Mathematics for Chemistry
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Module - 07
Lecture - 34
Hermite Polynomials, Solutions of Quantum Harmonic Oscillator

So in the last class I talked about associated legendre polynomials and which are also known as spherical harmonics, and I showed how you get the differential equation, how the differential equation naturally appears when you are solving quantum mechanical problem, and I outlined how you how the power series method can give you useful information about the solution.

So, I encourage each of you in the case of both the Legendre polynomials and the associated Legendre polynomials to actually take some standard textbooks, and try to see how they have worked it out and try to work out all the properties that are associated with that.

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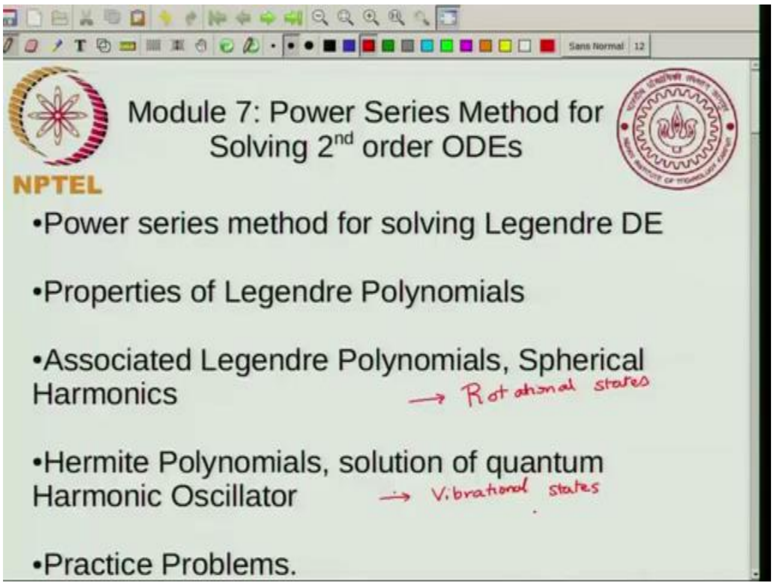

So, we would not have time in class to discuss all these things, but I would encourage each of you to look at various properties of each of these polynomials.

And today I will show another polynomial we will discuss today called the Hermite polynomial, which appears when you in another standard chemistry problem that is solution of the harmonic oscillator. And again I will just outline the solution and I would encourage each of you to read about it, incidentally I should mention that spherical harmonics. So, these are so, spherical harmonics are related to rotational states of molecules.

So, if you are doing any rotational spectroscopy then you can actually you probe the difference in rotational energy levels and these are related to solutions of these spherical harmonics. Similarly the quantum harmonic oscillator is related to vibrational states. So, if you are doing any infrared spectroscopy, then what you see it is related to the vibration levels which can be modelled very usefully as a harmonic oscillator. So, these are fairly well used equations in the physical chemistry.

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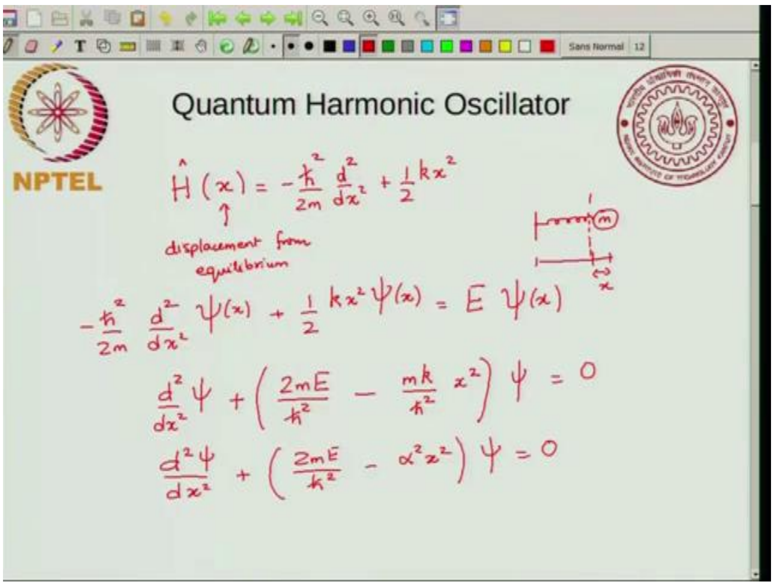

