Mathematics for Chemistry
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Lecture - 18

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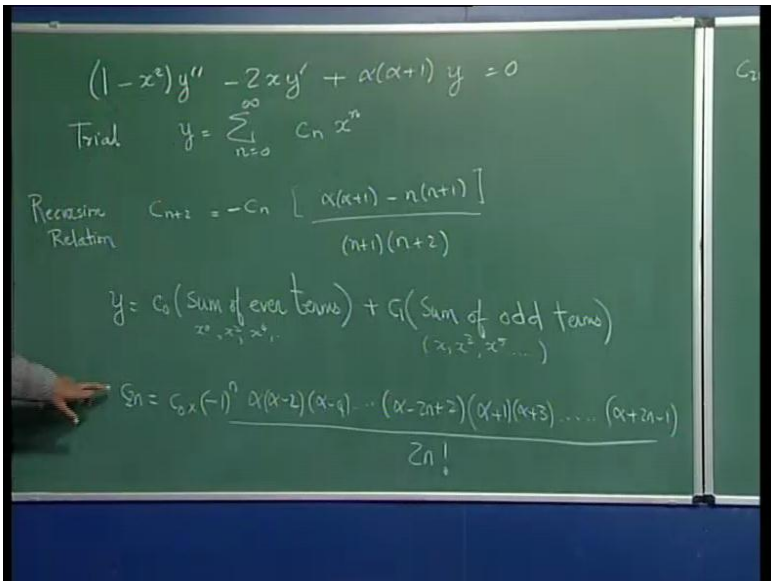

To summarize what we have been talking so far, we started with a differential equation of this form 1 minus x square y double prime minus 2 x y prime plus alpha alpha plus 1 y equal to 0. And in the power series method, we use a trial function of the form, y is equal to sum of sum over n equal to 0 to infinity C n x raise to n, and when you substitute this in this differential equation, then you get a relation between C n plus 2 and C n, we call this the recursion relation and this can be written in this form. So you can and what we saw is that all the odd terms are proportional to C 1 and all the even terms are proportional to C 0.

So, we can write your solution y as C 0 sum of even terms and even terms are polynomials of the form x raise to 0, x square etcetera x 4, so this is a polynomial containing only even powers of x, this is the polynomial containing only R powers of x like x, x cube, x 5 and so on. So, we will have C 1 x, C 3 x cube, C 3 x cube is C 3 is proportional to C 1, so there is a constant of proportionality times C 1 and so on.

We can just to formally you can show that, you can write C n is equal to if you have an even polynomial, if you have an even coefficient. So, C 2 n this is proportional to C 0, so this is C 0 multiplied by something, and that something is minus 1 raise to n. So, each time you go away 1 lower you get a minus 1 alpha, alpha minus 2 what you have is alpha alpha minus 2 alpha minus 4 all the way up to plus 2 and then you have…

So, this whole thing multiplied by alpha plus 1 alpha plus 3 this goes to alpha 2 n plus minus 1, this whole thing divided by 2 n factorial. So, essentially when you write C n plus 2 in terms of C n you have an n plus 1 n plus 2, then when you will write C n in terms of C n C n minus 2, you will have a n and n minus 1 and so on.. So, when you keep doing this all the way to C 0, then you will get a 2 n factorial, so all even coefficients can be expressed in terms of C 0.

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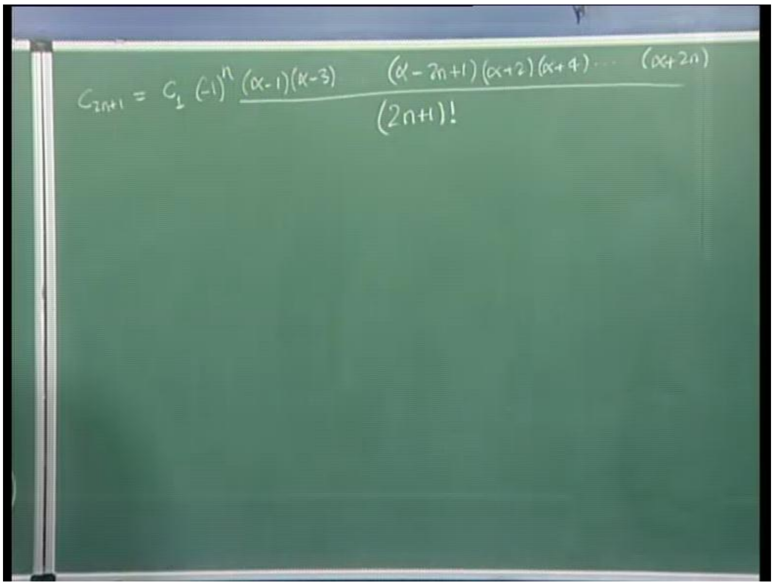

And similarly, all the odd coefficients can be written in terms of C 1 and this is minus 1 raise to n alpha minus 1 alpha minus 3 alpha minus 2 n plus 1 and alpha plus 2 alpha plus 4 alpha plus 2 n divided by 2 n plus 1 factorial.

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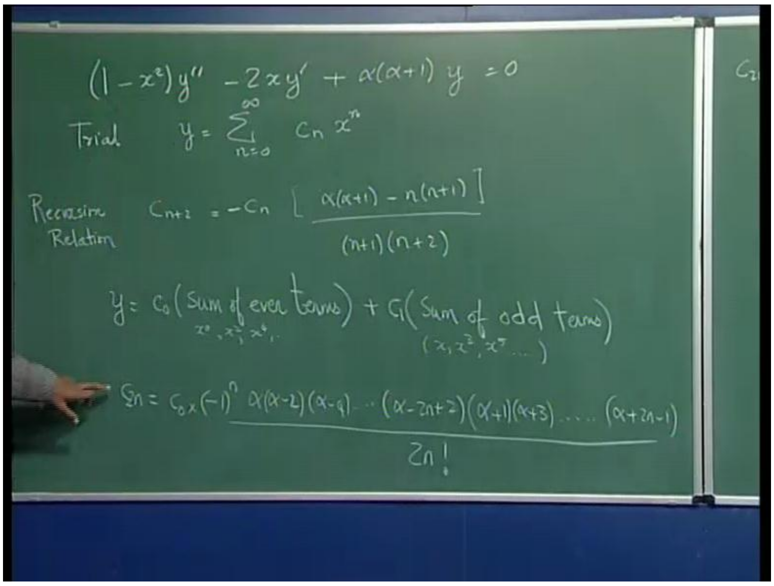

So, suppose you want to find the coefficient of x raise to 10 that will be C 10. So, C 10 means, you put n equal to 5 so you put n equal to 5, you can find the coefficient of C 10 so you can write C 10.

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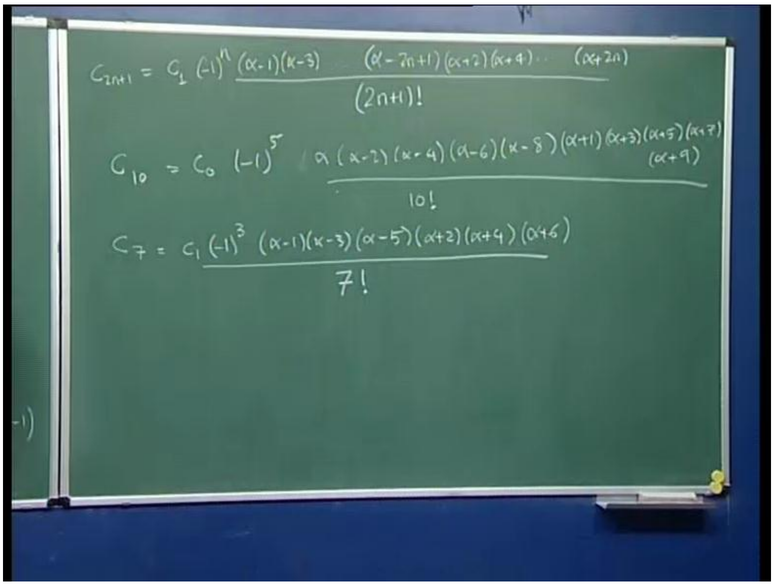

So, if I put n equal to 5 here then I have equal to C 0 minus 1 raise to 5 and then what we will have is alpha alpha minus 2 minus 4 alpha minus 6 alpha 8. So, it goes all the way to alpha minus 2 n, alpha minus 2 n is 10 plus 2, so it goes all the way to alpha minus 8 and then you have plus 3 7 alpha plus 9. So, all the way to alpha plus 2 n is alpha plus 10 minus 1 is 9. So, it goes all the way to alpha plus 9 this whole thing divided by 2 n factorial that is 10 factorial.

So, C 10 can be expressed in terms of C 0 notice that all this is just a constant, it is just depends on alpha so it is some constant that depends on alpha times C 0 similarly, if I want to write C 7, I can write it in terms of C 1. Now when so if you want to calculate C 7 then n has to be equal to 3, so 2 n plus 1 is 7, and if n equal to 3 then you have C 1 minus 1 cube alpha minus 1 alpha minus 3. Now, 2 n plus minus 2 n is 3, so alpha minus 3 alpha minus 6 plus 1, so it goes up to alpha minus 5.

