Symmetry and Group Theory
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Lecture – 34
Symmetry of Normal Modes: D3h

Character table, what are the character table? **"Professor - student conversation starts"** for classing them. What was that? Cyclic groups character tables in which we have imaginary characters that is one thing, right. Are we all okay with that? What else did we learn. Imaginary. I just said imaginary. What is the real thing that we learnt? Reducible. How to reduce irreducible representations into representations that are not reducible, right.

How to reduce irreducible representations into representations that are not reducible, that is what we learnt. How do we reduce reducible representations to irreducible representations? Yes? Block, block factorization? How do I do block factorization? But did we do similarity transformation? **"Professor - student conversation ends."**

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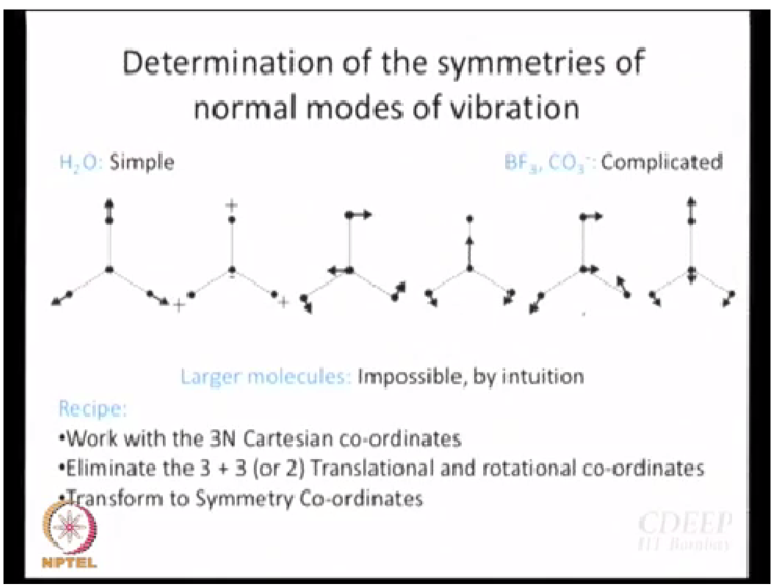

What we said is that if you want to do similarity transformation, that is the right thing to do. But it can become very complicated. So in case you have gone through that example that I suggested you to go through before mid sem in Harris and Bertolucci, then you will understand how complicated it can become. It is extremely difficult to find the matrices that are actually supposed to be used to perform the similarity transformation. We took an easier way out.

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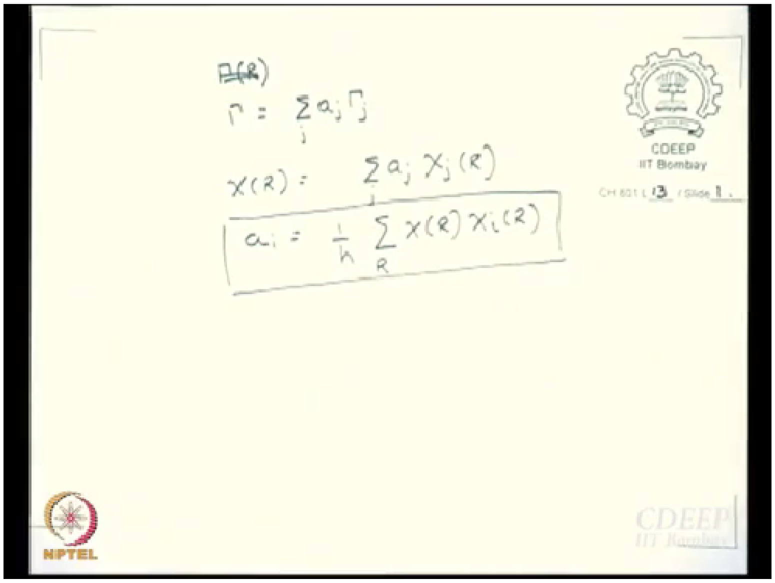

We said that if this is the reducible representation or rather if this is the reducible representation gamma that, and if it is written as sum over j aj gamma j, what is gamma j? gamma j is the jth irreducible representation which makes up the reducible representation. Earlier we have said it that you can construct irreducible representations by block addition of the reducible representations, right.

