Group Theory Methods in Physics
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Lecture - 29
Molecular vibration normal modes: Classical Mechanics approach

We did see the video last time, right. You remember now? So, given n atoms in a molecule each one has 3 degrees of freedom. If you are in three dimensional space, 3-Nn degrees of freedom and then the center of mass of the molecule will remove how many? 3 of the degrees of freedom right which is the you can move the whole molecule from place a to place b center of mass is what?

Center of mass of the molecule is what is moving and that is not going to change the vibrational degrees of freedoms. So, three translational degrees of freedom associated a center of mass of the molecule is not playing a role in vibration motion. Other thing is you rotate the whole molecule. If it is linear, the rotation about the access of that linear molecule will not do anything.

So, only you will have two rotations if it is linear molecule. If it is non-linear molecule, you have three access of rotation. So, you have to remove the rotational degrees of freedom also from the system. So, totally 3 N minus 6 where N is the number of atoms in a molecule that place the role for vibrational degrees of freedom if it is non-linear molecule. Is that clear?.

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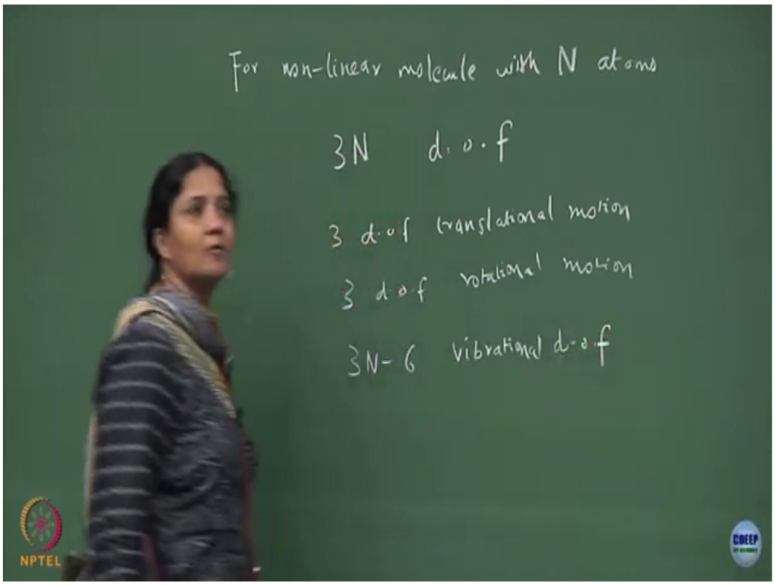

For non-linear molecule with N atoms

3N d.o.f

3 d.o.f translational motion

3 d.o.f rotational motion

3N- 6 vibrational d.o.f

Atoms 3N degrees of freedom is total and then 3 degrees of freedom is for translations translational motion, 3 for rotational motion. So, 3 N minus 6 is the vibrational degrees of freedom, if it is linear molecules.

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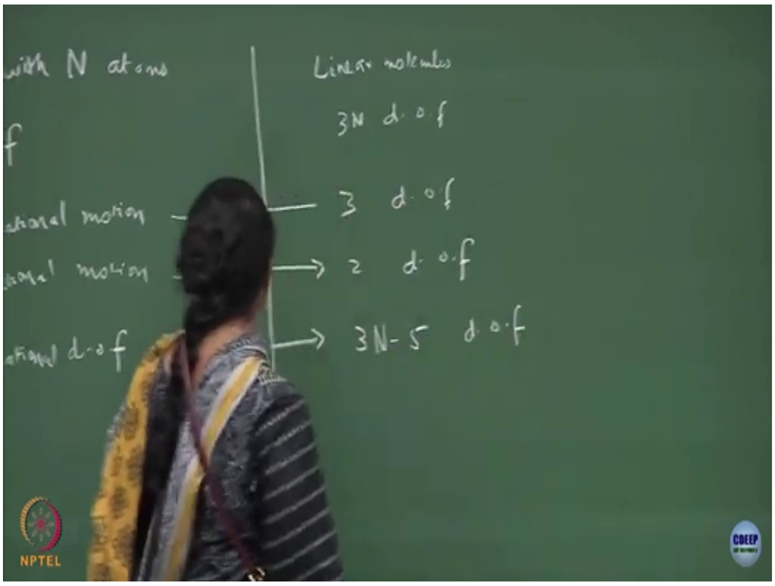

So, I am looking at all these molecules in three dimensional space, ok. So, linear molecule in three dimensions again 3 N to start with. This one will be again 3, this one will become 2 degrees of freedom because one about its own access. It does not give you for a linear molecule like carbon monoxide nothing happens.

