Advanced Mathematical Methods for Chemistry
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Module - 05
Lecture - 05
Hydrogen Atom, Recap of Module 5

In the last lecture of module 5, I am going to do a very pertinent example of the use of solutions of differential equations and this is an example from quantum mechanics you will see this in your elementary quantum mechanics course. But what I want to do today is to work out the problem that you see in your elementary quantum mechanics course and highlight where we use lot of our knowledge of differential equations in this problem. And the problem that I will be taking is the solution of the Schrodinger equation for the hydrogen atom. The hydrogen atom has 1 electron and 1 nucleus, the nucleus is considered fixed and you can write the Schrodinger equation for the electron in terms of the wave function of the electron.

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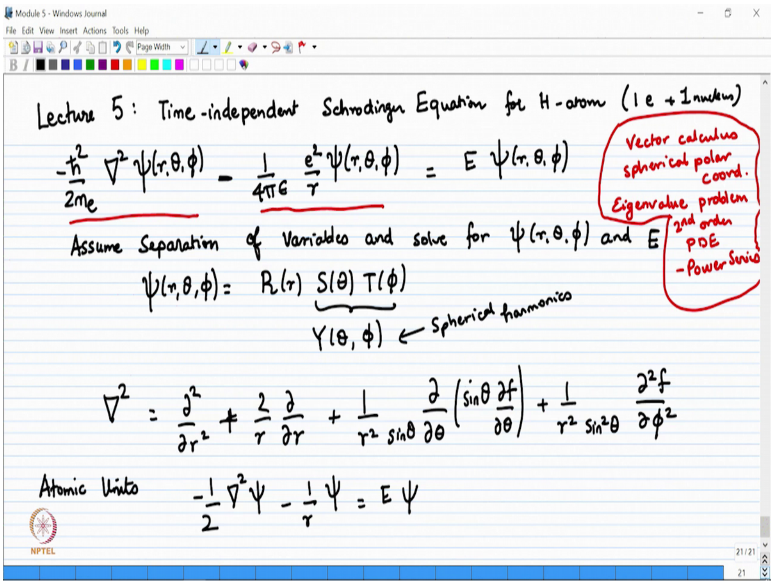

So, now I can show this is the wave function for the electron in a hydrogen atom the first term is the kinetic energy term. So, the wave function is psi I have written it in terms of the coordinates of the electron and the electron coordinates are written in spherical polar coordinates. So, the first term is the kinetic energy and it has a Laplacian operator. So, the gradients square operator. And now the next term is the is the potential energy term and this is written in terms of this constant 1 over 4 pi epsilon e square, E is the charge on the electron and the nucleus end over r multiplied by the wave function. And this should be equal to some constant E which is the eigenvalue of the energy times psi.

So, you can immediately see there are lots of aspects. So, you see vector calculus in terms of gradient tap operator, you see spherical polar coordinates polar coordinates, we see some elements of eigenvalue, eigenvalue problem not in terms of matrices, but in terms of differential equations. You see second order ODEs order actually it is the P d e which will which when we solve it we will see techniques of second order ODE and in particular we will see power series power series method. So, all these aspects, all these mathematical aspects will be seen as you work out, as you work out this problem. So, all these various mathematical aspects will be seen in this problem and that is the reason I want to really highlight this problem.

Now let us start. So, we will be using a technique. So, this is a partial differential equation it is a function of r theta phi. So, we will assume separation of variables to solve for psi of r theta phi. So, so what we will write is psi of r theta phi as a product of 3 functions 1 as a function only of r the other is only a function of theta and the third is only a function of phi. So, I will just used R S and T. Incidentally this term the theta phi term is sometimes combined in books to and with a symbol y of theta phi and this is something called spherical harmonics this is something called spherical harmonics, but you know we will not bother with this much here. Now the Laplacian the square Laplacian that appears in this equation it has to be written in spherical polar coordinates and you will get all these terms.

So, now, one of the things you know before we go to solve this equation we see all these constants h 2 m e 4 pi epsilon e square all these constants. So, what we will do is we will use what are called atomic units and we will set all these constants to one. So, what happens is the differential equation in atomic units it looks much nicer del square psi minus 1 by r psi equal to E psi.

So, I mean these 2 equations are essentially the same only all these constants I have removed them if you want you can keep the constants, but then the expressions become more tedious. So, it is essentially the same equation without those constants. So, what we will do is we will work with this equation and now we will start applying the various methods. So, before we apply the methods let me say a few things what our overall strategy is going to be. So, I will just explain the overall strategy of this of this solution. So, what we are going to do is we are going to take this equation. So, we are going to use 3 steps - first step is separation of variables, variables this is the technique that you will learn more formally when you are dealing partial differential equations, but you know this is a very common technique.

