Chemistry I

Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 33

Diatomic Vibration

Morse Oscillator Model

Prof. Mangala Sunder Krishnan,

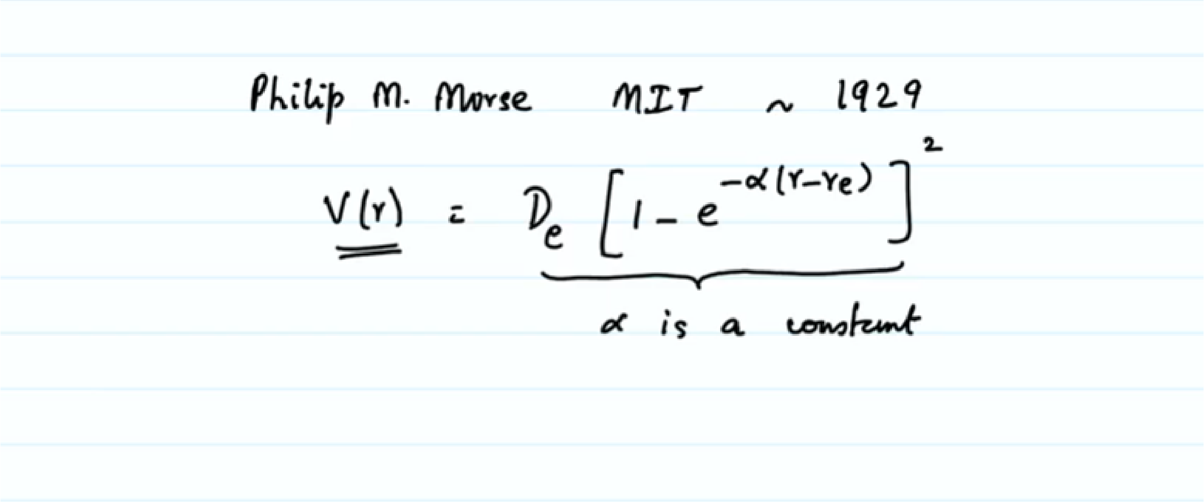
Department of Chemistry,

Indian Institute of Technology Madras

Welcome back to the lecture on chemistry and introduction to molecular spectroscopy. We shall continue the lecture from the harmonic vibrational spectroscopy of a diatomic molecule, o look at one model for the harmonic vibration and this model is due to Professor Philip M. Morse from MIT around 1929. He came up with the molecular motion being enharmonic and the vibrational motion eventually leading to for very large frequencies of vibration or very large energies of vibrational quantum number with very large quantum number. The molecule eventually dissociate, in the harmonic model. Dissociation does not exist because no matter how high the energy is. The parabolic nature of the harmonic potential energy curve, tells you that the molecule eventually reaches back to its equilibrium state and therefore there is nothing called the dissociation or a breakaway of the diatomic molecule accounted for in the harmonic model.

Therefore it is very important for vibrationally induced dissociation of chemical structures that the vibrational motion being a harmonic and the model that was proposed to by Philip Morse.

(Refer Slide Time: 01:40)

