Chemistry Atomic Structure and Chemical Bonding

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Lecture -29
Hermites Differential Equation

Welcome to the lectures in chemistry and the one the topic of atomic structure and chemical bonding. My name is Mangala Sunder and the I am in the Department of Chemistry Indian Institute of Technology as a professor of chemistry. The email ids are given below for you to write to me or for any other contact related to the course materials. This lecture is a follow-up on the last lecture on the infinite series representation and infinite series solution.

What is known as the power series solution for the differential equations. As the first serious example we shall look at the Hermite's differential equation, which is the basis for solving the harmonic oscillator problem and also getting the exact eigen functions.

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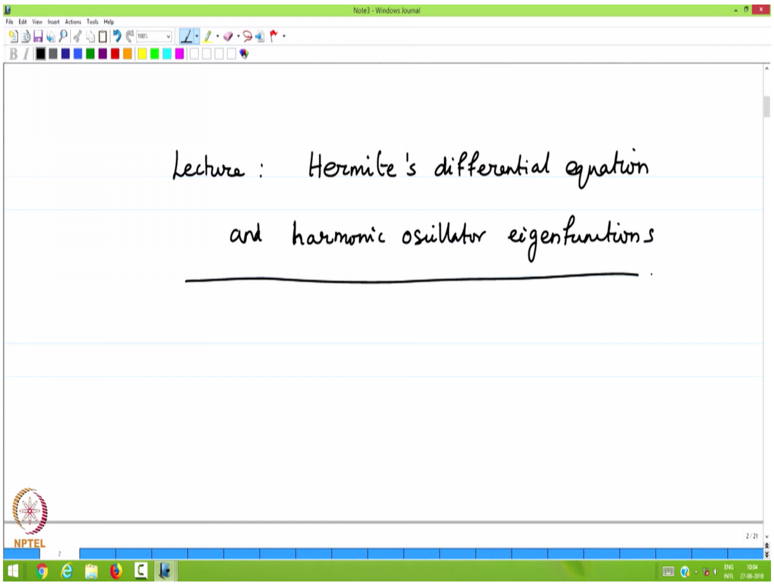

So, please remember the 2 most important aspects of the last lecture on power series or 1.

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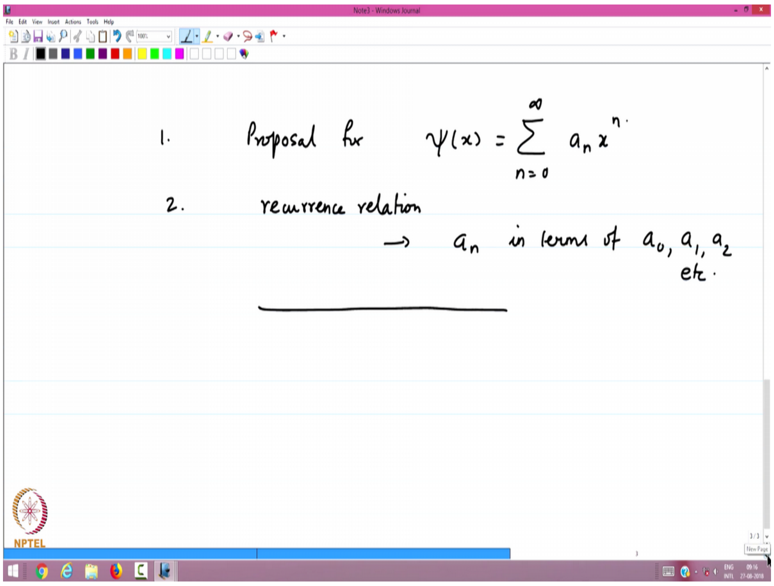

A proposal for the wave function solution, in terms of say in the case of 1 dimension as an x coordinate a solution in terms of an infinite series indexed by the integer n in x raise to n and then the second is a recurrence relation, which determines coefficients a n in terms of other coefficients.

In terms of a naught a 1 etcetera a 2 etcetera. So, these 2 things will be again the important aspects of today's this lecture on the Hermite's differential equation.

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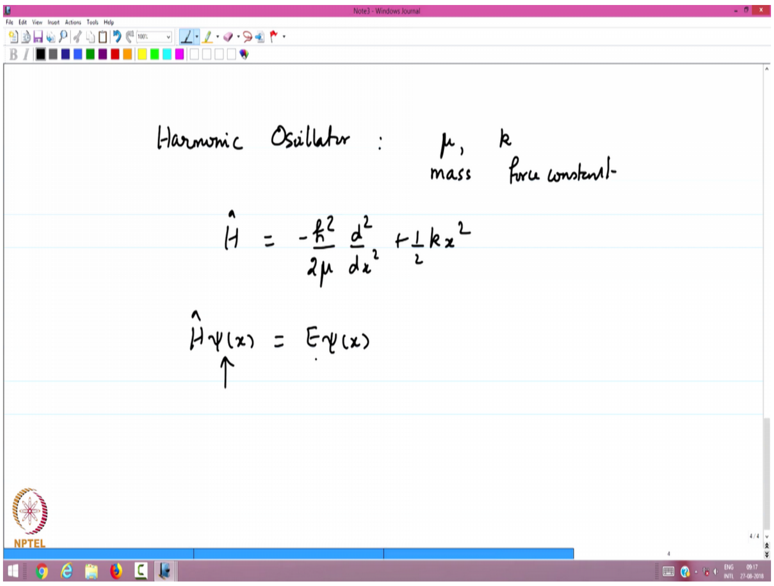

First let us recall the harmonic oscillator, Hamiltonian for a an oscillator with the mass mu and a force constant k, the Hamiltonian is minus H bar square by 2 mu d square by dx square plus half kx square kinetic energy and the potential energy. Therefore, the solution that we are looking for is the H psi of x is equal to e psi of x, this is the differential equation and the solutions are psi and e.

