| Group Theory Methods in Physics |
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| Lecture – 31 |
| Molecular vibration modes using Projection operator |

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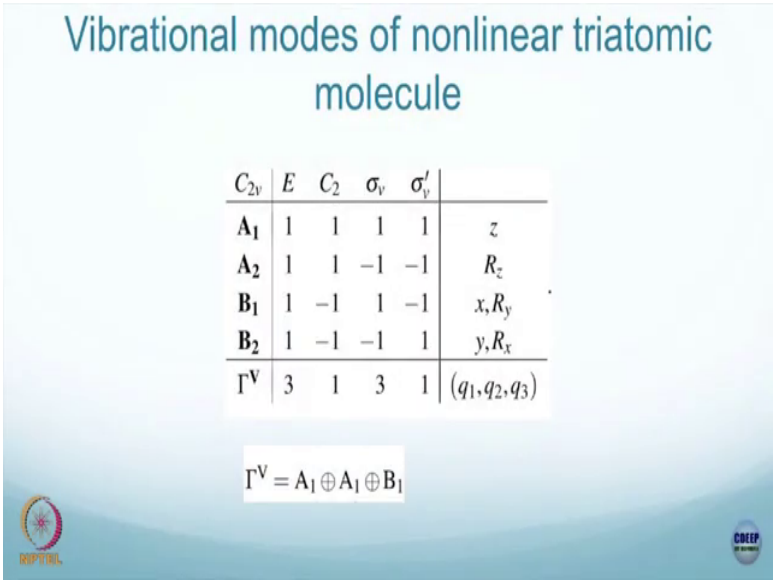


Now, I have still would like to see this in that bending asymmetric stretching, symmetric stretching and so on. So, the best way I knew from the long method q 1 q 2 q 3 are an independent variable if you have to right. That is why I worked out with q 1 q 2 q 3, where q 1 q 2 q 3 are this, this is, this information came from the long method already. I will not have this information also in general, you agree?

So, is it better to work not with some partial information from doing the mechanics explicitly, but to do it, as if I am doing only group theory we are going to do that. Is that clear? This q 1

q 2 q 3 information I got because of my solving it as a method in mechanics, I do not want to do that, ok. I want to do it as if I am doing a group theory problem which has 6 degrees of freedom in the xz plane, fair enough. And then I want to see symmetric asymmetric stretching everything in that language, ok. So, that is the next step.

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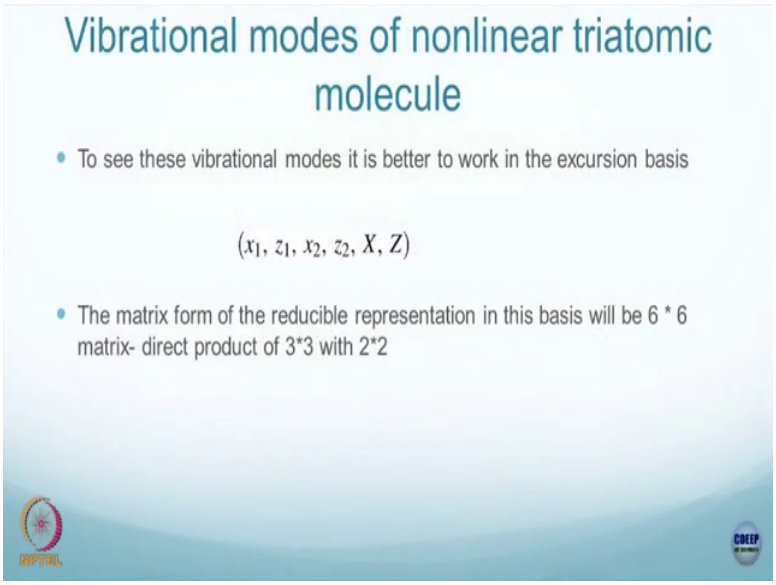


So, I am going to get onto that step to see these vibrational modes is better to work with excursion coordinates, excursion means displacement about its mean positions, ok. I am going to choose this column or this row as the basis vector. What is this, atom 1 x 1 z 1 followed by atom 2 x 2 z 2 followed by atom 3 capital X capital Z.

How can I see this basis as a tensor product? Tell me, can I see this as a tensor product? So, I am going to do something like this atom 1, 2 and 3 tensor product with x and z, ok.