So, that is a last term then you have alpha plus 2 alpha 4 and alpha plus 2 n, so alpha plus 2 n is alpha plus 6, so the last term is alpha plus 6, so that is whole divided by 7 factorial.

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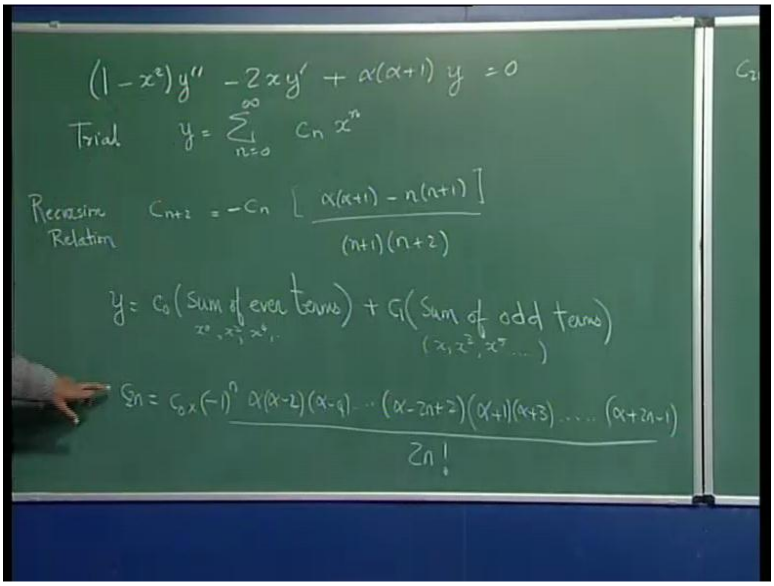

So, we can write both even and odd coefficients in the form of this power series, in this power series method we can write even coefficients is proportional to C 0 and the odd coefficients proportional to c 1.

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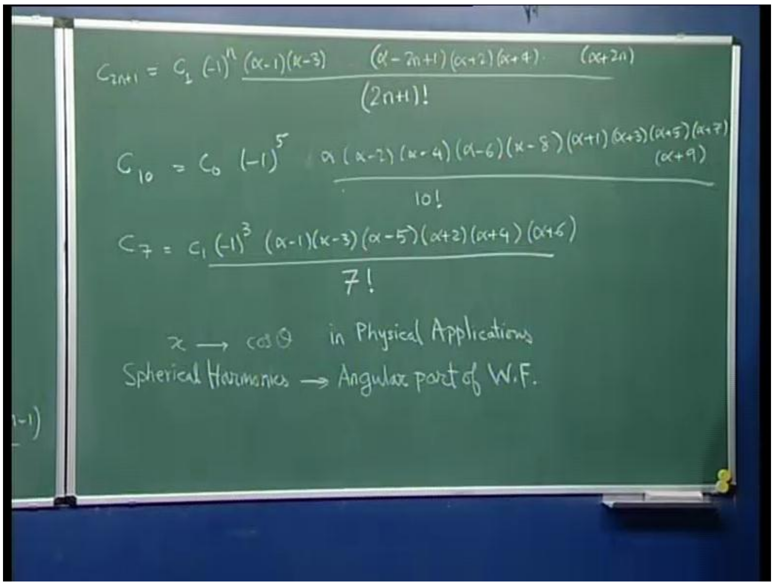

And notice that whenever you have a coefficient always the corresponding factorial appears in that denominator and then what you have in the numerator are various terms like alpha, alpha minus something and terms that look like alpha plus something so if alpha minus odd numbers, alpha plus even numbers. So, there is always this kind of symmetry in this relation.

So, the now the Legendre this equation it appears very naturally in the solution of the wave equation in the spherical coordinates and this appears to in the solution of the angular part of the of the wave equation. And so in the quantum mechanics courses it appears, when you are solving for the angular parts of the wave function for any spherically symmetric system. So for example, if you are solving for the hydrogen atom and, you are solving for the angular part of the wave function then the Legendre polynomials appear and Legendre differential equation appears, so typically when this appears your x, the argument x, x is actually cos of theta, so in the spherical.

So, what you call x in the differential equation is physical in applications so applications what appears is cos theta and what you have is a differential equation, where the argument is cos theta so you have the wave function is a function of cos theta and all these derivatives are with respect to cos theta. So, this leads to the spherical harmonic switch are which are related to the angular part of the wave function.

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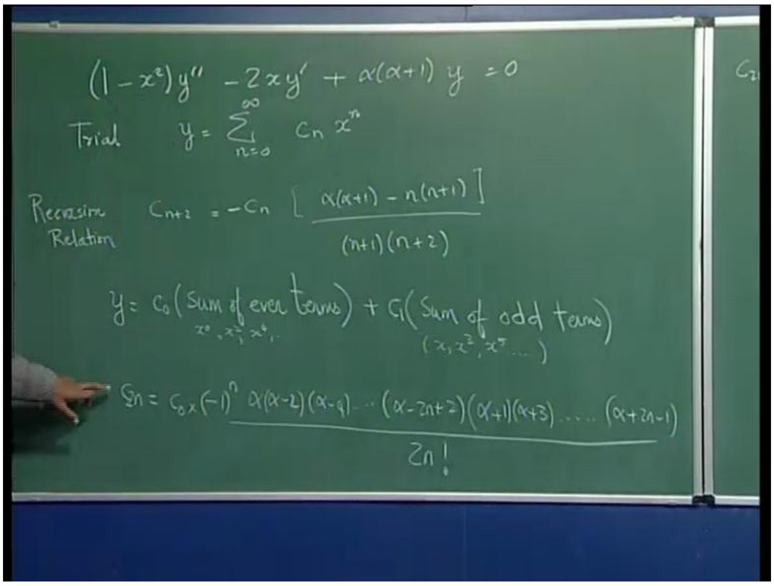

So, the angular part of the wave function of wave function, now 1 of the things that you have to think about, whenever you have a series like this whenever you have a power series of this form, the immediate question that you should ask is this does this series converge or does it diverge. So, what you mean is that this series as x becomes very large does it goes to plus or minus infinity or does it go to some finite number. So, that is the question that you immediately should ask, whenever you see a power series.

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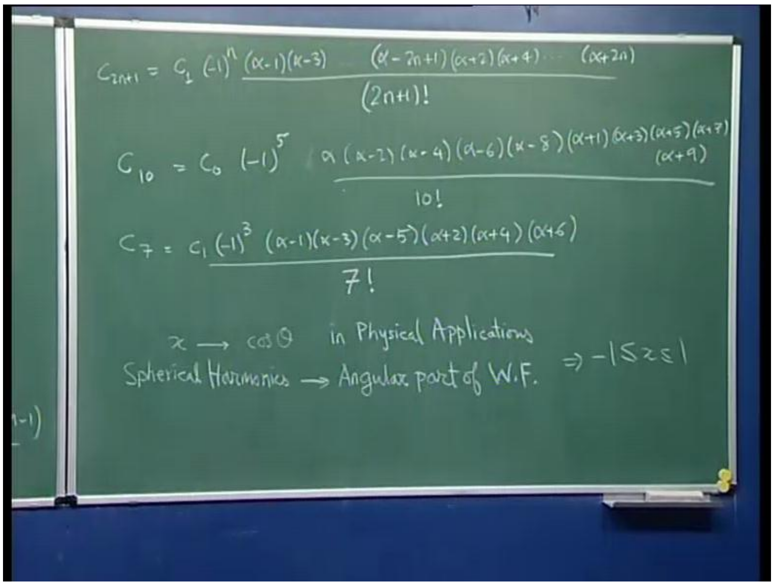

Now in these kind of as I said in physical application sin the spherical harmonics x is, x corresponds to cos of theta and so the argument x varies between minus 1 and plus 1, so cos theta is between plus and minus 1.

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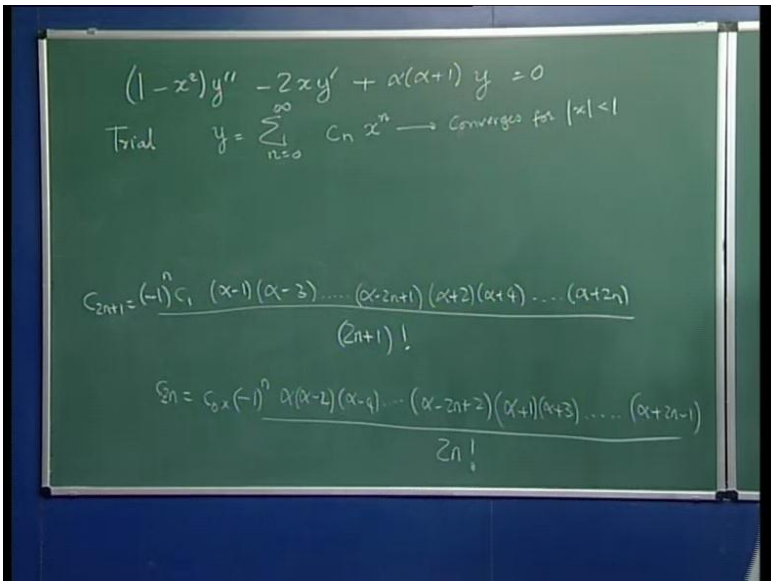

So, what this implies is minus 1 less than equal to x, less than equal to 1 and if x goes between minus 1 and plus 1 if, x goes between minus 1 and plus 1. Now so long as x is less than 1 so long as x is strictly less than 1, x is strictly less than 1 or rather or it is strictly greater than minus 1 then this series will converge. So, this with this power series if x is less than 1 if, absolute value of x is less than 1, so this converges for it always converges. So, whatever power series you take it will always converge if, a absolute value of x is less than 1.

