Introductory Quantum Chemistry
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Lecture - 19
Harmonic Oscillator – Generating Function

So, we were actually looking at the recursion relationship, we wanted to terminate the series at sum finite power of Xi and we managed to by putting lambda is equal to 2n plus 1. This ensures that we have an acceptable solution and that actually means 2 e by H nu must be equal to 2 n plus 1; which implies that, e must be equal to n plus half nu. So, therefore, you are able to get acceptable solutions only for these values of energy and there are no acceptable values for any other values of energy. And, so, we say that the energy of the harmonic oscillate is quantized, it has to be equal to n plus half H nu; otherwise no acceptable solution.

And, further if lambda is equal to 2 n plus 1; you can actually substitute it here. And, you can replace this lambda minus 1 with 2n; sorry you can replace this lambda in here with 2 n plus 1 and you will get differential equation which will read like. So, therefore, we know that H, the function H is a polynomial; it will satisfy this differential equation. And, if you want to determine H, actually what we can do is you can use the recursion relationship. You will take a value for a 0 and then use the recursion relationship to determine the polynomial. But it so happens that the functions which obey this differential equation were very well known to mathematicians, right. Even before quantum mechanics, came up people mathematicians had studied those differential equations and the associated polynomials.

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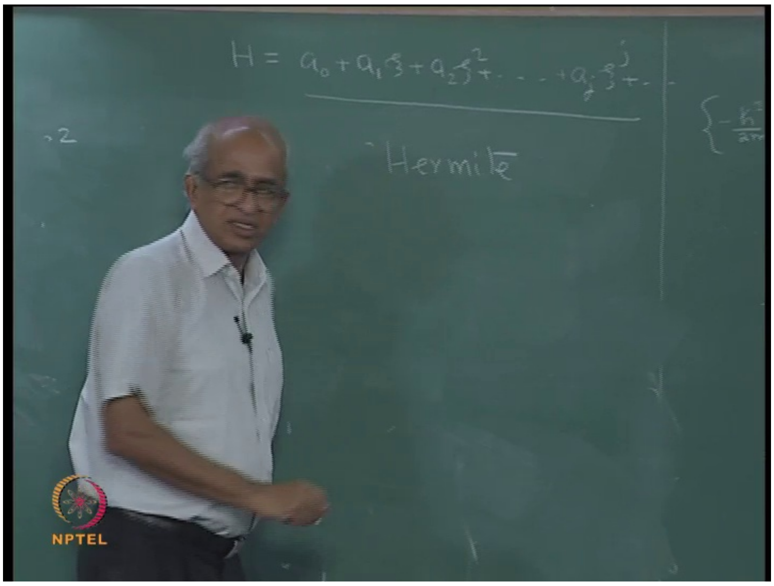

And, they were studied by a person called Hermite and these polynomials are called Hermites polynomials. So, I will spend a little bit time maybe 15, 20 minutes describing the properties of this polynomial. I will not go into that much detail, when we encounter other polynomials later on in the course. But this one, I will describe in all its details; just to give an idea as to how one works with these kinds of polynomials.

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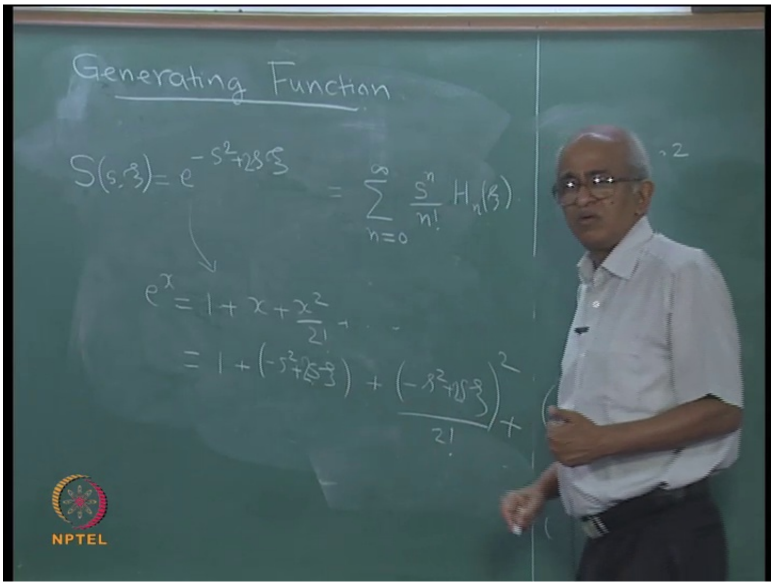

So, what I will do is I will start with, what is occurred to as a generating function. See here I have function which depends on 2 variables; one variable is S and the other variable is C. It is a function of 2 variables and therefore, I am going to write this as sum S which depends on s and c. S is the function, s and Xi are 2 variables and this S obviously depends upon these 2 variables. Now, you know that if I had e to the power of minus x, I can expand it as series. Similarly, this also if you want, you can expand it and you will get a series, suppose I do that and write this as a series in s.

