Engineering Chemistry - 1

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Lecture - 6

Module 1 Atoms and Molecules

Hydrogen Atom

Welcome back to the lecture series on the topic of Engineering Chemistry. This is a series of lectures being given to Under Graduate Science and Engineering students in the country and elsewhere and is part of the National Programme on Technology Enhanced Learning the project funded by the Ministry of Human Resource Development Government of India. I have been giving the series of lectures on the first module on Engineering Chemistry the module being the Atoms and Molecules and on the fundamental atomic structure principles and principles of Quantum Chemistry which we would hope that all Engineering students should be familiar with.

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In today's lecture we will continue with the hydrogen atom that we started in the last lecture namely lecture number 5. I introduced the spherical polar coordinate system for the study of hydrogen atom stating that this coordinate system enables us to solve the Schrödinger equation for the hydrogen atom rather in a straight forward manner by affiliating the Mathematics with Mathematical equations that have been known are quite sometime. The Schrödinger equation for the hydrogen atom is also the first real contact with systems of atomic nature and in which the full the Mathematical machinery can be employed to show analytical solutions. (Refer Slide Time: 3:16)

We will not solve the problem here we will state the problem and we will state the solutions as has been the tone of these series of lectures. It is an introductory lecture or this course is an introductory course. The solutions for the Mathematical equations that enter in hydrogen atom are a bit more detailed than the Mathematics you are already familiar with. The differential equations that come into the picture require solutions using slightly more advance methods which I hope as Engineering or Science students pursuing your higher degree you will see them in later years particularly in special function techniques, orthogonal polynomials, these are all Mathematical methods in the solutions of differential equations.

We will only state the solutions but more importantly we will try and understand what the pattern in all these solutions is and how we can make sense out of these solution in terms of the orbital picture that your are familiar with from your preliminary or the previous encounter that you had with hydrogen atom.

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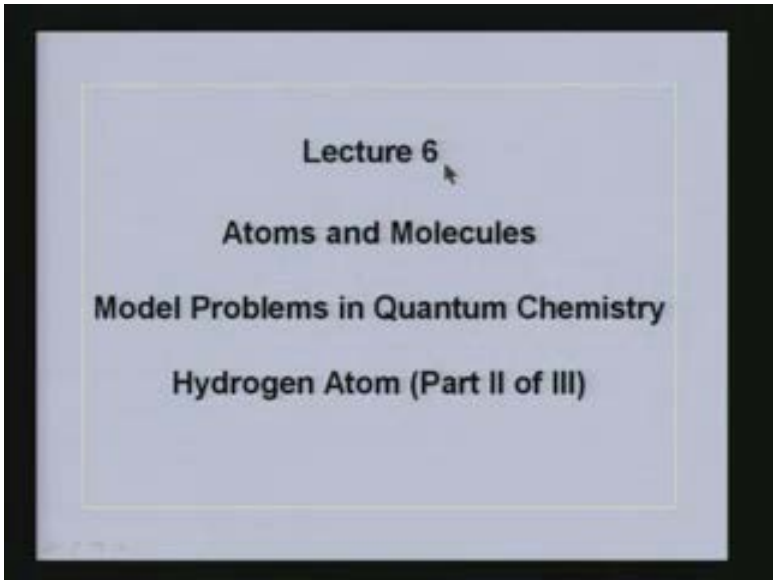

So in today's lecture which is lecture number 6 on Atoms and Molecules is part of the model problems in Quantum Chemistry. We will continue to look at the hydrogen atom.

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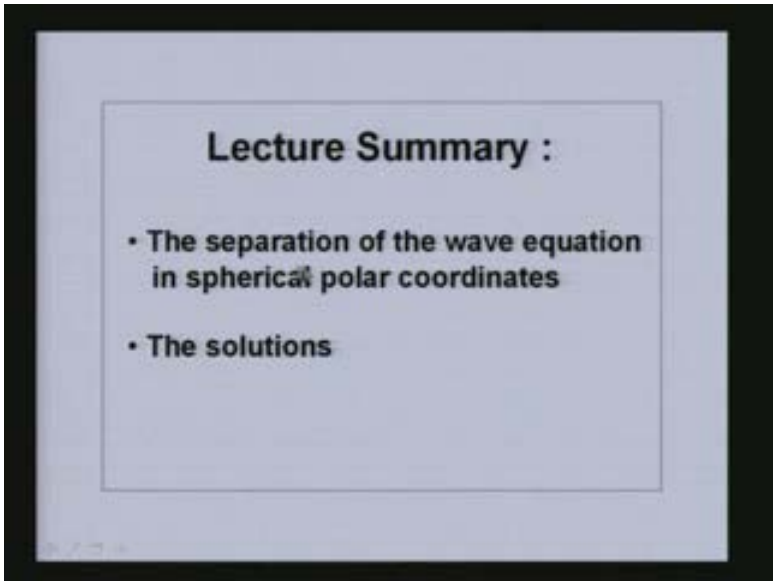

And in this lecture we are only going to look at two things; one is the separation of the wave equation expressed in spherical polar coordinates r, θ and ø. The second part is the radial solution. We will not look at the angular solution and we will not have the time to do the angular solutions but we shall examine the radial solutions and make sense out of the results. So the radial equation, the Hamiltonian for the hydrogen atom if you recall from the previous lecture the kinetic energy was written as $-\hbar/2m_e[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2]$ where m is the mass of the electron, and the momentum is taken as in terms of x components, y components and the z components. The whole of this is the kinetic energy and a potential energy term which is $-e^2/4\pi\varepsilon_0 r$ that is of course the charge of the nucleus is z but that is equals to 1 in this case and r is the radial distance of the electron as a dot from the nucleus with a classical model classical picture expressed in Quantum mechanical representation.

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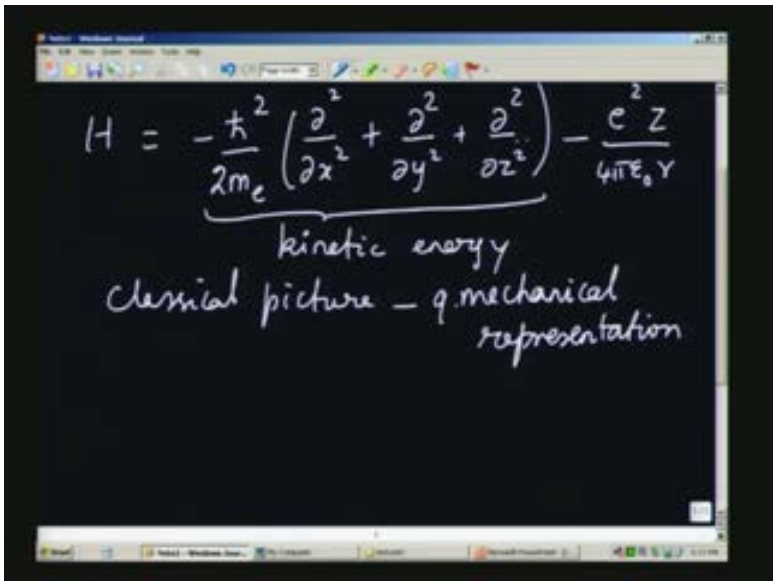

It is because we have written the momentum in the form of the derivatives.

Now, this was converted into the (r θ ø) coordinate system. I would like to rewrite or to write the Hamiltonian using the radial coordinate system or the polar coordinate system as $-\hbar^2/2m\{[\mathbf{1}/r^2\ \partial/\partial r(r^2\ \partial/\partial r)]+[\mathbf{1}/(r^2\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta)]+[\mathbf{1}/(r^2\sin^2\theta)\ \partial^2/\partial ø^2]\}$.

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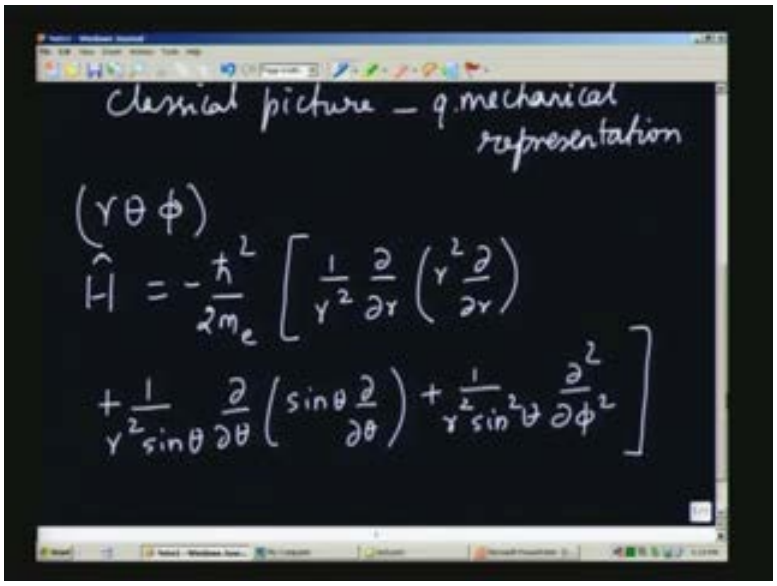

This is the polar coordinate representation of this term, the kinetic energy term that you have in the r, θ, ø representation. And then of course this is the kinetic energy term and what we are left with is the potential energy term which is $-Ze^2/4\pi\varepsilon_0 r$ and you know r is equal to $\sqrt{(x^2+y^2+z^2)}$.

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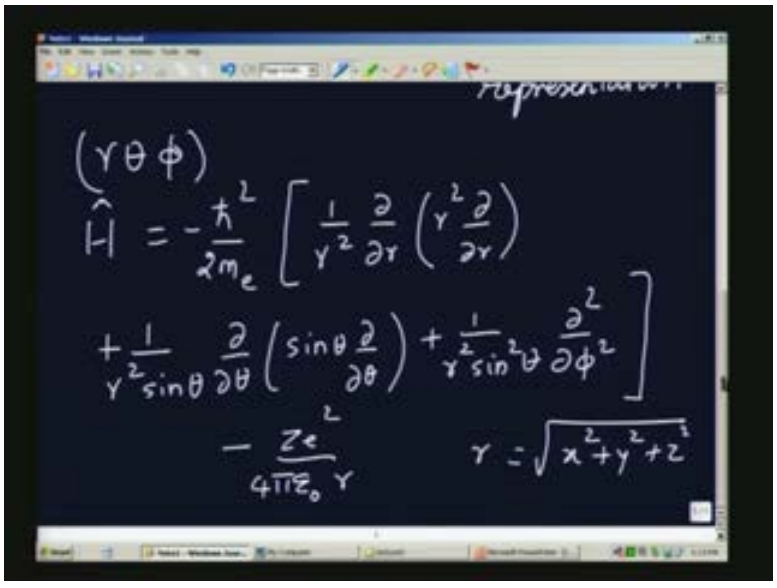

Now, when we say that the purpose of going into the polar coordinate system is to simplify the Schrödinger equation and separate it from the form that I just wrote down does not look like any simpler than the form that you have in Cartesian coordinate system. Actually the kinetic energy part is extremely simple looking in the Cartesian coordinate system. What causes the problem in that representation is r which is the $\sqrt{(x^2+y^2+z^2)}$. So even though the kinetic energy form and the

potential energy form are simple looking and they are not separable in the way they are written in the Cartesian coordinates. What do we mean by this? You have to recall the particle in a 2D box where we employed a wave function $\psi(x, y)$ as a product of one coordinate only the x function and a product of the y coordinate only and we were able to write the equation as $-\hbar/2m[\partial^2/\partial x^2 + \partial^2/\partial y^2]$ acting on ψ giving you the $E\psi$ for the particle in a 2D box free particle and bounded by v = infinity at the edges. This was separable when we assumed the wave function to be of this form.