So, now let me let us go to the quantum harmonic oscillator. So, the quantum harmonic oscillator as a wave functions; so the Hamiltonian for a quantum harmonic oscillator, so the Hamiltonian operator it depends on one coordinate x, x is actually the displacement from mean from equilibrium. So, if you can think of a one dimensional harmonic oscillator as a spring mass system. So, you have a mass and this is. So, there is some equilibrium length. So, this displacement from this equilibrium length is what is called the x. So, if you just leave the spring then it comes to rest at some distance and the displacement from that equilibrium position is what corresponds to the x variable. In any case the Hamiltonian operator can be written and this case as minus h Cross Square by 2 m, m is the mass of the particle times d square by d x square this is the kinetic energies operator, and then you have a potential energy term that is plus half k x square.

So, it is a typical spring energy that is half k x square. So, the Hamiltonian has a simple form and so you can write the Schrodinger equation the time independent Schrodinger equation for this quantum harmonic oscillator, as minus h bar square by 2 m, d square by d x square times psi of x, plus half k x square psi of x is equal to e which is the energy of the harmonic oscillator, times psi of x and our goal is to solve this problem and find out and what you will realize is that on the certain cases you have certain allowed values of e.

So, let me rewrite this differential equation in a slightly different form. So, what I will say is write this as d square by d x square of psi, I would not write the dependence on x plus, now I will take the 2 m e by h bar square. So, I take the 2 m and an a h bar to the other side as bring the e this side. So, what I will have is 2 m E by h bar square multiplying psi. So, and what else multiply psi. So, the other term that multiplies psi. So, when I multiply out this 2 m E by h bar square. So, then what I will get is minus now what I will get is something that looks like m k by h bar square x square, this whole thing multiplying by psi equal to 0.

So, I will just write it in this form I just rewrote the equation in this form now I will call this m k by h bar square is the alpha square. So, my everything should be positive m should be positive, k should be positive, h bar square is positive. So, I can write this as d square psi by d x square, plus 2 m E by h bar square minus alpha square x square, psi equal to 0.

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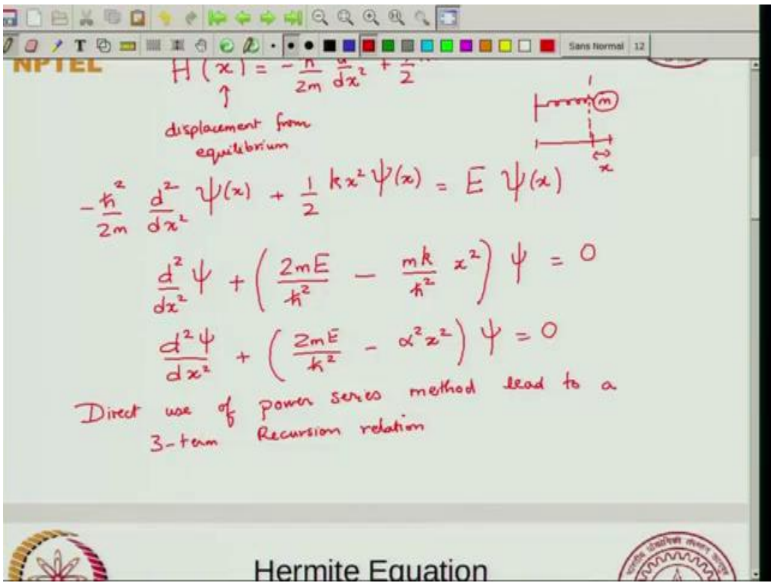

Now this is a second order differential equation and you can see from this differential equation that you can try the power series method to solve it; now if you directly use the power series method then one of the issues that you will get is you will get a 3 term recursion. So, you will get a recursion relation that has three coefficients. So, instead of a recursion relation having only 2 coefficients you will get a recursion relation having three coefficients.

So, I will just mentioned this at direct use of power series method leads to a 3 term recursion relation, and I encourage you to try this on your own I am not going to do that, but what I will. So, what you do is you make a substitution.

