Introductory Quantum Chemistry
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Lecture - 20
Harmonic Oscillator – Orthogonality of Eigen Functions

Now, we have seen that the wave function has this particular form. And we have to determine this normalization constant which I have been denoted by the symbol N with the subscript n. So, what is the normalization condition?

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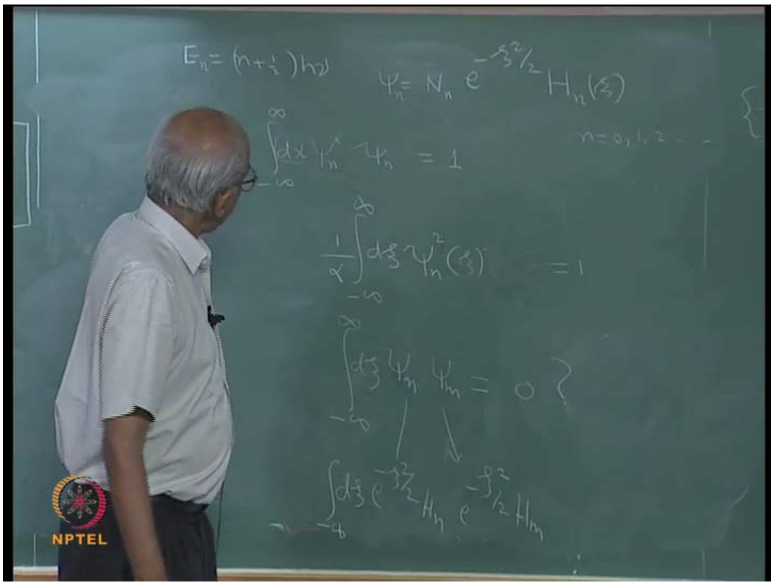

Well, normalization condition would imply that if I took psi star multiplied by psi; then remember I have to multiply it by d x integrate from minus infinity to plus infinity. And I have to ensure that this is equal to 1; that is the normalization condition. Now, to be very clear regarding the nature of the psi you see this is the way function for the nth stage that is indicate by the subscript n. So, it is better that I put a subscript n there also. And not only that as per as my allowed energy levels are concerned it is best if I put a subscript n; to indicate that this n depends upon the quantum number n. So, that means I am going to have an n here as well as there. But when you look at the form of psi you see you we are have been writing in terms X i everything is in terms of X i. And therefore even this d X i want to express it in terms of d X i right. **And** that is very easy because here I have the relationship X i is equals to alpha times x. So, that means d x must be d X i divided by alpha.

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So, therefore you will have integral d X i divided by alpha. So, let me put a 1 by alpha here minus infinity to plus infinity psi n star of X i psi n of X i equal to 1; this is the condition that I need to satisfy. And in fact what happens is in this case the wave function does not depend upon there is no square root of minus 1 occurring in psi. So, therefore this star is irrelevant, star does not affect the function because everything in there is real. So, I can remove the star. And therefore effectively what it means is that I would have the condition; I would have the things psi n square sitting there. But then suppose I have taken psi n and multiply it by psi m and then d X i integrated from minus infinity to plus infinity. What would you expect to happen; n and m are not the same; remember we discussed the same kind of thing in case of particle in a box. And we would expect that the 2 functions are orthogonal and therefore, this should be equal to 0; this is something that we would expect, we have no proof of that, but this is something that we suspect is varied.

So, therefore you look at this if you are looking at this expression what happens is you have e to the power of minus X i square by 2 right; psi n would have e to the power minus X i square by 2 and H n correct. And this one would have and e to the power of minus X i square by 2 and H m. So, therefore I want to evaluate the integral from minus infinity to plus infinity of a product which involves e to the power of minus X i square by 2 times effectively e to the power of minus X i square multiplied by H n, multiplied by H m. And I want to integrate it from minus infinity to plus infinity this is what I want to evaluate.

But H n itself you see the expression is not very simple, it is somewhat complicated. Because we have seen the expression today morning; it is there in your notes, H n may be obtained by this kind of formula right. Well, maybe I should just write it to remind you how it looks like?

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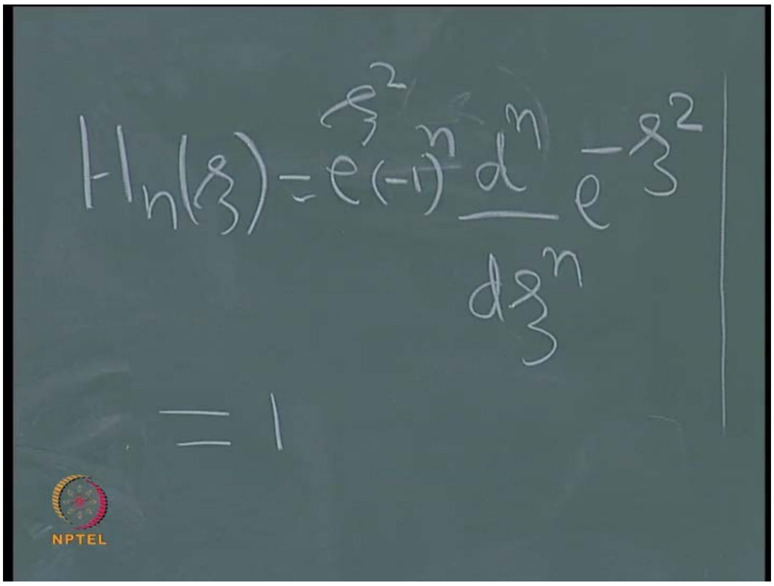