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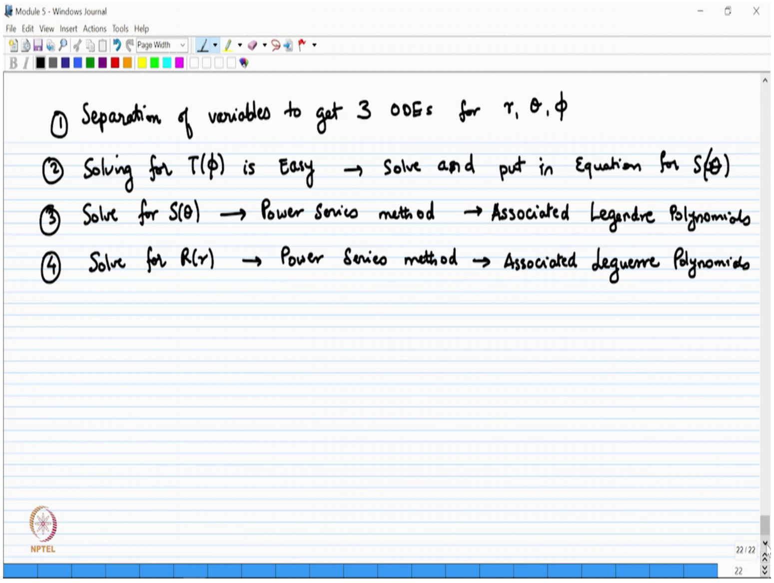

So, separation of variables to get and what will give you is 3 ODEs for r theta and phi. So, where 3 ODEs in one of them the independent variable will be r and then the other independent variables will be theta and in the third the independent variable will be phi. So, we will get 3 ODEs that is what we are going to do. Then we can easily I will write, it write it here. So, solving for T phi is easy. So, this is this can be easily done. So, now, then you solve for T phi. So, solve and substitute and put in equation for S theta then solve for S theta. Now, this involves power series method and the third and the last step is to solve for R of r this also involves the power series method.

In particular this involves something called the Associated Legendre Polynomials and this involves something called the Associated Laguerre Polynomials. So, I have not explained you what these Legendre polynomials are, but through this at least I will do the Legendre polynomials in detail the Laguerre polynomials will be we leave it as an exercise. So, I will just I will. So, these are the 4 steps and we are going to go through these steps one by one in solving this in, solving this partial differential equation.

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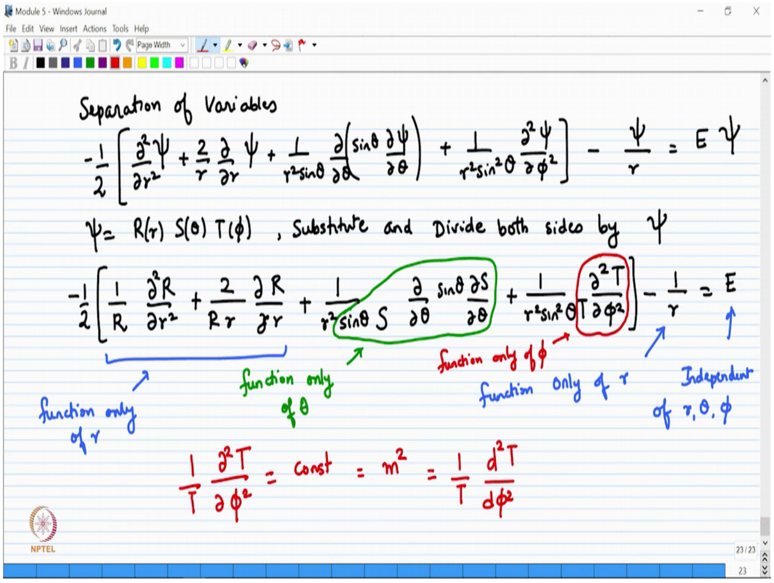

So, let us get to the first step. So, for those, the first step is the separation of variables. So, let me do this. So, separation of variables, our differential equation was 1 over 2. Now you had del square, now del square has this long expression because it is dou square by dou r square psi plus 2 by r dou by dou r of psi plus 1 over r square sin theta dou by dou theta of sin theta dou psi by dou theta dou by dou theta of this whole thing plus 1 over r square sin square theta dou square psi by dou phi square minus psi by r is equal to E psi.

So, now this differential equation what we see is that if you substitute the expression for psi. So, psi is equal to R of r, S of theta T of phi. So, if you substitute this expression then whenever you have a derivative with respect to r it will only operate on the r coordinate, so the S and theta can be taken outside. So, I will substitute and to substitute and divide the entire equation divide both sides by psi. So, psi is R times S times T. So, let us look at the first term. So, when I substitute, what I will get is I will have the minus half.

Now, when I take a d square by d r square. So, what will happen is I will get S T times dou square r by dou r square that will be this first term and you know you will get all the other terms. But what will happen is when I divide by psi then I will divide this by psi.

So, when I divide S T by psi I will just get 1 over r. So, what will happen it just become 1 over r.