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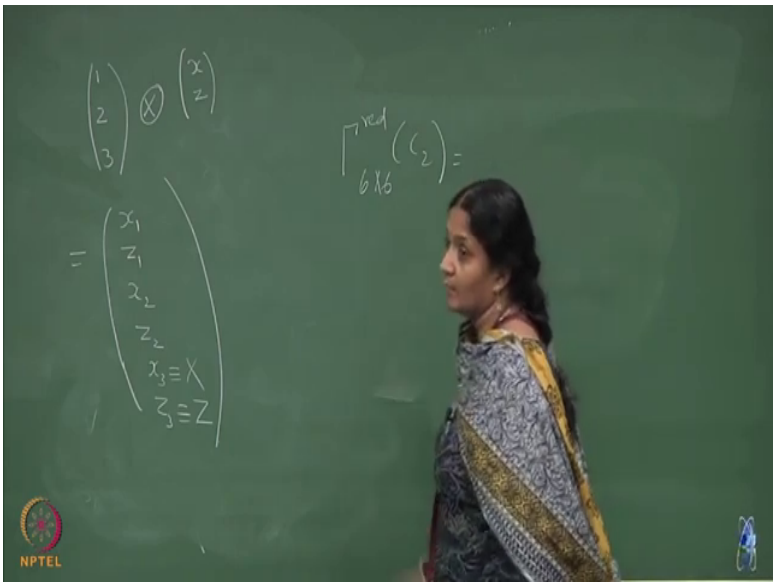

What is the meaning of this? If I write it in the long winding language, what is this x and this 1 I am going to put it as a subscript, x 2 z 2 x 3 which is what I am calling it as capital X and Z 3 which I am calling it as capital Z. Is that ok?

So, now you see how tensor product gets in to looking and the basis state of displacements of all atoms is a six dimensional vector space, but that six dimensional vector space can be looked at as a tensor product of the number of atoms in a molecule tensor product with each of their coordinates x and z and this basis which I get can be viewed this way,.

So, now you can do the reducible representation which will be a 6 cross 6 matrix for c 2 what will that be

Student: Ma'am (Refer Time: 04:42) independent (Refer Time: 04:44).

Not independent no.

Student: basis (Refer Time: 04:50).

It is a basis in the reducible basis in some sense, ok. The 6 dimensional vector space, the matrix representation which I am going to write will be a reducible matrix and this vector space will also be reducible, ok. In that sense it is. They are all you know I can write a six dimensional basis here and then I want to look at what are the irreducible basis associated with c 2 v symmetric.

If you are looking at some higher groups this could also be a valid basis, right, but for me I am looking at like regular representation I am looking at a non-linear triatomic molecule which has 6 degrees of freedom let me write my matrixes which is 6 cross 6 matrixes. And from there I would like to do all those rules of or the tools of character table projectors decomposition into irreducible representation and fix which linear combination is actually the basis for the vibrational modes of your water molecule.

Is that clear? Are you all with me.? Some bit, I can see faces are is it math is ok, but physics part of mechanics if you keep on remembering it then you will appreciate what I am doing, ok. I am doing this because I am assuming that I did not go through the long method of determining q 1 q 2 q 3. See there in the long method help me to say that the vibrational mode should be some linear combination of q 1 q 2 q 3 only, but I am not doing that now. I am going to derive that from this higher vector space which is 6 dimensional vector space. 6 dimensional vector spaces associated with the 6 degrees of freedom of this molecule, ok. So, how will you write the c 2 element? So, I can split this up into a 3 cross 3 of c 2 and another 2 cross 2 of c 2, right.

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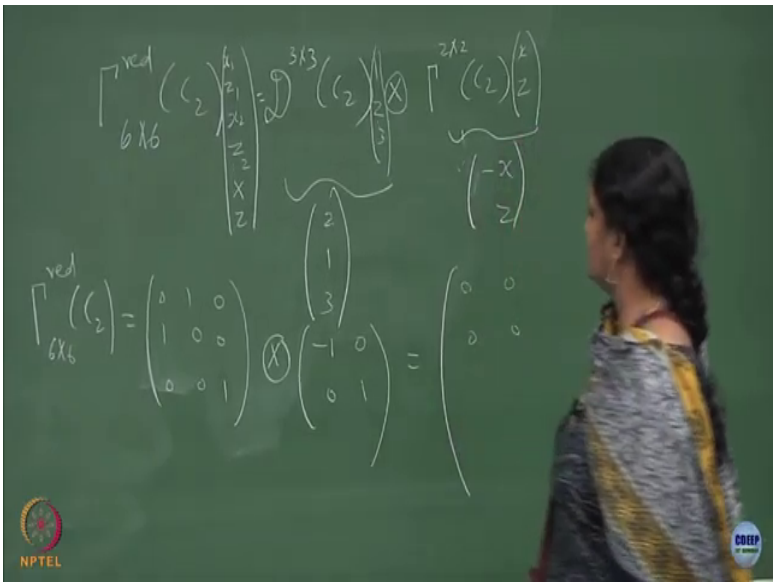

It will act on 1 2 3, this will act on x z. Are you all with me? And I am doing c 2 in the z axis. So, what will this matrix be?