So, this is the formula for H n. So, if I try to evaluate this integral by the usual methods, it is rather difficult. And that is where the generating function is extremely useful; all the integral that you want in connection with normalization, orthogonality everything can be evaluated in an extremely simple fashion. And so let me demonstrate that to you see this is my S, this expression is my S. So, suppose I write this generating function once more; this time what I will do is I will not use the variable s, but I will use a different variable.

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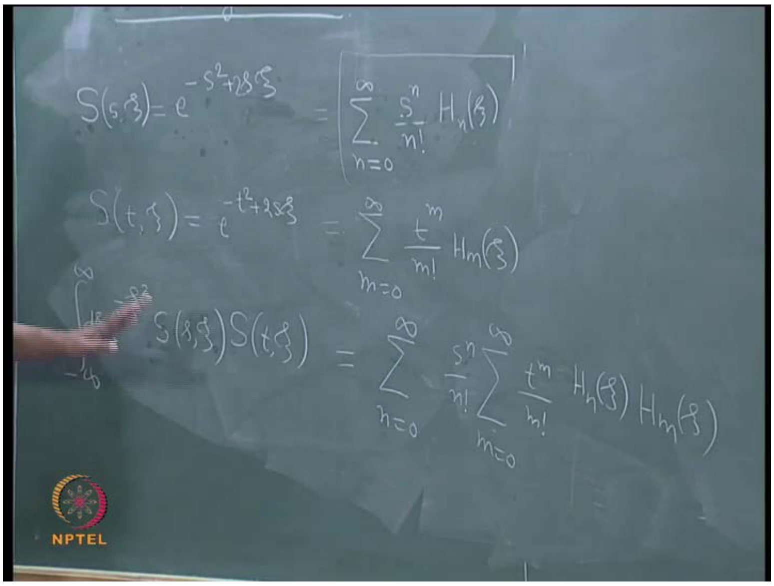

So, suppose I write this generating function once more; this time what I will do is I will not use the variable S. But I will use a different variable which I shall denote as t and I shall write an expression for S (t, X i); it would naturally be given by e to the power of minus X i square plus 2 t X i. And this you have to expand as a power series; earlier the expansion was a power series involved a power series in S. But now it will involve a power series in t; and what I will do is I will say I will write t to the power of m divided by m factorial multiplied by H m X i. And naturally you see you have the all some over all possible values of m which will run from 0 to infinity. And you will find that you see these 2 functions as the I have written are extremely useful and we are going to use it.

Now, you look at the integral that I want to evaluate I want to have an H n and I want to have an H m. So, you would realize that if I multiply these 2; I would definitely have H n and H m occurring in the product that is the idea right. But I want not only H n and H m I also want which one I want e to the power of. If you look at this integral there is H n there is H m these 2 together is e to the power minus X i square. So, I want that also. So, therefore what I will do is I will think of this integral e to the power of minus X i square into S of s X i S of t into X i. And I will multiply this into d X i integrate from minus infinity to plus infinity right; why do I do that it is fairly obvious now.

Because the right hand side will be sigma first one may be written as sigma n going from 0 to infinity; s to the power of n by n factorial. And that will be multiplied by H n of X i right and then I will have sigma m going from 0 to infinity multiplied by t to the power of m by m factorial and H m of X i. All that I have done is I have just substituted the expansions for these two nothing more, no manipulations, nothing has been done; all that I am doing is this is defined to be equal to that, while that is defined to be equal to that. So, just multiply the two together and you get this result. And then of course you will have to put in e to the power of minus X i square right because you have to have that. And then what we would do you will multiply by d X i and integrate from minus infinity to plus infinity. But you see none of these things are dependent up on X i. So, the integral will actually come here right.

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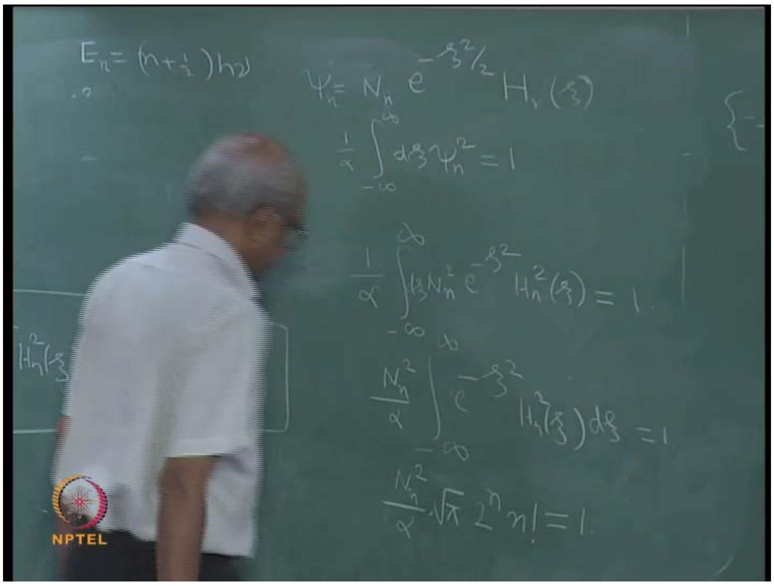

I do have problems with space may be the normalization condition I can shift and write somewhere else. Normalization condition actually says this is the normalization condition; over this expression I am going to write appear.

