Fundamentals of Spectroscopy

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Lecture-31

Vibration of a Diatomic Molecule and Derivation of the Vibrational Selection Rule

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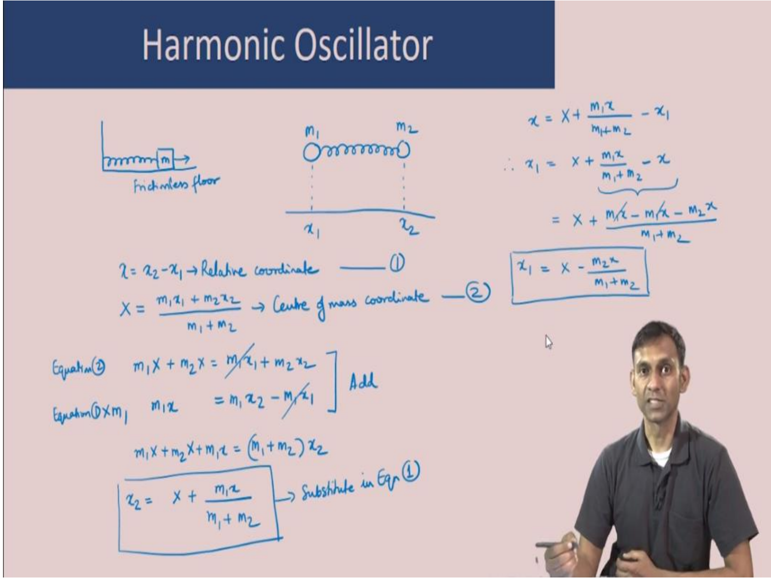

Harmonic Oscillator

$x = x_2 - x_1 \rightarrow$ Relative coordinate — ①

$X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \rightarrow$ Centre of mass coordinate — ②

Equation ② $\quad m_1X + m_2X = \cancel{m_1x_1} + m_2x_2$

Equation ① $\times m_1 \quad m_1x = m_1x_2 - \cancel{m_1x_1}$] Add

$m_1X + m_2X + m_1x = (m_1 + m_2)x_2$

$\boxed{x_2 = X + \frac{m_1x}{m_1 + m_2}} \rightarrow$ Substitute in Eqn ①

$x = X + \frac{m_1x}{m_1+m_2} - x_1$

$\therefore x_1 = X + \underbrace{\frac{m_1x}{m_1+m_2} - x}$

$= X + \frac{\cancel{m_1x} - \cancel{m_1x} - m_2x}{m_1+m_2}$

$\boxed{x_1 = X - \frac{m_2x}{m_1+m_2}}$

During the previous discussion, we have solved the quantum harmonic oscillator problem. In other words, we have found the eigenvalues and eigenfunctions of the Hamiltonian of the particle of a single particle which moves in a harmonic potential. Now, this is as I have mentioned connected very deeply to vibrational spectroscopy. So, what is the connection, we will show now, that the harmonic oscillator problem that is the single particle moving in a harmonic potential corresponds exactly to the vibration of a diatomic molecule.

We will see that even for a polyatomic molecule, the harmonic oscillator model is absolutely relevant and the vibration of a polyatomic molecule can be written as a sum of harmonic oscillator Hamiltonians where there are n internal degrees of freedom. Let us start with a diatomic molecule and we will later look at polyatomic systems, the picture of a single mass moving in a harmonic potential looks something like this which we have discussed before there is a mass m connected by a spring to a rigid wall and this moves on a frictionless floor.

Now, a diatomic molecule does not quite look like this. In fact, a diatomic molecule looks like this where you have 2 masses m 1 and m 2 and these are connected by a spring like this and these 2 particles move according to the force due to the spring and we assume that there is no other forces acting on this 2 particles. Now, our goal is to show that this system of 2 particles attached by a spring is actually identical to the system of 1 particle attached by a spring and another problem of an overall translation of centre of mass.

