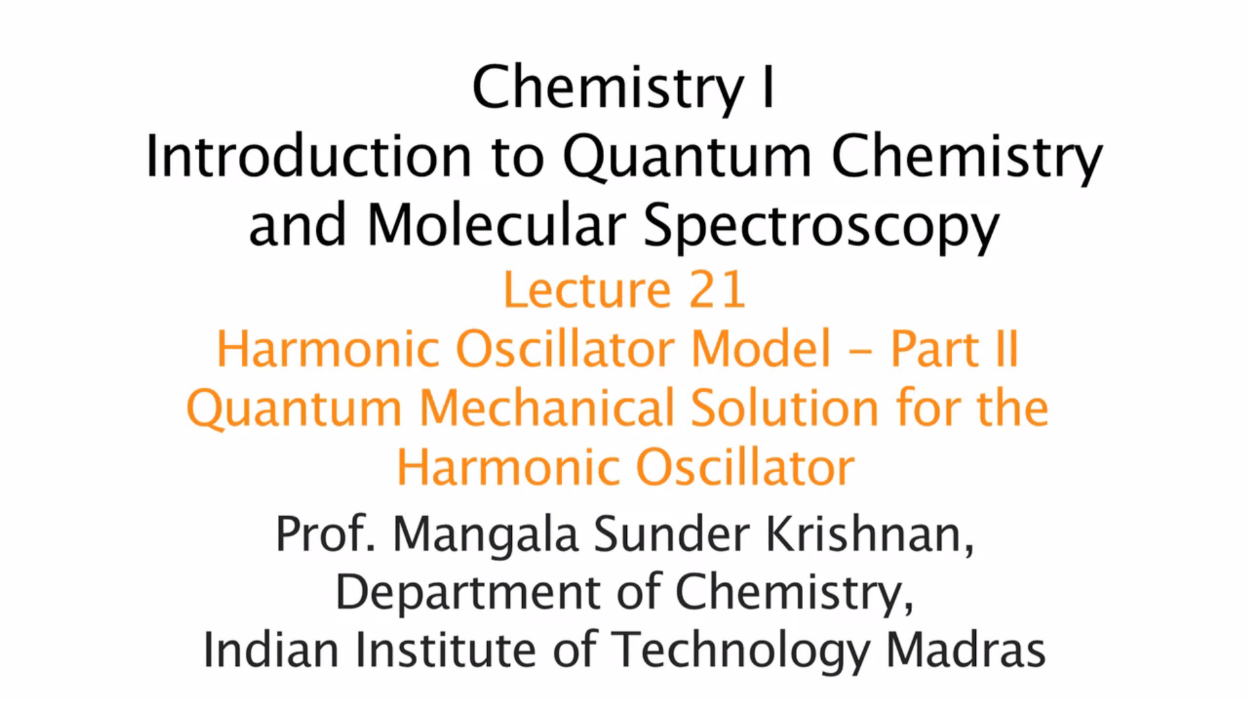

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 21
Harmonic Oscillator Model – Part II
Quantum Mechanical Solution for the Harmonic Oscillator

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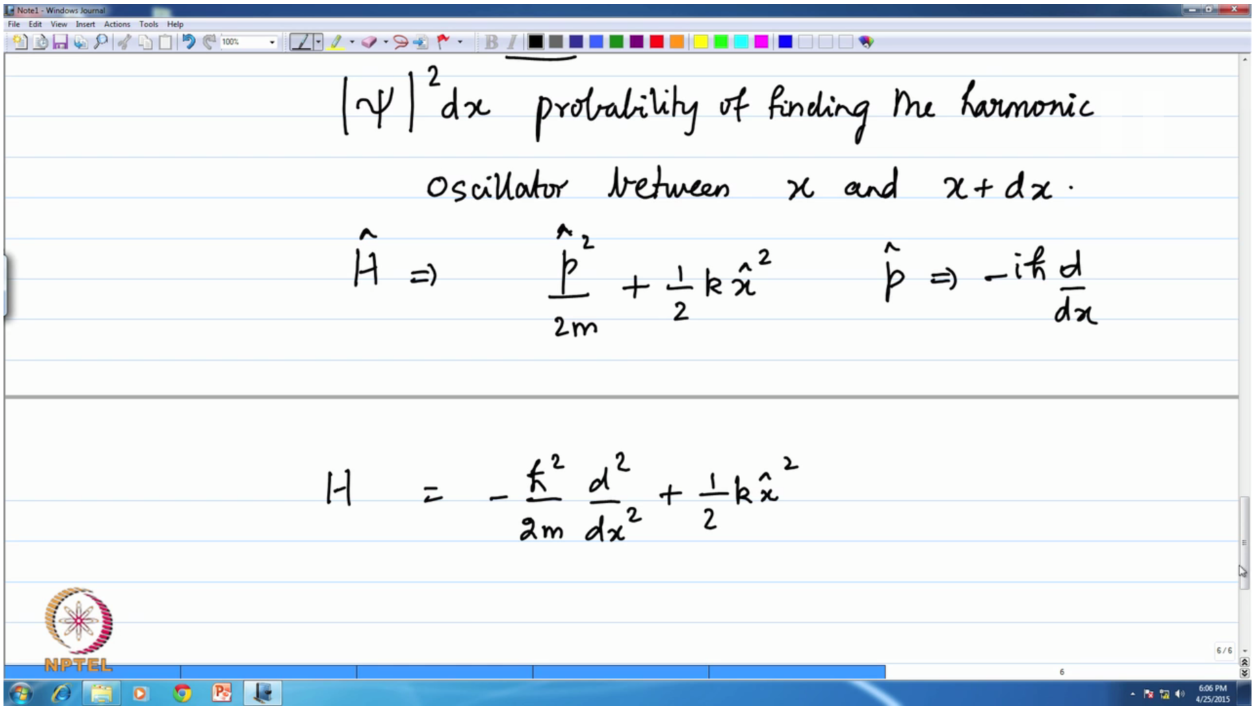