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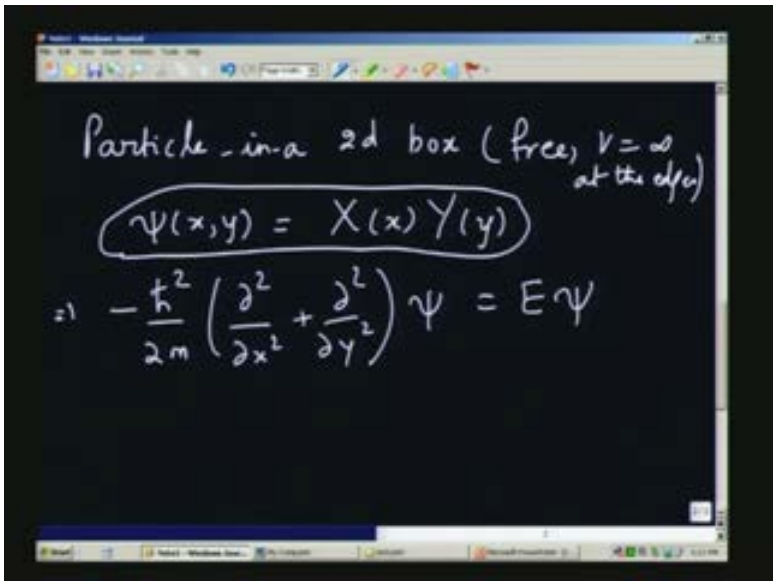

The equation separated into two one dimensional equations involving an X(x) only giving you an energy component E_x in terms of the $(h^2/8mL^2)n_1^2$ and likewise $(h^2/8mL^2)n_2^2$ for E_y and then the total energy was of course the sum of these two terms $h^2/8mL^2 (n_1^2 + n_2^2)$.

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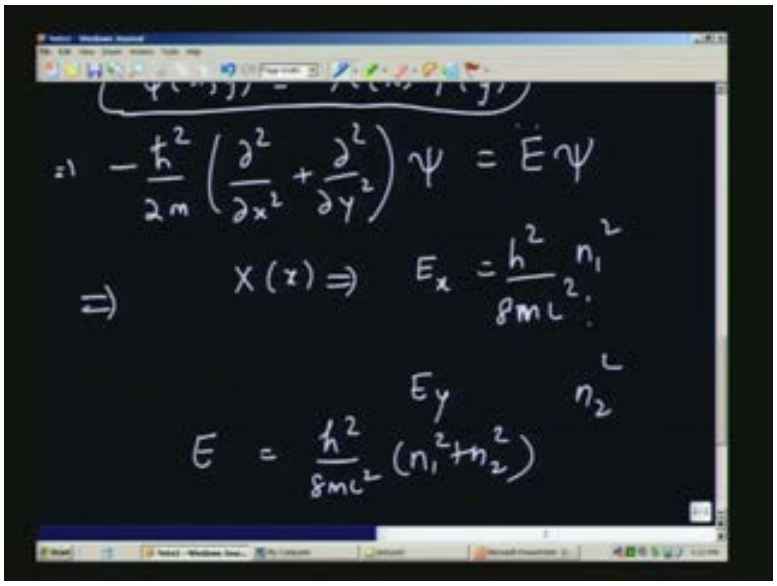

But the nice thing is that the representation of this wave equation could be simplified into two one dimensional wave equations by the proposition that the wave function ψ is a product of two wave functions each of which depends only on one coordinate. You recall that this is called the method of separation of variables in that lecture. Now, even though the hydrogen atom equation that you have here the Hamiltonian that you have here looks far more complicated in terms of the derivatives appearing in all places like this, the nice thing about this representation is that this can be separated into an or dependent equation only, a θ dependent equation only and a ø dependent equation only. It may not be obvious but we will go through that part rather elaborately to show that the equation is in fact separable. Now let us try and separate these equations one step at a time.

The first step is, let us multiply the Schrödinger equation by r^2. And in the second step let us write the overall wave function as ψ(r, θ, ø), let us for the time being write this as a radial function only and a function which depends on θ and θ and we will not separate this now we will do it later but we will write this as a product of a radial function or a function r which depends only on the radial coordinate and a function which depends on θ and θ and substitute this in Hψ = Eψ.

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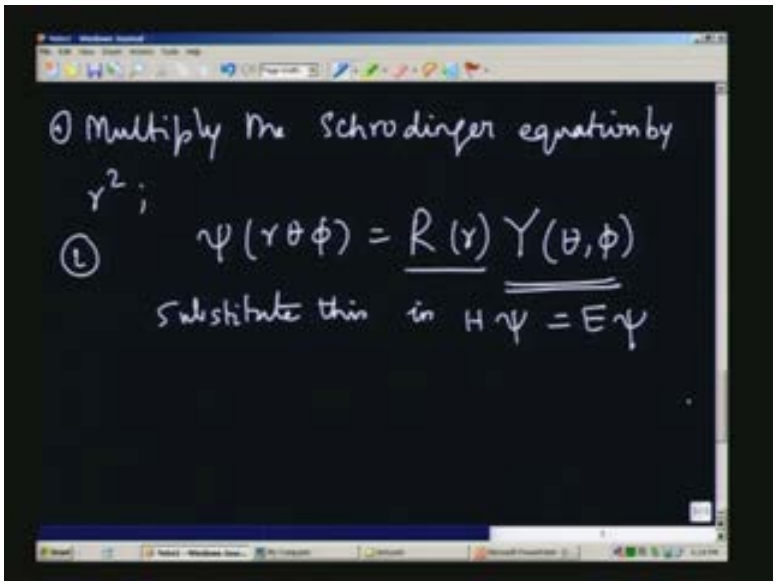

So let us write this equation. When you multiply by this by r what you have is $-\hbar^2/2m_e[\partial/\partial r(r^2 \partial/\partial r)]$ acting on radial function R(r) and Y(θ ø). Now it is quite clear that the radial derivative will act only on the radial function and with respect to this function this is of course the total derivative. So we might as well write this in a slightly different way by taking into account the full derivative and keeping all the other things outside namely $-\hbar^2/2m_e[d/dr(r^2 dR/dr)]$ so that is the radial part and this whole thing is multiplied by Y(θ ø), this is the first term.

Now if you do the same thing for the next term what you have is $-\hbar^2/2m_e$ $[\mathbf{1}/(\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial Y/\partial\theta)]$ R(r) since we have multiplied by r^2 we have only $\mathbf{1}/\sin\theta$. Now this is a $\partial/\partial\theta$ function. Since the function Y is a function of both θ and ø we will write this as a partial derivative $\partial Y/\partial\theta$ meaning that the ø part will be kept constant. And of course this will be multiplied by the radial part which is a multiple. (Refer Slide Time: 15:49 min). And likewise for the other angular part $-\hbar^2/2m_e[\mathbf{1}/\sin^2\theta\ \partial^2 Y/\partial ø^2]$ and of course this is also multiplied by the radial part, R(r). This is the entire kinetic energy acting on the wave function and the potential energy is $-Ze^2r/4\pi\varepsilon_0$ acting on the radial part R(r) and the angular part Y(θ ø).

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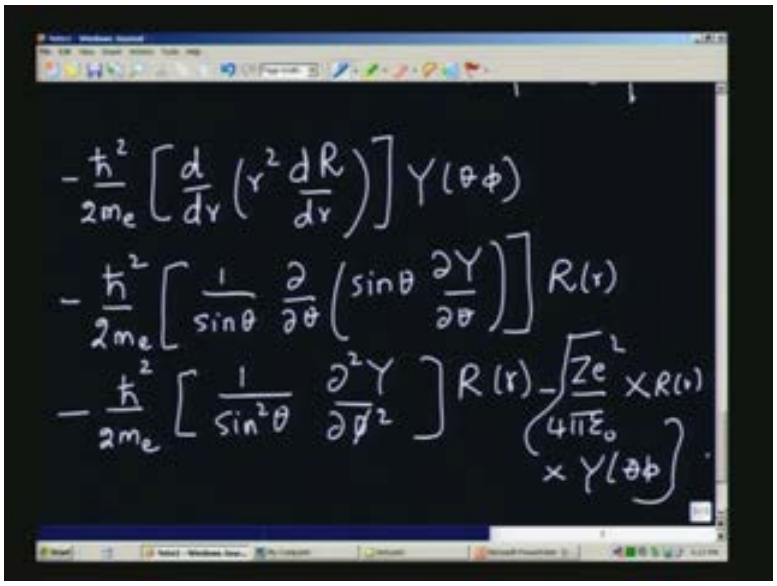

Since we multiplied everything by r^2 there is an r missing in denominator but we are multiplying this by r^2 so we will have the r here, and this becomes Er^2 R(r) Y(θ ø).

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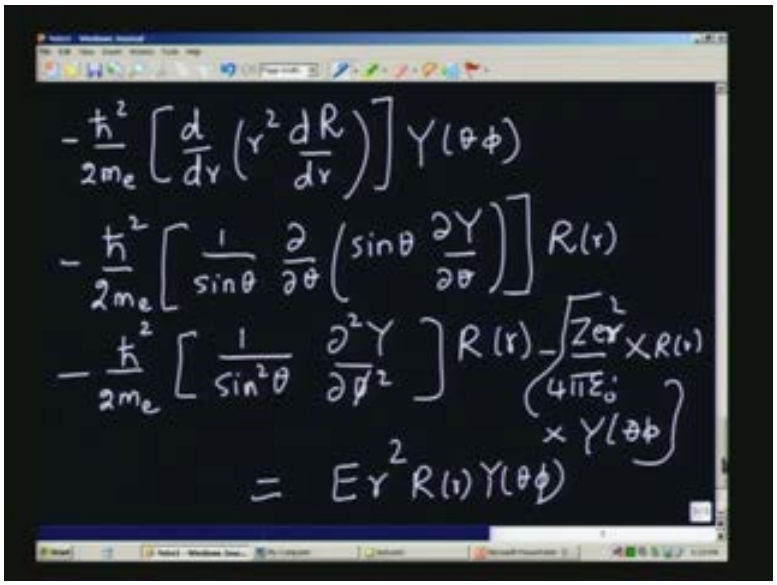

Now given this form you can see this in full screen that if you divide the whole equation by this R(r) Y(θ ø), let us divide the whole equation by that and what you will see is this Y will go away and there will be a 1/R here because you see this is dR/dr this is an operator you have to divide 1/R in first term and you will have a 1/Y here in θ part and you will have a 1/Y here in ø part, let us write that down. (Refer Slide Time: 17:51 min).

So, divide the above equation by R(r) Y(θ ø). So when you do that it is $-\hbar^2/2m_e 1/R[d/d\ r\ (r^2\ dR/dr)]$ and let me bring the other r dependent terms here namely $-Ze^2r/4\pi\varepsilon_0$ that is no factor here and then there is one more which was the energy term on the right hand side which if you have to bring it on this side it is $-Er^2$. So it is $\{-\hbar^2/2m_e 1/R[d/d\ r\ (r^2\ dR/dr)] - Ze^2r/4\pi\varepsilon_0 - Er^2\}$. All of these depend only on r and the leftover terms are $\{-\hbar^2/2m_e Y\ [1/(\sin\theta)\ \partial/\partial\theta(\sin\theta\ \partial Y/\partial\theta)]\}$, Of course there is a Y in the denominator when we divide the whole thing by R and Y.