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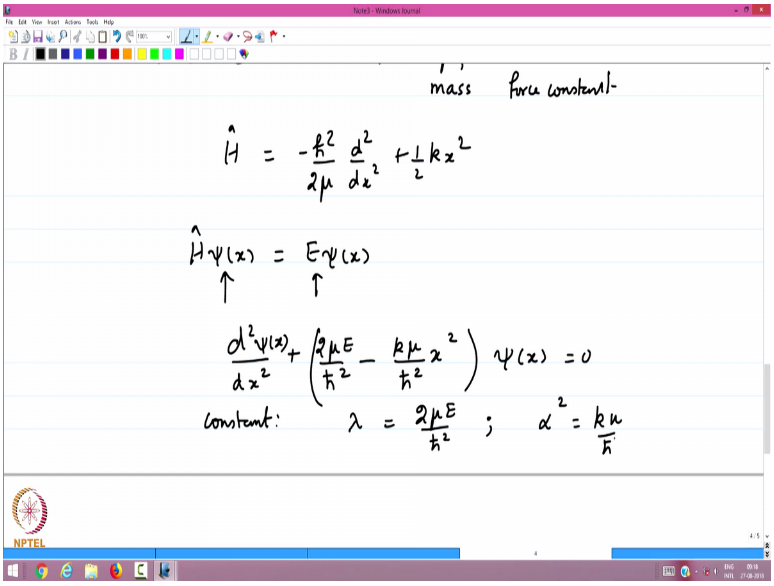

Therefore if we rewrite the differential equation we will have d square psi by d x square plus 2 mu e by h bar square minus k mu by h bar square x square psi of x is equal to 0 stay of x is equal to 0. Now let us introduce the constants, as introduced lambda as 2 mu E by h bar square and another constant alpha square as k mu by h bar square.

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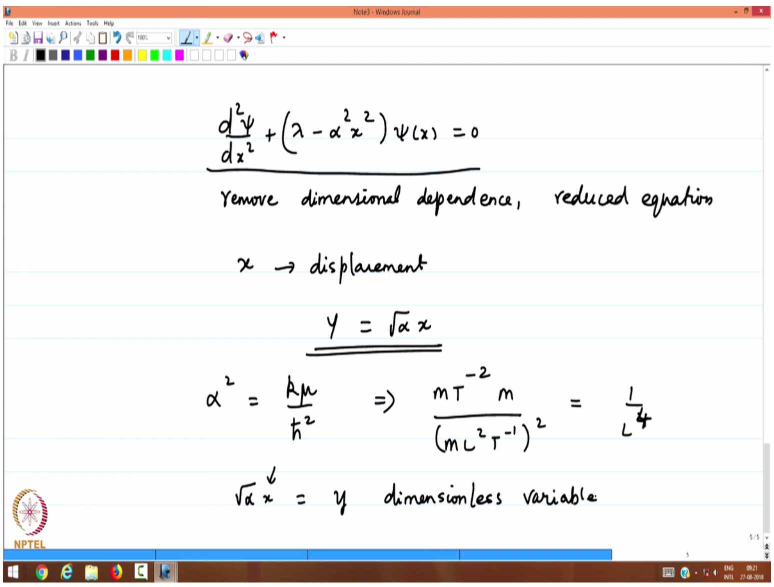

Then the differential equation is d square psi by d x square plus lambda minus alpha square x square psi of x is equal to 0.

Now, the idea of writing different constants and also the equation in a different way is to remove the dimensional dependence and write a reduced equation using variables which do not have dimensions. Here please remember x has the dimension of the displacement that is the length of the oscillator from the equilibrium displacement from equilibrium therefore, there is a physical aspect of the harmonic oscillator which is part of the mathematics and then you have the Planck's constant h bar, you have the energy which is also a dimension the quantity, the mass of the oscillator all these things are there which are specific to the oscillator itself.

Let us remove the oscillator specific details and we will write an equation which will be applicable to all oscillators independent about the masses and so on this is done in physics usually using dimensionless variables instead of the dimensional equation. So, let us introduce your dimensionless variable Y is equal to root alpha x and see Y it is a dimensionless variable. If you recall the definition of alpha it is alpha square is k mu by h bar square, alpha square k mu by h bar square, k is the force constant the dimension of k is mass per square inverse mass times inverse square of time and the reduced mass mu is also mass and h bar square leaving the angles out, it is basically mass length square T minus 1 whole square because it is a square of the plancks constant.

So, the definition of alpha square is such that the dimension of alpha square is 1 by L square and 1 by L to the 4 because the other things cancel off. Therefore, root alpha times x if you define that as y x having the dimension of the length and square root of alpha being one by length y is dimension to the dimensionless variable. Therefore, to do that let us go back and write the differential equation again.

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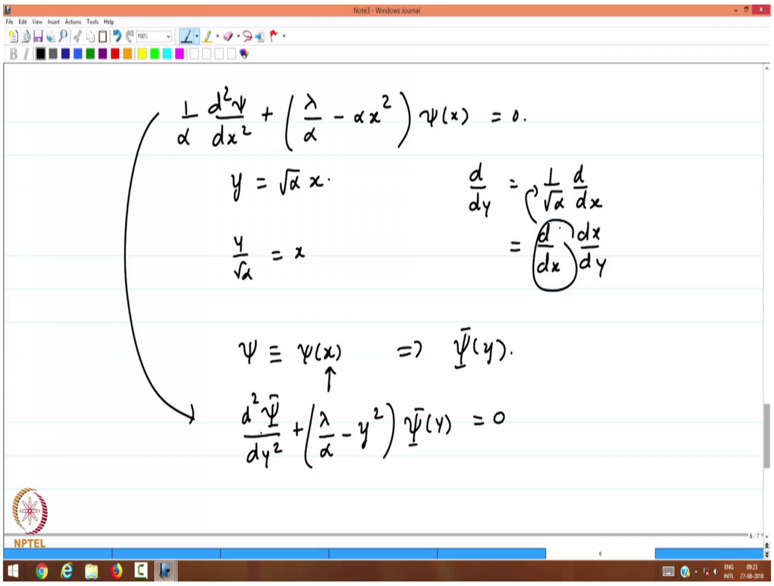

D square psi by dx square times 1 by alpha plus lambda by alpha minus alpha x square psi of x is equal to 0 and then introduce now y is equal to root alpha times x, therefore, d by dy will be one by root alpha d by dx ok, d by dy is d by dx and dx by dy and you know x therefore, this is that.

So, the equation now becomes the function psi is a function of x. Now we replace x by y it is a different function, so let us call this a psi of y. Therefore, the differential equation this one becomes d square psi by dy square plus lambda by alpha minus y square psi of y is equal to 0. So, this is the differential equation in which the parameters related to the harmonic oscillators have all been removed, there is of course, lambda by alpha, but we will find that out. So, how to handle it, but the variable y is a dimensionless variable.