Student: (Refer Time: 07:52)

This is rotation by 180 degrees in this about the z axis. So, it will become this will give you this thing will give you minus x and z. What about this?

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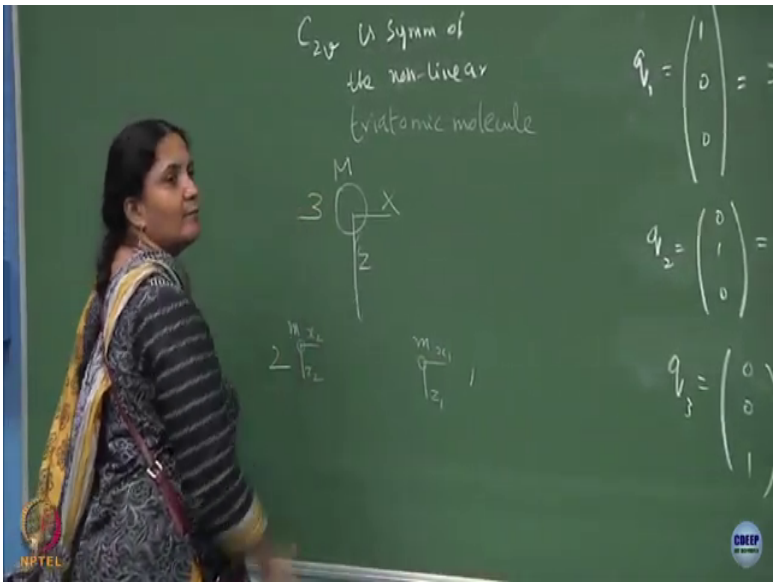


So, let me also call what are the atoms? This is atom 1 atom 2 and atom 3. So, what happens when you do about z axis, axis as shown in this figure 3 is untouched 1 and 2 get exchanged, clear? So, what will that matrix be? This whole thing should give you 2 1 3. So, what will be the matrix. So, this acts on x 1 z 1 x 2 z 2 x and z and this is what is the long winded thing and I need to determine this. So, let us write what is this. So, this clearly tells me it is 0 1 1 0 that is the matrix which will take. Is that right?

Student: (Refer Time: 09:28)

No I will do it. Then 0, no minus 1 0 0 1

Student: 0 0 1.

Yeah thank you, yeah. So, now, you multiply and write the 6 cross 6 matrix.

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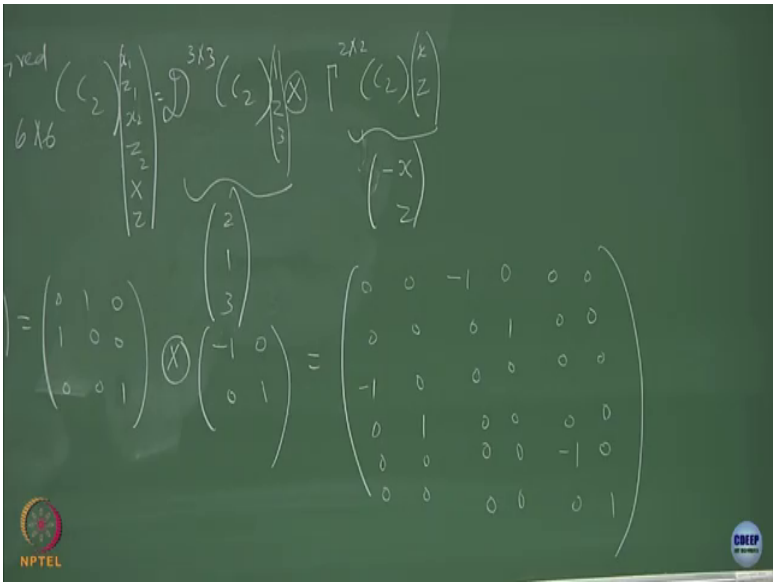

The first is this then you have a minus 1 0 0 1 0 0. How I have generated the, how I have generated this is clear I have using the tensor product power, ok. If you are using some kind of a permutation things here subset of the symmetry group permutation elements. I am doing these tensor product to generate my matrix which acts on the complete 2 n degrees of freedom for the triatomic non-linear molecule ok, ok.