So, what is going to happen, as I will have a series which will involve any power of s. Imagine we expand this as a series, then what is going to happen is that you will have s power 0, s power 1, s power 2, s power 3 etcetera. So, imagine I can write this as a series involving s to the power of n divided by n factorial summed from n going from 0 to infinity; correct? It should be possible to do that.

Then, if I write it like this, there will be some co-efficients here, but those co-efficients you will realize have to be functions of the other variable, right. If you want I can illustrate the point to, what I am saying. See, if you had expanded this series would be 1. I mean, I know e to the power of x is equal to 1 plus x plus 2 factorial plus etc and all that is happening is that here x is actually minus x square plus S c; that is all. So, the first time will be that plus the second time will be minus s square plus s into; my first mistake is there is a 2 here. So, that is the definition. So, there is a 2 here, there is a 2 there.

So, this is what the series is correct. And, what I can do is I can, if I can write the full series and expand and then collect together all the times which have the same power of s. For example, s to the power of 3, I can collect them together. If I collected them together, then there will be a coefficient. And, that co efficient will depend up on the other variable c; that is all. So, therefore, this can be written, this function can be written as a power series in s and there are going to be coefficients. And, thus co efficient actually, I am going to denote them as H n (c), right. And, interestingly what happens is that these co efficient are just your Hermite polynomials. That is why we think of these generating functions, right. These co efficient, they are introduced this way; they are just functions which obey this differential equation with a 2 n here. So, therefore, these function are just the ones which occur there as the coefficients.

Well, this is not enough to make this claim; I should prove that as I said in the next 15 or 20 minutes, I will actually show that that is the way it is. Now, suppose I take this function, this is a generating function and this is extremely useful. In fact, later on we will encounter Laguerre polynomials and legendary polynomials; they all have their own generating functions. They all have similar things; that is the reason why I thought this is a nice thing to introduce.

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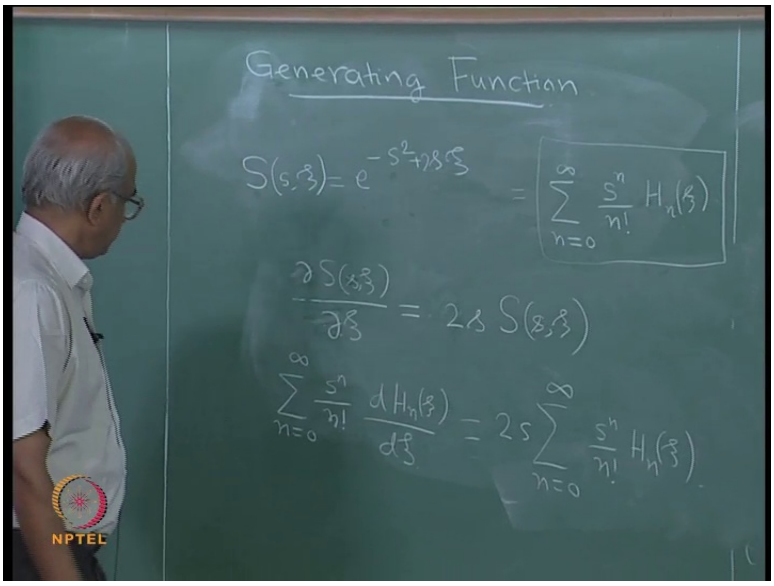

So, suppose I take this function and differentiate with respect to c, what will be the answer? Well, here if you differentiate, the answer is going to be minus; sorry, there is no negative sign. It is going to be 2 times s times this object and that is nothing but your s, correct. This is definitely valid. But then I know that, this is given by this expression. So, therefore, I can say that the left hand side, I can evaluate using that expression right. So, if you evaluated the left hand side using that expression, what is the answer you are going to get? You are going to have sum n going from 0 to infinity s to the power of n divided by n factorial, correct. You are differentiating with respect to c, you are not doing anything with respect to s. So, maybe what I should do is, I should change this to partial differentiation notation. That is better; so that there is no chance of any confusion. Am differentiating partially with respect to Xi and not changing s.