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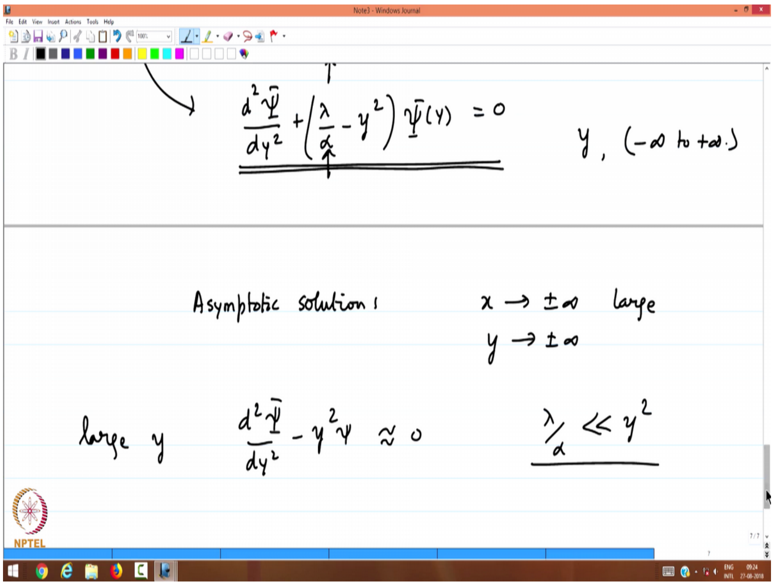

So, this differential equation namely this is valid for all values of y namely from minus infinity to plus infinity. So, in dealing with differential equations of this kind which take the entire range of real very real values the first is to look at the asymptotic solutions.

Asymptotic solutions refer to x going to plus or minus infinity large values. For very large here of course, is y that goes to plus minus infinity therefore, for very large values of y is possible to ignore this contribution which is a constant and write the differential equation as d square psi by dy square minus y squared psi is approximately 0 and because lambda by alpha is much much less than y square large y.

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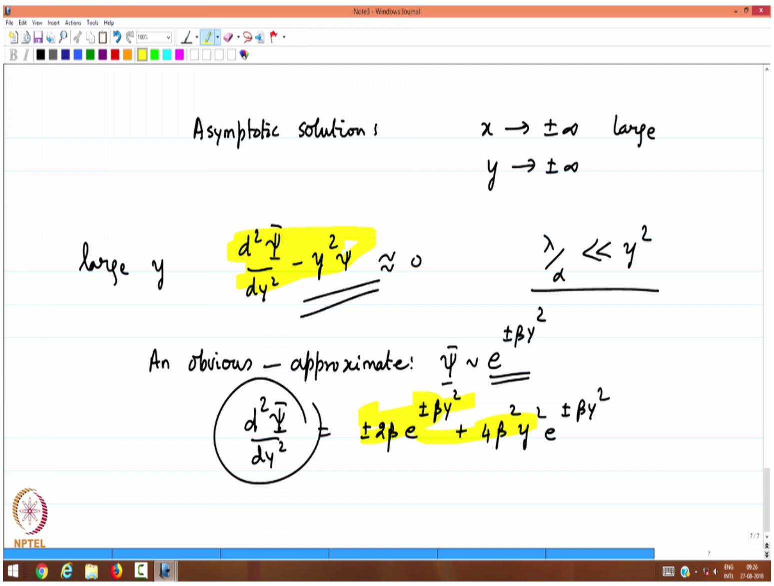

And for this equation an obvious solution, an obvious I would say approximate solution is e to the plus or minus beta y square. If we consider this psi to be approximately of this form e to the plus or minus beta Y square then you can immediately write d square psi by dy square is plus or minus 2 beta it is a simple derivative.

So, let me write the result e to the plus or minus beta y square plus four beta squared y square e to the plus or minus beta y square, that is this term and minus y square psi. So, if you want to write to the differential equation with the this and that.

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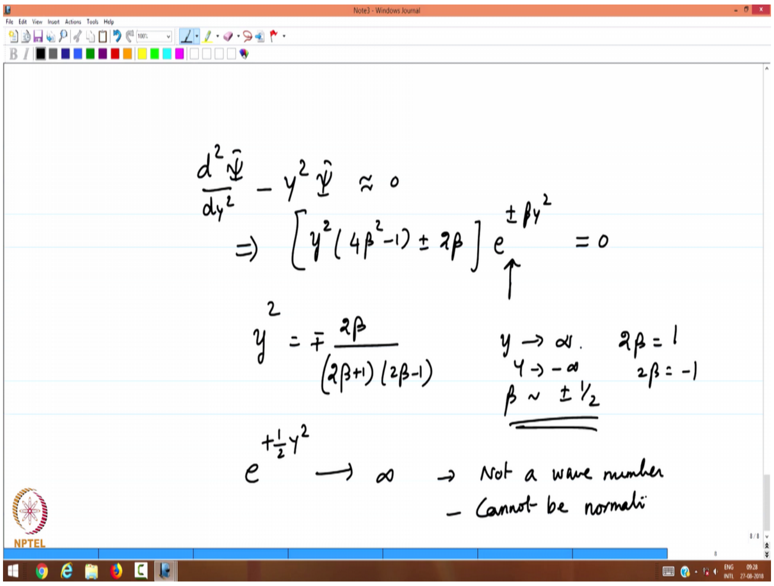

You will see that the equation that we have to write is d square psi by dy square minus y square psi is equal to 0 goes over to the condition that y square into 4 beta squared minus 1 plus or minus 2 beta times e to the plus minus beta y square is equal to 0. This never goes to 0 except that infinity.

Therefore the solution that you have to look at is y is equal to 2 beta or y square is equal to 2 beta by 2 beta plus 1 3 beta minus 1, this is a also the here this is y square. So, it is minus plus and the for y going to infinity; obviously, 2 beta is equal to 1 and you can see that the solution beta is plus minus half. It is y going to minus infinity of course, its 2 beta is equal to minus 1. Therefore, either way you have this, but the exponential function e to the plus half beta square half y square goes to infinity, therefore, it is not a wave function that we need or we would considered cannot be normalized.

