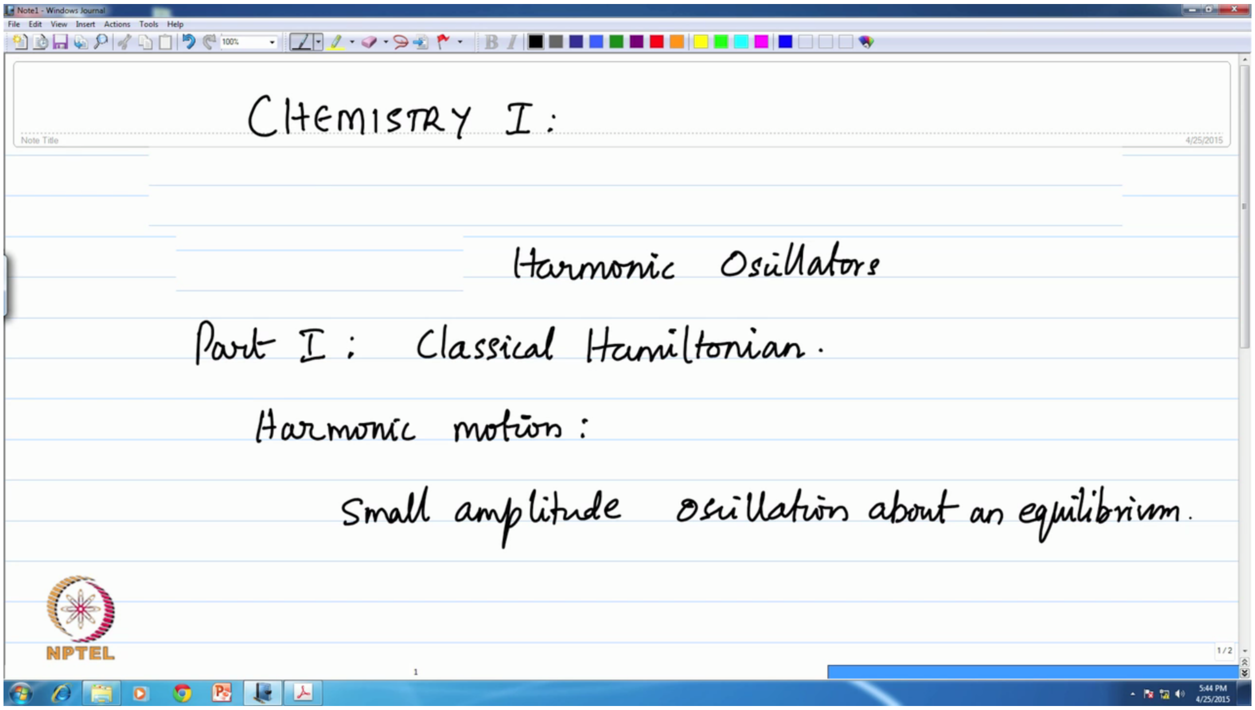
Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 20
Harmonic Oscillator Model
Part I: Classical Hamiltonian