So, then what is going to happen is, you see when I calculate the derivative using this expression s to the power of n by n factorial will remain unchanged. But the derivative operator is going to operate upon H n. So, therefore, what you are going to get is, d H n Xi by d c. So, that is your left hand side and that must be equal to 2 times s times s; correct. And, therefore, what is that? That is actually sigma going from 0 to infinity, right; s to the power of n divided by n factorial H n c; right. And, this s if you like you can take it inside. Because s is there; so, why should it be sitting outside, I can put it into the summation, inside the summation and say as n plus 1. So, here you see on the left hand side, you have power series here; right hand side you have a power series in s. So, if you think of one power series; if you say one power series is equal to another power series; then, what should happen? All the coefficient, if you think of coefficient of s to the power of 4; whatever is there on the right hand side it has to be equal to whatever is there on the left hand side.

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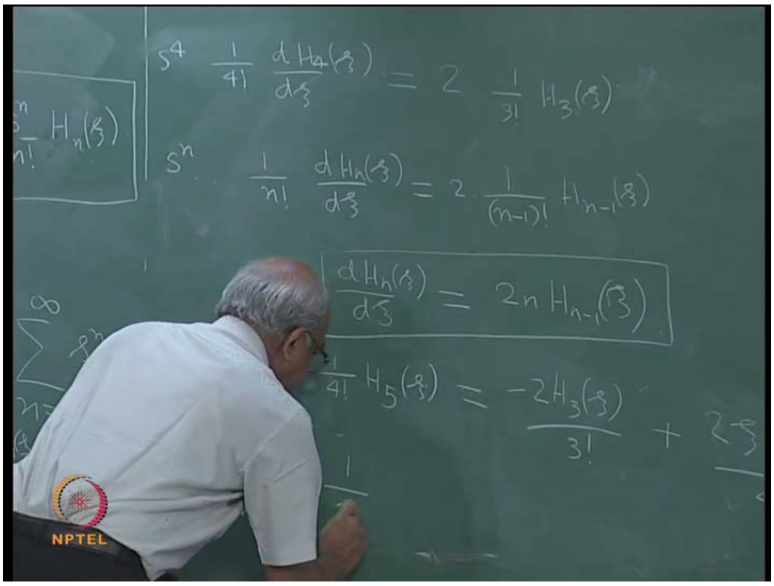

So, therefore, let us say I want to look at the co-efficient of s to the power of 4 on the left hand side; what is it? It is actually 1 by 4 factorial d H 4 by d c, right. That is the co efficient of s to the power of 4 on the on the left hand side. What will be the time on the right hand side? Coefficient of s to the power of 4. You will get, 2 you will get; this n plus 1 should be equal to 4. That means, n should be equal to 3 and therefore, you are going to get 1 by 3 factorial H 3 c, correct. This is what you are going to get; that means, d H 4 by d Xi is actually equal to something in terms of H 3, right. So, instead of equating the power of s to the power of 4; suppose I had equated power of s to the power of n. Here, I have just illustrated the point by equating the powers H to the power of 4 equating the coefficients of s to the power of 4. But instead of that, suppose I had equated the coefficients of s to the power of n; what would be the result? The result would be very simple.

I would have the result 1 by n factorial d H n by d Xi is equal to 2 divided by n minus 1 factorial H n minus 1 c, right. So, therefore, what this says is the first derivative of H n, right. These functions H n are such that the first derivation is actually equal to 2 n times minus H n minus 1 c, correct. So, I have proved this relationship; how did I prove it? I used the generating function; that is why generating function is useful. You took the first derivative of this H n, the answer is H n minus 1 into; there a mistake. Now, this I have done by differentiating with respect to c, but now we will differentiate with respect to s partially and see what the answer is…

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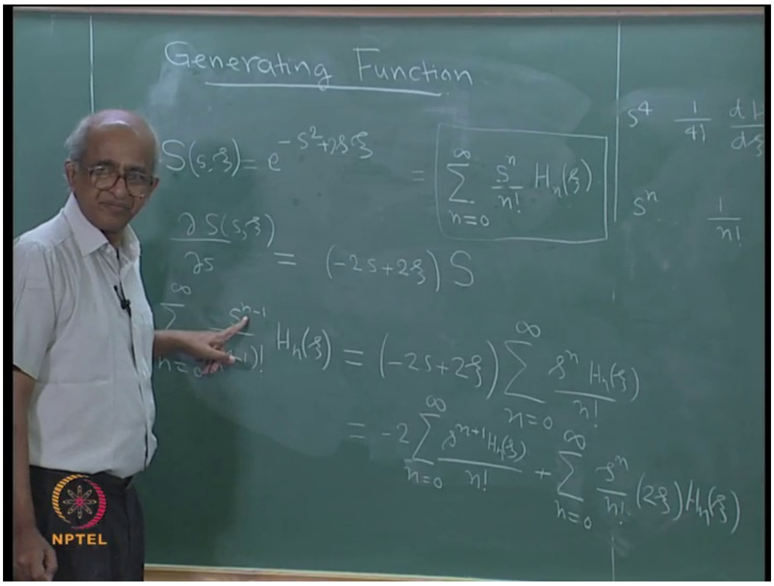