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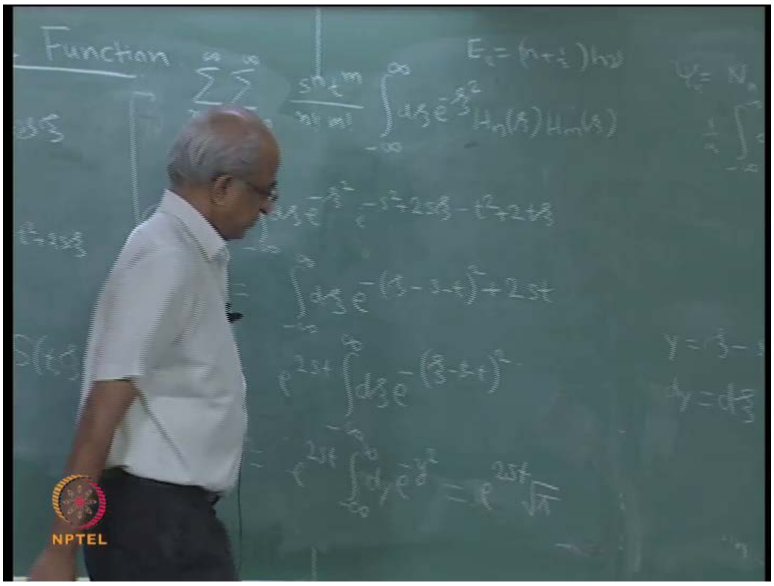

It is just a double sum with n going from 0 to infinity, m going from 0 to infinity, s to the power of n, t to the power of m divided by n factorial into m factorial. And integral d X i to the power of minus X i square H n of X i, H m of X i that is all. And what I am interested in is this is the value of this integral; I want to know the how much it is? In fact, I would like to know when n is equal to m; I would also like to know when n is not equal to m. In fact, I expect that the answer must be 0; when n is not equal to m. Now, you look at the left hand side, the left hand side is this on the left hand on the left hand side you find the variables S, X i, t and X i but X i you have integrated over. So, therefore the left hand side will depend upon the variables S and t. So, it is a function of S and t right. And the if you look at the right hand side you see the it is a function of S and t. And it is actually represented as a series involving s to the power of n, t to the power of m with n varying from 0 to infinity both varying from 0 to infinity.

So, suppose I find this function exactly what this function is and expanded it as a series. And looked at the coefficient of s to the power of n, and t to the power of m that coefficient should be equal to the integral that I want to evaluate correct. I can repeat the argument if you look at the right hand side it is an a series involving s to the power of n, t to the power of m. The left hand side if I evaluated it and then I will find a function. And that function if I can expand it as a series and find the coefficient of s to the power of n, t to the power of m that will be equal to the value of the integral that you want to evaluate. So, let us see whether I can evaluate this integral. In fact, what happens is this integral is easy to perform. Let us see why this is so easy to perform.

Let us see that let us look at the integral. So, this integral is equal to integral minus infinity to plus infinity d X i e to the power of minus X i square S is written here e to the power of minus s square plus 2 s X i. And the second function also is written there that is actually minus t square plus 2 t X i; that is all the integral is just that; I have just substituted for this s and that s that is all I have not done anything else. And now if you look at this you will find that it is minus infinity to plus infinity d X i; e to the power of interestingly what happens is that you can write the quantity in the exponent as X i minus s minus t the whole square. If you look at this expression there is a minus X i square minus s square minus t square. So, you can write it in this form, but that is not complete. In fact, everything will be fine; if I you just add it with a 2 s t the way to check that is you expand this and see that the answer is the same fine.

And, then you realize that t to the power of 2 s t is not depended upon the variable of integration. So, you can take it out. So, t to the power of 2 s t integral minus infinity to plus infinity d X i e to the power of minus X i minus s minus to t the whole square; that is what it is the integral. And now you can say the integral this makes the substitution X i minus s minus t is equal to y; X i is your variable of integration I am changing the variable of integration to a new variable which is y right; as far as this integral is concerned s and t are just constants I am going to integrate over X i. So, s and t are kept constant they are not going to affected. So, if you have y equal to psi minus s minus t then d y; obviously, will be equal to d X i. So, what will happen to this integral; it is going to be equal to e to the power of 2 s t into integral minus infinity to plus infinity d y, e to the power of minus y square that is all right.

And, this is a very easy integrant fragment I should not say very easy. Because it is not a what do we say it is not very straight forward to evaluate this. But because this is very well known I tend to say that is very easy; because it is very well known integral and the answer is actually square root of pi. So, you get the integral to be e to the power of 2 s t into square of pi. Any questions on this any points which is not clear?