So, the number of degrees of freedom vibrational degrees of freedom for a linear molecule will be 3 N minus 5 degrees of freedom will be the vibrational degrees of freedom, ok. Suppose I tell you that you are in a hypothetical situation that you are going to move only in the 2 dimensional plane then what happens?.

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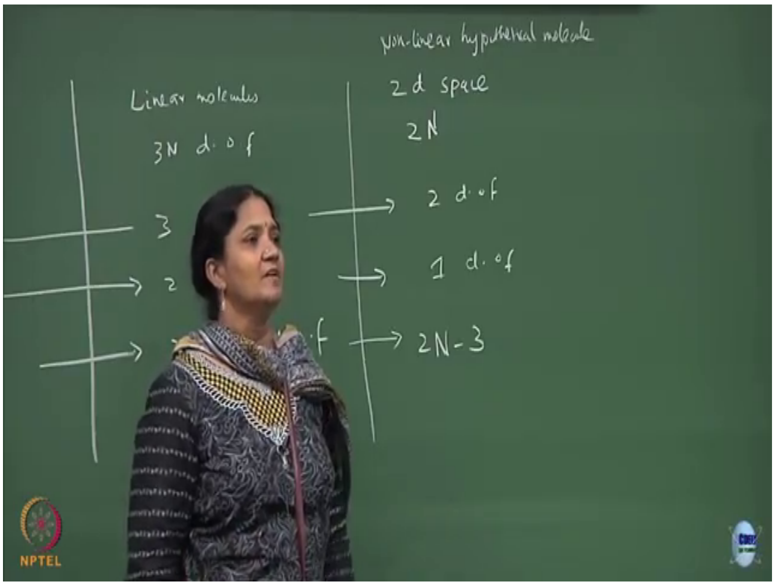

Suppose I say that 2 d space is where you can move around ok, then what all modifications will happen? 3 N will become 2 N and so on ok. Translational degrees of freedom will become 2 degrees of freedom. Let me look at non-linear hypothetical molecule ok. How many rotational degrees of freedom? 1.

So, totally vibrational degrees of freedom for a molecule with atoms on a plane let us say will be non-linear molecule. What I am taking it is on a plane, but not lying along a line. It is on some equilateral triangle or on a square, but it is just confined to the x y plane order and we have seen various things pictorially or in the video. The relative motions of the atoms without altering the center of mass of the molecule are the one's where we have to also rotation does not alter the rotations.

Those are the once which is going to tell you exactly whether there is stretching bending which are called breathing modes asymmetric stretching symmetric stretching. You saw some of these pictures on the video. Can we understand this from your character, table, projection, operators, reducible representations tends a product of representations. That is the theme of today's lecture.

So, assumption is you have not forgotten character table, you know tenser product, you know how to get from the reducible representation in the irreducible representations and then we will see whether we could get the asymmetric stretching, symmetric stretching. All these things you could like to understand.

Student: What about on the plane

On the plane you will have about the point rotations. That is all.

Student: but there are two point particles.

Ha.

Student: one can rotate like this, another can rotate like this.

No, but you have to keep it on the plane. You are looking at in 3 dimension just confined that I am on this floor. All the atoms are nothing beyond this floor. No going up or down.

Student: But still I am if I came on the plane like if particle is fixed like one can rotate like this other can rotate like this if say if.

No those will be the relative motions.

Student: Ok.

The whole molecule you can, you cannot rotate relatively different atoms in the molecule. That is what you are doing. You take the whole molecule, rotate the whole molecule. The system is intact, take the molecule, translate the whole molecule, the system is intact. So, those two are the 3 degrees of freedom, those two are the 3 degrees of freedom which you have to worry about for translation which is like center of mass of the molecule.

Similarly you have a rotational. What I will do see whether this works ok. Is that clear? Not the relative rotation, all those relative motions are like you know displacements about its mean position which will give you the vibrational degrees of freedom. It would not give you the total rotation of the point. If you have seen the video, it is just that the access on which the whole molecule is rotating, not relative atoms in the molecule. Is that all right? Fine.

So, now I am going to try and do well little bit of warm up on classical mechanics to tell you how difficult or how cumbersome it is to solve equations and then, I will lead you to group theory to show how simpler it is it can work for many complex polyatomic molecules, ok. This is the theme on which I am going to pitch today's lecture, ok.