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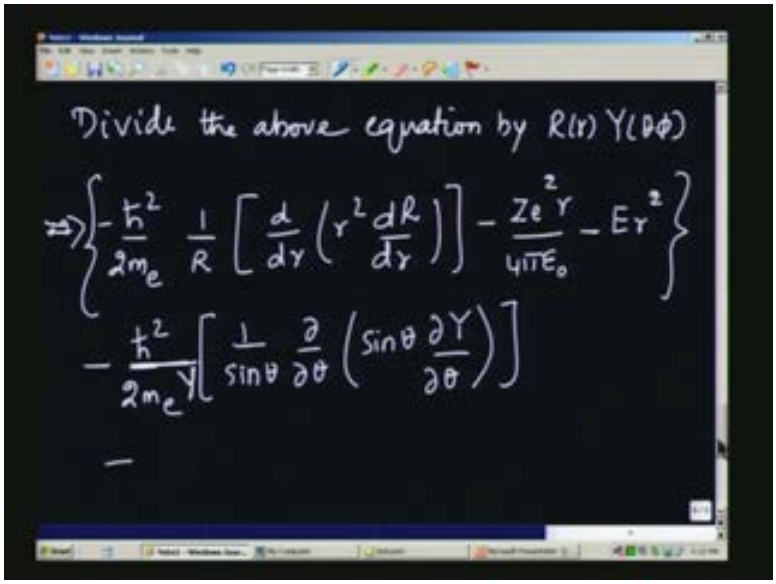

And then there is one more term which is $-\hbar^2/(2m_e Y)[1/\sin^2\theta\ (\partial^2 Y/\partial ø^2)]$. The whole thing is equal to zero as we brought the E on this side already. So, now you have an equation which if you look at it carefully as a term which depends only on the r and has two terms which depend only on θ and ø.

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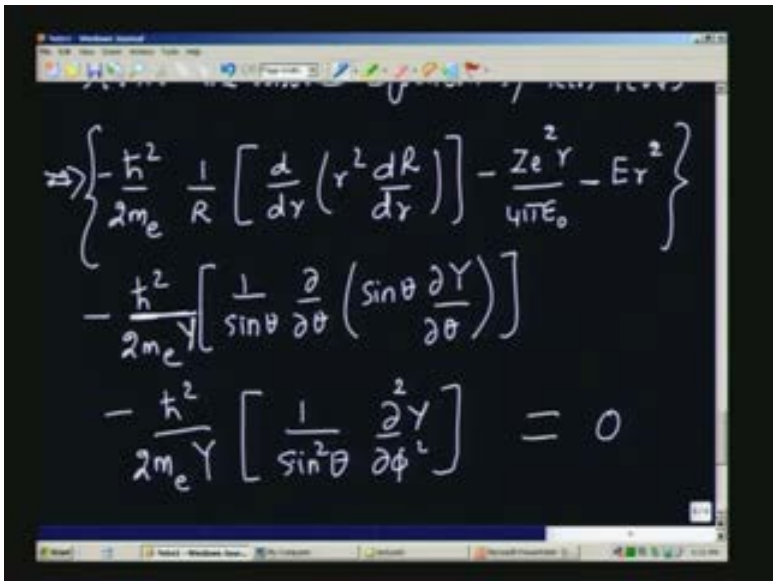

And remember that r, θ, ø are independent coordinates. Therefore you see that this equation has separated the terms according to r dependent terms only and θ, ø dependent terms only. Therefore if you write this as something like a quantity which depends only on a function of r and another which is a function of θ and ø if you do this symbolically is equals to 0 and this is valid for all values of r and all values of θ and ø which is in the hydrogen atom case r goes from 0 to ∞, θ goes from 0 to π and ø goes from 0 to 2π. (Refer Slide Time: 20:40 min)

If it is true then the only possibility for this equation to be solved consistently is that this whole thing is equal to a constant and the other whole thing is equal to a negative of the constant so that the constants $\beta - \beta = 0$. So now you see what is meant by the separation of variables in the case of the hydrogen atom when you express the kinetic energy in a rather complicated form using the r, θ, ø coordinates which was not there and if you were to write this using the (x, y, z) coordinates system. It is not over yet we have only separated r and θ and ø. Now we can do further by writing the θ, ø equation and trying to separate this into a function which depends only on θ and a function depends only on ø.

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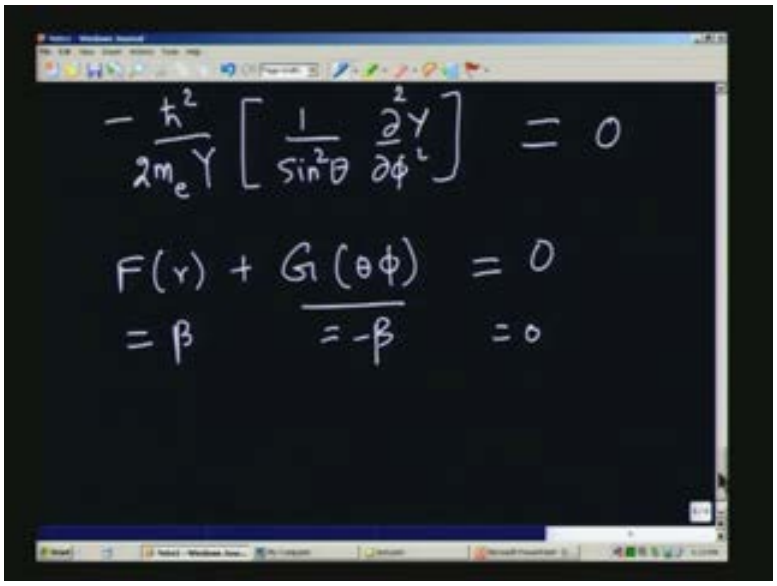

Let us keep in my mind that we call this whole θ dependent quantity as equal to –β, so let us write the (θ ø) equation. So (θ ø) equation is $-\hbar^2/2m_e Y$ [**1/(**sinθ) ∂/∂θ(sinθ ∂Y/∂θ)], this is the first term of the (θ ø) equation and then you have $-\hbar^2/(2m_e Y)[1/\sin^2\theta\ (\partial^2 Y/\partial ø^2)]$ and these are equal to –β that is what we set this equal to a function G(θ ø) = –β. So the total equation we can write as $\{-\hbar^2/(2m_e Y)$ [**1/(**sinθ) ∂/∂θ(sinθ ∂Y/∂θ)]} $-\{\hbar^2/(2m_e Y)[1/\sin^2\theta\ (\partial^2 Y/\partial ø^2)]\}$ = –β. Now, if we have Y(θ ø) expressed in the same way as we did earlier namely write as a function of θ only and a function of ø only.

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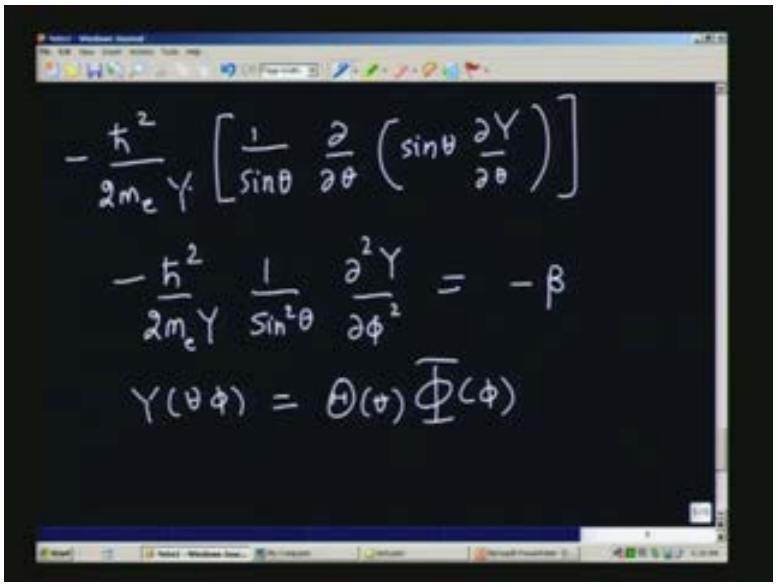

Then this equation can be separated further into two equations one dependent on θ and one dependent on ø. Then the separation of the three dimensional (r θ ø) problem of the hydrogen atom into three one dimensional problems each of which depends only on one coordinates is complete. And afterwards of course you have to think about solving such equation. Fortunately there are methods that Physicist found out and they knew earlier and those methods could be applied directly here. Let us just do the separation on the θ and ø.

So, if you substitute again you have to do the same thing you substitute and then you divide by θ and ø basically both sides. Substitute, divide by Θ(θ) and Φ(ø) so what you get is $-\hbar^2/2m_e$ and you will get a Θ(θ) in the denominator and you will get $[^1/\sin\theta\ \partial/\partial\theta(\sin\theta\ \partial\Theta/\partial\theta)]$. So this is $\{-\hbar^2/(2m_e\Theta)\ [^1/\sin\theta\ \partial/\partial\theta(\sin\theta\ \partial\Theta/\partial\theta)]\}$. This is the first term and the next term will be $-\{\hbar^2/(2m_e\Phi)[^1/\sin^2\theta\ (\partial^2\Phi/\partial ø^2)]\}$ and these two are equal to –β. (Refer Slide Time: 25:03 min).

But then it is obvious from this equation that if you multiply this by $\sin^2\theta$ throughout, let us do that, we multiply this by $\sin^2\theta$ what we get is sinθ here instead of $^1/\sin\theta$ and what we get here is this $^1/\sin^2\theta$ goes away and what you get on the other side is $-\beta\sin^2\theta$. So now you see that this is easily separated into a θ dependent term only by clubbing these two together this first term and $-\beta\sin^2\theta$ as a function which depends only on θ and then a function which depends only on ø. And then you have the same thing that $G_1(\theta) + G_2(ø) = 0$. Therefore this $G_1(\theta)$ is equal to a constant and the other $G_2(ø)$ is equal to the negative of that constant.

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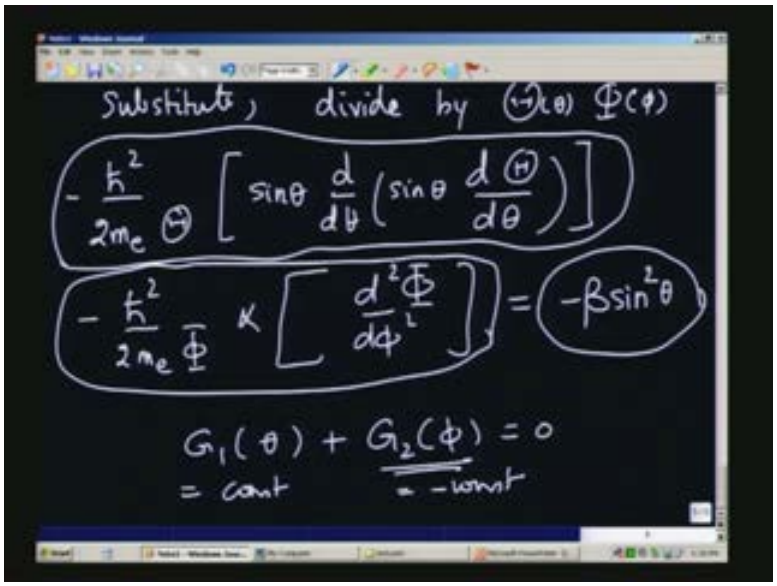

So then the three equations are completely separated. What is the result? Let us go and take a look at those equations in the slide here.