So, the only concern is what happens, when x equal to 1 now if you look at these terms. So, you have to consider what happens to these coefficients, when x equal to 1 you just have y equal to sum over n equal to 0 to infinity C n and so you have to look at this series of coefficients and you have to decide, whether they converge or they diverge. So, the point is this series it converges for x is for absolute value of x less than 1 now, when x is equal to 1, then this series becomes sum over n equal to 0 to infinity C n and C n. Since I mean it has infinitely many terms and depending up on the value of alpha these terms either they either there are infinite terms or there are finite number of terms.

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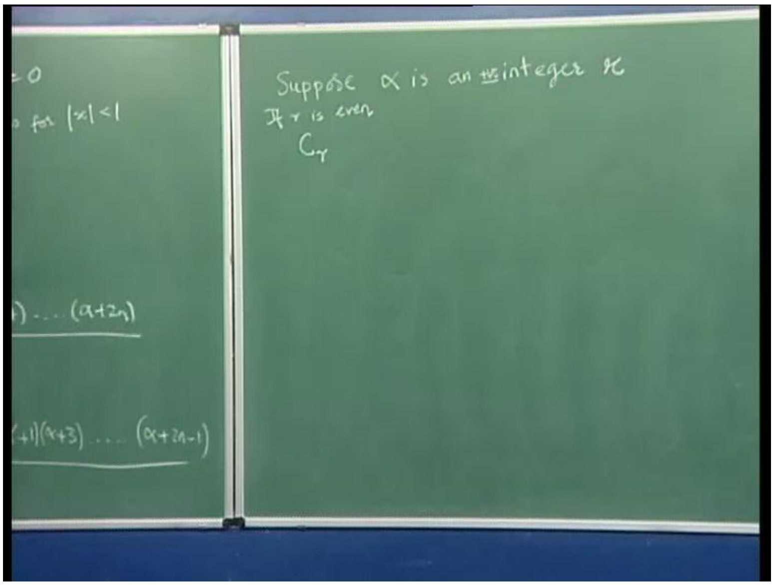

So, suppose alpha is an integer r. And lets I will just choose a positive integer a r so what that would imply is that C of r, now if r is even.

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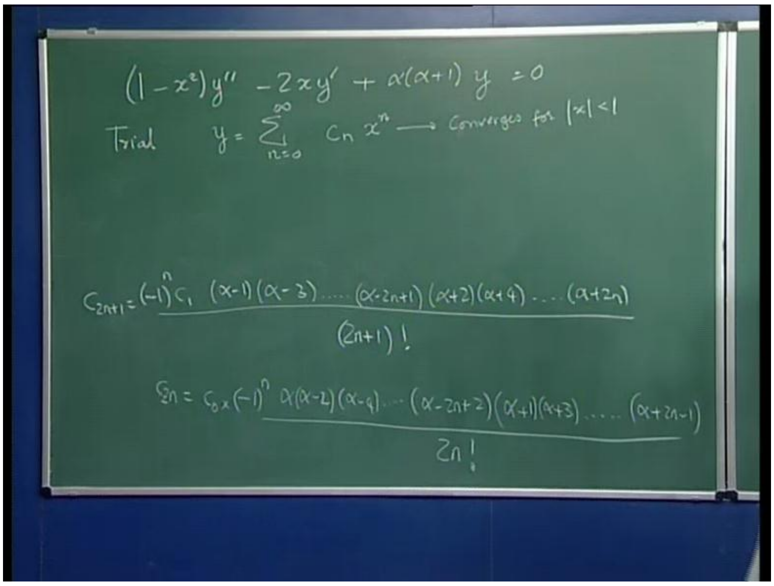

C of r can be written in this form so C of then instead of n, I put r by 2, I can write this form.

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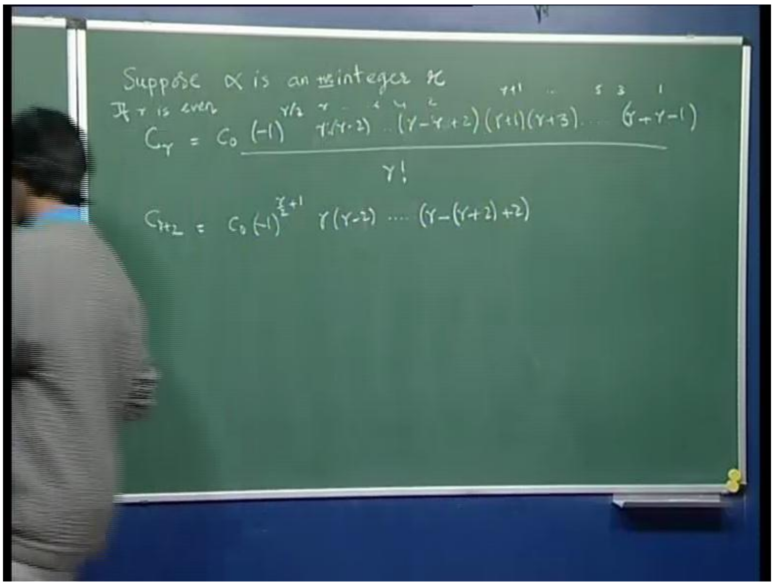

So, C of r can be written as C 0 r by 2, all the way up to alpha minus 2 n plus 2 or r plus 2 and what we have said is that r alpha is equal to r. Now, if alpha equal to r then I replace all the alphas by r and what I get is r minus 2 all the way to r minus r plus 2 and then you have r plus 1 r plus 3 r plus 2 n is same as, r minus 1. So, you notice divided by r factorial. So, it goes from r minus 2 all the way up to 2, so basically this series looks like 2 4 6 all the way up to r. r is an even number.

So, it is a product of all even numbers smaller than r and this goes from 1. So, this is 1 3 5 all the way up to r plus 1 so this is a product of all odd numbers, so that is what you get, if you do this now what about C r plus 2, what about C r plus 2. Now, if you had r plus 2 then this would be C 0 minus 1 raise to r plus 2 is r plus 2 by 2 is r by 2 plus 1 and here, you have r plus 2 r minus 2, all the way tor plus 2 or sorry you have alpha is equal to r. So, you have r minus 2 all the way up to r minus now 2 n 2 n is r is 2 into r by 2 plus 1. So, that is that is 2 n, so 2 n is r plus 2, so minus r minus 2 plus 2, so where I had 2 n i put r plus 2 so this term alpha minus 2 n plus 1.

So, that is alpha minus r plus r plus 2, so that is alpha is r minus r plus 2 so I just make it explicit I put it this way and I had a plus 2 or plus 1 r sorry r. So, you have no sorry no plus 2 r plus 2.

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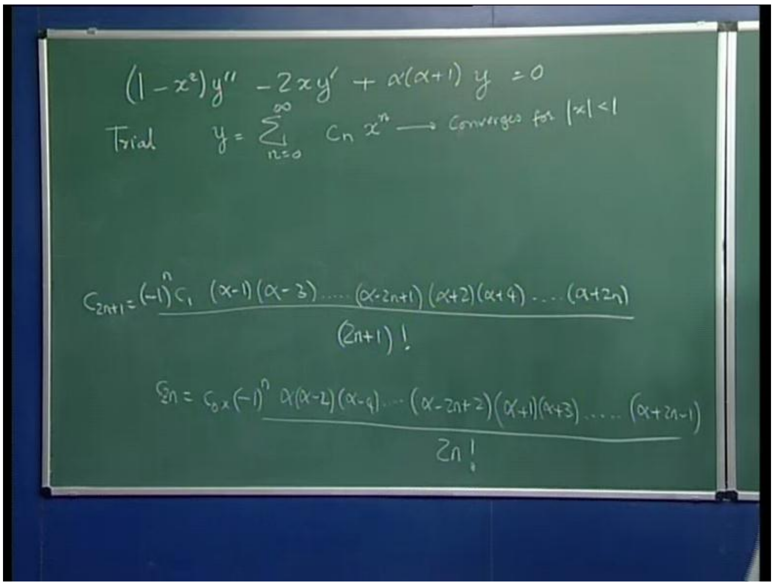

So, what you have here is alpha minus 2 n plus 2 so you have alpha alpha minus 2 alpha minus 4 alpha minus 6 alpha minus 8, it keeps going on all the way to alpha minus 2 n plus 2.