Is not it? So this is how I can write it. So if this is the case, what we said is that X of R=Sum over j aj Xj of R and hence what we found was ai=1/h sum over i, i is the specific number. It cannot be sum over i. Sum over R, XR, X of R Xi of R. This is how we break up reducible representations into their constituent irreducible representations. Alright? Okay. And this is the golden rule.

I need you to remember this. So today what we are going to do is, we are going to generate irreducible representation to start with. So what we will do is, we will generate a reducible representation and this reducible representation is going to be something that is relevant to chemistry and then we will see how we will break it down into its components. So now we are really getting into applications of all these things that we have studied so far.

I had actually planned to do it at the end. But then for different reasons I thought I do it now because then something that is very easy and then it is something that can give you a lot of food for thought and I can give homework assignments which you can solve over the next couple of weeks. Yes? So this is what we are going to learn today. Then determination of the symmetries of normal modes of vibration.

What is the meaning of normal modes of vibration? I think we have discussed that in this class. What is the meaning of normal modes of vibration? **"Professor - student conversation starts"** That are linearly… **"Professor - student conversation ends."** Linearly independent ways of vibration. Mode means way. Normal means you already know what is the meaning of normal, right, the independent.

So you can write this set of vibrations and you can say that this set of vibrations are linearly independent and for water, we already know what are the normal modes of vibration, I think we worked that out, right. And I think we also what we did was we found a symmetry classification of this normal modes of water. Is not it? The total, the symmetric stretch, to which symmetric species does it belong? A1.

What about the asymmetric stretch? V1. And what about the bent? A1. So you know how to perform the symmetry classification of normal modes of water at least. Right? Now I think you will agree with me if I say that we can do it fairly easily, right. We did it quite simply, right. In a matter of few minutes just before mid sem. So water, it was simple. However, if you just add, water, how many atoms are there in water? 3.

If you make it a 4 atom system and of course, you can make it a 4 atom system in 2 different ways. Right? You can generate a Td group or you can generate, what is this group? Say BF3 of carbonate. It is D3h, right? Because we have D3 perpendicular to the plane of the molecule, right. Each of these bonds is a C2. Molecular plane is a plane which is horizontal. So it is D3h. For D3h molecule, what I will show you now is the normal modes of vibration.

Are they simple? Can you guess what they will look like if I do not tell you? This one you might be able to guess. So this is like symmetric stretch. It is just that there is another bond. So you, that will be also stretching. Even this you might be able to guess? What is this kind of motion? It is doming motion. Doming motion, dome, you know dome? You go to hostel 15, this thing, mess hall. There is a dome on top.

Of course, there is no reason why you have to go to hostel 15. There is a dome on top. Or if you see many buildings in Andheri, they have this dome on top. So this is doming motion, right. So it is like this.

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So, I think this is easier than that. This is the molecule, is not it? Carbonate of BF3, whatever it is. What is the third one? I remember, cannot even see it. Okay. Can you see all 3? Right. So doming motion will be like this. All 3 go out of plane, then come back and all 3 come behind the plane also. You understand what is doming motion. Actually it is a planar molecule. If it goes out of plane, then you get what is doming motion.

Whatever, this bond going that way and these bond coming this way, is that in normal mode of vibration. This bond going this way and these bonds coming this way, is actually vibration plus rotation. It is like the molecule is rotating, okay. So all 3 going one way, symmetrically. This is + phase and this is - phase. This is doming motion. Okay, understood, Jenniver. **"Professor - student conversation starts"** Yes, sir but that kind of, symmetry will change.

Symmetry will change but then do not forget we are talking about simple harmonic oscillation. What are the essential condition for simple harmonic oscillation? This is a very very good question. No, not coming back to the same position. I have something else in mind. Good. **“Professor - student conversation ends.”** So this one perhaps you can see. Understand the meaning of this + and -, right.

It does not mean that this has 3+ stretch and this is 1- stretch. This one is going behind the plane, the central atom. The other 3 atoms are coming above the plane. Those who have studied CH442, either with me or with Arindam, for them this is the repetition, this class but then whoever have studied it long ago when he was much younger. So it is good that he is studying it again.