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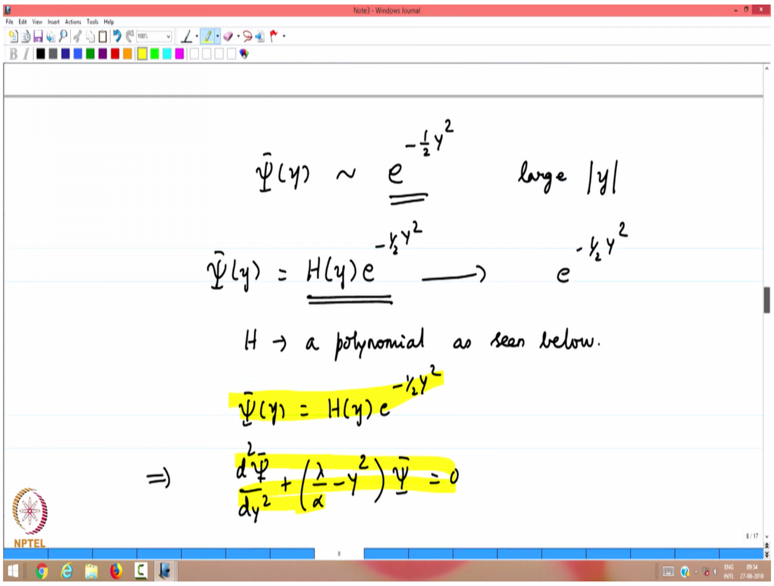

Therefore, let us take the solution psi of y for large values of y e to the minus half y square large y absolute value of y, to plus minus y does not matter the function has the same value. What is the exact solution that we are looking for therefore, psi of y is some function of y multiplied by e to the minus half y square such that for very large values of y this function behaves like e to the minus half y square. So, we need to introduce this function H and this H will turn out to be your polynomial as we will see soon. So, let us use this definition namely psi of y as H of y times e to the minus half y square and now consider the full differential equation d square psi by dy square plus lambda by alpha minus 1 minus y square psi is equal to 0.

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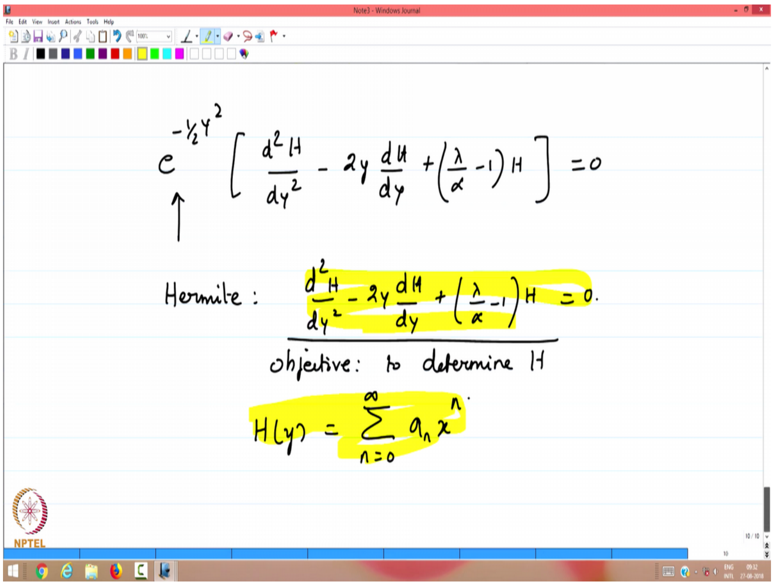

If you take the derivatives, you can see immediately this result namely e to the minus half y square times the second derivative of the function H minus 2 y the h by dy plus lambda by alpha minus 1 H. This would be 0, this is substituting this function in this equation. The differential equation that you get is the following and since this is valid for all values of y and this does not go to 0, the differential equation known as Hermite's differential equation is this for 1 d square H by dy square minus 2 y d H by dy plus lambda by alpha minus 1 H is equal to 0 therefore, our objective is to find out H to determine H.

Now, for doing that let us propose H of y is a power series namely sum over n equal to 0 to infinity, sum constant a n times x raised to n. So, at this point now you see that this is a starting point from the previous lecture on the power series therefore, this is a differential equation that we have to solve and this solution H if you recall is part of this solution namely the full solution the wave function is H of y multiplied by the Gaussian function e to the minus half y square therefore, the that the chain should be clear one should be able to follow the trails quite carefully.

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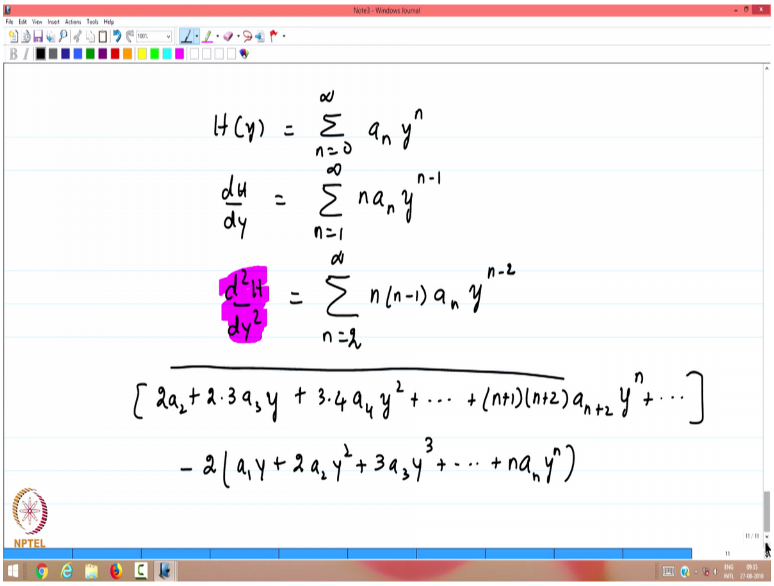

So, let us look at H of y given by this definition and then substitute the derivatives and the second derivatives and so on so. This is n equal to 0 to infinity a n x y raise to n, I am sorry it is not x it is y.

Where is to n and I think in the previous this is also y raise to n. d H by d y is the sum n equal to 1 to infinity n a n y n minus 1 and d square H by dy square is the second derivative namely n equal to 2 to infinity n into n minus 1 a n y n minus 2 ok. This we will substitute in the differential equation here a square H minus 2 yd H by dy this one. So, when you do that the substitution gives you the following, 2 a 2 plus 2 into 3 a 3 y plus 3 times 4 3 into 4 a 4 y square plus etcetera plus n plus 1 into n plus 2 a n plus 2 y raise to n plus etcetera.

This is the first term and this term is essentially this one, d square H by dy square. The next term is minus 2 d H by if you recall the next term is minus 2 y d H by d y therefore, d H by d y every term is multiplied by y to give you a 1 y plus 2 a 2 y square plus 3 a 3 y cube plus plus n a n varies to n and the last term is of course, the H itself multiplied by lambda by alpha minus 1.