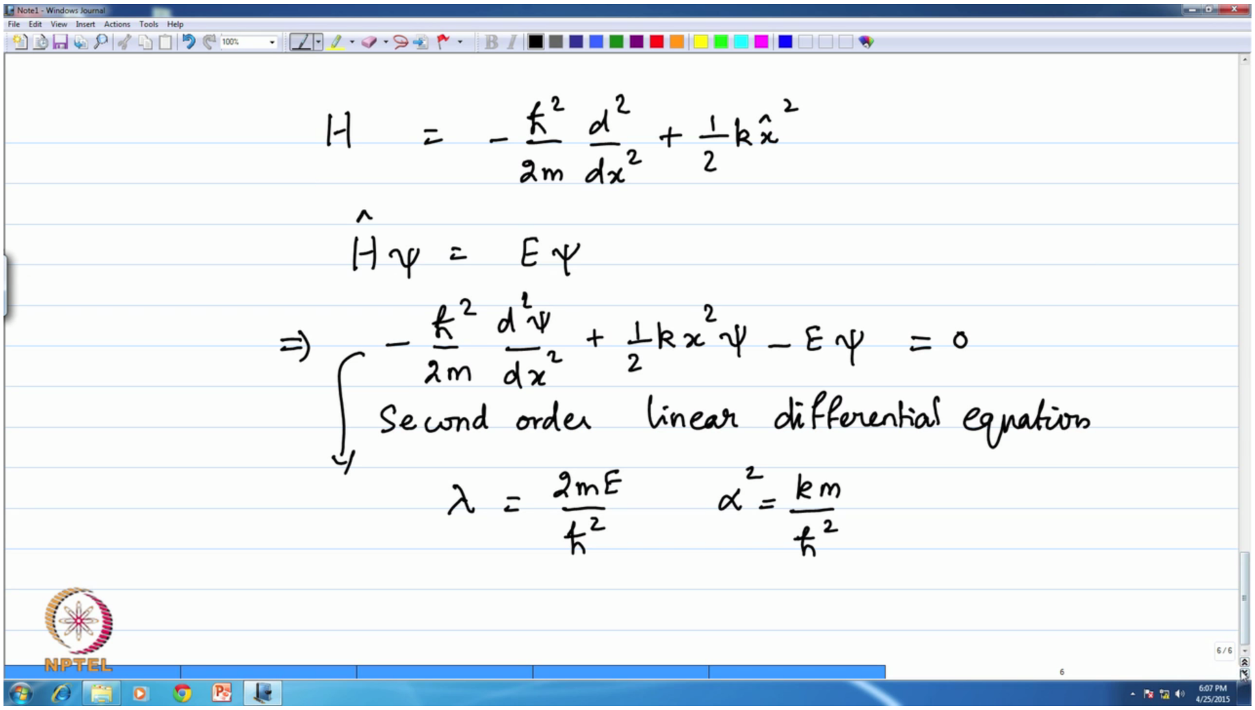
$|\psi|^2 dx$ probability of finding the harmonic oscillator between x and $x+dx$.

$$\hat{H} \Rightarrow \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 \qquad \hat{p} \Rightarrow -i\hbar\frac{d}{dx}$$

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

Prof. Mangala Sunder Krishnan: In this segment, let us look at the solutions for the harmonic oscillator using the quantum mechanical methods and the solution of the Schrodinger equation time-independent $h\psi(x) = E\psi(x)$. The x is the position coordinate for the harmonic oscillator motion and the wave function is function associated with the harmonic oscillator and it has the same probability interpretation as you have with the particle in a one dimensional box, namely $(\psi)^2dx$ represents the probability of finding the harmonic oscillator between x and x+dx.

The H is of course the Hamiltonian operator and the Hamiltonian operator in quantum mechanics is obtained from the classical Hamiltonian, which is $P^2/2m$ by changing the momentum to the operator and also ½ kx^2 where x is the position operator. In quantum mechanics of course in this case P is to be replaced by the standard representation in coordinate with the derivative -ħd/dx. It's one dimension so we don't need the partial derivative. It’s ħd/dx, which leads to immediately this formula, namely H is $-\hbar^2/2m\ d^2/dx^2$ as you had it in the particle in the one dimensional box with ½ kx^2, which is the potential energy associated with the harmonic oscillator.



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

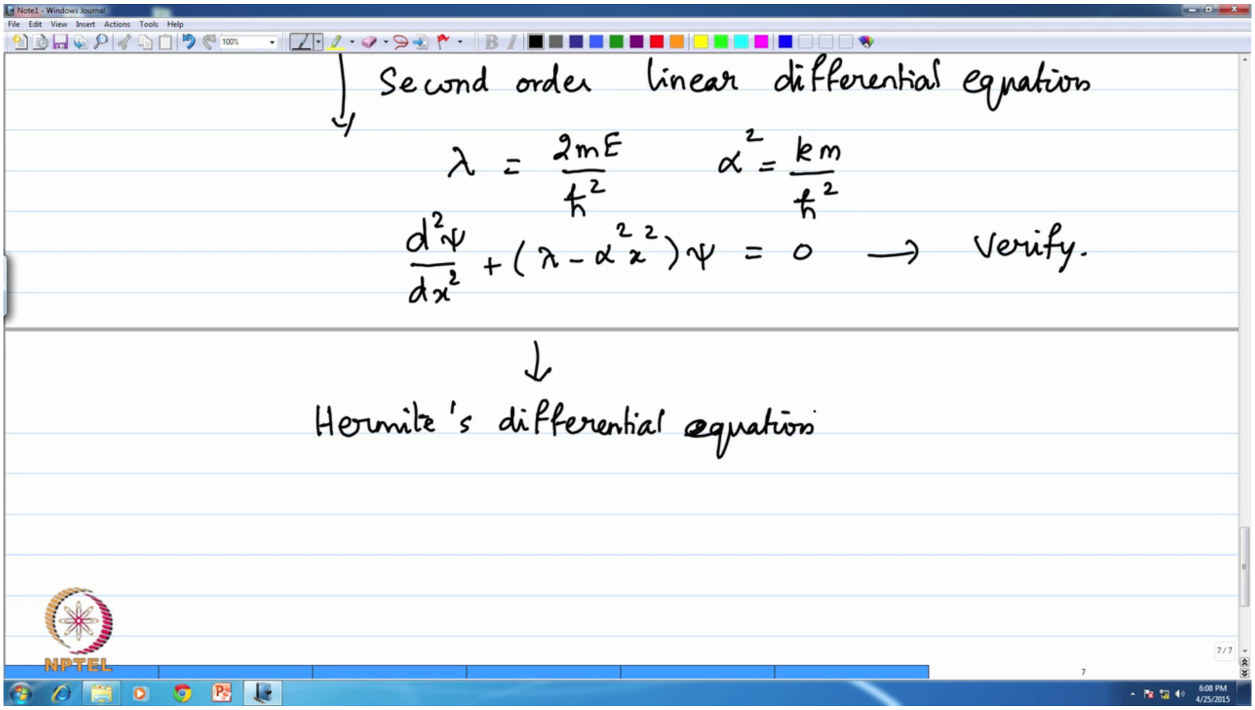
$$\hat{H}\psi = E\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi - E\psi = 0$$

Second order linear differential equation

$$\lambda = \frac{2mE}{\hbar^2} \qquad \alpha^2 = \frac{km}{\hbar^2}$$

Therefore, the solution that you have to obtain is the solution that $\hat{H}\psi = E\psi$, sorry no cap on the ψ, is equal to Eψ is the solution of the differential equation namely $-\hbar^2/2m\ d^2\psi/dx^2 + ½kx^2\psi - E\psi = 0$. So second order linear differential equation. This lecture will not tell you how to solve this differential equation, but it will tell you that if you rewrite this by introducing a simple parameter say for example lambda = $2mE/\hbar^2$ and another constant α or α^2 as $km/\hbar^2$.



