Introductory Quantum Mechanics and Spectroscopy

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Lecture 5: Part V
The Quantum Mechanics of Hydrogen Atom

Welcome back to the lectures. We will conclude the elementary part of the quantum mechanics of hydrogen atom with this part five where, I shall give a brief description of radial functions and radial distributions of the hydrogen atom.

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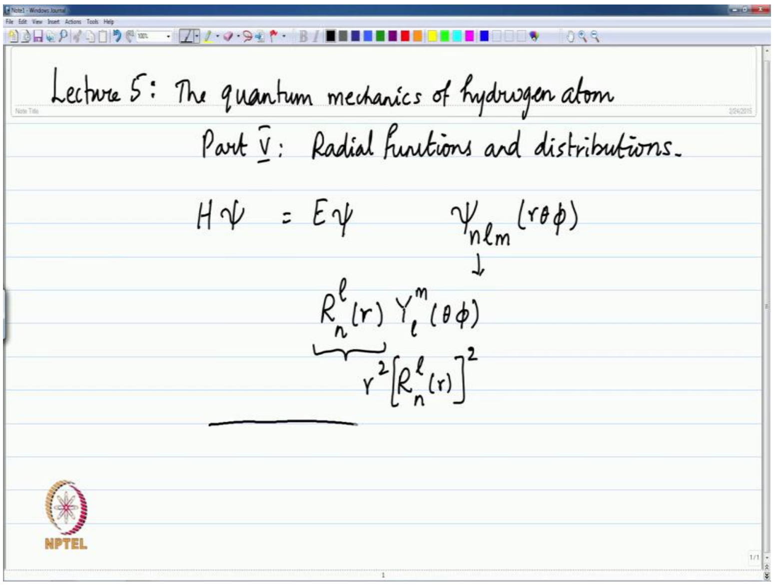

Lecture 5: The quantum mechanics of hydrogen atom

Part V: Radial functions and distributions.

$$H\psi = E\psi \qquad \psi_{n\ell m}(r\theta\phi)$$

$$\downarrow$$

$$\underbrace{R_n^{\ell}(r)}_{r^2\left[R_n^{\ell}(r)\right]^2} Y_{\ell}^{m}(\theta\phi)$$

Now, recall that the hydrogen atom wave functions for the Schrodinger equation, that is, the solutions have been earlier represented by psi with three quantum numbers n, l and m as the function of the three co-ordinates r, theta and phi. And, this was written as R n l of the radial co-ordinate r n y l m theta phi. This phi or phi, I seem to have mixing these two things but, remember phi or phi in the context both mean the same thing in this lecture. The radial function R n l r and the radial distribution that we will consider in this lecture namely, it is r square R n l of r square; are the probability distribution, the wave function component and the probability distribution for the radial part.

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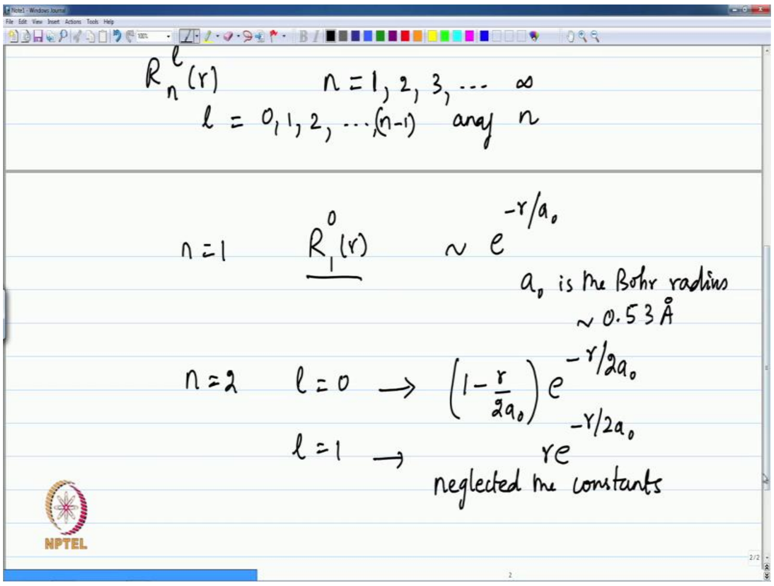

$R_n^l(r)$ $n = 1, 2, 3, \ldots \infty$

$l = 0, 1, 2, \ldots (n-1)$ any n

$n=1$ $\underline{R_1^0(r)}$ $\sim e^{-r/a_0}$

a_0 is the Bohr radius

~ 0.53 Å

$n=2$ $l=0 \rightarrow \left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$

$l=1 \rightarrow re^{-r/2a_0}$

neglected the constants

Now, we have not talked about the solutions of these earlier, other than briefly mentioning that, the radial functions have; with the quantum number n, l and r have the range for the quantum numbers as n equal to 1, 2, 3 all the way up to infinity. And, l is equal to 0, 1, 2 up to n minus 1 for any n. Therefore, when n is 1 we have the radial function, which is R 1 0 of r. And, the solution of the radial Schrodinger equation using the calculus of differential equations in the solution of differential equation gives us what are known as Laguerre polynomials and the exponentials. And, this particular function R 1 r is like exponential minus r by a naught; where a naught is the Bohr radius and 0 point 53 Armstrong. For n equal to 2, we have two solutions namely l equal to 0 and l equal to 1. And, the function for l equal to 0 is 1 minus r by 2 a naught times e to the minus r by 2 a naught. For l equal to 1, the radial function happens to be r times e to the minus r by 2 a naught. I have neglected the normalization constants of the pre factors; constants.