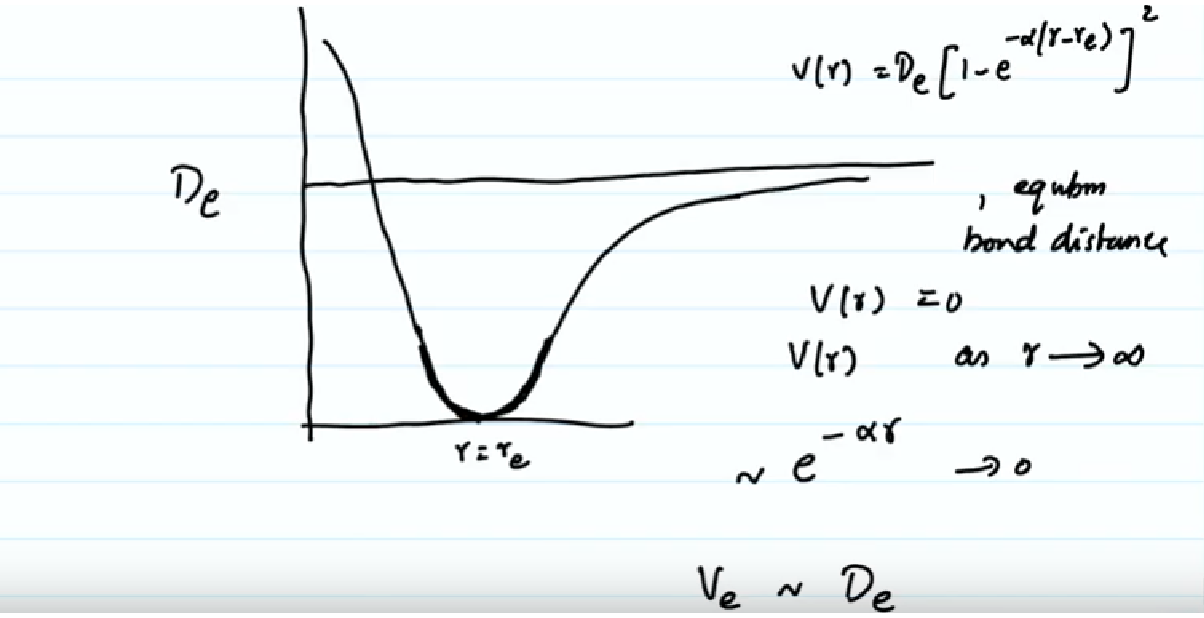


Philip M. Morse MIT ~ 1929

$$\underline{\underline{V(r)}} = D_e \underbrace{\left[1 - e^{-\alpha(r-r_e)}\right]^2}_{\alpha \text{ is a constant}}$$

Has the following form for the potential energy as a function of the distance from the equilibrium. The V(r) is given by the specific functional form a constant De multiplied by this particular mathematical quantity alpha exponential of minus alpha r minus re Whole Square. So the potential energy has a very specific form, due to exponential and alpha is a constant, which we shall see in a minute, how it is identified with the equilibrium or which is called the harmonic oscillator frequency.

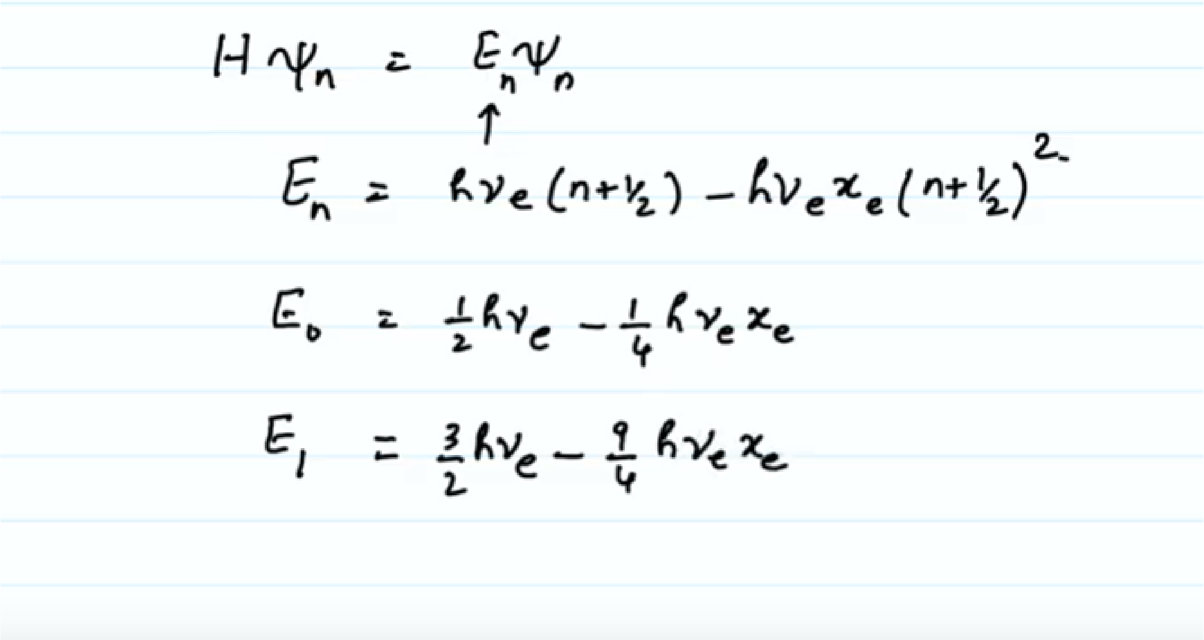
(Refer Slide Time: 02:43)