So, dou s by dou s is equal to, differentiate partially; what will happen? You are going to get minus 2 s plus 2 c, right. The derivative of this exponent is minus 2 s plus 2 c; because I am differentiating partially with respect to s with s into S, right. Procedure is just the same as before. Now, I will evaluate the left hand side using this expression, I will substitute the same expression into here and then equate the coefficients of s to the power n, correct. This is what I will do; let me see what the result is. So, because we understand the procedure, we can proceed quickly. Sigma n equal to 0 to infinity, I have to differentiate this with respect to s. So, the answer is going to be s to the power of n minus 1. One n will come down, but then you have n factorial, right. So, what will happen? This n and that n minus, I am anticipating the result; that is why I am saying n minus 1 factorial. This n and n factorial will be combined and you will get n minus 1 factorial.

And, the coefficient will be H n Xi and that is equal to minus 2 s plus 2 Xi sum n going from 0 to infinity s to the power of n H n Xi divided by n factorial. The right hand side, let me just rewrite by splitting the terms, you will have this term; minus 2 sigma n going from 0 to infinity. We took this as inside, you are going to get s to the power of n plus 1 H n Xi divided by n factorial plus sigma.

Well, there is a Xi sitting outside; maybe I will take it inside. These 2 Xi I will take inside; so, I will have s to the power of n by n factorial 2 Xi H n c, right. Tell me if I have made mistakes. So, just as before, I mean maybe we will just look at the co-efficient of s to the power of 4 on the left hand side as well as the right hand side. Equate the two and see what happens and then generalize it. So, what will be the co efficient of s to the power of 4 here? It is going to be 1 by 4 factorial, right. You have to say n minus 1 here; that is equal to 4. Because I want o get the co efficient of s to the power of 4.

So, n minus 1 is 4 that means I will get 1 by 4 factorial H 5 Xi is equal to the right hand side. In the right hand side you see, you have to have s to the power of 4. That means, you will have to put n plus 1 should be equal to 1; that means, it is 3 right. s is 3 right. So, you will get H 3 Xi divided by 3 factorial right. Because n plus 1 has to be 4 to get s to the power of 4 and as well as this time is concerned to get s to the power of 4; it is quite straightforward you just have to put n equal to 4. So, there is a minus 2 here, thank you for reminding me; plus 2 Xi H 4 Xi divided by 4 factorial. Is that ok?

I hope there are no mistakes. I am tempted to check from the book. So, let us now generalize; in general what will happen, I will have 1 by n factorial. I am going to equate the powers of s to the powers of n. This is for s to the powers of 4. So, what is going to happen is, I will have H n plus 1 Xi equal to minus 2 H n minus 1 Xi divided by n minus 1 factorial plus 2 Xi H n Xi divided by n factorial, right. This is what will happen if we equate it; the coefficients of s to the power of n. And, this relationship you can, what will you do? You will multiply throughout by n factorial and to look at the result.

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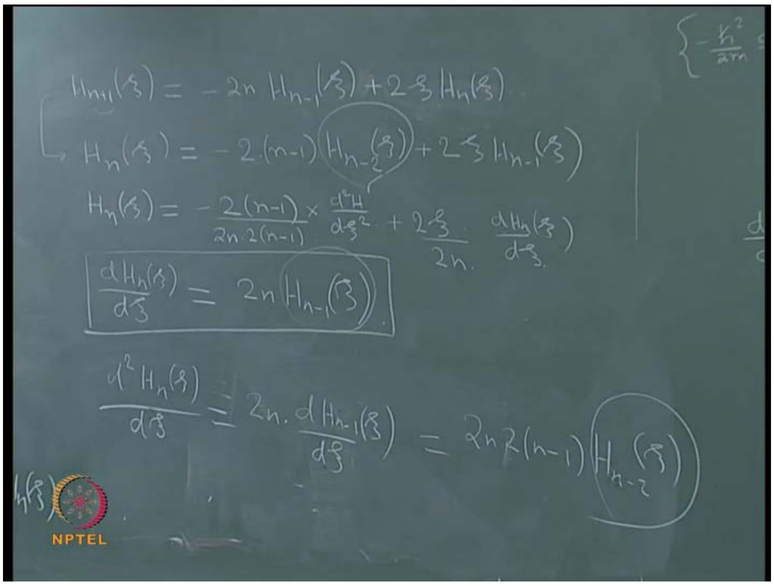

So, if you multiply throughout, your answer is going to be H n plus 1 Xi is equal to how much; right. Now, my ultimate aim is to show that H n actually obeys this equation. That is what I want to show each n obeys; this is what I want to show. So, how will I do that? I have these 2 equations and I can use these 2 equations I can manipulate them and then get that differential equation.

