Chemistry Atomic Structure and Chemical Bonding
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Lecture – 30
Legendre and Associated Legendre Equation

Welcome back to the lectures in chemistry on the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am in the Department of Chemistry of The Indian Institute of Technology, Madras, as a professor. The email contacts for you are given in this page.

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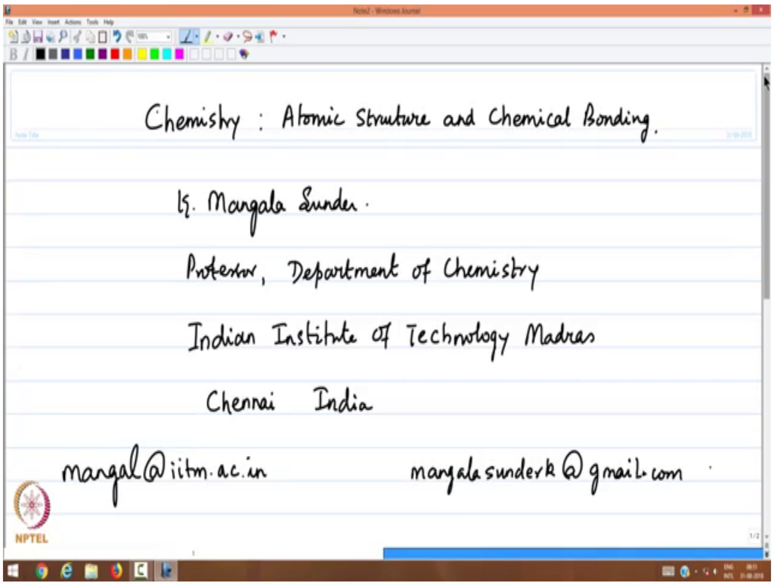

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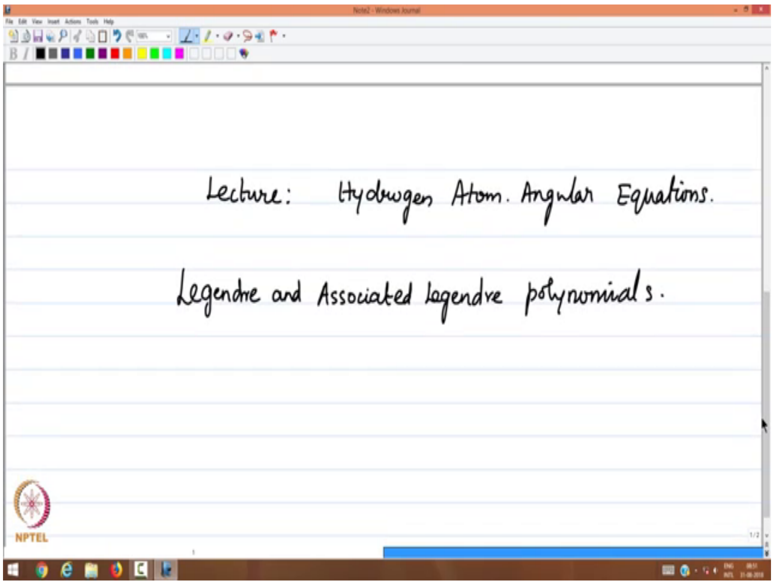

The lecture now, we will continue on the Power Series Method for Solving Differential Equations, related to some of the important model problems of Quantum Mechanics. We have been looking at. And we looked at the Hermite polynomials in a previous lecture and, in this lecture we shall look at the angular part of the hydrogen atom problem and the Schrodinger equation, but some review of that has to be done before we get to the details of Legendre and the associated Legendre polynomials ok.

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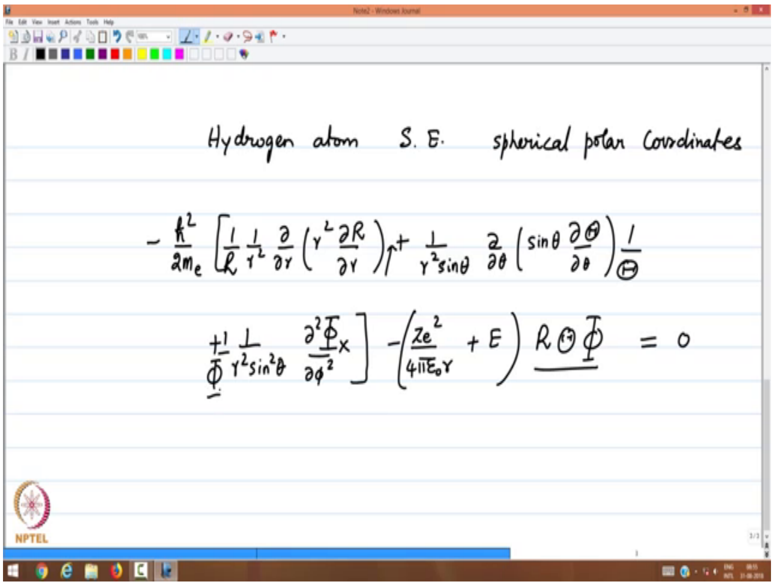

So, let me recall from what was done a few lectures earlier. The hydrogen atom Schrodinger equation and this was done in, spherical polar coordinates and in one of the lectures I had suggested, how this could be separated into 3 equations. So, let us recall the equation the kinetic energy term is given by the derivative terms that you have been r theta and phi as 1 over r square dou by dou r, r square dou R by dou r where r is the r only dependent.

There is a radial coordinate only dependent function, then you had 1 over r square sin theta dou by dou theta of sin theta dou theta by dou theta this is a function of the polar angle and then we have the last term 1 over r square sin square theta dou square phi by dou phi square. This is the Azimuthal angle which is the other angular coordinate in the spherical system.

All of this was kinetic energy and then we had the potential energy term minus Z e square, minus Z e square 4 pi epsilon naught r plus E of the radial functions or the angular function theta and the phi function and if I have to do that, then I must also have in this a theta and a phi function a radial and a phi function and here multiplied by here radial function and a theta function, ok, and this was set to 0.

Now, if you recall that we separated this by dividing the whole thing, with the R theta phi and what we got was essentially the following equation. So, let me remove this and what will be left here is a 1 by capital R, because this is of course, a derivative function.

So, R cannot be cancelled from here. This is a theta function, theta cannot be canceled from here. Therefore, you will have a 1 by theta and then you had the third term, without these, but with 1 by phi and of course, when you did that all of this enter y is equal to 0.

