Quantum Mechanics and Molecular Spectroscopy

Prof. G NareshPatwani
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture No -30
Molecular Vibrations (Part 1)

Hello, welcome to the lecture number 30 of the course quantum mechanics and molecular spectroscopy. In the previous lecture we were looking at the rotational transitions and the associated selection rules.

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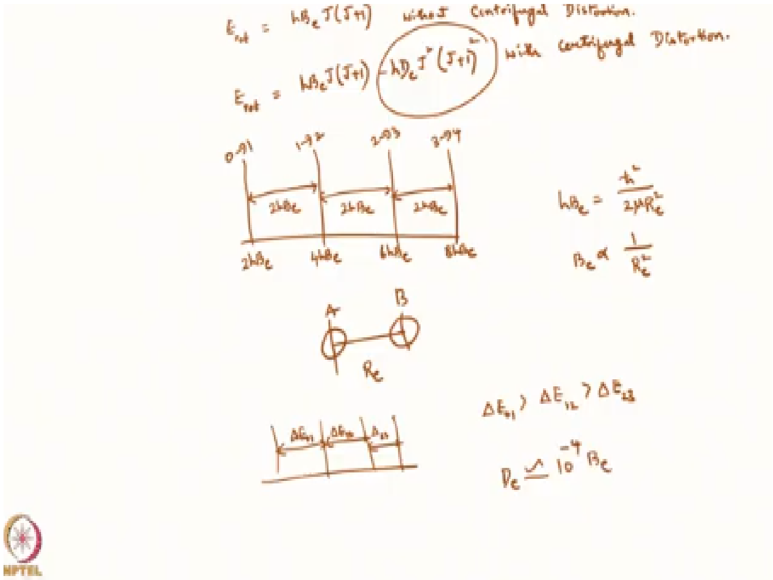

So we had, E rotation or E rotor was given by h B e J into J + 1 and when we had this is without Centrifugal Distortion and when we had Centrifugal distortion E rotational was given by h B e J into J + 1 - h D e J square into J + 1 whole square, so when we figured out that this is with Centrifugal Distortion. Now, we figured out that when there is no centrifugal distortion, the rotational lines will be evenly spaced.

So this is going from J is equal to 0 to 1, 1 to 2, 2 to 3, and 3 to 4 this will be 2h B e, 4h B e, 6h B e, 8h B e and the difference is given by 2h B e, so we will have equally spaced lines 2h B e and we know that h B e is equal to h bar square by 2 mu R e square. So from B e is proportional to 1 over R e square, so one can get the where R e is the A and B, and R e is the equilibrium distance or equilibrium geometry. So by measuring the rotational spectrum one can get the bond distance or in general for polyatomical molecule, you can get geometrical parameters.

Now it turns out that rotation spectroscopy is the only spectroscopic method by which one can measure geometrical parameters or bond lengths in particle, there is no other spectroscopic technique that will allow this. Now what happens when you have the centrifugal distortion when the centrifugal distortion is there, so it kind of effects, because this term effects larger J transitions more than the lower J. So what happens is this lines become more and more packed.

So the distance or the energy difference between the subsequent lines keeps decreasing. So this is delta E 0 1, delta E 1 2 and this is delta E 2 3. So delta E 0 1 will be greater than delta E 1 2, will be greater than, delta E 2 3, of course you know by looking at the pattern one can also figure out the centrifugal distortion and which is generally, so D e is approximately equal to 10 power -4 times B e.