So, let us look into this precisely and we will map this problem of 2 particles attached by a spring to a harmonic oscillator problem. So, let us assume that these 2 masses have positions x 1 and x 2 for masses m 1 and m 2. Now, we can define a relative coordinate x, which is x 2 – x 1, which is the difference in the position of the 2 coordinates. This relative coordinate is a measure of how much the spring is stretched or compressed, and therefore tells us how much force is acting on the 2 masses.

For this system, there is also another important coordinate, which is the centre of mass coordinate. And by definition, the centre of mass coordinate here is m 1 x 1 + m 2 x 2 divided by m 1 + m 2. So, this is the centre of mass coordinate our goal to write the Hamiltonian of this 2 mass problem in terms of these new coordinates, which are the relative coordinates and the centre of mass coordinates.

So, let us see how we can go about doing that, we will express the x 1 and x 2 coordinate in terms of the relative coordinate and the centre of mass court. So, let us call this as equation 1 and this is equation 2. So, let us let me begin with equation 2 and I will rearrange this as m 1 x + m 2 x = m 1 x 1 + m 2 x 2 and I take equation 1 and I multiply by m 1 and write that on the next line and that I then I get m 1 x = m 1 x 2 - m 1 x 1.

Now, if I add these 2 equations, then you see that these 2 terms will cancel and I get m 1 x + m 2 X + m 1 x = m 1 + m 2 times x 2. Now, if I solve for x 2, I get x 2 = X + m 1 x divided by m 1 + m 2. Here is the equation for x 2 and I will substitute in equation 1 to get now an expression for x 1. So, on substituting I get x = X + m 1 x divided by m 1 + m 2 - x 1. So, x 1 = X + m 1 x divided by m 1 + m 2 - x. let us simplify these 2 terms.

So, this gives X + m 1 x - m 1 x - m 2 x divided by m 1 + m 2 and these 2 terms cancel giving an expression for x 1, which is X - m 2 x divided by m 1 + m 2. So, now, in these 2 boxes, we have the expressions for the coordinates of the 2 masses in terms of the centre of mass coordinate and the relative coordinate of the 2 masses.

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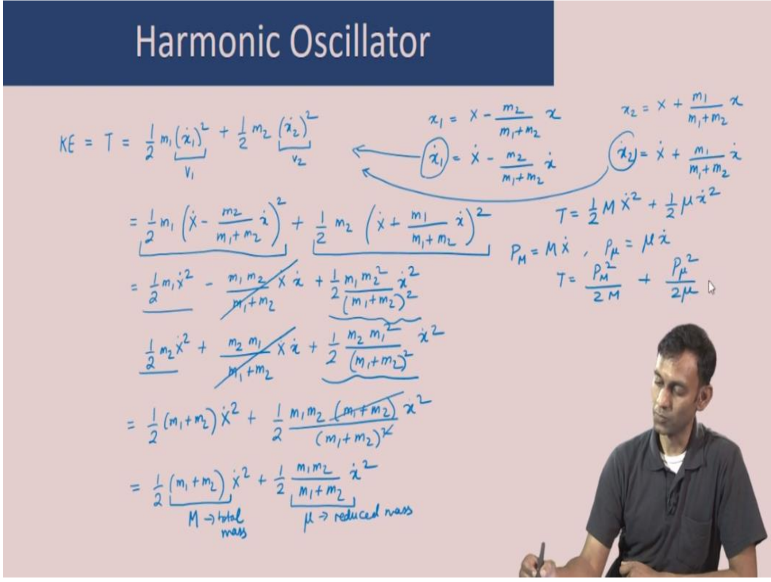