This was the radial equation and the angular equation together and you can see immediately that the separation that we are worried about was writing this and these, as the radial part. If we multiply everything by r square which is also d1, that way here let us do that, if you multiply everything by R square this goes away, this goes away, and this also goes away, but then you have to multiply the rest by R square.

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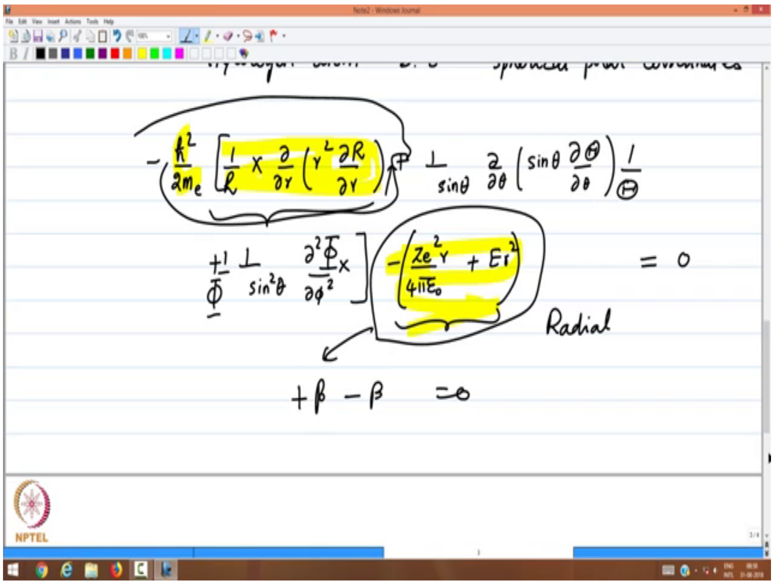

So, you have an r square here, r square and you have and r here that is called r. So, now, you can identify the radial equation as I recalled the radial equation has terms containing, these multiplied by this constant and the terms containing at these as the radial equation.

This is what you had seen in one of the lectures earlier and the rest of it is the angular equation. So, let me now for this lecture, we concentrate on the angular part and you must know that the radial part which depends only on the r coordinate is obviously, independent of the theta and phi coordinates. Therefore, varying theta and phi for this part of the equation has no consequence for this part.

So, all of this is equal to a constant and the rest of it is equal to minus of that constant. So, that if you write the radial part it is equal to plus beta and therefore, the angular part was equal to minus beta and that for that is equal to 0. So, everything that you see in the yellow here everything this plus this was equal to plus beta and therefore, everything which is left out is equal to minus beta.

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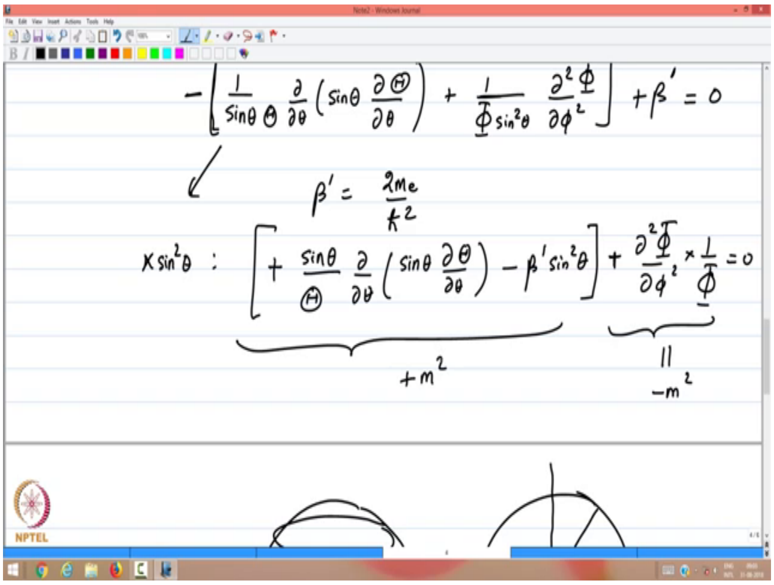

So, let us collect the angular part and look at the angular part more closely. It is a minus h bar square by 2 m e 1 by sin theta and the capital function theta dou by dou theta of sin theta dou capital theta by dou theta plus 1 by phi sin square theta dou square by dou phi square of the capital phi function plus beta, all of this is the kinetic energy term with the minus h bar square 2 me plus beta is equal to 0.

And of course, since we multiply this by the constant h bars 2 m e by h bar square. So, let us defined beta prime as 2 m e by h bar square and then you can easily get rid of this term,, and write the minus sign here, but then you call this as beta prime is equal to 0.

Now, again, if you multiply the whole thing by sin square theta, you can see that the separates further into the theta phi has 2 different parts. So, what you have is minus sin theta by capital theta dou by dou theta of sin theta dou capital theta by small theta variable minus also minus sign therefore, minus beta prime sin square theta. All of this depend only on theta and since we multiplied by sin square theta.

The remaining term is essentially minus dou square capital phi by dou phi square times 1 by capital phi if we do the minus sign I think we should remove that and you should put this as plus, because then we have changed the sign of this whole term ok. So, this is equal to 0. Now you see, this is only theta part and this is only phi part again the theta comp1nt is independent of the phi comp1nt. Therefore, this is equal to a constant and this is equal to a constant, remember the phi coordinates.

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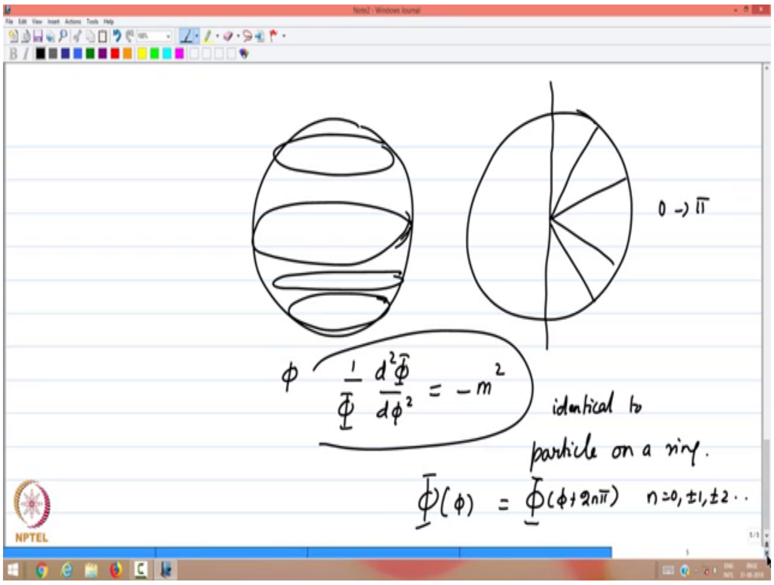

If you recall the spherical coordinate system that you have the theta was essentially let me draw the sphere again. So, circle of course, it is a 3-dimensional, you recall that the theta part was essentially going from this to this to this to this.