↓ Second order linear differential equation

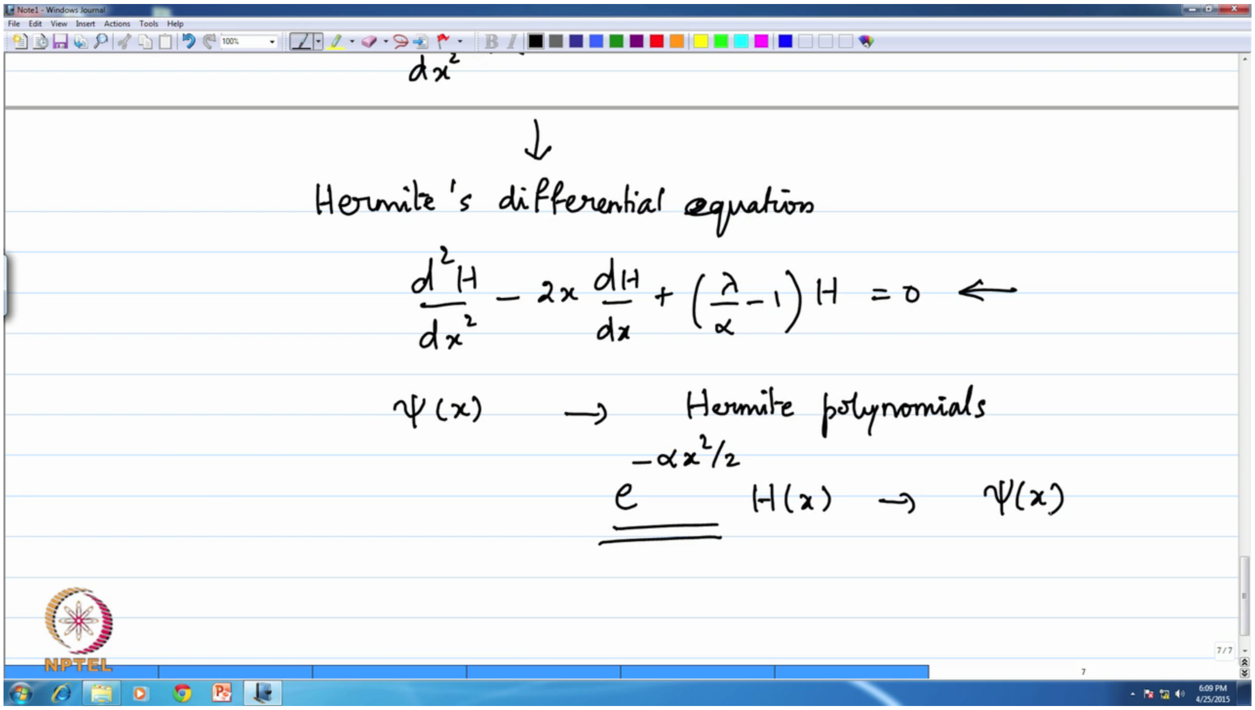
$$\lambda = \frac{2mE}{\hbar^2} \qquad \alpha^2 = \frac{km}{\hbar^2}$$

$$\frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2)\psi = 0 \longrightarrow \text{Verify.}$$

↓

Hermite's differential equation

If you introduce two new constant, then it's possible for you to write the differential equation as d²ψ/dx² + (lambda-α²x²)ψ = 0. I think verify, this will be one of the items for you to check.



dx^2

↓

Hermite's differential equation

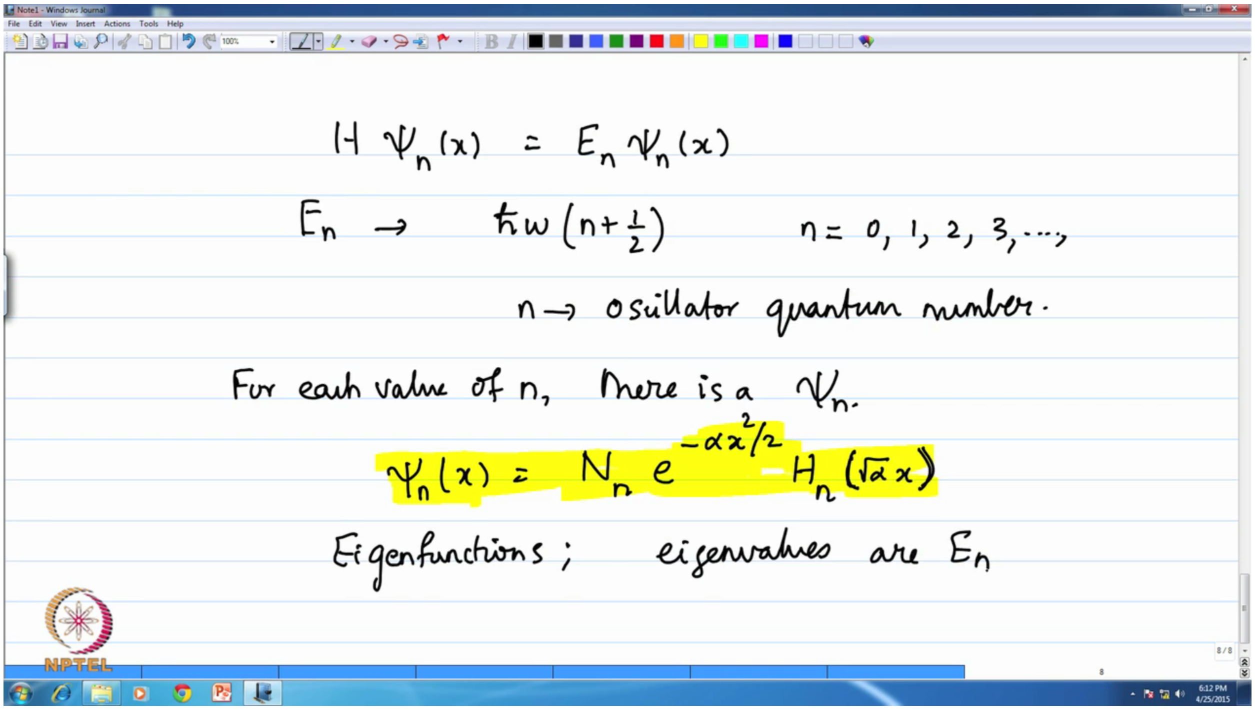
$$\frac{d^2H}{dx^2} - 2x\frac{dH}{dx} + \left(\frac{\lambda}{\alpha} - 1\right)H = 0 \longleftarrow$$