So, S T divided by psi psi is R times S times T, so I will just get 1 over r. Now the next term will become 2 by R r, dou R by dou r plus now what I will get is 1 over r square sin theta now I will have S, S of theta and dou by dou theta of sin theta dou S by dou theta because here the here that d by d theta will only act on the S term plus 1 over r square sin square theta dou square T by dou phi square and I will have a T and now the next term will just be minus 1 over r equal to E.

So, now what we see is that the right hand side is a constant it is independent of r theta and phi. So, this constant is independent of r theta phi this term is purely a function of r, this is only or a function only of r only of r. Now at the same time we can also see that I will put it in green. So, if you see this term this is a function only of theta this term and theta this term is function only of phi ok.

So, this is a function only of phi. So, what you see is that if you and again all this is, all this whole thing is function only of r. So, I want I means, I think what I want to say is fairly obvious. So, we have a left hand side that has 1 term that is a function only of r. The second term that is a that has a function of r multiplied by a function only of theta third term has a function of r that is r square function of theta that is sin square theta and a function that is only a function of phi and then you have another term that is also a function only of r. So, what you can say is that if this whole thing has to give a function which is a constant then you can immediately say that all the terms that is only a function of r or the all the term that is only a function of phi there should be no dependence on phi on this equation.

So, immediately you can say that, immediately you can say that d square T by d phi square 1 by T dou square T by dou phi square is a constant. So, that is the first thing you can say because this is the only term that depends on phi and nowhere else you have phi in the whole expression. So, this has to be a constant there should be no dependence of phi on phi on the equation. For convenience let us call this constant as m square, we will take it as m square for now let us just let us start with this we will there is an understanding of why this should be a positive constant, but we will not bother with that right now. So, this is the equation for phi.

Now we are into the second we are into the second step of the solution that is solving for T phi is easy. So, this is an equation I should I be a little careful when I write these should really be whole derivatives or now when I write because r is only a function of, r is only a function of r. So, these are actually not partial derivatives because T is only dependent on phi. So, this I can write as 1 over T, d square T by d phi square.

So, all these derivatives of S with respect to theta is a d by d theta because there is only a theta dependence. So, all these derivatives become regular derivatives.

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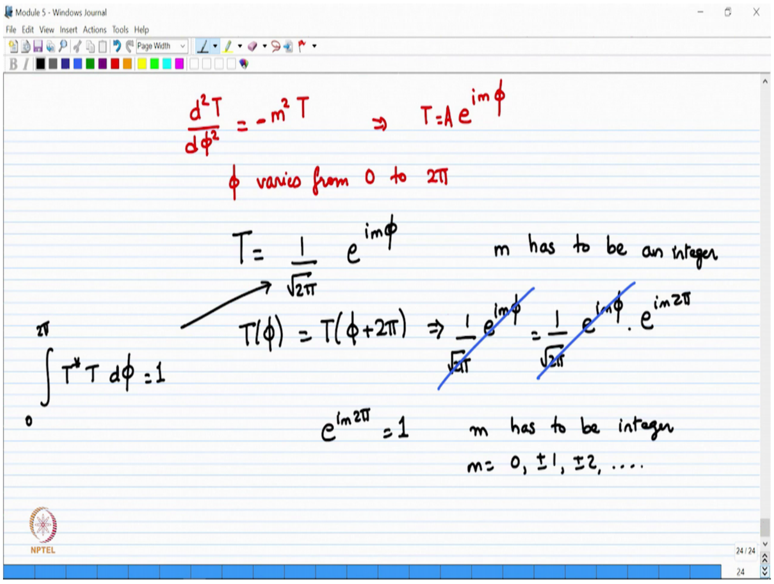

Now let us go to the next step that is solving for phi you have d square T by d phi square is equal to m square T. So, this implies T is equal to e to i, this constant I will set as minus m square I am sorry I (Refer Time: 16:30) want to set this as minus m square. So, with this we will come to it later why this constant should be negative, but we will set this constant as minus m square. So, if you set it as minus m square you can immediately see that T should be e to the i m phi. So, T of phi is e to the i m phi multiplied by some constant A. So, the A is a normalization constant.

So, now phi, now, phi varies from 0 to 2 pi. So, this gives T is equal to 1 by root 2 pi e to the i m phi, m has to be an integer. Now why does m have to be an integer because you should have T of phi is equal to T of phi plus 2 pi. So, phi should satisfy this condition. So, this implies. So, T of phi is 1 over root 2 pi e to the i m phi this should be equal to 1 over root 2 pi e to the i m phi times e to the i m 2 pi. So, if these 2 have to be equal then you can immediately see that you can cancel these and you get you get the condition e to the i m 2 pi equal to 1. Now e to the 2 pi is just 1, so you get m has to be an integer; m equal to 0 plus minus 1 plus minus 2 etcetera.

So, in this normalization constant of 1 by 2 pi is, 1 by root 2 pi is there to satisfy. So, this constant comes from integral T star T d phi from 0 to 2 pi this should be equal to 1 this is the normalization condition for this wave function. So, T star T equal to 1, therefore, now T star is just e to the i m phi and you can clearly see that that in this a has to be equal to 1 by root 2 pi. So, this completes the solution for phi.