Harmonic Oscillator

$$KE = T = \frac{1}{2}m_1\underbrace{(\dot{x}_1)}_{v_1}^2 + \frac{1}{2}m_2\underbrace{(\dot{x}_2)}_{v_2}^2$$

$$x_1 = X - \frac{m_2}{m_1+m_2}x \qquad x_2 = X + \frac{m_1}{m_1+m_2}x$$

$$\boxed{\dot{x}_1} = \dot{X} - \frac{m_2}{m_1+m_2}\dot{x} \qquad \boxed{\dot{x}_2} = \dot{X} + \frac{m_1}{m_1+m_2}\dot{x}$$

$$= \underbrace{\frac{1}{2}m_1\left(\dot{X} - \frac{m_2}{m_1+m_2}\dot{x}\right)^2} + \underbrace{\frac{1}{2}m_2\left(\dot{X} + \frac{m_1}{m_1+m_2}\dot{x}\right)^2}$$

$$= \underline{\frac{1}{2}m_1\dot{X}^2} - \cancel{\frac{m_1 m_2}{m_1+m_2}}\dot{X}\dot{x} + \frac{1}{2}\frac{m_1 m_2^2}{(m_1+m_2)^2}\dot{x}^2$$

$$\underline{\frac{1}{2}m_2\dot{X}^2} + \cancel{\frac{m_2 m_1}{m_1+m_2}}\dot{X}\dot{x} + \frac{1}{2}\frac{m_2 m_1^2}{(m_1+m_2)^2}\dot{x}^2$$

$$= \frac{1}{2}(m_1+m_2)\dot{X}^2 + \frac{1}{2}\frac{m_1 m_2\cancel{(m_1+m_2)}}{(m_1+m_2)^{\cancel{2}}}\dot{x}^2$$

$$= \frac{1}{2}\underbrace{(m_1+m_2)}_{M \rightarrow \text{total mass}}\dot{X}^2 + \frac{1}{2}\underbrace{\frac{m_1 m_2}{m_1+m_2}}_{\mu \rightarrow \text{reduced mass}}\dot{x}^2$$

$$T = \frac{1}{2}M\dot{X}^2 + \frac{1}{2}\mu\dot{x}^2$$

$$P_M = M\dot{X}, \quad P_\mu = \mu\dot{x}$$

$$T = \frac{P_M^2}{2M} + \frac{P_\mu^2}{2\mu}$$

Let us now consider what the Hamiltonian looks like of these 2 mass system in terms of these new coordinates. So, let us write the Hamiltonian now, and as you know the Hamiltonian has the kinetic energy operator and the potential energy operator. So, let us start with the kinetic energy operator. So, the kinetic energy of the 2 mass system which I will do Notice T, I will first write the classical expression for kinetic energy.

And then as you know, we can convert to the quantum operator by substituting the classical variables with the quantum operator. So here is the classical kinetic energy, which is half m 1, x 1 dot square + half m 2 x 2 dot square x 1.is the first derivative of the position with respect to time, so it is just the velocity 1 and this x 2 dot is the velocity 2, we have obtained the value of x 1 as X - m 2 divided by m 1 + m 2 x. So, the first derivative with respect to time = X dot - m 2 divided by m 1 + m 2 x dot.

And similarly, we have x 2 = X + m 1 divided by m 1 + m 2 x and x 2 dot will be X dot + m 1 divided by m 1 + m 2 x dot so if we substitute the expressions for x 1 dot and x 2 dot into the kinetic energy expression, we get the kinetic energy value is half m 1 X dot - m 2 divided by m 1 + m 2 x dot square + half m x dot + m 1 + divided by m 1 + m 2 x dot square expanding this out, we get half m 1 x dot square - m 1 m 2 divided by m 1 + m 2 x dot x dot.

Here the half outside cancels with the 2, which comes when you open the square and + half m 1 m 2 square divided by m 1 + m 2 x dot square. These 3 terms come from the first term in the previous line, we now expand the second term and that gives half m 2 x dot square + m 2 m 1 divided by m 1 + m 2 x dot x dot + half m 2 m 1 square divided by m 1 + m 2 whole square x dot square. In the previous term, this m 1 + m 2 in the denominator should also be whole square.

This expression can now be simplified further by noting that these 2 terms actually cancel each other. And we can combine now the, these 2 terms here, and the last 2 terms together. So we can write this as half of m 1 + m 2, X dot square + half m 1 m 2. And then we can write this as m 1 + m 2 x dot square divided by m 1 + m 2 whole squares. And one of the terms in the numerator and denominator m 1 + m 2 cancels.