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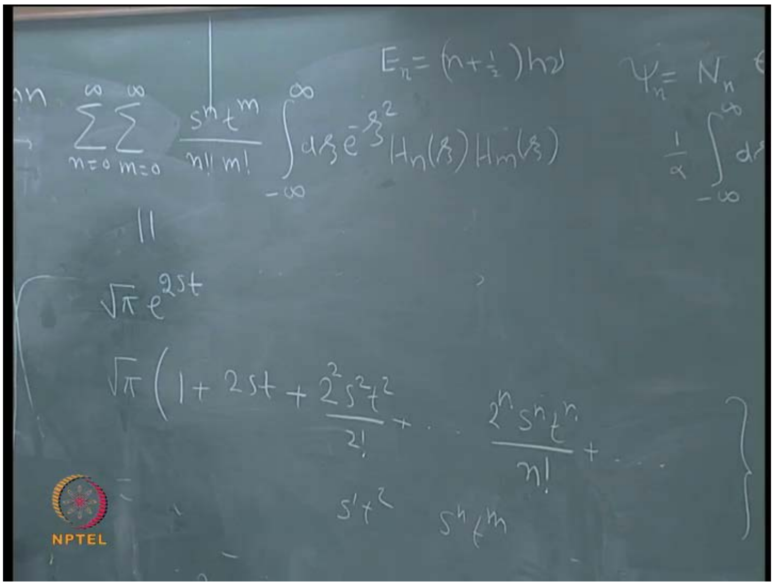

So, therefore what is happened is this series see I have never evaluated this series, the sum of the series is actually nothing but; this is nothing but how much root pi into e to the power of 2 s t right; this is actually equal to square root of pi into e to the power of 2 s t. But e to the power of 2 s t I know how to expand it? So, what will happen is I will get root pi into 1 plus 2 s t plus 2 s square sorry 2 square s square t square divided by 2 factorial plus in general 2 to the power of n, s to the power of n, t to the power of n divided by n factorial this is the series right. So, what do you find? You find that there are only terms which contain the same power of s and t; you do not have a term like s to the power of 1, t to the power of 2; you do not have such a term right or you do not have a term of the form s to the power of n, t to the power of m with n and m being different; such a term is not there in this expansion.

So, what is the conclusion? The conclusion is that an integral involving n and m different has to be 0, right. So, that is the way we evaluate this integral. And if n is equal to m what is the value? If n is equal to m then what will happen is that this actually has the value if n is equal to m the coefficient of s to the power n, t to the power of m is how much? See when n is equal to m let us say I will have s to the power of n, t to the power of n and you will have 2 to the power of n divided by n factorial multiplied by square root of pi, correct. So, therefore what happens is that is that I take the term with the n equal to m here right. If n is equal to m the term that is occurring to go occurring.

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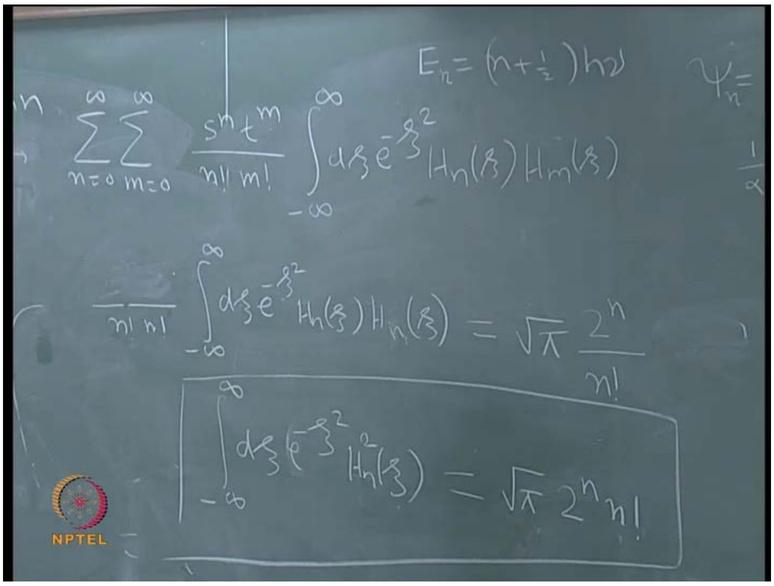

If n is equal to m the term that is occurring to go occurring there is if n equal to m that the term occurring there is s to the power of n, t to the power of n divided by n factorial divided by m factorial. Because n and m are the same integral minus infinity to plus infinity d X i to the power of minus X i square H n of X i H m of X i is equal to what? You will have that square root of pi which is sitting there 2 to the power of n divided by n factorial with of course, I mean I should say s to the power of n, t to the power of n. Because I have put s to the power of n here and t to the power of n there. So, this is what is going to happen and obviously that means, when I have made a slight mistake it is not m, but I have put m is equal to n here. So, you can actually remove s to the power of n and t to the power of n. And so what do you find? You find the answer that you wanted minus infinity to plus infinity d X i e to the power of minus X i square H n X i square is equal to how much? That is there are there is 1 by n factorial 2 times here. So, therefore you will actually get the answer root pi 2 to the power of n this 1 by n factorial square actually can be taken to the other side and you will get an n factorial.

