Chemistry Atomic Structure and Chemical Bonding
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Lecture - 47
Introduction to Quantum Mechanical Perturbation Theory

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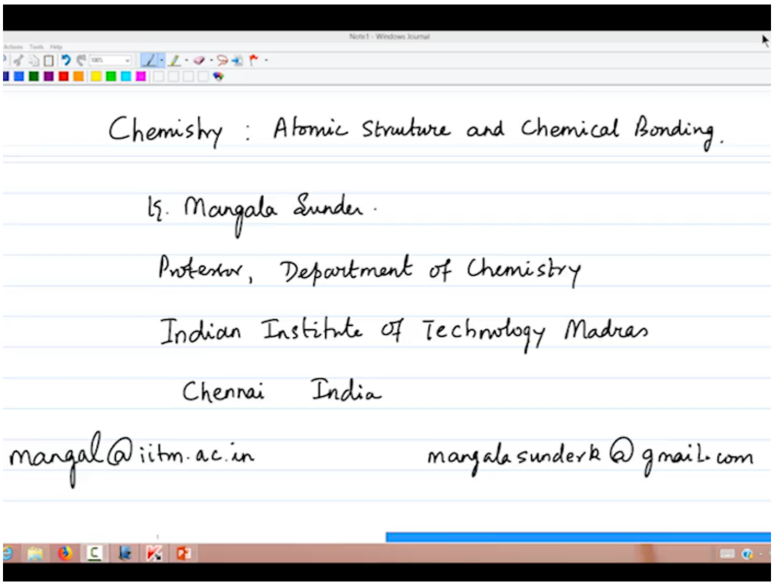

Chemistry : Atomic Structure and Chemical Bonding.

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Welcome back to the lectures in Chemistry and on the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder. I am from the Department of Chemistry, Indian Institute of Technology, Madras. I would like to discuss a little bit on the approximation methods.

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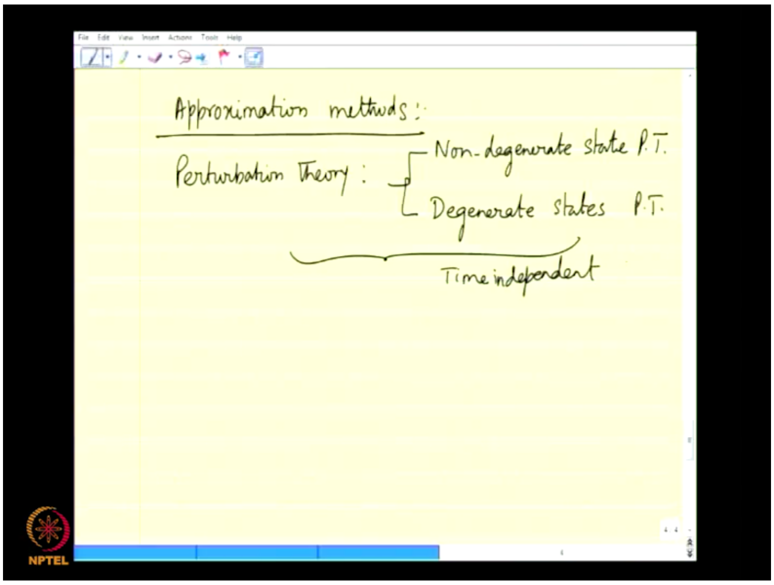

Approximation methods:

Perturbation Theory:
- Non-degenerate state P.T.
- Degenerate states P.T.

Time independent

But this lecture I would like to introduce what is called the perturbation theory. There are 3 possible cases that we have to consider; one is called non degenerate state perturbation theory ok. There is a slight variation of this is the degenerate state perturbation theory. And these are both time independent Schrodinger equation solutions and in molecular spectroscopy, where we have some basic relations that can be obtained from solving quantum mechanical problems. We need to study what are known as first order sorry.