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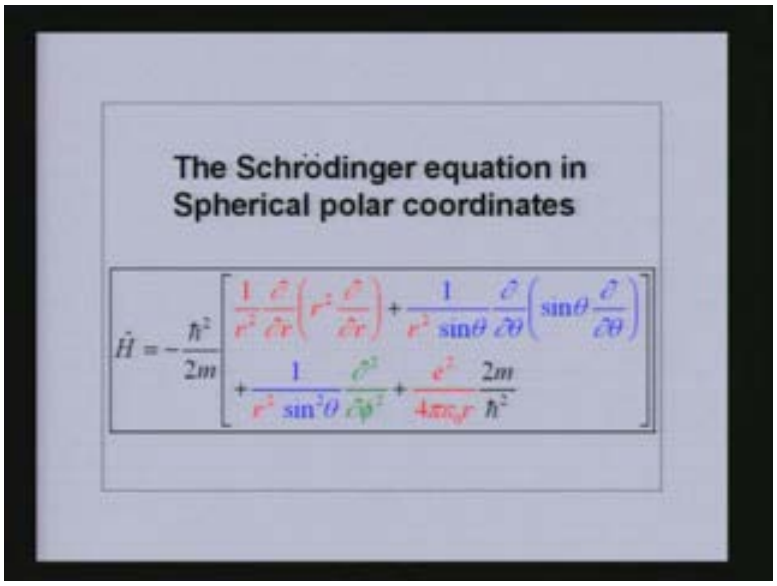

So this is the same equation that I have written down with a $-\hbar^2/2m$ the mass of the electron and here the e subscript is not here but you can add that. And this equation is something you have seen already.

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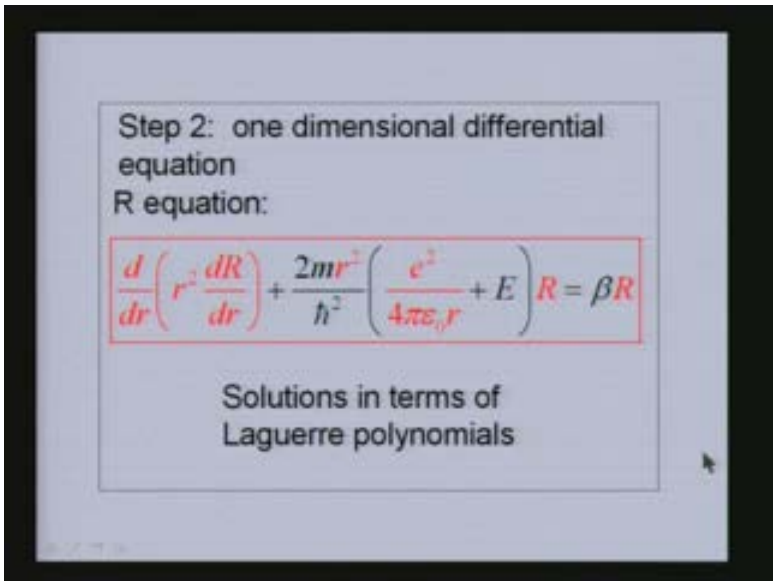

And the r part that I have written down of course the constant β here you must have a minus sign but it does not matter we will call this as a new constant β so the radial part is the $-\hbar^2/2m_e$ has been some sort of multiplied out here and this β contains that with some sign changes so the β that you have here can be associated with this term that you multiply with $-2m_e\beta/\hbar^2$ then this is the constant present in the slide.

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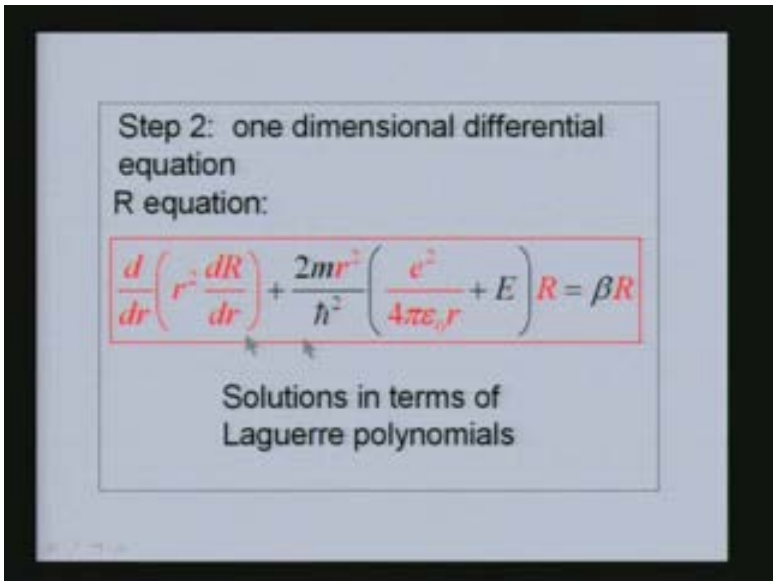

The point is that this is a solution for the radial coordinate. And later on we will learn that the solutions are given in terms of the orthogonal polynomials known as the Laguerre polynomials.

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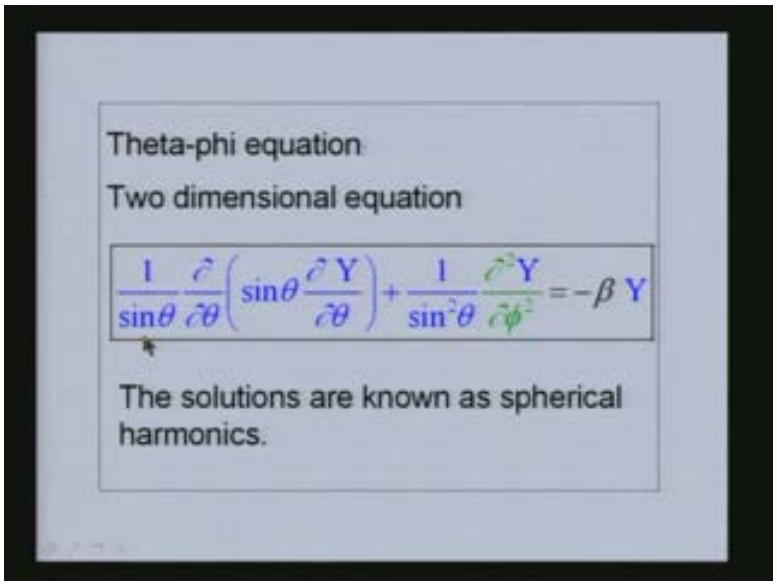

Likewise the θ equation $^{1}/\sin\theta\ \partial/\partial\theta(\sin\theta\ \partial Y/\partial\theta)$ and the separation of this when we did that we got this into two independent equations but the solutions Y which contains both θ in blue and ø in green these are two variables to show you Y depends on both of them. This solution Y is known as spherical harmonics in the Mathematics that we deal with. (Refer Slide Time: 28:15 min).

Let us now look at the radial functions. The radial equation contains a constant called the β, this constant is related to the θ equation and the constant also appears in the θ equation. If you look at the solution for the θø equation it can be obtained analytically, here this equation has the θ part or the ø part and together the sum of this is equal to 0. This can be obtained analytically if this β has the special form namely a number integer l(l+1) where l can have values 0, 1, 2, 3 etc integers only.

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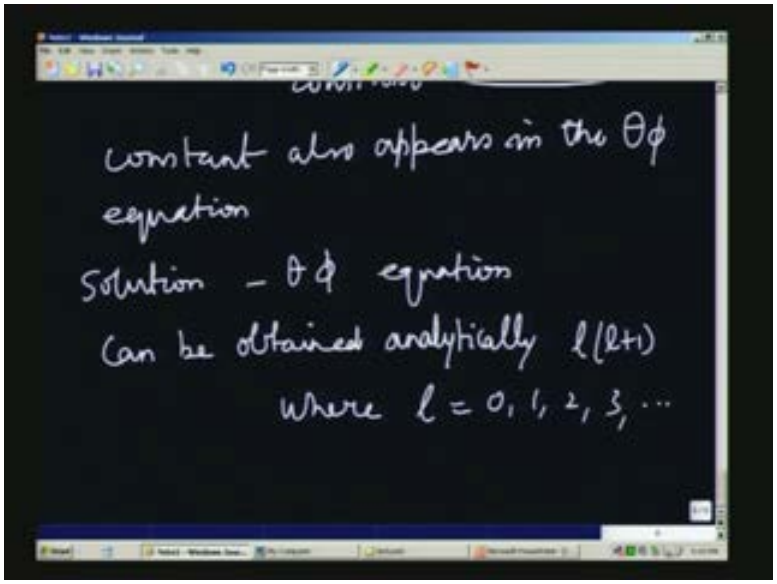

This l has a result of the solution of the θø equation also controls the radial functions because the l appears in the radial equation here. Therefore the radial functions depend on two quantum numbers; one that comes with the l from the θø equation and one with the radial equation itself. (Refer Slide Time: 30:29 min).

Radial equation comes out with a quantum number requirement n which is 1, 2, 3 etc and l which is 0, 1, 2, 3 etc. But since the l is part of the radial equation coming from the θø so l cannot be arbitrary but for any n the l has to have the value 0, 1, 2 etc up to n – 1 only for satisfactory solution of the problem, solutions ψ in terms of the radial functions and the angular function.

This is part of the Mathematics and our purpose is that up to this point we can understand the Mathematics of separation.

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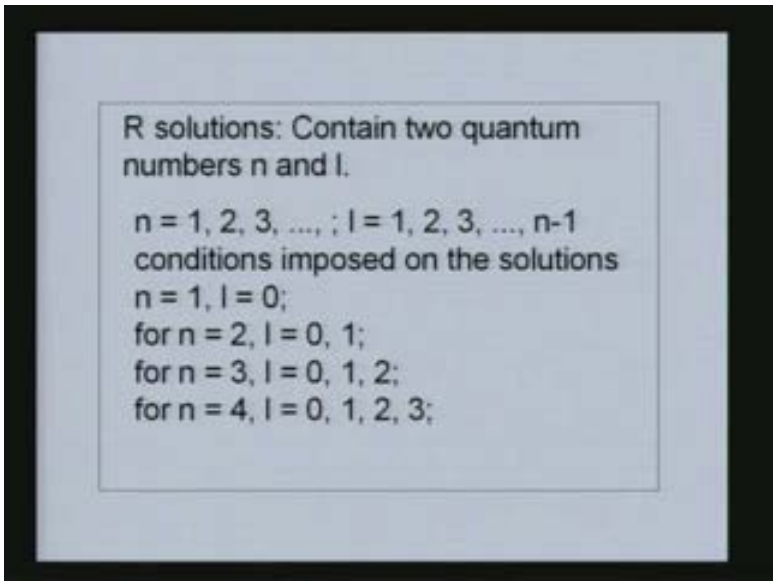

The solutions are, the radial solutions contain two quantum numbers n and l. The values of n can be integers there is no n = 0 it starts with 1, 2, 3 etc where I is bounded by the requirement of the n namely up to n – 1. Here l should be 0 which is also allowed. So n = 1then the only solution is l = 0. If n = 2 the quantum number l can have two values 0 and 1 and for n = 3 the quantum numbers can be anyone of the three 0, 1, 2 and so on.

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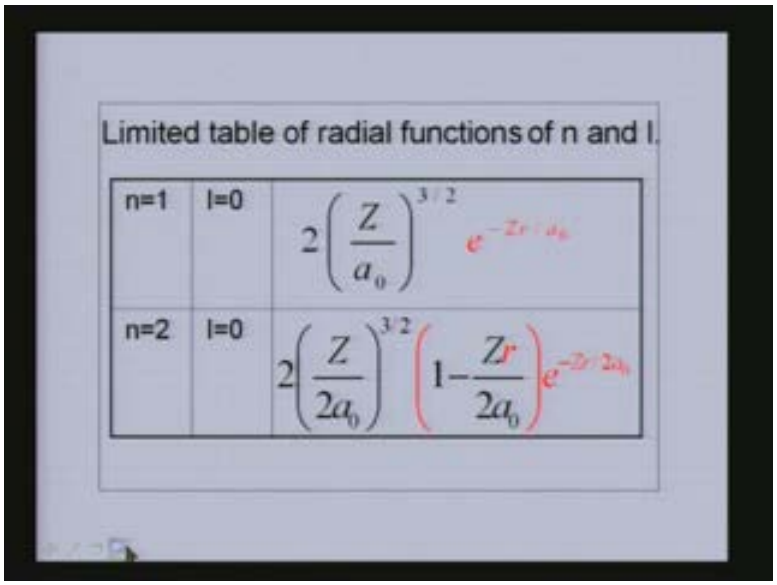

What are the radial solutions? Let us look at the radial solutions by the actual functional form obtained by solving the radial equation. The radial solutions contain two parts; one which is exponential namely $\exp(-r/na_0)$ where a_0 is the Bohr radius. You can look for the expression for

the Bohr radius in terms of the constants that we have given namely the ħ, the mass of the electron, the charge and things like that so this whole thing comes out from the constants in the Hamiltonian.

