

Introductory Quantum Mechanics and Spectroscopy
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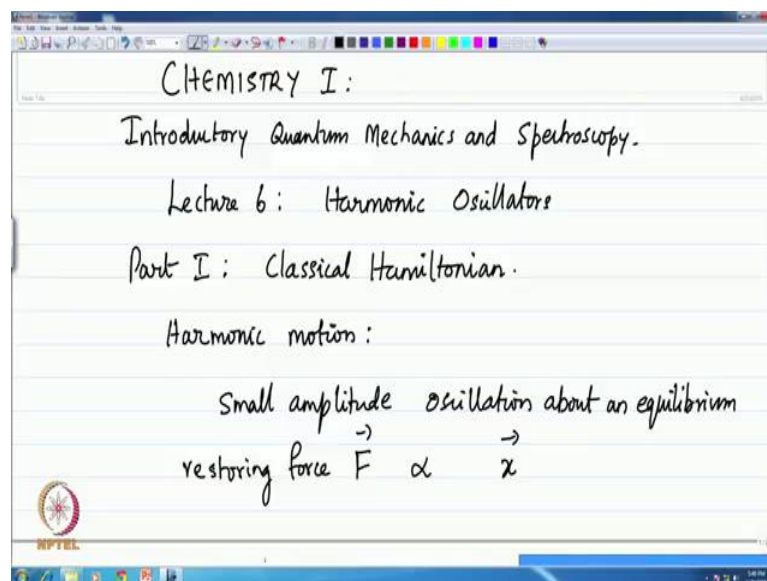
Lecture - 6
Harmonic Oscillators
Part 1: Classical Hamiltonian

Welcome back to the lectures in chemistry, the first course on elementary principles. In this series of lectures, we have been looking at introductory quantum mechanics and spectroscopy. So far we have studied a couple of model problems namely, the particle on the one-dimensional box, two-dimensional boxes, and also the electron in the hydrogen atom. Basically, we looked at the solutions and try to understand what was meant by quantization and energies and transitions between the energy levels and so on.

The other extremely important model problem, both from physics and chemistry is the problem of harmonic oscillators, which is also well known from the classical mechanics. What we would do is to study the elementary quantum mechanical aspects of harmonic oscillator using the wave function method. Later, in an advance lecture I would talk a little about the different types of rising and lowering operator formalisms of harmonic oscillator, but in this set we would look at it as a wave function method. And as has always been in the last lectures, few lectures, we start by looking at the energy of the harmonic oscillator from a classical mechanical point of view and then convert that into a quantum mechanical Hamiltonian and look at the solutions.

The harmonic oscillator by definition is about small amplitude oscillator motion about an equilibrium position or periodic motion, such as motion on a circle. These things can be easily understood as cost by a restoring force, which is propositional to the displacement away from the equilibrium, but in the opposite direction.

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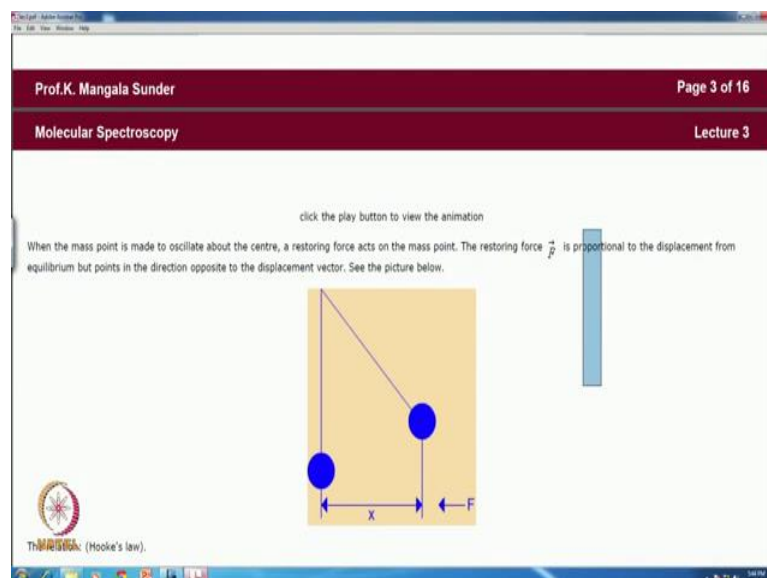


CHEMISTRY I:
Introductory Quantum Mechanics and Spectroscopy.
Lecture 6: Harmonic Oscillators
Part I: Classical Hamiltonian.
Harmonic motion:
Small amplitude oscillation about an equilibrium
restoring force $\vec{F} \propto \vec{x}$

The image shows a digital whiteboard with handwritten text in black ink. The text is organized into a structured list. At the bottom left, there is a small circular logo with a star-like pattern and the text 'NPTEL' below it. The whiteboard interface includes a toolbar at the top with various drawing tools and a status bar at the bottom.