$$\psi(x) \longrightarrow \text{Hermite polynomials}$$

$$\underline{e^{-\alpha x^2/2}}\; H(x) \longrightarrow \psi(x)$$

It is possible to transform this into what is known as the Hermite’s differential equation for which solutions have been known for more than hundred years when this itself was proposed. In fact, the Hermite differential equation, let me write that down, Hermite differential equation is d^2H, the Hermite function, dx^2 - 2x dH/dx + (lambda/α - 1) H = 0. Now I have just pulled this out of nowhere, but it does not matter what is important is the wave functions ψ are going to be associated with what are known as the Hermite functions or Hermite polynomials, and will also have a component called the Gaussian, which is $e^{-\alpha x2/2}$, this Gaussian and the Hermite polynomial x will determine the solutions of the harmonic oscillator.

The mathematics is involved. We don't need to worry about it. What I would do is to write down directly the solution of this equation, which you have here, this equation. And then we will only examine the nature of the solutions and the consequences of the solutions rather than solving the differential equation itself. This can be referred to at a later time.



$$H\,\psi_n(x) = E_n\,\psi_n(x)$$

$$E_n \rightarrow \hbar w\left(n+\frac{1}{2}\right) \qquad n = 0, 1, 2, 3, \ldots,$$

$n \rightarrow$ oscillator quantum number.

For each value of n, there is a ψ_n.

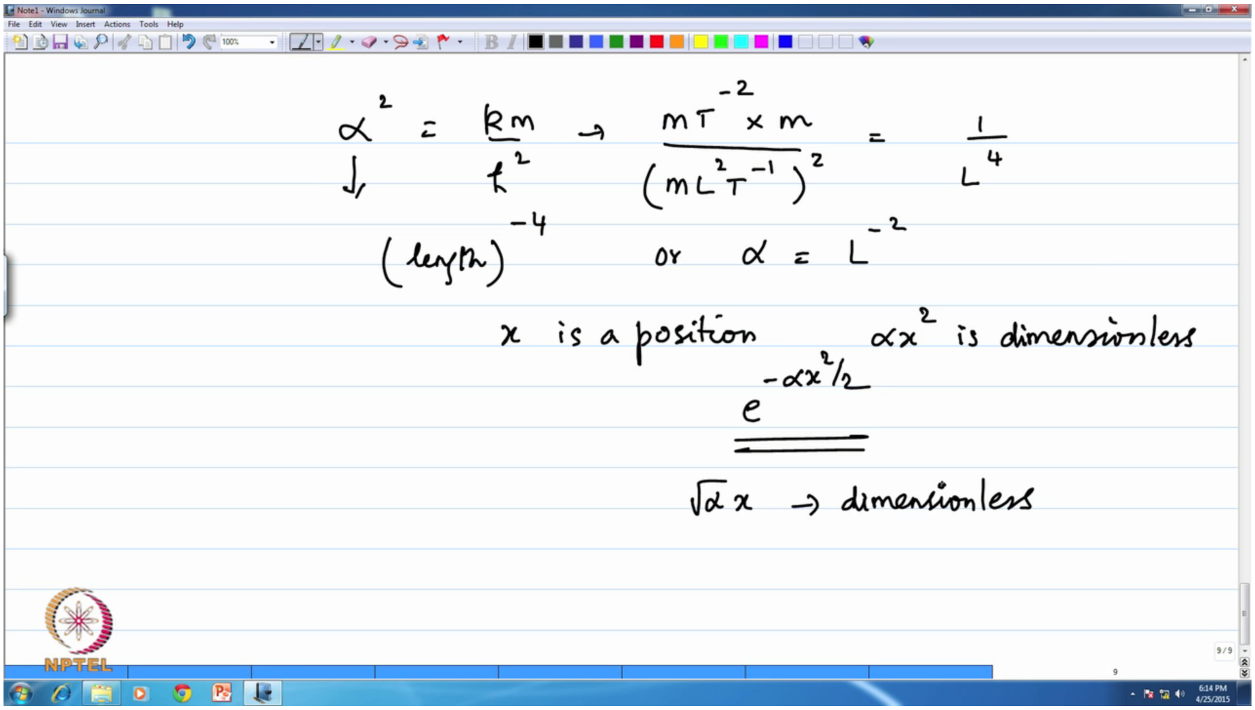
$$\psi_n(x) = N_n\, e^{-\alpha x^2/2}\, H_n(\sqrt{\alpha}\, x)$$

Eigenfunctions ; eigenvalues are E_n

So what are the solutions for the harmonic oscillator?

First of all, there are an infinity of solutions. H $\psi_n(x) = E_n\, \psi n(x)$ and the formula for E_n turns out to be, when you solve the Schrodinger equation, E_n is ℏω (n+½) and n is the quantum number, which can take values 0, 1, 2, to infinity, n is the oscillator quantum number. And for each value of n, there is a ψ_n, there is a wave function ψ_n. The general formula for ψ_n when you do the mathematics is given by a normalization constant, which also depends on this quantum number n and an exponential of $-\alpha x^2/2$ times the Hermite polynomials H_n (√αx), okay.

These are the solutions or in whatever we have described so far these are also known as the eigenfunctions of the harmonic oscillator Hamiltonian. The eigenvalues are E_n.



$$\alpha^2 = \frac{km}{\hbar^2} \rightarrow \frac{mT^{-2} \times m}{(mL^2T^{-1})^2} = \frac{1}{L^4}$$