But the thing is the exponential now has the arguments which are dimensionless that is r/a_0 where a_0 being a radius itself of a constant radius 0.53 A°, want to know what it is and the quantum number n is 1, 2, 3 etc. There is one part to the radial function and the other part is the part of what is known as the Laguerre polynomials. (Refer Slide Time: 34:14 min)

The harmonic oscillator solution also had two parts, a Gaussian function an $\exp(-x^2)$. And there was a function called Hermite polynomial which keeps changing or it actually is a polynomial with increasing powers of x as we increase the quantum number n = 1, 2, 3 etc. The same way here the Laguerre polynomials are also polynomials of certain power and the exponential is such that the whole wave function eventually vanishes when r becomes very large.

The boundary conditions are important in all the problems we solve in Quantum Mechanics. The boundary condition in this particular case tells you that the wave function must vanish at the boundary, but where is the boundary? The boundary is $r = \infty$. So the wave function must go to 0 at $r = \infty$, nothing better than an exponential function. In fact it comes out from the solution obtained that it is $\exp(-r/na_0)$. Recall if you have a function have $\exp(-r/a_0)$ and if you have a polynomial of r/a0 again you see which is essentially r/a0 to the n^{th} power being the leading term where n is 1, 2, 3 etc. So we can write it as $\exp(-r/a_0)$ $[f(-r/a_0)/(-r/a_0)^n]$.

Remember that eventually $\exp(-r/a_0)$ makes this full product vanish. Only one thing is that as n increases the value of r/a_0 for which the exponential starts dominating over the polynomial becomes farther and farther that is higher and higher. For small values of n the exponential drops off very quickly but for very large values of n the exponential does not dominate this whole product and the wave function stays big or increases for much larger values and then only it decreases.

But for any finite power of n the exponential eventually kills the wave function giving you the right boundary that the hydrogen atom wave function the radial part vanishes. Whatever be the angular part the angular parts are between theta and phi they do not go to infinity and they are bounded and therefore the overall wave function vanishes at the boundaries for a sphere of infinite radius irrespective of what the values of the θ and the ø coordinate. So the boundary condition is contained in the solution.

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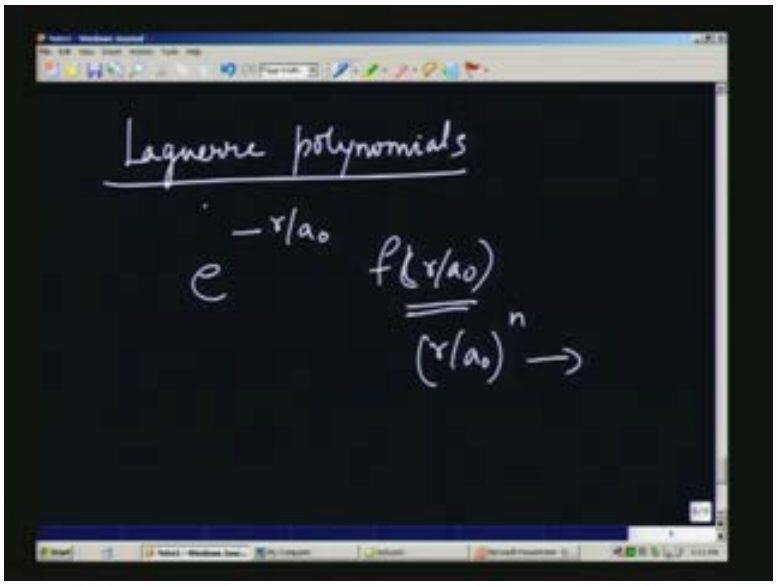

Let us try and understand what the solutions convey in meaning they contain the right boundary condition, is the first thing. The second part for n = 1 there is only one radial solution, for n = 2 there are two radial solutions namely corresponding to (n = 2 and l = 0) as one set and (n = 2 and l = 1) which is another set. And the successive cases as you increase n to 3, 4 and 5 etc the total number of solution is n corresponding l = 0, 1, 2, 3, 4 and up to n–1. So there are n solutions for any radial wave function with the principle quantum number n. The values of l of course are 0 to n–1 (Refer Slide Time: 38:30 min).

The other thing is, the radial and angular part also control the other ø part. the ø equation will introduce its own quantum number in the solution of the ø part but that quantum number m will be limited by the n and l such that if n is 1, 2, 3 etc and if l is 0, 1, 2, 3 etc.

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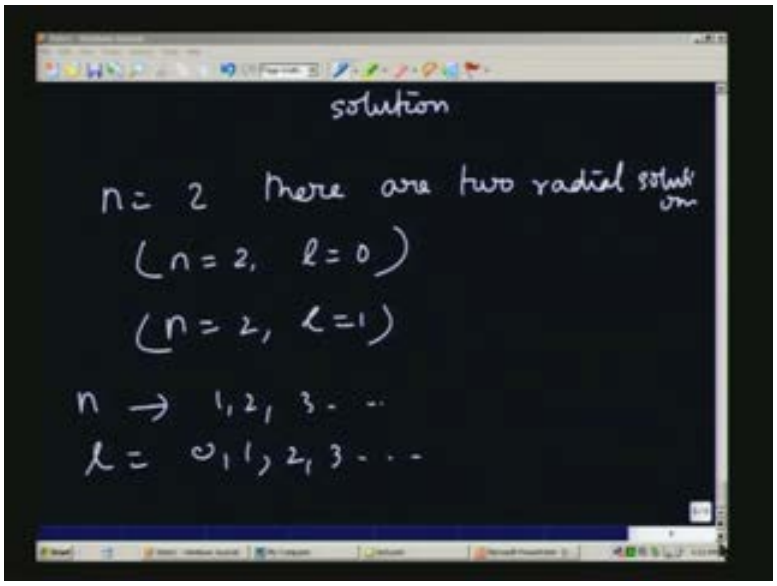

The ø part contains a quantum number m which goes from 0, ±1, ±2 up to l for any value of n. So this is the hierarchy of the quantum numbers in the case of hydrogen atom. Go back and look at the ø equation if you are doubtful. Here is the ø part, you see that θø part contain the sinθ and $\beta\sin^2\theta$ all these things are the θ part and then there is a ø part. So this whole equation on the θ part of it if you said it is equal to a constant then this is said to be equal to the negative of the constant with that the sum of these two is equal to 0.

Therefore the ø has a certain constant associated with that and the ø equation ultimately can be written as basically $-\hbar^2/2m_e\ (\partial^2\Phi/\partial ø^2) - k^2\Phi = 0$. Such equations are known to have a very simple equation. Let me write this in the form of a slightly simpler quantity in the form of $(k')^2$ then $(\partial^2\Phi/\partial ø^2) + (k')^2\Phi = 0$ and this equation also has the boundary condition you remember Φ depends on the value ø and the value of ø is between 0 and 2π that is our spherical system.

Therefore any other value of ø for example 4π or 6π or anything greater than 2π should be represented for what you call as the single valued and continuous function the wave function ø part must satisfy (ø+2nπ) where n can be 0, ±1, ±2 etc.

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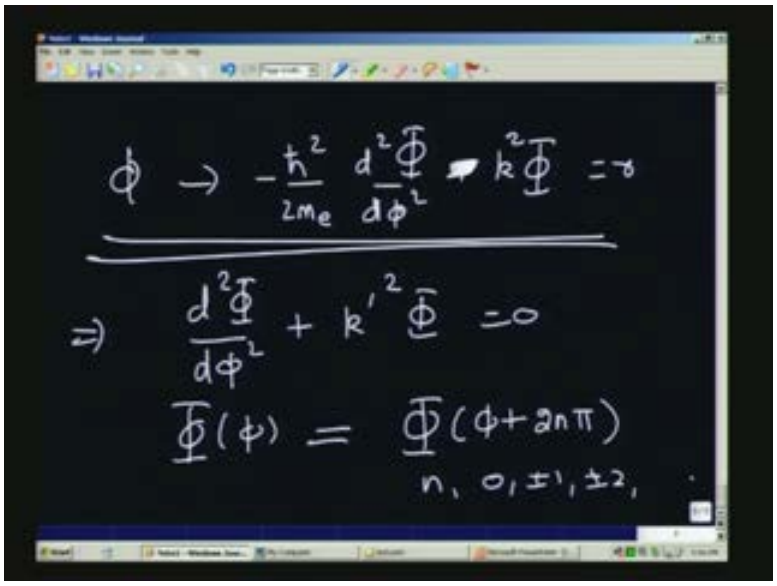

Therefore this introduces a quantum number for the ø part m just written down here as 0, ±1, ±2 etc up to l.

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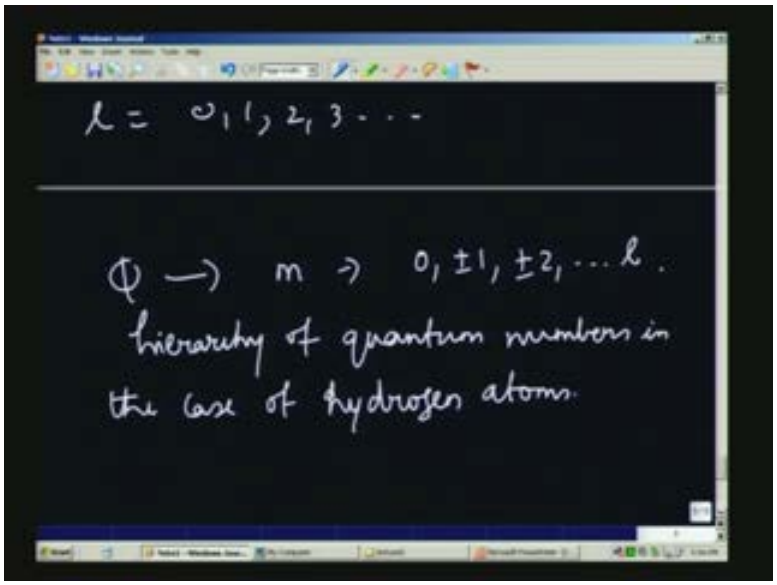

So, given hierarchy of all the equations and the results now let me look at the radial part first then we will look at the angular part and then we will go to the angular part with the ø part.