Therefore, the polar coordinate is from 0 to pi, but the phi solution was basically for any theta value the phi will take a circular system. All values of 2 pi 0 to 2 pi all values of them, ok. Therefore, the phi equation which is written as 1 by capital phi d squared phi by d phi square is equated to a number minus m square there m is a positive constant.

This form is very similar or identical to that of the particle on a ring and with the same condition's boundary condition or the cyclic boundary condition, namely phi of phi is equal to phi of phi plus 2 n pi where n is 0, plus minus 1 plus minus 2 and so on.

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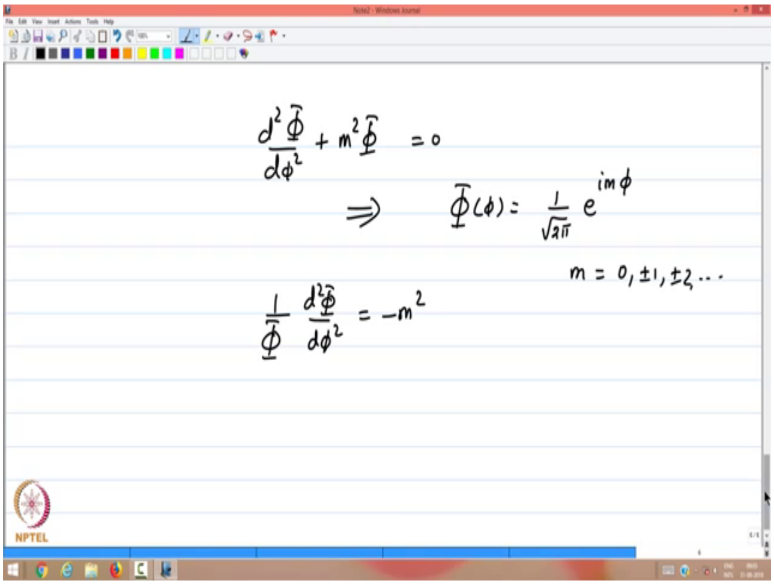

Therefore, the solution to the phi equation is immediate namely, d square phi by d phi square by plus m square phi is equal to 0, will give you from the particle in the ring solution, if you recall the eigen functions of the phi to be phi of phi as 1 by root 2 pi e to the i m phi, where m is now 0, plus minus 1, plus minus 2 and so on.

Therefore, m square has to be an integer, ok. If we put this equation namely, 1 by phi d square phi by d phi square as minus m square, then you go back to the angular equation here we have equated this whole thing to minus m square and therefore, this is plus m square and ms m is a constant and for the phi equation, tells you m is an integer, plus or minus, but then that is part of the angular theta equation and therefore, the equation that we now want to solve in this lecture of course, in detail can be written in its final form.

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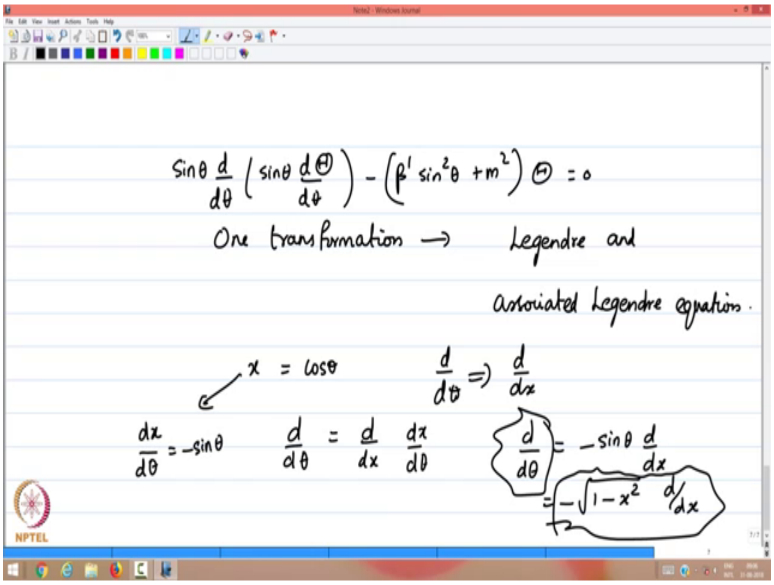

In the theta variable, as sin theta d by d thetas the partial derivative goes away, because the function is only a function of theta and therefore, you have sin theta d theta by d theta minus beta prime, sin square theta plus m square theta is equal to 0.

1 transformation, we shall make to identify this, to an equation which has been solved 100s of years before at least 100-150 years before will convert this into what is known as the Legendre and, associated Legendre equation which was studied in mathematics earlier and Schrodinger found out that the transformation of the hydrogen atom, problem into spherical polar coordinates. Eventually leads these equations to well identified well known equations of the an earlier mathematical literature and therefore, he could immediately obtain the solutions from that ok.

So, now, you make the transformation that x is equal to cos theta and write to the d by d theta in terms of d by dx, replace them. Now you know that d by d theta is going to be d by d x dx by d theta and dx by d theta for this x is equal to cos theta. So, therefore, if you take the derivative of this with respect to theta, it is minus sin theta. Therefore, d by d theta is now replaced by minus sin theta d by dx and of course, sin theta itself is in terms of the x it is minus 1 by minus square root of 1 minus x square d by dx.

So, this substitution for d by d theta is what we wanted to make throughout and change this equation into x variable and 1 last thing you have to look at is please remember theta has a limiting I mean the values all possible values between 0 and pi and therefore, if you change x to cos theta then x has a value from cos 0 to cos pi and therefore, x has a value from 1 to minus 1 the limit of x is from 1 to minus 1 and d x.