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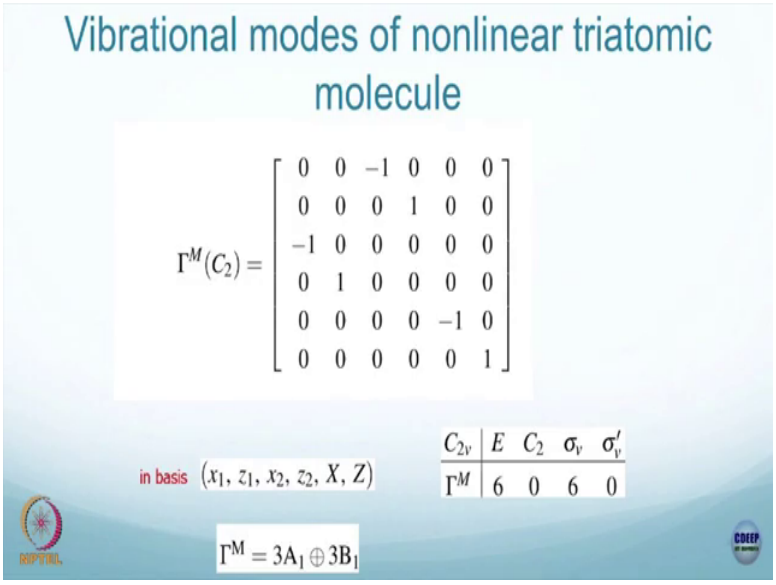


So, now getting back to the screen now; so, I have elaborated for you how we got this. I am calling this reducible one with the letter capital M, this is just to keep the nomenclature that earlier one I called it as v, but it has nothing to do with you can call whatever letter you want, here I am following M. So, I have written this matrix and I have taught you how to write the 6 cross 6 matrix, right.

Student: Ma'am.

Yeah

Student: This case (Refer Time: 12:00) is that how (Refer Time: 12:01). So, instead of considering a 6 dimension, (Refer Time: 12:06) we have considered a 4 dimension (Refer Time: 12:11).

Capital X and capital Z is not quite invariant X also changes to minus X under C 2, ok.

Student: Larger molecule will be fixed.

Which one?

Student: Larger molecule will be fixed that is why.

No, the larger molecule remains fixed the x coordinate is going to get 2 minus x, z will not change. So, there is some subtlety let us go through this and then we will come back by a shortcut method which you are already getting on to in the next class. So, there is another shortcut way of doing it will come to it. Once you appreciate this then I can get to that other method ok, are you all with me, ok.

So, I have written this 6 cross 6 matrix now you have to redo this form identity element is of course, trivial identity element trace will be the character will be 6. Similarly, sigma v will also be 6, because it will both be almost same. This character c 2 turns out to be that these two are diagonal elements they add up to be 0 clear. So, that is why I put the c 2 character to be 0 for the reducible representation and sigma v prime will also turn out to be 0 please check it, ok.

Again break do the decomposition of this reducible representation using the character table of c 3 v c 2 v to find how many times which irreps appear, ok; so, that I will leave it to you as an exercise.

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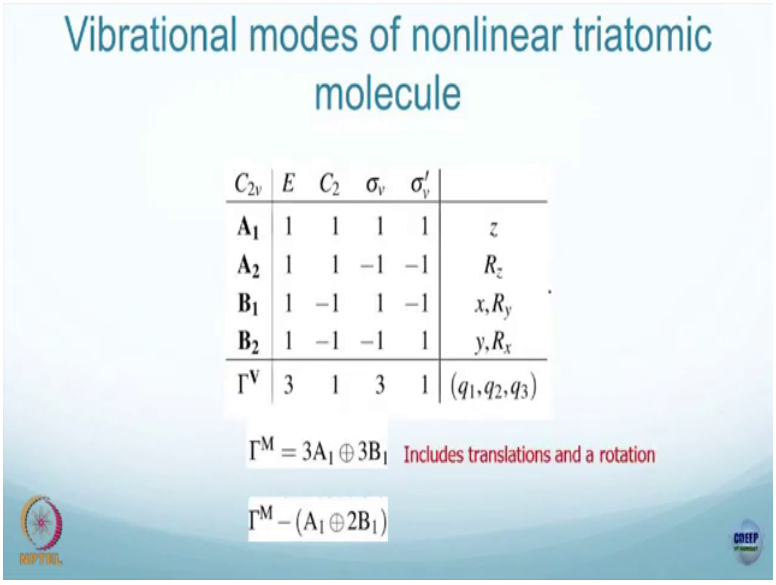


So, please try it out.

Student: (Refer Time: 14:16).

Student: Sigma v (Refer Time: 14:19).