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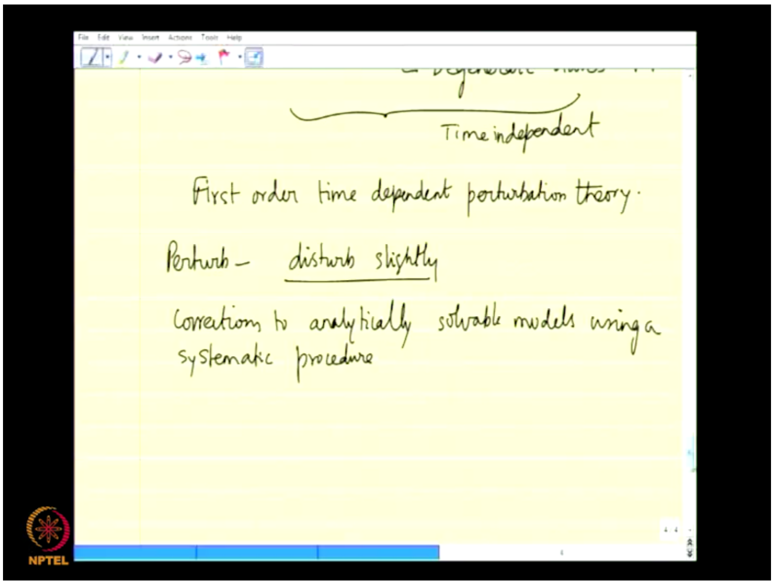

Time independent

First order time dependent perturbation theory.

Perturb – disturb slightly

Corrections to analytically solvable models using a systematic procedure

What are known as the first order time dependent perturbation theory, ok. Perturb means, disturb very slightly. Otherwise, it is not perturbation it is a disturbance and all kinds of things. What we mean by that is in order to understand to the basic philosophy of perturbation theory, one must also go back and recall that in quantum mechanics only a few problems that can be solved exactly.

You recall from your earlier quantum chemistry that you have done the particle in a one dimensional box, the particle in probably n dimensional box with infinite potentials boundaries and with no potentials in between in the region and perhaps with some potentials in the region and you study slightly more complicated problems but, the moment you put in put the potential energy it is not possible to solve this for arbitrary potential energies exactly.

Therefore, potential free particle in the box problem is an exactly solvable problem; 1 dimension, 2 dimensions. The particle on a 1 dimension 1 dimensional that is a single (Refer Slide Time: 03:40) or on the surface of a sphere for example, these are solutions that can be solved exactly using mathematical methods.

And the harmonic oscillator, a simple harmonic oscillator can be studied by analytical method, analytic methods in quantum mechanics and the last of course that you have seen is the hydrogen atom in which the atomic orbitals are obtained in precise mathematical forms by solving the 3 dimensional Schrodinger equation in a spherical coordinate system using r, theta and v.

So, these are the problems for which exact solutions are available. Now, if you place the hydrogen atom in a magnetic field or in an electric field and you want to study how these energy levels of the hydrogen atoms are changed or disturbed or different in the presence of the feed then, one has to use the premises of the exact solution that is the field free solution and then build corrections to the field present cases and that is possible in certain cases, namely when the fields applied are very small and they do not disturb the energy levels by a large amount and also the fields are such that they do not change the entire basic structure of the quantum system.

So, exactly solvable models in quantum are few and perturbation theory builds on adding corrections to analytically solvable models; exactly mean analytically solvable models using a systematic procedure. In order to do the mathematics, semi formally, accurately I it is not possible for me to do the mathematics very precisely using the theorems and so on, the theory of perturbation operators and so on ;leave the leave all those things out.

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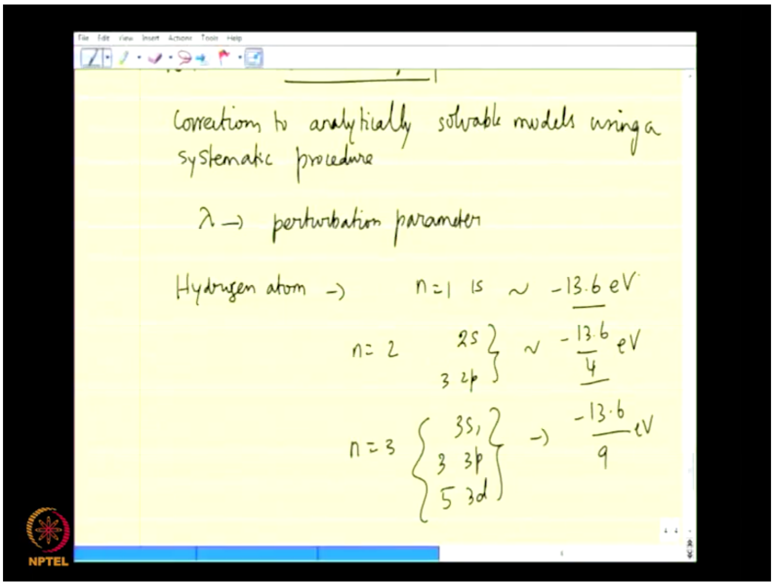