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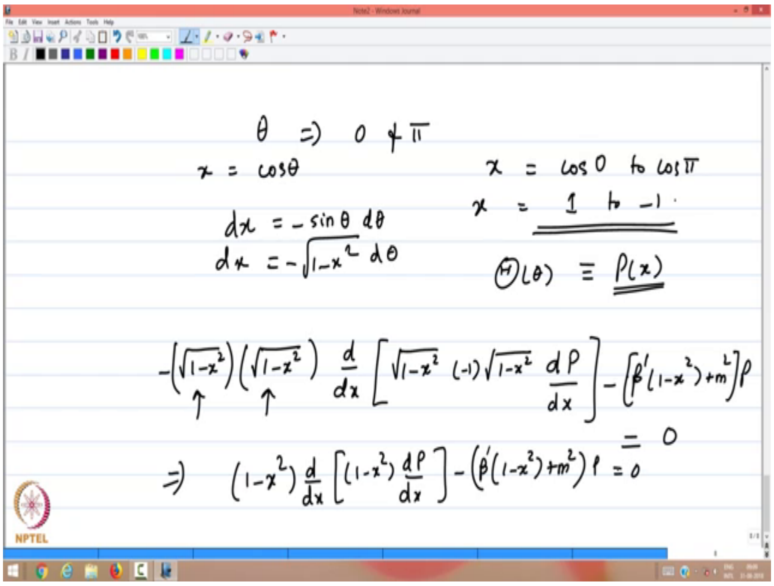

You can also see, we have seen the dx if we have to later integrate this equation with respect to theta d x is minus sin theta d theta. That is what you have here and therefore, that is going to be minus square root of 1 minus x square d theta. So, dx will be replaced by d theta will be replaced by that ok. So, now, with this change you can therefore, write to the equation as the angular equation please see this, there is a sin theta in front and there is a sin theta inside the derivative, but preceding the other derivative and then there is a sin square theta.

Therefore, if you substitute for all of that what you would get is minus square root of 1 minus x square and you have square root of 1 minus x square. This comes from the d by dx expression this comes from the sin theta that is already there and then you have the d by dx acting on the square root of 1 minus x square.

This is the sin theta expression and then there is a minus sign for the d by d theta which will also have a 1 minus x square and now let us call the theta function in terms of x variable the theta of theta. Since, we are replacing theta by x we will call that as the P of x.

So, the function that we are looking at is the function P of x and then the left remaining term minus beta prime into sin square theta is 1 minus x square and then you have m square acting on P or multiplied by P this is equal to 0, which, if you simplify becomes the well-known equation 1 minus x square d by d x of 1 minus x square d P by d x minus beta times 1 minus x square plus m square P is equal to 0 and the last line now is the Legendre equation.

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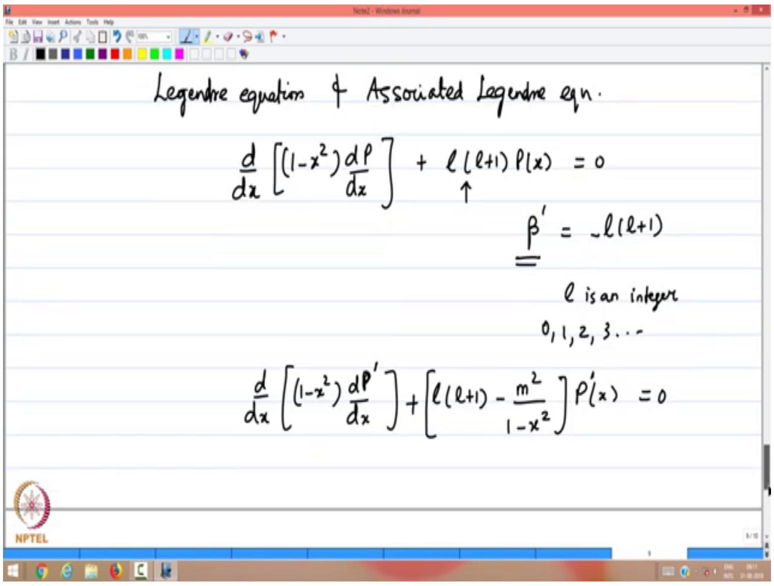

And, we associated Legendre equation, Legendre they are 1 d by dx of 1 minus x square d P by dx plus l into l plus 1 P of x is equal to 0. If we identify the term beta prime to be minus l into l plus 1, because beta prime, that is an arbitrary constant, but the Legendre equation is an equation which has an arbitrary integer l is an integer and it takes values 0 1, 2, 3 etcetera.

And the corresponding solutions for different values of l's are known as the Legendre polynomials and the associated Legendre equation is the 1 in which the m square is also included namely d by d x into 1 minus x square d P by d x minus or plus l into l plus 1 minus m square by 1 minus x square P of x is equal to 0 of course, we are using the same symbol P.

So, I would not do that I would call it as by a different symbol, say maybe P prime or P prime, because when m is not 0 this is, different from this. This equation becomes that, only when m is equal to 0 therefore, P prime becomes P for m equal to 0 and m equal to

0 is the solution, known as the Legendre function and for m non-zero the solutions are known as associated Legendre functions. This is the failure.

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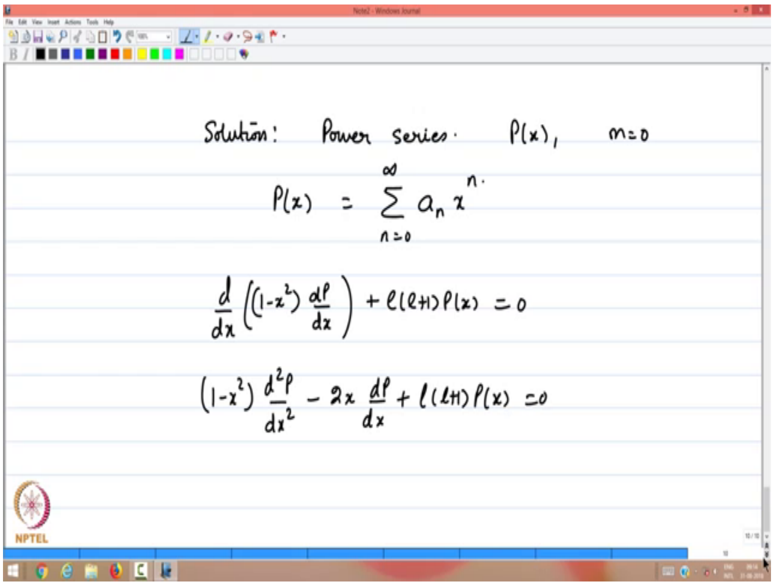

Now the solution; now, we will go back to the power series method that we have for P of x, P of x and let us assume that m equal to 0. So, the solution is in the same way, that we did for the other the series solutions namely P of x is written as an infinite series n equal to 0 to infinity a n x raise to n and the equation that we are going to solve is the equation d by dx let me rewrite to this equation d by dx of 1 minus x square times dP by dx plus l into l plus 1 P of x is equal to 0. We will write this as explicit derivatives.