Sigma v, sigma v was different in q 1 q 2 q 3 basis where I have removed the translation degrees and rotational degrees. Now I am not doing anything, I am just taking the 6 degrees of freedom and I am finding out how the reducible representation which preserves the c 2 v symmetry breaks into irreps of c 2 v. Now I have to remove the translation and rotation which we will do, ok. So, that is the additional work you have to do if I want to do this piece of work ok. Anything else? Ok.

So, back to the character table of c 2 v and gamma m, you can break it up and write 3 times A 1 and 3 times B 1, but as he already pointed it out. This is a 6 degree of freedom to start with unlike the gamma v which involved 3 degrees of freedom. The 6 degrees of freedom 3 of them belongs to the A 1 irrep 3 degrees of freedom and 3 degrees of freedom will belong to the B 1 irrep. But, you have to remember it includes translation and a rotation because I am doing it like a 2 D plane, rotation about y axis, is that right rotation about y axis and translation in the xz plane.

So, translation along x direction, if you look at this character table and this basis function translation along the x direction is similar to the B 1 irrep, ok. Translation along z direction is like an A 1 irrep. So, you can subtract the A 1 under B 1 and rotation about y axis is also the r y belongs to the B 1 irrep. So, you will subtract additional b 1 here that is why I put a 2 times B 1. These subtractions are to remove the translation degrees of freedom and rotation degrees of freedom, ok.

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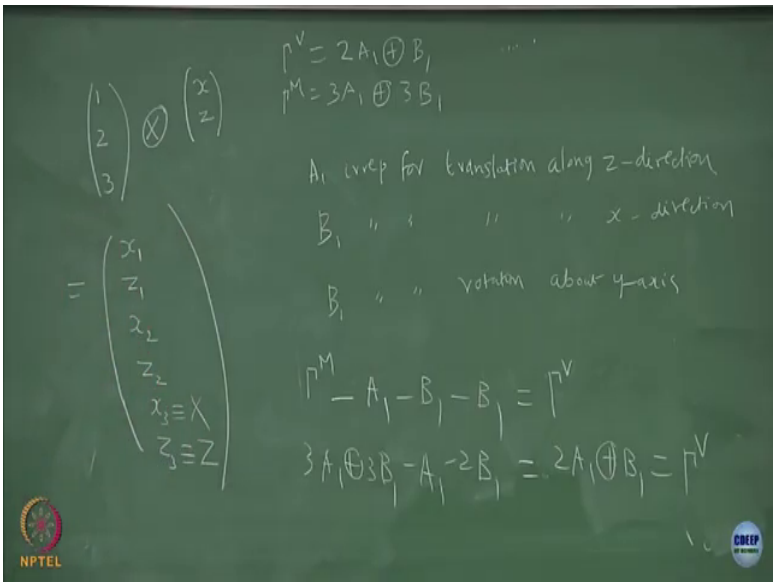


So, essentially if you subtract from 3 A 1 plus 3 B 1 the aA1 and 2 B 1, you have to get back the answer which you got for what did the answer come for gamma v. Gamma v was 2 A 1 plus B 1 gamma M is 3 A 1 plus B 1 3 B 1, yeah. And then this includes translation. So, A 1 is for translation, ok. So, gamma M minus A 1 minus B 1 again another B 1 this will be the, this will contain only the vibrational degrees of freedom and I am claiming that this should be same as your gamma v. Can we check that?

So, 3 A 1 plus 3 B 1 minus A 1 minus 2 B 1 turns out to be 2 A 1 plus B 1, ok. Still I do not know q 1 q 2 q 3 I can still say that whatever physics you did with q 1 q 2 q 3 essentially comes out after I subtract out the translation and rotation irreps out of the system.

Student: (Refer Time: 19:47).

I am looking at only that know the molecule is in the x z plane. So, I am just doing only a 2 d problem kind, right yeah.

Student: (Refer Time: 20:04).

Yeah so, we if I am looking at 6 degrees of freedom in a 2 d system 3 in 2 3 atoms into 2 2 n, right 6 and then you have to subtract out translation which is to subtract out rotation. And you have to look at 2 into n minus 3 degrees of freedom which are the vibrational degrees of freedom; I have not done the subtraction. So, whatever I am going to get out of this will have translations rotations and vibrations. To look at the vibrations of atoms within the molecules without touching without altering the center of mass of the system or rotating the system, you need to subtract those degrees of freedom.

So, the irreps associated with a vibrational degrees of freedom which you did from here mechanically belongs to A 1 2 and B 1, but here it will be 3 A 1 and 3 B 1, but it includes translation and rotations. You have to remove the translation and rotation if you want to compare these two, clear? Still I have not shown you the picture how to get the q q 1 q 2 q 3 that also we will do, this is clear.