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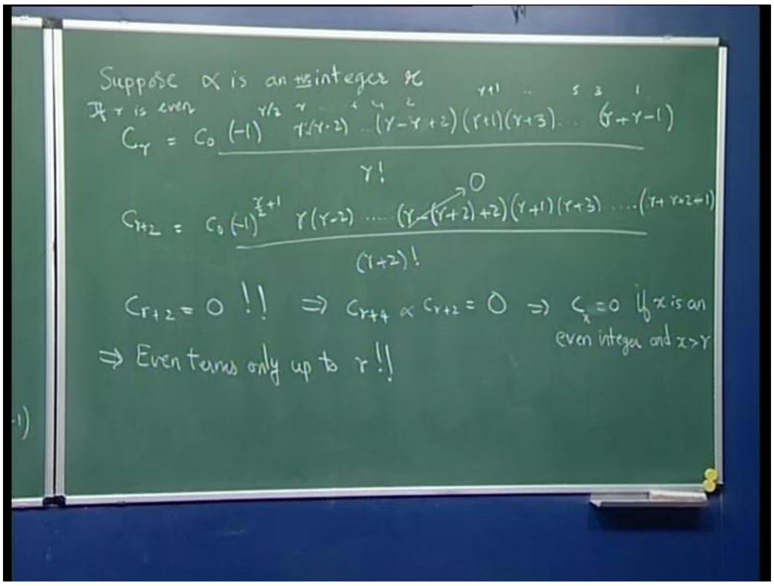

So it this is alpha alpha minus 2 then alpha minus 4 alpha minus 6, all the way to alpha minus this is 2 n alpha minus 2 n 2 n is same as r plus 2. So, alpha minus r plus 2 plus 2 and then you have all the other terms like alpha plus 1 or alpha plus 1 is r plus 1 up to r plus r plus 2 minus 1,this whole thing divided by r plus 2 factorial right.

So, notice that the C r plus 2 term has this term so this is r plus 2 minus r plus 2, so this term goes to 0, so that implies c r plus 2 equal to 0, so this is the result that you see if, r if alpha is a positive integer r and r is even, then C of r plus 2 is 0. And this immediately implies C r plus 4 is proportional to C r plus 2 equal to 0 C r plus 4 is just a multiple of C r plus 2 and that is also equal to 0 and so implies C of C of any C of x equal to 0 if, x is an even integer and x greater than r. So that means, all the even terms for which, are greater than r are all 0 that is implies even terms only up to r so the series. So, the sum of even terms that goes only up to r.

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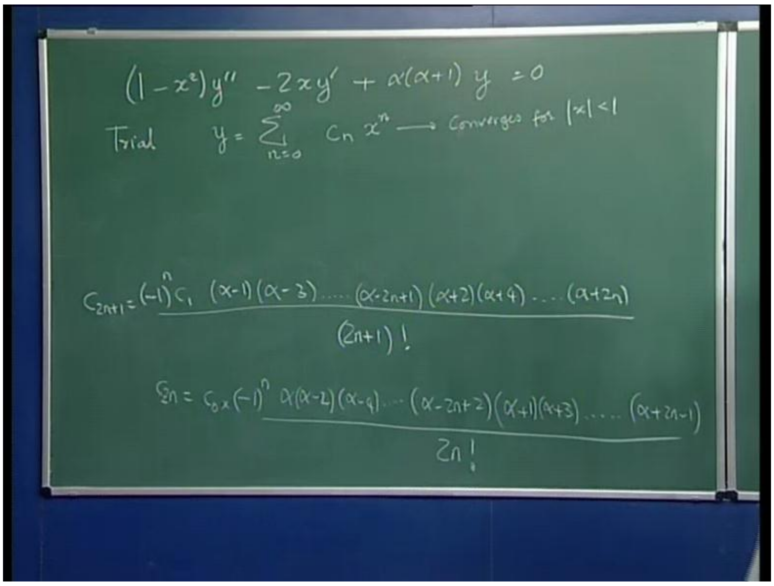

So, this is an important property that if alpha is an integer, if alpha is a positive.

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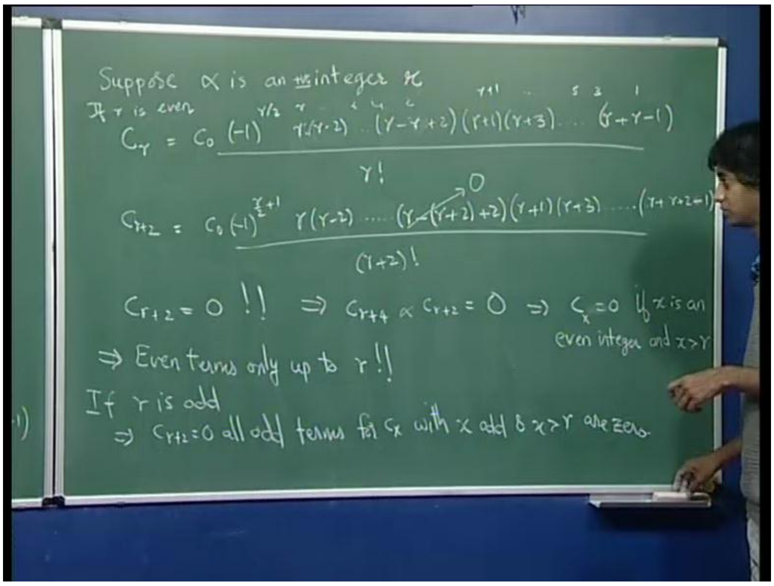

If alpha is an even integer then your then the even series truncates at alpha equal to r now if, alpha is an odd integer, if r is odd then you can show that then it is easy to show you can go by the same arguments, if r is an odd integer. Then when you take C of r plus 2, which will be another odd integer that will be equal to 0 odd 0, all odd terms for C x with x odd and x greater than r are 0. So, essentially if r is an odd integer then also all the odd terms all that are where the power of x is greater than r are 0, and if alpha is an even integer then all the even terms with power greater than r are 0.

So, what this means is that if, you choose alpha to be an integer so if alpha is an integer r then your series truncates at r then 1 of the 2 series truncates at r. Now, we come back to our solution we know that if alpha is an integer then depending on if it is even then the even series truncates at r, if it is an odd integer. Then the odd series truncates at r and this is what is used in order to motivate solutions of this Legendre equation in real physical problems.

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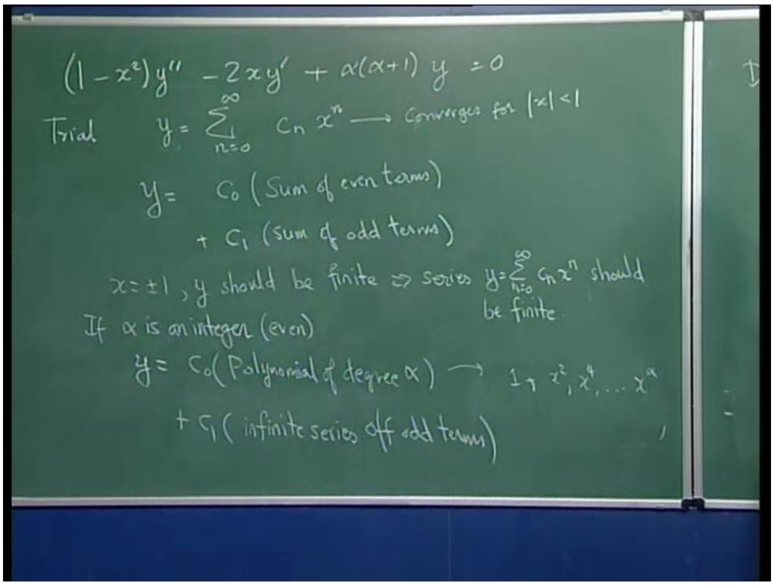

So, now y we had y is equal to C 0, sum of even terms plus C 1 sum of odd terms and so if r is an integer then 1 of these series terminates at 1 point so 1 of these series will terminate if, r is an integer. Now how do we use this fact, when we are applying it to real physical problems so suppose you are applying it to spherical harmonics then 1 of the things you will say is that your y is actually corresponds to a wave function, and the boundaries at x equal to plus minus 1 y should be finite.

Now, suppose this series does not truncate so suppose you had an infinite series of coefficients, then you can show that is a divergent series. So, implies a series should be finite so this is particular case of this Legendre polynomial in the of this differential equation, where we had a particular Gaussian relation.

So, you can have convergence series but the series that we considered that turns out to be divergent if, at x equal to 1 so that implies so if alpha is an integer y is equal to and let us say choose even for now. So, then y equal to C 0 times a polynomial of degree alpha this is the polynomial of degree alpha that means, it has terms like 1 x square x 4 all the way up to x raise to alpha. Alpha is an even integer and then you have C 1 times, this is a series this is an infinite series of odd terms.