Correction to analytically solvable models using a systematic procedure

$\lambda \rightarrow$ perturbation parameter

Hydrogen atom $\rightarrow$ $n=1$ 1s $\sim -\underline{13.6}\,eV$

$n=2$ $\left.\begin{matrix} 2s \\ 3\ 2p \end{matrix}\right\} \sim -\dfrac{13.6}{\underline{4}}\,eV$

$n=3$ $\left\{\begin{matrix} 3s, \\ 3\ 3p \\ 5\ 3d \end{matrix}\right\} \rightarrow \dfrac{-13.6}{9}\,eV$

Some what is to me formally in order to do this, we introduce a parameter called perturbation parameter ok. Typically what is meant by a perturbation parameter? Let us take the hydrogen atom case. The hydrogen atom if you recall, the ground state has n equal to 1, l equal to 0 and m is 0. These are the angular quantum numbers both of which are 0 and that is the 1 s orbital the energy is given as minus 13.6 e V, you know that from your textbook quantum solutions.

The next one when you go to n equal to 2, there are 4 energy states, the 2 s and the 3 2 p orbitals, all of which have the energy minus 13.6 by 4 e V ok. What about the next one n equal to 3. There are 9 solutions, all of which are identical namely 3 s, 3 3 p and 5 3 d solutions. They all have the same total energy and that is given by minus 13.6 by n square where n is 3; therefore it is 9 e V ok.

Now, when you say we put the hydrogen atom in an external magnetic field or in an electric field and say that it perturbs the states of the hydrogen atom, it does something to disturb the energy levels of this the degenerate energy levels and or something to that. The order of magnitude of correction that is the perturbation has to be roughly if you take any 2 levels, which are to be studied through some transitions and so on.

The order of magnitude that you can think of is the difference between the 2 energy levels that you have, here it is minus 13.6 and minus 13.6 by 4; the difference between the 2 is minus 13.6 by 3, 3 by 4 times 13.6. The perturbation has to be at least 10 times smaller than this difference between the 2 energies. In order for this to be treated by the methods that I am going to describe ok.

So, if you are thinking of many energy levels in a quantum system and if you want to study simultaneously the transitions that take place due to external influence, which cannot be solved analytically. You can use perturbation theory provided the magnitude of the perturbation divided by the pair of energy levels that this perturbation may actually disturb.

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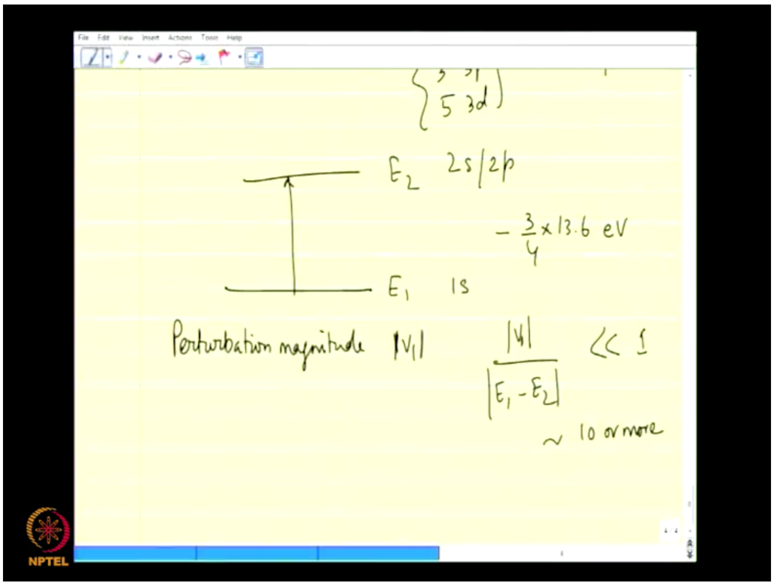

Suppose you have 2 energy levels, E 1 and E 2, in this case, 1 s and 2 p, 2 s or 2 p ok; this difference which is given by minus 3 by 4 times 13.6 e V ok. The perturbation magnitude which you call by some quantity say the magnitude of perturbation as V 1, the magnitude can be treated as perturbing provided V1 by E 1 minus E 2 is much less than one is of the order of 10 or more ok, here magnitude E 1 minus E 2.