So, how will I manipulate them? Obviously, you see I need the second derivative of H n. Because you look at the differential equation, it has second derivative of H. So, that means, I will differentiate this once more. Will be equal to what? It is going to be equal to 2 n, right; n is just a number, d H n minus 1 by d Xi right, if you just differentiate this is going to be the answer. I will give you the reason for doing this; I want to get the second derivate of H n. Why because the second derivate is there in this differential equation. But then if you are interested in the second derivative of Hermite polynomial, right; it is now related to the first derivative of the Hermite polynomial. But the first derivative itself can be written in terms of Hermite polynomial.

So, in this equation what I need to do is put instead of n you will put n minus 1. So, if you put n minus 1 what will happen? You are going to get 2 n. This derivative I am going to use that equation and get 2 into 2 n minus 1 in to H n minus 2 c; that is all. Now, what I will do is I will take this equation wherever n plus 1 is occurring; I am going to replace it with n. So, that means, see I am going to write this as n; is that right. Instead of n plus 1, I want n here. So, that means, wherever n is occurring, I shall put n minus 1; replace it with n minus 1. So, naturally what happens is I shall get an equation like 2 n minus 1 H n minus 2 Xi H n minus 1 c. So, this first equation is valid for any n. So, therefore, even if I replace any n with n minus 1, the equation has to be valid and I did that and I get this as the answer, correct.

And, now if I look at this equation, you will find that there is H n minus 2 sitting there. And, you have H n minus 2 related to the second derivative of H n. Look at this; H n minus 2 is related to the second derivative of H n. So, therefore, the H n minus 2 occurring there can be replaced with that; right. You can replace it with that and you have an H n minus sitting there, but H n minus 1 is related to the first derivative. So, you can use this relationship; get rid of H n minus 1. So, if you do that, what is the answer? H n minus 2 I am going to get rid of it using this equation. So, I have to replace H n minus 2 with second derivative of H n, but divided by 2 n into 2 into n minus 1.

So, d square H by d Xi square divided by 2 n into 2 into n minus 1 plus 2 Xi H n minus 1; I am going to use this equation get rid of H n minus 1. So, naturally I shall get d H n by d Xi by using this equation see I will H n minus 1 is here, but I see this equation and replace the H n minus 1 occurring there. So, the answer is just this divided by 2 n; is that fine? So, if I have done that well again I have run out of space; I will, I do not think I shall need this equation anymore. So, maybe, but I will keep it somewhere in case I need it later. So, where will I write it? Yes, this relationship is there I will write this equation on top of that.

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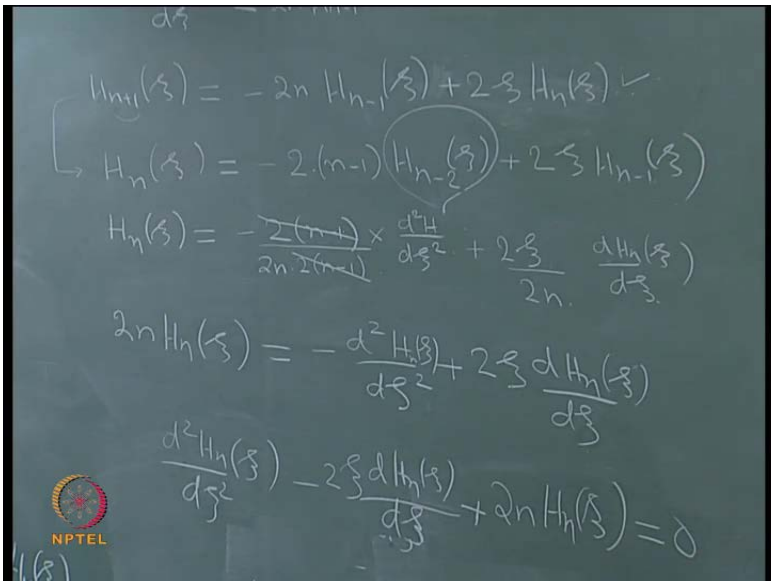

So, having done that I can remove this equation and try to simplify the equation which I have just now obtained, this is the equation, you can simplify it very, very easily, but before you do any simplification let me remove 2 into n minus 1 there and that. And, let me now multiply throughout by 2 n. So, if you multiply throughout by 2 n, you are going to get 2 n H n Xi on the left hand side and that is equal to minus d square H divided by d Xi square plus 2 Xi d H n by d Xi d Xi; this is the result. And, just take these 2 terms to the left hand side. You are going to get d square H n by d Xi square right and that is the answer that I wanted.