And those who have studied it this year, they have not come. So it is okay. But now you can guess this may be. With a little effort, you might be able to guess this also. But then when it is bending, see here it is bending, here also it is bending. What is the difference? The difference is that this atom is fixed and the central atom is moving and in this case, both the atoms are moving.

So even if you can guess that this bending motion will be there, it is not very easy to guess whether the outer atom will move or whether the central atom will move. And if you can actually guess these, this and this one, then we should interchange places. Can you guess this? I tell you sketch the normal modes of BF3? Will you be able to draw these arrows, like this, this and this particular angle that in that particular angle. Not easy.

I cannot guess this if I do not know anything else. So the problem is just increasing one atom makes it so complicated, so if you want to talk about symmetry of normal mode of wing molecules, how do we do it? We cannot guess unlike water. We need something else. And that is where symmetry itself helps us out. That is what we have learnt today, right. That is where character table comes very, very handy.

Mobile phone inside your pocket, it is impossible. You cannot work with larger molecules by intuition, it is impossible, just impossible, right. So what do you do? You need a recipe. Once again we like recipes. We love recipes. Right? Now it is time for one more recipe. Now how many normal modes would an N atomic molecule have? **“Professor - student conversation starts”** Sir linearly, 3N and -5.

If it is linear, then it is 3N -5. If it is non-linear, then is 3N -6. What is so, where did 3N come from. Degree of motion. Vibrational. Number of degrees of motion. No, no, with that, it will, yes. Vibration-translation is fine. Where did 3N come from, you tell me that first? Degree of vibration. Degree of freedom. Total number of degrees of freedom is 3N, right. What is the meaning of total number of degrees of freedom?

No, no, no, no. That, that is also, those are also degrees of freedom but how did you get 3N, that is what I am asking? I have an N atomic molecule; why do I say that it must have 3N number of degrees of freedom. Once again, it is easier than what you are thinking. Sir 3. Yes, x y z. Each atom can go in x y z direction, right. **“Professor - student conversation ends.”** Now when all the atoms move the same distance along x, same distance along y, same distance along z, then it is translation.

Otherwise, it is rotation or vibration. Is not it? That is all. So your starting point even in this 3N -6 is the x y and z axis attached to each and every atom. You understand that. So what we do is you can start with 3N number of Cartesian coordinates. 3 for each on the N atoms. Okay with that? Then what will I do? Then I am going to eliminate the translational and rotational coordinates.

It is very easy to do that from the character table because you already know where x y z belongs, where Rx Ry Rz belong. And then transformation to symmetry coordinates is something that we are not going to do but we will actually talk about you know already, right, that, you know, you have studied the IR spectroscopy. At some level or the other. So if in a carbonyl molecule, what is that 1700 bend.

So how do we do that. How do we say that that is because of carbonyl and something else is because of CF or whatever? We will learn a little bit of that. To start with 3N Cartesian coordinates, build a reducible representation then decompose it. Okay, so here goes. This is my molecule; I have just given it 4 numbers instead of writing the atoms.

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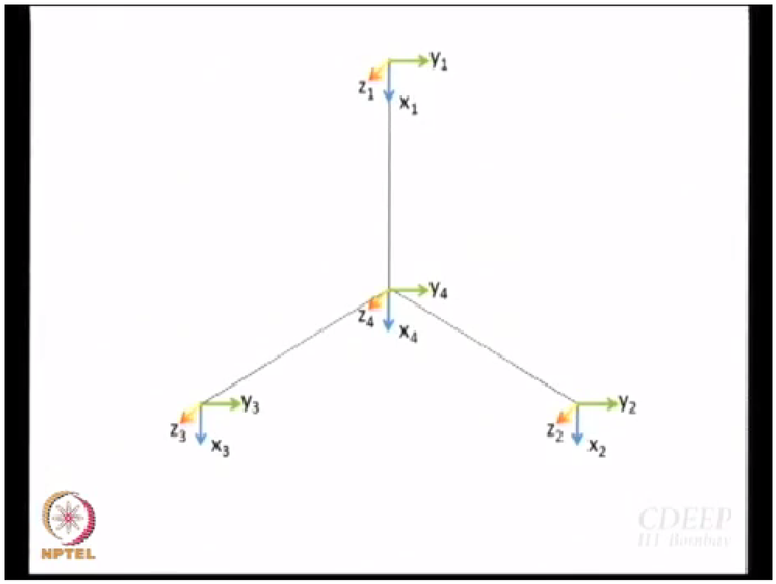