This is a rough guide to tell you that perturbation theory works very well if this ratio is about 10. If this ratio is about is smaller than that it is even better, but if the ratio is larger say about 5 or 4, you have to watch the perturbation corrections that you calculate may not be sufficient in that you may not be it may not be enough to calculate 3 terms or 4 term maybe you need much more.

But if the correction term is of the order of magnitude same as that energy difference, you have a serious problem perturbation theory is not very useful for such cases ok, there are other methods for dealing with them. So, when you define what is meant by a small magnitude or when you meant when you say what is perturbation, this is what is to be kept in mind that, if multiple energy levels of a quantum system are studied and the disturbance between these energy levels due to an external influence, how these energy levels change due to that.

Then the magnitude of the perturbation divided by the corresponding differences cannot be more than I mean, cannot be less than about 8 to 10. This is a rough guide for you and there can be maybe 1 or 2 problems I will have that in the lecture notes when I give the assignments and so please refer to my website for some problems related to that ok.

Now, in the remaining time of 5 minutes, I will just tell you, I will just summarize some of the solutions that we have to recall in order to study perturbation theory formally.

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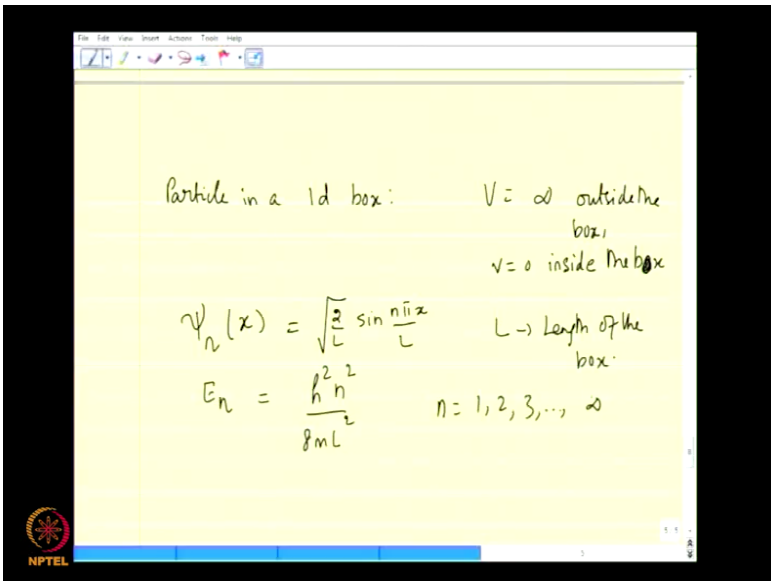

Particle in a 1d box:

$V = \infty$ outside the box, $V = 0$ inside the box

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$L \to$ Length of the box.

$$E_n = \frac{h^2 n^2}{8mL^2}$$

$n = 1, 2, 3, \ldots, \infty$

So, I will just summarize the solutions of the particle in a 1 dimensional box in d box, which is if you recall V is infinity outside the boxes and V is 0 inside the box. So, the boundary region is inside the box, the boundary region is the infinite potential region and you remember that the solutions psi n, n goes from 1 to infinity of the particle coordinate if you call it x the 1 the meant 1 degree of freedom coordinate in the inside the particle inside the box that is given by root 2 by L where L is the length of the box sin n pi x by L, L length of the box. And the energy is E n or given by h square n square by 8 m L square n is equal to 1 2 3 to infinity, all the energy levels of the particle in a one dimensional box.