$$\downarrow$$

$$(\text{length})^{-4} \quad \text{or} \quad \alpha = L^{-2}$$

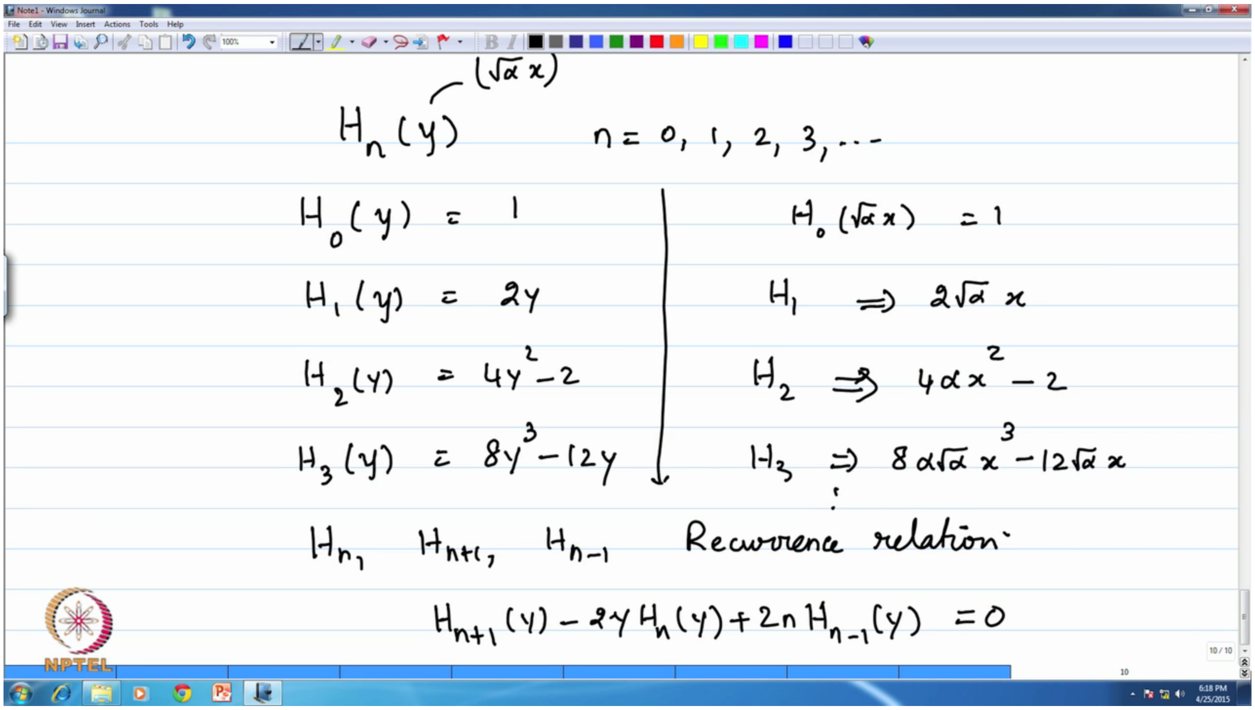
x is a position αx^2 is dimensionless

$$\underline{\underline{e^{-\alpha x^2/2}}}$$

$\sqrt{\alpha}\, x \rightarrow$ dimensionless

Go back and look at the constants α and lambda. Alph^2 is km/$\hbar^2$, α^2 is km/$\hbar^2$, okay. K is the force constant, which is mT^{-2} x m and ħ is $(mL^2T\text{-}1)^2$. So what you have is $1/L^4$. Therefore, α^2 has the unit $(\text{length})^{-4}$ or α has the dimension -- I mean α^2 has a dimension of $(\text{length})^{-4}$ and α has a dimension of L^{-2}. That should make sense because x is a position and therefore it is also the length from the equilibrium, a distance from the equilibrium. Therefore, you see that αx^2 is dimensionless. Otherwise, $e^{-\alpha x2/2}$ doesn't make sense, okay.

So the constants have been chosen to get some of these physical parameters clear and the Hermite polynomial, which is a function of position is multiplied by square √ of α and you can see that square √ of α is length inverse, okay, length inverse therefore, square √ of αx is also dimensionless so that you can add various powers.



$$H_n(\overset{(\sqrt{\alpha}\,x)}{y}) \qquad n = 0, 1, 2, 3, \ldots$$

$$H_0(y) = 1 \qquad H_0(\sqrt{\alpha}\,x) = 1$$

$$H_1(y) = 2y \qquad H_1 \Rightarrow 2\sqrt{\alpha}\,x$$

$$H_2(y) = 4y^2 - 2 \qquad H_2 \Rightarrow 4\alpha x^2 - 2$$

$$H_3(y) = 8y^3 - 12y \qquad H_3 \Rightarrow 8\alpha\sqrt{\alpha}\,x^3 - 12\sqrt{\alpha}\,x$$

$\vdots$

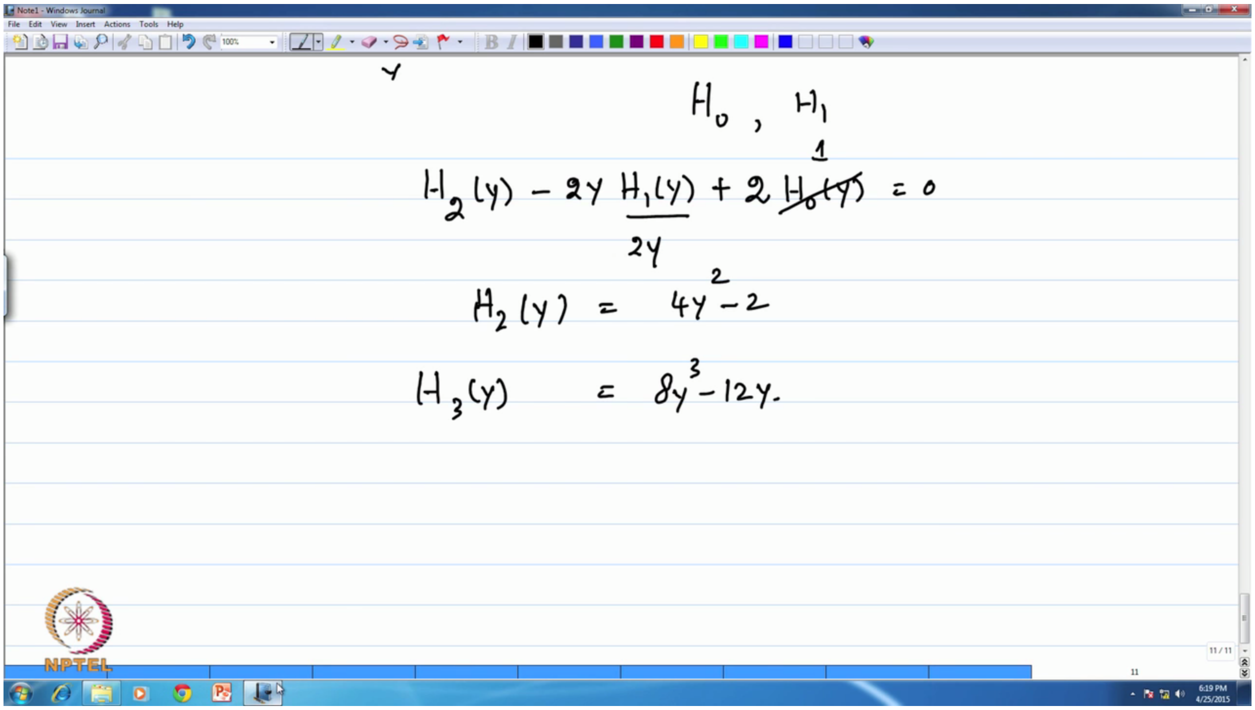
H_n, H_{n+1}, H_{n-1} Recurrence relation:

$$H_{n+1}(y) - 2yH_n(y) + 2nH_{n-1}(y) = 0$$

The Hermite polynomials are solutions of what is known as the Hermite equation, which I wrote down earlier and the Hermite polynomials are defined for various values of say let me write $H_n(y)$ if I put the argument as y instead of √ αx, okay. Why is √ αx in this case? If I write $H_n(y)$ and n = 1, 2, 3, et cetera, then the results are already known namely $H_0(y) = 1$, $H_1(y) = 2y$, $H_2(y) = 4y^2 - 2$, $H_3(y) = 8y^3 - 12y$ and so on, okay. So if you write this in terms of √ αx H_0 (√α x) = 1, H_1 is 2√α xm, H_2 is $4\alpha x^2 - 2$, and H_3 is 8√α -- α √α, that is $\alpha^3/2$ x 3 - 12√α x and so on.

There are relations that the polynomial satisfy between H_n, H_n+1 and H_n-1, there is a relation called recurrence relation. Stop for a minute.

The recurrence relation between these is also known in mathematics it is $H_n+1(y) - 2yH_n(y) + 2_n\ H_n-1(y) = 0$.



y

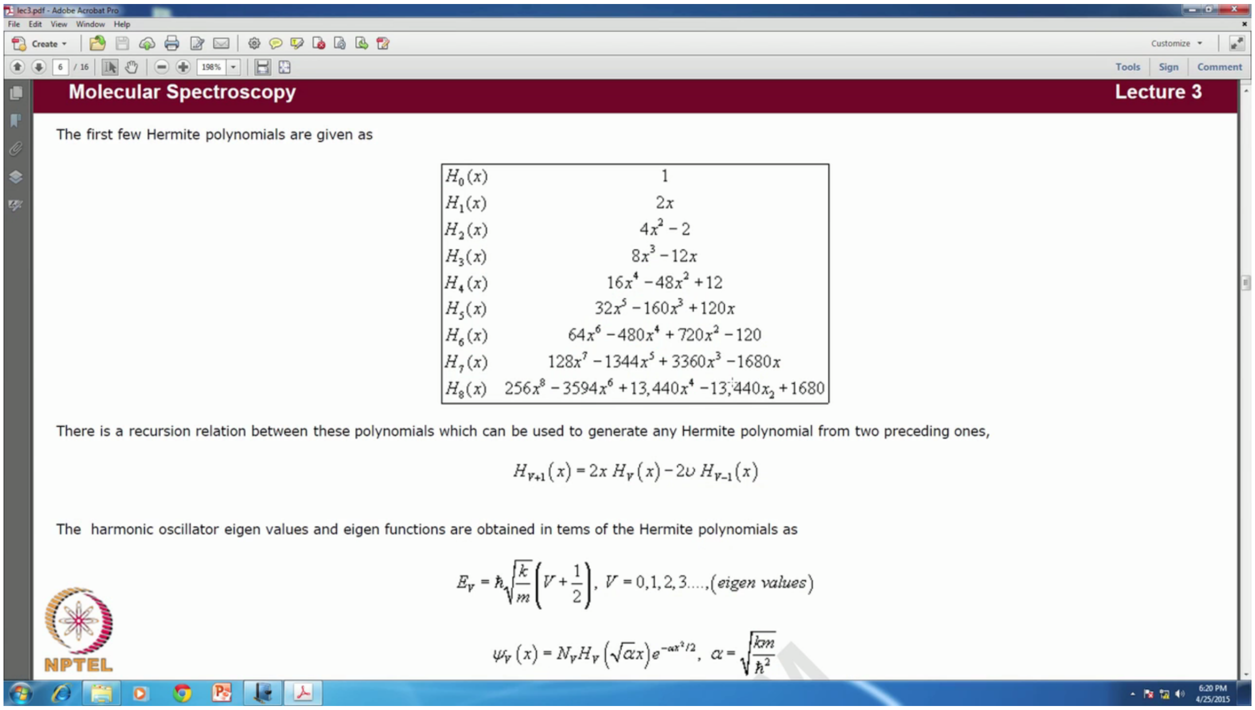
H_0 , H_1

$$H_2(y) - 2y\,\underbrace{H_1(y)}_{2y} + 2\,\overset{1}{\cancel{H_0(y)}} = 0$$

$$H_2(y) = 4y^2 - 2$$

$$H_3(y) = 8y^3 - 12y.$$

What this tells you is to obtain harmonic oscillators for higher values, I mean larger values of n from the harmonic oscillator -- the Hermite polynomials for smaller values. For example H_0 and H_1 if you know, then you can calculate $H_2(y)$ - 2y $H_1(y)$ + 2, since n is 1, this is 2 $H_0(y) = 0$, and this is 1 and $H_1(y)$ is known as 2y, therefore you see $H_2(y)$ is $4y^2 - 2$, which is what I had written down earlier, okay, see that. So if we knew H_0 and H_1 from mathematics and also from the recurrence relation, if we know the recurrence relation, then in principle we can calculate any Hermite polynomials H_n from the previous two Hermite polynomials. And so one exercise would be to show that $H_3(y) = 8y^3 - 12y$ and so on.



Molecular Spectroscopy **Lecture 3**

The first few Hermite polynomials are given as

$H_0(x)$	1
$H_1(x)$	$2x$
$H_2(x)$	$4x^2 - 2$
$H_3(x)$	$8x^3 - 12x$
$H_4(x)$	$16x^4 - 48x^2 + 12$
$H_5(x)$	$32x^5 - 160x^3 + 120x$
$H_6(x)$	$64x^6 - 480x^4 + 720x^2 - 120$
$H_7(x)$	$128x^7 - 1344x^5 + 3360x^3 - 1680x$
$H_8(x)$	$256x^8 - 3594x^6 + 13,440x^4 - 13,440x_2 + 1680$