And finally, we have this is equal to half m 1 + m 2 X square + half m 1 m 2 divided by m 1 + m 2 x square, we can now define a total mass of the system, m 1 + m 2, which is m, this is the total mass. And we can define another quantity, which is for m 1 m 2 divided by m 1 + m 2, which we will call mu, which we will call the reduced mass of the system. And with that, the kinetic energy T becomes half M x dot square + half mu x dot square by using momentum, P m is equal to mass times velocity similarly, p mu = mu times velocity x dot we can write the kinetic energy as p m square / 2 m + P mu square / 2 mu.

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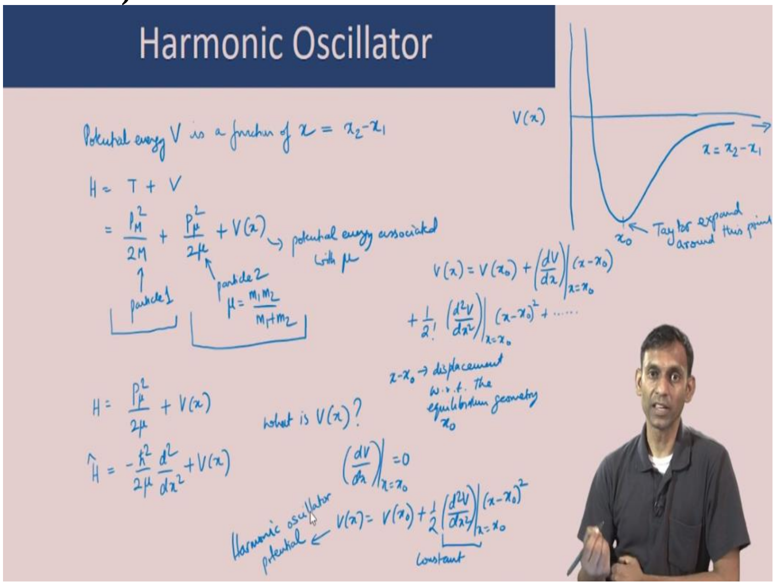

Harmonic Oscillator

Potential energy V is a function of $x = x_2 - x_1$

$H = T + V$

$= \frac{P_M^2}{2M} + \frac{P_\mu^2}{2\mu} + V(x)$ → potential energy associated with μ

particle 1

particle 2

$\mu = \frac{m_1 m_2}{m_1 + m_2}$

$H = \frac{P_\mu^2}{2\mu} + V(x)$

$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x)$

what is $V(x)$?

$V(x) = V(x_0) + \left(\frac{dV}{dx}\right)\Big|_{x=x_0}(x-x_0) + \frac{1}{2!}\left(\frac{d^2V}{dx^2}\right)\Big|_{x=x_0}(x-x_0)^2 + \ldots\ldots$

$x - x_0$ → displacement w.r.t. the equilibrium geometry x_0

$\left(\frac{dV}{dx}\right)\Big|_{x=x_0} = 0$

Harmonic oscillator potential ← $V(x) = V(x_0) + \frac{1}{2}\underbrace{\left(\frac{d^2V}{dx^2}\right)\Big|_{x=x_0}}_{\text{constant}}(x-x_0)^2$

The potential energy in the case of the 2 mass system connected by a spring depends only on the relative separation between the 2 masses. So, in other words, the potential energy V is a function of the relative coordinate x which is = x 2 - x 1. So, the Hamiltonian which is sum of the kinetic energy plus potential energy is = P m square / 2 m + P mu square / 2 mu + V of x if we look at the expression for this Hamiltonian.

We can observe that this is equivalent to the Hamiltonian of a system of 2 particles, one of which is a particle of mass m and another which is of mass mu. And the particle of mass M particle 1 does not have any potential energy, so, it is moving without any force acting on it. And the particle with mass mu has a potential energy V x. So, this is the potential energy associated with mu.