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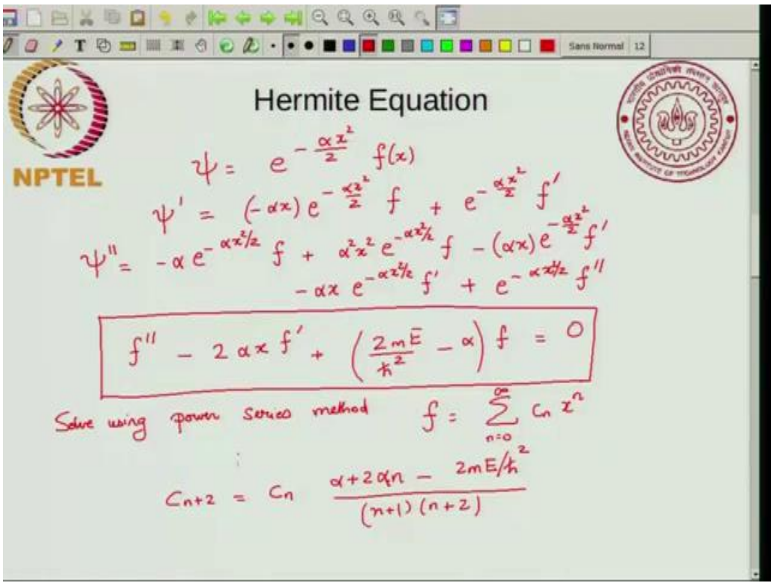

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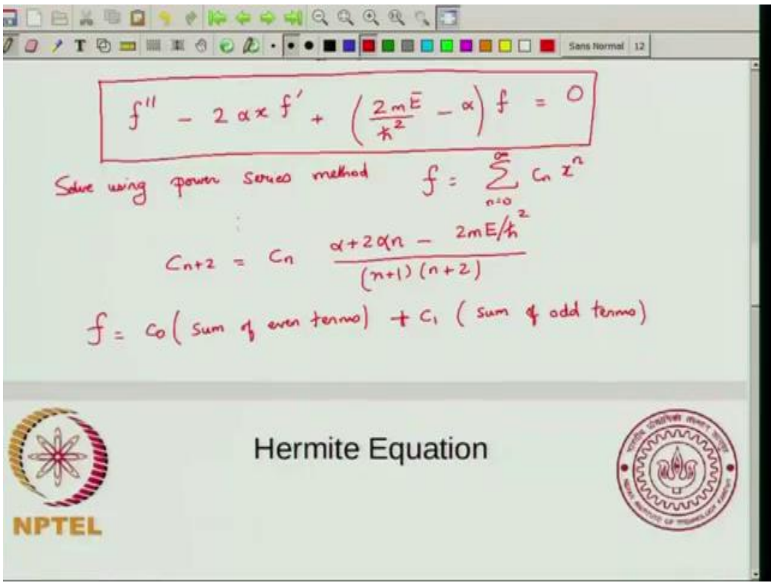

So, you make a change. So, you write psi is equal to e to the minus alpha x square by 2 f of x. So, psi of x is this ok.

So, what I did is I wrote the psi in this form and you can see what happens when you do e to the minus alpha x square by 2, you take 2 derivatives of this you will get an alpha square x square, we will get 2 alpha x and then you will get again you will get alpha x and you will get alpha square x square. So, one of the terms will be that, but when you take this and you substitute in this relation (Refer Time: 07:49) you will get a differential equation for f. So, I want again, what you will do is you will calculate psi prime. So, this will have 2 terms it will have derivative of this. So, derivative of this is minus alpha x times e to the minus alpha x square by 2 times f.

Then you will have another term that looks like plus e to the minus alpha x square by 2 f f prime, then again you take the derivative if you take a derivative the second time, now you will have to you will get lot of terms. So, just from this you will get 2 terms, then this is multiplying this. So, you will get another 2 into 2 four terms plus another 2 terms. So, I would not bother writing out all the terms so, but you can do this process and then you can take your psi double prime. So, you can take your psi double prime.

