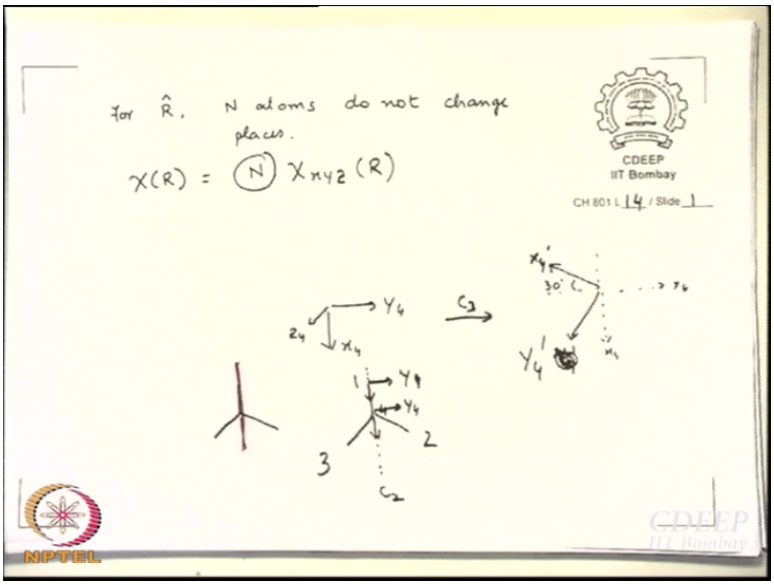
Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 37
Recap: Reducible Representation for Normal Modes

(Refer Slide Time: 00:18)



What were we doing? We are dealing with the 3N number of normal modes. For each operation let us say, for an operation R, let us say N number of atoms do not change places. So what is going to be chi (R)? What is going to chi (R). Anup, do not violate Ahvah principle. What is chi(R)? N. N multiplied by what? Shall I call it chi xyz (R) will you allow me to call it chi xyz (R). Is that what we wrote last day? We have forgot that I do not remember what I wrote.

Remember what we did for BF3 unfortunately today is one day where I have not brought my laptop, but what did we do? We fixed unit vectors on every atom we call them x1y1z1, x2y2z2, x3y3z3, x4y4z4 and then we perform whatever operation we have to perform. Think of C3 for example. When we applied C3 what happened? 1 moved to the original position of 2, 2 moved to the original position of 3, 3 moved to the original position of 1 and so remain what it was and then I think we had worked out the entire 12 x 12 matrix there was it 12 x 12?

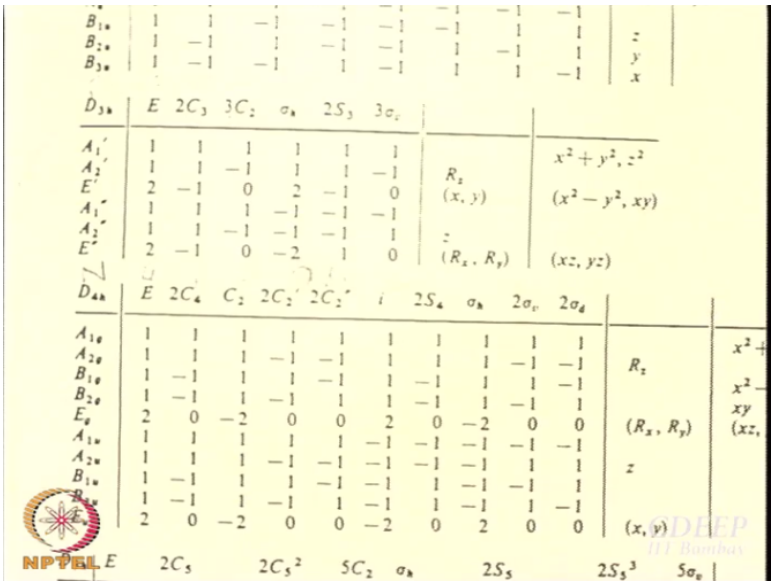
We worked out that entire 12 x 12 matrix and we have said that whichever atom changes position upon that symmetry operation does not contribute. Does not contribute to what to the character? Do you remember that? Because they go off diagonal and in character only the diagonal elements will contribute. Now what do I get? What is it that contributes then? For C3 operation for example for 1, 2, 3, 4 only atom number 4 contributes is it right?

If atom number 4 is the only one that is contribute what is it that we are using as the basis? Xyz? X, y, z. This is how we had held it or no, this is how we held it, x below, y pointing this way, and z pointing this way and then we say that we rotate it by 120 degrees. So basically what we are doing is we are working with a set of xyz for 4 only and 4 is the only atom that does not change place. And how will this xyz transform.

Exactly in the same way as is given in the character table. Right or wrong? Right. So say that. Now if I take what I am doing essentially is the N part clear that only those atoms that do not change places will contribute and then think of C3 that is what I am saying. Think of C3 in C3, E, in D3H. So in for atom number 4 what we said was this was x4, this was y4, and this was z4. You give the C3 rotation what do you get? z4 remains z4 I will not even draw it.

