v''	C_3^2	E	C_3	σ_v'''	σ_v'
C	C	D	F	E	A	B	C	σ_v'''	C_3	C_3^2	E	σ_v'	σ_v''
D	D	C	A	B	F	E	C_3	C_3	σ_v'''	σ_v'	σ_v''	C_3^2	E
F	F	B	C	A	E	D	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.

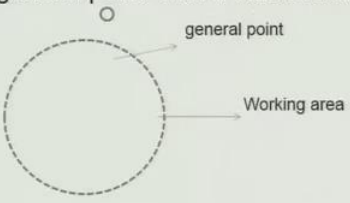
Like you know for group 3, group 4, group 5, group 6, we learnt a certain number of such a group multiplication tables are possible. Once we learnt this technique, how to form this group multiplication table, then if we encounter with any particular group of having any particular order, then it should 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.

(Refer Slide Time: 12:49)

Chemical Applications of Symmetry and Group Theory

Stereographic projections

- The **stereographic projection** is a particular mapping (function) that projects a sphere onto a plane.
- We start by defining a “working area” with a dashed circle, and marking some “general point” with a little circle.



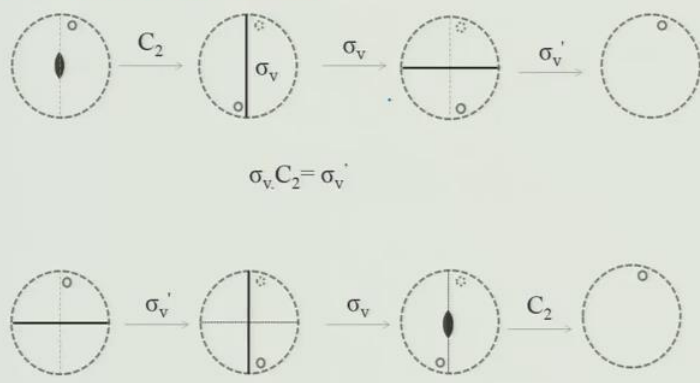
The diagram shows a dashed circle representing the 'Working area'. A small circle inside it represents the 'general point'.

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, I 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.

(Refer Slide Time: 13:45)

Chemical Applications of Symmetry and Group Theory

Product of symmetry operations using stereographic projection



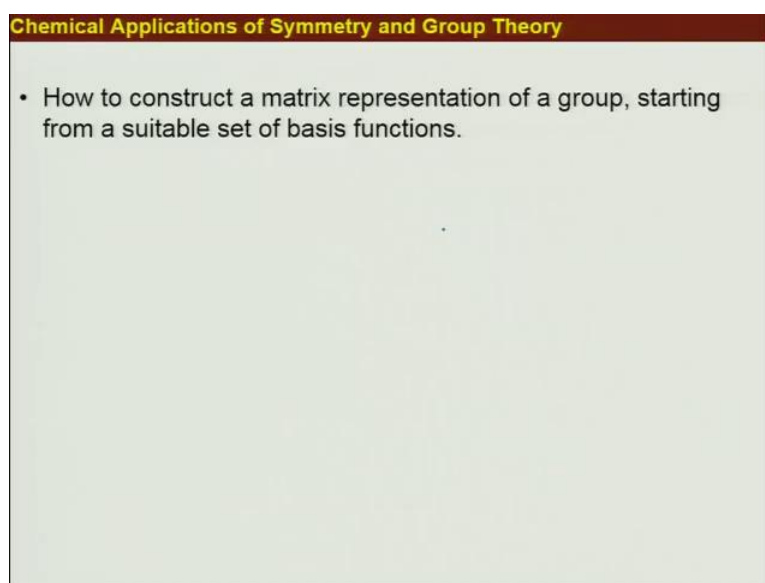
The diagram illustrates the product of symmetry operations using stereographic projection. It shows two sequences of operations:

Sequence 1: C_2 followed by σ_v results in σ_v' . The equation $\sigma_v C_2 = \sigma_v'$ is shown below.

Sequence 2: σ_v' followed by σ_v results in C_2 . The equation $\sigma_v \sigma_v' = C_2$ is shown below.

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 σ_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.

(Refer Slide Time: 14:39)



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.

(Refer Slide Time: 16:08)

Chemical Applications of Symmetry and Group Theory

Representation of Group

- A representation of group may be defined as the set of matrices, each corresponding to a single operation in the group, that can be combined among themselves in a manner parallel to the way in which group elements (symmetry operations) combine.
- We worked out the representation of C_{2v}

Considering that the principal axis coincides with z axis, σ_v be the xz plane, and σ_v' be the yz plane the matrices corresponding to all the operations in C_{2v} were found to be:

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2: \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
$$\sigma_v: \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v': \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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_{2v} and σ_v and σ_v' 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.