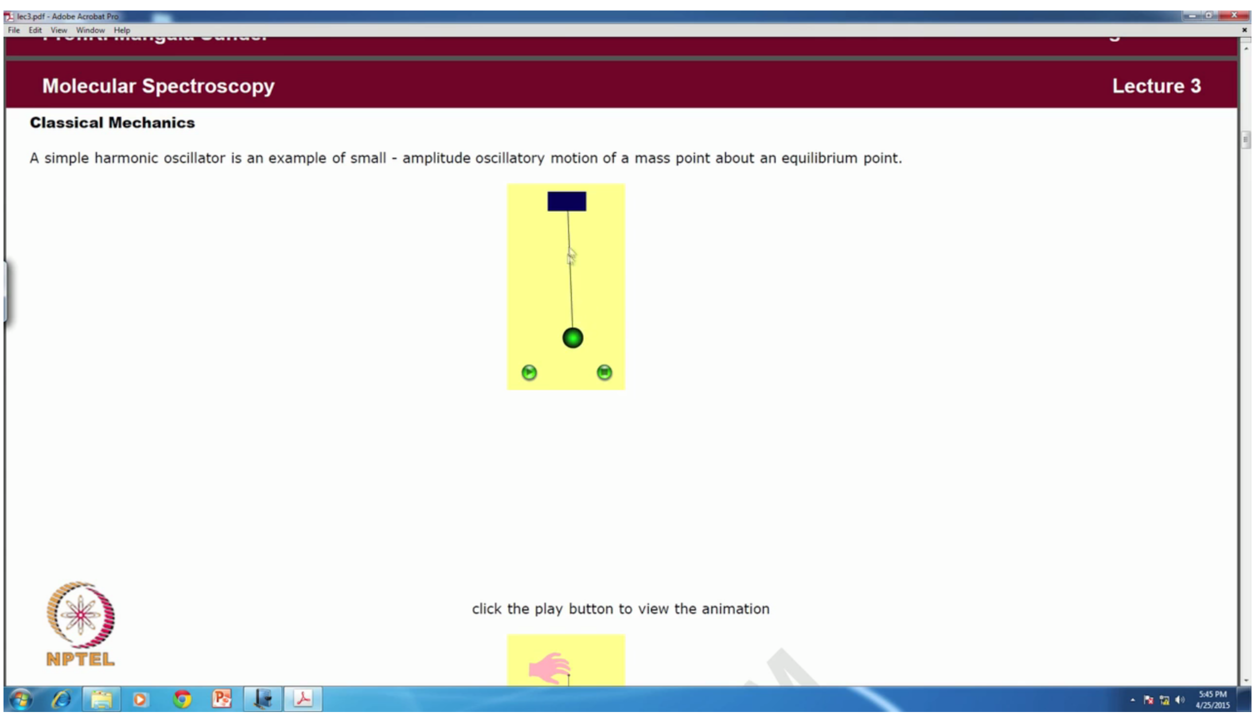
Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

Prof. Mangala Sunder Krishnan: Welcome back to the lectures in chemistry, the first course on Elementary Principles. In this series of lectures, we have we studied a couple of model problems, namely the particle in a 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.

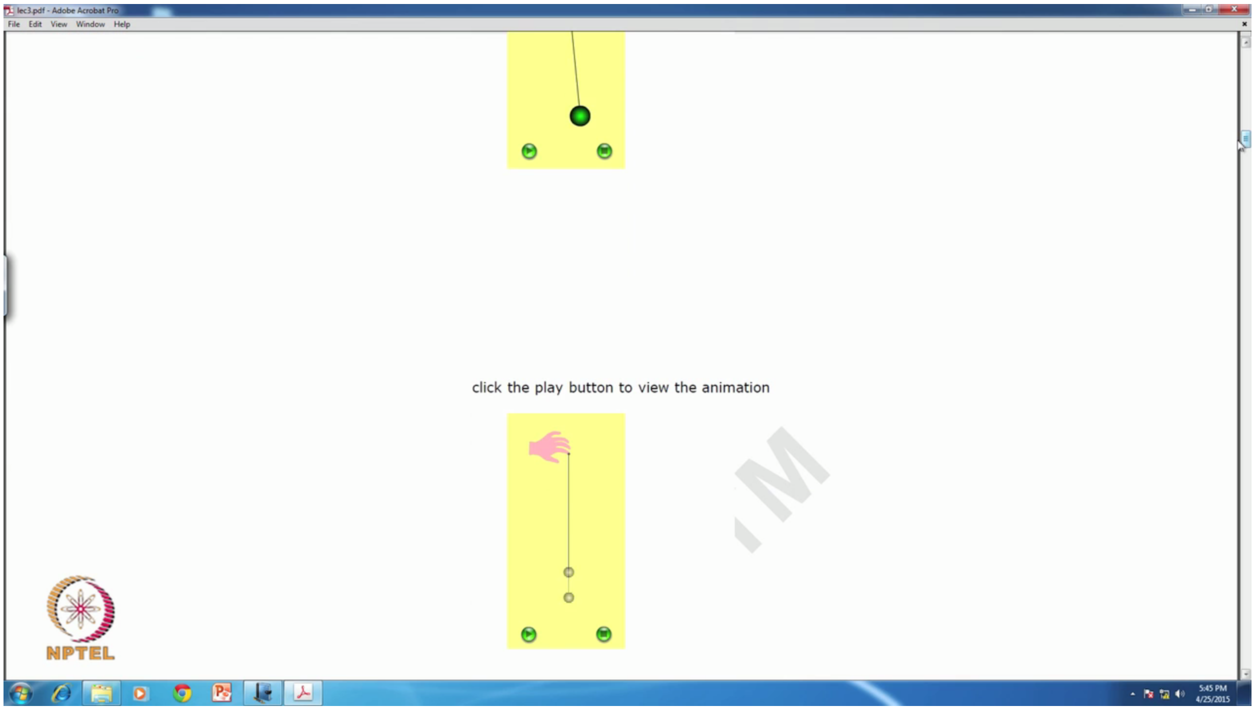
What we would do is to study the elementary quantum mechanical aspects of harmonic oscillator using the wave function method. Later in an advanced lecture, I will talk a little bit about the different types of raising and lowering operator formalisms of harmonic oscillator, but in this set, we would look at it as a wave function method. And as has always been in the last 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.