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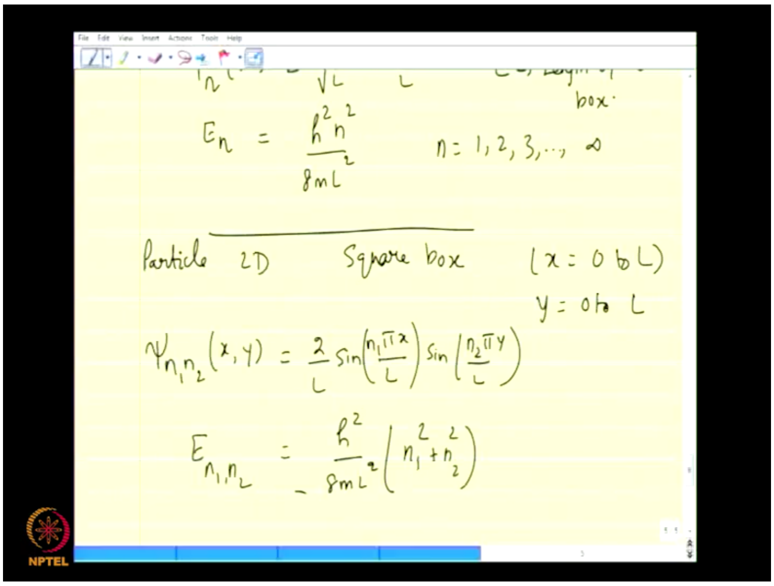

box.

$$E_n = \frac{h^2 n^2}{8mL^2} \qquad n = 1, 2, 3, \ldots, \infty$$

Particle 2D Square box (x = 0 to L)
y = 0 to L

$$\psi_{n_1 n_2}(x, y) = \frac{2}{L} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right)$$

$$E_{n_1, n_2} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2\right)$$

And likewise for a particle in a 2D box so, let us take a square box that is x is from 0 to L and y is also from 0 to L, that is the box that you talk about a planar region which is a square region then the wave functions are now given by 2 quantum numbers psi n 1 and n 2 and because it is planar the 2 orthogonal coordinates in the plane, we can write as x and y and in terms of x and y you remember that the wave function solution is 2 by L sin n 1 pi x by L sin n 2 pi y by L.

And the energy which is also a function of the 2 quantum numbers now, E n 1 and n 2 is given by h square by 8 m L square within brackets n 1 square plus n 2 square. You remember the solutions and likewise the solutions for a simple harmonic oscillator model may be recalled.

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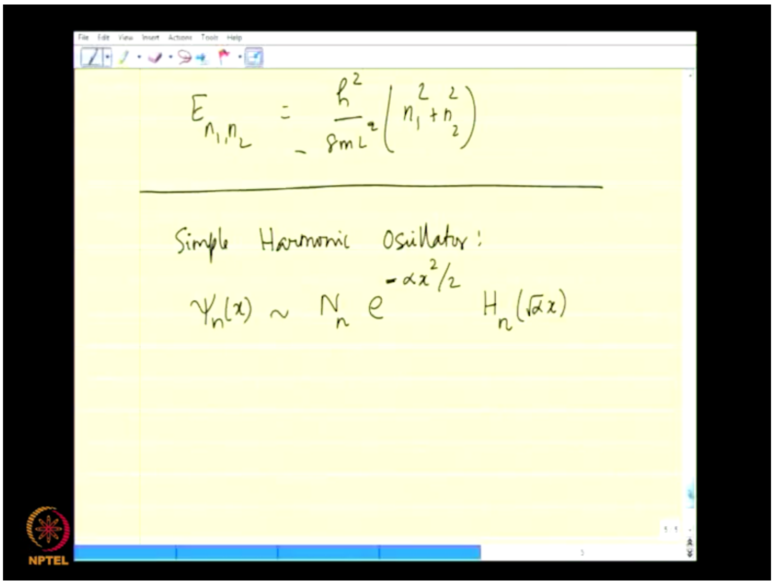

$$E_{n_1,n_2} = \frac{\hbar^2}{8mL^2}\left(n_1^2+n_2^2\right)$$

Simple Harmonic Osillator:

$$\Psi_n(x) \sim N_n\, e^{-\alpha x^2/2}\, H_n(\sqrt{\alpha}x)$$

The wave functions are given by a normalization constant which itself is a function of the quantum number N and is given by an exponential factor which I will write using a constant alpha x square by 2, psi n is a function of the harmonic oscillator coordinate x and then it is also multiplied by the Hermite polynomial root alpha x, 1 is the alpha to get the notation correct let us write these things carefully.