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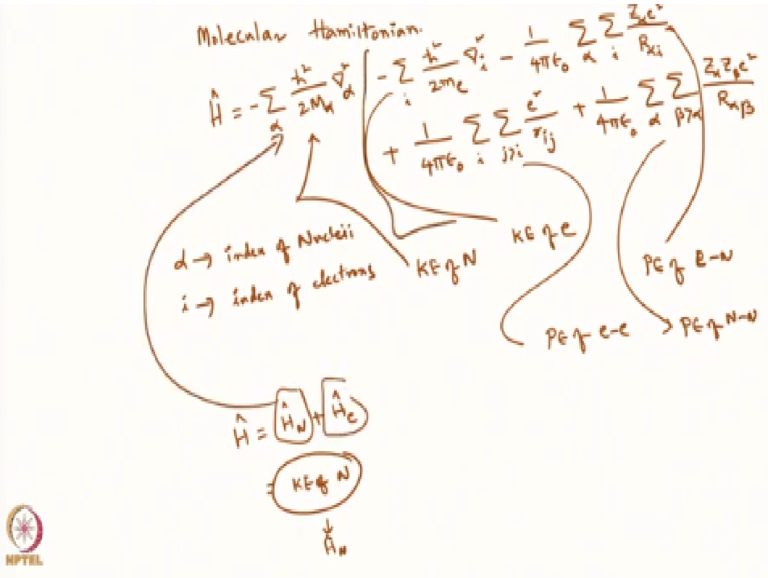

Now when we go back to the molecular Hamiltonian, it had many terms so H was equal to sum over alpha h bar square by 2M alpha del square alpha, negative of this minus sum over i h bar square by 2me Del square i - 1 by 4 pi epsilon 0 sigma over alpha and sigma over i, z alpha e square by R alpha i + 1 by 4 pi epsilon 0 sigma over i, sigma over j greater than i, e square by r i j + 1 by 4 pi epsilon 0 sum over alpha, sum over beta greater than alpha, z alpha, z beta e square by R alpha beta.

Now this term corresponds to where alpha is the index of nuclei and i is index of electrons. Now we know that this is nothing but kinetic energy of nuclei, this one is kinetic energy of electrons and this is P E of electron and nucleus, this is P E of electron and electron, this is nothing but P E of nucleus and nucleus. This whole Hamiltonian is written as H is equal to H nuclear + H electron, so this will be nothing but K E of nucleus, this will correspond to H nucleus.

And all the rest of the terms Kinetic energy of the electrons, potential energy between the electrons between the nuclei and the electrons in the nuclei will constitute to the H electron. So this one will be only with this term and this will be 1, 2, 3, 4 terms.

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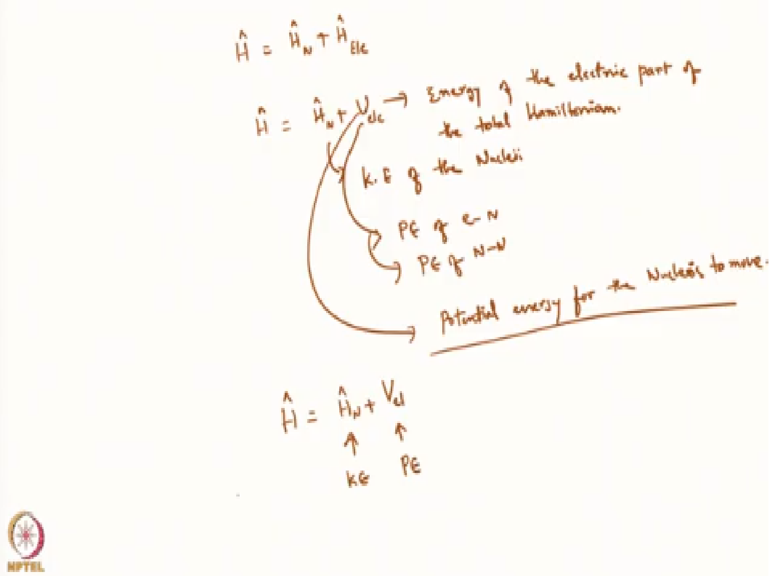

Now one can think of that is within the Born oppenheimer approximation, so one can think of it so your total Hamiltonian edge is H nuclear + H electronic, now if you solve this so one can think of this as H is equal to H nuclear plus, when you solve this will give some energy that is waterless as oil qualitative as a U electronic energy of the electronic part of the total Hamiltonian. Now can think of the total Hamiltonian will be nothing but the nuclear Hamilton, here is only the kinetic energy of the nuclear.

