**Mathematics for Chemistry**
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**Module - 08**
**Lecture - 39**
**Leguerre Polynomials Solution to Radial Part of H-atom**

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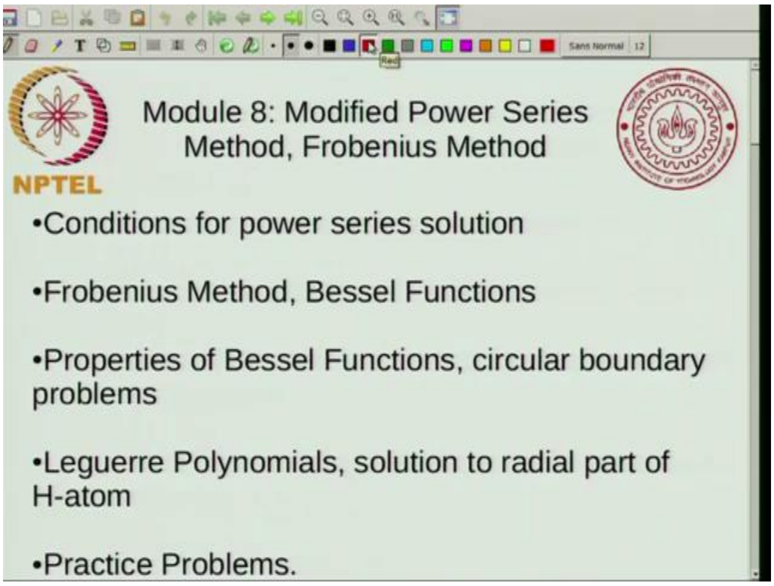


So, in today's class I am going to talk about Leguerre polynomials and how they appear in the solution to the radial part of the hydrogen atom problem in quantum mechanics.

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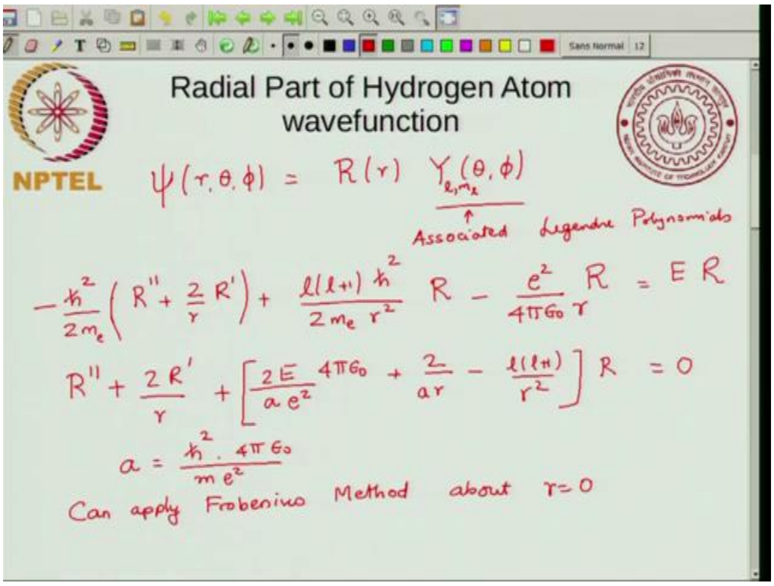


So, let us just remind our self. So, what is the, so the wave function for the hydrogen atom depends on r, theta and phi and this is written as a product of a radial part that depends only on r, times an angular part that depends on theta and phi; and this angular part we already saw the solution of the angular part. So, this was related to the angular momentum Eigen functions and these are related to the spherical harmonics and they have their 2 quantum numbers l and m; l and m l probably is probably the right notation. So, these are related to associated Legendre polynomials, you can solve these using the power series method.

Now, the radial part; so the radial part is what we are going to focus on today. So, let us write a Schrodinger equation I will write it in spherical polar coordinates, and I will just write the expression h cross square by 2 m, m e is a mass of the electron and I have R double prime plus 2 by r, R prime plus now the angular part. So, the angular part since you know the solution we take we use at solution and write this as l, l plus 1, h bar square divided by 2 m e r square times R, and then you have an additional term. So, that looks like e square. So, all these comes from the kinetic energy then you have the potential energy e square by 4 pi epsilon 0 r times R, this is equal to E times R.

