Group Theory Methods in Physics
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Lecture – 30
Molecular vibration normal modes: Group theory approach

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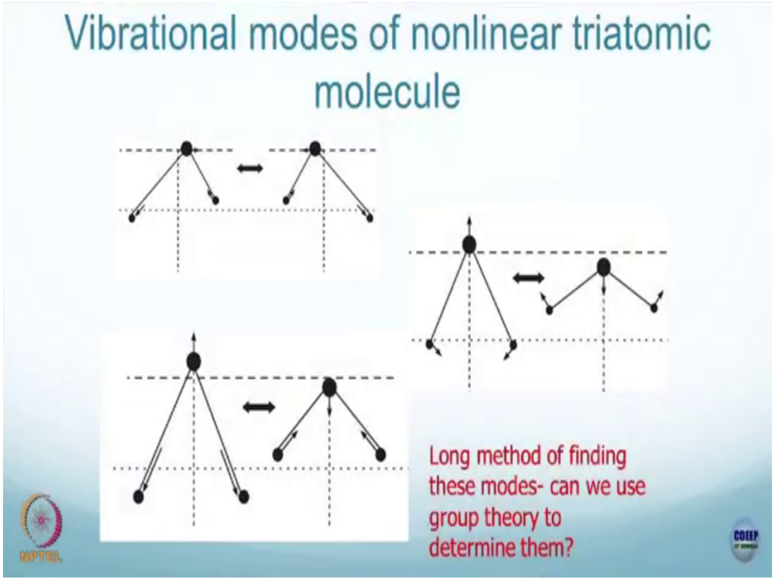

So just to recall for you that for this particular molecule with three atoms. I have shown a big mass with a bigger circle and two identical mass with a smaller circle. These are like the bond length changing this is you know is an asymmetric kind of it is going here, in an asymmetric way this one is going in and this one is coming out ok.

These are bond length changing, this is bond angle changing and these are symmetric stretching ok. So, this you would have seen in the video also. So, we would like to see how to get these pictures from group theory. You know it for physically for these three atomic you know non-linear molecule with three atoms very nicely I have given a simple example and it is a true if I give you a complex.

If I give it in your exam some ten atoms will you able to do it, is the question you will all be a little worried. But I am trying to simplify it and tell you now this methodology of what I am going to show in the next few slides, will show you how simple and powerful the tool of character table tends a products actually plays a lot of role. It is just manipulating only matrices and you can see that you can get these diagrams drawn from those matrices ok.

Still it is a suspense, but you will see it today by the end of today's lecture. I hope I can drive in the fact that normal modes of at least the non-linear three tri atomic molecule you can understand from this picture. So, long method I have gone through right now. So far whatever I have done in the last half an hour is a really a long method and can we use group theory to determine them ok.

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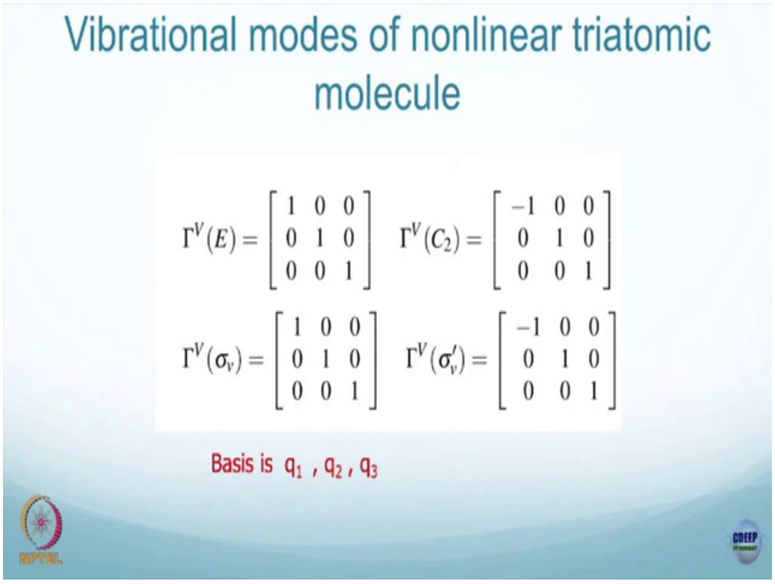

Student: (Refer Time: 02:42).

Now comes the matrix representation, I have tried to use the basis. So, I am going to use the basis q 1. Since I did the long method first let me confine to this long method and I will use the basis. So, this was x 1 plus x 2 right, these things where derived by the long method.