So, let me write down. Harmonic motion, small amplitude, oscillation about equilibrium, an equilibrium. If you want to visualize that here are some simple pictures.

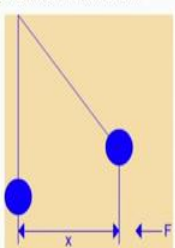
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Molecular Spectroscopy Lecture 3

click the play button to view the animation

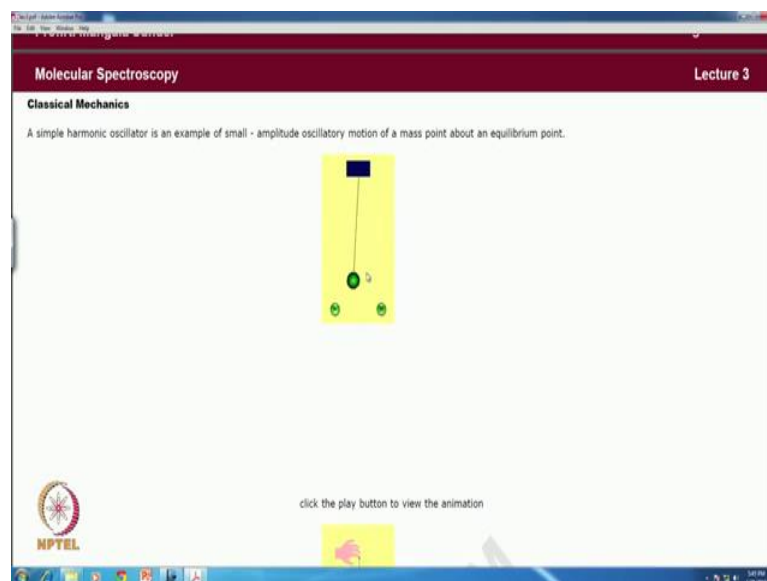
When the mass point is made to oscillate about the centre, a restoring force acts on the mass point. The restoring force \vec{F} is proportional to the displacement from equilibrium but points in the direction opposite to the displacement vector. See the picture below.



The diagram shows a mass-spring system. A blue mass point is attached to a spring. The spring is shown in its relaxed state (vertical line) and its extended state (diagonal line). The displacement from equilibrium is labeled x . The restoring force F is shown as a vector pointing towards the equilibrium position. The text 'Hooke's law' is visible at the bottom left of the diagram area.

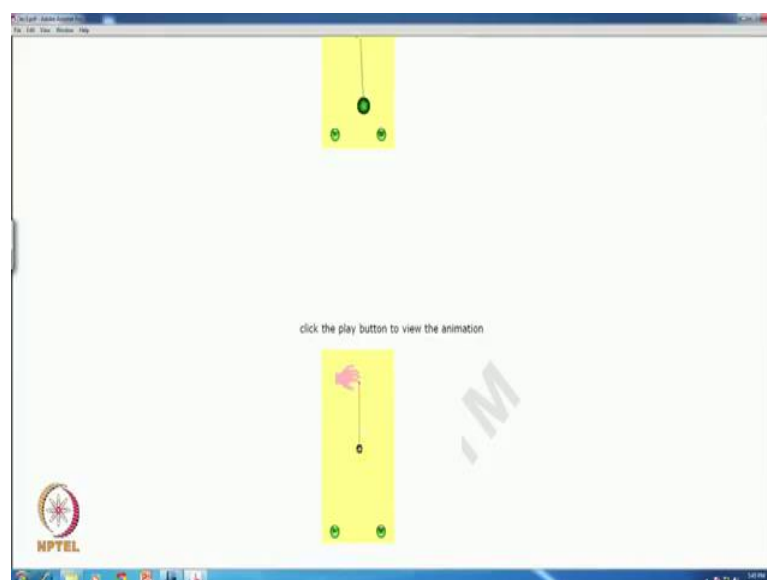
The slide has a dark red header with the text 'Prof.K. Mangala Sunder' and 'Page 3 of 16'. Below the header, there is a dark red bar with the text 'Molecular Spectroscopy' and 'Lecture 3'. The main content area is white and contains the text and diagram described above. At the bottom left, there is a small circular logo with a star-like pattern and the text 'NPTEL' below it. The slide interface includes a toolbar at the top with various drawing tools and a status bar at the bottom.