Now, now what we do is we take the solution. So, we use this form of T in this equation and we write the remaining part of the equation. So, let us write the remaining part of the equation and what I will do is I will collect the r terms together, so that you can see the expression. So, let me write the remaining part of the equation.

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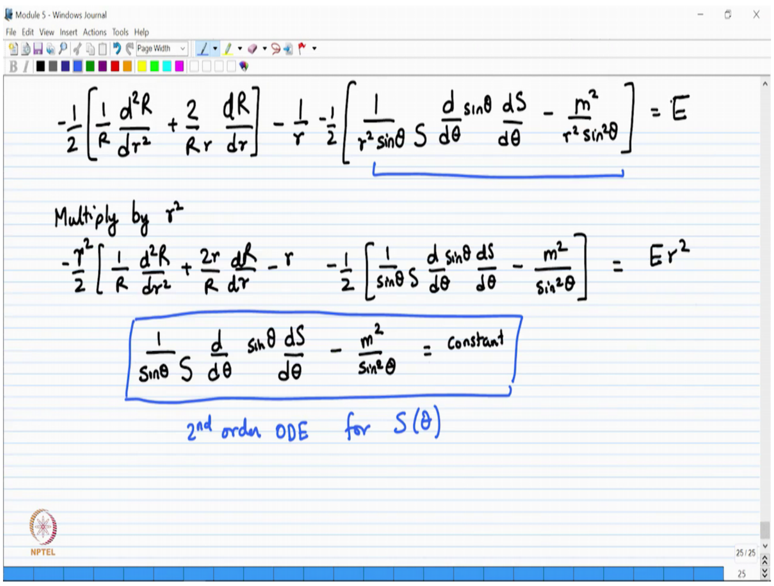

So, I will get minus half, now let me write in terms of d square R by d r square times 1 by r plus 2 by R r, d R by d r and I have a minus 1 by r. So, these are all the terms are defined only on r. Then I have the other term that is 1 over r square sin theta then I have an S d by d theta of sin theta d S by d theta.

Then I have a 1 over r square sin square theta, per head was I had, these I had d square T by d phi square and 1 over t, but that is just equal to minus m square. So, what we said is that 1 over td square T by d phi squared is just minus m square. So, I will just substitute minus m square. So, what I will minus half. So, we have the minus half and what I have here is I have minus m square equal to e. So, this is the next expression and what we want to do is to solve this for theta. Now you can see again what you can see that the same trick that we had earlier can be used because what we see is that this is the only part that depends on theta, these 2 are the only terms that contain theta and, so whatever you have the theta dependence here that should actually be a constant. So, what we will do is multiply by r square by r square.

So, if you multiply this whole thing by r square then what you will see is that the part or that depends on theta is just contained in this term and that that should be a constant. So, what you will get is that you will get minus half and I will just put an r square and you have a 1 by R d square R by d r square plus 2 r by R d R by d r by d r minus r. And then you have a minus half and now what you have is what you have is something that depends only on theta d by theta of sin theta d S by d theta minus m square by sin square theta equal to e times r square.

So, the right hand side is only depends on r's r left hand side has 1 term that depends only on r, second term that depends only on theta. So, this has to be a constant this has to be a constant so. So, therefore, we can immediately say that 1 over sin theta S d by d theta of sin theta d S by d theta minus m square m square by sin square theta this is a constant. So, the next thing that we want to do is to actually solve this equation. So, that will be the next part. So, the next part is this, this is the equation for theta for S, this is second order ODE for S of theta and this is what we want to solve. So, this is the third step of this problem that is to solve for S of theta and it turns out that this is a slightly more complicated solution.

So, this is what we are going to do next. So, the next step is to solve the second order ODE for theta. So, what we have seen is that we have a differential equation for theta and now what we want to do is to go ahead and solve with this. Now this will be solved using the power series method, but before solving using the power series method, we will make a couple of small substitute, we will make 1 substitution of variables 1 change of variables. What we will do is we will let cos theta equal to x and S of theta we will write this as P of x.

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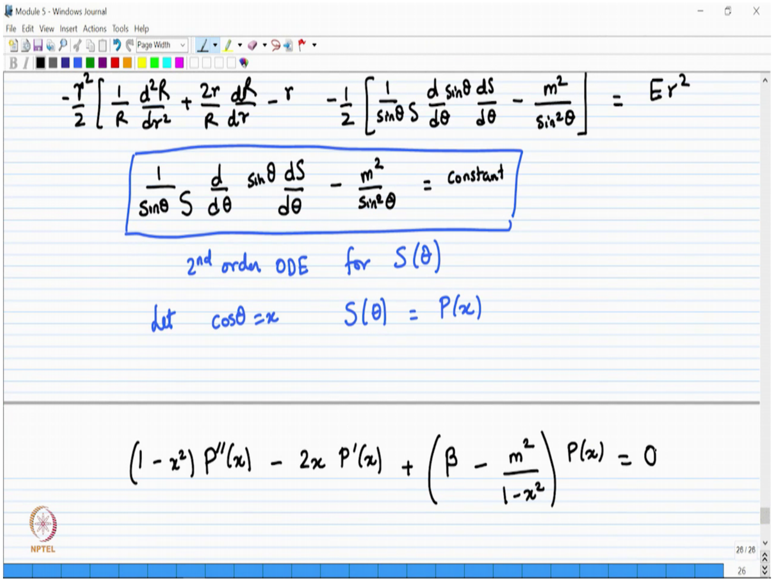