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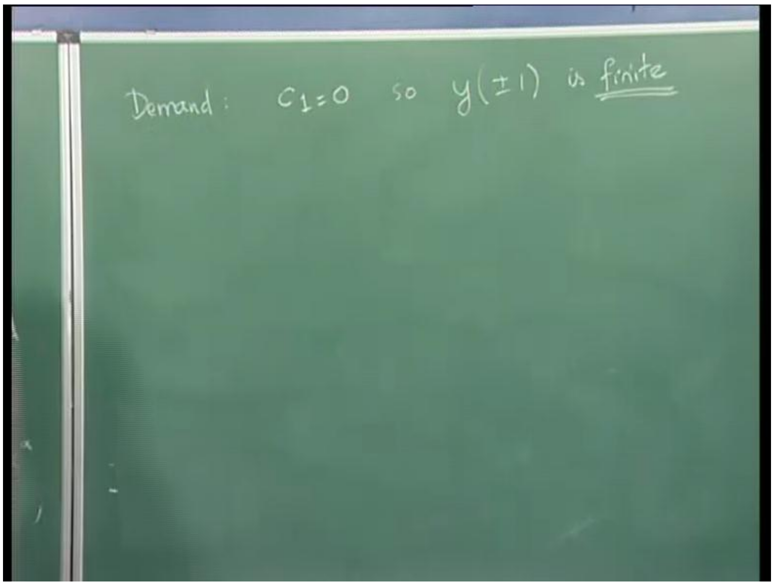

So, this is an infinite series of odd terms. And what we will demand is that C 1 equal to 0. So, if C 1 equal to 0 so we choose C 1 equal to 0 and then that will ensure that your y is finite at the boundary. So, y of plus minus 1 is finite.

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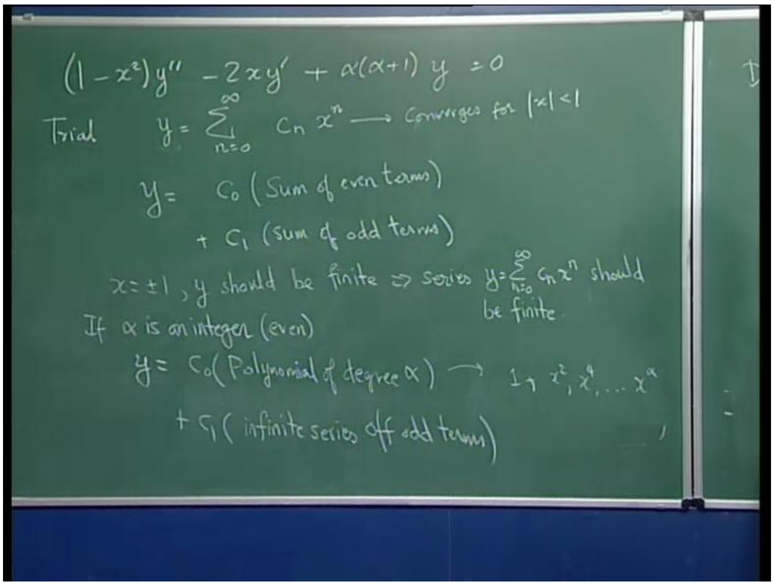

So, if you did not have C 1 equal to 0 if, C 1 was not equal to 0 then the then you would have an infinite series of odd terms and when, x equal to 1 this series will go to plus or minus infinity. So, therefore you by you force C 1 equal to 0, so that you only have this.

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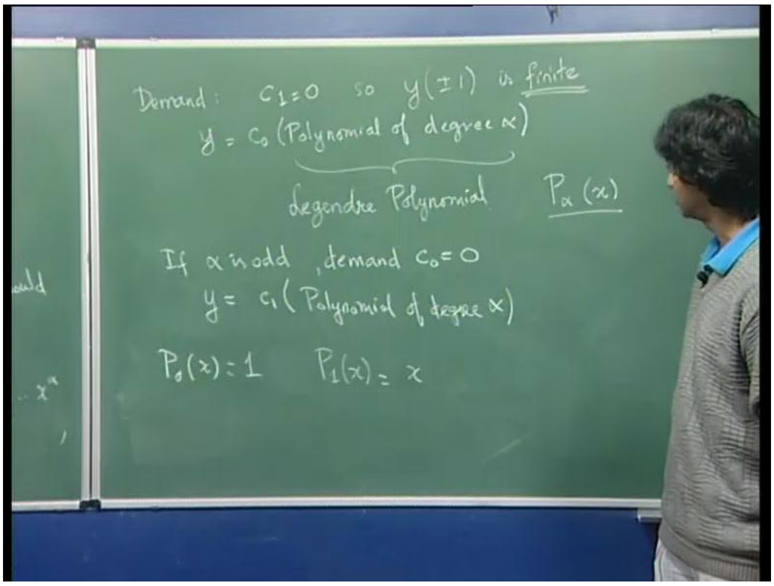

And so y is equal to C 0 times polynomial of degree alpha and this polynomial of degree, alpha is called a Legendre polynomial so it is a polynomial it is a function of x so it is a function of x so it is denoted by P alpha of x. So it is a function of x and it is a polynomial function it is denoted by P alpha. Alpha is because it is a polynomial of degree alpha you can similarly, you can do this for odd also, if alpha is odd y.

So, you demand C 0 equal to 0, so y is equal to C 1 times polynomial of degree alpha and this is also Legendre polynomial. So, the Legendre polynomial is a polynomial function and it has degree alpha and so it is given this name because it appears quite often. Now, the we can write the first few Legendre polynomials, so P 0 of x this is chosen to be 1, so P 0 of x is 1 P 1 of x, this is x so remember we had an obituary choice for C 0 and C 1.

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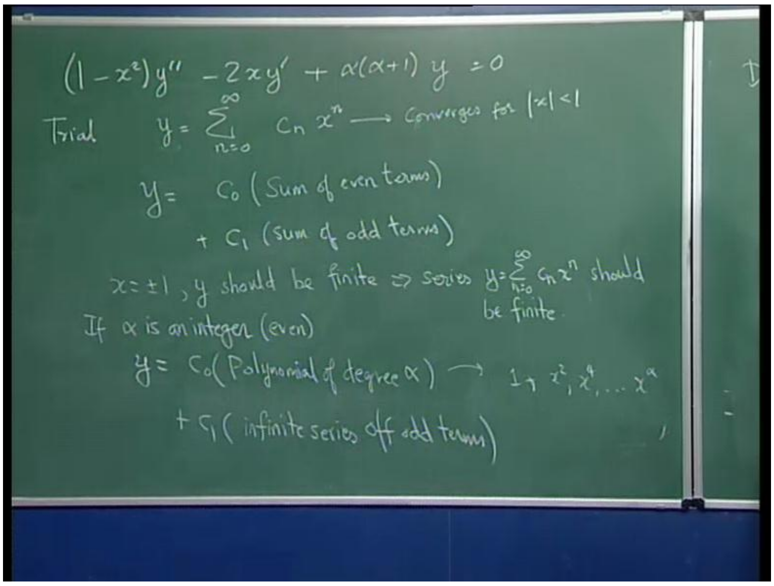

And P 0 means, a polynomial just of degree 0, so that is just a constant and that constant is chosen to be 1 similarly, P 1 is also chosen to be 1.

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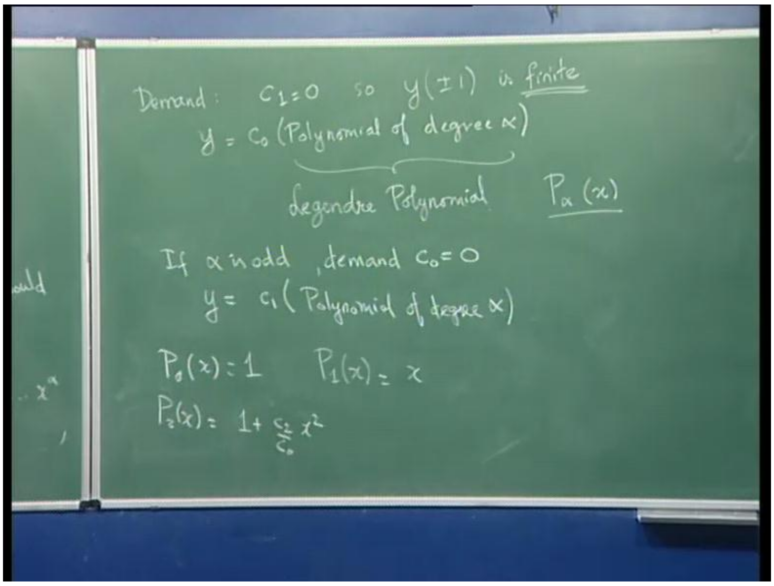

And this gives you P 2, so you can work out P 2 once you know P 0, you can work out P 2. In fact you can use the recursion relation to write you can go back to the recursion relation and you can write that P 2 is minus 1 into P 0 the coefficient of 0th polynomial. So, I think we would be little more careful, so P 2 of x is equal to C 0 plus C, so 1 plus C 2 by C 0 x square. So, what I did is I wrote y is C 0 times, a polynomial of degree alpha.