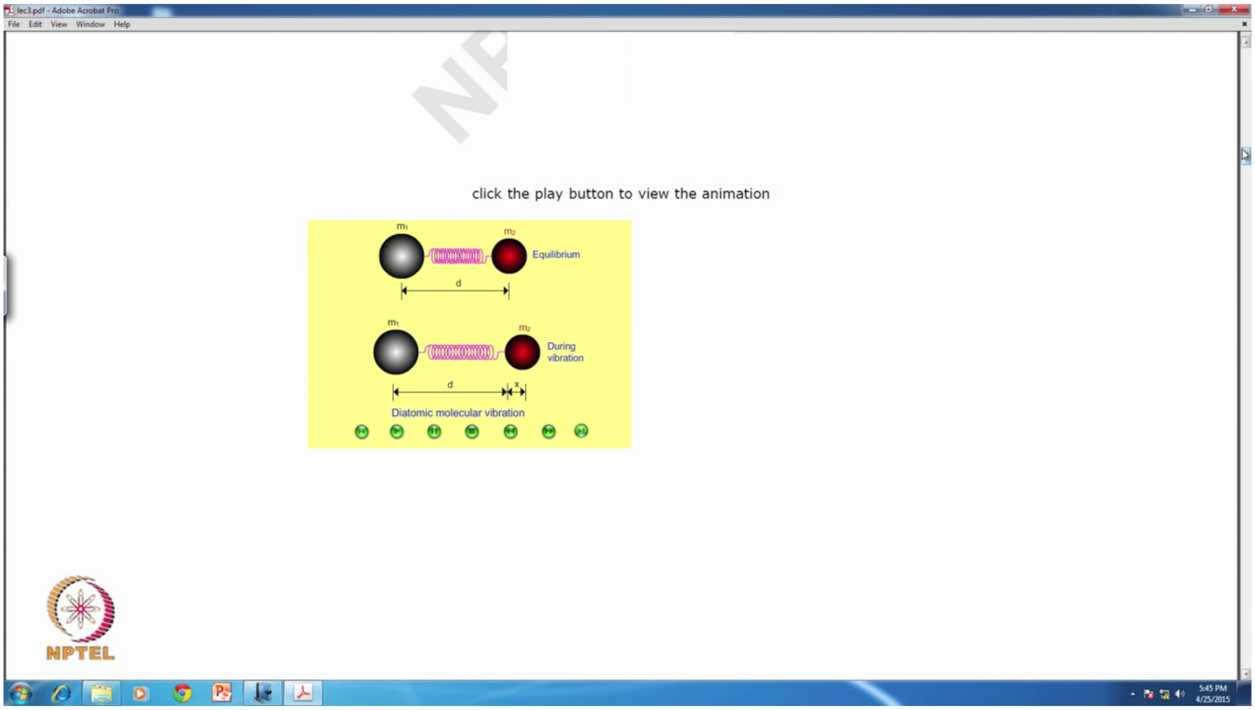
The harmonic oscillator by definition is about small amplitude oscillatory motion about an equilibrium position, or periodic motion such as motion on a circle. These things can be easily understood as caused by a restoring force, which is proportional to the displacement away from the equilibrium, but in the opposite direction. So let me write down, harmonic motion, small amplitude, oscillation about an equilibrium.