So, the left hand side is the Hamiltonian times operated on r, and right hand side is e times r. Remember r is a function this capital R is a function of small r; and r prime r double prime is just d square by d r square and r prime is d by d r. Now I will just rearrange this a bit. So, just take this minus h cross square by 2 m e to the right side and then just pull everything over to the left. So, I get differential equation the following form R double prime plus 2 R prime by r. So, this is the only term that. So, since I took this over here. So, this is the only term that has R double prime and the only term that has R prime plus ok.

Now, the h cross square by 2 m e will cancel with this, we have minus h cross square by 2 m e and you have h cross square l l plus 1, you when you write the remaining terms now I will have 2 e multiplied by 2 m e by h cross square; and what I will do is I will further I will take this factor over there. So, I will write this in the following form write this whole thing multiplied by R equal to 0. So, what I wanted to do is to write something multiplying R. So, since I just want r what I will the write is a following. So, I will write 2 e by a e square times 4 pi epsilon 0, plus 2 by a r I will tell you what a is in a minute plus l l plus 1 by r square ok.

So, a is the bore radius and that is related to h bar square times 4 pi epsilon 0 divided by m e square. So, this is the a, so I just use this and rearrange things in a bit to write it in this form. Now do not worry about all these constant, but what is important is that this looks like a second order differential equation and it is something that you can solve using the power series method, because you notice that this has a 1 by r. So, since I have a one here. So, I at R equal to 0 this does not vary this does not go to infinity faster than 1 by r. Similarly I have a 1 by r square that is the highest power of r and that is not go to 0 faster than one by r square. So, basically with this you can see that you can apply the frobenius method about r equal to 0 ok.

Now, you can apply the Frobenius method about r equal to 0. So, I will just mention this can apply Frobenius method about r equal to 0, but instead of doing that we will make things a little simpler. So, you can do this, but you will get some very complicated recursions. So, instead of that we will separate some factors just like we did in the case of the harmonic oscillator.

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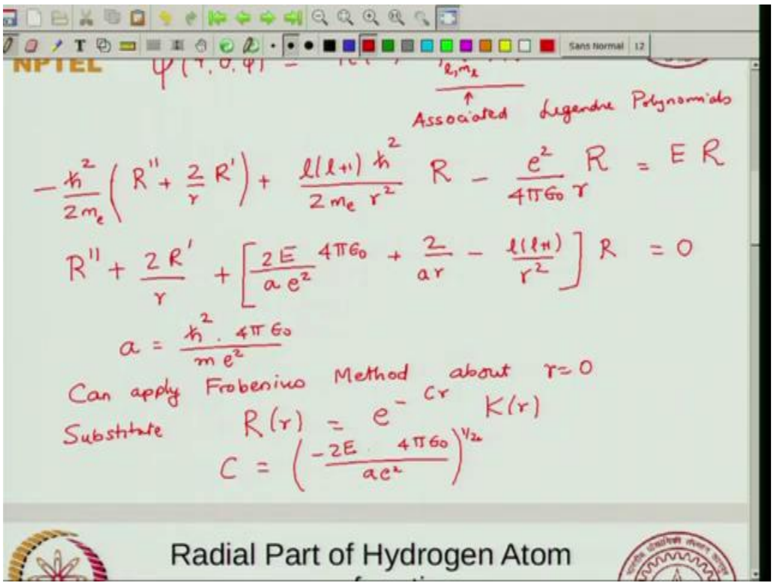


So, what we will say is you substitute R of r is equal to e to the minus c r times K of r. Where C is equal to minus 2 E times 4 pi epsilon divided by a e square the whole thing raised to half and you can you can probably see why we took this form; because suppose you take large r. So, suppose you take r going to infinity. So, if r is going to infinity then this term will be negligible, all these 1 by r terms will also be negligible, so what you will get is R double prime is just some constant times r and so you will get an exponential d K you will get an exponential d k. So, it will exponentially go to 0 and that power of this exponential is exactly this ok.