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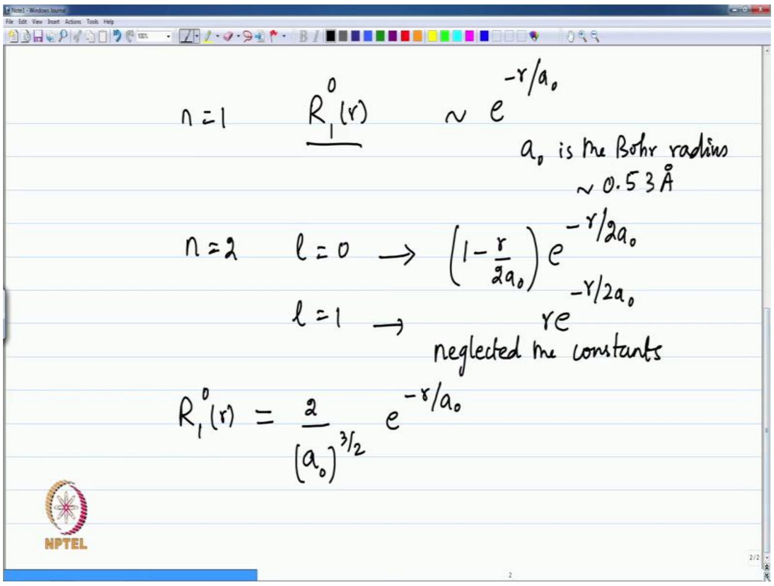

$n = 1$ $\quad \underline{R_1^0(r)} \quad \sim e^{-r/a_0}$

a_0 is the Bohr radius ~ 0.53 Å

$n = 2 \quad l = 0 \rightarrow \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$

$l = 1 \rightarrow re^{-r/2a_0}$

neglected the constants

$$R_1^0(r) = \frac{2}{(a_0)^{3/2}} e^{-r/a_0}$$

But if I do not; if I have to write this exactly, then R 1 0 of r is equal to 2 by a naught is to 3 by 2 e to the minus r by a naught.

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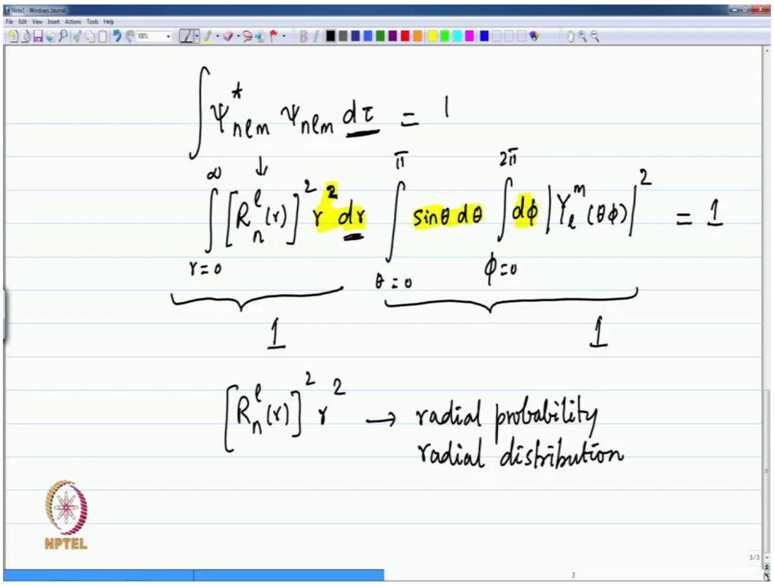

$$\int \psi^*_{nlm} \psi_{nlm} \, \underline{d\tau} = 1$$

$$\downarrow$$

$$\underbrace{\int_{r=0}^{\infty} [R_n^l(r)]^2 r^2 \, \underline{dr}}_{1} \; \underbrace{\int_{\theta=0}^{\pi} \sin\theta \, d\theta \int_{\phi=0}^{2\pi} d\phi \, |Y_l^m(\theta\phi)|^2}_{1} = 1$$

$[R_n^l(r)]^2 r^2 \rightarrow$ radial probability
radial distribution

This normalization constant is obtained by the following procedure namely the psi star n l m psi n l m d tau. The integral is equal to 1, which when we use of the spherical polar coordinates has the following form; r equal to 0 to infinity. The radial function n l of r square because this is real. And r squared d r, which is the radial path for the d tau, then you have theta is equal to 0 to pi sin theta d theta integral phi is equal to 0 to 2 pi d phi Y l m theta phi the absolute square. This has to be 1.

Now, you see that the d tau is essentially r square dr d theta sin theta d phi. Then, the rest of it is psi star n l m psi n l m. Therefore when you do this integral independently of this, the theta phi integral, note that the definition of Y l m, Y l m are such that this part is one. And therefore, the radial path is given by this one. And, now you can see immediately why the quantity R n l of r square r square is called the radial probability or the radial distribution; because this probability, when it is calculated for all values of r from 0 to infinity is equal to 1. Therefore, you see the radial probability in the case of the hydrogen atom is not just the r l m square, but it is multiplied by the r square. And, that is important to remember. It is not just square of the function. Let us look at these functions in the pictorial form.

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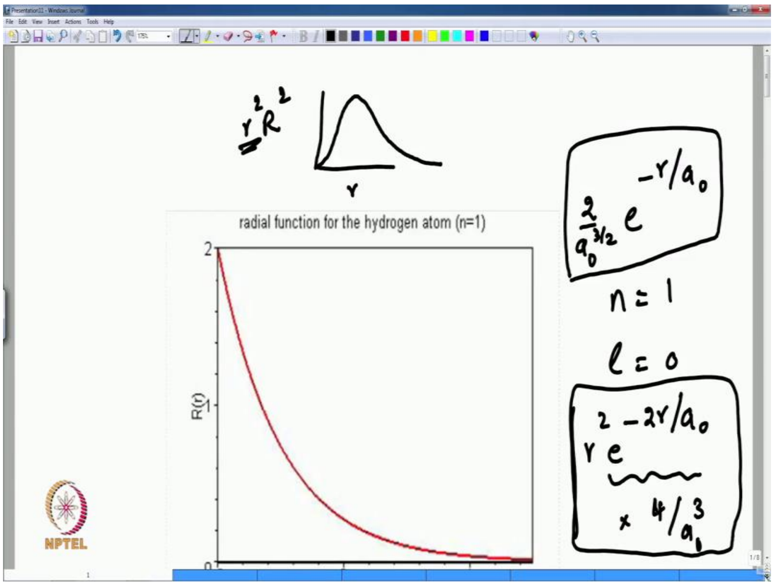

In the pictorial form, the first one is like exponential minus r by a naught. This is n is 1; l is 0. And, this is the straight forward exponential, the radial function. And the integral, the square of this function if you write to the formalization constant also, if you write that remember it is 2 by a naught to the 3 by 2. Therefore if you do that, the integral that you have to worry about for radial probability is r square e to the minus 2 r by a naught. This is the square of the radial function. And then, you have the multiplied by 4 by a naught cube. So, this is the radial probability; this is the radial function.