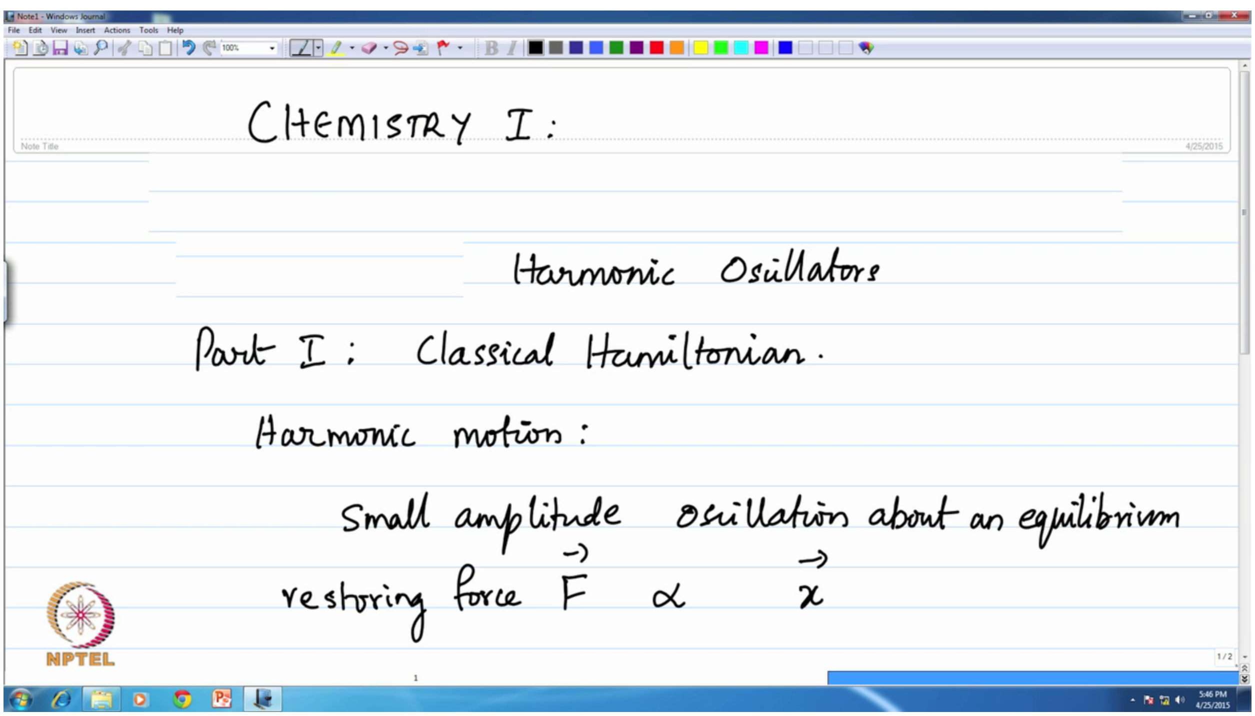
If you want to visualize that, here are some simple pictures. So the equilibrium position in the first picture is the vertical distance, and you can see that the ball oscillates between two extremes rather with a small amplitude.



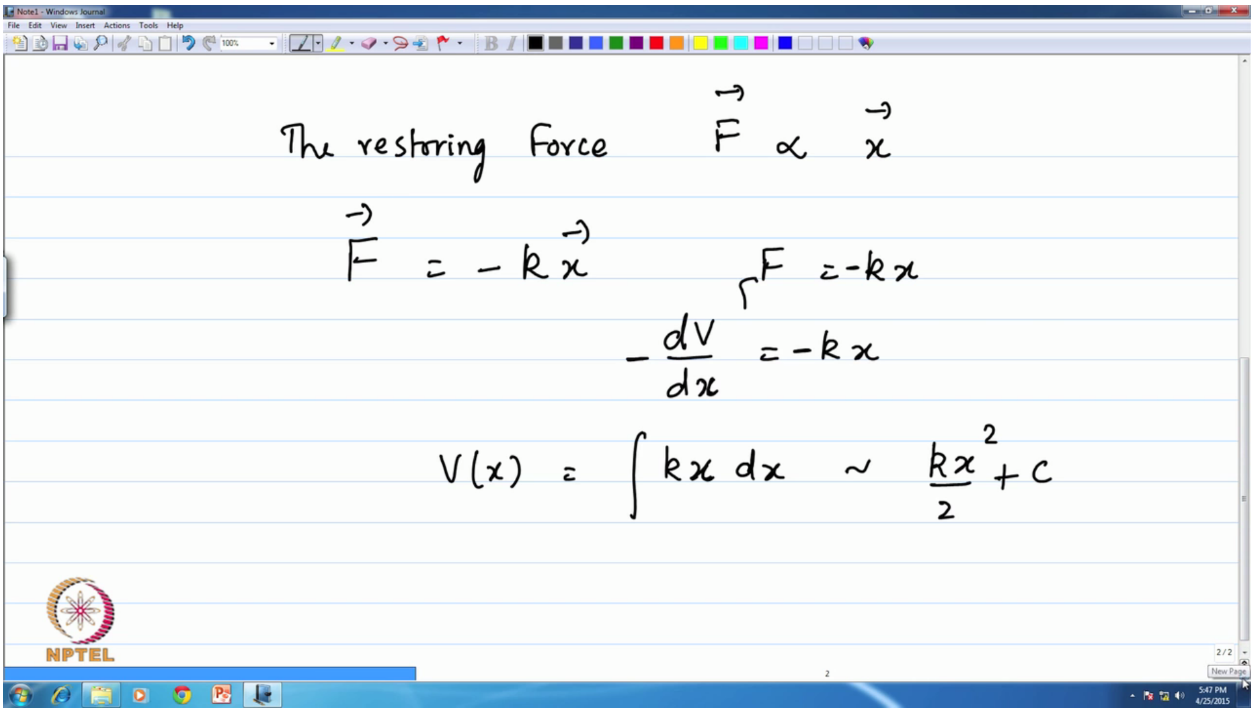
Another example is the usual play that you have with the spring ball and the motion of the spring ball is also harmonic.