Now one of the things that we have to see that U electronic has also nucleus in it two ways, one is the PE of electron and nucleus, the second one is PE of nucleus and nucleus. This U electron will constitute a potential in which the nuclei will move, so this is nothing but the potential energy for the nucleus to move or nuclei to move. So this is the potential, so think of it the total H Hamiltonian is like kinetic energy operator plus the potential energy operator which I will call it as V electron or U electron.

So this is the K E and this is the P E, so the electronic part of the Hamiltonian gives you the potential in which the nuclei will move.

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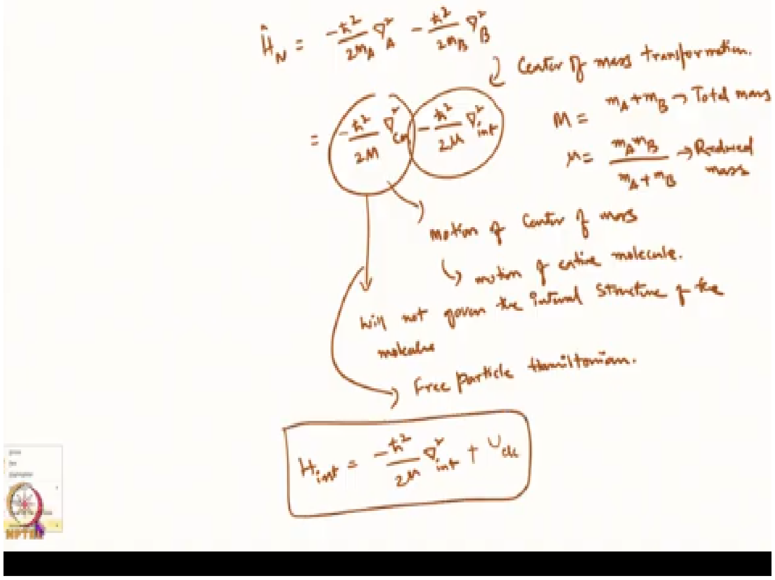

$$\hat{H}_N = \frac{-\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2$$

Center of mass transformation.

$$= -\frac{\hbar^2}{2M}\nabla_{cm}^2 - \frac{\hbar^2}{2\mu}\nabla_{int}^2$$

$M = m_A + m_B \rightarrow$ Total mass

$\mu = \frac{m_A m_B}{m_A + m_B} \rightarrow$ Reduced mass

motion of center of mass

motion of entire molecule.

Will not govern the internal structure of the molecule

Free particle Hamiltonian.

$$\boxed{H_{int} = \frac{-\hbar^2}{2\mu}\nabla_{int}^2 + U_{ele}}$$

As I told you the kinetic energy part or the H nuclei will be nothing but for a diatomic molecule A B will be nothing but minus h bar square by 2 M A Del square A - h bar square by 2 M B del square B. So this we said that we could do in terms of center of mass separation when you do center of mass transformation, what will get is - h bar square by 2 M, total mass del square center of mass - h bar square by 2 mu del square internal.

Where captain M is given by m A + m B and mu is given by m A m B divided by m A + m B, so this is nothing but total mass and this is nothing but reduced mass. Now, this is motion of center of mass, which is nothing but the motion of entire molecule. Now think of it like this, if there is a hydrogen atom has internal structure of several orbitals 1 S2, 2 S2 but thus are independent of the hydrogen atom is going to be moving or is to be stationary.

So this particular quantity will not affect or will not govern the internal structure of the molecule, and basically it is a free particle Hamiltonian. Now what we are left with only this, so what I have is H internal is equal to - h bar square by 2 mu del square internal and this is exactly what we had? When we had the rotational motion however, when we are considering the vibrational motion this will be also added up with the U electronic.

Because for nuclei to vibrate you know, a potential energy for them should be provided by the electrons, so the electrons provide the potential energy electrons in the sense very loosely the electronic energy which will also consist of the electron nuclear attraction and the nuclear-nuclear attraction. So, this is your H internal.