So, therefore, you see that the generating function is very useful; I can derive differential equations. And, in fact, the differential equation we have obtained by doing all the manipulations earlier. And, therefore, this H is nothing but the Hermite polynomial; H n. As I told you, these things were already known to mathematicians and therefore, people who were doing quantum physics had to grow their knowledge that is all. But then you may say well, what is the fun, after all you could have solve the equation directly; why should you take this? The answer is that once you have this expression, you can derive a very simple for the Hermite polynomial itself; which I will do now. Starting from here I can derive, a simple formula for Hermite polynomial.

If you want to calculate any Hermite polynomial, I can give you a formula; that is the first thing. The other thing is that in quantum mechanics, you always have integrals to be evaluated. And, evaluation of any integral involving the Hermite polynomial is easy to perform using the generating function. That also I shall demonstrate just for this case. But in other cases, but the other cases we will discuss later like legendary or Laguerre polynomial same procedure is valid. But I will not go in to the details. So, what is the formula that I have for evaluating the Hermite polynomial.

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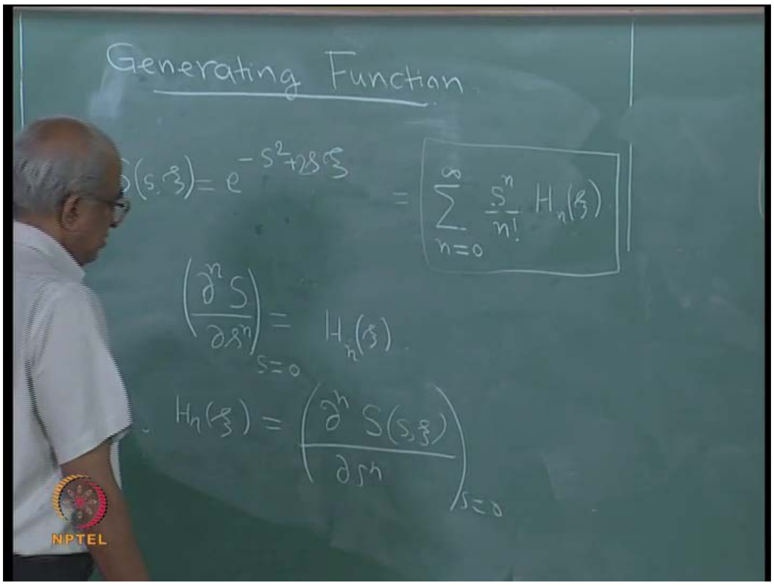

Well, suppose I take this function and differentiate it partially with respect to s, after which I will put s equal to 0. What will be the answer? I suggest that you try this. If you differentiate s partially, use this right hand side; use this expression. Imagine that I differentiate this partially with respect to s, after doing the differentiation I will put s is equal to 0. You can imagine what is going to happen? You will find that the answer must be equal to H 1. Because you look at the series; maybe this one will become clearer if I wrote the series; 1 plus s by 1 factorial H 1 plus s square by 2 factorial into H 2 plus etc; that is the form of the series of this series.

So, if you are differentiating with respect to s, this 1 will go this term will survive. It will survive as H 1 and then you will have a time involving s and then higher order times involving s square etc. But the moment s is equal 0; this is going to disappear and therefore, you going to be left with only H 1. So, therefore, if you differentiate once with respect to s and put the derivative equal to 0, you are going o get H 1 (Xi).

If you differentiate it 2 times with respect to s and put the derivative equal to 0; what will you get? You are going to get H 2; differentiate n times and put the derivative. Sorry, differentiate n times and put s is equal to 0. What will happen? You will get H n, right. So, that is the nice thing. You just have to take this function differentiate it n times with respect to s, correct. Put s is equal to 0 you are going to get H n. But that is not the nicest thing actually. The nicest thing is a formula I am going to show now. So, I can say that H n Xi is equal to dou to the power of n s by dou s to the power of n with s equal to 0. And, that is equal to well I do not need these things anymore that is your S correct.

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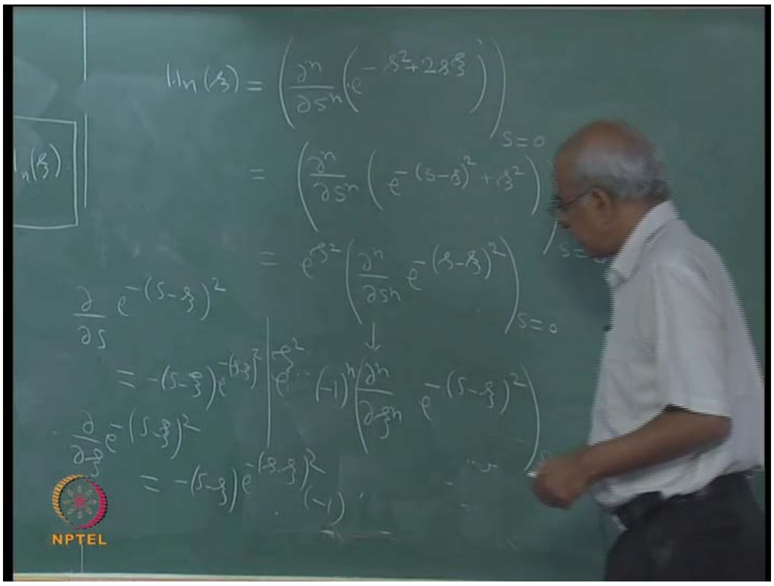