The radial function is given like this and, the radial probability if you have to plot it, if I have to make brief plot of this, I do not have it in the screen here. If I do the plotting as a function of r, if I do the r square R square, the radial probability is like that it is 0. At r equal to 0; the function, the radial function itself is not 0 at r equal to 0. But, the radial probability because of this r square is always 0 at the nucleus as the value. The probability density is 0 and probability distribution is that this is r square R square. The area of this for all work under this graph is equal to 1. That is the normalization.

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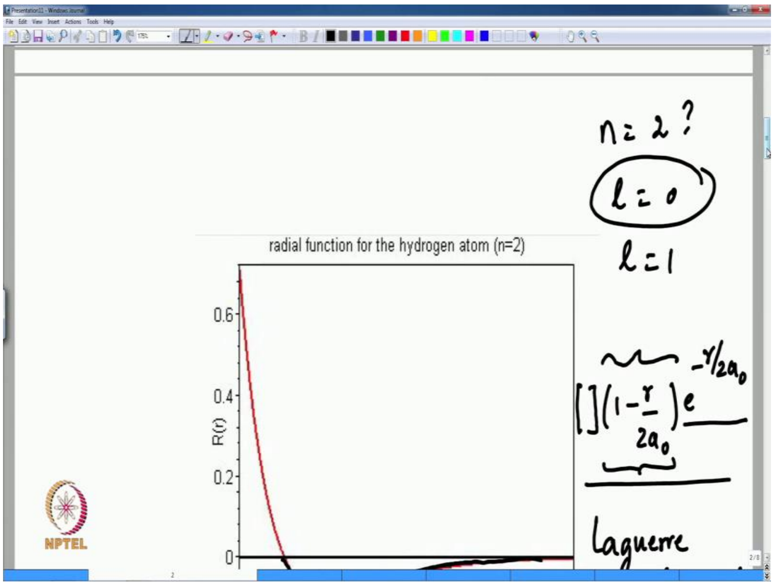

What about the radial function for the hydrogen atom at n equal to 2? There are two values; l equal to 0 and l equal to 1.

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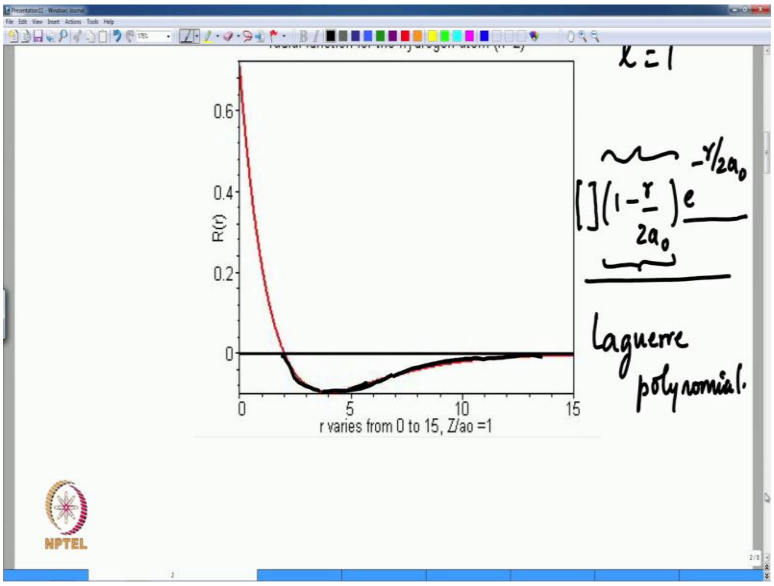

$l = 1$

$[\;]\underbrace{\left(1-\frac{r}{2a_0}\right)}e^{-r/2a_0}$

Laguerre polynomial.

So, if I have to look at to the l equal to 2, the functional form if you remember I wrote down is 1 minus r by 2 a naught e to the minus r by 2 a naught. You can see clearly that when r is 0, this is 1. So, you start with some number, depending on what the constant in front of this; that is the maximum here. But, at r equal to 2 a naught as r increases from 0 to 2 a naught, you say that the function drops off while, the exponential is also minus r by 2 a naught. So, you see that this function goes down. But for all values, sorry, yeah for all values of r greater than 2 a naught, this will increase; because this will increase, but the exponential will decrease. Therefore, after some time the function goes such that the exponential (Refer Time: 11:00). So, this initial increase is due to this. This is the part of what is the known as the Laguerre polynomial, which are solutions for the radial equation. For l equal to; this is l equal to 0, I am sorry, this is the function for l equal to 0.

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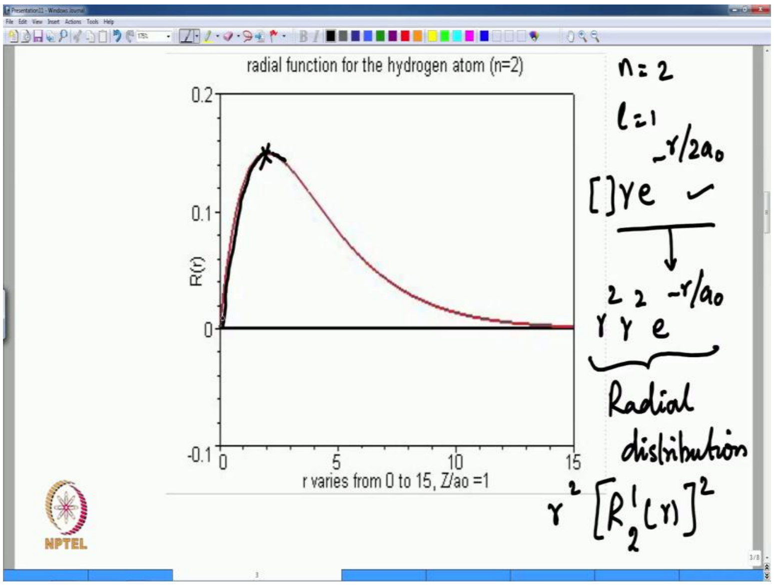