So, the coefficient of the exponent is this and basically this immediately tells you that E should be less than 0. So, the energy of these electron in the hydrogen atom should be less than 0 and that basically says that the electron is bound it is not free to go. So, you see this and when you make this substitution, and you substitute in this differential equation you will get a differential equation for K and I will just write what that differential equation is you can actually go ahead and work it out ok.

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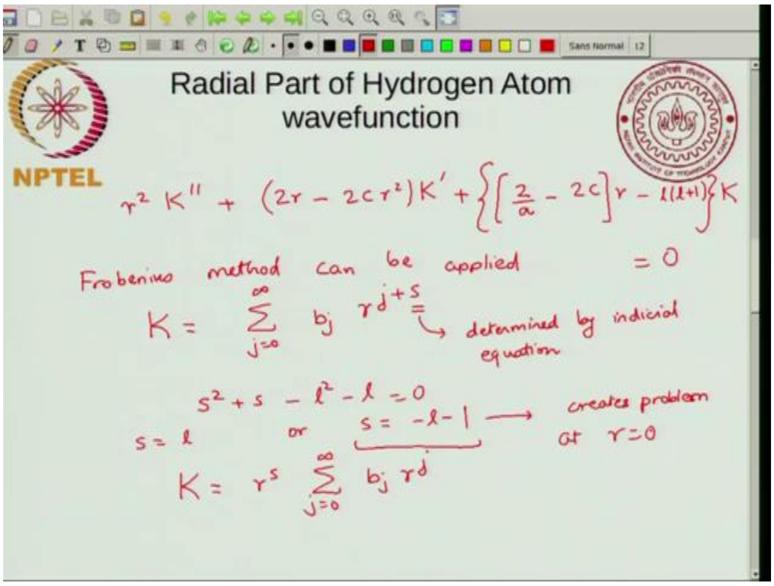


So, let us write down what that differential equation is. So, it looks like the following r square K double prime plus 2 r minus 2 c r square K prime, plus 2 by a minus 2 c r minus l, l plus 1 the whole thing multiplied by K equal to 0. So, I wrote it as r square times K double prime plus something I do not have just an R K prime I have a r and an r square K prime and I have something else equal to 0 ok.

So, this is where you can apply the power series method again you can verify that is Frobenius method can be applied, can be applied, and if you apply the Frobenius method what you will says that K equal to I am not writing the K of r. So, j equal to 0 to infinity b of j, r raised to j plus s. So, remember you had x raised to n plus v. So, this is the same thing instead of n I am using j, instead of v I am using instead of r I am using s the point is. So, s is what is going to be determined from the determined by the indicial equation. I just want to emphasize that if you actually want to solve the hydrogen atom problem when you want to get what the 1 s wave function looks like, what is the 2 s wave function looks likes and so on.

Then you have to go through this procedure. So, this procedure is actually necessary. So, we usually directly write the solutions, but actually if you want to derive the solutions you have to go through this procedure. So, what does the indicial equation work outs. So, if you substitute in this equation your indicial equation looks like this. So, it is looks like s square plus s, minus l square minus l equal to 0 and you will get basically 2 conditions you will get s equal to l or s equal to minus l minus 1. So, these are the 2 possibilities that you can get for the indicial equation ok.

So, now this s equal to minus l minus 1, remember here what it means that you have a K equal to r to the s times sum over j equal to 0 to infinity b j r raised to j. So, basically when j equal to 0 you have r raised to s. So, r raised to s is a leading term now you can actually show that when s equal to minus l minus 1 then you will have a problem at r equal to 0. So, s equal to minus l minus 1 creates problem at r equal to 0, and you know you can show for various reasons that this is not this is not of interest.