It is a little more convenient, okay. So if it is BF3, then this atom number 4 is B, 1 2 3 are F. If it is carbonate, then atom number 4 is C, 1 2 3 are O. Okay. Now what do I need to do? I need to draw the x y and z axis on them. I will draw them like this. You can draw it anyway you want; it does not matter. Okay. This discussion today is entirely from Cotton's book, okay. Cotton's book on Symmetry.

It is clear enough, is not it, yes. So what I have drawn? I have drawn x1 along this bond. So it is basically pointing downwards. y1 perpendicular to it. z1 is pointing towards us. Okay. So everybody is clear about x1 y1 z1, x2 y2 z2, x3 y3 z3 and x4 y4 z4. Right, okay. Now what we will do is, we are going to see how this coordinates move. So what are, basically what we have taken is?

We have taken unit vectors along x y and z for every atom. They are all unit vectors remember that. We will see how they transform? If I now want to make a representation out of this. If, suppose I want to make a basis out of this? Unfortunately, people who ask those relevant questions are not here today. What to do? They can watch the video. If I want to make a basis out of these x's and y's and z's, then what will be the dimensionality of that basis?

No, 12, 12. So now if using that if I try to make a representation, how we will make the representation? We are going to work out the transformation coordinates. If I make the representations using that, what will be the dimensionality of that reducible representation? 12, right. For D3h, what are the symmetry elements that are there, symmetry operations that are there? E, C3 and how many operations for C3? C3 square, then S3.

< 12, right. Let me show you the character table, then it will be a little easier. **"Professor - student conversation starts"** Sir S3 (()) (15:45) S3 square. Yes, of course. You cannot deny S3 square.

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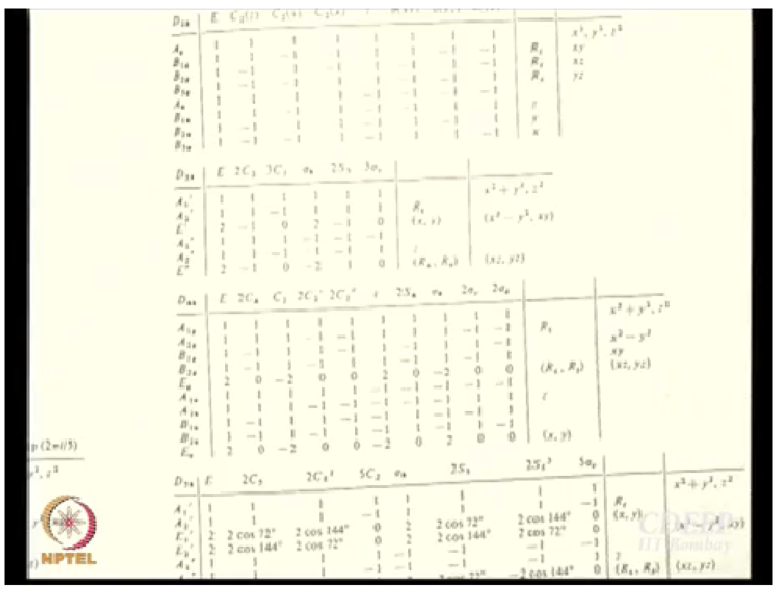

You see D3h? Yes. What do I have? You have E 2C3. 2C3 means C3 and C3 square. Then you have 3C2. 3C2 you can see easily along the bonds. Then you have sigma h. How many sigma h, 1. Then you have 2S3 similarly and you have 3 sigma v's. What is the total? 12. 1 2 3 4 5 6 7 8 9 10 11 12. Okay. So this is the case where h is 12 and we are working with a representation which is also of the same order.

Okay. We will have to write something. Or do I need the character table first? I think I need the character table first. Yes. So let us leave this in this zoom length. **"Professor - student**

conversation ends." So E is very easy. What will be the matrix for E? So you understand what we are doing, right? What will be the dimensionality of the matrices now? **"Professor - student conversation starts"** So you are going to write down not 12*12 matrices and Dolla is not at all amused at that prospect.