So, this is the answer and the answer is very general it is violet for any n; and that is why I said it is the generated function technique is a very nice technique. Because I did not have to look at a particular value for the n I got the answers for all possible n in one shot; not only that I also found that the functions are all orthogonal. They all are orthogonal to one another which is another nice thing; I got all these results generating function. So, I finally what is the normalization factor? So, well there is my normalization condition. The normalization condition is here right and the way it is written is this. So, let us rewrite this I mean write this once more 1 by alpha integral minus infinity to plus infinity; psi n is given by that expression psi n is given by this expression. So, therefore I will put n n square into the power of minus X i square H n square X i is equal to 1; this is the normalization condition.

So, I can take this n n square out and n n square by alpha integral minus infinity to plus infinity e to the power of minus X i square H n X i square d X i is equal to o1. You see d X i is missing in this equation I better write it; but just we evaluated this part and that is written here. So, therefore m square by alpha times root pi 2 to the power of n; n factorial is equal to 1 or n n itself is equal to alpha by root pi 2 to the power of n; n factorial m half that is the normalization factor. And so finally what is the wave function for the nth state?

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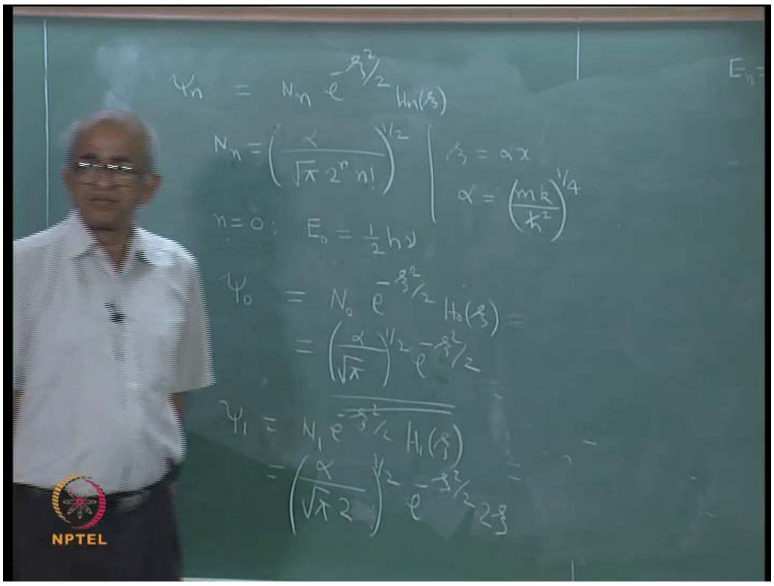

The wave function for the nth state psi n is equal to that n n into e to the power of X i square by 2 H n of X i. And n n is equal to alpha divided root pi 2 to the power of n n factorial to the power of half. And just to remind you X i is equal to alpha x; alpha is equal to m k divided by H cross square to the power of 1 by 4 right. We have to completely solve the Schrodinger equation for the harmonic oscillators that we want is here now. And then we look at the I mean it is not just enough to solve the equation; we have to look at the different possible levels of the system. Let us look at that. So, will I do not need this anymore.

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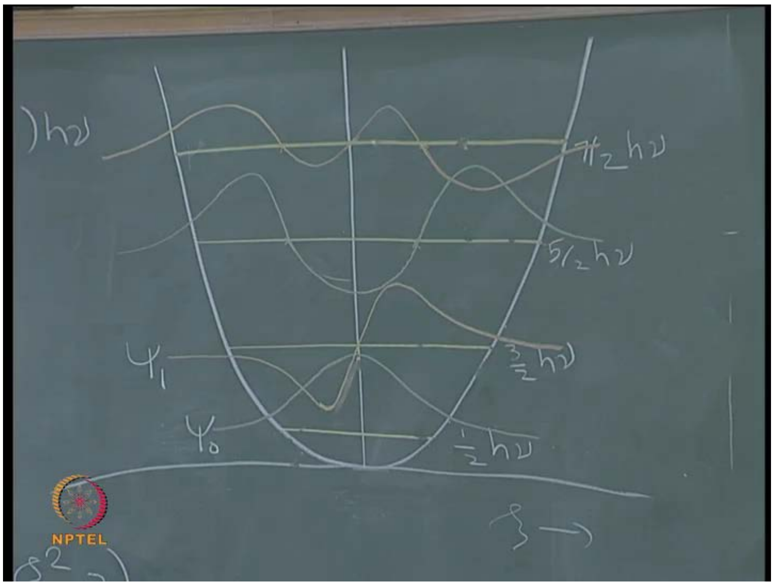

So, this is the potential energy of the harmonic oscillator latest look at the situation where n is equal to 0. What will happen? The energy will be having lowest value because energy is of the form n plus half H nu; n can take the values 0 1, 2, 3, 4 extras. So, n is 0 is the lowest possible state. So, we always say that that is the ground state of the system. So, the energy will be E 0 and it should be equal to half H nu. Now, noticed that the energy lowest possible states energy is not 0. So, the system has what we effort to have 0 point energy; as I said in the case of the particle in a one-dimensional works this is nothing but a consequence of the answer to be principle where the particle simply cannot be sitting at rest. It is not possible because that will violate the answer in differentiable.