So, f of theta is P of x. So, if you change the variable then the function will have a slightly different form. So, we just call it P of x. So, with this substitution you can substitute in this differential equation and you can take the appropriate derivatives and then what you will get is you will get a differential equation that has this form 1 minus x square I will write P double prime of x double prime means second derivative with respect to x minus 2 x P prime of x and let me call this constant as beta. So, I will call this constant as minus beta, so then this will become plus beta minus m square over 1 minus x square times P of x. So, sin square theta is 1 minus cos square theta. So, that is how you get this and you will get a differential equation like this and this equal to 0.

And you can immediately see that this is a homogeneous second order differential equation in P of x and we will solve this using the power series method. Now you can solve this for a general value of m, you can solve this for an arbitrary value of m, but it turns out to be a little more involved.

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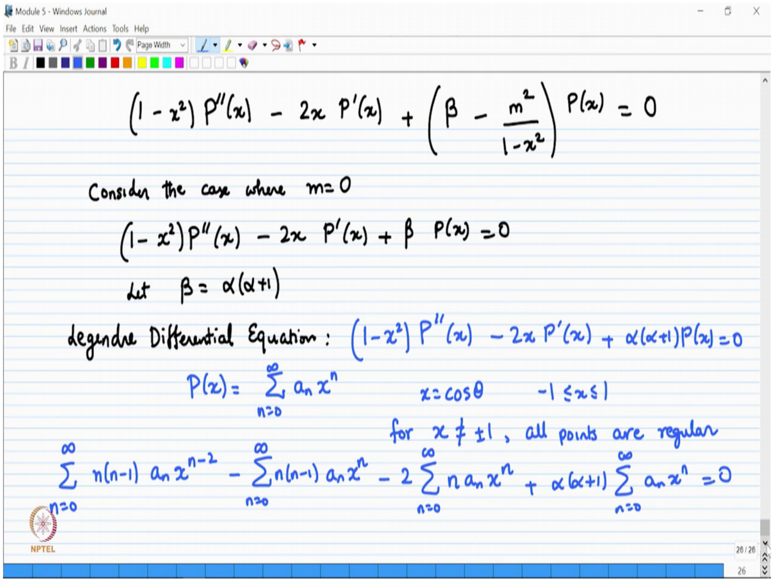

So, we will take the case of, consider the case of case where m equal to 0.

So, when m equal to 0 then this differential equation has this form, P double prime of x minus 2 x P prime of x plus alpha P of x equal to 0 oh sorry plus beta. So, what we are going to do is we are going to let beta equal to alpha times alpha plus 1, you can always do this you can always write beta in this form. So, alpha is beta is some real number alpha is also a real number. So, if you let this form then you are then what you get is called the Legendre differential equation, this turns out to be a very famous differential equation in engineering that was discovered many centuries ago - 1 minus S square P double prime of x minus 2 x P prime of x plus alpha alpha plus 1 P of x equal to 0.

Now, these equation as I said is a very famous differential equation and this has been solved nearly 200 years ago. So, let us look at how we can solve this differential equation and what we will do is we will apply the power series method at this point. So, the power series method will be applied only when the differential equation is in this form. So, what we will say is let P of x is equal to sum over a n x raise to n, yes and I forgot one thing, so n equal to 0 to infinity. Before we do this we can see that that x equal to cos theta. So, therefore, minus 1 less than equal to x less than equal to 1. Now for x not equal to plus minus 1 this is a regular then all points. So, all points are regular.

So, any point except x equal to plus minus 1 is a regular point. So, that means, where we are interested that is minus 1 2 to 1 except at the boundaries all the points are the regular points and they are not singular points. So, we can write the differential equation solution we can write the solution in this form as an ordinary power series without the x raise to r term. So, now, you can do this and you can substitute for P prime of x and P double prime of x and I will just I will just write the expression.

So, I have 1 times P double prime of x. So, I will write that as sum over n equal to 0 to infinity and I have n n minus 1 a n x raise to n minus 2. Now I have x square, so minus sum over n equal to 0 to infinity n n minus 1 a n x raise to n minus 2 into x square that is x raise to n and then I have minus 2 x into P prime. So, P prime will give me n times, I will write minus 2 sum or n equal to 0 to infinity. Now I have n a n x raise to I had x raise to n minus 1 because of P prime now we will become multiplied by x will give me x raise to n and then I have plus alpha alpha plus 1 sum over n equal to 0 to infinity an x raise to n equal to 0.