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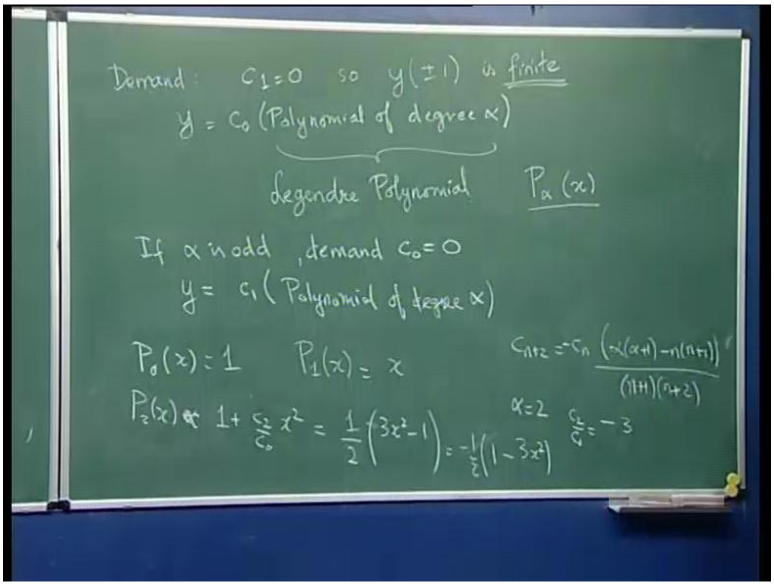

Now if, this polynomial truncates at 2 since alpha equal 2 this polynomial will end at 2. So, P 2 looks in looks of this form and so what you need is C 2 by C 0 and so this works out to 1 minus. So, this works out to half 3 x square minus 1 so you can work this out and show that this is need the case for this.

So, what we have seen is that you can construct each of the polynomials 1 by 1 and you can take this series further on, so there are many interesting properties, that you can derive these are just based on the recursion relation. And I just want to remind you the recursion relation was a relation that related C n plus 2 equal to C n times something and that something was minus C n times alpha alpha plus 1 minus n n plus 1 divided by n plus 1 n plus 2.

So, this was the recursion relation so you could calculate C 2 by C 0 using this relation so C 2 by C 0 means n equal to 0 n equal to 0, you have alpha alpha plus 1 divided by 2 and if, you had alpha equal to 2 then you just have 2 into 3 by 2 that is 3. So, that is where you get this from. So, you can use this so starting with this recursion relation you can calculate all the polynomials.

So, what we said is that P 2 of x is actually proportional to this so there is an arbitrary constant of proportionality that you can add. So, it is proportional to 1 plus C 2 by C 0 x square. So, and then P 2 is actually equal to half 3 x square minus 1. Now or I can write this as minus half 1 minus 3 x square so now I said that this constant before, this 1 is arbitrary.

So, this constant is chosen arbitrarily, the in fact there are some ways that, we will talk about later, how we choose these constants, but essentially what you have is 1 minus 3 x square now the 1, we got from the 1 corresponds to the leading term in this polynomial series, the second term is C 2 by C 0. So, this C 2 by C 0 now, this C 2 by C 0, you can calculate C 2 by C 0, if you want to calculate C 2 by C 0, you use a recursion relation.

So, C n plus 2 is related to C 0 and to C n in this way, now you put n equal to 0, when you have C 2 equal to C 0 times something, n equal to 0. So, this term will go away, now when alpha equal to 2 so since we are calculating P 2 you need to put alpha equal to 2. So, you put alpha equal to 2 then C 2 by C 0 becomes minus 3 and that is this minus 3 here.

So except for this constant of proportionality you know, how to get the Legendre polynomials so except for this constant of proportionality you can derive the Legendre polynomial. Using this method now this pretty much is the entire way of how to use the power series method and it is a very powerful method, it can be used for many different kinds of problems and what I have illustrated here is the is the basics of the techniques.

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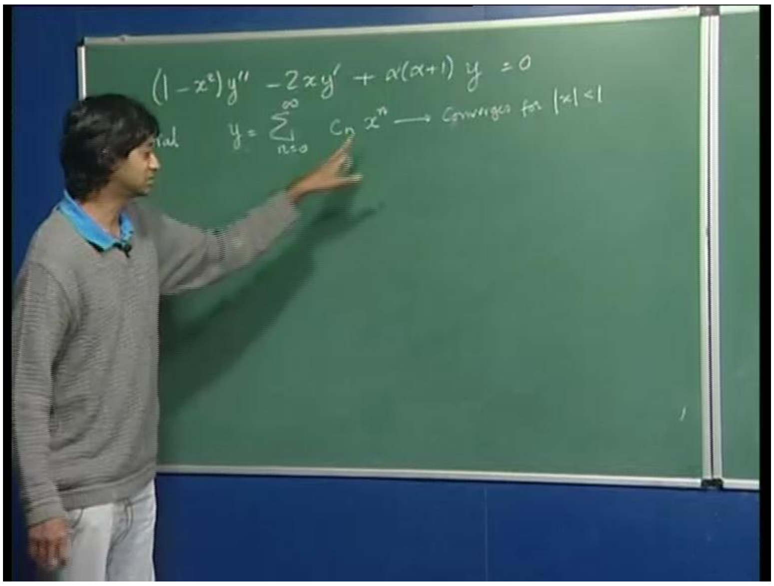

So, you start by assuming a trial function of this form and then you get various recursion relations.

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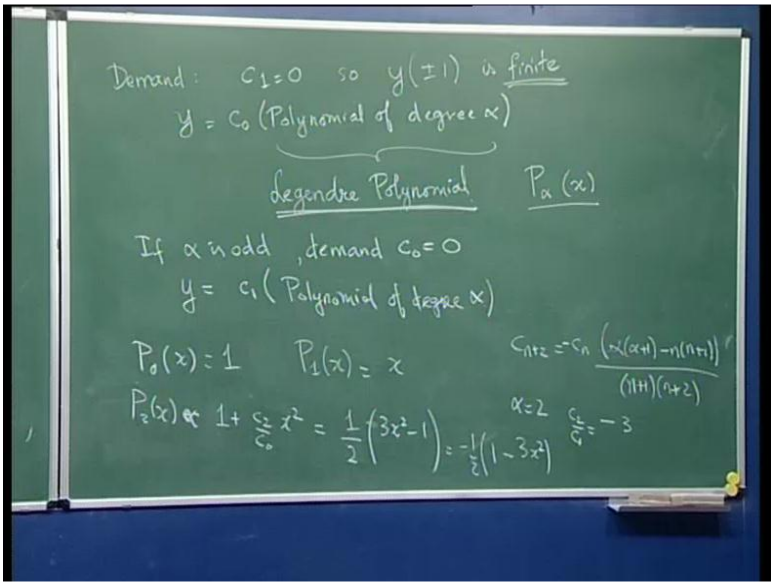

And actually starting from this recursion relation, you can derive all the polynomials individually. Remember that we had to impose the condition that if alpha is an integer then this series truncates at some value and that allowed us, to set to 1 of the coefficients to 0 and that is what gave us these Legendre polynomials. So, these polynomials are quite since, they appear in the solutions of these equations they are given a name and these equations are quite important in various applications. Now, there are some interesting properties of these polynomials so when you take polynomials of different degrees like P 0, P 2, P 3, P 4 and so on; they satisfy some interesting relations.

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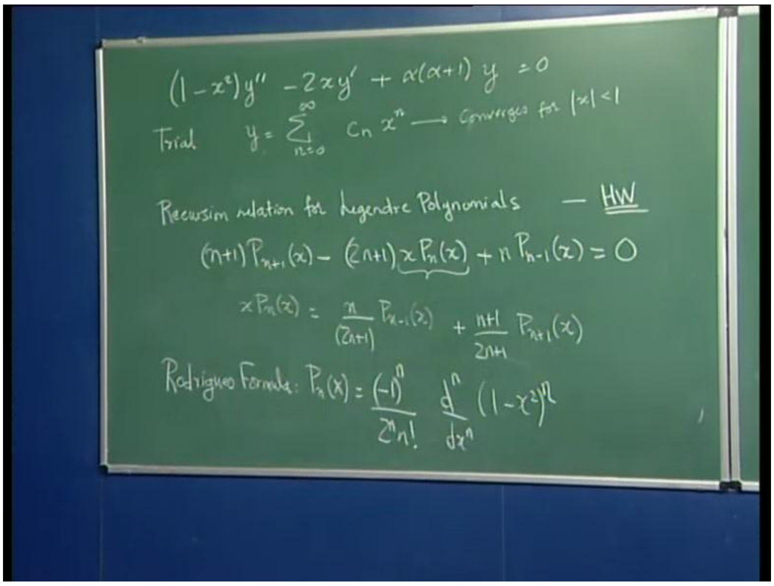

So, 1 of them is also called a recursion relation or Legendre, and this is something that you should try to work out as a home work you can try to work out, I will give you the relation n plus 1 2 n plus 1 x P n and this is plus n P n minus 1 x. So, this is something that you can derive this based on the these expressions for the polynomials, it is not that straight forward to derive but we will just assume that it is possible to derive these notice.

Now this is a very interesting relation because it relates P n plus 1 to P n and P n minus 1. So, if you have a polynomial for or in other words that is relates P n to P n minus 1 and P n plus 1 so if you have x times P n then it is a liner combination of P n minus 1 and P n plus 1 so I will write this in a slightly different way. So, x times P n of x is equal to n divided by 2 n plus 1 P n minus 1 of x plus n plus 1 divided by 2 n plus 1 P n plus 1 of x.

So, x times P n is linear combination of p n minus 1 and p n plus 1. So, this is the very interesting relation and it turns out that, there is 1 relation is turns out to be very important, when we are deriving selection rules and spectroscopic transactions. So we will come back and we will see this relation, at that point to or similar relations involving other polynomials, the other there are some more interesting ways interesting properties of these Legendre polynomial, I will just summarize 3 of them and before we go to the next part of this power series solution. So, the 3 of them first is what is called the Rodriguez formula and this is also, something that, so this is a formula that gives your p n. So, by 2 raise to n factorial 1 minus x square raise 2 n 1 minus x square so the point is that If, you want to derive any polynomial and my polynomial.