$n = 2$

$l = 1$

$[\,]\, r e^{-r/2a_0}$ ✓

$\downarrow$

$\underbrace{r^2 r^2 e^{-r/a_0}}$

Radial distribution

$r^2 \left[R_2^1(r)\right]^2$

And for l equal to 1, n equal to 2, the radial function that you have is r e to the minus r by 2 a naught with again some pre factors there is a normalization constant. You can see that this function is 0 at r equal to 0. As r increases, this increases; but this decreases. So, there is a competition between the increasing r up to the point; that is a maximum. And then, the function is reducing due to the exponential; even though r is increasing, the exponential dominates and therefore, the function goes back; goes to 0 for large values of r. This is the radial function for l equal to 2, l equal to 1 and, the radial distribution is r square multiplied by the square of this function, which is again another r square and e to the minus r by a naught. This is the radial distribution. This is R 2 1 radial function square multiplied by r square. So, again the maximum that happens is quite far away from the 0.

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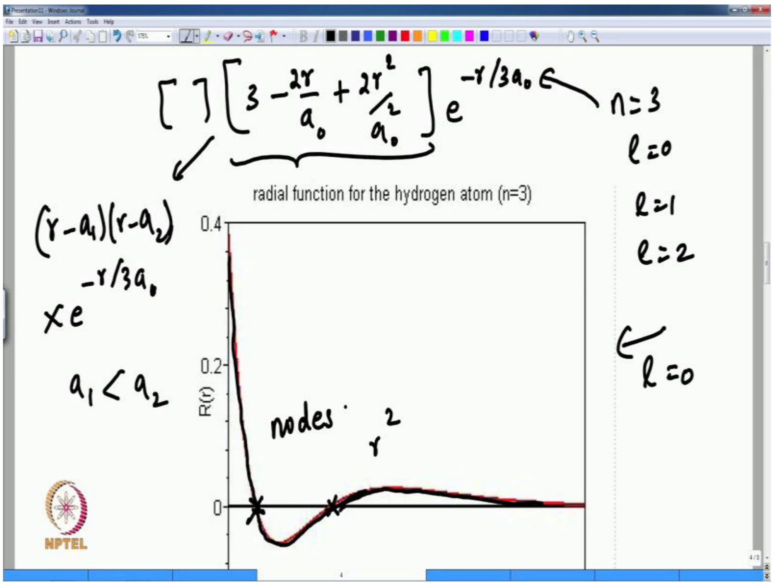

$$[\ ]\underbrace{\left[3-\frac{2r}{a_0}+\frac{2r^2}{a_0^2}\right]}e^{-r/3a_0}$$

n = 3
l = 0
l = 1
l = 2
l = 0

$(r-a_1)(r-a_2)$
$\times e^{-r/3a_0}$
$a_1 < a_2$

nodes
r^2

n is equal to 3 has three possible functions namely l equal to 0, l equal to 1 and l equal to 2. This one is l equal to 0. The form of the radial function is essentially 3 minus r by 2, sorry, 2 r by a naught plus 2 r squared by a naught square. This is the quadratic in front of the function multiplied by e to the minus r by 3 a naught n equal to 3. The quadratic has two solutions; both of which are positive and, you can see that those two solutions are these. That is the quadratic goes to 0 for these 2 values of r.

If you factor this quadratic with the two roots, these are the two roots. And, you can see that when r is 0, the function is positive. It is non 0 because of the 3 and the pre factor in front of the normalization factor in front of it, it is somewhere here. And then, as r increases; if you write this as the two roots, so quadratic r minus a 1 times r minus a 2 times e to the minus r by 3 a naught. And if a one is less than a 2, you can see for r less than a 1 and r is also less than a 2, therefore this product is positive. And, the exponential is always positive, but it is a small number. The function is positive between 0 and the first one; first root. Between the first and the second root because this product is negative, r is greater than a 1; but less than a 2, the function is negative. But, it is also multiplied by e to the minus r 1 3 a naught. And for r greater than a 2, this is positive. So, the function tends to increase this r square. However, e to the minus r by 3 a naught eventually brings it down to 0. So, it has two roots called nodes.

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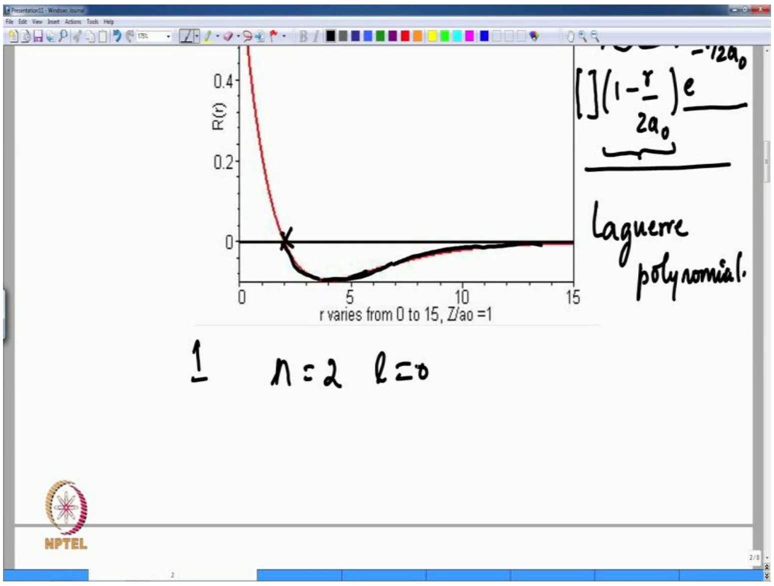

$[\,]\underbrace{(1-\frac{r}{2a_0})}e^{-r/2a_0}$

Laguerre polynomial.

$\underline{1}$ $n=2$ $l=0$

The previous one has one node. n equal to2; l equal to 0.