Now, this is the expression with which you start and now let us try to compare it term by term this is the most this is the first step in the power series method of solution. Now what we will do is compare term by term. So, let us say x raise to 0 terms.

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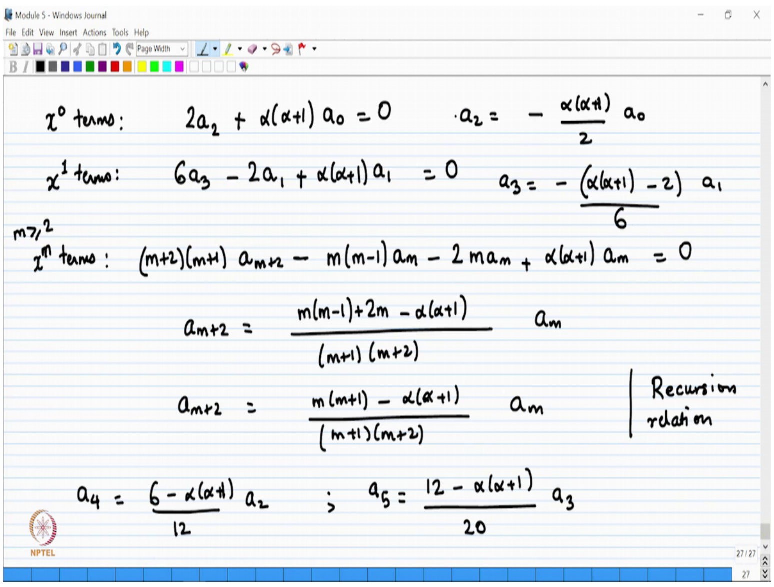

So, on the left hand side if you want x raise to 0 then n has to be equal to 2. So, if you want to term that has x raise to 0 then n has to be equal to 2. So, you have 2 into 1 into a n. So, you have 2 a n that is the first term. In this term if you want x raise to 0 then n has to be 0, but if n is 0 this n into n, a n times n minus 1 is 0. So, you do not have any term with x raise to 0 here. Similarly if you want x raise to 0 then n has to be 0 in the third term n has to 0 mean n being 0 means the third term goes to 0. Then you have plus alpha alpha plus 1 a 0 equal to 0. So, here n equal to 0 you have a 0, oh there should n equal to 2. So, there should be 2 a 2. So, this is what is the term looks like and so what you get is that a 2 is equal to minus alpha alpha plus 1 by 2 a 0.

Now we can go ahead what about x raise to 1 terms. Now what you will get if you want x raise to 1 in this then n has to be equal to 3. So, you have 3 into 2 that is 6 and a 3, you have 6 a 3. In this case if you want then a in the second expression n has to be 1, but if n is equal to 1 then n times n minus 1 goes to 0. So, you do not have any n equal to 1 term here. The third term will give you again if you have to have n equal to a x raise n has to be equal to 1, you get a 1. So, you have minus 2 a 1 and in the last term you will get plus alpha alpha plus 1 times a 1 this has to be equal to 0, so all the terms because right hand side has no x raise to 1 term, so plus 1.

So, what you get you get a 3 is equal to minus a 1 times minus a 1 times. Now what you have is alpha alpha plus 1 minus 2 divided by 6. So, I have chosen to write it in this form, but basically a 3 is related to a 1. So, a 2 is related to a 0 a 3 is related to a 1. Now suppose you consider a general let us say x raise to n terms or x raise to let me call it x raise to m terms just to distinguish from that variable. So, if you look at all terms that have x raise to m. So, if you have, if you want to have x raise to m then what you should have is in this should be n should be equal to m plus 2. So, you have m plus 2 m plus 1 a m plus 2 minus if you want x raise to m, so x raise to m of course, we are saying m is greater than 2, m greater than equal to 2.

So, then in this case you will have if you want x raise to m then you should have m m minus 1 a m minus 2 m a m plus alpha alpha plus 1 a n equal to 0. Now what you see is you have a m plus 2 and you have a m. So, what I can do is I can write a m plus 2 is equal to a m times some quantity now the denominator is m plus 1 m plus 2. Now what I have in the numerator? So I have m m minus 1 plus 2 m. So, that is. So, what I have is m m minus 1 plus 2 m minus alpha alpha plus 1.

So, what this looks like is m times m plus 1 minus alpha times alpha plus 1 divided by m plus 1 m plus 2 times a m. So, this is called the recursion relation, this is called the recursion relation and notice this is the recursion relation of this of this differential equation of the Legendre differential equation. So, we had the Legendre differential equation we made the substitution and then what we noticed was that when we make this when we use the power series method we get a recursion relation that relates the coefficients. So, notice that when you have the power series method what your goal your goal is to determine these coefficients a n.