Let us write it down. So, I will get a term where I take the derivative with respect to this part. So, I will get minus alpha e to the minus alpha x square by 2 f, then I will get a term where I take the derivative with respect to this. So, I will get plus alpha square x square e to the minus alpha x square by 2 times f, then I will get a term where I have a derivative with respect to f. So, I will get minus alpha x, e to the minus alpha x square over 2 f prime and so all these come from the first term.

Now, from the second term you again you will get 2 terms. So, the 2 terms you will get or one term that will look like which will look exactly like this. So, it looks like minus alpha x, e to the minus alpha x square by 2 f prime. So, that came from the derivative of e to the minus alpha x square, and then you will get one last term that looks like plus e to the minus alpha x square over 2 f double prime.

So, these are the terms that you get in psi double prime notice that with that each of the term contains e to the minus alpha x square by 2, each of these terms in the day. So, when you substitute in the differential equation every term will contain this factor of e to the minus alpha x square by 2, even on the right hand side your psi other psi term that is not the derivative term. So, that will also have e to the minus alpha x square by 2.

So, what this means is that you can cancel the factor of e to the minus alpha x square by 2, and you will get a differential equation that involves only f; and I will just write that [ex/expression] expression I mean it is not very difficult to show. So, I will just say f double prime minus 2 alpha x, f prime plus 2 m E by h bar square minus alpha f equal to 0. This is the differential equation for f and this is related to the hermite polynomials. So, f is closely related to the hermite polynomials, and I will just quickly go ahead and tell you what you do next. So, what you will do is you will write. So, this is the differential equation that we will solve using the power series method. So, this is solve using power series method; f is equal to sum over n equal to 0 to infinity, c n x raise to n and when you do this what you will get is you do this you take the derivative, you take the second derivative a substitute in the power series, and you will get a recursion relation that looks like this.

So, when you substitute this you have to you should encourage each of you to go back and try all these steps. C n plus 2 equal to c n, times alpha plus 2 n 2 alpha n, minus 2 m E by h bar square divided by n plus 1 n plus 2. Now write it nicely n plus 1 I will solve write the alpha a little nicely. So, what you have is this expression; now this is the recursion relation and now again what you will get is this relates c n plus 2 to c n. So, what I will have is f can be written as c 0 times sum of even terms plus c 1 times some of odd terms, and what you did in the case of the legendre differential equation you said that if one of these series has to terminate. So, if one of these series has to terminate, so condition for termination of series is C n plus 2 equal to 0 or you can write alpha plus 2 alpha n minus 2 m E by h bar square equal to 0.

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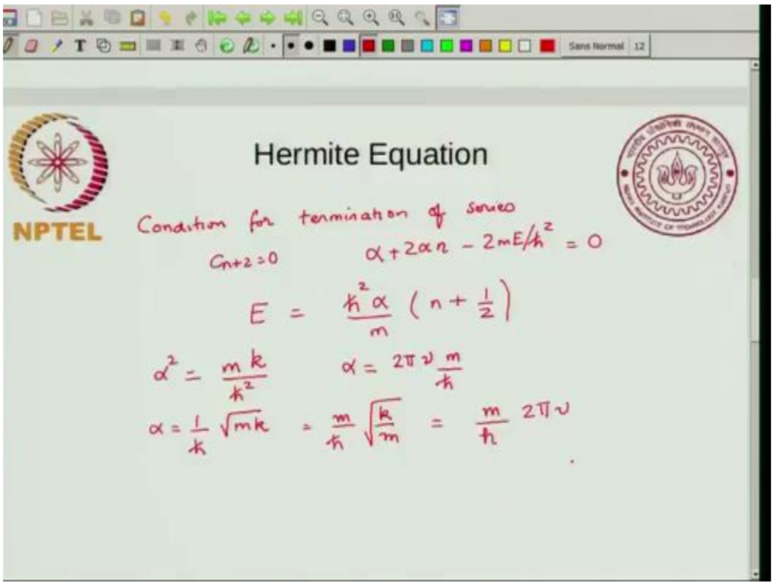