What about x? Where does x go. This was x4, this was y4. Where will x4 go? 90 degrees and then 30 degrees further. So it goes here. This here is your x4 dash. This is 30 degrees. Where is y4 go? I can tilt a little bit and I can simply draw a line that is perpendicular to x4 dash and this angle will also be 30 degrees naturally. So what is that we are transforming? We are transforming unit vectors along x, y, and z. So what I am trying to say is if you now look at the character table.

(Refer Slide Time: 06:13)



The problem is that I have zoom it again. D3h, see what happens? Z what is the character of C3 for z? 1. And what is the character for xy for C3 operation? -1. What I am saying I simply take those characters isn't it. So I am taking x, y and z together so you are basically adding 2 blocks. So what will be the total character? 0, -1 from xy and + 1 from z. The total character will be 0. Now think of what we have done at that time. Did we not get 0 after all that operation?

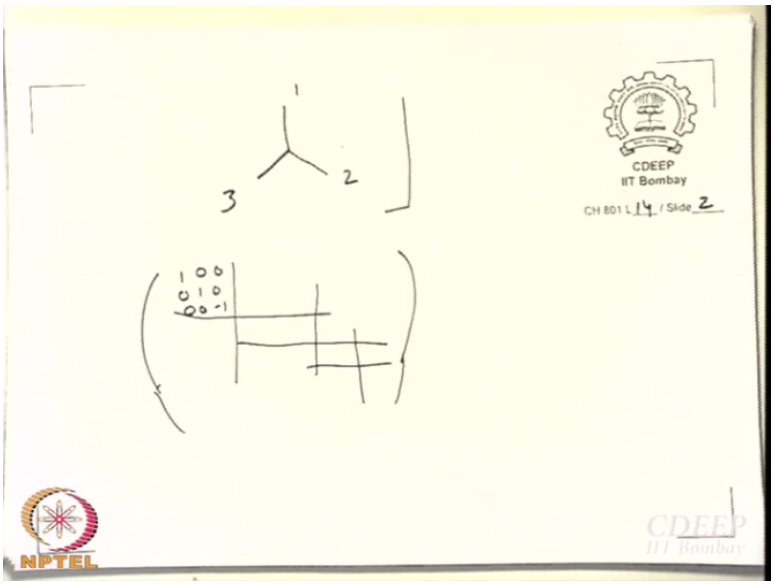
Yes, or no? Did we get 0 or not? So what I am saying is this is how we got the 0. Number of atoms that remain unchanged upon the symmetry operation multiplied by character that you get from x, y, z for the same operation. Now did you understand for C3? Now let us think of something else. What I got C2. This is my bad handwriting. Got it? Now let us think of something else. Think of C2. You have drawn out molecule like this and we have taken our C2 to be along since I have other colours I hope, is this a different colour?

You cannot make out it is a different colour, which means that this camera is as colour blind as I am. I do not know how to do it actually. Anyway, let me draw it again. This is my molecule. Then let us say if I draw like this we will be able to make out this isn't it? This here is my C2 axis, 1, 2, 3, and this one of course is 4. If I apply c2 then what will happen? 2 and 3 interchange places 1 and 4 do not interchange places. Now what happens to the vectors?

Where is x for 1. Where is x1? This is x1 where is x4. This is x4 do they change? They do not change. What about y1. Y1 becomes - y1. What about Y4 that becomes - Y4. So whatever happens to Y1 also happens to Y4 because essentially they are unit vectors that are parallel to each other isn't it. So now if I want the character what will I do?

I know what is the character for x, y, and for z for C2 operation. I will just read out from the character table here. For xy the character is 0 for C2 and for z the character is - 1. So what will be the character then? - 1 * 2 - 2. Did you not get - 2 earlier when we actually worked it out now is it starting to make sense? You understand what you are supposed to do? What was next? sigma v. No sigma h.

(Refer Slide Time: 11:04)

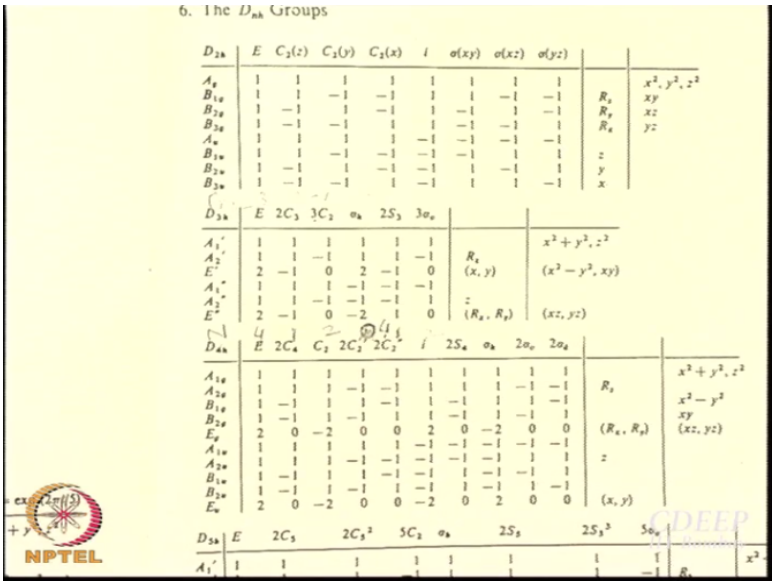


So, sigma h. So 1, 2, 3, this is 4 I won't even right. If you apply sigma h then what happens? Which plane is sigma h? xy plane. So now do you agree with me that x1 remains x1, x2 remains x2, x3 remains x3 and x4 remains x4. Similarly, y. What about y you do not like y after x you want to go to z that is not very good. So y1 remains y1, y2 remains y2, y3 remains y3, y4 remains y4.