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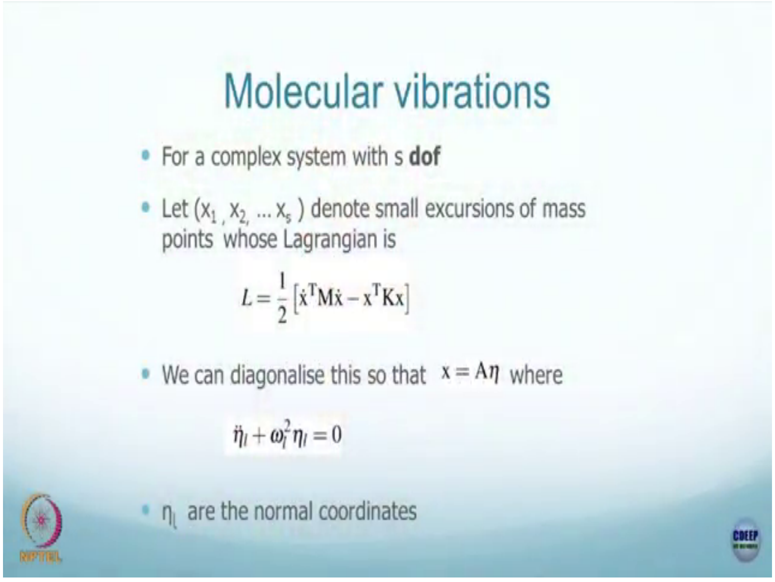

Molecular vibrations

- For a complex system with s **dof**
- Let (x_1, x_2, ... x_s) denote small excursions of mass points whose Lagrangian is

$$L = \frac{1}{2}\left[\dot{x}^T M \dot{x} - x^T K x\right]$$

- We can diagonalise this so that $x = A\eta$ where

$$\ddot{\eta}_l + \omega_l^2 \eta_l = 0$$

- η_l are the normal coordinates

So this is a warm up which we did last. I am also for a complex system. Anyway I have said this there are a number of degrees of freedom and that degrees of freedom will depend on your number of atoms and all these things have explained on board. So, given that there are s degrees of freedom. So, you just take them x 1 till xs are deviations from the mean positions of the atom.

So, it gives you displacements of the atom about its mean position in a molecule. So, those are what we call it has excursions of mass points and typically you will have a lagrangian which is dependent on x 1 x 2 xs which I have put it as a column vector and row vector. In between there will be a matrix, so that this whole thing will be some kind of number or is that right.

So, you have a matrix, a column vector multiplying the matrix. Here x dot is the time derivative of these s degrees of freedom and x dot transpose is a column vector and then, sorry row vector this is a column vector and this is s cross s matrix and similarly, you will have a kinetic potential energy term where it is only on the positions. So, displacements of the mean positions which I call it as excursion, this is a formal Lagrangian which you can write, it will be coupled set of you know if you try to find the equations of motion for this there will be a coupled set of second order equations to solve, right. You might have done this.

Only way you can make it into uncoupled equations like this is by doing a suitable diagonalization matrix and then find the basis eta for those diagonal eigen values. Diagonal eigen values are the frequencies. So, you would have done this. If you have not done, it just take at 2 d or 3 d system which is coupled, try to diagonalize the matrix, find the eigen values, then try to use the matrix which allows you to diagonalize such a matrix and that will define for you the position excursions over the etas; etas are what we call it as a normal modes. Is that clear?.

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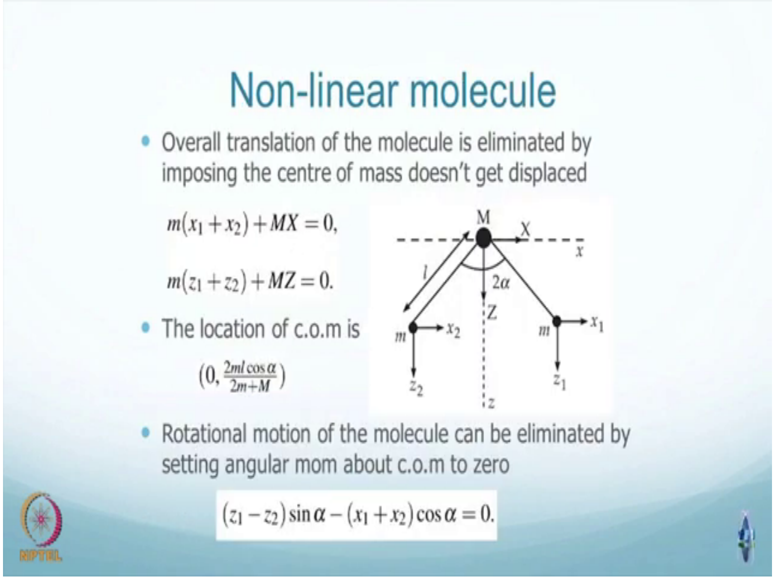