Now, what we saw was that we can write a 2 as some something times a 0 a 3 as something times a 1 and you can write any m plus 2 th term in terms of a m 4, m greater than or equal to 2 you can write the m plus 2 th term in terms of a m. Notice that m plus 2 th term they has not involved a m plus 1 you can write it distinctly in terms of a 2. So, what that means is that if I write a 4 I can write as a 4; that means, m equal to 2. So, 2 into 3 that is 6 minus alpha alpha plus 1 divided by 2 plus 3 into 4 that is 12 a 2. I can write a 5 equal to, 5 means m equal to 3, so m equal to 3, 3 into 4 that is 12 minus alpha alpha plus 1 divided by 3 plus 1, 4 into 5 - 20 a 3 and what you can do? You can do a few more things.

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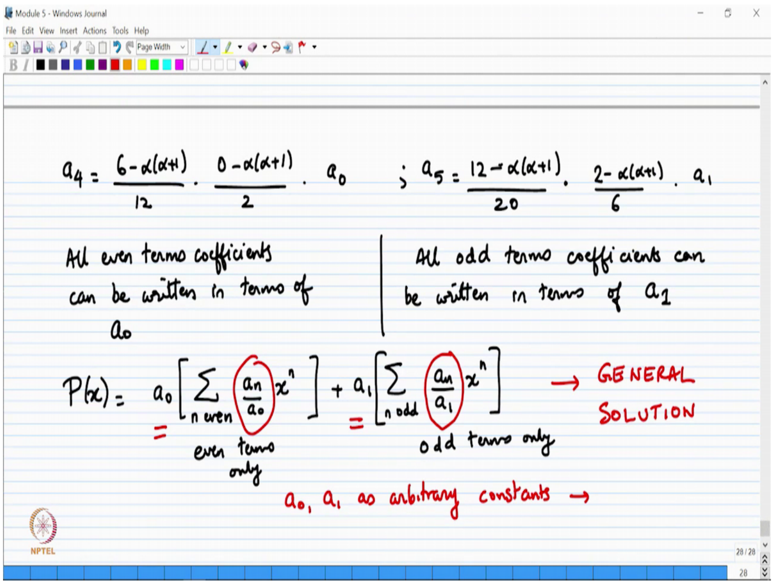

So, if you look at a 4 I can write as 6 minus alpha alpha plus 1 divided by 12. Now for a 2 I can use my expression for a 2 and I can write as minus alpha alpha plus 1 by 2. So, I will write this as 0 minus alpha alpha plus 1 divided by 2 times a 0 and I can write a 5 as 12 minus alpha alpha plus 1 divided by 12 times now, for a 3 I use this expression that I had before. So, all right is as 2 minus alpha alpha plus 1 by 6, 2 minus alpha alpha plus 1 by 6 times a 1. So, what this implies is that all even terms, even terms coefficients can be written in terms of a 0 and all odd terms coefficients can be written in terms of a 1 . So, what our power series will look like. So, I can write the power series in this form. So, P of x looks like this, a 0 times sum over only the even terms. So, I will just write I will just write n even and what I will get is e n by a 0 x raise to n plus.

So, a n by a 0 is some number that that depends on alpha and I have a 1 times sum over n odd a n by a 1 x raise to n. So, this contains only odd terms, this is even terms only and what is important is that these are not, these are just functions of these are just functions of alpha. So, I can use I can write this as, so this is a general solution if you can see if you think of a 0 and a 1 as, a 0 a 1 as arbitrary constants then this represents a general solution of this equation. So, this is a general solution.

So, the general solution has 2 linearly independent solutions. So, the polynomial the series with only even terms and the series with only odd terms are linearly independent. So, this is a general solution that is written in terms of a linear combination of these 2 solutions.

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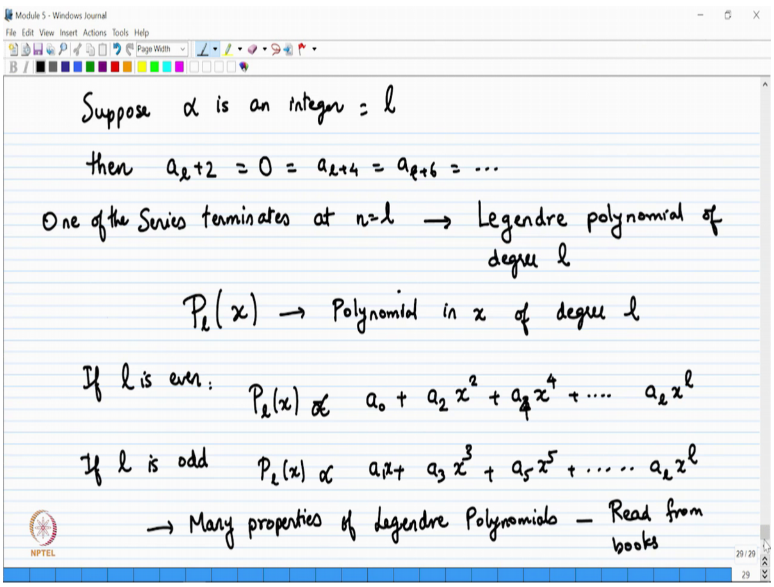

Now, let us consider the case let us go back here. So, now, suppose alpha is an integer alpha is an integer let us say equal to l then a l plus 2 equal to you can see from this expression. So, so when you look at a l plus 2 you will get l l plus 1 minus alpha alpha plus 1 is just l l plus 1. So, a l plus 2 equal to 0 equal to 0 and because a l plus 2 equal to

0, a l plus 4, a l plus 6 all these equal to 0. So, that implies that series terminates at n equal to l, 1 of the series. So, 1 of the series, 1 of the series terminates at n equal to l. This terminated series is called a Legendre polynomial of degree l.