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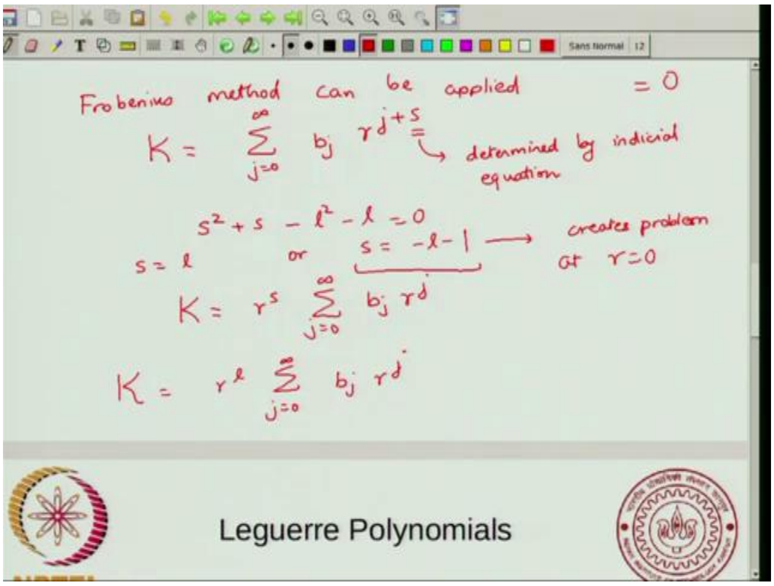


So, the solutions that are of interest look the following. So, K is equal to r raised to l times sum over j equal to 0 to infinity, b j r raised to j. So, this is the form of the solutions that we are actually interested in. So, we start with this now r raised to l this is the same l that appears in the differential equation.

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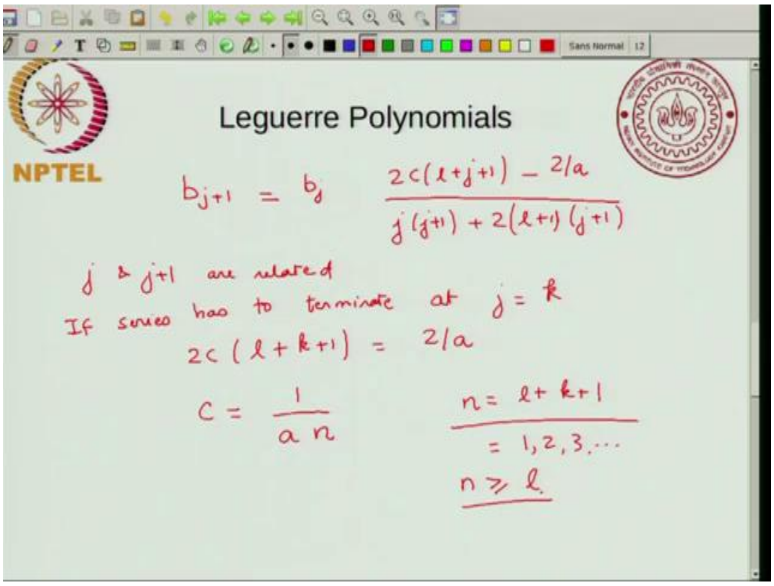


If you work it out then you will get b of j plus 1 you will get recursion relation that looks like a b of j plus 1 equal to b j times 2 c l plus j plus 1, minus 2 by a divided by j, j plus 1 plus 2, l plus 1, j plus 1.What is important is that this recursion relation is what you get and notice that here you have j and j plus 1 are related.

So, you do not have only odd terms or only even terms because the reason is your differentially equation had had a term that has an r K prime and an r square K prime and similarly it has an r K here. So, basically you get coupling between both j plus 1 and j not just j and j plus 2.

Now, we can say that if this series has to terminate. So, if series has to terminate at j equal to I will just call it k, then we should have 2 c times l plus k plus 1 is equal to 2 by a, or you will get c is equal to 1 by a times n, where n is equal to l plus k plus 1 . So, n equal to l plus k plus 1, now k can be anywhere from 0 onwards. So, l also can be 0, 1 2, 3 etcetera, basically n equal to 1, 2, 3 etcetera. So, these are the allowed value of n and also notice that n is greater than or equal to l. So, these will be familiar. So, n is what is called the principal quantum number, and you can you can immediately see from here that n has to be greater than or equal to l and n has to be a positive integer. So, this is the very nice thing that you got this quantization of n.