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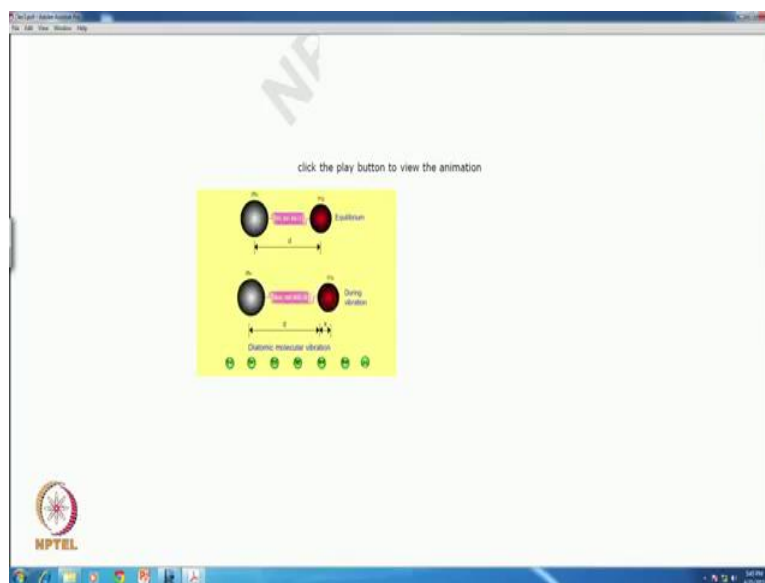
So, the equilibrium position in the first picture is the vertical distance, and you can see that the ball oscillates between two extremes rather with the small amplitude.

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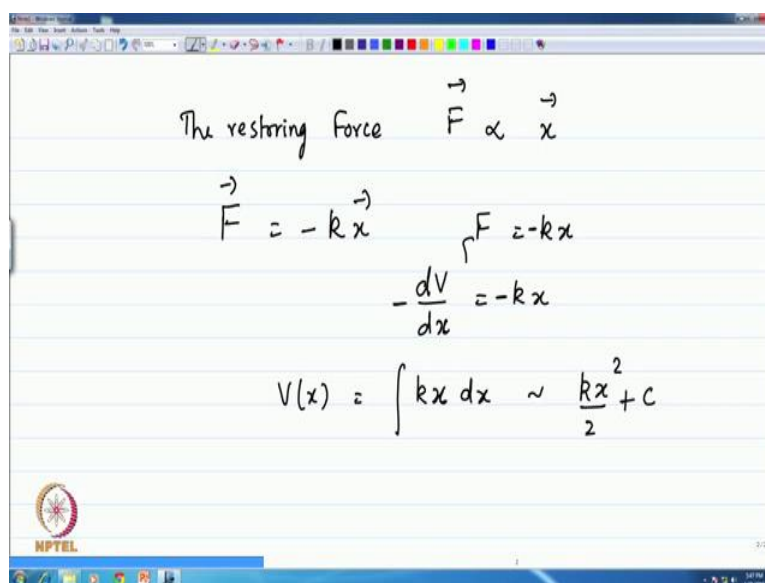
Another example is the usual play, that you have with the spring ball and the motion of the spring ball is also harmonic.

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From the point view of chemistry if you look at the diatomic molecular motion at very low temperatures is very nearly harmonic, and the amplitudes of vibration of a fairly stable bond that is about the equilibrium distances. They are also modeled using harmonic motion. So, these are some examples of what is meant by a small amplitude vibration or oscillation about an equilibrium position.

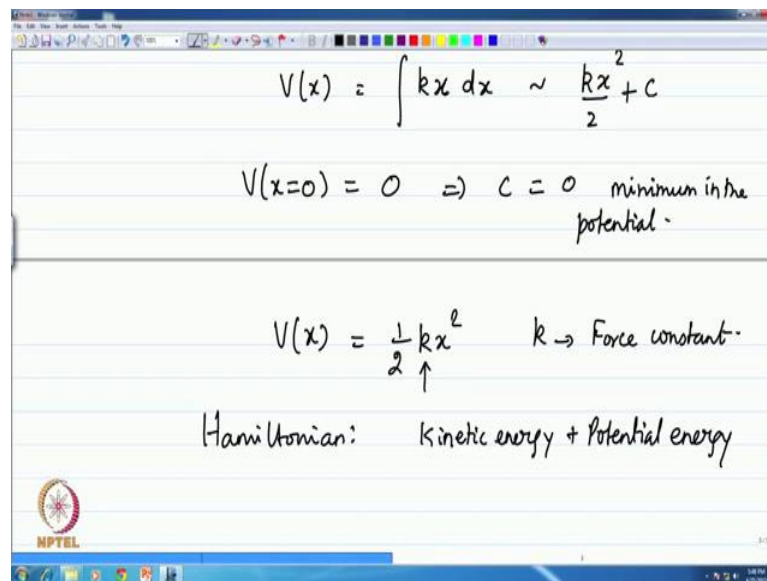
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Now, the restoring force F , if you write that, it is proportional to the displacement vector from the equilibrium. And the mathematics is that the proportionality constant is a constant, and since it is in the opposite direction, it is minus kx and in one dimension we would assume that the force is in a direction opposite to that of the displacements. So, we no need to worry about the vector arrow here.