So, what you get is this is represented as P l or l is put in the subscript P l of x is a polynomial in x of degree l and P l of x is 1 solution. So, it is 1 solution. So, basically the if l is even then P l of x is equal to a 0 plus a 2 x square plus a 3 x a 4 x 4 plus dot dot dot up to a l x raise to l if l is odd actually this is written slightly differently. So, P l is I will say proportional to this I will just say it is proportional to this if this is odd P l of x is proportional to a 1 plus a 3, a 1 x plus a 3 x cube plus a 5 x 5 plus dot dot dot up to a l x raise to l, with some constants of proportionality this is what your Legendre polynomials are.

So, we can go ahead and you can write lot of properties of Legendre polynomials. So, many properties of Legendre polynomials, but basically now I will just you can read and read from various books we will not be spending too much time on that.

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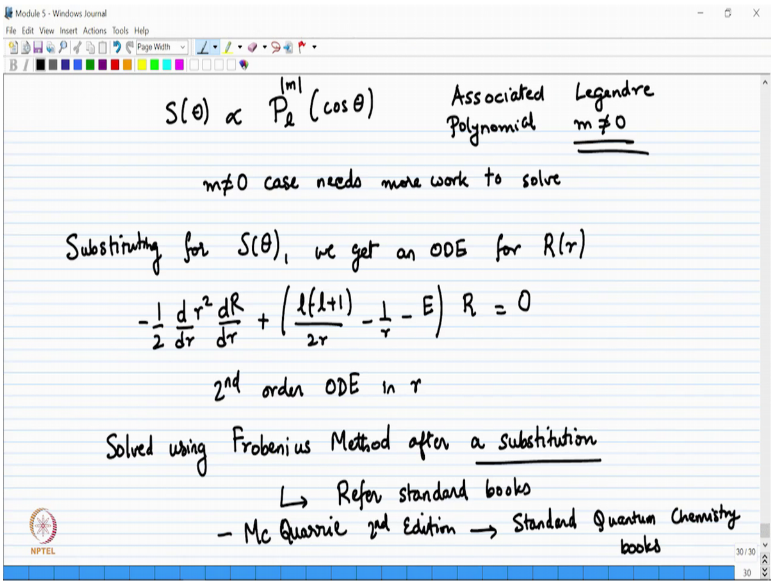

Rather what I will just write is that finally, what you will get is your S of theta is proportional to, now P l of m of cos theta now P l of m. So, remember we considered m equal to 0. So, this is Associated Legendre Polynomial, polynomial and this comes when m is not equal to 0. Now I have actually it turns out that that when you have a; when you have something like this when you have 2 series and alpha is an integer then 1 of these series will terminate and as I said a 0 and a 1 are arbitrary constants. So, what is done is you take the series that terminates you use that as the as the required solution, the other solution you can throw away from conditions on the wave function.

So, we use only the solution only the polynomial solution that which shows, which is due to the terminating series. So, now, what you get is here you have the associated Legendre polynomial that appears naturally in this equation I have not done the m naught equal to 0 case needs more work to solve which are not done to solve, but you can look up again in standard books. So, now, when you do this what we will get is that this whole thing when you use the solution and you put back in the day in the differential equation for theta what will happen is that this whole factor. So, this whole factor of will just be replaced by l l plus 1 and then you will get you will get an equation. So, substituting for S of theta we get an ODE for r and for actually R of r. So, the ODE for r has this form.

So, I will just write minus 1 by 2 d by d r of r square d R by d r plus l l plus 1 divided by 2 r minus 1 by r minus E times r equal to 0. Now you can expand this and you can clearly see that this is a second order ODE in r and this is actually the solution is solved using Frobenius method, but you know before that after a substitution. So, you first make a substitution and then you solve using Frobenius method. So, I will not do this explicitly this you can refer books, refer standard books. So, this is done in Mc Quarrie, Mc Quarrie has it and Mc Quarrie mathematical methods that is second edition has this topic also it is also there in standard quantum mechanics books, quantum chemistry books.

So, I will conclude this module here. So, what I have try to show in this module is the techniques to solve second order differential equations and I have just given you a very brief and very quick overview of the techniques. Now these are these are techniques that you can learn. So, with this background you can actually work out all these and you can actually show how to use all these techniques to solve second order ODEs. So, I will conclude this module here.

Thank you.