(Refer Slide Time: 18:17)

Chemical Applications of Symmetry and Group Theory

Character Table

- A **character table** is a two-dimensional table whose rows correspond to irreducible group representation, and whose columns correspond to conjugacy classes of group elements. The entries consist of characters, the trace of the matrices representing group elements of the column's class in the given row's group representation.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$
II		I		III	IV

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.

(Refer Slide Time: 19:42)

Chemical Applications of Symmetry and Group Theory

The Great Orthogonality Theorem

- The order of a group is denoted by h .
- The dimension of the i^{th} representation, which is the order of each of the matrices which constitute it, is denoted by l_i
- The various operations in the group are given a generic symbol R .
- The element in the m^{th} row and the n^{th} column in the matrix corresponding to the operation R in the i^{th} irreducible representation are denoted as $\Gamma_i(R)_{mn}$
- The Great Orthogonality Theorem can be stated as

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

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.

(Refer Slide Time: 20:15)

Chemical Applications of Symmetry and Group Theory

How to construct molecular orbitals by taking linear combinations of SALCs of the same symmetry species.

How to determine the irreducible representations (IRs) spanned by a basis set, and construct symmetry adapted linear combinations (SALCs) of the original basis functions that transform as the IR of the group.

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.

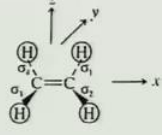
(Refer Slide Time: 20:45)

Chemical Applications of Symmetry and Group Theory

Constructing SALCs:
Sigma bonding in C₂H₄

Step 1: Identify the point group: D_{2h}

Step 2: Take 1s orbital as the basis for a representation (Γ); we choose the coordinates and label the σ functions as shown below. Form the representation, Γ.



Step 3: Reduce the representation to irreducible representations $\Gamma = A_g + B_{1g} + B_{2u} + B_{3u}$

Step 4: Apply projection operators to get the SALCs

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 C₂H₄, 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 1s 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.

(Refer Slide Time: 22:50)

Chemical Applications of Symmetry and Group Theory

- For each of the representations we have the following results

$$\hat{P}^{A_1}(\sigma_i) = (1)\sigma_1 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_4$$

$$= 2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \approx \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$

$$\hat{P}^{B_1}(\sigma_i) = (1)\sigma_1 + (1)\sigma_3 + (-1)\sigma_4 + (-1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (-1)\sigma_2 + (-1)\sigma_4$$

$$= 2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \approx \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$$

Similarly,

$$\hat{P}^{B_2}(\sigma_i) \approx \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4$$

$$\hat{P}^{B_3}(\sigma_i) \approx \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$$

(Refer Slide Time: 23:03)

Chemical Applications of Symmetry and Group Theory

How to set up and solve the secular equations for the molecule in order to find the molecular energy levels and orbital coefficients –

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.


(Refer Slide Time: 24:00)

Chemical Applications of Symmetry and Group Theory

The Hückel Approximation

All $H_{ij} = \alpha_{ij}$; if $i=j$
All $H_{ij} = \beta$; if i and j are adjacent
All $H_{ij} = 0$; if $i \neq j$
All $S_{ij} = 0$

To see how the Hückel approximation simplifies the treatment of a moderately complex problem, let's consider the π orbitals of Naphthalene



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.

(Refer Slide Time: 24:18)

Chemical Applications of Symmetry and Group Theory

SYMMETRY FACTORING OF SECULAR EQUATIONS

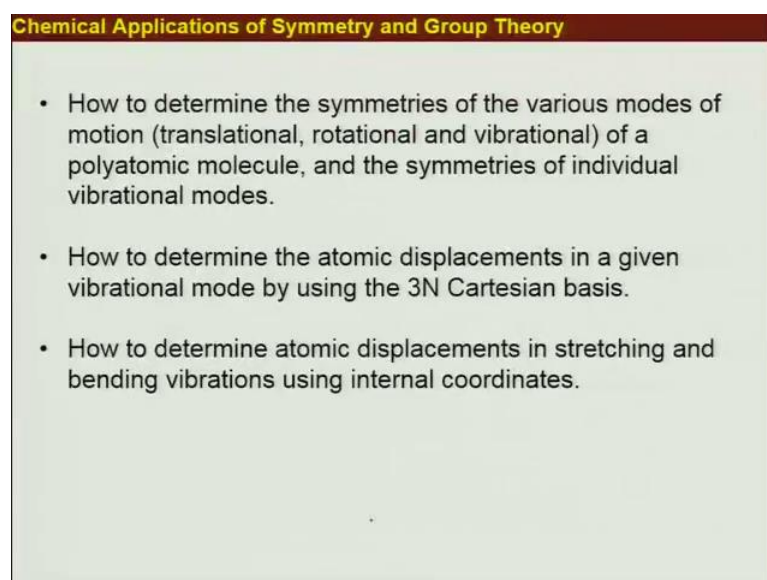
The three-step procedure for setting up a symmetry-factored secular equation:

- Use the set of atomic orbitals as the basis for a representation of the group, and reduce this representation to its irreducible components.
- Combine the basis orbitals into linear combinations corresponding to each of the irreducible representations. These SALCs can always be constructed systematically by using the projection operator technique.
- List the SALCs so that all those belonging to a given representation occur together in the list. Use this list to label the rows and columns of the secular determinant. Only the elements of the secular determinant that lie at the intersection of a row and a column belonging to the same irreducible representation can be nonzero, and these nonzero elements will lie in blocks along the principal diagonal. The secular determinant will therefore be block-factored.

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.

(Refer Slide Time: 26:20)



Chemical Applications of Symmetry and Group Theory

- How to determine the symmetries of the various modes of motion (translational, rotational and vibrational) of a polyatomic molecule, and the symmetries of individual vibrational modes.
- How to determine the atomic displacements in a given vibrational mode by using the $3N$ Cartesian basis.
- How to determine atomic displacements in stretching and bending vibrations using internal coordinates.

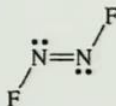
Then we learnt about the symmetry properties of various types of motions in the within the molecule. We talked about translational rotational and vibrational. Mostly we dealt

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.

(Refer Slide Time: 27:15)

Chemical Applications of Symmetry and Group Theory

• trans- N_2F_2



• Point group C_{2h}

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

For example, we took the case of trans planner N_2F_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.

(Refer Slide Time: 27:48)

Chemical Applications of Symmetry and Group Theory

- Total degrees of freedom = 12
- Total vibrational degrees of freedom = 6
- Taking 12 Cartesian vector as basis set; reducible representation.

C_{2h}	E	C_2	i	σ_h
Γ	12	0	0	4

- Which reduces to give
$$\Gamma_t = 4A_g + 2B_g + 2A_u + 4B_u$$
Out of these $A_g + 2B_g + A_u + 2B_u$ contributes to rotational and translational degrees of freedom hence subtracting them
$$\Gamma_v = 3A_g + A_u + 2B_u$$

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.

(Refer Slide Time: 28:46)

Chemical Applications of Symmetry and Group Theory

- To get the contribution of internal coordinates we take the basis sets as 2 N-F bond distance, 2 NNF bond angles and one N=N bond distance which will give reducible representation as

C_{2h}	E	C_2	i	σ_h
Γ_{NF}	2	0	0	2
Γ_{NNF}	2	0	0	2
Γ_{NN}	1	1	1	1

- Now it can be easily shown that the irreducible component corresponding to these reducible representations is given as

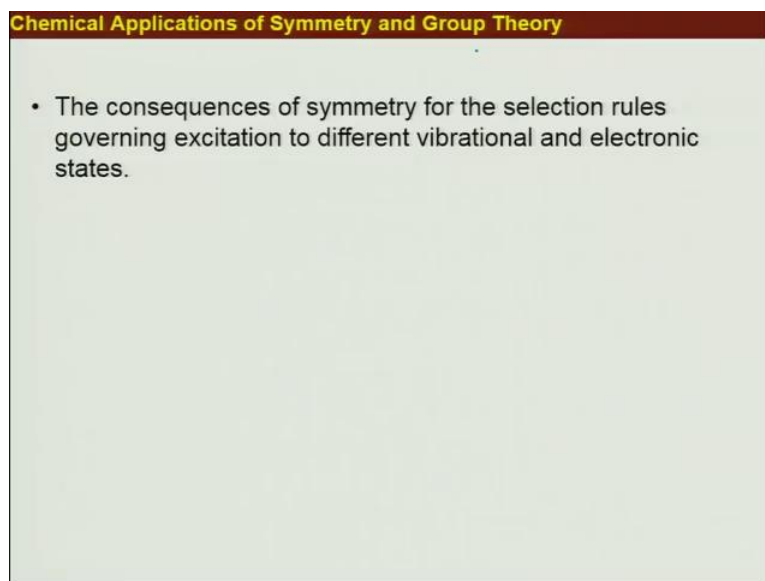
$$\begin{aligned}\Gamma_{NF} &= A_g + B_u \\ \Gamma_{NNF} &= A_g + B_u \\ \Gamma_{NN} &= A_g\end{aligned}$$

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 A_g or B_u symmetries knowing the property of this A_g and B_u 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 stretching 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.

(Refer Slide Time: 30:57)



Chemical Applications of Symmetry and Group Theory

- The consequences of symmetry for the selection rules governing excitation to different vibrational and electronic states.

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.