Non-linear molecule

- Overall translation of the molecule is eliminated by imposing the centre of mass doesn't get displaced

$$m(x_1+x_2)+MX=0,$$

$$m(z_1+z_2)+MZ=0.$$

- The location of c.o.m is

$$(0, \tfrac{2ml\cos\alpha}{2m+M})$$

- Rotational motion of the molecule can be eliminated by setting angular mom about c.o.m to zero

$$(z_1-z_2)\sin\alpha-(x_1+x_2)\cos\alpha=0.$$

So, with this in mind let us look at an example non-linear molecule ok. So, I said overall translation molecule is eliminated by imposing that the center of mass of the molecule does not get displaced. So, you put that to be zero origin. So, you have remember an example like a water molecule, right the two hydrogen atoms and this is the oxygen atom and be have this equation for center of mass with the molecule does not get displaced, ok.

So, you can determine what is I given the bond length in the undisplaced situation as l and the angle made with respect to the oxygen molecule I am calling angle subtended by the two hydrogen on the oxygen molecule is 2 alpha, clear. So, location of the center of mass of this molecule can be return down. We can find that the x is 0 and y will have this, sorry z I am taking this to be in the x and z coordinates ok.

So, now rotation this will clarify your question. Rotation of the molecule can be eliminated by putting angular momentum about center of mass of molecule to be 0 and if you try to use these two equations, you can simplify and write this constraint which has to be satisfied. So, basically what would we see you have 6 degrees of freedom, ok. You have 1, 2 and 3 constraints, clear.

So, essentially how many degrees of freedom you have with you which will be the vibrational degrees of freedom is 3 degrees of freedom. So, translation and one rotation puts three constraints on the 6 degrees of freedom. What are the 6 degrees of freedom? You have x 2 z 2 capital X capital Z x 1 z 1. I am looking at coordinate. So, why coordinate is remaining the same. If you take this, then you find that there are essentially 3 degrees of vibrations possible and we are interested in looking at the 3 degrees of vibrations, ok.

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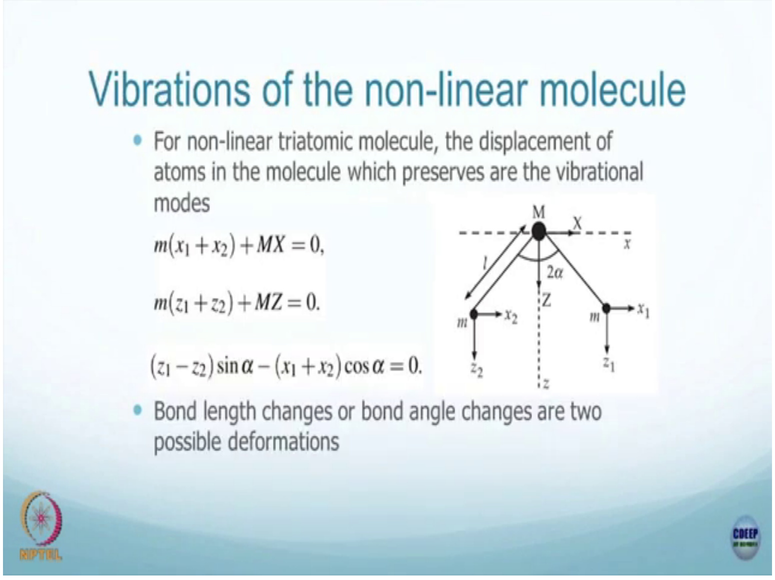

Vibrations of the non-linear molecule

- For non-linear triatomic molecule, the displacement of atoms in the molecule which preserves are the vibrational modes

$$m(x_1 + x_2) + MX = 0,$$

$$m(z_1 + z_2) + MZ = 0.$$

$$(z_1 - z_2)\sin\alpha - (x_1 + x_2)\cos\alpha = 0.$$

- Bond length changes or bond angle changes are two possible deformations

So, I am also trying to show you how systematically you can solve these situations in classical mechanics, so that you appreciate when I do the group theory that this is doable from group theory, ok. So, for non-linear triatomic molecule, so we have to have which preserves are the vibrational modes subjected to these three constraint.

So, the only motion where you are allowed the freedom of displacement or excursions of these atoms in the molecules are either the bond length, this length could change this length could independently change and you can also have the angle. 2 alpha could also change because of the relative displacements of the atoms in the molecule, clear.