Therefore, when the derivative acts on 1 minus x square it gives you minus 2 x, but if it acts on the dP it gives you 1 minus x square d square P by dx square. So, there are 2 terms to it minus 2 x dP by dx plus l into l plus 1 P of x is equal to 0.

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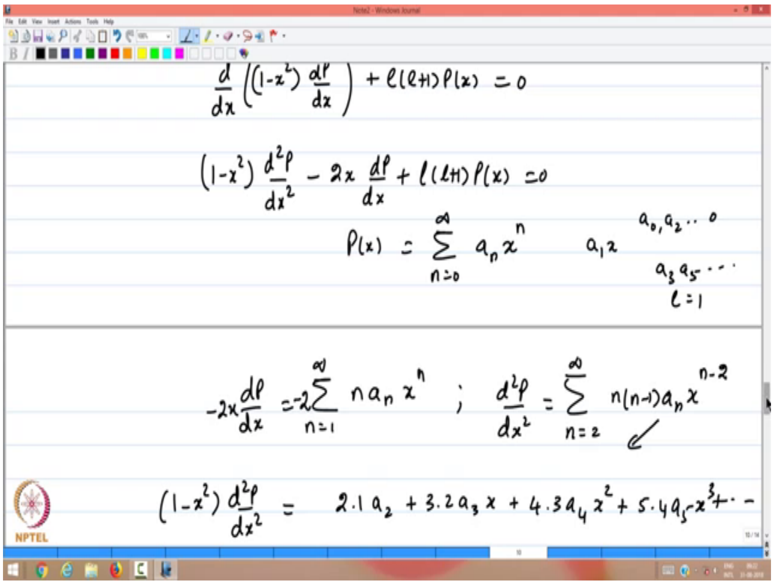

Writing this explicitly, helps us in getting the power series terms ordered and. Now, since p is already assumed to be this infinite series which we will have to truncate later for finite solutions dP by dx is of course, sum over n equal to 1 to infinity n a n x raise to n minus 1 and d square p by d x square is multiplied the sum n equal to 2 to infinity n into n minus 1 a n x raise to n minus 2.

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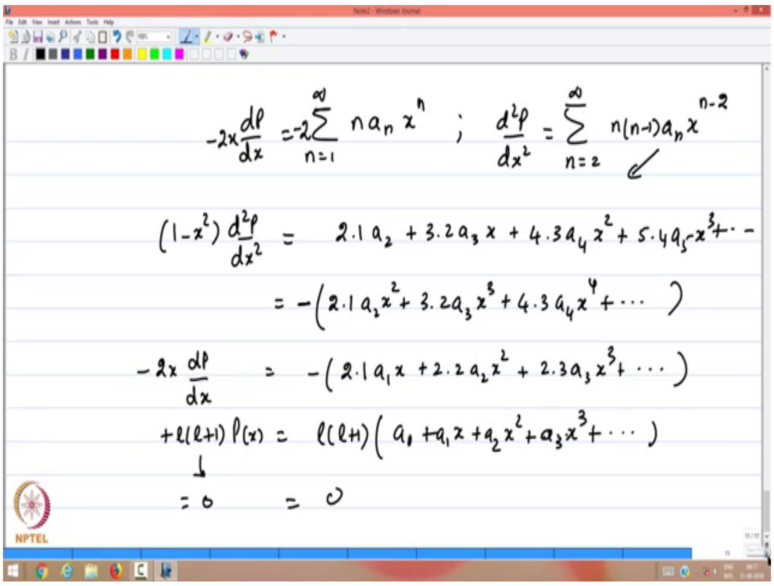

Therefore, the equation that we have to do is to find out the term 1 minus x square d square p by d x square. So, let us write this explicitly, the 1 times d square p the first term will be this namely 2 into 1 into a 2 plus 3 into 2 times a 3 x plus 4 times 3 a 4 x square that is the term,, and expanding this series plus 5 into 4 a 5 x cube plus etcetera. And the second 1 is the x square term which multiplies everything by x squared with the minus sign.

Therefore, we have a minus 2 1 a 2 x square plus 3 2 a 3 x cube plus 4 times 3 a 4 x 4r plus etcetera. So, that is this term then we have a minus 2 x dP by dx. Therefore, this series we have to multiplies by x. So, if you multiply this by minus 2 x, what you will get? You will get minus 2 x times minus 2 x.

So, you will get minus 2 and then this minus 1 will go away it will become x raise to n ok. So, minus 2 x will become minus 2 times 1 n is 1 therefore, a 1 x plus 2 times 2 a 2 x square plus 2 times 3 a 3 x cube plus etcetera and the last 1 is of course, plus l into l plus 1 P of x. So, you will have this is l into l plus 1 a naught plus a 1 x plus a 2 x square plus maybe 1 more term a 3 x cube plus so, on.

So, all of this added to 0 added to give you 0 therefore, the usual practice that we have followed is that individual powers of x each term the coefficients of individual parts of x each one of these set of coefficients goes to 0 and. So, let us write the first coefficient that we need to know.

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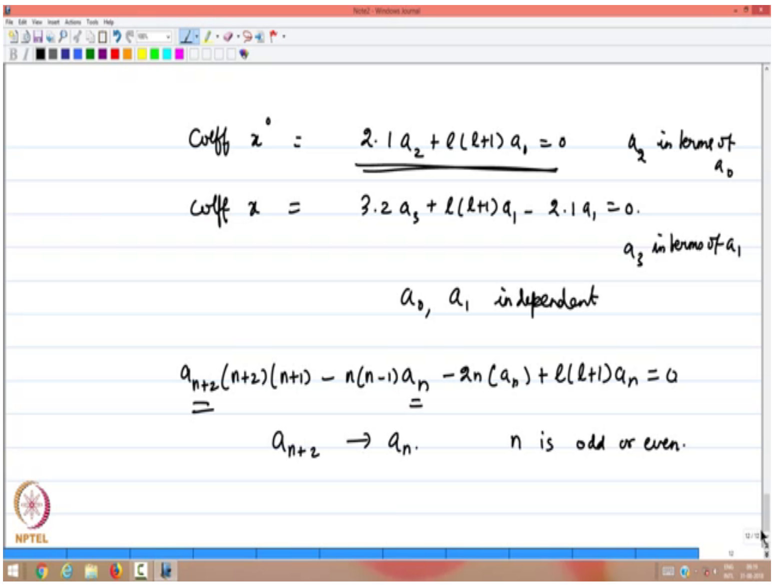

The coefficient of a 0 of course, in the x raise to 0, is going to be 2 times 1 a 2 plus l into l plus 1 a naught is equal to 0 and likewise coefficient of x is going to be 3 times 2 into a 3 plus l into l plus 1 times a 1 minus 2 times 1 a 1 is equal to 0 you can see immediately the trend that is coming up a 2 is connected to a naught a 2 in terms of a naught and a 3 in terms of a 1.