But as we will see, things will take care of themselves. Just wait and see. What will be the E matrix? 1 0 0 0 0 0 and all that 0 1 00 etc., etc. 0 0 1 etc., etc. What will be the character? 12. 12. Now that is easy. And see we worked out 1 matrix already. Next what do we have? We have C3 and for C3, we do not have to bother about C3 and C3 square separately. Just C3 is good enough because after all C3 and C3 square belong to the same class.

So character will be the same. Right. So what will happen if I apply C3? What will happen to say z4? z4 will remain z4. What about x4 and y4? They will turn by 120 degrees and then we know what the relationship will be, because we already worked this out earlier. Is not it? 120 degree rotation. Now what about say x1 y1 z1? y1 will become x2. Yes. y1 will become x2. No, no. z1 will become z2. **"Professor - student conversation ends."**

See do not forget that this x1 is along the bond, right. So when you are rotating, transform x1. x1 that will also be along this bond. So it will be a vector sum of x2 and y2. Is not it?

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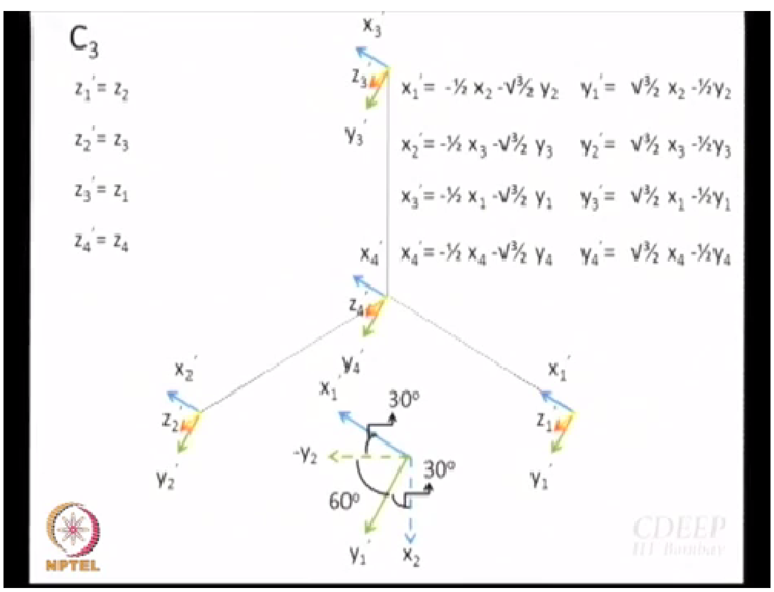

So let us just draw this. This is what it will be. This is where we started from. So just remember this. z1 is very easy. These are the z, so z1 become z2, z2 becomes z3, that is not a problem. Now then next is easy to see x1. x1 is along the bond. So x1- will be along this bond. Moreover, all the other axes will be parallel to x1. Is not it? The other way of thinking is that this x4 is going to be rotated by 120 degrees.

So if x4 is rotated by 120 degrees, where will it go? A little bit of high school geometry one again. What it will be like this? So forget everything else. Look at x4- and x1-. Right, they are along this bond. And then you can just confidently draw x2- parallel to x1- and x4-. Draw x3- parallel to x1- and x2-, right. These z's are very easy, z-. What about y? How do I write y? y also is very easy.

Because y has to be perpendicular to x, right. So it is very easy for me to draw y1- perpendicular to x1-. y4- perpendicular to x4- and the check is that the y should be parallel to each other. So now you see y4- here is parallel to y1- here. Then similarly you can draw y2- here and you can draw y3- here. Alright. So I have now rotated the molecule and I have rotated the coordinates as well.

Now let me without getting scared, let me construct that 12*12 matrix. What is easiest out of x y and z? **"Professor - student conversation starts"** z. z. So let me see. What is z1-? z1-=original coordinates z2, is not it? z1-=z2, will you agree with me? What is z2-? z3. z3- is z1. z4- is the easiest z4, right. Okay very easy. And in the other one is easy because we have already worked it out so many times.