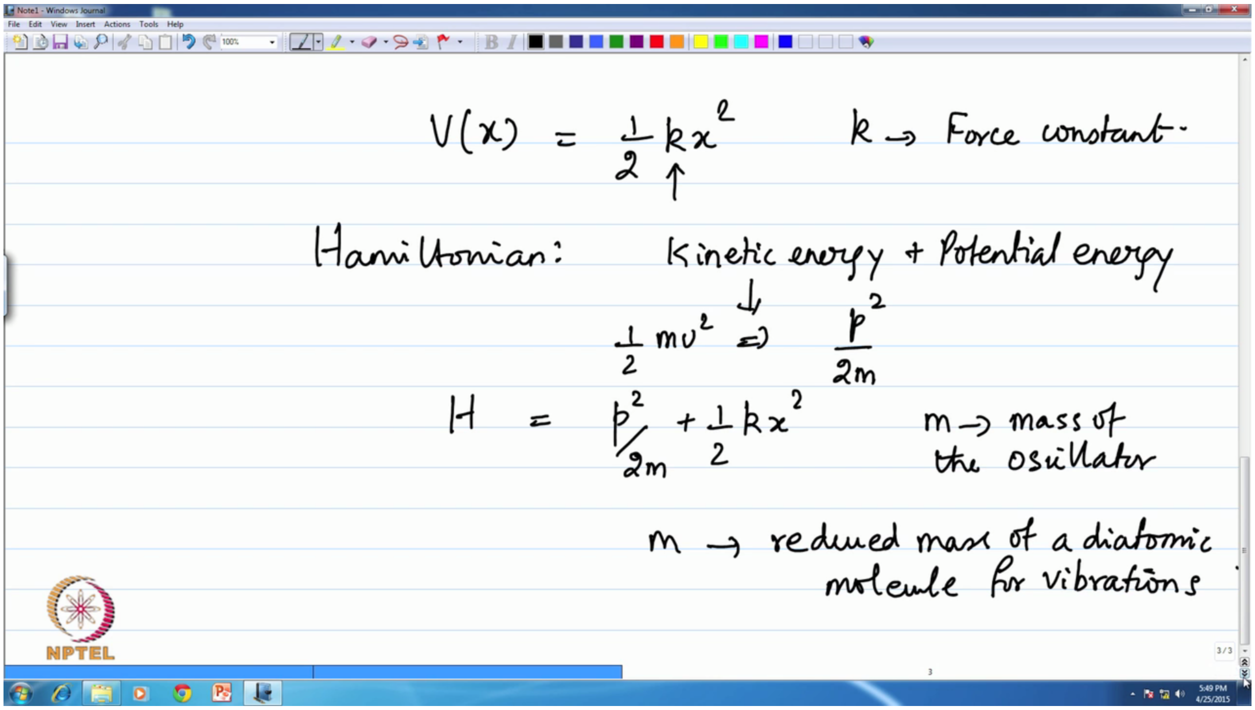
From the point of view of chemistry if you look at the diatomic molecular motion at very low temperatures is very nearly harmonic and the amplitudes of vibration of a fairly stable bond that is about the equilibrium distances. They are also modeled using harmonic motion. So these are some examples of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



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.