So whatever happens to 1 y happens to all the ys provided the atom has not moved from its original position and z changes sign. So had we said? You said we have 4 identical blocks. Isn't it? If we do not say that vertex is like this transformation matrix. We have this 4 identical blocks

and what are the blocks x remains what it is, y remains what it is, z changes sign. So 1, 1, 1. Isn't? So do not we get by the same relationship n * chi xyz, are?

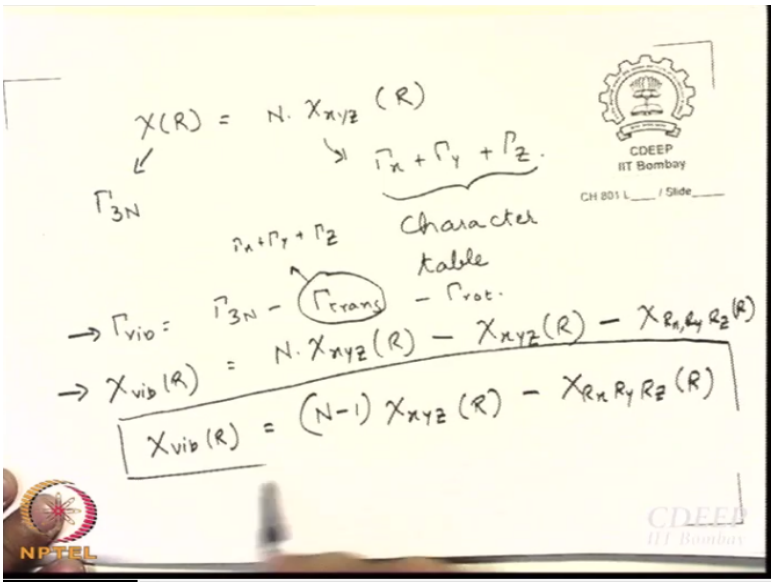
(Refer Slide Time: 12:39)



Let us see what is chi xyz, are? Can you read now? What is chi x, y for sigma h? 2 and what is chi for z so 2 - 1 is 1 and number of atoms unchanged this 4. So what is left? A little lazy instead of s3 let us do sigma v. I do not even draw now. Let us see if you can visualize it and think. You also do not draw. Let us see if we can do it in our minds. **"Professor - student conversation starts"** When I apply sigma v, sigma v along 1/4 then what happens? Atoms change places.

So how many atoms do not change places? 1/4. And which plane is sigma v in terms of x, y and z, zx right. So what will happen to x, what will happen to y, what will happen to z, x and z do not change sign, y changes sign. So what will be the character for each atom? 1, 1, - 1 so 1 and how many atoms do not change places 2. Do we get the same thing from here? **"Professor - student conversation ends"** Sigma v xy is 0, z is 1 so 1 * 2 understood, are you all okay now. So finally this is what we are using. We will write another slide.

(Refer Slide Time: 14:44)



Chi (R) = N * chi xyz, for (R). What is chi (R) it is the character in the reducible representation. Which reducible representation? This here we are talking about gamma 3N isn't it. This chi (R) when we write this chi(R) we are talking about the reducible representation that we generate from the 3N number of coordinates that are there in the molecule. What is N. N you know already?

Number of atoms that do not change places under symmetry operation R upon operation R and what is gamma xyz, this is going to come from gamma x + gamma y + gamma z from the character table. Now can we do this? Now what did you see. Now this is 3N fine. What you need to take out from this. How do I get gamma vib? Gamma vib = gamma 3N - gamma trans - gamma rot. So what you could do is you could work this out character by character.

What I can say now is that for chi vib (R) = N * chi xyz of (R) - will you allow me to write, chi xyz, (R) once again. Chi x, y, z (R) is the character for the particular symmetry operation R in the presentation that is generate by combining the irreducible representations of x and y and z. What is gamma trans? Is gamma trans rot gamma x + gamma y + gamma z. Are you all okay with this? Any question, any doubt, please ask now?

So instead of gamma trans for gamma trans I can write chi xyz. So do not forget what we are doing? This line is about the total representation. This line is about individual characters. So that

is saying is chi vib (R) the character for symmetry operation are in the reducible representation containing the 3N - 6 normal modes of the molecule are given by N * chi xyz, (R) - chi xyz (R) - chi Rx, Ry, Rz (R). So this can be simplified as chi vib (R) = (N - 1) chi xyz (R) - chi Rx, Ry, Rz (R).