Now it is important to visualize this potential energy first to understand why it was why it is meaningful. Now if you plot V of r as a function of r. It is De times 1 minus exponential of minus alpha r minus re whole square. Therefore at r is equal to re the equilibrium bond distance, V of r is zero because this becomes 1, because the exponent is 0, therefore 1 minus 1is 0. Therefore V of r is a minimum at r is equal to re and for very large values of r, V of r as or goes to very very large values or say the limit being infinity, you see that the exponential of minus alpha times r, approximately re is too small and as r goes to infinity this goes to 0. Therefore the potential energy Ve becomes De, which is a positive constant. Therefore for very large values of r, if we go back to the graph and as r increases from the equilibrium value you see the exponential of minus alpha re, therefore the potential energy and this is a square. Therefore as r is slightly different from re, this whole graph sort of goes up and eventually it reaches a plateau and the value which does not change for very large values of r equal to re is the asymptotic value, okay? Which you can call this, this graph reaches the asymptotic value. Then that value is De, for r less than re, this is negative and therefore the exponent, the exponent of the exponential becomes positive and is this becomes more negative the this increases forever and therefore what you see here is that . Okay? So this is the form of a potential energy for a given value of, alpha. If alpha is very large then you see that this graph is narrower. If alpha is very small this graph is more elongated, therefore the alpha gives the spread roughly between what is called the harmonic area. This area looks more like a parabola and therefore you can see that for small values of r minus re, this function will actually become parabolic in the limit of r minus re being very small and at r is equal to re this is the minimum.

Therefore, this is the parabolic potential which you have with the half Kx square, half Kr squared that you use for the harmonic oscillator model, it has that as the limit of small amplitude oscillations and for very large amplitude oscillations you see that the molecule is such that the atoms go far apart from each other and they never come back and this is the dissociation limit, okay?

(Refer Slide Time: 06:38)



$$H\psi_n = \underset{\uparrow}{E_n}\psi_n$$

$$E_n = h\nu_e(n+\tfrac{1}{2}) - h\nu_e x_e(n+\tfrac{1}{2})^2$$

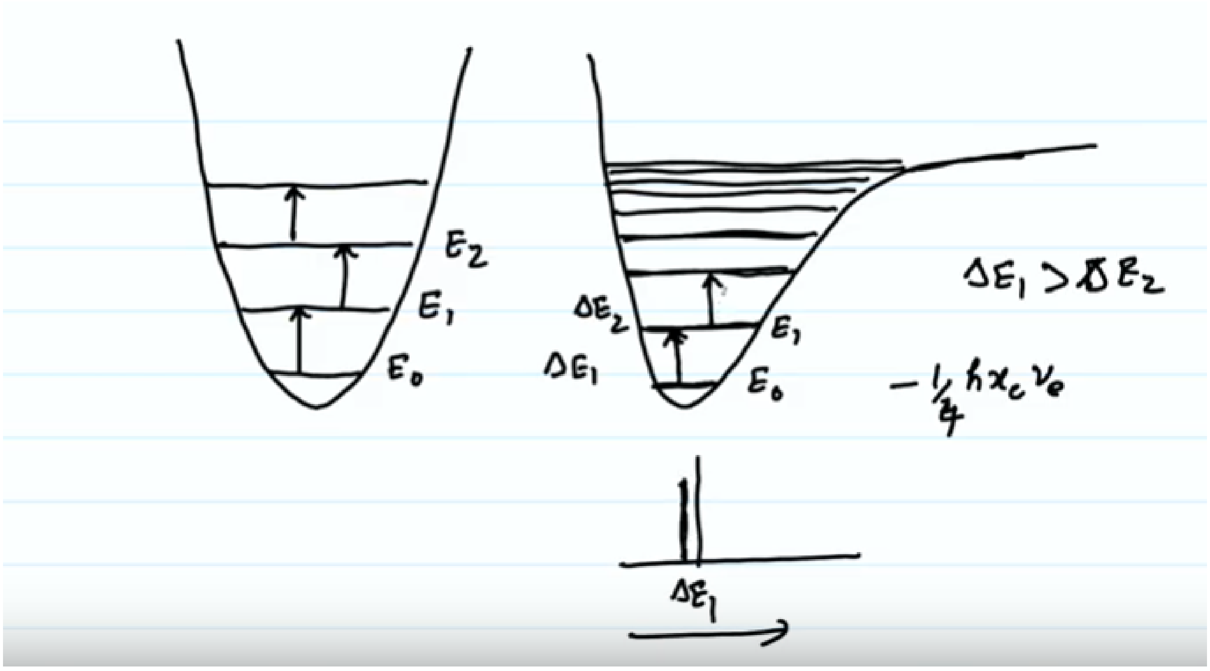
$$E_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$$