Is not it? So write it like this. What is x4-? **"Professor - student conversation ends."** Okay we will, since we want to start with one, let us do it like this. Just zooming in a little bit. So this x1- y1- and it will be easier if I draw the original coordinates also there, x2 and -y2. Is not it? x2 and -y2, is not it? This direction, this direction is -y2. Right or wrong? So now what will be the angles?

Between say x1- and -y2, x2 and y1-, what will these angles be? These will be the angles. Angle between x1- and -y2 is 30 degrees. That between x2 and y-, y1- is also 30 degrees and that between y1- and -y2 is 60 degrees. So now you can write? You have already done this. So tell me what is x1-? -1/2x2-root 3/2y2. Have you done this earlier or not? You have done it, right. It is very easy.

What happened? Okay. What is y1-? Root 3/2x2-1/2y2. Alright convinced. Convinced. Similarly, x2- will be -1/2x3-root 3/2y3. y2- will be root 3/2x3-1/2y3. x3-, y3-, you can write. You can write x4- y4- also. Are you all okay with this? But we are going a little fast, so please work it out yourself also, okay. Now are you all okay with this? Now what do I want to do now? I want to write this in matrix form.

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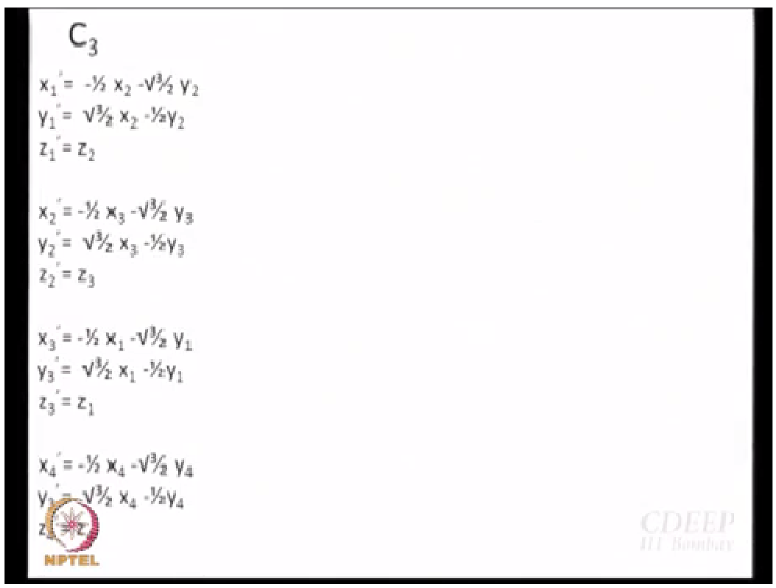

To do that, first let me get rid of the figure. Then let me write the equations of 1 2 3 and 4 together and if I want to write it as matrix, I have to put in all those terms where coefficients are 0's, right. Most of the terms are coefficients of 0, right. I will have to write it.

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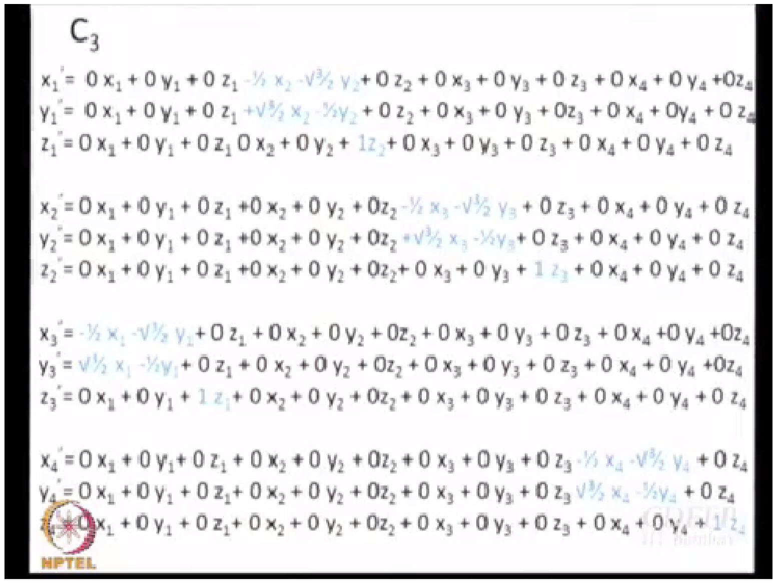