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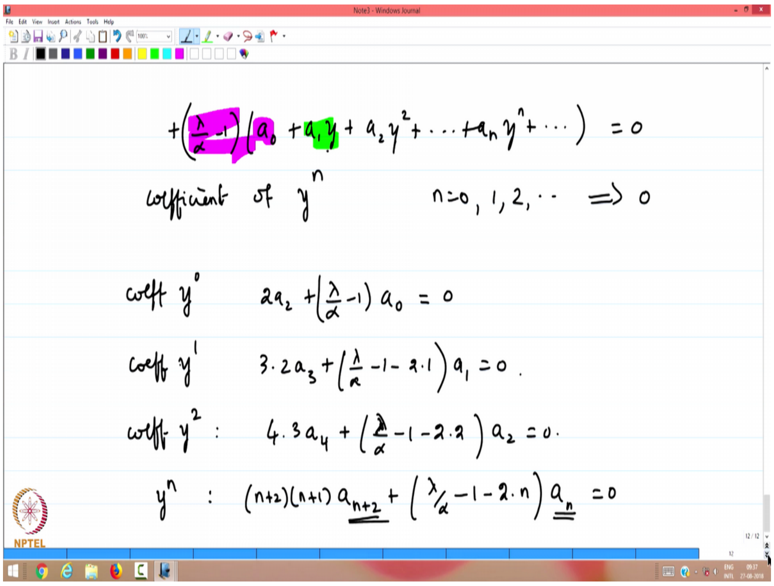

Therefore the last term is lambda by alpha minus 1, times H which is a naught plus a 1 y plus a 2 y square plus a n y raise to n plus so on is equal to 0.

As usual we will see that every term is either a constant or a power of y. So, we will equate each coefficient of y to the power n, n equal to 0, 1, 2, 3, etcetera, each one we will set it to 0 in order to obtain the solutions in final form therefore, the first term if you look at to the coefficient of y raise to 0 that is the constant term. If you look at you can see immediately that the terms are 2 a 2 there is no power of y here and then that is also lambda by alpha minus 1 times a 0. So, these are the only 2 terms without any y therefore, the first term is 2 a 2 plus lambda by alpha minus 1 a 0 is 0 and the coefficient of y to power 1 you can see it immediately here.

2 times 3 a 3 y minus 2 times 2 a 1 y and then there is a 1 y. So, again you can see this relation namely a 3 and a 1 are connected, a 2 and a 0 are connected and you can see this kind of odd even relationships and most of these equations coefficient of y 1 y raise to 1 namely coefficient of y itself is 3 time 2 a 3 plus lambda by alpha minus 1, minus 2 times 1 a 1 is equal to 0. So, let me write a couple of more coefficients here coefficient of y square is 4 times 3, a 4 plus lambda by alpha minus 1 minus 2 times 2 a 2 is 0 and likewise for the coefficient of y raise to n, the general term is n plus 2 into n plus 1 a n plus 2 plus lambda by alpha minus 1 minus 2 times n a n is equal to 0. N plus 2 and the n connected which means odd series and even series that you will have.

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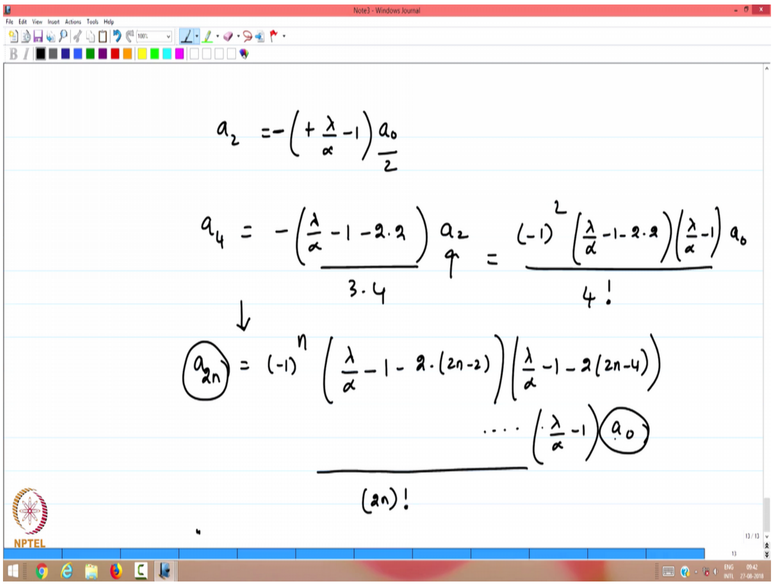

Therefore the coefficient a 2 is minus lambda by alpha minus 1 a naught by 2 and the coefficient a 4 is minus lambda by alpha minus 1 minus 2 times 2 a 2 by 3 times 4, which is given as minus 1 whole square if you substitute for a 2 from the above you get lambda by alpha minus 1 minus 2 times 2 times lambda by alpha minus 1 a naught divided by 4 factorial. The general term is a 2 n is equal to minus 1 raise to n half is a 4 is minus 1 square a 2 is minus here a 2 is minus 1 raise to n lambda by alpha minus 1 minus 2 times 2 n minus 2 lambda by alpha minus 1 minus 2 times 2 n minus 4. All the way down to the last one when the n is 0, n is 2 you will see that lambda by alpha minus 1 times a naught divided by 2 n factorial.

This is the recurrence relation between all the even coefficients a 0 a 2 a 4 etcetera all of them and of course, the old coefficient if you follow the same mathematics it is immediate to write this down.

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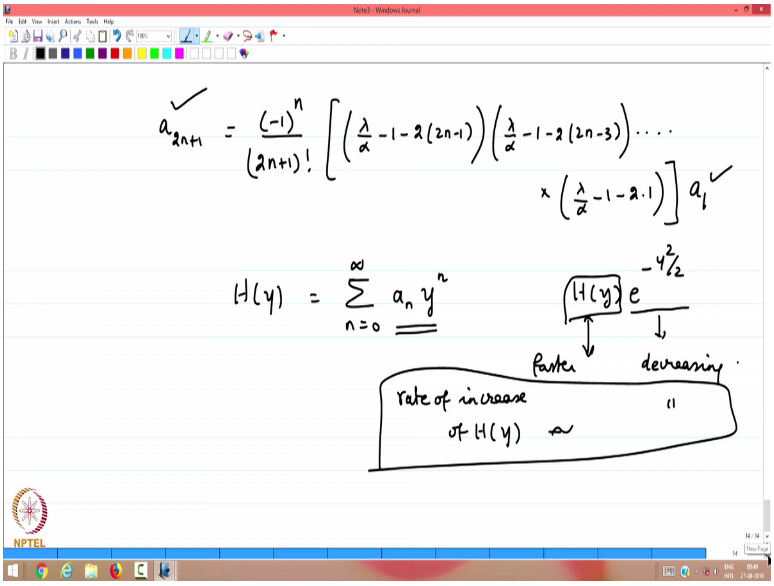

So, the coefficient a to the 2 n plus 1 is related to the coefficient a 1 by the formula, exactly the same way as above minus 1 is 2 n 2 n plus 1 factorial times lambda by alpha minus 1 minus 2 times 2 n minus 1 lambda by alpha minus 1 minus 2 times 2 n minus 3 all the way to lambda by alpha minus 1 minus 2 into 1 times a 1. Therefore, you have the relationship of a 1 to a 3 a 5 a 7, etcetera and the relationship of a naught to a 2 a 4 a 6, etcetera.