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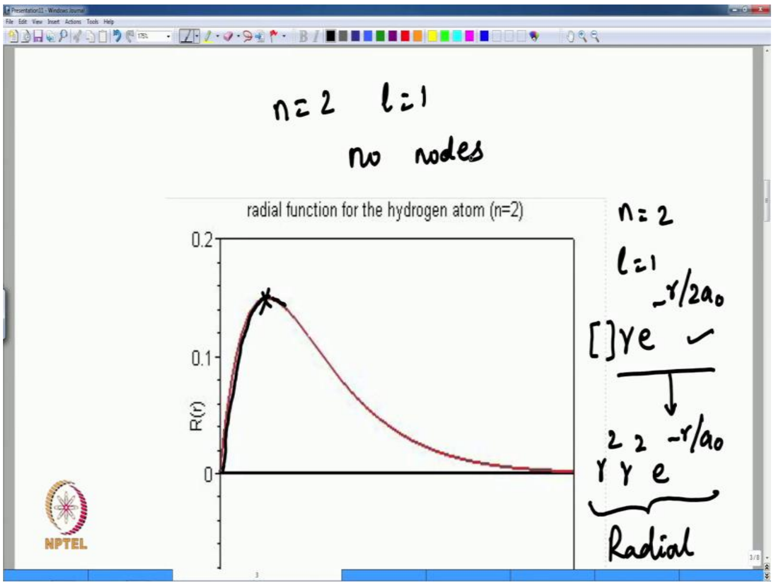

$n=2$ $l=1$

no nodes

$n=2$

$l=1$

$[\,]re^{-r/2a_0}$ ✓

$\downarrow$

$\underbrace{r^2 r^2 e^{-r/a_0}}_{\text{Radial}}$

When n equal to 2, and l equal to 1 no nodes.

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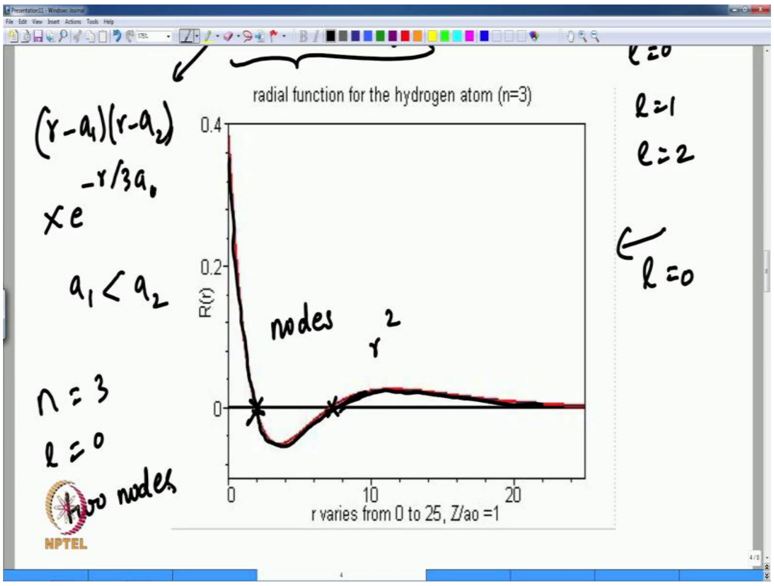

$(r-a_1)(r-a_2)$

$\times e^{-r/3a_0}$

$a_1 < a_2$

r^2

$n = 3$

$l = 0$

two nodes

$l = 0$

$l = 1$

$l = 2$

$l = 0$

When n is 3 and l is 0, there are two nodes.

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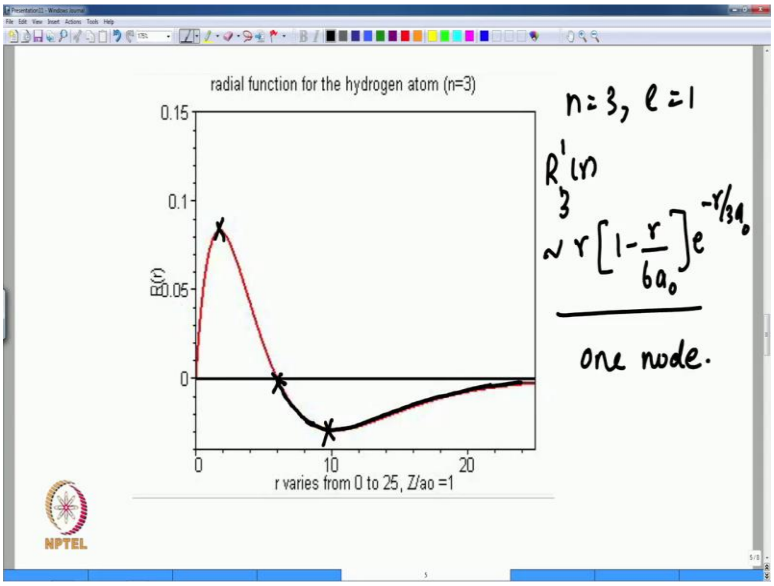

$n = 3, l = 1$

$R_3^1(r)$

$\sim r\left[1-\frac{r}{6a_0}\right]e^{-r/3a_0}$

one node.

When n is 3 and l is one, the radial function considered to be 3 1 of r; turns out to be the proportion, the normalization constant. It is r times 1 minus r by 6 a naught times e to the minus r by 3 a naught. So you can see that this is 0, when r is 0. And then, r is 6 a naught. So, between 0 and 6 a naught the function increases and, at r equal to 6 a naught, it goes to 0.

As for all values of r greater than 6 a naught, this whole thing is negative. And, you can see that the function decrease r square, but the exponential of minus r by 3 a naught eventually brings it back to 0. So, here is the maximum and then, the function goes to 0 r but only one node.