Let me for completeness write the basis for these and then worry about how to get these basis also in the next step ok. First sense we went through this long method we know that q 1 is one independent degree of freedom, q 2 is another independent degree of freedom and q 3 is the third independent degree of freedom q 2 is actually x 1 minus x 2nd this I think is z 1 plus z 2 ok.

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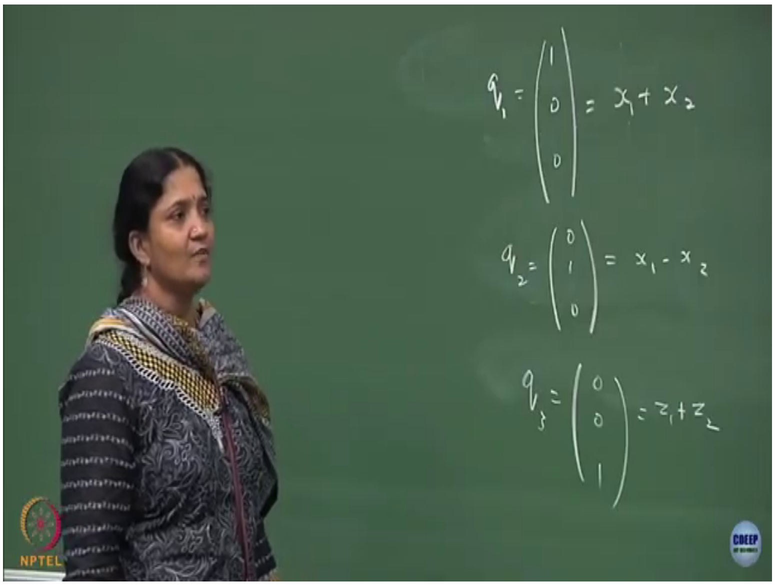

This was known the right hand side was known because of the long method. Now in these spaces I want to write the matrix representations of all the elements of this C 2 v symmetric of that molecule ok.

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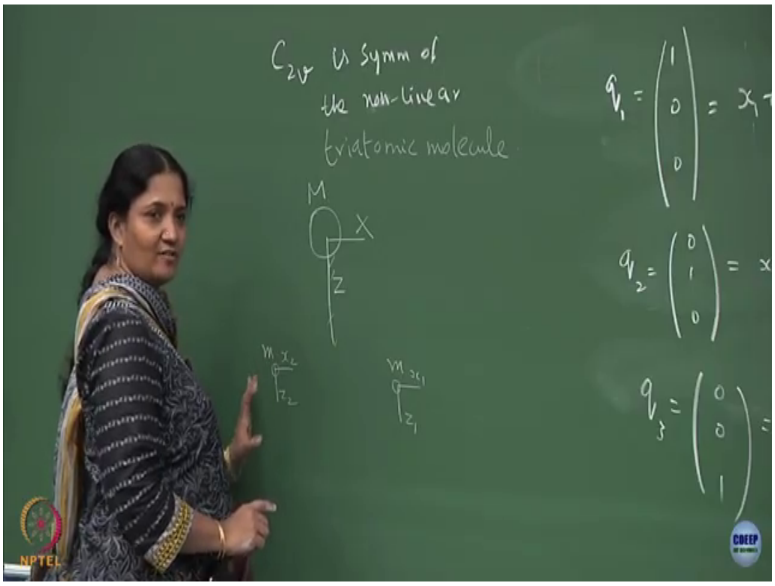

So, C2 v is a symmetric of the molecule of the tri linear non-linear tri atomic molecule. So, remember the picture I had a bigger mass here two small mass here and I have used a notation z axis x axis, I think this one was x 1 z 1 this one is z 2 x 2. So, this is what I am using as the degrees of freedom in the X Z plane for every atom in that molecule.

Student: Maam.

Yeah.

Student: (Refer Time: 05:35).

This is capital M this is identical that is right that is a way I am looking at it I am taking.

Student: (Refer Slide Time: 05:43).

It is you assume that the molecule is quite heavy and you are doing putting the axis through that molecule and do the rotation C 2.

Student: (Refer Slide Time: 05:56).

Correct I am assuming all those things. So, another way of seeing is that if I put an axis through this, if I do 180 degree rotation these two will exchange and if I put a mirror here. Then these two atom which are identical will going into each other and if I put a mirror on this plane this is like you know it remains it goes into itself this atoms goes into itself, this atom goes into itself that is also a symmetric. So, C 2 v is a symmetric of such a molecule and the consideration ok.