$$E_1 = \frac{3}{2}h\nu_e - \frac{9}{4}h\nu_e x_e$$

For this potential energy with this form if you write down the Hamiltonian as minus H bar square by 2 µ d square by dr square, plus the dissociation energy De times 1 minus e to the minus alpha r minus re square. The wave functions H ¥ n is equal to En ¥ n as actually closed form solutions, that is analytic solutions given by Philipe Mores and later corrected by professor Tear Hawk, that En is h Omega e times n plus ½ and there is another term which contains a small constant called, the enharmonic contains a small constant xe but with n plus ½ whole square, so you can see that the energy level is zero. For example is 1/2h. Let me a not right We, I think they have been using it for angular frequency so let us write this as nu E and nu E okay, Then Ian for a zero, when the n is 0. Is half H nu e remember this is ¼ h nu E ex e, what is the next energy level for this problem is, n is equal to 1, E 1 is 3 half H nu e Minus , this is 3 half, therefore it is 9 by 4 H nu e xe.

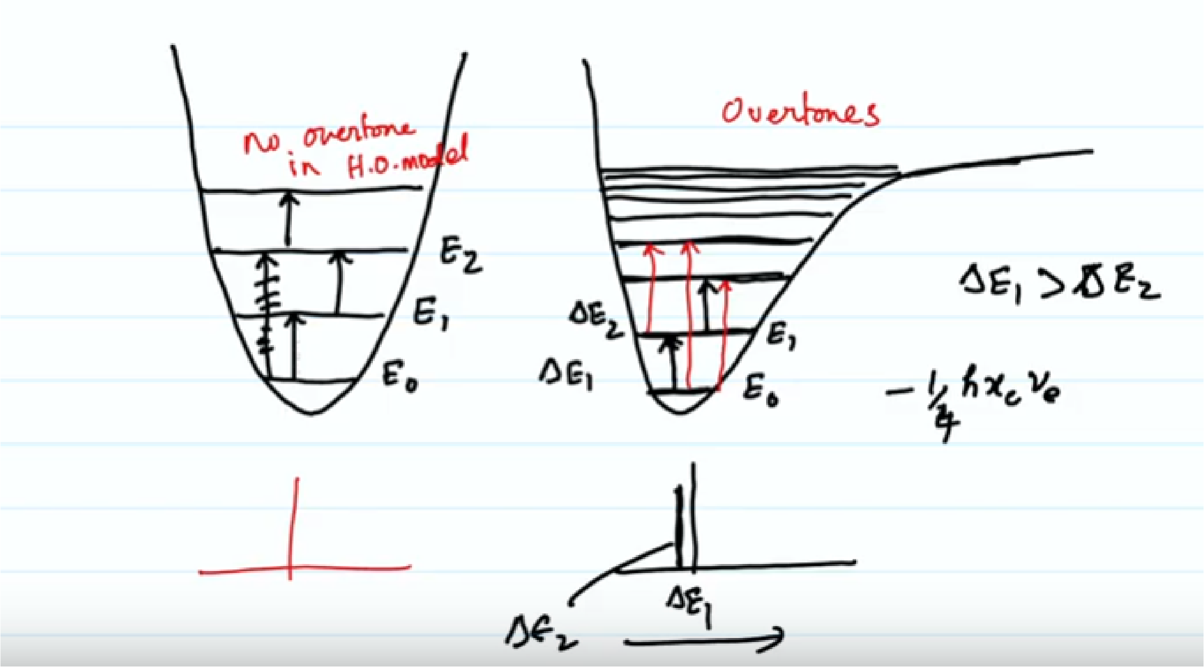
Please remember for motion very near equilibrium the xe is a small constant and it is called the enharmonic constant and therefore the energy is not precisely 1/2H nu, but it is like lower than 1/2H nu. xe is positive. Okay? Therefore you see that the energy levels as you go from 0,1,2,3, etc...Are more and more away from what is called the harmonic oscillator energy level?