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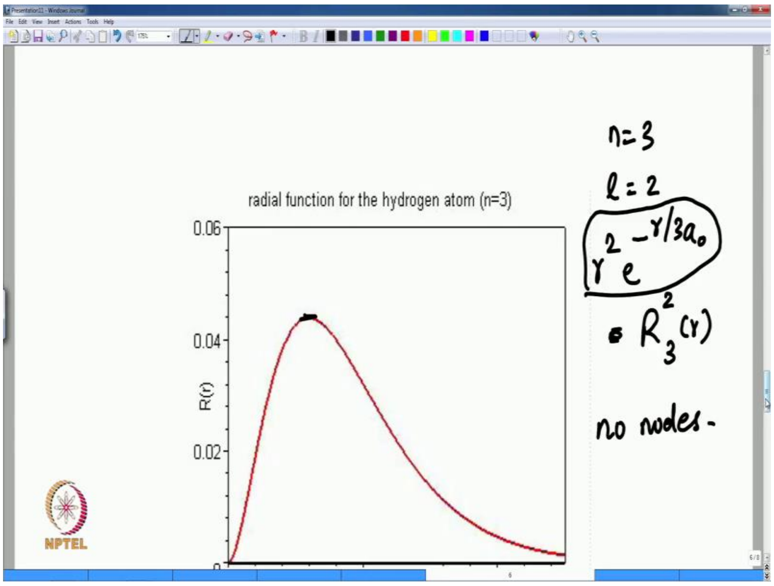

And the last one; when you look at n equal to 3, l equal to 2, the function is r square e to the minus r by 3 a naught. This is like the radial function R 3 2 of r. I have not put in the normalization constant, but that is what it is. And, this r square has only one maximum and then the exponential eventually goes to 0, no nodes.

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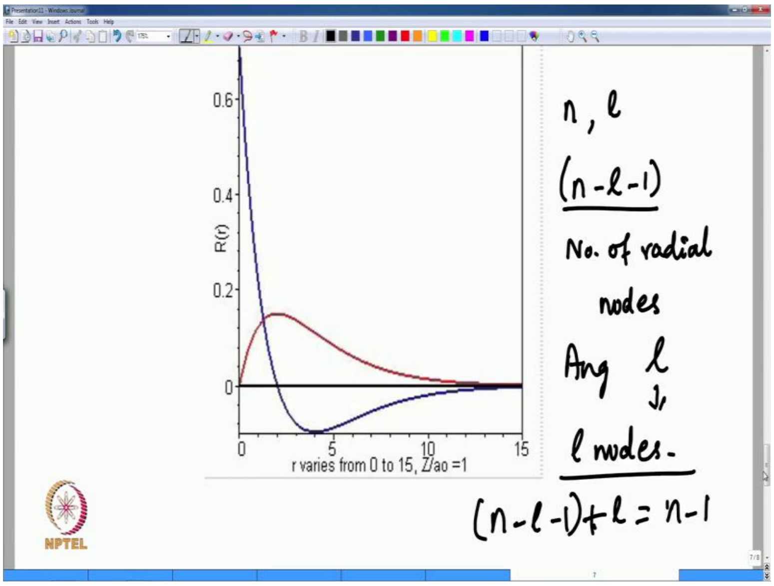

n, l

$(n-l-1)$

No. of radial nodes

Ang l

$\downarrow$

l nodes.

$(n-l-1)+l = n-1$

Therefore, the Laguerre polynomials which are there for various values of n and l are basically polynomials in the; to the order of the polynomial or the degree of the polynomial is n minus l minus 1. That is the number of radial nodes; because if the polynomial is of this degree, it has that many roots. So, you see that when n is 1, n is 0; there are no roots and no nodes. When n is 2, l is 0; 1 node, no node, then 2,1,0. When n is 4, you have 3,2, 0, 1, 0. So, the number of nodes, are like this.

Then, for angular functions we saw already for any l has l nodes. So, the total number of radial plus angular nodes for any function is n minus l minus 1 plus l, which is n minus one. These formulas are somewhat familiar from the elementary school introduction of the hydrogen atom functions as pictorial functions. But, you can see that the radial functions are like this and, the radial probability is the square of the radial function multiplied by r square.

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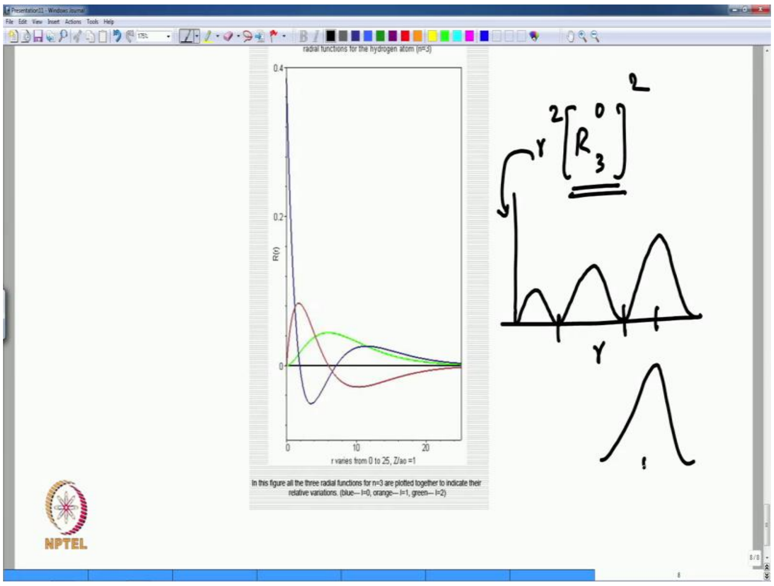

In this figure all the three radial functions for n=3 are plotted together to indicate their relative variations. (blue--- l=0, orange--- l=1, green--- l=2)

So, let me conclude by putting all these functions together for each value of n. So, this is for n equal to 2. The two functions are; this is l equal to 0 and l equal to 1, gives you an idea that the larger part are the maximum value of these functions are slightly farther from the maximum values that you would see for n equal to 1. This is a statement that the 2 s orbital is more extended than the 1 s orbital. The maximum for the 2 s orbital are the probabilities for the electron in the 2 s orbital are maximum. When, it is slightly farther away compared to the electron being in the 1 s orbital; where the maximum is closed to the Bohr radius. And, the same thing happens for n equal to 3. The maximum is even shifted further and there are two nodes.