So, it has to move and if it moves it has kinetic energy. So, therefore the energy cannot be 0. So, that will be the state let me represent that in the figure here the energy is 0, but that is not possible the first allowed energy level as n equal to 0. And I can probably represent it by this line the energy is half H nu the next allowed energy level; obviously will be equal to 3 by 2 H nu and I can represented it by this line. So, 3 by 2 H nu and next is of course, 5 by 2 H nu and 7 by 2 H nu and so on. Now, you should also notice that this spacing between these 2 successive energy levels; see if you look at these 2 energy levels the spacing is actually H nu. And it is saved for the next 2 energy levels and it is same for the next 2 energy levels and it is same for the next 2 energy levels. So, therefore you get a series of equally spaced energy levels; this is a specialty of harmonic oscillator. If you remember in the particle in a books what happened same energy level, but the spacing between them will be increasing as you went up; here the spacing is actually the same ok.

So, when n is equal to 1 as I told you the energy is 3 by 2 H nu and n is equal to 5 by 2 H nu and n is equal to 7 by 2 H nu and so on. Let us look at the wave function for the ground state what would be the wave function? And the wave function will be psi 0 which will be given by n 0 what I am you doing is I am using the expression where is my expression? Here, it is n 0 e to the power of minus X i square by 2 H 0 of X i correct; this is my expression. And you can actually evaluate n 0 where is the expression form 0 where this is the expression and that I have derived; just had to put n square or n equal to 0. Then, what will happen? You get alpha divided by root pi 2 to the power of 0 is unity, 0 factorial is also by definition it is unity.

So, therefore you get this to the power of half e to the power of minus X i square by 2 and H 0 we did evaluated in the morning it is equal to 1. So, therefore the wave function is this.

And if you want you can express it in terms of x how will you do that? You will replace X i here with alpha x, but why should we do that that term x we can just use X i it is proportional to the precision. So, therefore what we can do is we can say if X i is my horizontal since the alpha because one is proportional to the other. And then suppose if we make a float of this function against X or equivalently against X I; what is the answer that you are going to get? It is what is referred to as a Gaussian function e to the power of minus X i square by 2 it is a Gaussian function.

So, if you make a plot of such a Gaussian function what happens? When the value of X i is equal to 0 it has the largest value and you increase the value see; if it is in the positive direction the function will decrease or if you decrease the value of the X i in the negative direction again X i square will increase and therefore the function will decrease. So, therefore what happens is you will get the curve which looks like this.

So, that is the ground state of the system and it is also obvious to you that it is the we are put as symmetric state. If you replace it X i with minus X i you look at this expression replaced it X i by minus X i the function remains unchanged; that is reflected in the float that I have made; that is the ground state. So, the ground state wave function is symmetric with respect to replacement of X i by minus X i and it does not have any nodes we can see that also. What about the next one X i X i e to the power of minus X i square by 2 H 1 of X i and that is equal to alpha where is my dell expression? Here, is my dell expression alpha by root pi 2 into 1 factorial; 1 factorial is actually 1 to the power of half e to the power of minus X i square by 2 into H 1; H 1 if you look into your note you will find that it is 2 X i.

So, therefore the interesting part is this e to the power of minus X i square by 2 which actually says that function will be 0 at infinite distance from the equilibrium position e to the power of minus X i square by 2 is well behave. But in addition to that we have this X i see; if we have that X i what will happen it is at the origin X i is equal to 0 this function will vanish. And not only that you can see that if I can replace that X i with minus X i sign of the function will change for this is an anti symmetric function. So, how will it look like I will make a float, I hope this is not too confusing. Because I am plotting different functions in the same picture; if you find it confusing I will draw it separately. So, that is our psi 1, this lower one was psi 0. Then, we I will do one more psi 2 would be equal to alpha by root pi 2 square into 2 factorial which is 2. So, effectively you have 8.(No Audio From 35:48 to

35:58) So, this is the function remember H 2 I have written in the morning it is actually for psi square minus 2.

So, again you will notice that this is an even function first of all; the second thing is you where are those zeros of this function well when you have 4 psi square minus 2 is equal to 0; when this is equal to 0 you would have it equal to the function equal to 0. So, when does that happens? That happens when X i square is equal to one by 2 or X i is equal to plus or minus 1 by root 2; there are 2 nodes this is something that we would have expected. So, how will it how will the function look like? Well, these are the 2 nodes; the nodes are actually symmetrically located these are the 2 nodes. And the function would look like (No Audio From 37:01 to 37:10) that it is symmetric I mean the way I have drawn it may not appear completely symmetric. But it is symmetric and with that knowledge actually we can now go and draw the next one I will not try to write the expression; the next one would have 3 nodes. So, it is not difficult to draw.

So, that is the appearance of the next one and similarly you can go on plotting the other ones if you like; as the value of n increases what happens you have more and more nodes. In fact, the n th function would have n minus 1 nodes. Let us again go back to the ground state this one; what is the wave function? Well, I will think only of the ground state now; this is the wave function and as I have told you it is a symmetric function in x. So, suppose I imagine that I make a series of measurements of the positions of the particle and take its average.