But knowing that the force is the negative derivative of potential with respect to the distance or with respect to the position coordinate, this is equal to kx , and you can see therefore the potential energy V of x is with minus kx and the minus kx , therefore V of x is the integral $kx \, dx$, which gives you kx square by 2 plus a constant.

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Handwritten notes on a digital whiteboard showing the derivation of potential energy for a harmonic oscillator.

$$V(x) = \int kx \, dx \sim \frac{kx^2}{2} + c$$

$$V(x=0) = 0 \Rightarrow c = 0 \text{ minimum in the potential.}$$

$$V(x) = \frac{1}{2} kx^2 \quad k \rightarrow \text{Force constant.}$$

Hamiltonian: Kinetic energy + Potential energy

We can always choose that the potential about the equilibrium, that is ((Refer Time: 05:50)) equilibrium x is equal to 0, is 0, which means, that the constant can be chosen to be 0. This is the minimum or what is known as the minimum in the potential. And therefore, the potential energy for a harmonic oscillator as a function of the displacement from equilibrium is given by half kx square.

And k , you know is the force constant or the spring constant, if you are talking about spring's force constant. And you know the dimension of k , kx square is energy. So, it is

very clear what k should be. And the Hamiltonian if you have to write or the harmonic oscillator is obviously the kinetic energy plus the potential energy of the harmonic oscillator.

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Handwritten notes on a digital whiteboard showing the derivation of the Hamiltonian for a harmonic oscillator.

Potential energy: $V(x) = \frac{1}{2} k x^2$ where $k \rightarrow$ Force constant.

Hamiltonian: Kinetic energy + Potential energy

Kinetic energy: $\frac{1}{2} m v^2 \Rightarrow \frac{p^2}{2m}$

Hamiltonian: $H = \frac{p^2}{2m} + \frac{1}{2} k x^2$ where $m \rightarrow$ mass of the oscillator

$m \rightarrow$ reduced mass of a diatomic molecule for vibrations

And the potential energy is already given here. The kinetic energy is half $m v$ square or if you want to write it using momenta, it is p square by $2m$. And therefore, the Hamiltonian in a classical sense is p square by $2 m$ plus half $k x$ square, where m is the mass of the oscillator. If you are worried about the diatomic molecule or vibration of a diatomic species, then m is replaced by the reduced mass of the diatomic molecular system for vibrations.

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The image shows a digital whiteboard with handwritten notes. At the top, it defines the relationship between frequency ν and angular frequency ω : $\omega = 2\pi\nu$. An arrow points from ω to the text "angular frequency". Another arrow points from ν to the text "frequency per sec". Below this, the formula for frequency is given: $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$. The next line shows the classical Hamiltonian H in two forms: $H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$. The final line underlines the text "Classical Hamiltonian". The whiteboard interface includes a toolbar at the top and an NPTEL logo at the bottom left.

$$\omega = 2\pi\nu$$

angular frequency.

frequency per sec

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$
$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Classical Hamiltonian.

Also please remember, the harmonic oscillator is associated with a frequency ν or an angular frequency ω , which is 2π times ν . This is the angular frequency in radians per second. This is the frequency linear per second, the frequency of a harmonic oscillator in a classical form is something that you all know, it is $\frac{1}{2\pi}$ square root of the force constant by the mass.

You see that the two physical parameters for the harmonic oscillator or the extent of stiffness are the harmonicity given by k and the mass of the harmonic oscillator m and these are the only two parameters, that go in the classical Hamiltonian, namely p square by $2m$ plus half kx square. And p , of course is, as you know, it is this mass times the velocity, therefore it is the parameter for the harmonic oscillator are only the m and k . And if you want to write it using the angular frequency, you can write this by writing p square by $2m$ plus half $m\omega$ square x square. So, this is the classical Hamiltonian.