So, these are the only possibilities which I can pictorially see here which may not be visible when we go to complex polyatomic molecule, but let us understand in this simplest case and map it to group theory, so that you can believe in group for complex polyatomic molecule. So, bond length changes. This is one possibility which will be one vibrational degrees of freedom and then you can also have the bond angle changing ok. See the other two possible deformations of the molecule without altering the center of mass of the molecule and rotational degree of freedom, ok.

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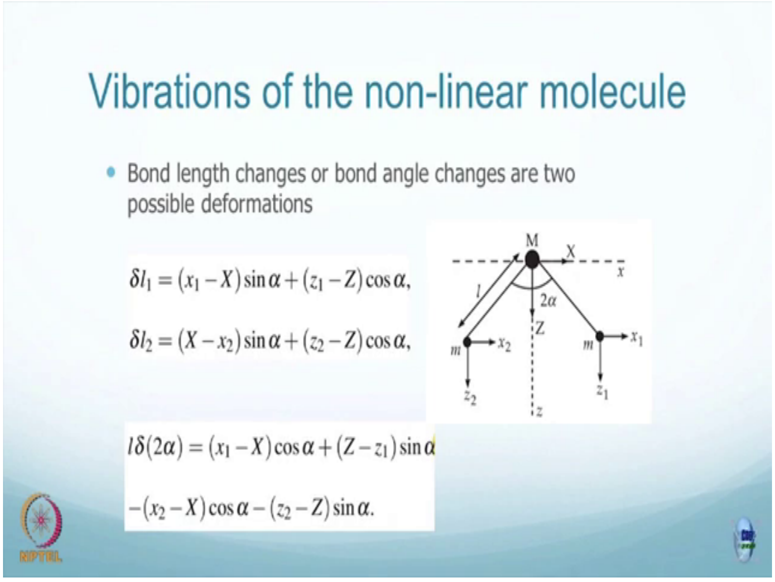

Vibrations of the non-linear molecule

- Bond length changes or bond angle changes are two possible deformations

$$\delta l_1 = (x_1 - X)\sin\alpha + (z_1 - Z)\cos\alpha,$$

$$\delta l_2 = (X - x_2)\sin\alpha + (z_2 - Z)\cos\alpha,$$

$$l\delta(2\alpha) = (x_1 - X)\cos\alpha + (Z - z_1)\sin\alpha$$
$$-(x_2 - X)\cos\alpha - (z_2 - Z)\sin\alpha.$$

So, how does bond length change? You can make this length to change. For example here which I call it as delta l 1 is the change in length of the bond, length between capital M and small m for this case and delta l 2 is the change in bond length for the mass with coordinates x 2 z 2 and the capital M with x and z, and you can also have a rotational constraint, ok.

So, in fact this is given explicitly in Landau Lifshitz mechanics book. In case somebody is I am only giving the final equations here. If anybody is interested to derive these things, you should go back and look at Landau Lifshitz mechanics, ok. So, the rotational deformation delta 2 alpha, this is given by these changes in which involves xxz, all this 6 degrees of freedom and the angle alpha, ok.

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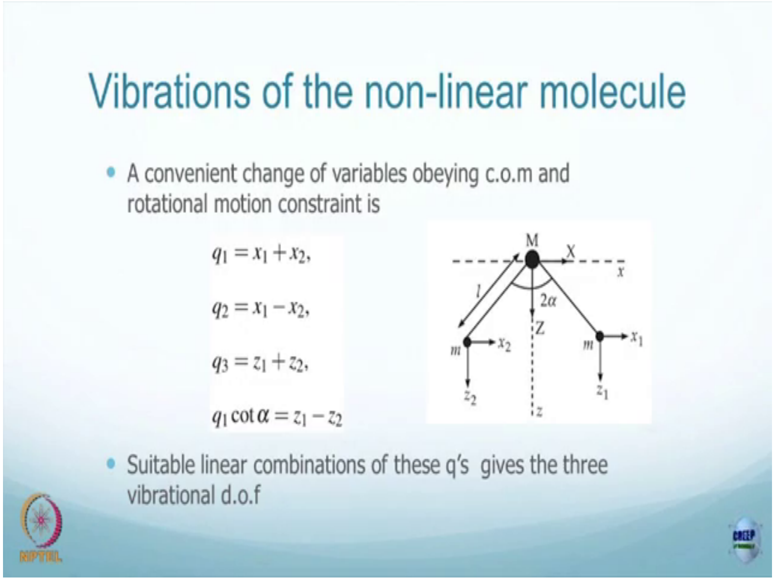