So, therefore, we know the H of y as an infinite series. The difficulty is that H of y is multiplying e to the minus y square by 2, it is important that H of y does not increase faster than e to the minus y square decreasing or at least the same as the rate. The rate of increase of H of y term by term if you look at it, it should be faster, it should not be even the same as that of this one because then the series will not converge, the product will not converge to give you a finite wave function, a the square of the wave function should go to a finite value when you integrate.

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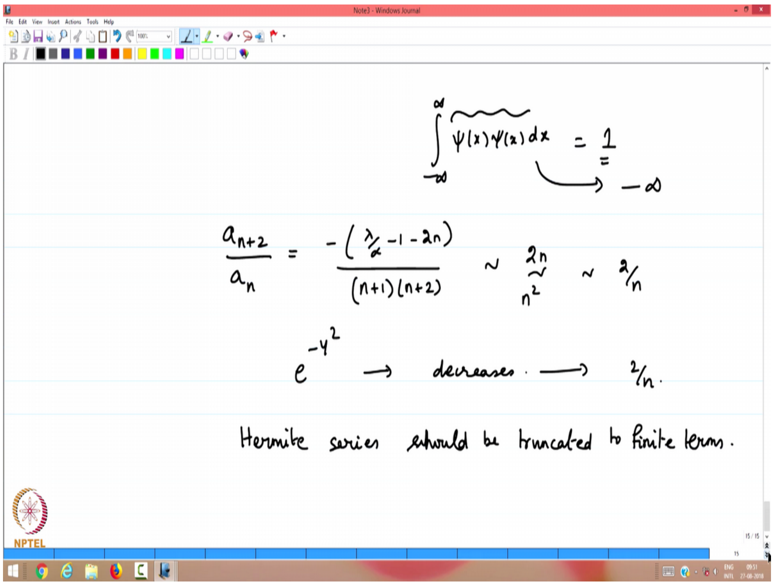

Remember ultimately we have to have this property psi of x dx from minus infinity to plus infinity this should be normalized to 1, if this tends to infinity then this function is not very good.

Take a quick look a n plus 2 if you take the ratio to a n then you will see that the term is minus lambda by alpha minus 1 minus 2 n divided by n plus 1 into n plus 2. So, this is of the order when n is very very large this lambda by alpha minus 1 is irrelevant, this is of the order 2 n by n square and the other terms can also go to they can be removed because the n is very large n square is the leading term. So, it is 2 by n. The unfortunate thing is exponential minus y square also decreases in the same order 2 by n.

So, we have problem if we take these two together that this function will not be Hermite polynomial, Hermite function the infinite series is not the right solution, but the Hermite function should be series should be truncated to finite terms. Only then the product function will be acceptable as a wave function for the harmonic oscillator problem.

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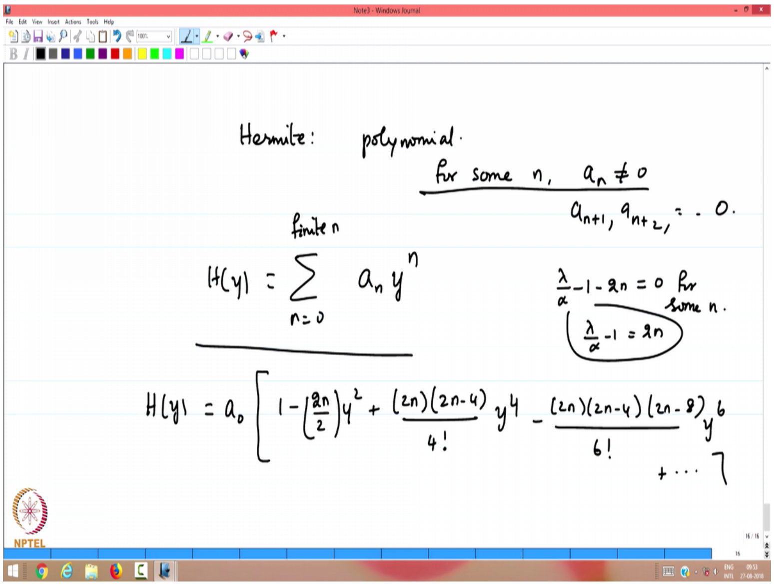

So, if you have to truncate this function then Hermite series should be a polynomial. What it means is that for some n a n may not be 0, but all the other terms a and plus 1 a n plus 2 all these coefficients should be 0 then the series is truncated to a finite value then you can write H of y as n equal to 0 to some finite n a n y raise to n. This will be the requirement in order for the wave function to be normalizable. So, if you have to make this to a finite value that is the right the H of y based on the a n s we have written down so far the even terms are all a n 1 minus 2 n by 2 y squared plus 2 n minus times 2 n minus 4 by 4 factorial y raise to 4 and so on. So, what we have assumed is that lambda by alpha minus 1 minus 2 n is 0 for some n and therefore, lambda by alpha minus 1 is equal to 2 n that is put in here.

Then you have let me write the next term for the series minus 2 n times 2 n minus 4 times 2 n minus 8 divided by 6 factorial y raise to 6 plus etcetera, this is the even number of terms.

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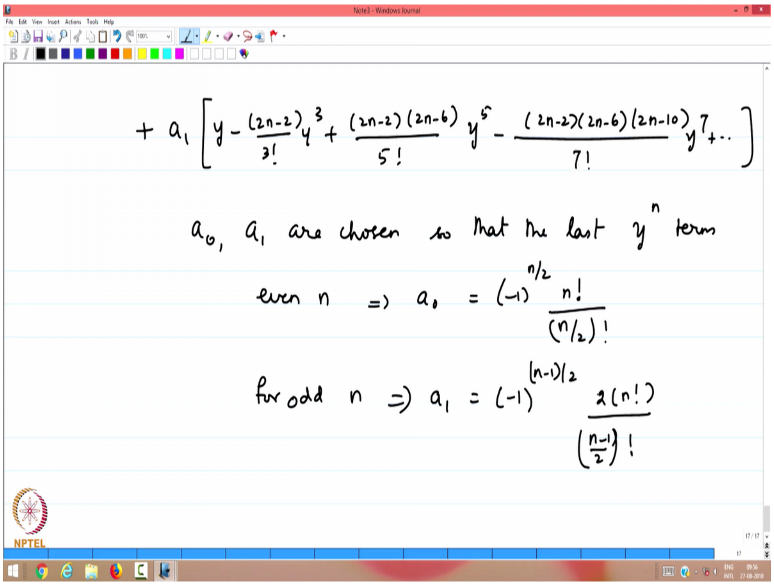