So, now how do I write in this basis in terms of the q 1 q 2 q 3 basis I want to write the matrix representations of all the element of C 2 v ok. So, identity element is trivial, but if you want to write the C 2 element what happens. So, what does C 2 do?

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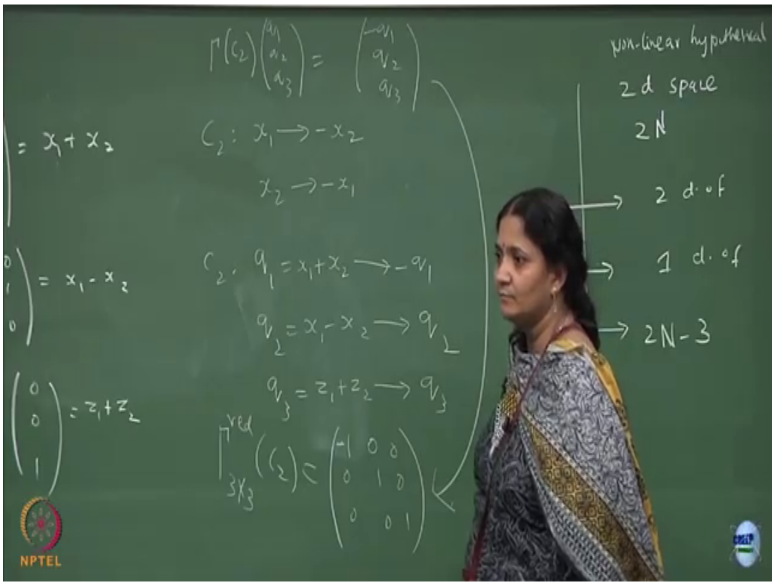

C 2 takes x 1 to minus x 2 x 2 to minus x 1, in the directions which I have taken. So, what will happen to q 1 which is x 1 plus x 2 under C 2 operation q 1 will go to minus q 1. What about q 2 that is the difference that will go to somebody, x 1 will go to minus x 2, x 2 will go to minus x 1. So, q 2 will go to q 2 no change what about q 3.

So, the corresponding matrix representation for this which is a 3 cross 3 matrix, it better be reduceable because C 2 v is an abelian group with each irrep being one dimensional you cannot get a 3 cross 3 matrix, 3 cross 3 has to be reduceable for the C 2 element. In this basis q 1 q 2 q 3 will be such that when it acts on q 1 it should go to minus q 1, q 2 should remain this q 3 should remain this.

Tell me what will be the matrix minus 1 0 0 0 1 0 0 0 1 is that clear. So, write it out for the sigma v treated to be the xz plane sigma v is also like the identity matrix as I shown in the screen. So, identity element is this C 2 element is this, which I worked it out elaborately now. Sigma v is the x z plane x z plane you will not change x y z coordinate, so q 1 q 2 q 3 will remain invariant.

But if you take the y z plane x coordinate is going to change sign right and you can show how the elements in q 1 q 2 q 3 are modified ok. So, this element I have not worked it out take it to be the y z plane and do the same exercise I did for C 2 and fix the in the q 1 q 2 q 3 basis write down this matrix ok.

So, what I have done by the long method I had found out that q 1 q 2 q 3 essentially will contain normal modes. Now I have written a reduceable representation for those three coordinates to find which linear combination of q 1 q 2 q 3 will actually give me the normal modes ok. Instead of doing that diagonalization of matrices I am going to now play around with matrix representations for the C 2 v group ok.

So, we need to find which linear combination. In fact, we should find the q 1 is untouched right, we know that also q 1 equation was completely decoupled from q 2 and q 3 right is that clear.

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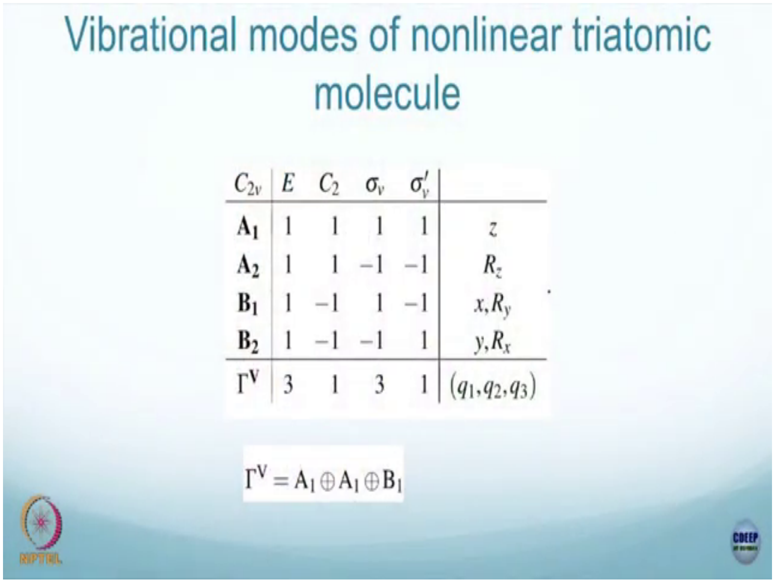

So, character table.