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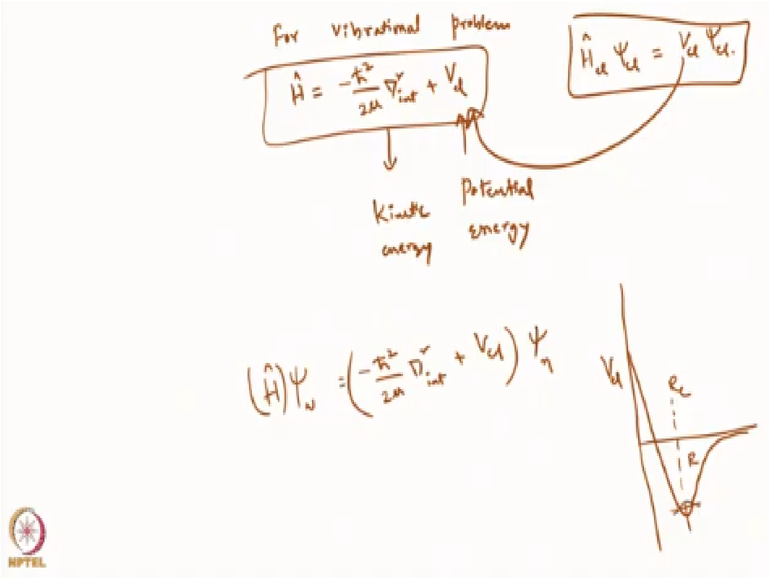

For vibrational problem

$$\boxed{\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{int} + V_{el}}$$

$$\boxed{\hat{H}_{el}\psi_{el} = V_{el}\psi_{el}.}$$

Kinetic energy

Potential energy

$$(\hat{H})\psi_{v} = \left(-\frac{\hbar^2}{2\mu}\nabla^2_{int} + V_{el}\right)\psi_{v}$$

So we have the Hamiltonian, so for the vibrational problem your Hamiltonian H is nothing but - h bar square by 2 mu del square internal plus, let us call it V electronic, and how do you get V electronic? V electronic is nothing but H electronics psi electronics will give you V Electronic and psi electronic**.** So that is the potential, so this is the kinetic energy operator and this is the potential energy, so we have to somehow solve this Hamiltonian.

So H is equal to - h bar square by 2 mu del square internal + V electronic, so this is the Hamiltonian so the corresponding Schrodinger equation would be that what we need to solve. Now if I want to plot, the function of R the V electronic that will come out to be something like this, so we all know so this is nothing but your R e or equilibrium geometry and in the rigid rotor case, we looked at this R e as the fixed distance between A and B, but that is not the case because the molecule A B will move in this potential, or vibrate in this potential, so what we have that is a curve something looks like this.

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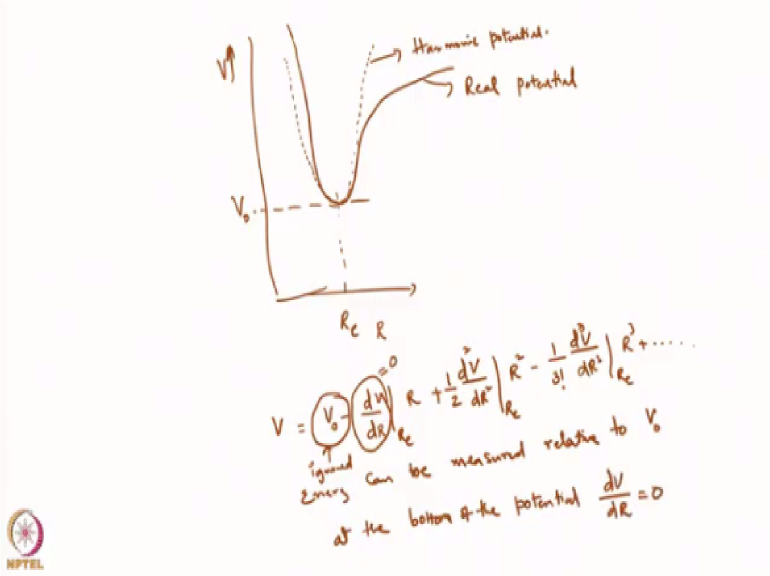

$$V = \boxed{V_0} - \overset{=0}{\boxed{\frac{dV}{dR}}}\Big|_{R_e} R + \frac{1}{2}\frac{d^2V}{dR^2}\Big|_{R_e} R^2 - \frac{1}{3!}\frac{d^3V}{dR^3}\Big|_{R_e} R^3 + \cdots\cdots$$