And the odd coefficients are all connected to a 1 they will be y minus 2 n minus 2 by 3 factorial y cube plus 2 n minus 2 times 2 n minus 6 by 5 factorial y raise to 5 minus 1 more term I will write 2 n minus 2 2 n minus 6 2 n minus 10 divided by 6 factorial y raise to 7 plus etcetera. But it is truncated to the value n, what is the value of n? n can be 0, n can be 1, n can be 2 each n gives you 1 Hermite polynomial. So, the truncation is important in the sense that the physical parameters lambda by alpha.

So, let me highlight these the physical parameters are there in lambda and alpha, remember lambda was given in terms of if you go back to the lecture very early on, you can see what was the definition of lambda. From the differential equation we had put in lambda is equal to 2 mu e by h bar square. So, here is the physical constant and alpha is k mu by h bar square. So, lambda and all for determine the physical parameters and the physical parameters are chosen such that this condition is approximately valid lambda by alpha minus 1 is 2 n then the Hermite polynomial is truncated to the last term, only to that term.

And the convention is to choose for Hermite polynomials the constants a naught and a 1 are chosen so that the maximum term, so that the last y raise to n term, has the coefficient as follows. For even n a naught is chosen as minus 1 raise to n by 2 n factorial by n by 2 factorial and for odd n is possible for us to write this. This is a convention in the choice of the Hermites solution a 1 is written as minus 1 to n minus 1 by 2 times 2 n factorial divided by n minus 1 by 2 factorial. This is the highest term that is the y raise to n th term therefore, with this convention now we can write the Hermite polynomial as follows.

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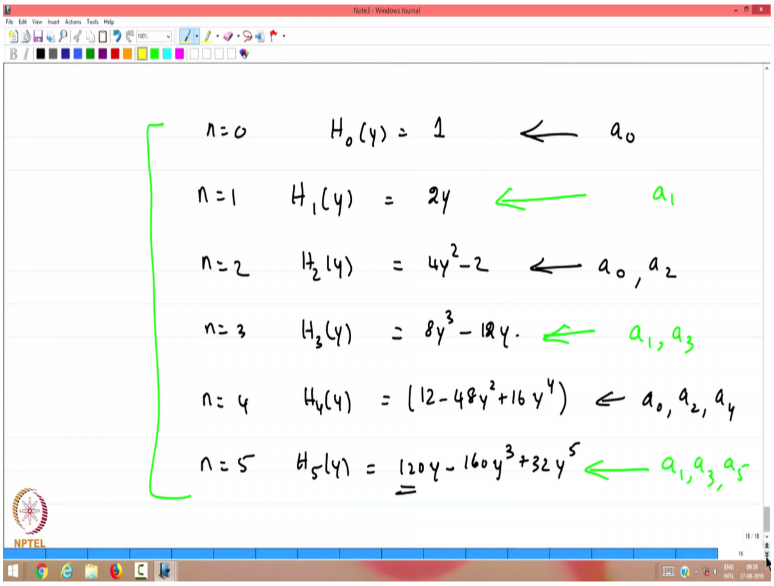

The first Hermite polynomial namely when n equal to 0 the H 0 of y will become 1 ok, it is just a naught.

Which you can see right away, that if n is 0 all of this gets to 1, 0 factorial is 1. If you choose n equal to 1 the H 1 of y will give you the value 2 y, which is also easy to see, you are only retaining the first term you are not keeping because now n is limited only to 1 therefore, when n is 2 this term goes to 0 all the other terms go to 0. So, when n is 1 you have the odd n here minus 1 raise to n minus 1 to n factorial is 1 and then you have n minus 1 by 2 factorial that is also 1. So, you have 2 therefore, the coefficient a 1 is 2 and therefore, the expression is 2 y. So, likewise n equal to 2 H 2 of y becomes 4 y square minus 2 n equal to 3 h 3 of y becomes 8 y cube minus 12 y.

You see that this means a naught this also means a naught and a 2 and let me write 1 more term n equal to 4 H 4 of y is equal to 12 minus 48 y square plus 16 y raise to 4, this means only these 3 coefficients a naught, a 2 and a 4 are chosen and n has the value and y n equal to 5 is the last term. I will write H 5 of y which is 120 y minus 160 y cube plus 32 y 5 and all these numbers come from the choice of those things therefore, this you can see now this is a 1 this is the choice of a 1 and a 3 this is the choice of a 1, a 3 and a 5. So, the Hermite polynomials are such that you see that the reason even polynomial the reason odd polynomial depending on which constant you choose and these coefficients are connected by the recurrence relations that we had earlier. This is the recurrence relation that we had and in this therefore, we have chosen the condition that lambda by alpha minus 1 is equal to 2 n. So, when n is 0 of course, you get a 0 when n is 1 you get a 1 and so on therefore, what is the final solution now?

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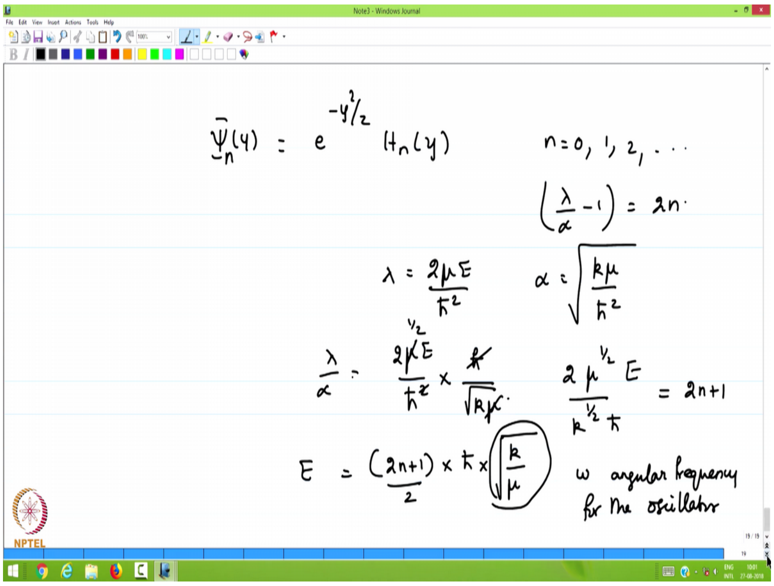

The final solution psi of y is e to the minus y square by 2 H n of y and since n is chosen as 0, 1, 2, 3, etcetera subject to the condition lambda by alpha minus 1 is equal to 2 n. Now let us look at lambda remember lambda is 2 mu E by h bar square and alpha is equal to alpha square was chosen as k mu by h bar square and alpha therefore, is basically square root of k mu by h bar square therefore, what is lambda by alpha if you do that its 2 mu e by h bar square into h bar divided by square root of k mu. So, you have mu to the one half this mu is gone and what is left over you have a h bar is gone.