I can actually get that average by calculating the expectation value of x. And what will that be for this particular problem I am going to calculate it. But is it necessary to calculate it is the question; see the you have the equilibrium position which is x is equal to 0. And then you have the wave function which is symmetric about the equilibrium position. So, when you make a measurement it is equally likely that the particle will be found on this side or on the other side. If it is found on this side its position coordinate is positive while on the other side the position coordinate will be negative.

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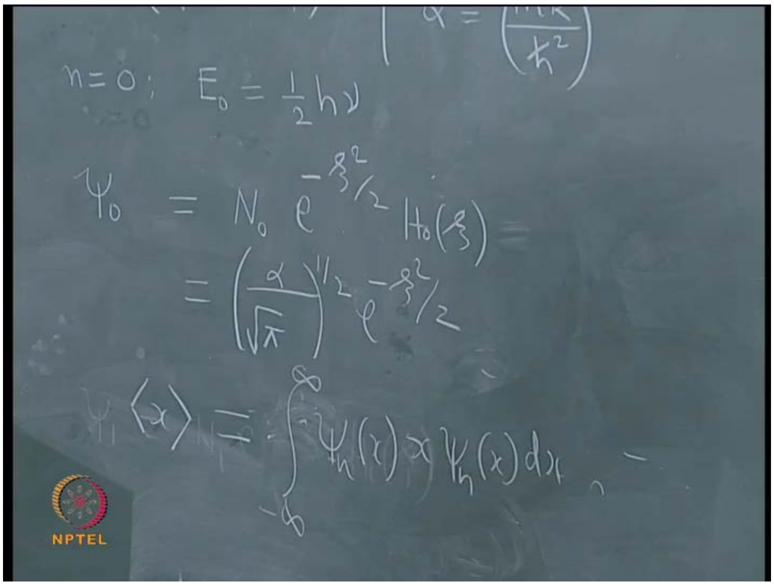

And, therefore on an average the expectation value of x you would expect is 0 right; that we can easily verify it is a parallelizable thing. How will you do that well well I do not think I need to do the integral. Because I can say that you look at the integrant is from minus infinity to plus infinity, but the integrant is an odd function of x correct; it is an odd function of x. And if I integrate the odd function from minus infinity to plus infinity what has to be the answer? The ever will be contribution from the negative x region and that will be cancelled by the exactly by the contribution from the positive x region and therefore, the answer has to be 0.

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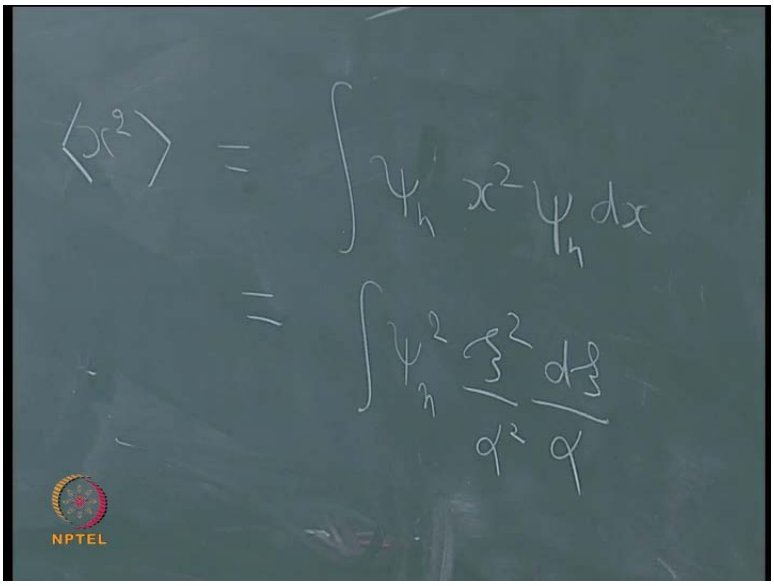

Similarly, if you if I thought of p x the average value of p x what would you expect if it is in the ground state? And the particle if you are measuring the momentum may be sometimes it will be moving in this direction. But it is not going to go away it will come back. So, it will go back in the reverse direction sometimes. So, therefore for average value of momentum you would expect is 0. What is more interesting is actually to calculate expectation value of x square; I will not actually evaluate it. But I will tell you how to evaluate it and then maybe you can do it as an exercise perhaps if you like. What is the definition of x square?

Let me say I am thinking of the n th state that is what I have written here actually I even though I said that I am going to speak about the 0 state I the expectation value that I did is wrote is general; and answer is valid for any general line. So, let us say I have phi n, x square psi n I am not going to put the star here because the function is real. And therefore the star has no effect if I want to evaluate this integral; that is the expectation value of x right. And here you have things written in terms of x you will have changeover to your X i that is better. So, therefore how will you do that you have x defined as X i by alpha. So, what will happen is you will have integral psi n square X I square by alpha square into d X i divided by alpha right; you are changing x square as well as d x into expressions in terms of X i and d X i.