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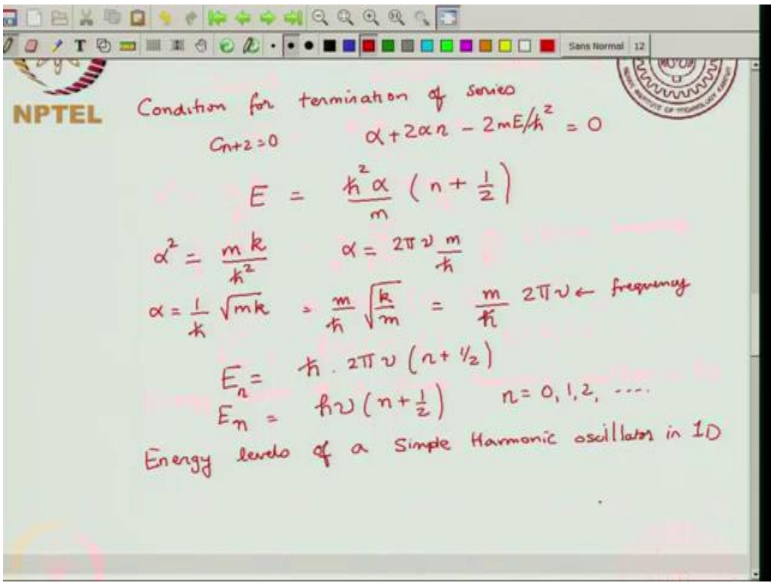

So, what you get is. So, I can write E is equal to h bar square alpha by 2 m into h bar no what I want to write it as h bar square alpha yeah. So, if I rearrange this what I will get is that e or 2 m e by h bar square is basically alpha times alpha plus 2 n. So, the then if I divide by 2 then what I will get is n plus half. So, I will get it in this form, now what we said is that the series terminates at n. So, series terminates at n. So, this is the condition for the series to terminate at n. Now alpha, alpha remember what we said was that alpha square was equal to was if you go back to where we got alpha from. So, we got we said alpha square is m k by h bar square. So, alpha square is m times k by h bar square. So, Alpha Square is m times k by h cross square.

So, then I can write this relation in a slightly different form. So, what I will says that alpha square is this and alpha I can write as I will write it in this form. So, 2 pi nu which is a frequency m by h bar. So, I mean you can you can see this in the following way. So, if I write alpha is equal to 1 over h bar square root of m k, and you can write this as this is m over h bar square root of k by m; and this square root of k by m for a simple harmonic oscillator is related to your frequency. So, this is 2 pi nu.

So, base. So, basically I can write alpha in this form, and the reason for doing this is (Refer Time: 16:28) it will become m by h bar. So, what you will get is your expression E will look like now h bar into 2 pi nu is the frequency. So, nu is the frequency times n plus half or I can write and then this is e that is terminating at n, so the energy corresponding to n. So, I can write this as h bar, h bar is h by 2 pi. So, I can write this as Planck's constant times nu which is a very typical m a energy expression and E n equal to h nu n plus half. So, this is the energy levels now n can be 0, 1, 2 etcetera. So, this is the energy levels of a harmonic oscillator of a simple harmonic oscillator in 1-D.

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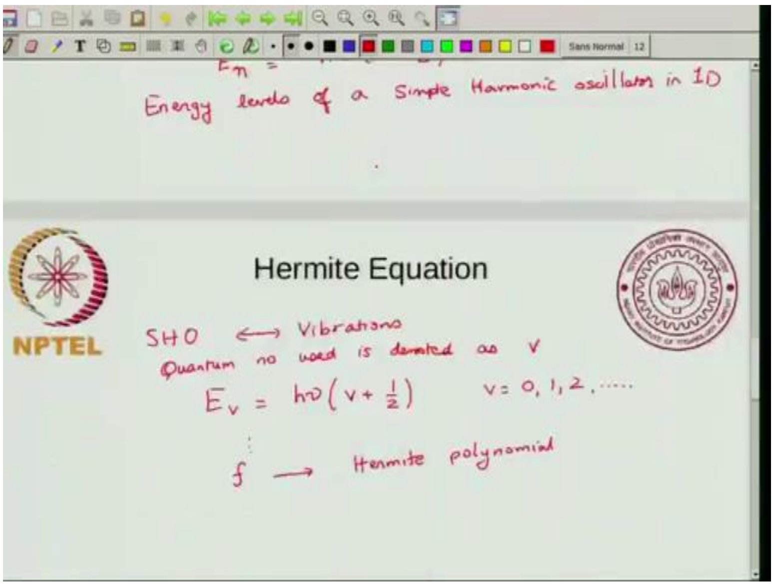