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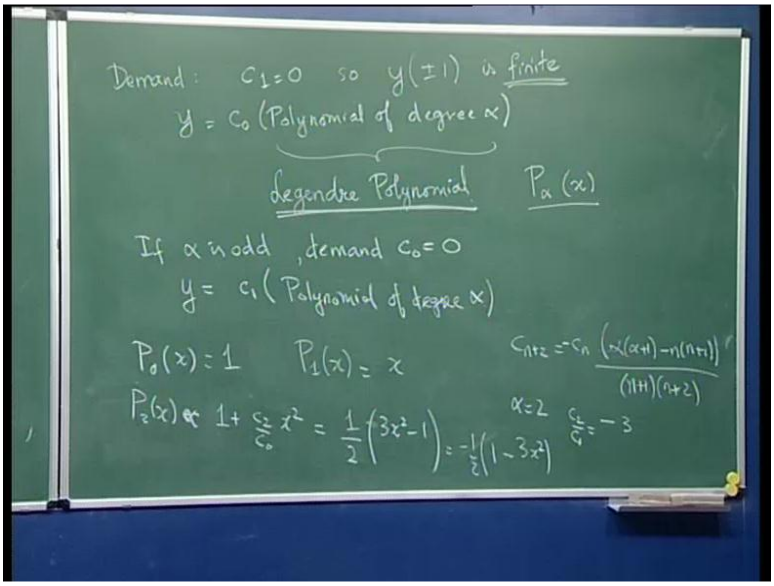

I mean the entire polynomial not just the individual coefficients, the entire polynomial you can derive it.

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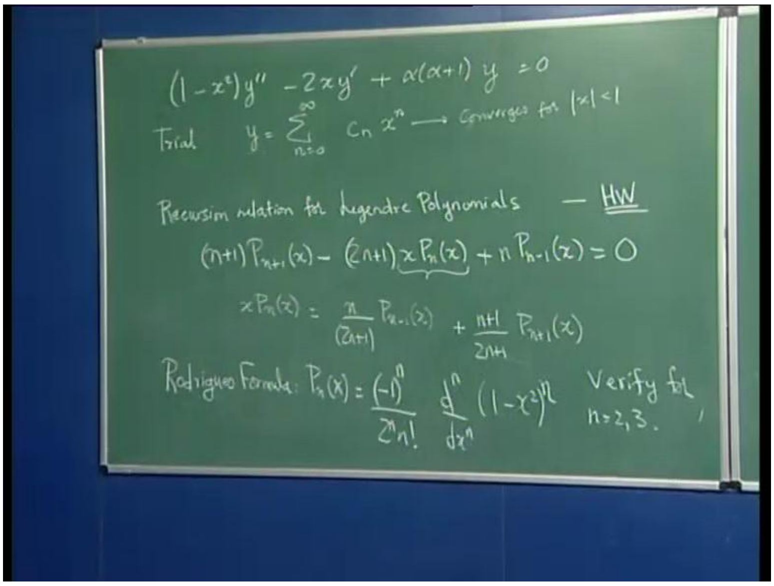

Starting with so suppose you want to write you want to find the value of p 4. So, then you just put n equal to 4. So, you take 1 minus x square raise to 4 you take the 4 derivative of that and then you multiply it by minus 1, raise to four 4 by 2 raise to 4 factorial and what you get will turn to be the Legendre polynomial. So, this was the formula that was derived by Rodriguez, you can verify it forever if, y for n equal to 2 3.

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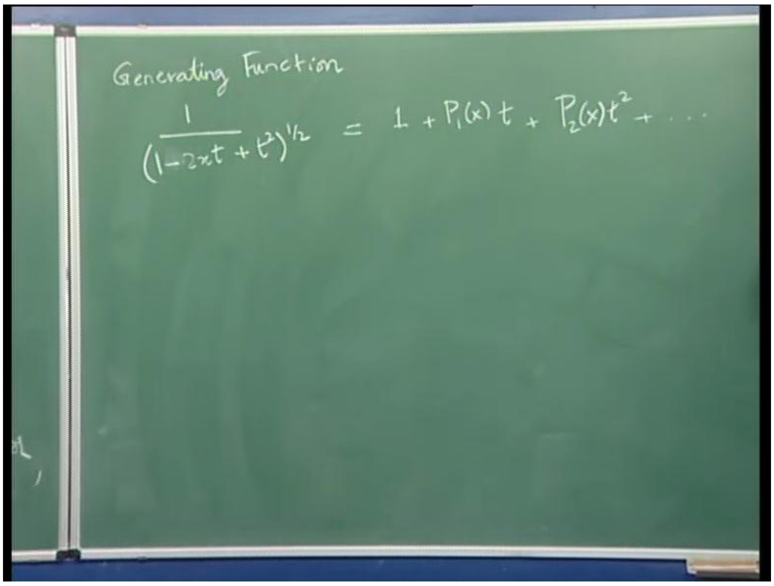

So, that is another exercise for you to do another interesting property of the Legendre polynomials is a property of a generating function and what you can show is that this function 1 over 1 plus 2 x t 1 minus 2 x t plus t square raise to half. So, if you take this function and you write this, as a Taylor expansion in t. So, if you write this as a Taylor expansion in t so it looks like 1 plus some constant into t plus some constant into t square plus.

So, here I am treating this as a function of t and this constant is a function of x and what appears, will I get the exactly the Legendre polynomials. So, if you write this as a Taylor series in t, then the then what appears in this Taylor series will be the Legendre polynomials and this is a direct consequence of this Rodriguez formula.

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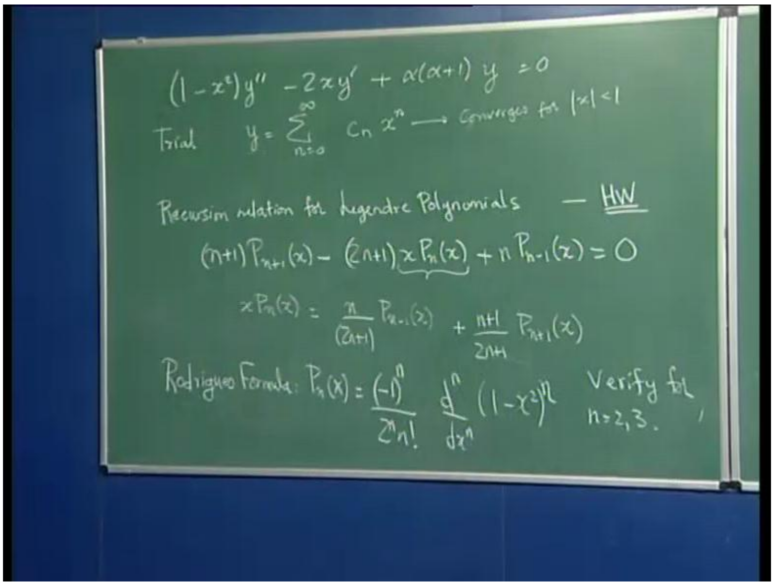

So, you can look at Rodriguez formula and that then you can show that you this is indeed a generating function.

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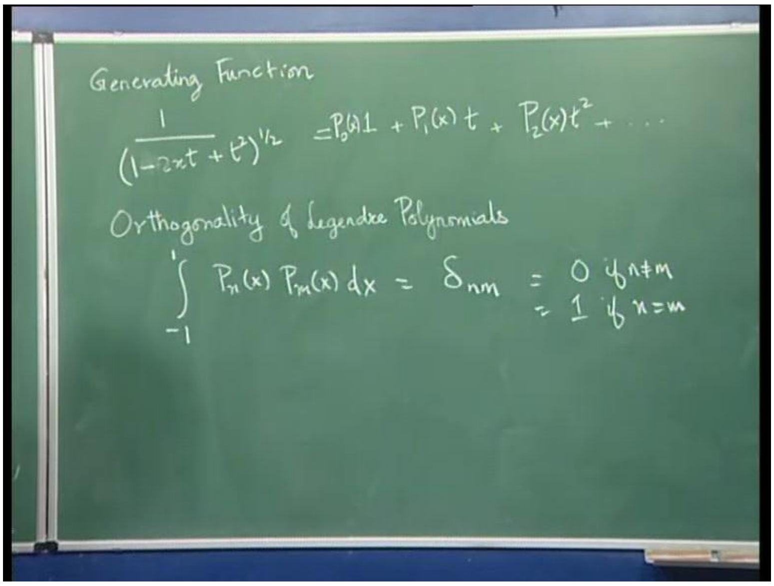

And interestingly 1 P 0 of x is just 1, so you can multiply this by P 0. So, all the polynomials can be generated from this simple looking function lastly, we will mention 1 property of Legendre polynomials that will that can be proved, and this property is the orthogonality of. So, this is integral minus 1 to 1 P n of x P m of x delta n m, so that means so this is equal to 0 if, n is not equal to m equal to 1 if, n equal to m. So, there are

2 things in this first of all if you take n and m to be different from each other then the integral will be 0, will be identically 0.