So, if you look at the radial square functions namely the r square, hence r 3 0 if you square, if you look at that function, the radial probability will look like this probability here. The radial probability will look somewhat like that with the two nodes corresponding to the (Refer Time: 21:27) where this polynomial, the radial functions goes to 0. And then, for 3 1 you have two maxima and for 3 3 3 2 only one maxima. But, the maxima’s are all towards the farther psi; meaning that the 3 s orbital is much more extended in space than the 2 s orbital, than the 1 s orbital. And, the maximum of the 3 s orbital is quite far away compared to that of the 2 s orbital and that is also far away compared to that of the 1 s orbital. So, this picture of Bohr having a circular orbits drawn, those circle essentially represent something close to a maximum. We have now replaced the circle by a probability distribution through a more exact treatment of

Schrodinger. Then, the only question that I would not be able to answer, why Schrodinger equations, we do not know the answer.

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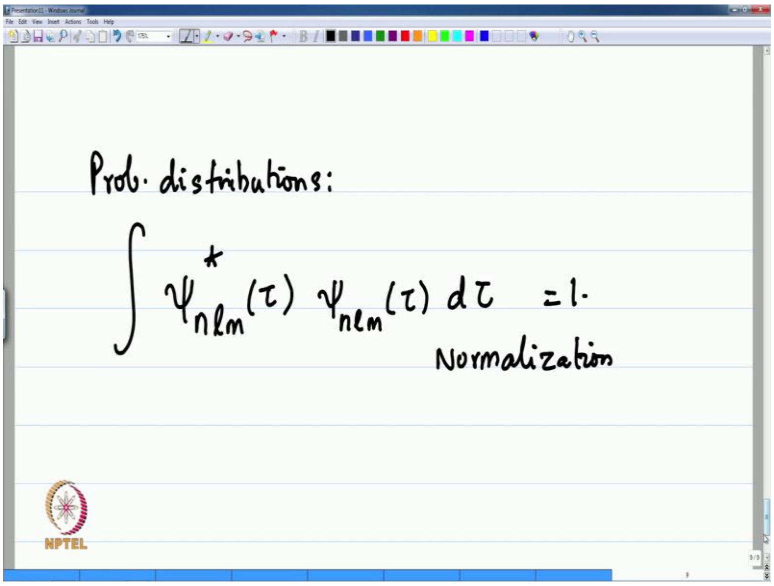

Prob. distributions:

$$\int \psi^{*}_{nlm}(\tau)\, \psi_{nlm}(\tau)\, d\tau = 1.$$

Normalization

Let me conclude this lecture with the note on the probability statement and probability distributions. The wave functions psi n l m are chosen to be normalized wave functions. So, if I put all the three coordinates by the abbreviated symbol tau, then it is psi n l m psi n l m tau d tau integral to the equal to 1, this is normalization.

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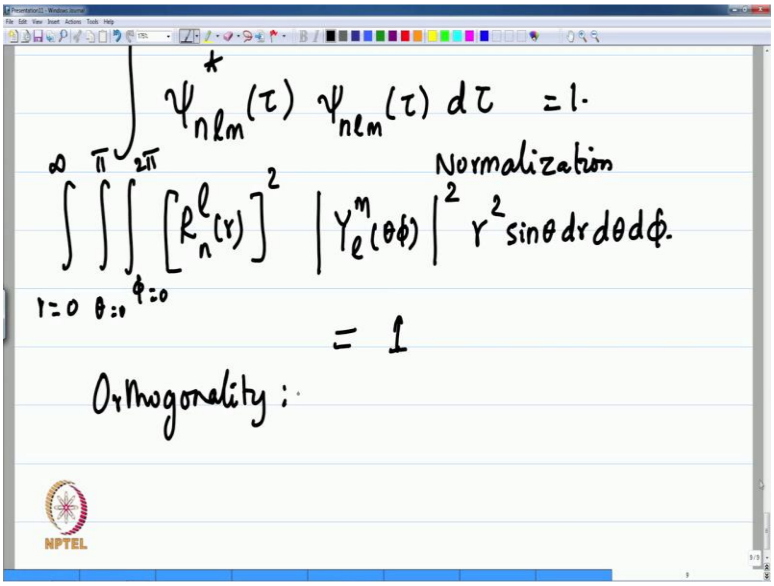

$$\int \psi^{*}_{nlm}(\tau)\, \psi_{nlm}(\tau)\, d\tau = 1.$$

Normalization

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \left[R^{l}_{n}(r)\right]^{2} \left|Y^{m}_{l}(\theta\phi)\right|^{2} r^{2}\sin\theta\, dr\, d\theta\, d\phi.$$

$$= 1$$

Orthogonality:

From the functions given in the lecture notes for the individual R n l r s and the y l m the integral node takes the specific representation is a triple integral r equal to 0 to infinity, theta is equal to 0 to pi and phi is equal to 0 to 2 pi. You have the radial functions square, you have the absolute value of the spherical harmonics; theta square absolute value multiplied by the theta which is r square sin theta d r d theta d phi; that is equal to 1. And, the orthogonality of these wave functions as being solutions of a Hamiltonian, which is the Hermitian - Hamiltonian.

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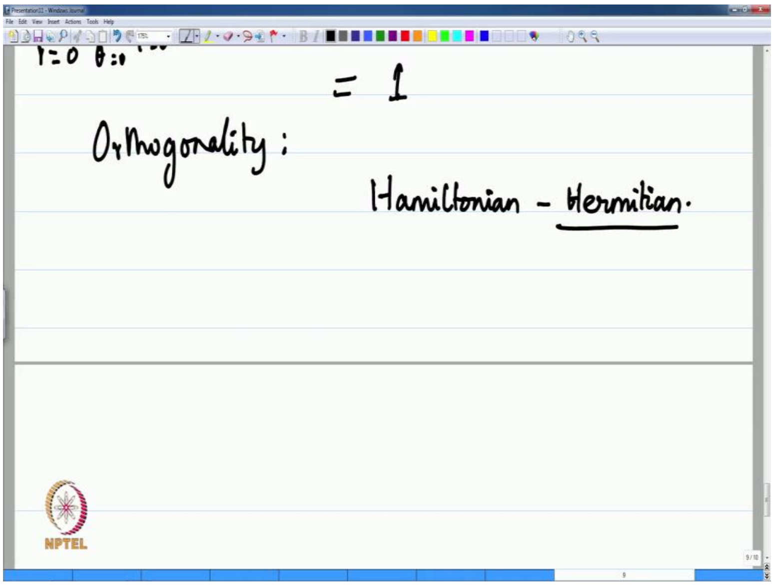

$r=0 \quad \theta=0$

$= 1$

Orthogonality :

Hamiltonian - Hermitian.