Vibrations of the non-linear molecule

- A convenient change of variables obeying c.o.m and rotational motion constraint is

$$q_1 = x_1 + x_2,$$

$$q_2 = x_1 - x_2,$$

$$q_3 = z_1 + z_2,$$

$$q_1 \cot\alpha = z_1 - z_2$$

- Suitable linear combinations of these q's gives the three vibrational d.o.f

So far so good. Looking at these constraint of center of mass angle of momentum being about the center of mass being 0, you can try to rewrite the Lagrangian. This looks adoque at present, but let us just make a change of variable to a new variable q 1 which is the sum of x 1 plus x 2, q 2 is the difference between x 1 and x 2, q 3 is a sum of z 1 plus z 2 and you will also see that the center of mass of the molecule and the angle of momentum about the center of mass being 0 will be putting some kind of a condition here between q 1 and z 1 minus z 2.

So, I am basically trying to say that if you had two coordinates, you could sum up the two coordinates and take the difference. They are two linearly independent objects, but when it comes here to z 1, the other one is actually related to q 1 and the angle alpha. So, it is not going to be a new degree of freedom, ok. Z 1 minus z 2 should not be a new degree of freedom. It is going to be constraint.

So, q 1 q 2 q 3 are essentially the 3 degrees of freedom which can capture the vibrations of this non-linear molecule made of three atoms to find the normal modes or actual vibrational degrees of freedom. It could be a linear combination of 1, 2 and 3 that I am not really looked that it, right. Now I just made a change of variable and then I can write for this system the Lagrangian, ok. So, the Lagrangian will have a potential energy. There will be potential energy due to vibrations which involves delta l 1 square, another vibration with delta l 2 square and there could also be a vibrational mode due to delta of the angle change, ok.

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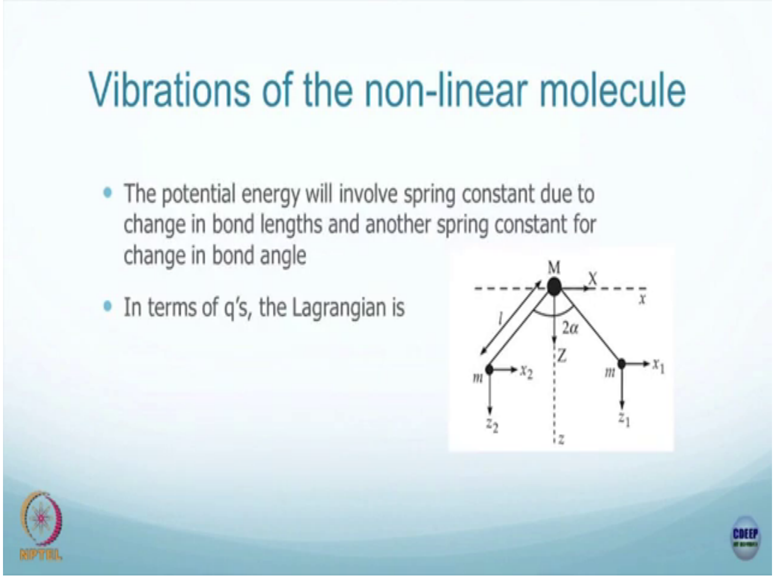

Vibrations of the non-linear molecule

- The potential energy will involve spring constant due to change in bond lengths and another spring constant for change in bond angle
- In terms of q's, the Lagrangian is

So, you will have those terms added into it. So, this is what I am saying in level spring constant. So, all simple harmonic let us take it to be small displacements that is not do a violent vibrational modes are like you know small displacements about its mean positions. So, they will all be simple harmonic, and let us take the spring constant due to change in bond lengths to be kappa subscript l another spring constant due to change in bond angle as another kappa alpha and in terms of q, you can write the Lagrangian for the system, ok.

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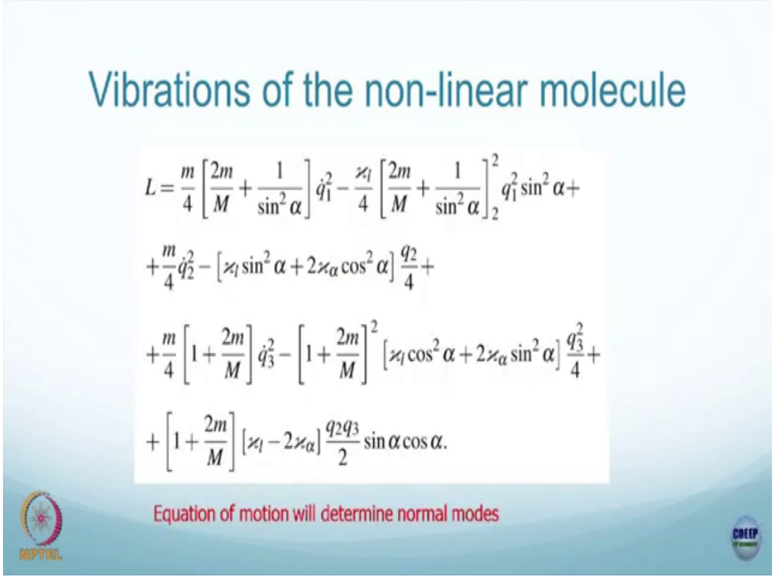