There is a recursion relation between these polynomials which can be used to generate any Hermite polynomial from two preceding ones,

$$H_{V+1}(x) = 2x\, H_V(x) - 2\upsilon\, H_{V-1}(x)$$

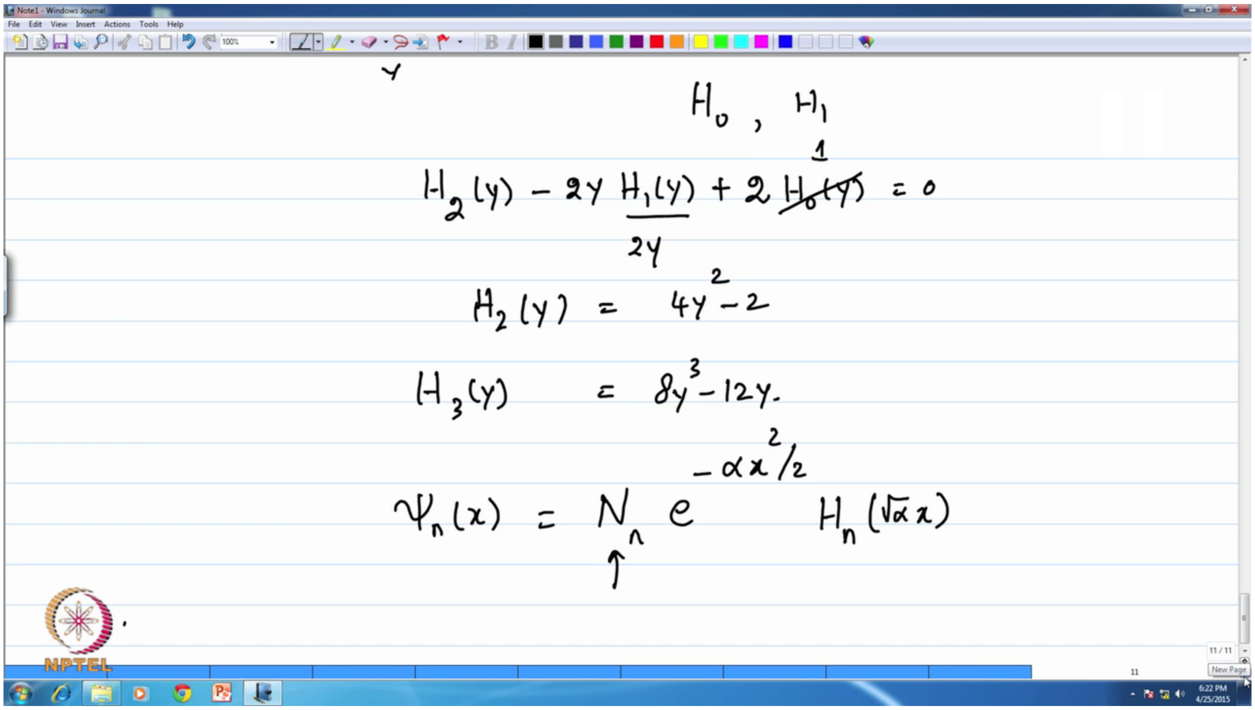
The harmonic oscillator eigen values and eigen functions are obtained in tems of the Hermite polynomials as

$$E_V = \hbar\sqrt{\frac{k}{m}}\left(V + \frac{1}{2}\right),\ V = 0,1,2,3....,(\textit{eigen values})$$

$$\psi_V(x) = N_V H_V\left(\sqrt{\alpha}x\right)e^{-\alpha x^2/2},\ \alpha = \sqrt{\frac{km}{\hbar^2}}$$

So one can reproduce these tables, and let me just show you from one of the lectures that I have had earlier. One can see the table here for various values of the Hermite polynomials. In this table of course y and x have been interchanged, you can see that H naught of X and one can go on and calculate H_0, H_1 and H_2 and what you see here is up to H_8.

One thing that should be noted is that the even-numbered polynomials 0, 2, 4, 6, 8 are all even functions of X $H_0(x) = 1$, $H_2(x) = 4x^2 - 2$, which doesn't change if X is negative or positive and if -x or +x. $H_4(x)$ again is x^4x^2, therefore, it’s an even function of x. $H_6(x)$ is even. Therefore the Hermite polynomials also give us a series of functions, which are odd or even depending on whether the quantum number associated with the harmonic oscillator problem is odd or even. This is something that we have to remember when we do some of the computations regarding probabilities and average values using harmonic oscillator eigenfunctions.



y

$$H_0 \,,\; H_1$$

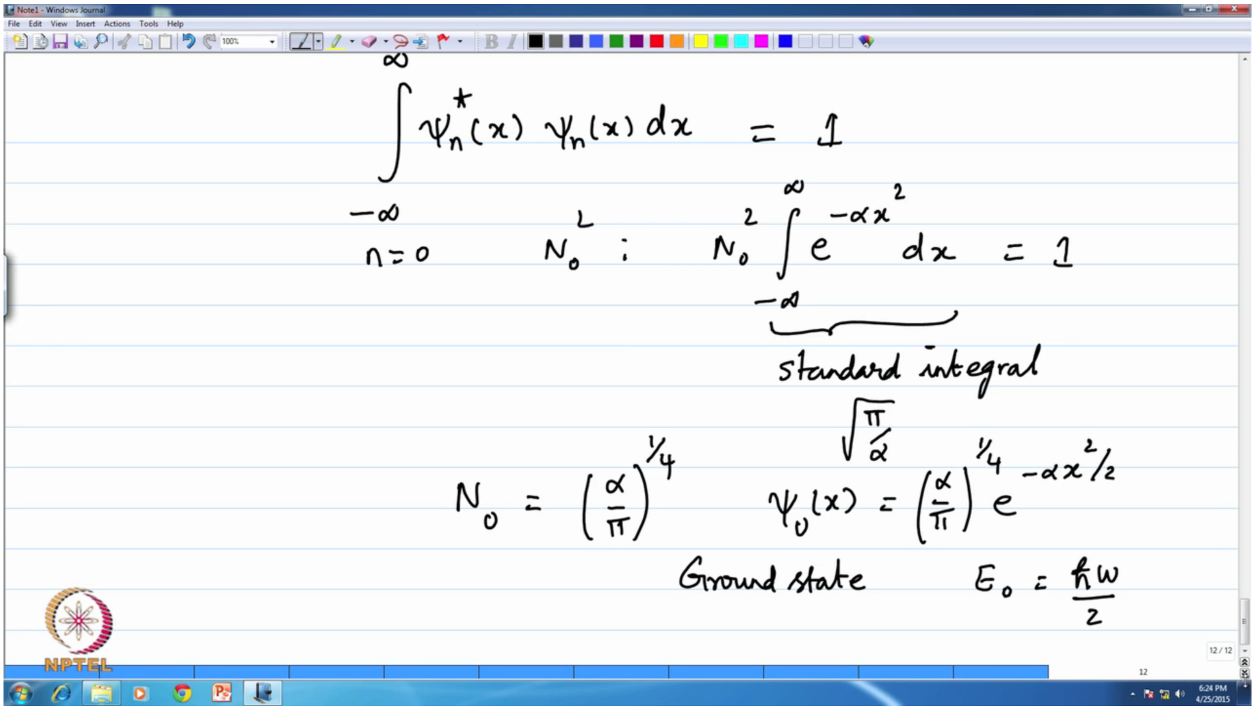
$$H_2(y) - 2y\,\underset{2y}{\underline{H_1(y)}} + 2\,\overset{1}{\cancel{H_0(y)}} = 0$$

$$H_2(y) = 4y^2 - 2$$

$$H_3(y) = 8y^3 - 12y.$$

$$\psi_n(x) = \underset{\uparrow}{N_n}\, e^{-\alpha x^2/2}\, H_n(\sqrt{\alpha}\,x)$$