Are you all getting some feel of how math's speaks physics? Actually speaking what you want in the lit in the language of physics we want to get those asymmetric symmetric modes and we are going to see that now, ok.

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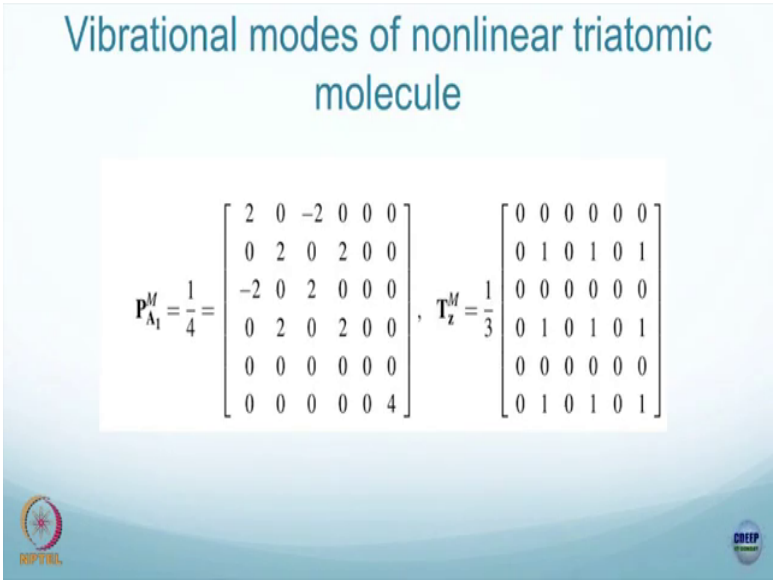


So, I want you to take this irrep, sorry reducible representation and find the projectors ok. I have given a projector for the A 1 sorry this should be one fourth multiplying this it is not equal to that 1 by 4 is because 4 is the order of the group, ok.

So, basically this matrix I will leave it to check will you do it just have to take I worked it out for you for the c 2 you have to work out for all the elements it is very simple sigma v prime will be almost same identity and sigma v are the identity operators. You just have to take the characters are all one; you just have to sum up all these matrices. If you sum up all these matrices, you will end up getting a projector of such a matrix I will leave it you to check this out, ok.

And once you get this projector, you have to look at translation what is the projector for translation suppose I am looking at translation along z direction because A 1 as I said is

associated with translation along z direction. The projector for conventional translation along z axis is just that you have to shift the z by some constant I am normalizing the constant to be 1, ok. So, this is will be a projector. What do I mean by a projector? The square of this matrix should be itself that is the definition of a project, am I right?

So, this matrix which I have written is a projector for the translation along z direction and translation along z direction belongs to A 1. So, I am going to subtract from this matrix which I have generated the translation projector which means one basis I have removed one linear combination I have removed, clear. Whatever remains that matrix should be having rank two and you should be able to find two linearly independent basis for that rank two matrix, ok.

So, this I am saying is a rank three and then I subtract the translation it becomes rank two should have two linearly independent basis, ok.

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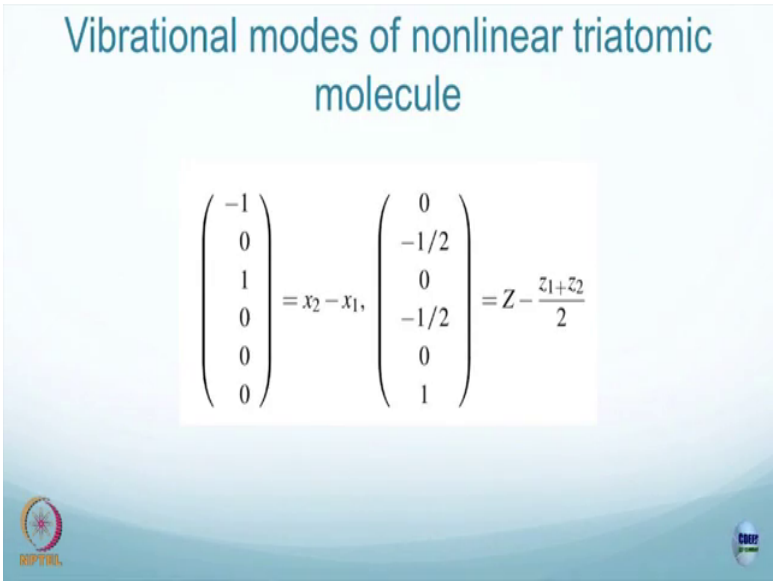

So, the two linearly independent basis in this basis ok. You go and look it up do it and you will see that you get minus 1 0 1 others are 0. In the notation of this basis I can equivalently write it as x 2 minus x 1 and that was nothing, but your q 2 up to an overall constant q 2 was x 1 minus x 2 is what I took what I get is that.