Vibrations of the non-linear molecule

$$L=\frac{m}{4}\left[\frac{2m}{M}+\frac{1}{\sin^2\alpha}\right]\dot{q}_1^2-\frac{\varkappa_l}{4}\left[\frac{2m}{M}+\frac{1}{\sin^2\alpha}\right]_2^2 q_1^2\sin^2\alpha+$$

$$+\frac{m}{4}\dot{q}_2^2-\left[\varkappa_l\sin^2\alpha+2\varkappa_\alpha\cos^2\alpha\right]\frac{q_2}{4}+$$

$$+\frac{m}{4}\left[1+\frac{2m}{M}\right]\dot{q}_3^2-\left[1+\frac{2m}{M}\right]^2\left[\varkappa_l\cos^2\alpha+2\varkappa_\alpha\sin^2\alpha\right]\frac{q_3^2}{4}+$$

$$+\left[1+\frac{2m}{M}\right]\left[\varkappa_l-2\varkappa_\alpha\right]\frac{q_2q_3}{2}\sin\alpha\cos\alpha.$$

Equation of motion will determine normal modes

So, try and redo this rewriting it for the system of three masses, you have two masses and a capital M. So, try to write it out explicitly and you will find that you have equations where you have a Lagrangian with q and dot square, you have a Lagrangian with q and square sin square alpha and kappa alpha kappa l is the spring constant for the change in bond length, and similarly for q 2 also you will have a piece which depends on kappa l, but you will also have a kappa alpha and so on.

So, you have this. What do you do next? Given a Lagrangian you try to find the equations of motion for q 1 q 2 and q 3. This is what you will do right. Everybody is bold looks like a everybody knows. So, good if you know at, it is good if you do not know. Do not worry, but this is the cumbersome process in which a mechanic students, classical mechanic student works out the normal modes in and I am sure they would have got problems in exams and for linear molecule finding the normal modes, yes or no? Yes ok.

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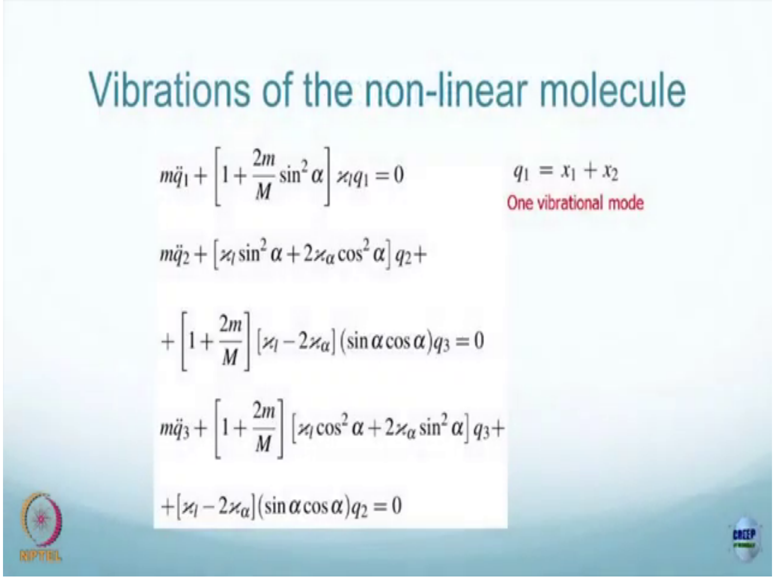