So let me do that. x1-=0x1+0y1+0z1-1/2x2-root 3/2y2+0*z2+0*x3 and I am tired, 0* everything else. It is so nice, the computer knows what I want, it writes itself. Alright, is this okay? Similarly, I can write it for y1- and z1- and everything else. The computer is really smart. Okay, these are the matrix equations. Do you see the non-0 blocks? These are the non-0 blocks. Okay. Alright, these are the non-o blocks. Anybody want to say anything at this point? Now it is very easy for you to write this equation in matrix form?

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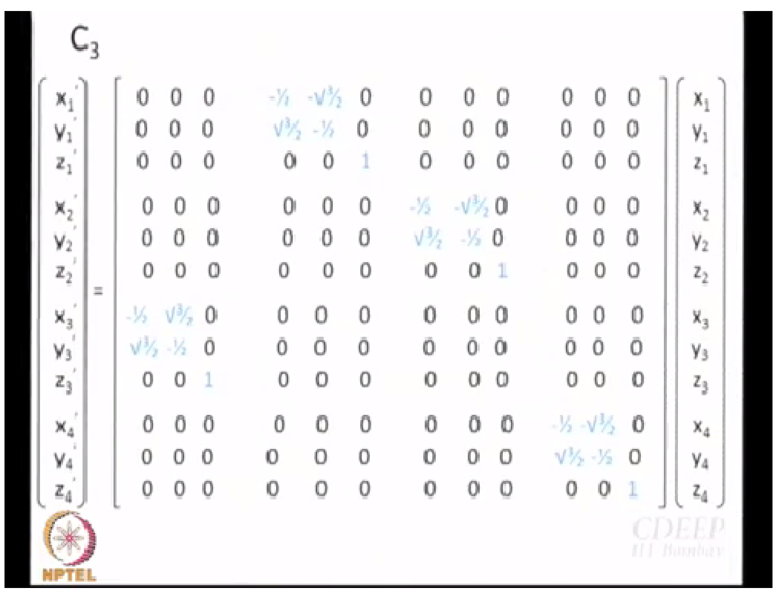

This is the equation in the matrix form. Non-0 blocks are still in blue, okay. These were the linear equations. Now I have written them in matrix form, that is all. Alright. You just have to believe me that I did not cunningly change some number somewhere and you can verify when I will send you the slides this evening. Now what do I want? I worked out the transformation matrix.

I worked out the transformation matrix. It was not all that difficult. 12*12 was easy. It will get easier after this. But before that tell me what is the character, what do I add? At this the case. Very difficult addition? **“Professor - student conversation starts”** 0. And answer comes to 0. Like many things in physical chemistry. **“Professor - student conversation ends.”** So here x comes out to be 0, right. x of C3=0.

Now what is the important lesson that we have learnt? In all this exercise. We have learnt that a rolling stone gathers no moss. What do the non-0 blocks stand for? The blue blocks? They stand for the contribution of the original coordinates in transform coordinates, right. So now what has happened here. As a result of application of C3, atom 1, what are the atoms that change places, do you remember?

1 2 and 3 change places. 4 did not change place. So what had happened is that the non-0 blocks have gone off diagonal for 1 and 2 and 3 because x1- y1- z1- are completely expressed in terms of x2 y2 z2. x2- y2- z2- are completely expressed in terms of x3 y3 z3. And similarly those in for atom 3 are completely expressed in those of in the coordinates of, in terms of coordinates of atom 1.

No? And since they have gone off diagonal, they cannot contribute to the (()) (27:20) X. The only atom that contributes to X is C4 which has not moved. So we have learnt that a rolling stone gathers no moss. Understood. So have you all learnt, do you now all believe in this ancient wisdom that a rolling stone gathers no moss? So off diagonal blocks do not contribute to X and that signifies our life very much.

For all types of (()) (27:57) operations what we will do is, we are only going to focus on those atoms which do not change places. Okay and that is how we have learnt to cheat and we are going to work out these big matrices without really working them out. And if you thought that was the end of the story, it is not. So "picture baaki hai, thora bahut." We will come to that a little later.