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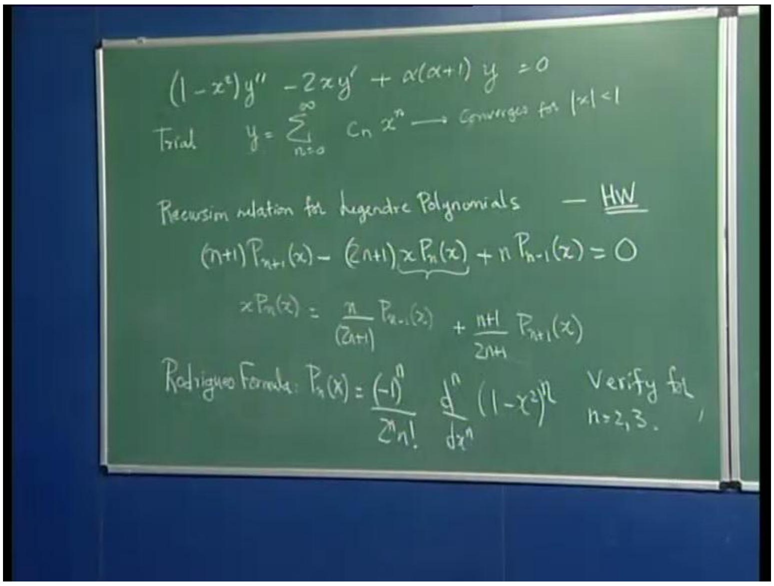

And in order to show this, you can use this relation and or you can use know.

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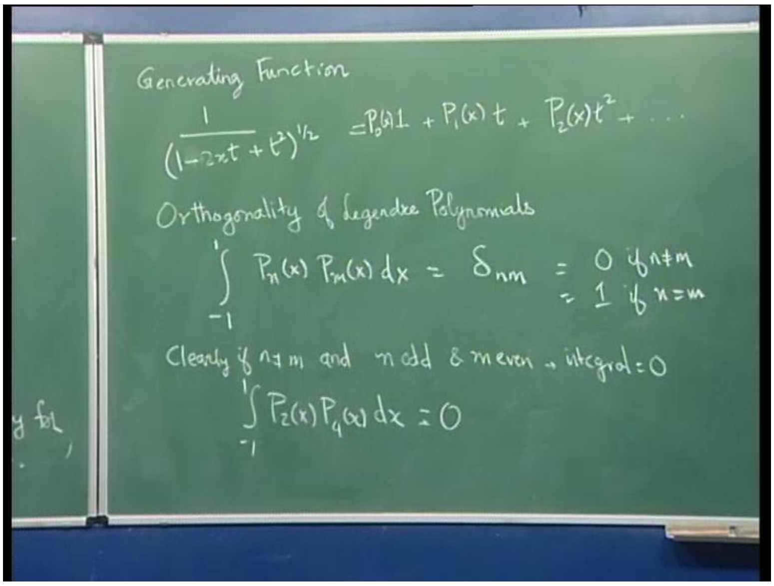

You can consider a case where so clearly so if n not equal to m and n is odd and m even or vice versa. So, if 1 of them is odd 1 of them is even, then you have an odd function multiplying an even function their product is an odd function, then clearly this is equal to 0, then integral is 0, equal to 0.

So, if 1 of them is odd 1 of them is even obviously, it is 0 but even if they are 2 even functions, even if both these are even functions but 1 is but n is not equal to m it is it turns out to be 0. So suppose I take P 2 times P 4 d x from minus 1 to 1 this turns out to be equal to 0.

Obviously, if I taken P 3 and P 4 you would have said that P 3 contains only odd terms. So, it is an odd function of x P 4 contains only even terms. So, it is an even function of x their product is 0 but even if you take any 2 different functions, that are both even. So this is also the whole integrant is an even functions still this, when you take 2 different polynomials their integral is 0.

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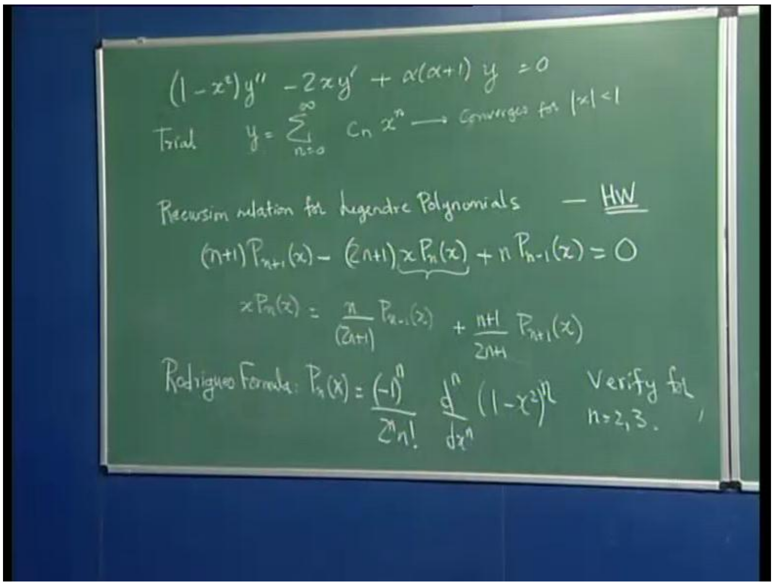

And to show that you can use such a relation, you can use a relation like this. So, you can write1 of these a sin terms of in terms of P n minus 1 and P n plus 1.

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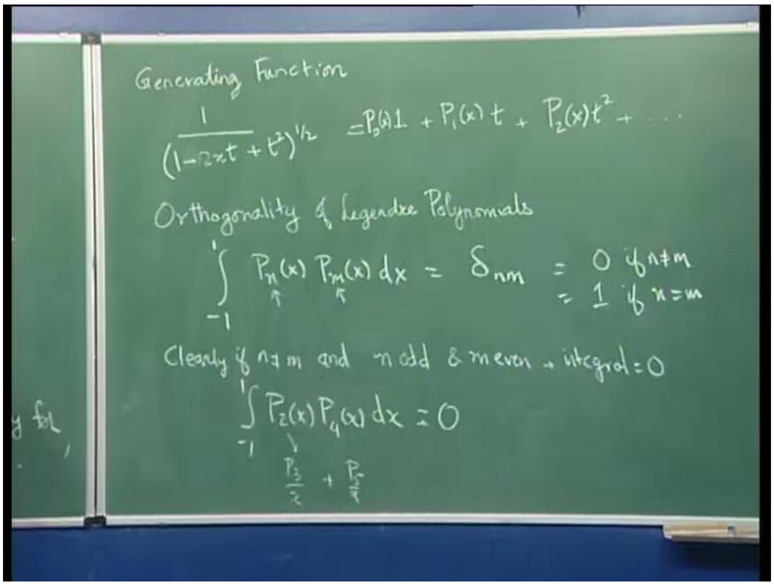

And clearly integral of integral over when ever so and that and each of those integrated with this will give you 0. So, in other words in I can write this a sin can write P 2 as some as P 3 divided by x plus P 5 by x, some constant times P 3 by x and P 5 by x and clearly, when you do these integrals, they individually go to 0. So, the point is that when you take any 2 different polynomials, any 2 different indices then it goes to 0, this integral goes to 0. Now, if you choose n is equal to m, that you just get P n square d x.

And this is where our choice of the constant multiplying P n comes into place. So, we choose our constants such that P n square d x equal to 1, this integral from minus 1 to 1 is 1, so this is as I want to say about Legendre polynomials and in the next class we will start looking at another power series method called the Frobenius method.

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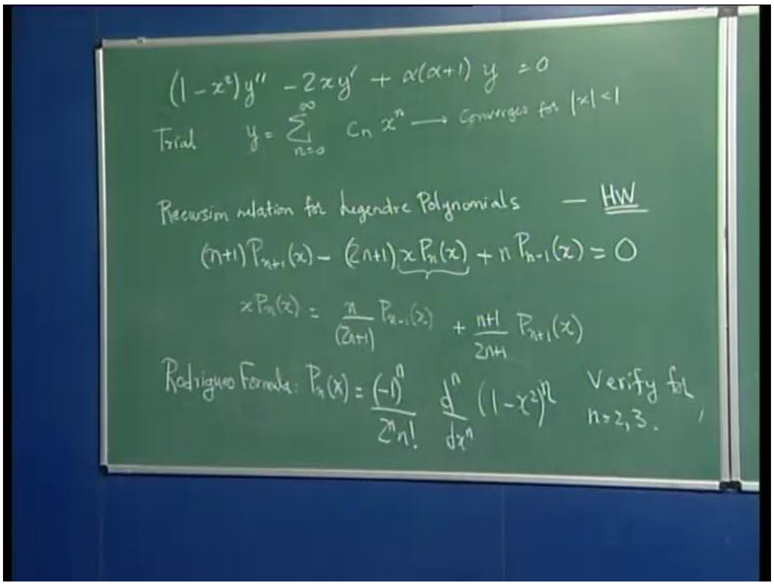

So, this it turns out that normal power series methods, works in some cases it is not, so useful and we have to do something called a Frobenius method. So, we will take that up in the next class.

Thank you.

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