Now, you can go further because c is related to your energy. So, basically if you substitute for c if you substitute the expression for c in term of e that is this expression that we had here that we had here. So, c goes as energy raised to half. So, energy goes as c square and with some constants you multiply all those constants out and you will get the expression for energy of a hydrogen atom.

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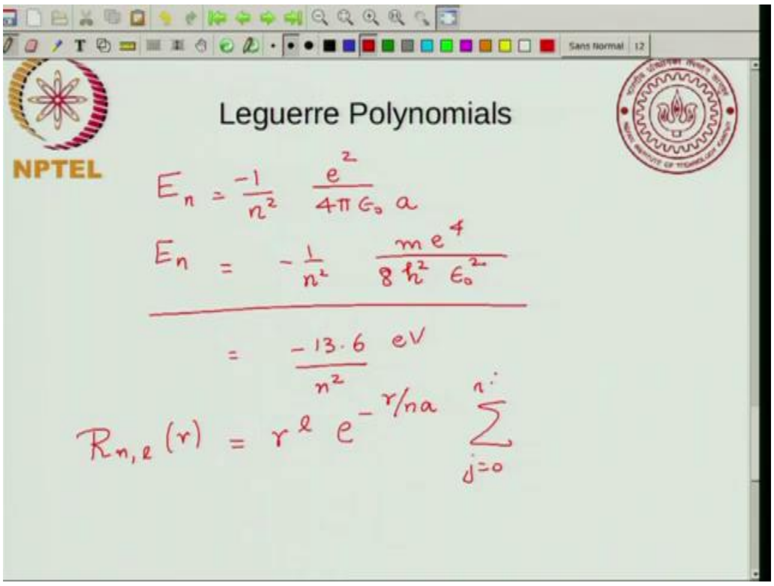


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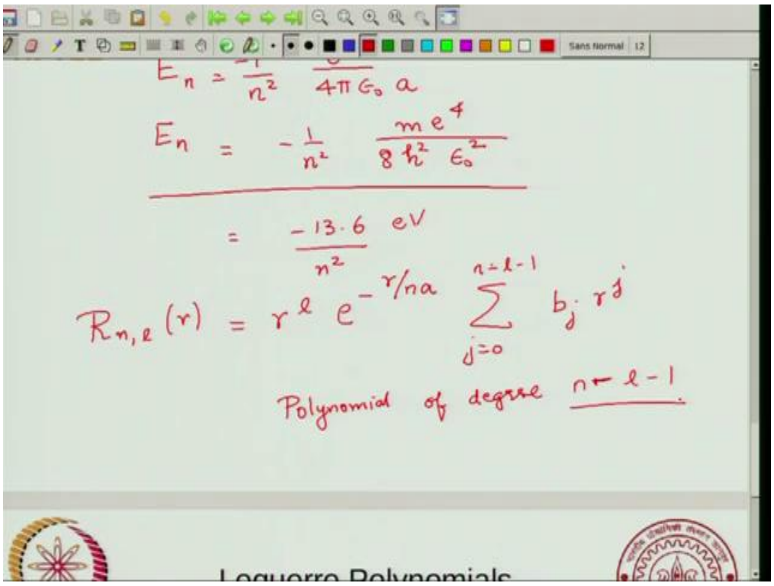


So, what you will get is that E goes as and I will put a subscript n. So, it goes as 1 by n square by the minus sign, and you will have e square by 4 pi epsilon 0 a; and if you substitute the value of a you will get minus 1over n square and what you will get is m e 4 divided by 8 h square h, h is epsilon 0 square ok.

And this is the usual energy expression for the bounds states. So, this is the usual. So, if you substitute all these values you will get it as a minus 13.6 electron volts divided by n square. So, you can substitute these values and get this, and what we are seen is that is that by this procedure we are able to get exactly the energy of an electron in hydrogen atom.

Now, next what about the wave functions? So, the wave functions, so your R now it is the functions of n and l of r. So, this has this form r, r raised to l e to the minus r by n a. So, you can show this n times a and you have sum over j equal to 0 to.