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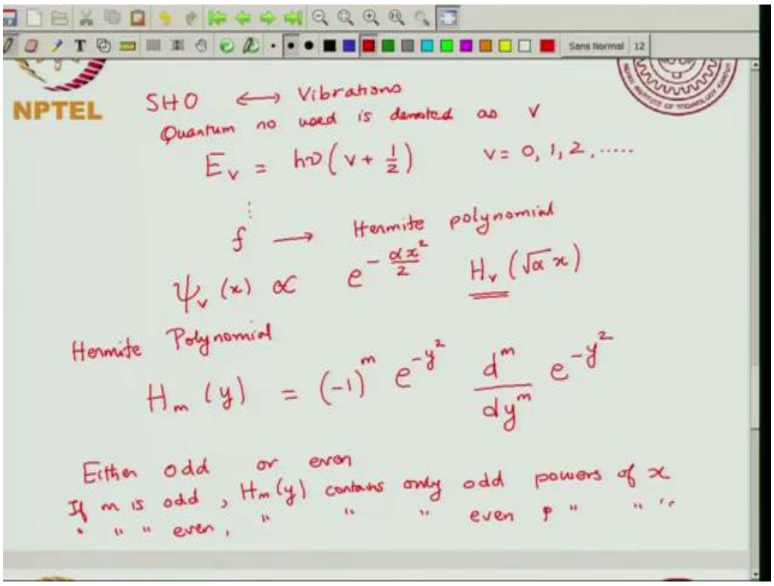

Now usually the quantum number that is used, since harmonica since simple harmonic oscillator is used to model vibrations; so the quantum number used is denoted as v. So, what we write is E v. So, instead of n v write e v equal to h nu v plus half, where v equal to 0, 1, 2 etcetera. Now we got the solution from the series that terminated. So, this was the condition for termination of the series that gave you this condition for energy it gave you quantization of energy levels of harmonic oscillator.

Now, what about the solution we have not solved it yet we just got the condition for E, but now you can go back and you can substitute and you can calculate each of the coefficients and calculate them you will get a polynomial, and this solution will this polynomial is referred to as a hermite polynomial, and if you write your solve for solve for f. So, and then the f a f is related to a hermite polynomial, and if you remember we got f by starting with the wave function starting with the psi and we made a transformation we converted from psi to f. So, the wave function is just e to the minus alpha x square times f of x.

So, the final form of the wave function is the following. So, psi of v of x has this form. So, I will I would not write the constant of proportionality, so it is proportional to e to the minus alpha x square by 2 H v of square root of alpha x. So, H v is called the hermite polynomial and what is the definition of the hermite polynomial. So, if you take H m of y this is equal to minus 1 rise to m, e to the minus y square, d m by d y raise to m, e to the minus y square. So, this is how we will define; now this is a hermite polynomial, but the variable is square root of alpha times x. So, this is the; and you can see that e to the minus alpha x square is e to the minus square root of alpha x the whole square. So, it is actually exactly equal to this what you get in the wave function.

Now, this is the expression for the hermite polynomials, and again just like the Legendre polynomials. So, it is either odd or even; that means odd polynomial. So, if m is odd, H m of y contains only odd powers and then if m is even then H m of y contains only even powers of x. So, basically the hermite polynomials will be either odd or even they will be either odd or even functions depending on whether m is odd or even.

So, now let us just write down a couple of properties of hermite polynomial and then we will stop for today.