So, we see that the system of 2 particles attached with a spring can be equivalently written as a system of 2 different particles, which are in some sense fictitious. One of these is a particle of mass m 1 + m 2, which is the total mass of the system. And that is moving without any force that is this part of the Hamiltonian. And there is another fictitious particle with a mass mu.

Which is the reduced mass particle 2 has mass mu = m 1 + m 2 divided by m 1 + m 2 and this is moving with a potential V x, which is which depends only on the relative distance between the 2 masses m 1 and m 2 the motion of the centre mass does not have any force acting on it. And therefore, it is just a translation with constant motion or the particle or the 2 masses may just be stationary.

And the real energy quantization is due to the internal motion of the 2 particles, which is in the second part of the Hamiltonian. The Hamiltonian of interest for now, us is H = P mu square divided by 2 mu + V of x and if we write the quantum mechanical Hamiltonian which is the operator this becomes - h bar square / 2 mu d square / dx square + V of x. The question is what is V of x for this, let us look at what potential energy looks like for a diatomic molecule for a typical diatomic molecule.

The potential energy V of x as a function of the distance between the 2 atoms looks something like this. So, the x axis here is the distance between the 2 atoms and you can call this as x the relative coordinate and the value at which the energy is the lowest is also called the equilibrium geometry of the diatomic molecule. And we can denote that as x 0 and if we make a Taylor expansion of this potential energy around the equilibrium geometry.

So, let us Taylor expand around this equilibrium geometry then V of x = V of x 0 + dv / dx at x = x 0 multiplied by x - x 0 + the second order term 1 over 2 factorial d 2 v / dx square at x = x 0 multiplied by x - x 0 whole square and then the higher order terms we notice here that x - x 0 is the displacement with respect to the equilibrium geometry and the equilibrium geometry is denoted by x 0 in our case.

So, at the equilibrium geometry as you can see from the figure, the first derivative is equal to 0. So, dv / dx at x = x 0 = 0. And therefore, the expansion of the potential energy in terms of a Taylor series, which is up to the second order simply becomes V of x = V of x 0, which is just the absolute energy at x 0 + half d square V / dx square x = x 0 which is a constant at the particular value x = x 0 and multiplied by x - x 0 square.

And this is good up to the second order, which is a fairly good approximation for a potential energy of the form that you see here. So, the potential energy is essentially that of a harmonic oscillator. The Hamiltonian is therefore, that of a particle moving in a harmonic oscillator potential.

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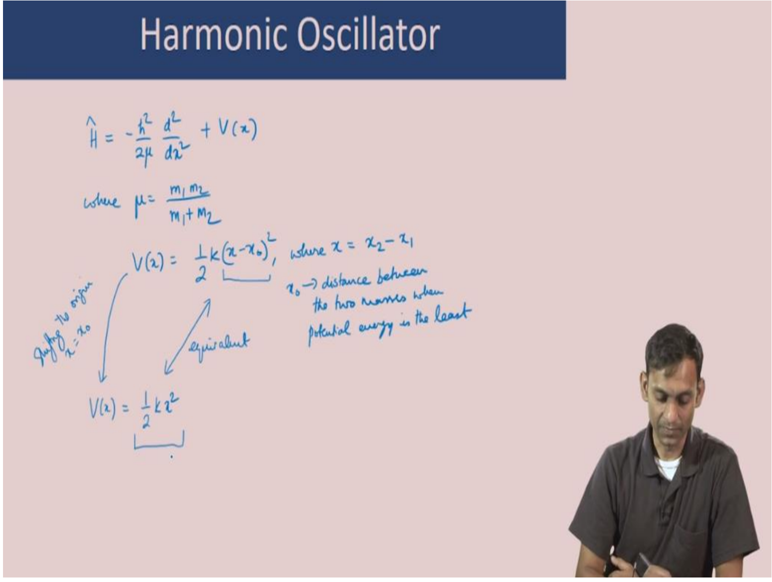

Harmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$$V(x) = \frac{1}{2}k\underbrace{(x-x_0)}^2, \text{ where } x = x_2 - x_1$$

$x_0 \rightarrow$ distance between the two masses when potential energy is the least

Shifting the origin $x = x_0$

equivalent

$$V(x) = \underbrace{\frac{1}{2}kx^2}$$

So to summarise the Hamiltonian of a diatomic molecule, which consists of 2 masses attached by a spring is essentially - h bar square / 2 mu d square / dx square 2 Last V of x, where mu is equal to the reduced mass m 1 m 2 divided by m 1 + m 2 and V of x = half k x - x 0 square, where x is the relative coordinate, which is the difference in the coordinate between x 2 - x 1 or in other words, it is the change in the distance between the 2 masses and x 0 is the distance between the 2 masses.

When the spring is not stretched and not compressed, or in other words, that is the lowest potential energy of the 2 mass system connected by the spring. So, this is the distance between the 2 masses when potential energies the least we can now understand that the vibration of a diatomic molecule can be modelled by the motion of a single particle moving in a harmonic potential.

Because we have seen that these 2 problems are essentially mathematically exactly equivalent, you have to keep in mind that you have to use the reduced mass of the system, which is given by m 1 m 2 divided by m 1 + m 2. The idea of modelling the vibration of a diatomic molecule by a particle moving in a harmonic potential can be extended to polyatomic molecules as well.

And in that case, you can see that the vibration can be modelled as a sum of several 1 dimensional oscillators, there is a point which we need to note here, we have seen that the harmonic oscillator potential energy, V of x = half k x square. Now here, the form that we have is half k x - x 0 square. The point is that these 2 potential energies are actually equivalent. And we can convert this potential energy V of x, which is half k x - x 0 square to this half k x square by shifting the origin to x = x 0. So, then the value at x 0 just becomes 0. And we have instead of x - x 0 x - 0 square, which is basically half the x square.

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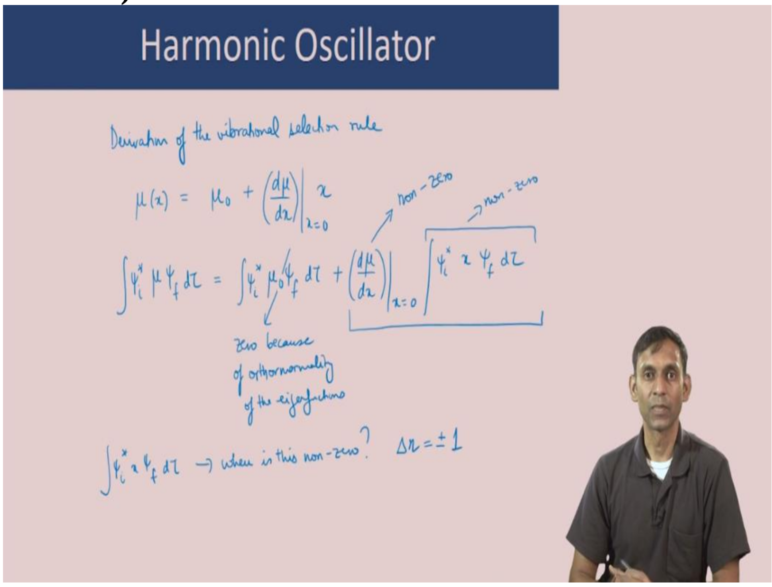

Harmonic Oscillator

Derivation of the vibrational selection rule

$$\mu(x) = \mu_0 + \left(\frac{d\mu}{dx}\right)\Big|_{x=0} x$$

$$\int \psi_i^* \mu \psi_f \, d\tau = \underbrace{\int \psi_i^* \mu_0 \psi_f \, d\tau}_{\substack{\text{zero because}\\ \text{of orthonormality}\\ \text{of the eigenfunctions}}} + \underbrace{\overset{\text{non-zero}}{\left(\frac{d\mu}{dx}\right)\Big|_{x=0}} \overset{\text{non-zero}}{\int \psi_i^* x \psi_f \, d\tau}}$$

$$\int \psi_i^* x \psi_f \, d\tau \rightarrow \text{when is this non-zero?} \quad \Delta n = \pm 1$$