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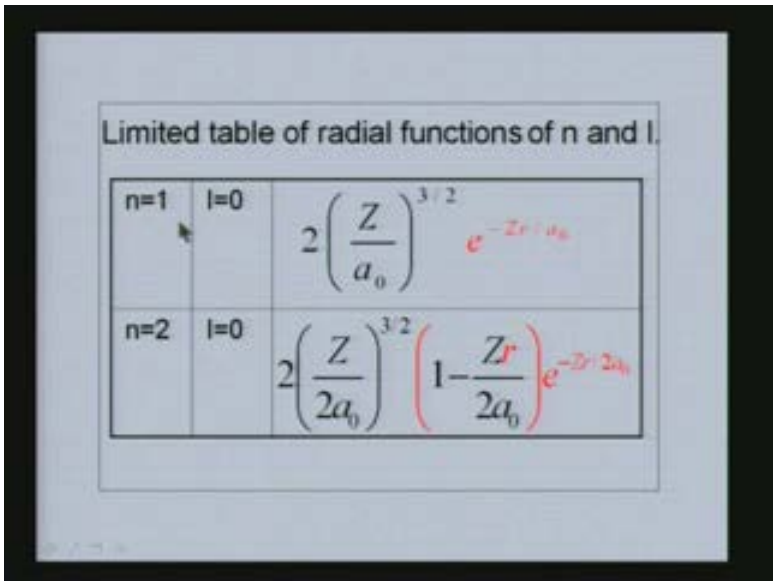

The radial solution $2(Z/a_0)^{3/2} \exp(-Zr/a_0)$ for n = 1 and l = 0 has of course the charge and the a_0 the Bohr radius a_0 and here $(Z/a_0)^{3/2}$ is a normalization constant which makes the wave function $\psi^*\psi\, d\tau$ integral into unity. But the wave function is $\exp(-Zr/a_0)$ where z which is a nuclear charge and the n = 1 here is r/na_0 is the general form for the exponential equation.

For n = 2 there are two solutions l = 0 and l = 1. Let us look at the l = 0 case, the l = 0 case has an $\exp(-Zr/2a_0)$ the n appears here. And it has a simple function $(1 - Zr/2a_0)$ so this is a monomer that is a function to the $r^{th\ 1}$.

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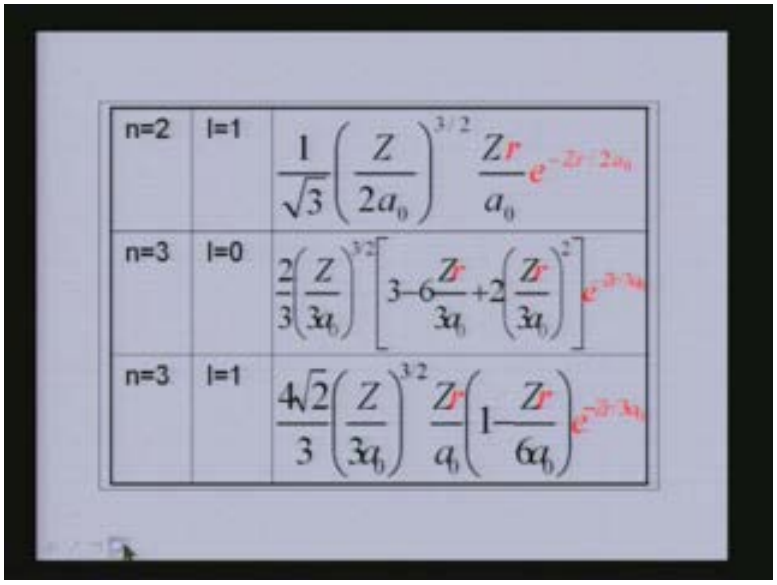

The other one n = 2, l = 1 is also $(Zr/a_0)\exp(-Zr/2a_0)$. But the point is, this function is 0 at r = 0 and it never goes to 0 for any value of r other than r =∞. This one on other hand n = 2, l = 0 which contains $(1 - Zr/2a_0)\exp(-Zr/2a_0)$ does not go to 0 at r = 0 in fact at r = 0 it is simply this constant this exponential is 1 so this is simply 1 but it does go to 0 when $r = 2a_0/Z$, where Z is charged therefore when $r = 2a_0$ this function goes to 0.

Therefore it has a radial node at an intermediate value. The radial node is there for the function l = 0 n = 2 is not there for the function l = 1, n = 2. (Refer Slide Time: 44:40 min)

What about the n = 3? You see that the pattern of the Laguerre polynomials and the exponential is such that the exponential is $\exp(-r/3a_0)$for n = 3, l = 0 you have that for n = 3, l = 1 you have that again.

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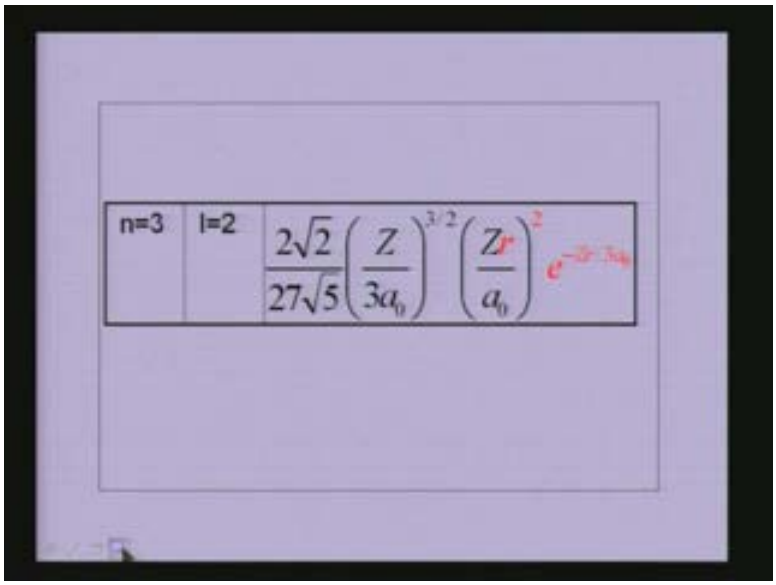

And for n = 3, l = 2 you have that again $Zr/3a_0$ but looking back from this side you see that the l = 2 contains an r^2 which goes to 0 at r = 0 but never anywhere else other than infinity. (Refer Slide Time: 45:20 min).

So n = 3, l = 1 and if you look at this it does go to 0 at r = 0, r =∞ and also one r in between them where this particular function $1 - Zr/6a_0$ is 0. Therefore this has one radial node for l = 1. (Refer Slide Time: 45:37 min).

The function for the n = 3, l = 0 is a quadratic function multiplying an exponential which does not go to 0 at r = 0 but it goes to 0 in two other places in between and then of course that r =∞. So this function has two radial nodes corresponding to the two roots of this quadratic equation. So the pattern now should be clear, immediately what it is for n = 4 for example. (Refer Slide Time: 45:10 min).

For n = 4 and l is maximum 3 you must have a term something like $r^3 \exp(-Zr/4a_0)$ here this n is always the principle quantum number associated with that. For l = 2, n = 4 you will have a function r and an equation something like $r^2(r/a_0 - c)\exp(-Zr/4a_0)$ that is it will have one radial node.

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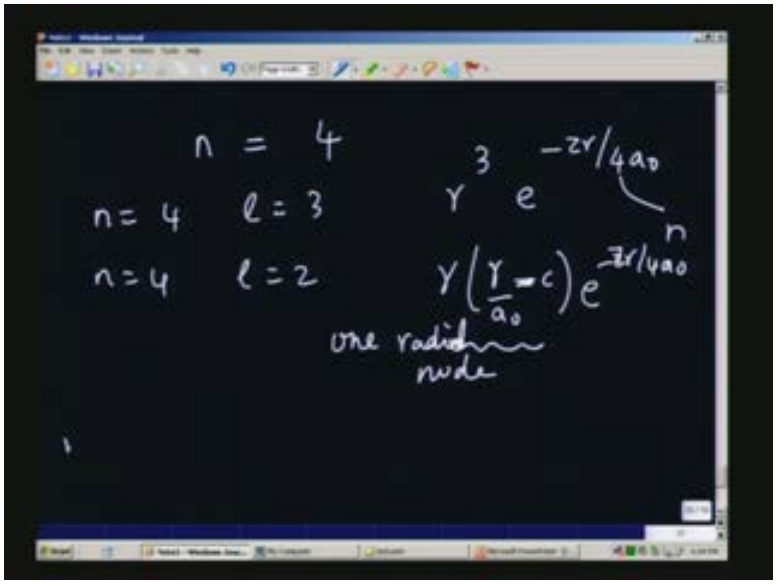

For n = 4, l = 1 you will have when you do the Mathematics and expand the Laguerre polynomials rightly it is r (quadratic in r)$\exp(-Zr/4a_0)$ has two radial nodes.

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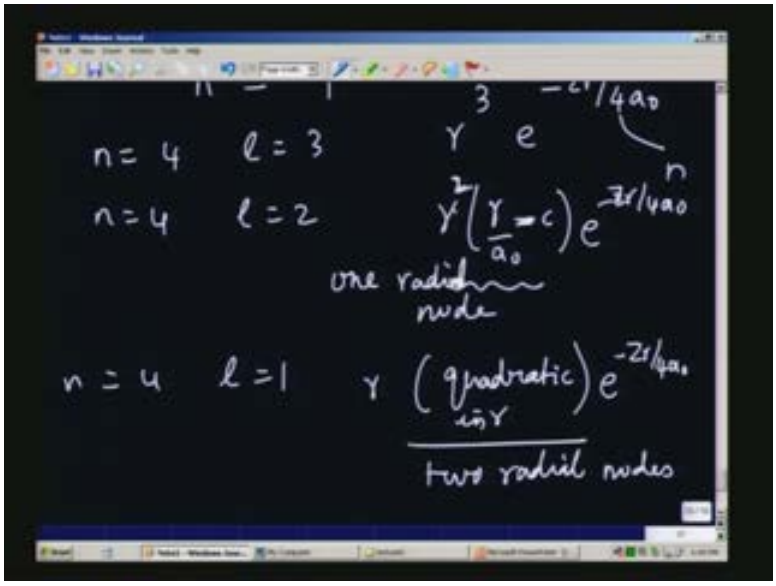

And for n = 4, l = 0 you have a (cubic in r) exp(–Zr/4a_0) and this has 3 radial nodes but this function is not equal to zero at r = 0.

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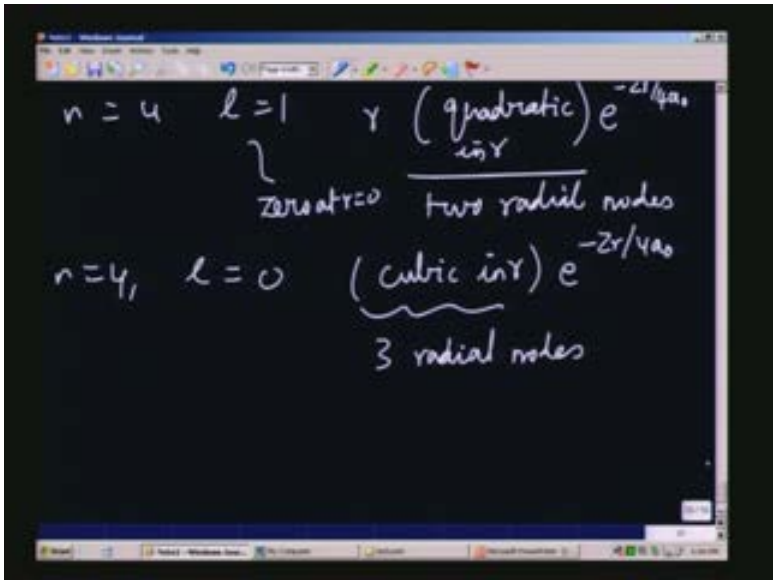

l = 2 is 0 at r = 0, l = 3 is also 0 at r = 0 and of course all of these go to 0 at r = ∞. So you have the number of radial nodes which you can immediately see for these functions the number of radial nodes other than 0 if it is applicable of course you see it does not exist for the l = 0 case and other than 0 and infinity, it is not a node because it is just where the function goes to 0 forever. And what you have is (n – l – 1) this is the number of radial nodes that you have. So when you have a function with l = 0 quantum number you have the maximum number of radial nodes corresponding to the l value maximum. In n – 1 if n is 4 and l is 0 it is three radial nodes. If n is 4 and l is 2 then one radial node and so on. So the pattern of these functions should be recognized. If we are unable to solve this equation using simple Mathematics we must understand how these functions were derived or how do they behave for different choices and recognize the pattern from them. Now, it is easier if we recognize this using a graphical representation of the same thing.