Therefore, there are 2 independent coefficients a naught and a 1 independent and everything else is a function is in terms of these coefficients and let me write a couple of terms or maybe I think, since you know this now let me write the general term that we have to worry about the general term for the coefficient of a n plus 2 times n plus 2 times n plus 1 minus n into n minus 1 a n a n plus 2 3 a n minus 2 n a n plus l into l plus 1 a n is equal to 0.

Therefore, a n plus 2 is expressed in terms of a n in irrespective of whether it is odd or even whether n is odd or even odd or even. So, the lowest is n is 0 the next 1 is a 1 except these 2 everything else is in terms of those 2 and the solution, therefore, is a n plus 2 for the coefficient is minus l into l plus 1 minus n into n plus 1 divided by n plus 2 into n plus 1 times a n you can see immediately why in Legendre equation l was chosen to be an integer, because n is an integer.

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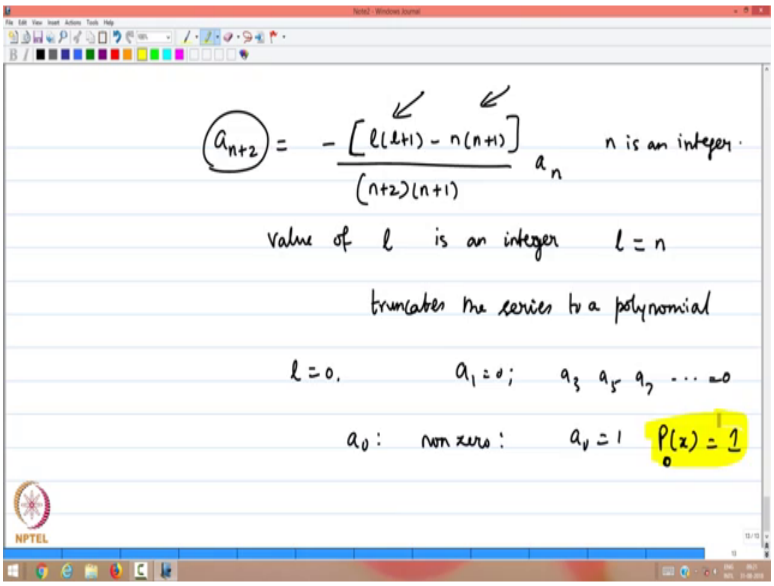

Therefore, this series truncates at some value of n if the n is chosen to be l a n is not 0, but a n plus 2 is 0 therefore, you see the value of l is an integer and the maximum the maximum value of l is to be n here truncates the series to a polynomial.

Now, you can see immediately, that if we choose l equal to 0 then we have a 1 will be 0 and therefore, a 3 a 5 5 a seven all of them go to 0 therefore, we have only 1 series of powers containing a naught is non0 and for l equal to 0 of course, a naught will be 1, because the polynomial p of x choosing l to be 0 we will denote that value of l to be here and that is equal to 1 this is important this is the lowest order polynomial constant. The next choice that we can have is l equal to 1.

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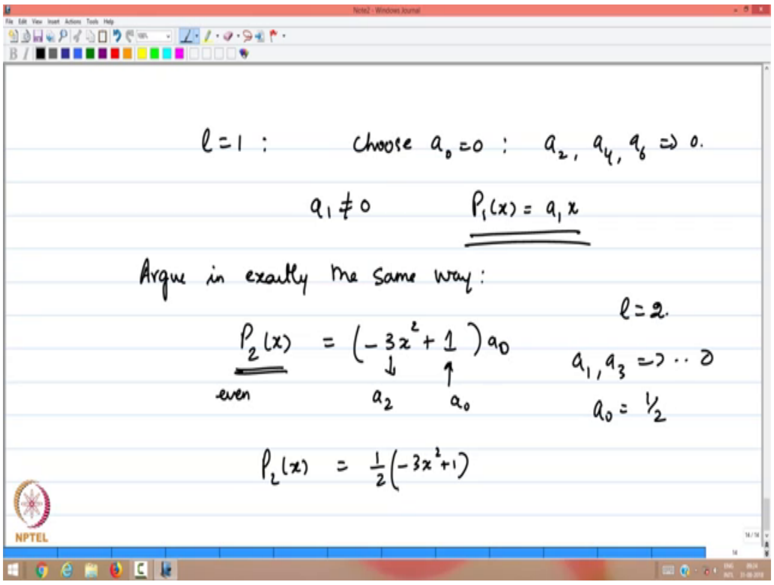

If he choose l equal to 1 then and we choose also a 2 to be a naught to be 0 then all the even a is a 2 a 4 a 6 or all 0 and therefore, a 1 not being 0 will give you P 1 of x as a 1 of x you can see, there when you choose l equal to 1 you will have a 1 which is independent and a 1 is part of the infinite series expression here and we have chosen in this series. Only the term a 1 of x a naught a 2 are all 0 a 3 a 4 5 are all 0, because l is 1, because of l equal to 1 this is 0 you can see that a 3 is 0 since the l is 1 n is 1 therefore, a 1 is non zero, but a 3 is 0.

So, you have only 1 term p 1 of x is equal to a 1 others argue in exactly the same way to arrive at various possible solutions and without any further explanation I can write the P

2 of x where l is chosen to be 2 the P 2 of x will have this formula namely, minus 3 x square plus 1.

So, this is a naught minus 3 is a 2 a 1s a 3s are all chosen to be 0 if a 1s are not chosen to be 0, but the even 1s are chosen 0 then you have the even the odd polynomials and the even polynomial. So, this is the even indexed polynomial n is 2 and likewise when n is 3 for this of course, we have chosen a naught to be 1 by 2 if we do that then the reason why this is d1 is of course, is to normalize these functions in a certain way then P 2 x becomes 1 by 2 minus 3 x square plus 1 this must have been a 1 a 2 a 0 and therefore, if you choose a 0 to be half this is what you will get.