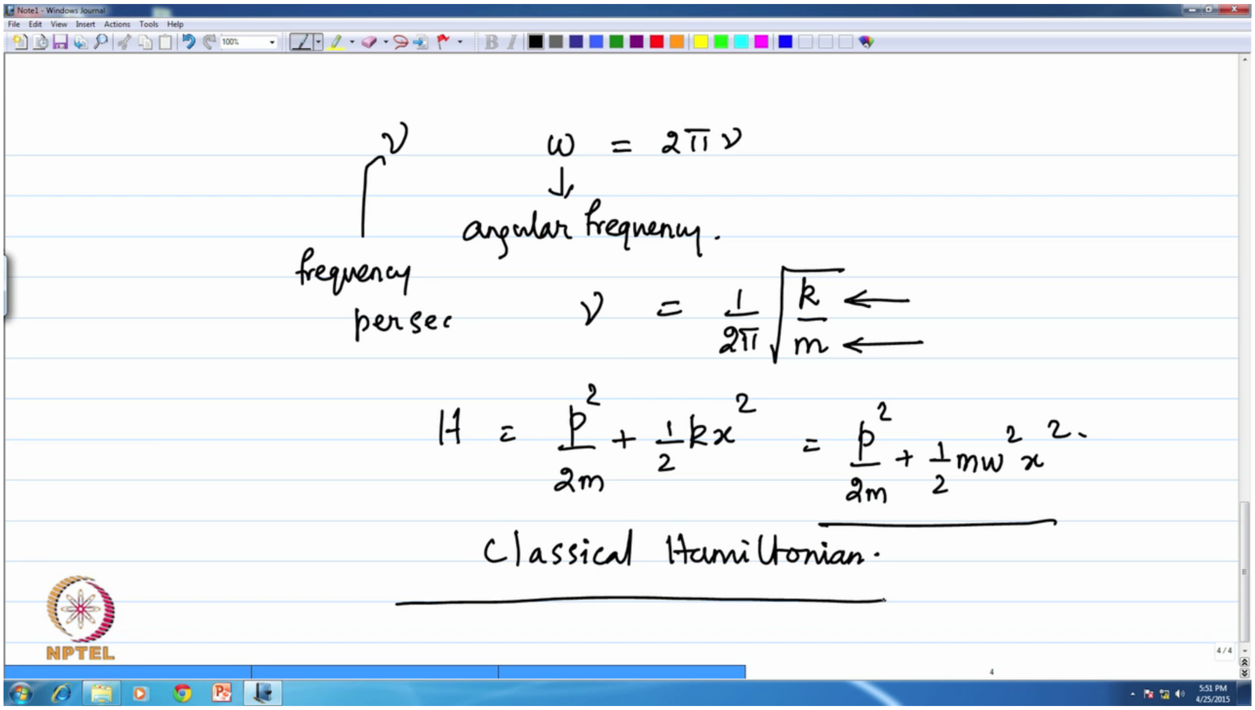


And since it is in the opposite direction, it is -kx, and one dimension, we would assume that the force is in a direction opposite to that of the displacement, so we don't need to worry about the vector arrow here, but knowing that the force is that negative derivative of potential with respect to the distance or with respect to the position coordinate, this is =kx, and you can see therefore, the potential energy V(x) is with -kx, and a -kx. Therefore, VF(x) is the <kx dx which gives you $kx^2/2$ plus a constant.



We can always choose that the potential about the equilibrium that is or at equilibrium X=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 ½ kx^2, and k you know is the force constant or the spring constant if you are talking about springs, force constant. And you know the dimension of k, kx^2 is energy so it's very clear what k should be. And the Hamiltonian if you have to write for the harmonic oscillator is obviously the kinetic energy plus the potential energy of the harmonic oscillator.

The potential energy is already given here. The kinetic energy is ½ mv^2 or if you want to write it using momenta, it is $P^2/2m$, and therefore, the Hamiltonian in a classical sense is $P^2/2m$ + ½ kx^2 where m is the mass of the oscillator. If you are worried about a diatomic molecule or vibration of a diatomic species, then m is replaced by reduced mass of the diatomic molecular system for vibrations, okay.



Also, please remember, the harmonic oscillator is associated with a frequency ν or an angular frequency ω, which is 2πν, 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's 1/2π 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 or 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 P2/2m + ½ kx2 and P of course, you know, it's mass times the velocity, therefore, it is the parameter for the harmonic oscillator or only the m and k, and if you want to write it using the angular frequency, you can write this by writing P2/2m + $1/2m\omega^2x^2$. So this is the classical Hamiltonian.