Energy can be measured relative to V_0

at the bottom of the potential $\frac{dV}{dR} = 0$

So we have a potential energy curve that looks like this, so this is my potential energy and this is my distance and this distance is R e. Now when you have that one can approximate this as a harmonic potential in that case the harmonic potential will look something like that bottom of the well, one can approximate the real potential or the potential in a molecule of A and B as a harmonic potential, so this is your real potential and this one is the harmonic potential.

Now, how do I get to this harmonic potential? Imagine there is a potential energy V and at the bottom of the well around R e, I want to expanded it as a Taylor series, So my V is now given as some value V0 + d by dR of V evaluated R e R + one half of d square V by dR square evaluated R e, r square + 1 over 3 factorial d square V by negative sign cube, dR cube at R e, R cube + etcetera. So one can write an expansion.

Now, what is V 0? V 0 is the bottom of the potential, this is V 0 now this two things that we can think energy is always measure relatively, So I can always measure energy can be measured relative to V0. So if I measure energy can be measure relative to V 0, then my V this term kind of ignored, can be ignored. Now what you have is the, now since we are located the bottom of the potential bottom of the potential when you know at the bottom of the potential the first derivative is 0, So dV by dR this is equal to 0, so at the bottom of the potential d V by d R = 0. So I can somehow ignore the two terms.

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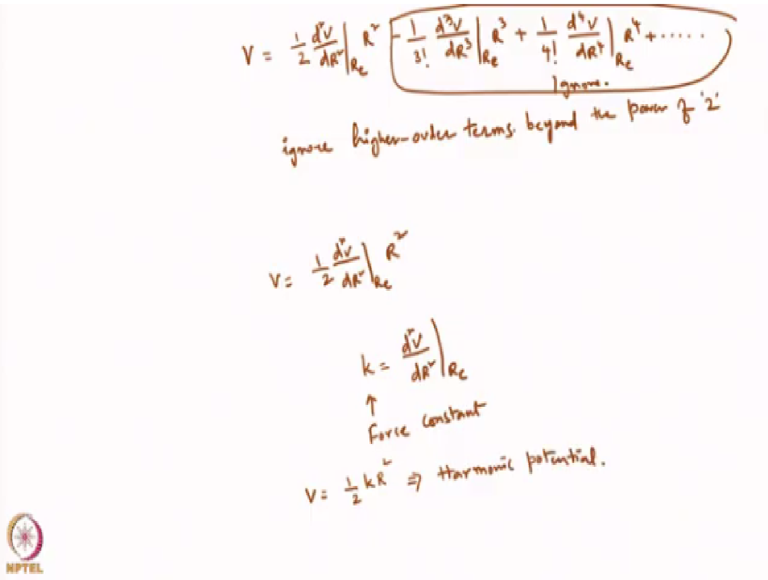

$$V = \frac{1}{2}\frac{d^2V}{dR^2}\Big|_{R_e} R^2 \underbrace{- \frac{1}{3!}\frac{d^3V}{dR^3}\Big|_{R_e} R^3 + \frac{1}{4!}\frac{d^4V}{dR^4}\Big|_{R_e} R^4 + \cdots}_{\text{Ignore.}}$$

ignore higher-order terms beyond the power of '2'

$$V = \frac{1}{2}\frac{d^2V}{dR^2}\Big|_{R_e} R^2$$

$$k = \frac{d^2V}{dR^2}\Big|_{R_e}$$

↑ Force constant

$$V = \frac{1}{2}kR^2 \Rightarrow \text{Harmonic potential.}$$

So what I am left with is Potential V is equal to, first term is V 0 I told you that we can measure it respect to V 0 so we ignore it and the second term is dV by dR and since we are at the bottom of the potential we will ignore the term because the first derivative will go to 0 at the bottom of the potential. So what I have is half d square V by dR square at R e into R square - 1 over 3 factorial d cube V by dR cube R e into R cube.