Now, the series terminates at terminates at j equal to k. So, and k is n minus l minus 1. So, I can write this as a sum that goes up to n minus l minus 1, and what you have is b j r raised to j. Now what you can do is you can go ahead and you can express these. So, this poly this is a polynomial of degree n minus l minus 1. So, this is the polynomial of degree n minus l minus 1 and this is what is closely related to something called the Leguerre polynomial.

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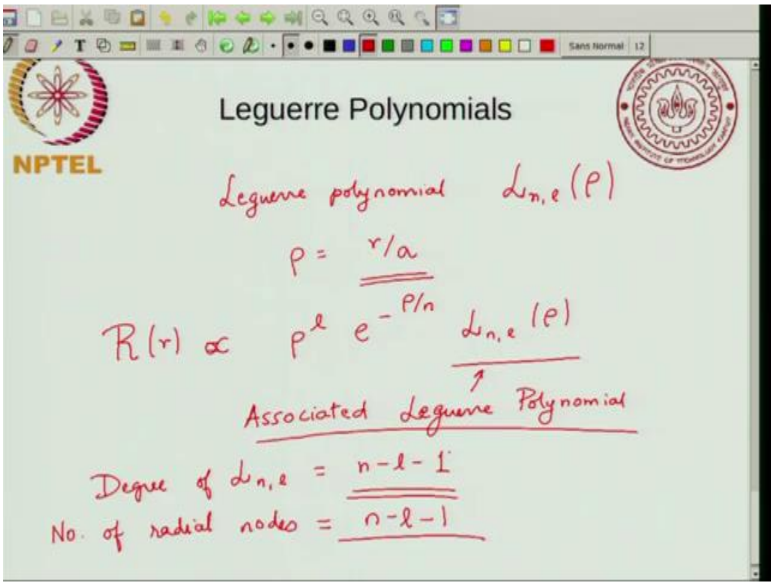


So, the Leguerre polynomial, so this polynomial So, you write Leguerre polynomial L and l depends on n and l and the argument of l is actually rho it is not r, this is just I mean rho is just a constant multiplied by r.

So, rho equal to r by a for the hydrogen atom; so for the hydrogen atom it is r by a and basically I can write my redial wave function of r as you know it is proportional to now I have rho raised to l e to the minus rho by n and then I have L n l of rho is just a change of variables that is used, but basically you can write the wave function in terms of these Leguerre polynomials. So, this is actually called an associated Leguerre polynomial just as you had the associated Legendre polynomial.

Now, I do not expect you to remember all these things about Leguerre polynomials, but as a student of physical chemistry it is expected that when you see the quantum mechanical problem for the hydrogen atom, you should realize that radial part of the solution contains Leguerre polynomials, and if you want you can go and work it out you can work out all the details you can work out all the properties of the Leguerre polynomials, what we know is that is Leguerre polynomial of l n l the associated Leguerre polynomial has degree n minus l minus 1. And these degree of this polynomial; so the degree of l n l is equal to n minus l minus 1 and this is actually very this degree turns out to be very important because if you have a polynomial of degree n minus l minus 1 then it will go to 0 at n minus l minus 1 points.

So; that means, number of nodes number of radial nodes equal to n minus l minus 1 and this is a very very useful result that you will see in your quantum mechanics courses. So, the other parts of R of r. So, rho raised to l goes to 0 only when l equal only when rho equal to 0, similarly e raised to minus rho by n goes to 0 only when rho goes to infinity, but it is this Leguerre polynomial that will give you the different nodes of the of the wave function.

So, again I will stop here I just want to emphasize that I have try to illustrate some of the applications of the Frobenius method, I do not expect you to remember all the properties of Leguerre polynomials and bessel functions, but I expect that you know with this knowledge you will be able to work them out whenever you need to. And you know in this in this few lectures I have try to give you various I have try to give u glimpses of the applications, but there are several applications if you read any book you will see that you know bessel functions and bessel equation there are several applications, it is in fact related to all kinds of series like the hyper geometric series or even the legendre polynomials and so on, but we have not try to do all those things, what I have try to do is try to give you a feel of where this Frobenius method is used in various chemical problems, and you know in the last lecture of this course I will do a few practice problems that had focused on the Frobenius method.

Thank you.