(Refer Slide Time: 09:04)



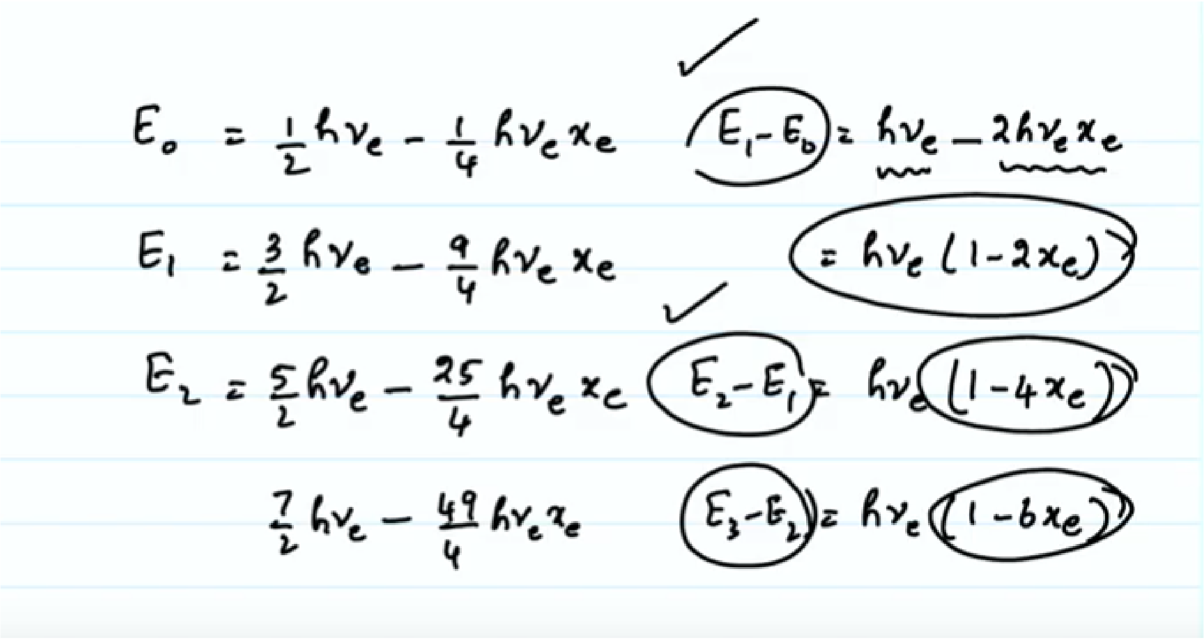
So if you look at the harmonic oscillator energy levels if you write that it's suppose you call this as e zero and then this is e1 and this is as e2 and compare that with the potential graph which goes something like that what you see is the lower level is the lowest level is slightly lower than the original E knot this is e not because it contains this minus half H X e nu e minus 1 by 4 sorry and then the e1 is even lower than the harmonic value of E 1 E2 is even closer and E3 is closer and so on and so finally you see that the energy levels become very dense and so on oh you can see that as you go further and further up if the hormone if the oscillation is sufficiently large if the amplitude of the oscillation is fairly large and the quantum energy levels are very high you see that the molecule eventually breaks down and a dissociation takes place. The therefore the energy differences which in the harmonic oscillator model we're identical between nearby levels are not so in the case of the Morse oscillator. This energy level is slightly more than this difference between the two energy levels E0 and E1 is definitely more, you call it as Delta E1 then this is more than Delta E2. therefore the frequency at which the molecule absorbs if it is an enharmonic molecule and if it satisfies this enharmonic model this frequency of absorption is slightly more than this frequency of absorption and therefore what you see here is of course a spectral line corresponding to Delta E1 ok if this is the increasing E the next is the Delta E2 if you see it is slightly lower than lesser than the Delta E1 and of course the intensities will also decrease because the higher the energy level is the fewer of the molecules are at any given temperature subject to thermal equilibrium conditions and that's almost Maxwell Boltzmann distribution law.