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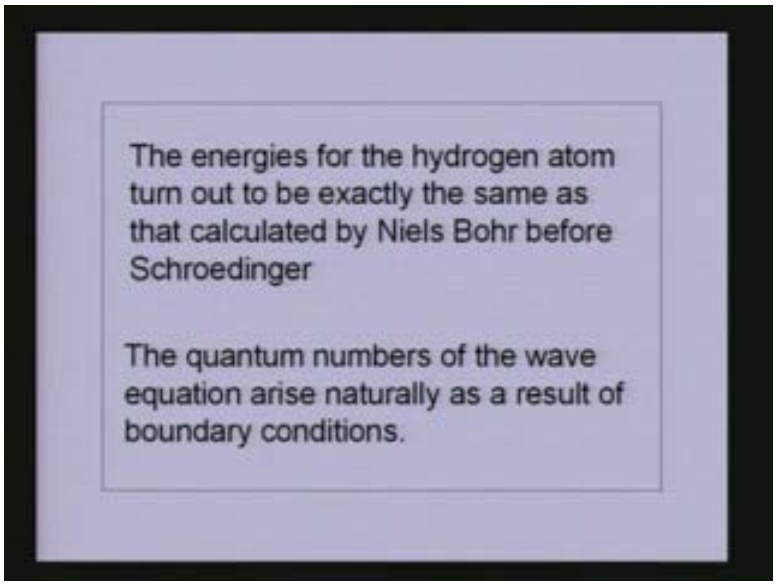

Before I do the graphical representation I would also want to point this namely the energies for the hydrogen atom i.e. E that you calculate which is a part of the radial equation. You remember that the $H\psi = E\psi$ that E got associated with the radial equation and not with the angular equation. The energy E turns out to be exactly the same expression as what Neils Bohr calculated using his ADHOC approximate or the method with the approximation that the angular momentum is quantized or the energies 1/n square form.

The quantum number of course in this particular case arises naturally by assuming that the wave function the Schrödinger equation is correct. The arbitrariness here is that we do not understand why the Schrödinger equation is correct. But if we understand that or we accept that it is correct then the rest of the solutions are naturally applicable and are derived from rigorous Mathematics.

This means that we are replacing the hypothesis of Bohr by the hypothesis that the Schrödinger equation itself is valid. but unlike that of the Bohr hypothesis the Schrödinger equation is found to be working for all atoms not just hydrogen atoms and the electrons in the hydrogen atom according to the Schrödinger equation is described by three quantum numbers and three only. This is a non relativistic Schrödinger equation and the three quantum numbers are n, l and the m and we are concentrating only on the n and l.

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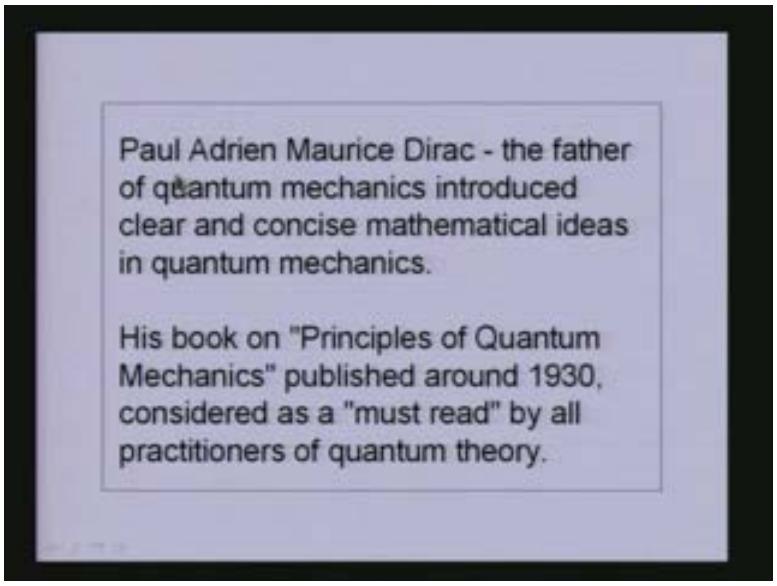

I would in passing make a remark which is very important in recognizing the fundamental contributions of Paul Adrien Maurice Dirac the English Physicist, the father of quantum mechanics introduced clear and concise mathematical ideas in quantum mechanics. He also generalized the Schrödinger equation to the relativistic motion of electron and derived the spin quantum as the 4^{th} quantum number through his formalism for which he eventually shared the Nobel Prize in 1933.

His book of course is one of the best known and probably the most Mathematical rigorous book on the principles of Quantum Mechanics. Dirac's book is still a classic book. Let us just quickly look at the plots of the radial function namely the $\exp(-Zr/a_0)$ in this case how does it look for the radial n =1 and the l = 0 in this case.

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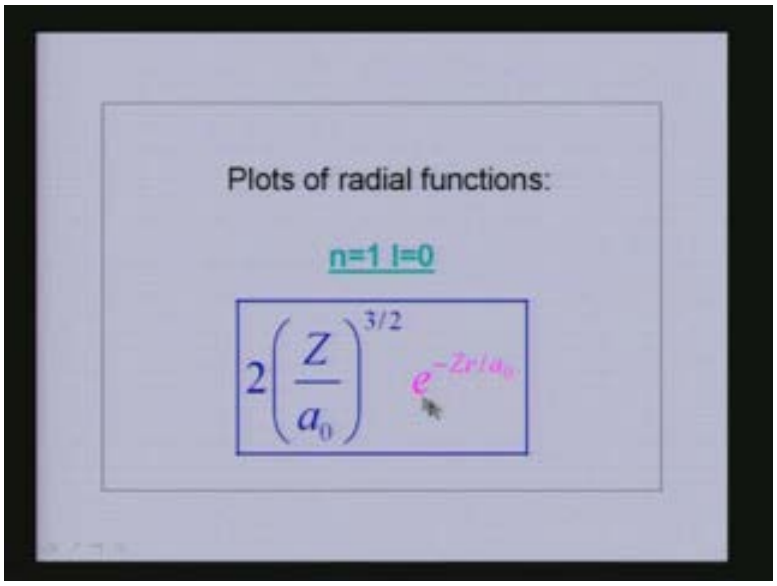

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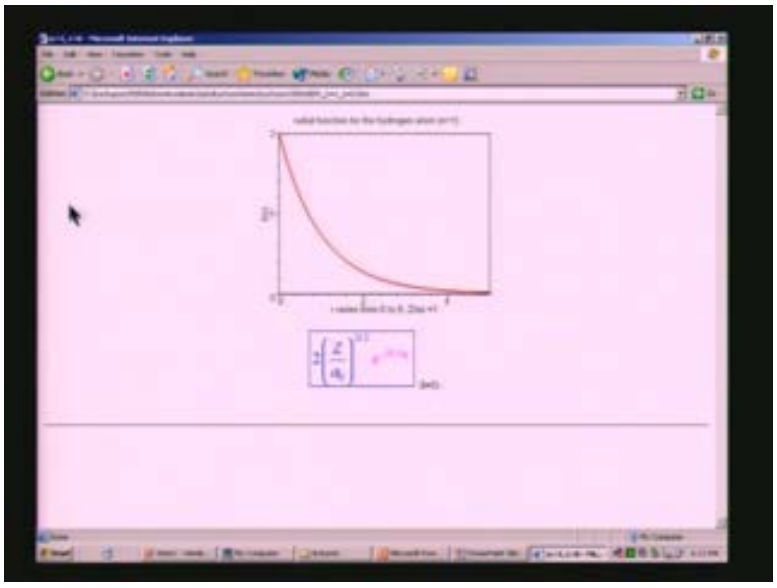

The radial part if I plot this as a function of r you see it is a straight forward exponential. There is nothing and as r/a_0 goes to something like 5 or 6 this wave function goes to 0.

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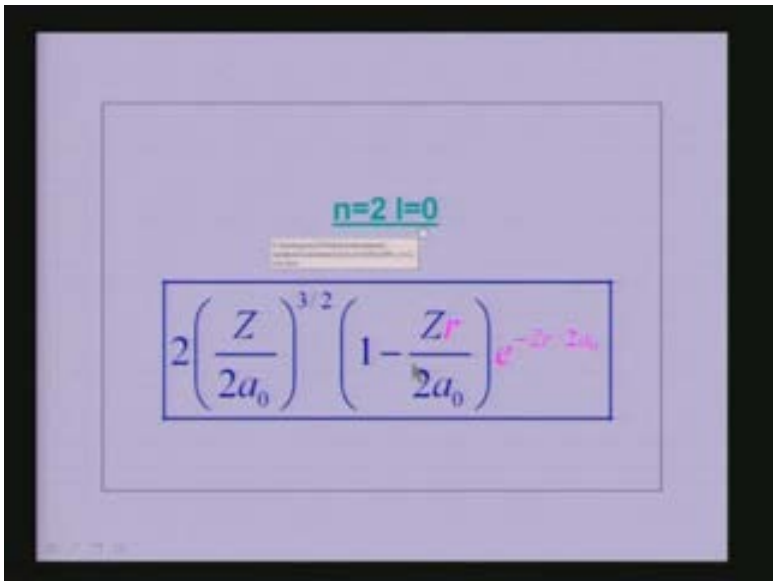

The next one is n = 2, l = 0 and the radial function is $(1–Zr/2a_0)\exp(–Zr/2a_0)$. Now as you increase from r = 0 to higher values you see this function becomes smaller but this function is not 0 it goes to 0 at $r = 2a_0$ and then it is negative for all values of r greater than $r = 2a_0$ it is negative.

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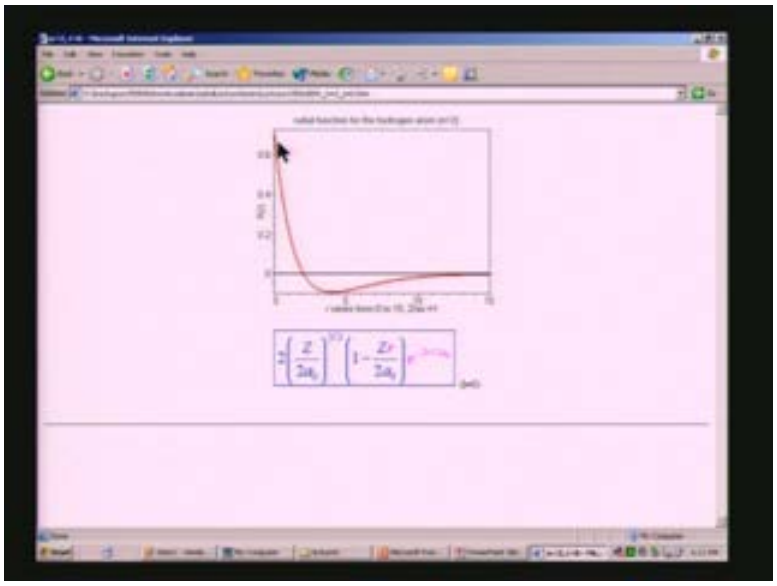

It goes down to 0 from a maximum to $r = 2a_0$ and then of course it stays negative it keeps increasing but the point is the $\exp(–Zr/2a_0)$ will eventually reduce it to 0, bring it to 0. Therefore this function has the radial node at this point r = 0.