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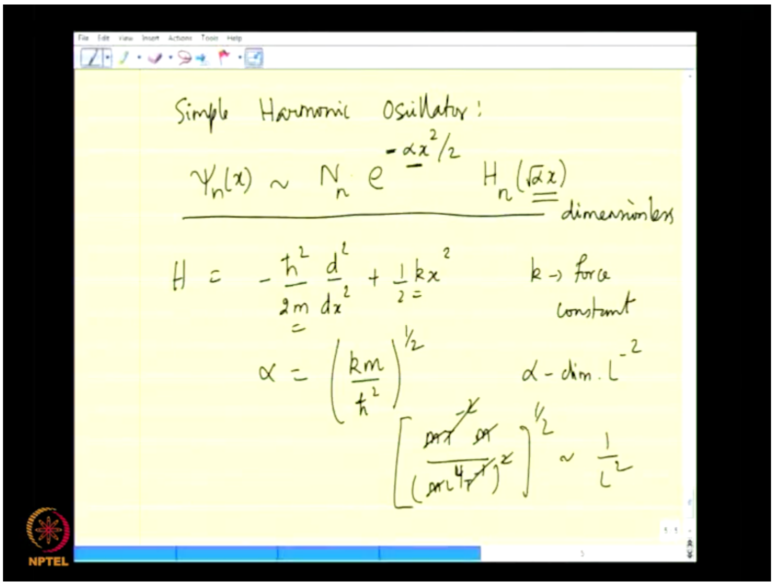

Simple Harmonic Osillator:

$$\Psi_n(x) \sim N_n\, e^{-\underline{\alpha} x^2/2}\, H_n(\underline{\underline{\sqrt{\alpha}x}})$$

dimensionless

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

k → force constant

$$\alpha = \left(\frac{km}{\hbar^2}\right)^{1/2}$$

α - dim. L^{-2}

$$\left[\frac{\cancel{M}\cancel{T^{-2}}\,\cancel{M}}{(\cancel{M}L^4\cancel{T^{-1}})^{\cancel{2}}}\right]^{1/2} \sim \frac{1}{L^2}$$

Let me see I think I should be able to do that the Hamiltonian for the harmonic oscillator is minus h bar square by 2 m d square by d x square which is the kinetic energy of the harmonic oscillator plus half k x square where k is the force constant ok.

So, if I recall the constant alpha, I think it is given by the constants in the Hamiltonian, I mean the physical system that we talked about it is in terms of k m by the planks constant squared, I believe it should be square root or if we have doubts, we can check because you see alpha root alpha x is to be dimensionless that is alpha x square that you see here is also dimensionless.

So, alpha has to have the dimension of 1 by L square x is the length displacement from the equilibrium, so alpha has to have the dimension of dimensionally not 1 by alpha is not equal to 1 by L square, sorry alpha must have the dimension of 1 by L square L to the minus 2.

So, you can check that the force constant you see force constants is the mass T to the minus 2, force constant times x square gives you the energy. So, m L square T to the minus 2 is energy and if you multiply by mass and h bar is m L square T to the minus 1 this whole square.

So, if you calculate this you see you are getting square root of this comes out to alpha as 1 by L square because, the m cancel out with the m square and the T to the minus 2 cancel out with the T to the minus 2 and the L square becomes L raise to 4 half of that is 1 by L square. So, sometimes you should do these things by looking at the dimensions and it is very easy afterwards not to forget these things.

So, the alpha is the parameter with which you define the harmonic oscillator wave function and alpha contains the physical information that is the mass of the particle and the force constant of the particle undergoing the simple harmonic motion. That is all the information that you need and everything else is given in terms of the physical content namely, the wave functions the energies and so on. So, what is the energy for the harmonic oscillator?

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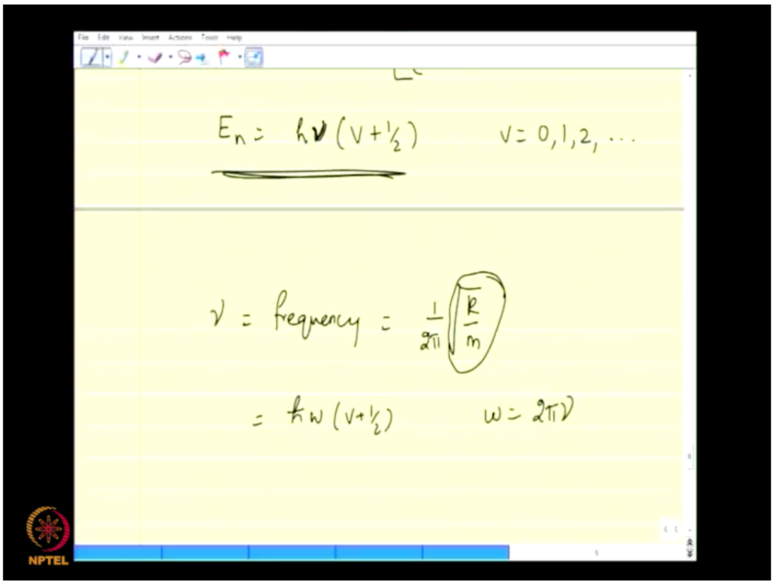