And if I want to include the next term it will be 1 over 4 factorial its d 4 V by dR 4 at R e, R to for a 4 etcetera. Now if I ignore higher order terms beyond the power of 2, so which means I will ignore these. Then what I have V is equal to half d square V by dR square, R e into R square, that is my potential V. Now, if I equate something called K is equal to d square V by dR square evaluated R e. So that is the second derivative of the potential with respect to R and this is the force constant, so which means your V is written as half K R square and that is called Harmonic potential.

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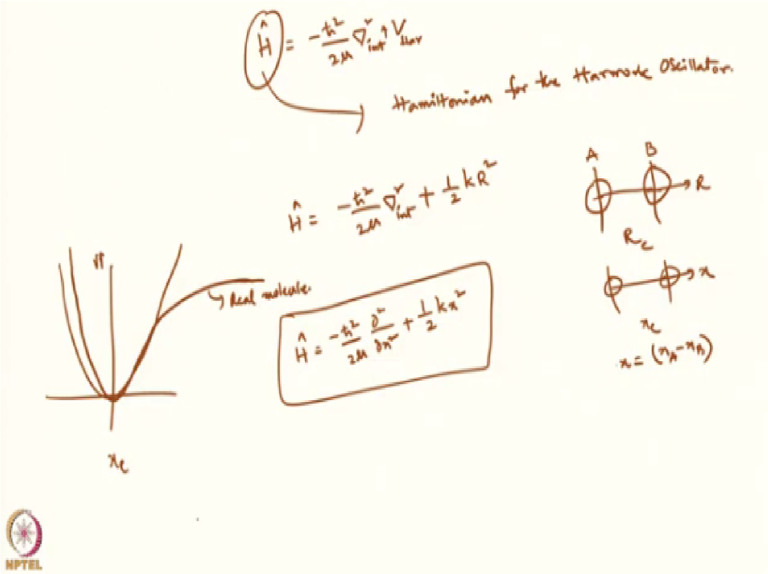

So therefore, your Hamiltonian H will now become - h bar square by 2 mu del square internal + V harmonic so, this is the Hamiltonian for the harmonic oscillation. So H will be - h bar square by 2 mu del square internal plus half K R square. Now if I have a, diatomic molecule A Band this is my direction, then what I am doing it? I doing this is my R e and this is the direction R, R is just a simply a choice is variable..

So I could in fact write it as my x e so one can write it as so this is my x e and this direction I can call it as x, because variables are dummy one can always interchange variable, so what will happen my H will now become minus h bar square by 2 mu, This is my direction. So when I have del square internal will become d square by dx square, where x is equal to x A - x B + half k x square. So, that is the Hamiltonian for which I need the solution. And that will give me the solutions of the harmonic oscillate.

But one must always remember that harmonic oscillator is an approximation, the actual molecule is not an harmonic oscillator. But harmonic oscillator potential something like this, so this is what I call it as a x e, it will never break, so harmonic oscillator potential does not break it all it can go up to infinity. This is your potential energy However, real molecules break, so when you go to some distance or some energy the A B bond will break, so then this is the real molecule.

So the harmonic oscillator approximation is only trying to represent the bottom of the potential. So if you go above, somewhat in energy then the harmonic oscillator approximation breaks down the other drastically. So when you are looking at the properties of a molecule at the bottom of the potential or when it is sitting in this well really the bottom of the well then one can approximate it to be a harmonic oscillate, even then it is only an approximation and it is not a real thing.

However this approximation works reasonably well for most of the molecules and this approximation can be used to evaluate the wave functions and the associated selection rules for vibration spectroscopy which will be continue in the next lecture and we will stop it here for now.