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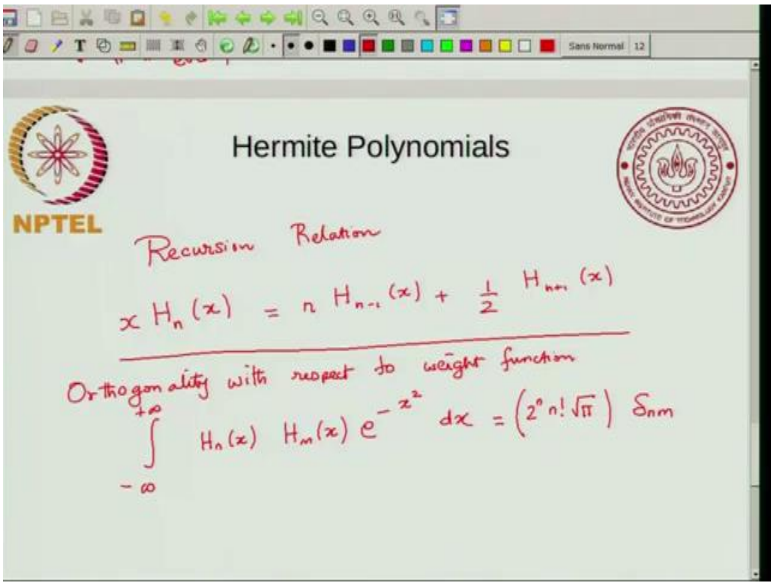

So, what are the properties? So, the hermite polynomials satisfy the recursion relation and this is a very important recursion relation in all of in vibrational spectroscopy this relation actually plays a very important role. So, I will just write the recursion relation for hermite polynomials, n times H n minus 1 of x plus half times H n plus 1 of x.

Now this recursion relation is actually extremely powerful and we will see uses of that in some of the practice problems, and I expect that you should know this recursion relation. So, you should remember this recursion relation, remember again what you do is you multiply x into H n then you get H you get a sum of 2 terms one that has H n plus 1 and 1 that has H n minus 1 there are some factors that multiply each of these. Now the hermite polynomials also satisfy orthogonality, and again this is another expression that I expect you to remember. So, minus infinity to plus infinity H n of x into H m of x; now what is important is this these are orthogonal with respect to weight function, and what is the weight function weight function is e to the minus x square d x.

So, this is the property of the polynomial. So, notice the range of the integration is minus infinity to plus infinity. So, this is some constant multiplied by delta n m. So, if n is not equal to m then it will be zero, if n is equal to m you have a constant that constant I will just write it, it is 2 raise to n, n factorials square root of pi. So, this is the constant I do not expect you to I mean. So, I mean this is a fairly simple relation and I expect you to remember this orthogonality relation with the constants.

So, this is the property of these hermite polynomials, and we will just conclude by saying that the hermite polynomials they satisfy this differential equations.

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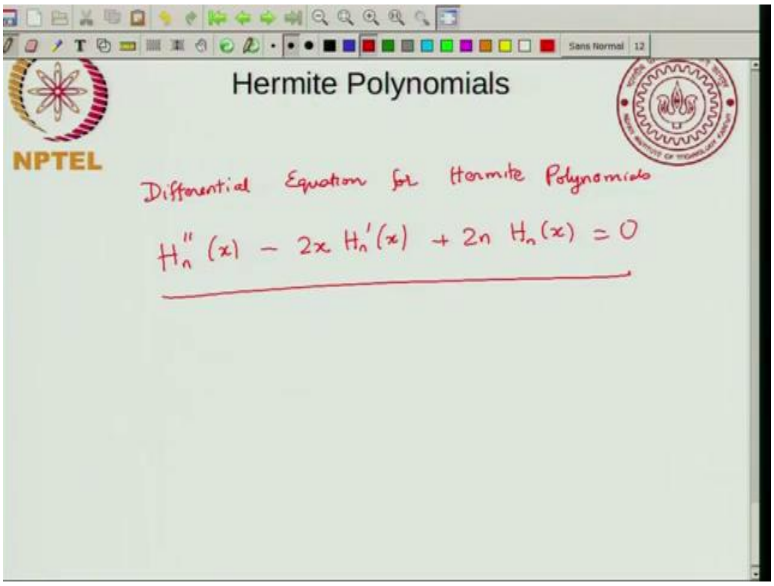

So, what is the differential equation? Equation for Hermite polynomials and it is also it is also called the hermite differential equations equation. So, I will just write this H n double prime of x minus 2 x, H n prime of x, plus 2 n H n of x equal to 0. So, this is the hermite differential equation and you can see from the differential equation that f satisfied that if you put all the conditions at the series has to terminate, you will get exactly this differential equation for f. So, with this I will stop here in the next class I will do a few practice problems.

Thank you.