So let me summarize this with the only other thing that I have not yet mentioned namely if we write $\psi_n(x)$ as a normalization constant N and an exponential $e^{-\alpha x^2/2}$ multiplied by the Hermite polynomial $H_n(\sqrt{\alpha}x)$. The one more unknown quantity that we have is the normalization constant N.



$$\int_{-\infty}^{\infty} \psi_n^*(x)\,\psi_n(x)\,dx = 1$$

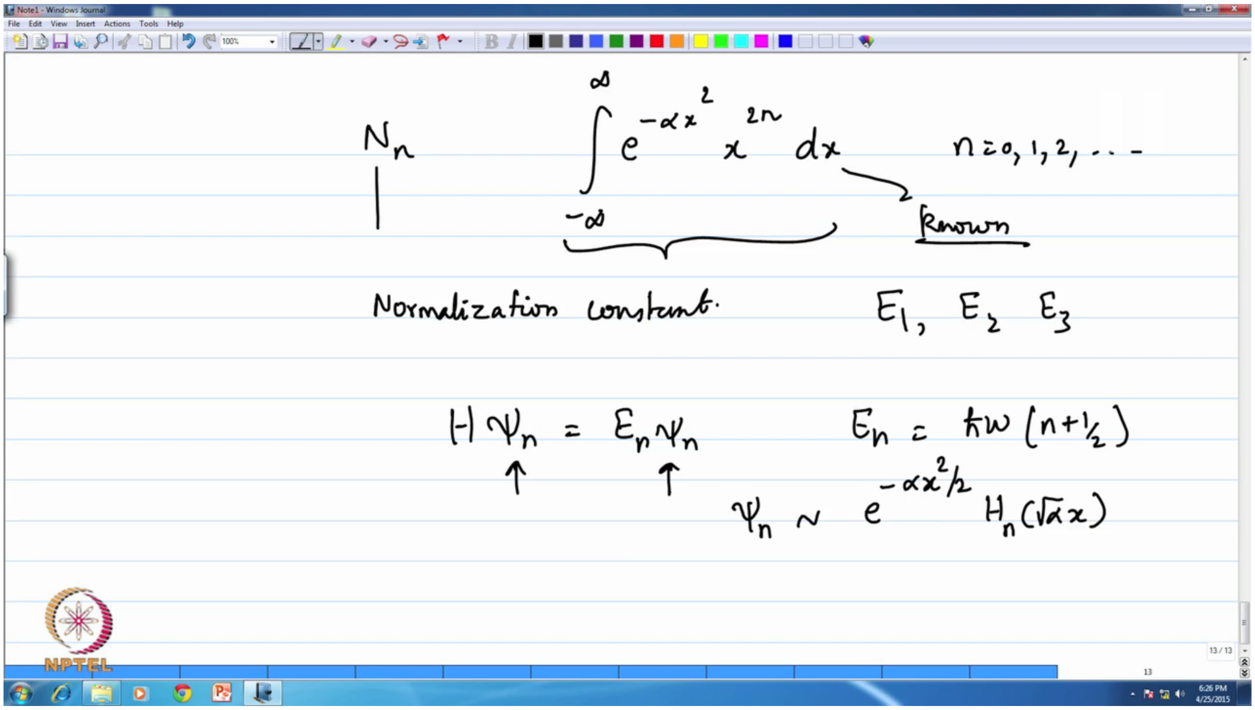
$$n=0 \qquad N_0^2 : \qquad N_0^2 \underbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2}\,dx}_{\text{standard integral}} = 1$$

$$\sqrt{\frac{\pi}{\alpha}}$$

$$N_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} \qquad \psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

Ground state $\quad E_0 = \dfrac{\hbar\omega}{2}$

And of course N is such that the ∫ ψ_n^*, which this case is the same as $\psi_n(x)$ $\psi_n(x)dx$ between the limits - ∞ to ∞, because the harmonic oscillator position coordinate can go the negative direction as well as in the positive direction, and if you take this theoretical limit that the x can go all the way to - ∞ and to ∞, then the normalization constant requires this condition namely -- can be obtained from this condition namely $\psi^*_n(x)$ $\psi_n(x)dx = 1$, which for n=0, for example if you want to know what dm_0^2 is that's obtained as follows, namely $N_0^2 \int e^{-\alpha x2}$ dx between - ∞ to ∞ is 1, because the Hermite polynomial for n=1 is 1, and this is a standard integral. Its value is known. This integral is $\sqrt{\pi/\alpha}$, therefore, the harmonic oscillator normalization constant $N_0 = (\alpha/\pi)^{1/4}$, okay. Thus, ψ_0 what is called the ground state wave function or the lowest energy solution. $E_0 - \hbar\omega/2$, because n + ½ will give you only ½, n is 0, $0 = \hbar\omega/2$ and $\psi_0(x) = (\alpha/\pi)^{1/4} e^{-\alpha x2/2}$, okay.



N_n

$$\underbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2} x^{2n}\, dx}_{} \rightarrow \underline{\text{Known}} \qquad n = 0, 1, 2, \ldots$$

Normalization constant.

$E_1,\ E_2\ \ E_3$

$$\underset{\uparrow}{H\psi_n} = \underset{\uparrow}{E_n\psi_n} \qquad E_n = \hbar\omega\left(n+\tfrac{1}{2}\right)$$

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

In a similar fashion, one can calculate N_n by having the normalization constant evaluated using these types of integrals, $e^{-\alpha x2}$ x^2n -∞ to ∞ dx. If you know the value of this integral for all values n = 0, 1, 2, 3 et cetera, then it's possible for you to calculate the normalization constant N_n.

In some of the problems and quizzes that follow this lecture, I would suggest that you calculate these constants for the first excited state or the second energy state like E1, E2, E3 et cetera. You can easily calculate this using simple integral formulas and this integral is known from integral tables, okay. You can also calculate this using elementary integration. So the solutions therefore $H\psi_n = E_n\psi_n$ or given as $\hbar\omega$ (n+½) and the ψ_n as $e^{-\alpha x2/2}$ $H_n(\sqrt{\alpha}x)$.

In the next part, we will see what these things mean in terms of a pictorial representations and also what the probabilities and an important concept known as the zero-point energy. Thank you.