(Refer Slide Time: 09:04)



Therefore you see that Delta E2 if this is called Delta E2 - and then Delta E3 is even smaller and so on, but something else also happens, in the harmonic oscillator model it's not possible for us to actually undergo a Transition, actually force a molecule to undergo a transition from E0 to E2 this doesn't exist, it cannot be seen, the dipole moment operator does not connect to that, however in the enharmonic oscillator model in the most oscillator model it is possible for you to see this transition it is also possible for you to see let me put it on a medium point with some other colour it is also possible for you to see this transition, it is possible for you to see this transition and even this and so on and these are vibrational overtones. There is no overtone in harmonic oscillator model, there's only one line what you see is only one line Corresponding to this Delta E and that is the same for every other transition as well. Therefore the Morse oscillator provides you a slightly more realistic, what is called, ‘Vibrational Spectroscopy’, and the vibrational spectrum that you see in the case of diatomic molecules, but please remember we have kept the rotational motion completely out of this picture. We assume that the molecule is purely vibrating and we do not worry about the rotational energies associated to that but after we know the microwave spectroscopy we will see how to look at the vibrational rotational spectrum together, but for the time being the simple picture of the harmonic oscillator model gives you no transition other than one line the enharmonic model due to Morse oscillator gives you several energy levels which are different from each other and therefore the gap between them is also different. So let us calculate that gap for a simple example.

(Refer Slide Time: 13:48)



✓

$$E_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e \qquad \boxed{E_1 - E_0} = h\nu_e - 2h\nu_e x_e$$

$$E_1 = \frac{3}{2}h\nu_e - \frac{9}{4}h\nu_e x_e \qquad \boxed{= h\nu_e(1-2x_e)}$$