So, therefore what happens is you will get 1 by alpha cube integral psi n square X i square d X i from minus infinity to plus infinity. And this is actually equal to 1 by alpha cube minus infinity to plus infinity; let me substitute for psi n square. So, actually psi to the power of minus psi square H n psi square right this is the psi n square there must be a normalization factor which you will write as n m square right; normalization factor has to be there then you will get this. And this is multiplied by psi square that is the integral that you will have to evaluate fine. Now, this is almost a normalization integral if it is not for the factor of X i square and this alpha cube this X i square is there. So, you have a different integral not the normalization integral but you have this integral. So, the question is how will you evaluate this? For that we can make use of one of the identities that I have derived earlier; the identities that I can use is to be taken from the book I had shown this in the morning.

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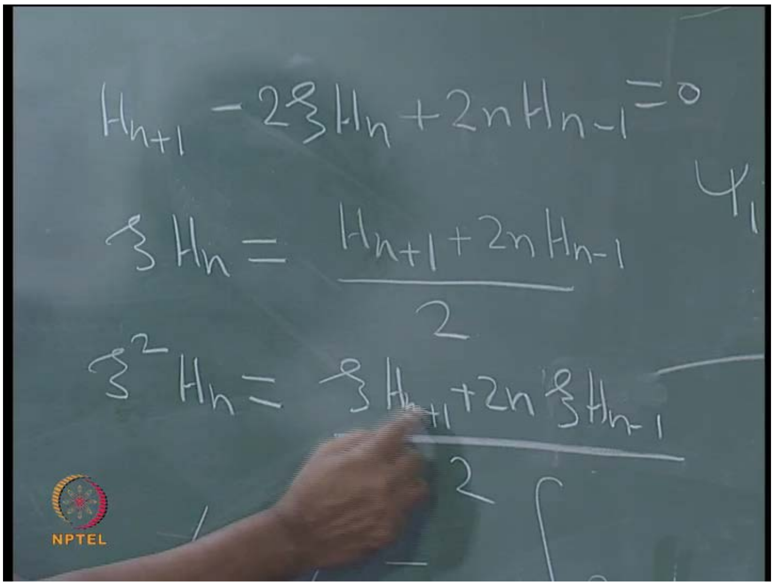

It says that H n plus 1minus 2 X i H n plus n H n is equal to 0 right; this is an identity that we have derived in the morning. So, therefore I can rewrite this and say this means that X i times H n is equal to how much H n plus 1 plus 2 n H n plus 1 divided by divided by how much? So, X i times H n I can write like this. And therefore if you multiply this X i square X i square H n will be X i H n plus 1 plus 2 n X i H n minus 1 divided by 2 fine. And then for each 1 of these X i into H n plus you can again you can again make use of this identity; and for that also I can make use of same kind of identity. So, it is a little bit of lengthy algebra which I am not going to do.

But if you did it that way ultimately what will happen your X i square will disappear. And you will have things written in terms of the hermit polynomial alone and then you can use the orthogonality theorem; and get the answer. This is how the calculation will proceed; if you wanted to calculate expectation value of x square. But I can tell you what the answer will be. I think I has spent enough time on the harmonic oscillator. So, therefore I am not going to evaluate this, but the answer is actually the following.

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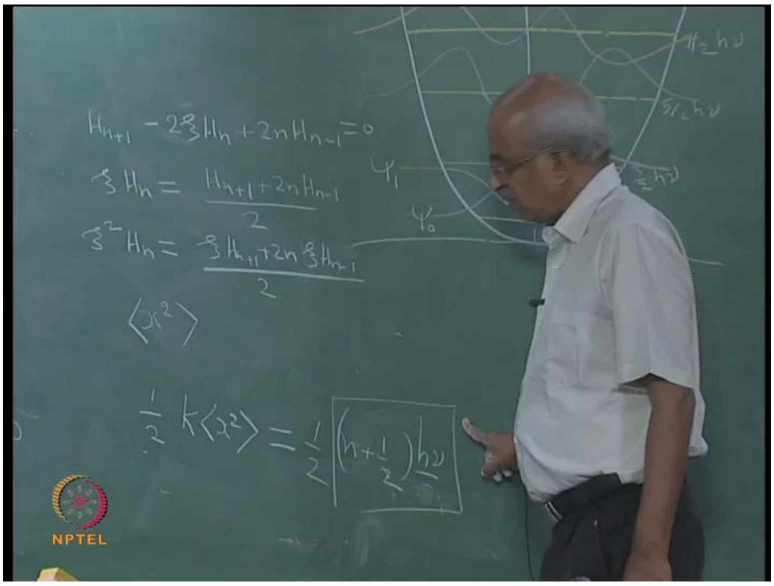

In fact, the answer can be written in this form half k x square average is equal to n plus half H nu divided by 2; that is the way in which you can write this; you see I mean this is not very surprising. Because n plus half H nu is the total energy of the system half k x square is the potential energy, average value of potential energy. So, it says that average value of the potential energy is equal to half the total energy which is not surprising. Because the system has kinetic energy and potential energies and for the system it is such that the average value of the potential energy is equal to this average sorry the average value of potential energy is half the total energy; that is what happened. And you will get this result if you evaluate this integral. I think I will stop my discussion of harmonic oscillator at this point then discuss start a discussion of hydrogen atom in my next class.

Thank you for listening.