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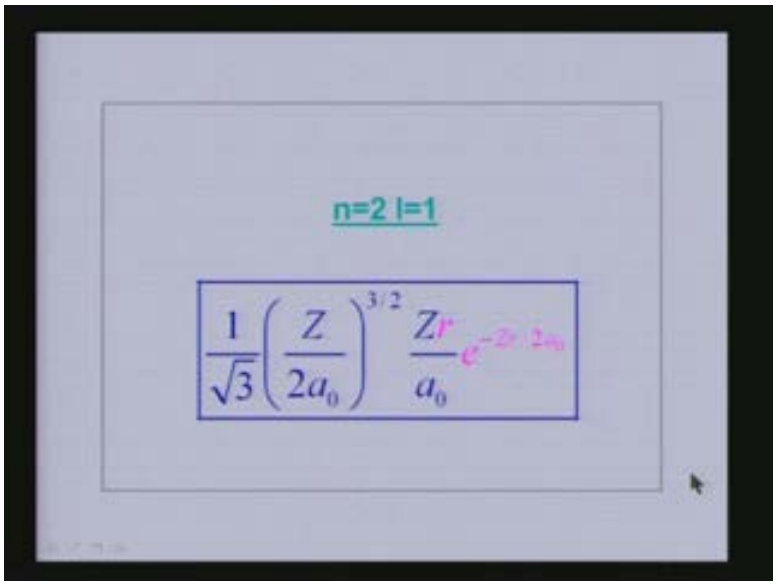

Here n = 2, l = 1 is simply r times exp(–Zr/2a_0), it starts from 0 increases as r increases but this eventually tapers of the function so what you have is starting from 0 and it goes from 0 to a maximum value and then it goes back to 0 as r increases, this is the radial function for n = 2, l = 1.

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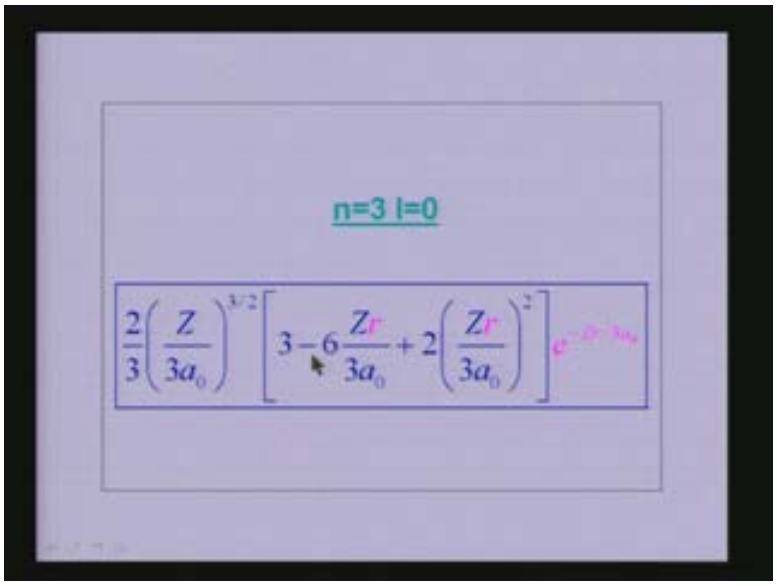

And then n = 3, l = 0 is a quadratic exp(–Zr/3a_0) if you plot this then this quadratic has two roots so the first root and the second root are such that the function is negative between the first and the second roots. The function can be written for n = 3 and l = 0 as a function (r – a_1)(r – a_2) exp(–Zr/3a_0) where these are the roots to the quadratic. And if we assume that the $a_1 < a_2$ and if

this is the radial function R(r) you see that the radial function is when r is less than a_1 and a_2 from 0 to a_1 this $(r - a_1)$ function is positive between the a_1 and a_2 this $(r - a_2)$ function is negative and at a_2 this function is 0 and when r is greater that a_2 this function keeps on increasing as r^2. But eventually the exponential goes down and this function goes to 0. (Refer Slide Time: 55:41 min)

Therefore what you have is you have a positive part, a negative part and then a positive part. n = 3, l = 0 it starts from a non zero value goes to 0 at a_1 increases but then decreases at a_2 it becomes 0 but it keeps on increasing at r^2 but the exponential eventually decreases you can see that. So these are the two radial nodes for the quadratic function that you have here. And it is quiet clear that when you do this for n = 3, l = 1 you will have one radial node namely it starts from 0 increases up to a certain value and then this function eventually for a value of $r = 6a_0/Z$ this whole thing goes to 0 so you will have one radial node and then this function is negative and it goes back to 0 at infinite r.

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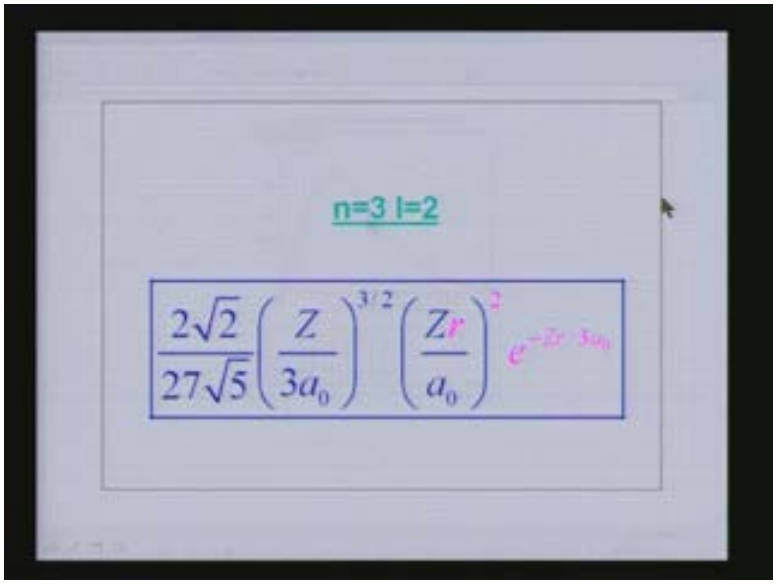

And the last one is n = 3, l = 2 is $r^2\exp(-Zr/3a_0)$, you see where the maxima occurs the maxima keeps on shifting because it is now r square and the function grows much more before it is killed by the $\exp(-Zr/3a_0)$,.

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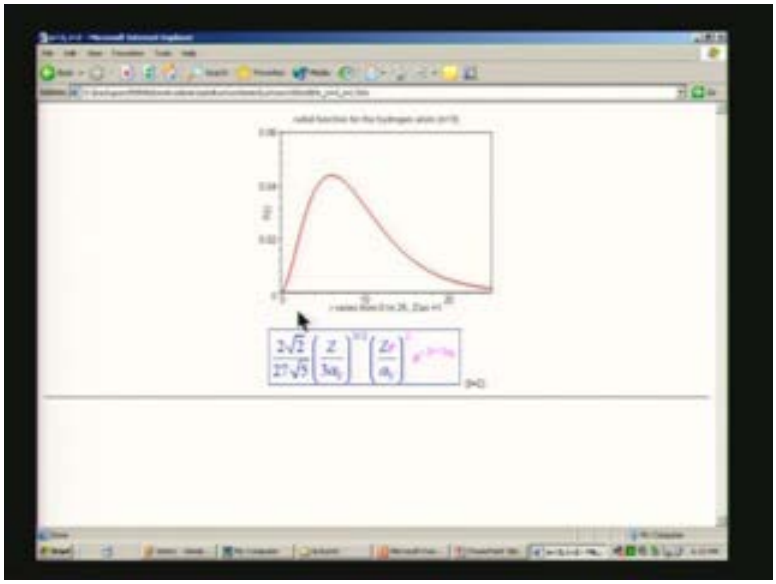

So you have no radial node for this but it is starts from 0. You can see this together,

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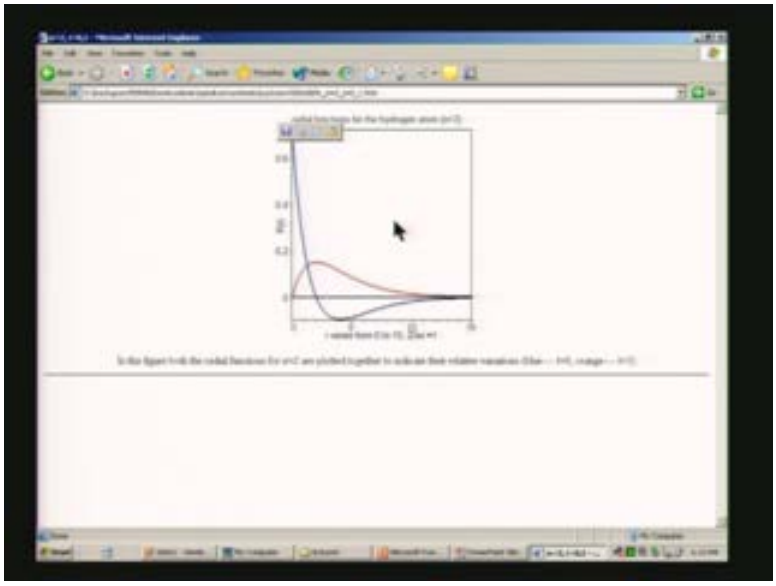

In the case of n = 2 you see the radial function for the l = 0 and l = 1 case together and likewise see the three together namely n = 3, l = 0, 1, 2 all three of them.

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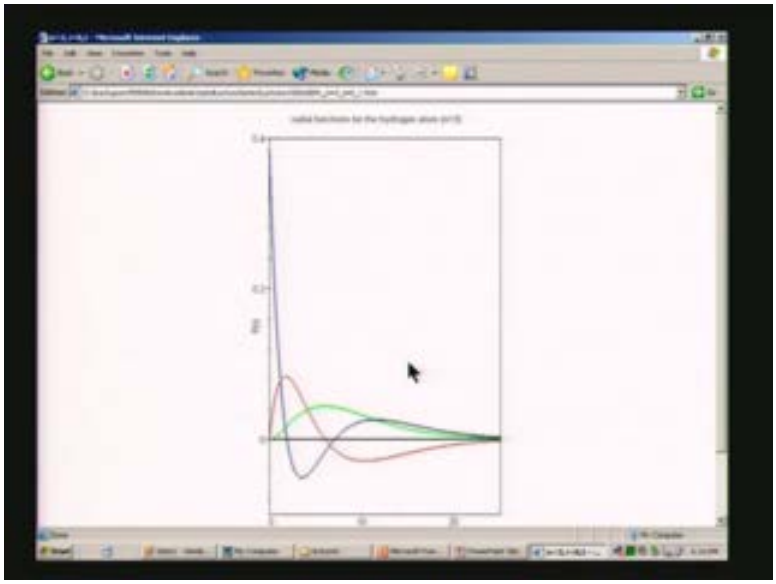

The 0 is the one that starts from non zero value at r = 0 and the rest of them are both from this value 0 and you see there is one radial node in this pink colored or whatever this pink colored function whereas the green color shows you that there is no radial node l = 2, this is l = 1 and this is l = 0. These are the radial functions that we have. Now the angular part we have not done yet, in the lecture we will continue this with the angular part.

The angular part now contains two quantum numbers l and m and the wave function for completeness let me write in this lecture before closing it. The wave ψ depends on three quantum numbers n, l and m and is written by the two quantum numbers $R_n^l(r)$ corresponding to 1, 0 all these things and the angular quantum numbers $Y_l^m(\theta\phi)$. This is the complete solution. The radial parts we have described today, the angular parts we will describe in the next lecture along with the pictorial representations for the real part the angular distribution and the angular wave functions. And these are the shapes that you normally see for the s orbitals, p orbitals, d orbitals etc.

With that we will sort of understand qualitatively why the Schrödinger equation hydrogen atom has the solutions that it has and how it could be obtained from the spherical polar representation of the Schrödinger equation Hamiltonian. And then we will move on to doing simple calculations by using these in order to understand a little bit globally the Mathematics associated with the hydrogen atom.

It is very important for Chemist and people who understand Chemistry or who require chemical understanding at a slightly higher level to see that the angular shapes and the radial shapes come from exact solutions to the Schrödinger equation to the hydrogen atom.