So, object that I have written is my S; you will have to do the differentiation. And, after doing the differentiation you will have to put s equal to 0. The way it is looks is tedious to perform this differentiation because the expression appears very messy. But there is a very nice trick which will enable me to evaluate this derivative. This object I am going to write this as, is that ok? Because you see if you had expanded this you are going to get like that. So, that is obvious. Now, e to the power of plus e square is there, but you see you are differentiating partially with respect to s. So, this e to the power of Xi square is not going to be affected. So, I can take it out. So, you will get e to the power of Xi square dou to the power of n by dou s to the power of n e to the power of minus s minus Xi whole square, right.

Now, you look at this expression. You see you are differentiating with respect to s. But in the function, what happens is that the function depends upon s minus Xi, right. If I wanted I can say instead of differentiating with respect to s, I can differentiate with respect to minus Xi. Because you see it is a function involving s minus Xi. So, therefore, I can even say that instead of differentiating with respect to this, I can differentiate with respect to Xi; the only thing is that an additional negative sign has to be put right. Therefore, this derivative I can say it is actually dou H by dou Xi to the power of n, right. But with each differentiation X i there is going to be a minus 1 coming out.

So, therefore, what is going to happen is that I will say this minus 1 to the power of n e to the power of X i square, e to the power of minus s minus X i the whole square. And, of course I shall have to put s equal to 0 is that ok. The argument is see when going from here to there you are actually differentiating with respect to s. But in the function the combination s minus Xi is occurring that is all that is occurring. And, therefore it is not necessary to differentiate with respect to s, but I can differentiate with respect to X i but X i is occurring with the opposite sign.

So, therefore if I am deciding to differentiate with respect to X i I shall put that sign also right. If you want you can verify this very easily look at e to the power of s minus X i the whole square differentiated once with respect to s. What will be the answer? The answer is going to be minus s minus X i e to the power of minus s minus X i the whole square this is the answer. If we differentiate with respect to s; if you differentiate it with respect to X I what will be the answer? The answer will be minus s minus X i into e to the power of s minus X i the whole square, but your differentiating was respect to X i that means, you will have to put an additional minus 1.

So, therefore instead of carrying out differentiation with respect to s you can carry out differentiation with respect to Xi as well as this function is concerned. The only thing is we have to account for that minus 1 each differentiation is going to give you such a minus 1. So, therefore I take this and say that here I can differentiate with respect to X i. Why did I put a minus 1 to the power of n? But then again you see that this is very very nice because what is the expression that we have arrive at. The expression that we have arrived at is e to the power of Xi square minus 1 to the power of n dou to the power of n by dou X i to the power of n e to the power of minus s minus psi whole square s equal to 0, but you see now there is no differentiation with respect to s.

So, straightaway I can put s is equal to 0 in here; I mean if you had differentiation then you have to be careful. But there is no differentiation with respect to s anymore. So, I will just put s is equal to 0 and then what will happen I will get a formula which is quite nice; what does it say? It says e to the power of X i square minus n to the power of n dou the power of n dou psi to the power of n e to the power of e square. And, even partial derivation notation is not necessary now. Because the derivatives are operating only upon a function of X i. Therefore, if you like you can say this d to the power of n d X i to the power of n. So, what is the result that I have obtained?

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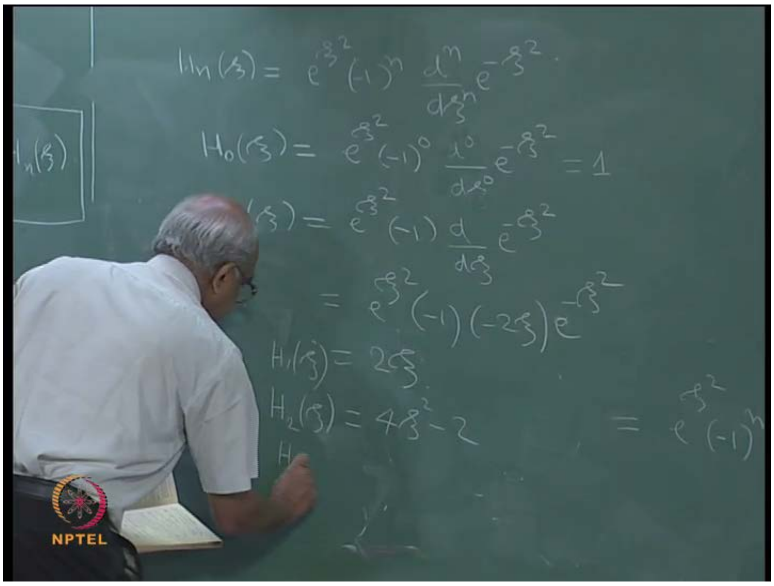