So, this projector which I am doing you can put an overall sign or overall factor. So, x 1 minus x 2 which I took as a basis turns out to be coming naturally from here. And again you can do the other basis for the a 1 and that turns out to be you know I get a minus half and a minus half and a 1. So, you can rewrite it as z minus z 1 plus z 2 by 2. So, basically it depends on the q this z can be eliminated, but this is depending on the q 3, right.

So, I am just trying to give you a flavor that how without even finding that q 1 q 2 q 3 by long method you can still work out the projectors and find the basis functions. And then you can say that the normal modes are these basis or linear combination of this basis. Once I have this x 2 minus x 1 I can draw the diagram which I showed you, sorry this one.

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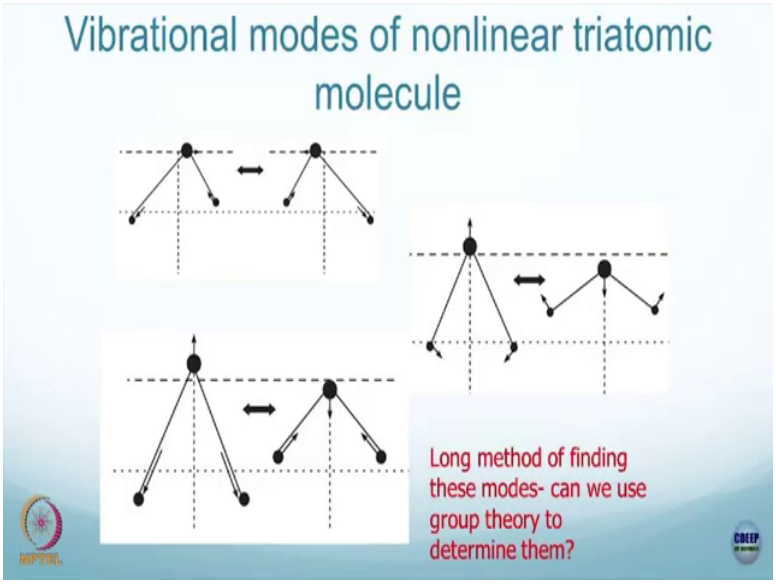


So, if x 1 so, you can resolve this component into x 1 and z 1 if x 1 as going to in the in this direction, you can see that x 2 is going in the same direction, right. So, this is one and another one you can see is another one you can see is that the x this is x 2 x 2 will be going in the negative direction and this one is going in the positive direction. So, you can net write it as x 1 minus x 2 and this one as x 1 plus x 2 and so on, ok.

So, I did not do the PB, PB 1 try that out PB 1 also. You should know how to write the corresponding projector for the in the PB 1, you have one x translation that you can subtract it out. We should also write the projector for rotation about y axis. Subtract both of them from the PB and you should get one rank one matrix and then that basis should give you x 1 plus x 2, ok. Is that clear?

So, I have shown you that q 2 and q 3 basis are obtained from PA 1, I want you to see that q 1 basis you will get it from PB 1 after subtracting translation along x axis operator and rotation about y axis operator which I have not done now. I want you to do it and check it out and you should get the q 1 coordinate from there q 1 is x 1 that will be 1. So, basically in this notation it will be 1 0 1 0 0 0, this you should get when you are doing the.

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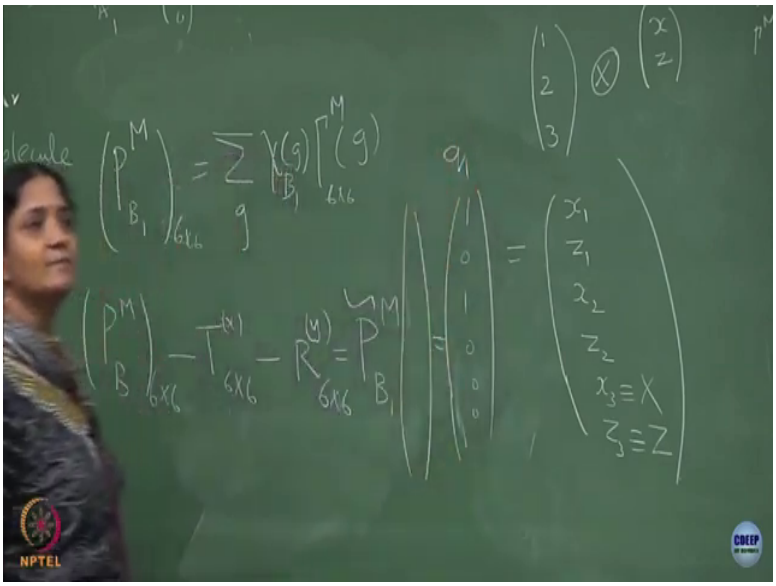