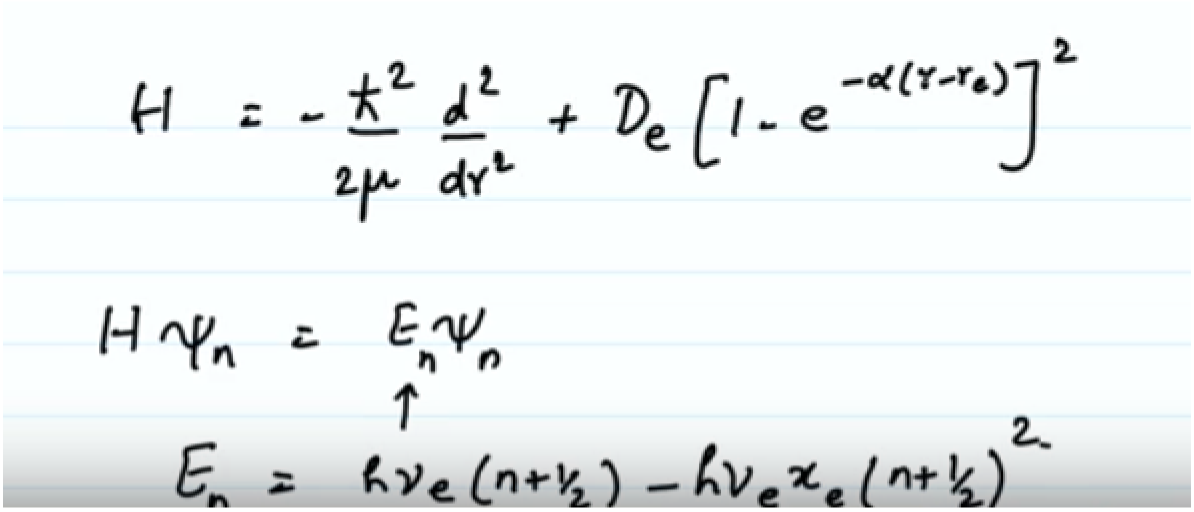
✓

$$E_2 = \frac{5}{2}h\nu_e - \frac{25}{4}h\nu_e x_e \qquad \boxed{E_2 - E_1} = h\nu_e\boxed{(1-4x_e)}$$

$$\frac{7}{2}h\nu_e - \frac{49}{4}h\nu_e x_e \qquad \boxed{E_3 - E_2} = h\nu_e\boxed{(1-6x_e)}$$

say E0 was written as h nu e minus 1 by 4 h nu e xe E1 was written as h nu e 3 by 2 sorry this is half h nu he this is 3 by 2 h nu e minus 9 by 4 h nu e Xe, e and E2 is written as 3 by 2 so then it's 5 by 2 h nu yi minus 25 by 4 n plus 1/2 whole Square, therefore it's 5 by 2 whole square is h nu e Xe and so on. Therefore if you calculate E1 minus E 0 the answer is h nu e, minus 9 by 4 minus 1 by 4 so you get 2h nu e, Xe XE is a very small number therefore this is an extremely small number compared to H nu e. Ok. essentially you can write this as H nu e times 1 minus 2 Xe, Xe being very small this is close to H nu e, but what about E2 minus E1? If you look at that that's a game H nu e, but the difference is 25 by 4 minus 9 by 4 therefore you get 1 minus 4 x e. Okay the difference is 16 by 4 and the next one if you want to write e and it is 49 by 4h nu e xe and therefore you E3 minus E2 is h nu e times 49 minus 25 is 24 therefore you get 1 minus 6xe. see how the successive energy differences are becoming smaller and smaller due to the larger contribution of xe, this is minus 2 xe here it's minus 4 xe and here it's minus 6 xe, therefore it's possible for us to actually obtain values for nu e and xe if get to experimental spectral lines if he get in transition due to this and if you get a transition due to this then the two equations involving the new E and nu E xe can be solved and it's possible for us to obtain numerical values for the anharmonicity constant and therefore use it for fitting experimental spectra of diatomic molecules where the motion is likely and harmonic. there are molecular problems where the motion is very highly and enharmonic and in the case of polyatomic molecule we will come to look at at least for a brief moment what are called non rigid molecular motions and so on. Therefore it is important to understand that vibrational spectroscopy starts with the elementary the model of a harmonic oscillator but then the corrections to the harmonic oscillator and the real molecular spectrum are usually taken into account by correcting the potential energy in such a way that enharmonic Corrections can be done. The previous lecture in the previous lecture I mentioned the enharmonic Corrections can be X cubed like terms.

(Refer Slide Time: 17:18)



$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2$$

$$H\psi_n = E_n\psi_n$$

$$\uparrow$$

$$E_n = h\nu_e(n+\tfrac{1}{2}) - h\nu_e x_e(n+\tfrac{1}{2})^2$$

The potential energy terms that you have here that is r minus re cubed terms or minus re to the power 4 terms and so on they are called the cubic and harmonists and quadratic and Harmonicity and the r minus re square is called the quadratic harmonic term. So keep this in mind in solving some of the problems related to enharmonic vibrational motion offer diatomic molecule. In the next lecture we will continue this and look at polyatomic molecular motion and then in a similar way we will extend the harmonic oscillator model to molecules with many vibrational degrees of freedom, what are called the normal modes of vibration? We will also some picture pictorial representations of some of the normal modes of vibration through a calculational tool, that is quite well known today called the, Gaussian zero-nine. The Gaussian program and the Gaussian program is a computational chemistry program which allows you to calculate molecular properties quite accurately. We will see the harmonic oscillator for model for a polyatomic molecule in the next lecture following this until then, thank you very much.