H bar square you have a h bar down here therefore, lambda by alpha turns out to be 2 mu to the one half E by k to the one half and h bar and that is lambda by alpha and that is equal to 2 n plus 1. Therefore, what is E? E is equal to 2 n plus 1 into h bar into square root of k by mu divided by 2 and square root of k by mu you know is the angular frequency for the harmonic oscillator, for the oscillator.

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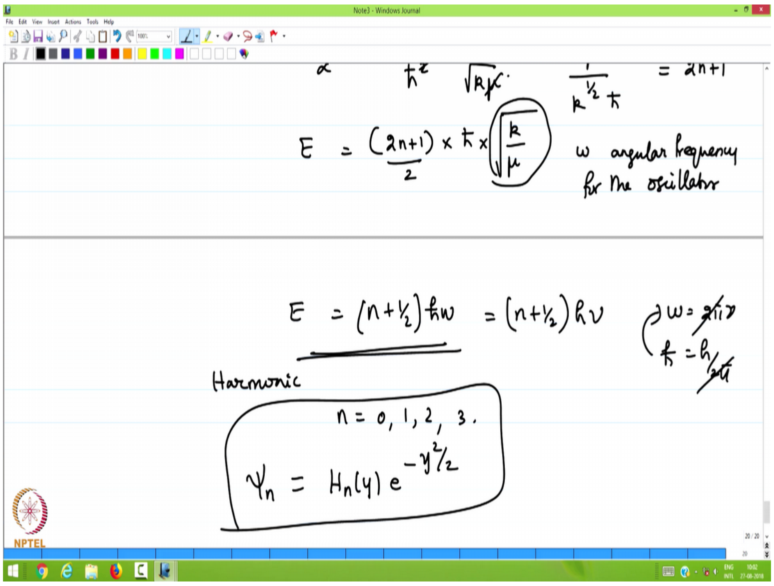

Therefore what you have is the energy E now in terms of the n values that you have chosen, E is given as n plus a half h bar omega, which is the same as n plus a half h nu since omega is equal to 2 pi nu and h bar is h by 2 pi therefore, they cancel out when you take the product of these 2.

So, you see that the energy expression for the harmonic oscillator is now given in terms of the n plus a half where the possible values of n or 0, 1, 2, 3 etcetera and the wave function psi n corresponding to this e n plus a half or this n is; obviously, H n of y e to the minus y square by 2. So, this is the sum and substance of the harmonic oscillator problem that we have the rest of it of course, I have already discussed in the harmonic oscillator model, how to normalize these functions and how to visualize the wave function as well as the square of the wave function and so on. Therefore, now you can connect to this let me leave you with the last conversion namely remember y is equal to root alpha x.

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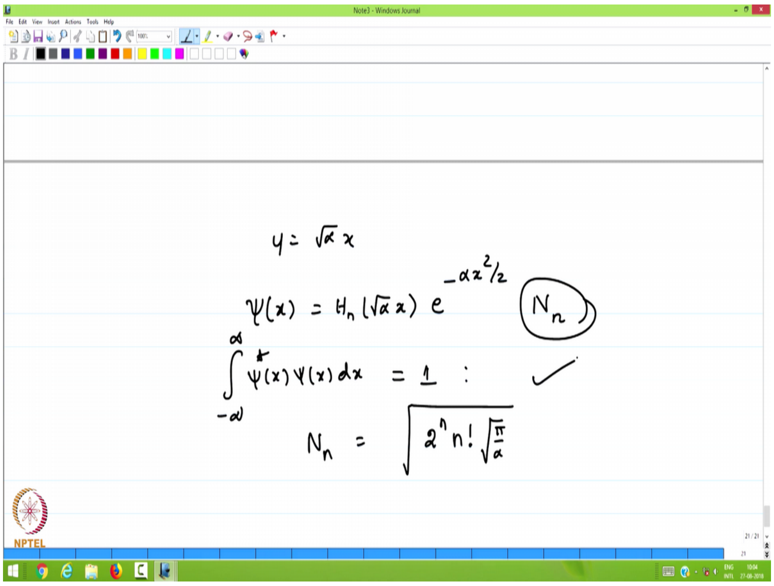

Therefore the wave function that we are talking about psi of x is now in terms of the variables that we have here it is H n of root alpha x and e to the minus alpha x square by 2.

The only thing that is missing is the normalization constant n such that psi of x psi of x integral d x psi star is of course, these are all real functions or we do not need to worry about the stock this is equal to 1. Therefore, you can calculate N of n and the general expression for N of n when you do the mathematics is also available and let me write that down. The general expression for N is 2 raise to n n factorial times root pi by alpha the whole square root that is the general factorial and therefore, you can see that the harmonic oscillator wave function, the harmonic oscillator energies are all obtained from the very simple differential equation namely the Hermite differential equation.

So, this whole exercise is to actually take you through the mathematics as in as detailed a manner as possible without worrying too much about to be the mathematical properties of some of these terms. But remember where the series comes from the series comes from the fact that the Hermite the infinite series is truncated to give a finite polynomial and the truncation means you truncate at various powers of n and various values of n.

Therefore you get a whole series of polynomials. What is the maximum value of n, n can go up to infinity all it means is that the harmonic oscillator will remain as a harmonic oscillator even for extremely large values of x, but that is a mathematical limit. Molecules do not oscillators do not they all become an harmonic even after a small amplitude therefore, these functions are important in understanding the one important part of the analytics analytical solution to the economic chemical problem namely the differential equation for the harmonic oscillator and the Schrodinger equation.

We will see only one more such equation namely the spherical harmonics which is also very important for all the angular momentum problems and therefore, I will take you through the infinite series solutions for the Legendre. And the associated Legendre polynomials in the next lecture and with that this part of mathematics is to give you a feel that things are not hands or I mean they are not you do not wave your hands, but you actually sit down and do the mathematics carefully.

Thank you very much.