It is a nice formula H and X i is given by e to the power psi square minus 1 to the power of n d to the power of n by d X i to the power of n e to the power of minus X i square; this is the formula I can use. If you want any Hermite polynomial you can evaluate it using this formula. And, just to illustrate suppose you can go H 0.

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This will be H 0 which is actually really unnecessary for me to write it down. Because it is so simple E to the power of 0 means you are not carrying out any differentiation; and minus 1 to the power of 0 is 1. And, so e to the power of X i square e to the power of minus X i square the 2 will cancel. And, you will get the answer as 1 simple and straight forward. We may just quickly verify H 1.

You just differentiate this once e to the power of minus e square minus 2 X i will come down. And, this and that are going to cancel and you will be left with 2 X i. So, this is your H 1 ok. Now, it is very easy all that you have to do is go on differentiating; if you wanted H 10 the only thing is you have to differentiate 10 times which you may say it is not very easy to differentiate 10 times. But there are as I said the other day that there are programs like mathematic can evaluate even the hundredth derivative expressions will be messy, but you can do it. Now, you can evaluate H 2 well I think it stands out to be I will check this. Because I do not want to make a mistake you can easily evaluate it. But maybe I will just copy it from the book that is H 2. Similarly, H 3 it goes on.

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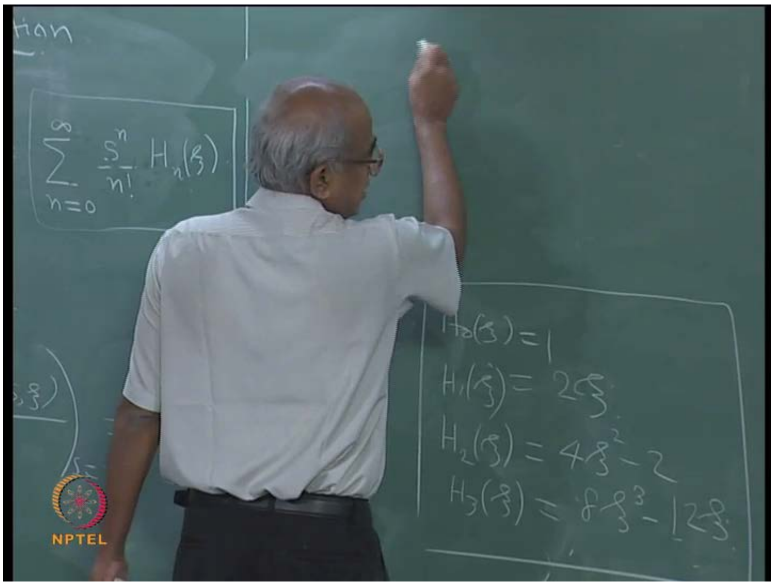

So, now let us summarize what we have found? What we have found is that the solutions are acceptable only I e is given by n plus half H nu. And, then what is the solution the solution is actually psi equal e to the power of minus X i square by 2 multiplied by H; this H is in general a polynomial if you are thinking you have a particular value of n, the polynomial will actually be a Hermite polynomial H n of X i which has a degree equal to n; the degree of the polynomial which is the highest power of X i will be n. And, it will be this H n you can evaluate it using the formula which was originally derived by Hermite I believe formula is it were of is square minus n to the power of n d by d X i to the power of n e to the power of is square this is H n.

But then once you have the wave function what do you do you try to get physical information out of it the function; you have to ensure that it is normalized in the way this psi is written it is not normalized. So, there will be a normalization factor I will introduce it now. I will call I mean this is just normalization factor give me any wave function I will normalize it. Then, the normalization factor will in general will depend upon the number n; this number is a quantum number. See that you should also remember that this is a quantum number that has arisen.

How did it arise? I imposed the acceptability conditions. And, then in the process of solution this number came out naturally right. It was there in the solution when you imposed the acceptability condition that the wave function is acceptable it will automatically got number; this solution was dependent upon that number. And, this number can take on the values in the case of harmonic oscillator; it can take on the values 0, 1, 2, 3 etc right. I think this is a right point for me to stop. I shall continue in the afternoon.

Thank you for listening.