Again introduced the new term called the Hamiltonian as a Hermitian operator, which has real Eigen values; for all the Eigen values are real.

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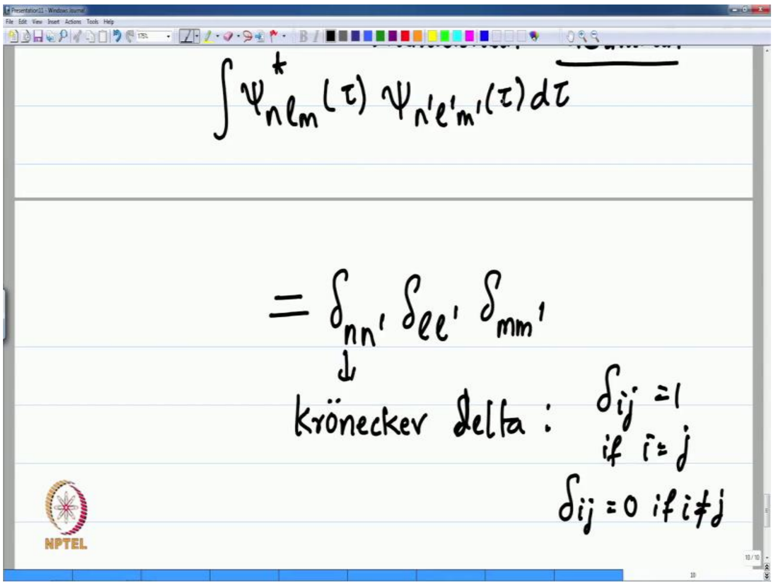

$$\int \psi^*_{n\ell m}(\tau)\,\psi_{n'\ell'm'}(\tau)\,d\tau$$

$$= \underset{\Downarrow}{\delta_{nn'}}\,\delta_{\ell\ell'}\,\delta_{mm'}$$

Krönecker delta : $\delta_{ij}=1$ if $i=j$

$\delta_{ij}=0$ if $i\neq j$

The Hamiltonian operator, the wave function is psi n l m tau psi star psi n prime l prime m prime tau d tau is; these functions are orthogonal to each other. And, if I have to write that in the integral notation, the answer is the Kronecker delta n n prime Kronecker delta l l prime m m prime this is Kronecker delta. The delta i j is 1, if i is equal to j delta i j is equal to 0, if i is not equal to j. Therefore if n is not equal to n prime, if l is not equal to l prime, if m is not equal to m prime, any one of them, any pair of them if they are not equal the wave functions, they are, wave functions are orthogonal.

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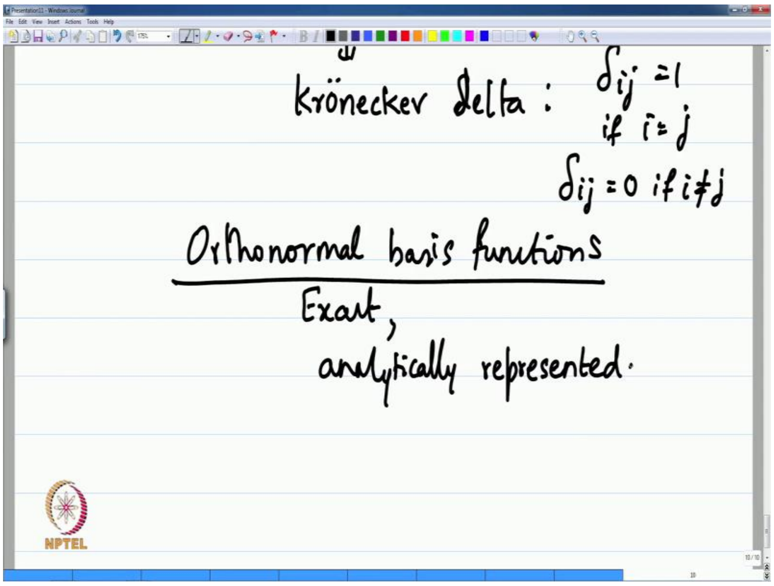

Krönecker delta : $\delta_{ij}=1$ if $i=j$

$\delta_{ij}=0$ if $i\neq j$

Orthonormal basis functions

Exact,

analytically represented.

And therefore, the wave functions being already normalized are thus known as orthonormal basis functions of all other problems of atoms. If you need to, we can always use the hydrogen atom wave functions as the basis functions; orthonormal basis functions as representing the wave functions for any other atom or any other system of nuclear and electrons together we wish to; we will not use that. But, these are analytically known that is, analytically represented and, we do not have much more of such analytic representations for other atoms.

In fact, for any other atoms which, has more than one electron, we do not have such analytic solutions. Therefore, the hydrogen atom solutions are extremely important. I have not covered the hydrogen atom here, in the form of the actual Mathematics and the solution of the differential equation that is usually given in a higher and slightly more advanced course. But please remember, we were trying to study the functions and represent them and look at their properties with the confidence that, these functions have been derived by the mathematician and physicists and have been shown to be exact.

Hydrogen atom is an extremely important problem in the understanding of the quantum mechanics of the atoms and molecules and the angular distributions, the radial probabilities, the radial distributions. All these things enhance one's capability in using similar mathematical techniques and tools in the understanding of atoms with many electrons. And, the only method that we can use for such studies are known as approximation methods. We do not have exact solutions for the differential equations. We use approximation methods known as perturbation methods or variational methods. But, those will form part of another course. And, as for as this elementary introduction to hydrogen atoms is concerned, I will leave the hydrogen atom in this point and move on to looking at the harmonic oscillator in the next set of lectures.

Until then, thank you very much.