Vibrations of the non-linear molecule

$$m\ddot{q}_1+\left[1+\frac{2m}{M}\sin^2\alpha\right]\varkappa_l q_1=0$$

$q_1 = x_1 + x_2$

One vibrational mode

$$m\ddot{q}_2+\left[\varkappa_l\sin^2\alpha+2\varkappa_\alpha\cos^2\alpha\right]q_2+$$

$$+\left[1+\frac{2m}{M}\right]\left[\varkappa_l-2\varkappa_\alpha\right](\sin\alpha\cos\alpha)q_3=0$$

$$m\ddot{q}_3+\left[1+\frac{2m}{M}\right]\left[\varkappa_l\cos^2\alpha+2\varkappa_\alpha\sin^2\alpha\right]q_3+$$

$$+\left[\varkappa_l-2\varkappa_\alpha\right](\sin\alpha\cos\alpha)q_2=0$$

So, equations of motion for that Lagrangian interestingly you see that this first equation is completely decoupled. It has no coupling to q 2 or q 3. So, straight away from here you can read off that q 1 which was defined to be x 1 plus x 2 should be one vibrational mode with this frequency, and again this equation has a coupling between q 2 and q 3 and this one has beading q 3 and q 2. So, they are coupled set of deferential equations, then you know how to solve it. What would you do? You write the determinant, you try to find normal modes by diagonalising such a matrix, right.

So, I will leave it you to check this. I will put this slide. I want you to check because it will help you to understand the group theory way of do it better, ok. Right now it is still mechanics whatever I have said it. So, you see the steps I have gone through. I have gone through systematically, but it is a little tedious.

You need to literally do these things to figure out that q 1 is a normal mode with coordinate x 1 plus x 2, but what we will see is from group theory we can actually get x 1 plus x 2 and then because we have done this hard work, you can appreciate x 1 plus x 2 is a normal mode I get from group theory, ok. Is that clear?.

So, some of the steps of math I am not going through right now here because it is not a mechanics course, but anybody is interested you can come and bother me if you are not getting in between steps, but you can look at Landau Lifshitz and you will be able to get these steps,. So, I am not doing the diagonalization of this coupled set of two equations to determine what are the normal modes which will be a linear combination of q 2 and q 3 and an orthogonal linear combination involving another mode, ok.

So, this I am not doing at now and when you diagonalize set, you will find two eigen values. If the two eigen values are different, then only you call it non degenerate right. Do you accept it to be different or do you accept it to be same for this molecule which we are looking at? C 2 v is a symmetry the character table tells you that you should have only 1 d IR reps.

So, you better get all these eigen values to be different ok. It has to be different. It cannot be degenerated, ok. Check it out. I am sure you can take this and diagonalisz it an find the frequencies, ok. So, 3 vibrational degrees of freedom will involve q 1 q 2 q 3 turns out that q 1 itself is a vibrational mode which is one frequency. What is the frequency? Frequency is going to involve this factor times. This one is omega squared, ok.

So, this is non-degenerate one, normal mode or one vibrational mode which is straight away q 1. Q 1 is not talking to, q 2 and q 3 linear combination of q 2 and q 3 what linear combination you have to diagonalise this and find out and what are the frequencies, ok. I am trying to tell you that you will find each one to have a distinct frequency. You cannot have the same frequency if you are doing other molecules like methane which is the shown in the video.

You will start seeing if you do this regress exercise, there will be some frequencies which will occur three times because there is a 3 d IR rep in the character type, or if you had C 3 v symmetry you will get 2 times which is associated with the frequency should repeat twice and you should be able to find two distinct normal mode sharing the same frequency.

That is the way they start doing that mixing and joining together you know. You remember and you can see that in the methane molecule there are three degenerate vibrational modes and they combine together and so on when will you get degenerate comes from the symmetry of the molecule, ok. I hope you are you know appreciating what I am trying to driven how simple looking, how complex looking where group theory can play very important.

Student: One problem that you have 2 dimension.

You can treat it be a 2 dimension or you can also treat it to be a 3 dimension, but then you have to remove the translation along the y direction and the rotations which is involving the others.

Student: What about C 2 v.

I will come to it C 2 V in the sense that this is an example of a water molecule and I know that the two I put it as two identical lengths. If you do as C 2 about this z axis, you do see that this hydrogen goes into the other hydrogen and vice versa.

Student: There will be 2 dimensional.

It will be still if you treat the z axis to be the c 2 axis, it is still true and sigma v to be like the axis z plane it is still true, ok. Is that clear? So, I am just looking at it from purely from the action of the group theory also and you can treat it like a 3 d problem, then you have to remove those. I have to put the center of mass coordinate for the y also.

So, basically I could have given x 1 y 1 z 1 and complicate the situation instead I thought anyway y is not playing a role with all these symmetries of this molecule like you look at it as a c 2 axis on the z axis which takes the two hydrogen atoms to each other. So, I thought it is better to and find to a simpler 2 d situation, but you can extra pull it to 3 d dimension.