We have seen the derivation of the eigenfunctions of the harmonic oscillator and how the harmonic oscillator is a good model for a vibrating diatomic molecule and how it can be a good model for the vibration of a polyatomic molecule. Let us know derive the vibrational selection rule. In a previous lecture, it has been discussed that the dipole moment of a molecule depends on the geometry of the molecule.

And let us focus on a diatomic molecule where there is only one geometrical coordinate, which is the distance between the 2 atoms which we denote as x. And then this dipole moment can be written as a constant plus a derivative d mu by dx first derivative at x = 0 multiplied by x. And then there are higher order terms, the intensity of a vibrational transition depends on the square of the transition dipole moment integral.

Which is psi i star mu psi f d tau, where psi i is the initial vibrational state psi f is the final vibration state and mu is the dipole moment operator. And if we expand the dipole moment operator like we have written here and use this in the integral then this becomes psi i star mu 0 psi f d tau plus the second term which is d mu / dx at x = 0 and psi i star x times psi f d tau. Then we notice that this first term is 0, because of orthonormality of the eigenfunctions.

And the transition dipole moment depends primarily on this term where again there are 2 terms. The first is this and this term is the derivative of the dipole moment with respect to the geometry. And this first term should be nonzero for this entire term to be nonzero. And it implies that the dipole moment gradient should be nonzero. So, with the change in geometry, the dipole movement should actually change for this term to be nonzero?

This is what is called the gross selection rule and as discussed in a previous lecture and the second part, which is here, should also be nonzero. And the question we ask now is, when is this psi i star x psi f d tau when is this nonzero because this will give us the specific selection rule, which is that the quantum number change between the initial state and the final state is plus or minus 1. Let us go ahead and derive this result.

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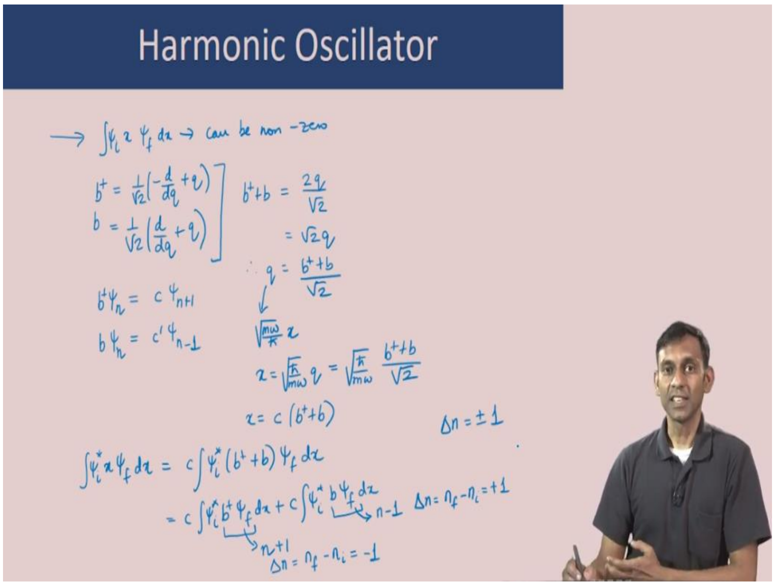