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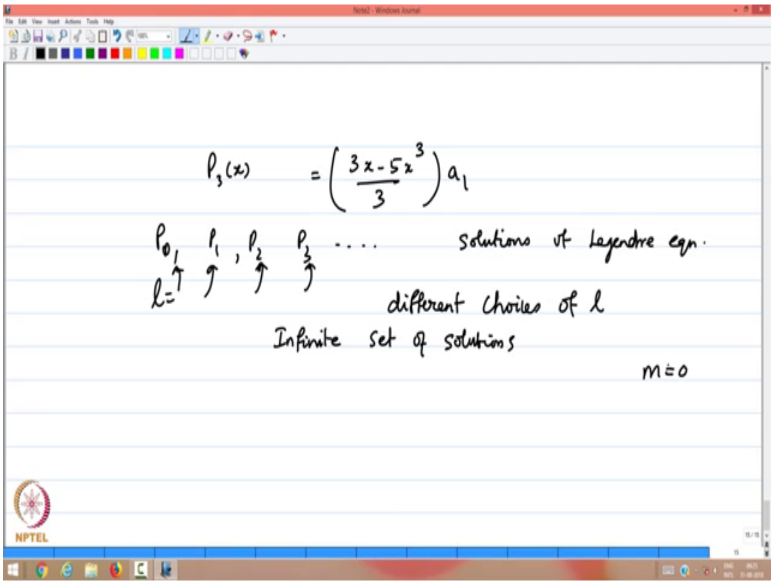

So, P 2 is chosen this way likewise P 3 of x were only the odd as are chosen you will see that it is 3 x minus 5 x cube by 3 times a 1 therefore, now you see that a whole series of solutions P 1 P 0 P 1 P 2 P 3. There are all solutions of the Legendre equation for different choices of l l and l is actually given by this index the super the subscript and therefore, you can see that the polynomials formed an infinite set of solutions for the differential equation this is all with m equal to 0 m equal to 0 I have given a fairly detailed lecture nodes.

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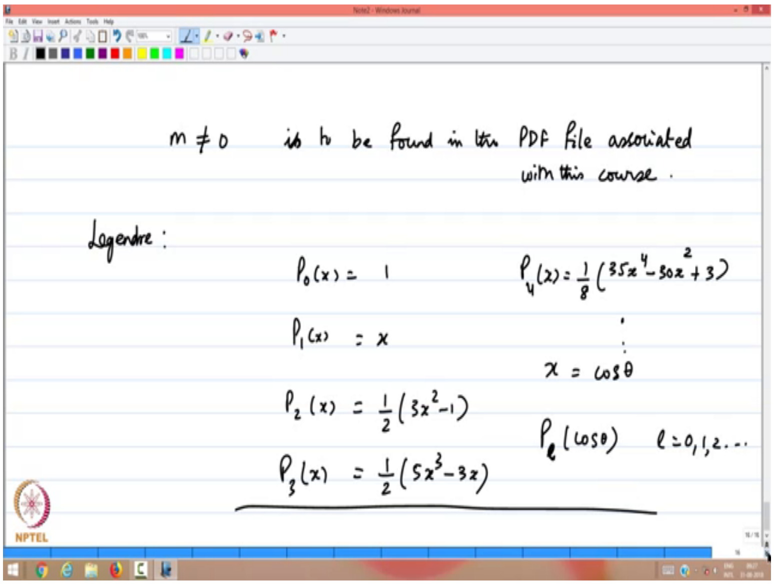

In which m naught equal to 0 is to be found in the lecture PDF file associated with this course,, and since the arguments are identical to what I have already presented let me complete this the arguments are exactly the same as what was d1, I let me write the final solutions for Legendre functions the following.

P naught of x is 1 P 1 of x is x P 2 of x is 1 by 2 3 x square minus 1 P 3 of x is equal to 1 by 2 5 x cube minus 3 x P 4 of x is equal to 1 by 835 x raise to 4 minus 30 x square plus 3 and so, on. Now recall x is equal to cos theta therefore, all of these things P l indexed this way namely, the variable is theta cos theta and the polynomials Legendre polynomials are l index l equal to 0 1 2 3 etcetera.

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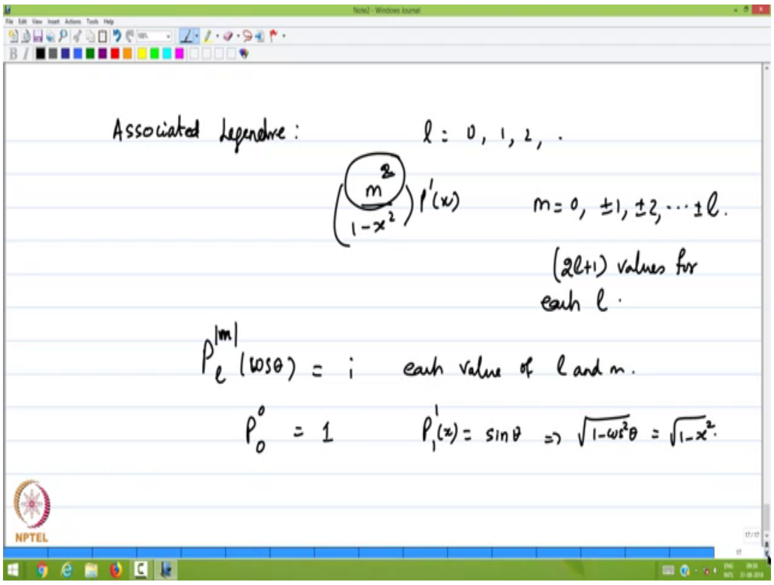

Now this is for the Legendre function and the associated Legendre functions with the m values or each m you will see that given a choice of l equal to 0 or 1 or 2 the differential equation with the m m square by 1 minus x square P prime x is there in the differential equation let me go back and show that this 1 the equation contains as you see it the Legendre equation part of it and the minus m square part of it.

Therefore, the polynomial now is indexed for 1 value of l and 1 value of m and the same argument regarding termination of the infinite series to truncation and finite powers will ensure that m takes only those possible values namely since m square is given m takes only those possible values namely m equal to 0 plus minus 1 plus minus 2 until plus minus l the plus minus is, because m appears in this whole equation as m square.