Student: (Refer Time: 10:59).

Which matrix this matrix, so I have to do the gamma of C 2 when acts on q 1 q 2 q 3 should give me minus q 1 q 2 and q 3 this is the meaning of this, q 1 goes to minus q 1 q 2 x 1 goes to minus x 2 C 2 goes to minus x 1. So, x 1 minus x 2 remain same.

So, I need a matrix which when acts on q 1 q 2 q 3 should give me this. So, what is that matrix? So, you have to make this diagonal because they are all diagonal and first the element has to be minus 1 the 2 2 element has to be plus 1 and 3 3 element has to be plus 1. This means this is the matrix is that clear. Any other question? Should we go ahead? So, back to our character table basis states and so on.

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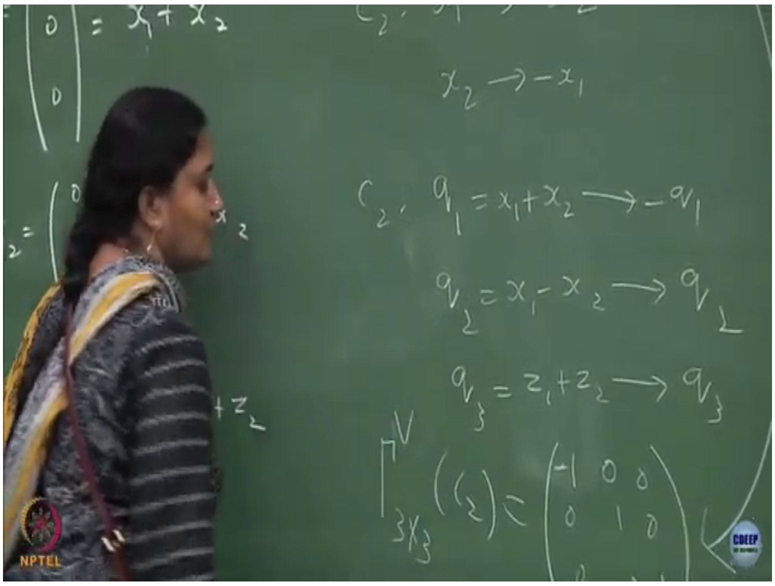

This representation reduceable I am calling it as the notation I am using on the slide is v it is a reduceable representation and you can find the characters for the identity element. Of course, trace of the 3 cross 3 matrix is identity and why xz plane will also be an identity matrix. So, that trace is also 3 this one trace. Of course, you can see that the trace turns out to be 1 right, for the C 2 trace is 1 and similarly for sigma v prime which is the is the y z plane you can find out what is a trace.

So, once I have this what do I have to do, I have to find out what is the number of times any of these irreps occurs in the reduceable representation ok. Then it will tell me what are the irrep language for the vibrational degree of freedom or the normal modes ok. So, do that exercise break that gamma v, A 1 appears twice A 1 appears twice and you have B1 which appears once. So, totally a rank 3 is broken up into 3 rank 1 irreducible representation, so this is the first step.

The next step is what if I want to find the actual degrees of freedom what. What you have to do? You can write a projector in the space in these matrices which I have you can write a projector and do the projection to get the basis states in the q 1 q 2 q 3 ok. I leave it to check it out and see what you get you understood.

So, given this you can write a projector for the A1 representation, this projector will involve character of A1 times the gamma v 3 cross 3 ok. Check the rank of this matrix, because v is broken up into A1 twice I would think that the rank is two and find the basis states.

Will you do that so p a 1 on an arbitrary vector should give me a piece which is 1 0 0. What does that mean? This is q 1 one of the vibrational modes is exactly q 1. So, q 1 is x 1 plus x 2 clear one of the vibrational mode is exactly q 1, if you find this but I am going to leave it you to check this out. And if it is rank 2 matrix you should be able to find two independent basis linearly independent basis, the other basis should involve not this one, but the q 2 and the q 3 is that clear.

So, this part I am not doing it, but please check it out and then do that long winded diagonalization to see whether you get the same linear combination of q 2 and q 3.