Harmonic Oscillator

$\rightarrow \int \psi_i x \psi_f \, dx \rightarrow$ can be non-zero

$$\left.\begin{aligned} b^+ &= \frac{1}{\sqrt{2}}\left(-\frac{d}{dq}+q\right) \\ b &= \frac{1}{\sqrt{2}}\left(\frac{d}{dq}+q\right) \end{aligned}\right] \quad b^+ + b = \frac{2q}{\sqrt{2}} = \sqrt{2}q$$

$$\therefore q = \frac{b^+ + b}{\sqrt{2}}$$

$$\downarrow$$

$$\sqrt{\frac{m\omega}{\hbar}}\, x$$

$$b^+\psi_n = c\,\psi_{n+1}$$

$$b\,\psi_n = c'\,\psi_{n-1}$$

$$x = \sqrt{\frac{\hbar}{m\omega}}\, q = \sqrt{\frac{\hbar}{m\omega}}\, \frac{b^+ + b}{\sqrt{2}}$$

$$x = c\,(b^+ + b)$$

$\Delta n = \pm 1$

$$\int \psi_i^* x \psi_f \, dx = c \int \psi_i^* (b^+ + b) \psi_f \, dx$$

$$= c \int \psi_i^* \underbrace{b^+ \psi_f}_{\to\, n+1} dx + c \int \psi_i^* \underbrace{b \psi_f}_{\to\, n-1} dx$$

$\Delta n = n_f - n_i = +1$

$\Delta n = n_f - n_i = -1$

We are looking for the condition when the integrals psi i x psi f dx can be nonzero when psi i and psi f are eigenfunctions of the harmonic oscillator Hamiltonian. So, for this, we recall that we define these 2 operators, the ladder up operator and the ladder down operator and we write their specific forms which are b dagger = 1 over square root of 2 - d / dq + q and b = 1 over square root of 2 d / d q + q.

We further recall that the b dagger operator acting on an eigenfunction of the harmonic oscillator with quantum numbers n gives an eigenfunction with quantum number n + 1 and the ladder down operator b operates on the eigenfunction with quantum number in and gives an eigenfunction with quantum number n - 1. Now, using these definitions of the b dagger and b operator, we can easily write q as a sum of these operators.

So, if you take b dagger + b, the - d / dq cancels with the d / dq and you get 2q divided by square root of 2 or in other words, this is equal to square root of 2q and therefore, q = b dagger + b divided by square root of 2 further q = square root of m omega / h bar x. So, x is equal to square root of h bar divided by m omega q or that is equal to square root of h / m omega b dagger + b divided by square root of 2.

The important point is that x can be written as some constant times the sum of the raising and lowering operators. Using this it is quite easy to derive the specific vibrational selection rule. So, for this, let us substitute in the integral that we are interested in. So, psi x psi f dx which is what we had here is some constant psi b dagger + b divided multiplied by psi f dx that is equal to c times psi i b dagger psi f dx + c times psi i all of these should be stars b psi f dx, now be dagger of psi f gives an eigenfunction with the quantum number increased by 1.

So, if psi f had quantum number n be dagger of psi f increases the quantum number 2 n + 1. Now, the only way that this integral would be nonzero is if the quantum number of psi i and b dagger of psi f are the same. And that would be possible if psi f has a quantum number 1 less than psi 1 so that when b dagger operates on psi f it increases the quantum number by 1. So, this is implies that the delta the change in the quantum number, which is the quantum number of final minus quantum number of initial should be - 1.

Similarly, if we consider this second integral, then the b operator acting on psi f decreases the quantum number by 1. So, if the quantum number of psi f was n, then be operating on psi f gives the quantum number n - 1. And this integral would be nonzero if the quantum number of psi f to begin with was 1 greater than psi. So, after b operates on psi f, the quantum number would decrease by 1 and make it equivalent to psi i and then the integral would be nonzero this gives delta n = n f – n i = + 1.

And that is the origin of the specific selection rule that for a vibrational transition to occur, delta n should be plus or minus 1. If the quantum number of psi f is more than one unit greater than psi i, then the b operator operating on it cannot lower it to make it equivalent to the psi i and therefore, the integral will be 0 and no transition will occur. So, we have seen that the specific selection rule delta n is equal to plus or minus 1 can be derived quite easily using the ladder up and ladder down operators, which were used in the derivation of the eigenfunctions of the harmonic oscillator Hamiltonian.