$$E_n = h\nu\left(v+\tfrac{1}{2}\right) \qquad v = 0,1,2,\ldots$$

$$\nu = \text{frequency} = \frac{1}{2\pi}\boxed{\sqrt{\frac{k}{m}}}$$

$$= \hbar\omega\left(v+\tfrac{1}{2}\right) \qquad \omega = 2\pi\nu$$

En’s are given by h nu into V plus half, where the quantum number V is 0, 1, 2, 3 etcetera and what is nu? nu is a frequency factor and again this frequency is given in terms of 1 by 2 pi square root of k by m again the physical constants of the problem that you talked about.

So, if the system has a higher force constant and a smaller mass, its harmonic frequency is much higher, if it has a larger k, a smaller k and the larger m it has a lower frequency and so on. But this is the harmonic oscillator solution, this is an exact solution and you can all often also write this as h bar omega times V plus half in terms of the angular velocity omega which is obviously, 2 pi times nu because, this there is no trick here, h bar omega is basically h by 2 pi times 2 pi nu and see it is nothing other than is what you have written now h nu into a V plus half ok.

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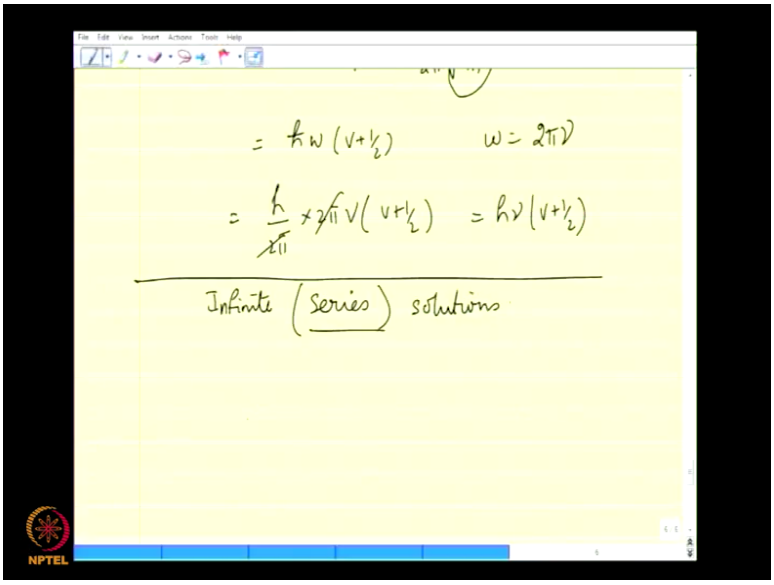

$$= \hbar\omega\left(v+\tfrac{1}{2}\right) \qquad \omega = 2\pi\nu$$

$$= \frac{h}{\cancel{2\pi}} \times \cancel{2\pi}\,\nu\left(v+\tfrac{1}{2}\right) = h\nu\left(v+\tfrac{1}{2}\right)$$

Infinite $\left(\underline{\text{Series}}\right)$ solutions

So, angular frequencies are like that. So this is the harmonic oscillator solution which you have to remember, when we talk about perturbation theory and likewise in the next lecture I will also discuss the hydrogen atom solution when we need to know; that is, we need to know solutions of what are known as model problems which are perturbation free and then when we put in the perturbation, how do we solve the system, systematically, term by term, using an infinite series is what I will do in the next lecture.

So, perturbation theory will be in the form of a series solution. For I mean thankfully we will not do infinite series, we will only do a series solution with 1 or 2 terms. The first term is called the first order perturbation theory, the second term is known under the second order perturbation theory and so on, until then.

Thank you very much.