Therefore, both the values or both the sins are accepted therefore, m is going to take 2 l plus 1 values for each l and such a polynomial is usually written in terms of P l and you write it with the magnitude of m cos theta and those polynomials are of course, now obtained in exactly the same way and let me just give you the final result that P l m cos theta are given as follows let me write them down for each value of l and m. So, P 0 of course, well l is 0 m is 0 this is 1 trivial P 1 of 1 is in our form of x if you were to write, but now we are writing it in the form of theta.

It will be sin theta and which is square root of 1 minus cos square theta or where root of 1 minus x if you have tried this in the form of x square and likewise you can determine through the same way.

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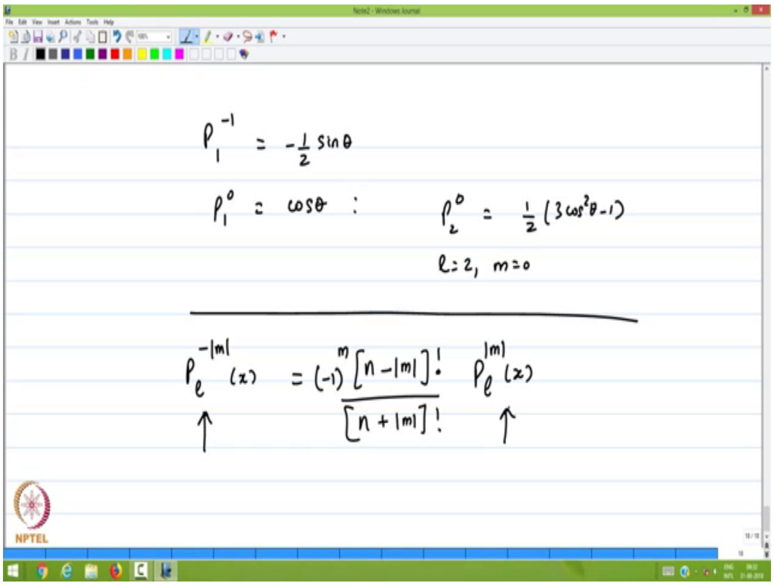

The minus P 1 minus 1 will turn out to be minus half sin theta P 1 0 will turn out to be cos theta and l last expression p 2 0 l is 2 m is 0 this is 1 by 2 3 cos square theta minus 1 the rest of the details of the associated Legendre polynomials or in the lecture notes then there is mathematically there is some the, the constants are chosen in such a way that these functions have this general property namely P l of minus m x are expressed in terms of the P l of m of x without the sign that is the positive and the negative m values are expressed as minus 1 raised to m.

Then you have n minus the absolute value of m factorial divided by n plus the absolute m factorial times. So, this is a general relation that is established between these after going through some of the mathematics in detail and you have already seen these expressions.

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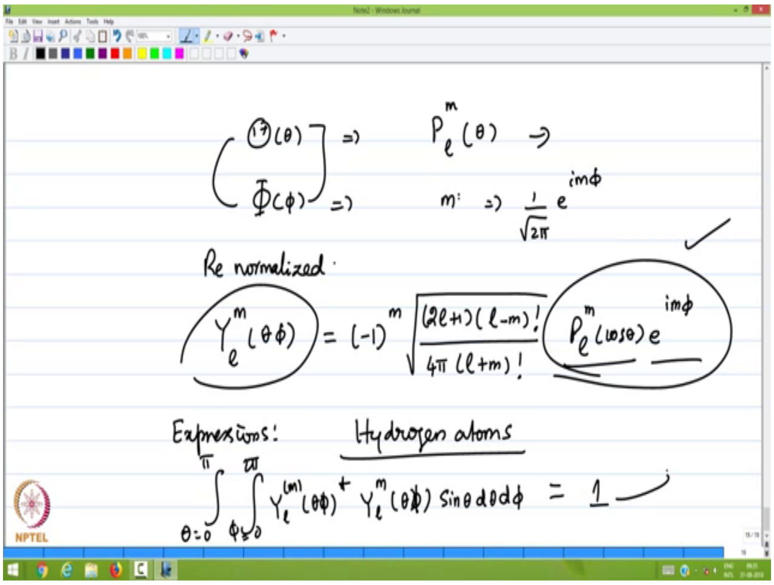

So, let me come to the last part of this namely a couple of minutes. Now, we have the function theta of theta which is expressed in terms of 2 coordinates l 2 quantum numbers l and m and the theta this is the associated Legendre polynomial and then we have the phi function which was expressed in terms of the m coordinate this m and this m are the same please remember they were connected to each other in the separation of the original equation.

Therefore, this is 1 by root 2 pi e to the i m phi. Now the conventional practice is to put these 2 things together and do a renormalization renormalize the whole integral and call these as the spherical harmonics Y l m theta phi and the Y l m theta phi in terms of the functions is defined to be minus 1 raised to m square root of 2 n plus 1 times n minus m factorial divided by 4 pi into n plus m factorial times P n m cos theta e raise to i m phi.

So, here is the theta part here is the phi part and I have used n instead of l. So, let me sorry this is l. So, let me write this consistently using l its 2 l plus 1 and this will be l minus m and this will also be l ok.

So, you have Y l m theta phi in terms of the P l cos theta e to the i m phi expressions for all of these where given in the detailed lecture nodes on the hydrogen atom which runs into about some 30-35 pages that is there in your website and this lecture these functions have been explicitly given. The property of these functions most important is Y lm theta phi is of course, it is a complex function.

Therefore, the normalization of Y lm theta phi is Y lm theta phi star Y lm theta phi and you have sin theta d theta d phi with the variable limits theta is equal to 0 to pi phi is equal to 0 to 2 pi this should be chosen to be 1 and this ensures that the wave functions for the hydrogen atom containing the angular part or independently normalized with the angular part and likewise for the radial part the radial equation is solved.

Now, I will not solve the radial equation in this course, because now I have given enough samples for the Hermite polynomial as well as for the Legendre polynomial and the lecture notes provided in the course contains probably some of the radial solutions as well please go through them and attempt to some of the assignments themselves yourselves and the radial equation. Please solve these equations yourself following the arguments given in order to feel more comfortable with the mathematics.

Therefore, I have basically not left any the hidden parts in this lecture all the mathematics have been given as an applied mathematician or a physicist would look at in solving the problem not as a mathematician who would look after the problem in the form of proofs theorems and details have not done that there is a lot of hands on in the whole processes, but it is still such that we can follow the algebra by yourself these are important in understanding the problems of the other the atomic and molecular bonding characteristics.

Therefore, I hope I have given you enough details will continue now with the spin angular momentum and orbital angular momentum in the next set of lectures this is part of the course until then.

Thank you very much.