So, first of all write for the reducible representation which I called for the B 1 which will be a 6 cross 6 matrix which will involve summation over all the elements character for B 1 for every element and the 6 cross 6 matrix for every element first write that out. And then subtract translation mode along the x direction which will be again a 6 cross 6 matrix, ok. And then rotation about y axis in this basis should also be a projector. What does is the

definition of a projector T 2 if you do twice it should be same that is the definition of a projector.

So, please fix this and find what it does that I will call it as P tilde B 1 M and if it operates on arbitrary state I have to get this. I have not shown this, but you should try and check it out and that will convince you that this is nothing, but your q 1 in the earlier language and you get q 1 basis to be the irrep belonging to B 1, q 2 and q 3 are the basis which belongs to irrep of the other 2 A 1, is that right? So, just to summarize what we did today.

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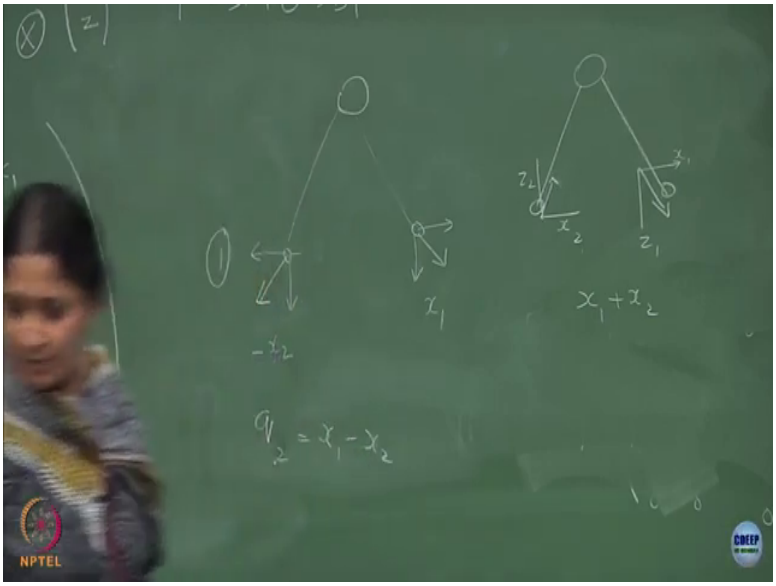


So, taking this atom you are looking at the vibrational modes of these molecules there could be vibrational modes which are symmetric that is one possibility. Second possibility is by this I mean there is a bond connecting them and then there is a relative motion between the atoms

in the molecule without touching the center of mass of the molecule or doing a rotation to the molecule, ok.

So, this is one vibrational mode if you try to resolve them. So, this will go this way and this will go this way and this will be this way and this will be this way. So, you see that x 1 is becoming this is the this is x 2, right in my notation this was x 1 and this one is minus x 2, that is 1. And this as a normal mode, we write it as q 2 which is x 1 minus x 2. The other one is where you have a this goes this way this goes this way, right the two atoms the bond it is an asymmetric stretching.

So, if you try to resolve this is x 2 z 2. So, you can see that x 1 plus x 2 is a good thing for this, ok. And then what else, the other one is the bond change which could be the other option and that also should involve for you the, the way of writing it you should see that, ok. So, let me show the picture again maybe now it will be visible in this language you can resolve it and see what is happening here what is happening here these two are one and the same no change up to an overall sign does not matter.

Similarly, these two stretching and shrinking in the same direction are one and the same because it is going through a simple harmonic motion, right. These are the bending modes where this angle is reducing and this angle is increasing that is also another simple harmonic motion and you will see that two of them will be a linear combination of q 2 and q 3, one of them will be purely q 1 which is x 1 plus x 2, ok.

I hope I have driven the point that you need character table you need first to know the group symmetry of the molecule character table the basis functions you need to know how to do the decomposition of a reduce reducible representation in the basis which corresponds to three n degrees of freedom for a molecule. And, then you use projectors remove translation projectors. To remove the translation projectors you should also know which irrep the translation belongs by looking at the basis states. Once you do that you can fix all the normal modes by just doing those projectors and you can draw those diagrams.