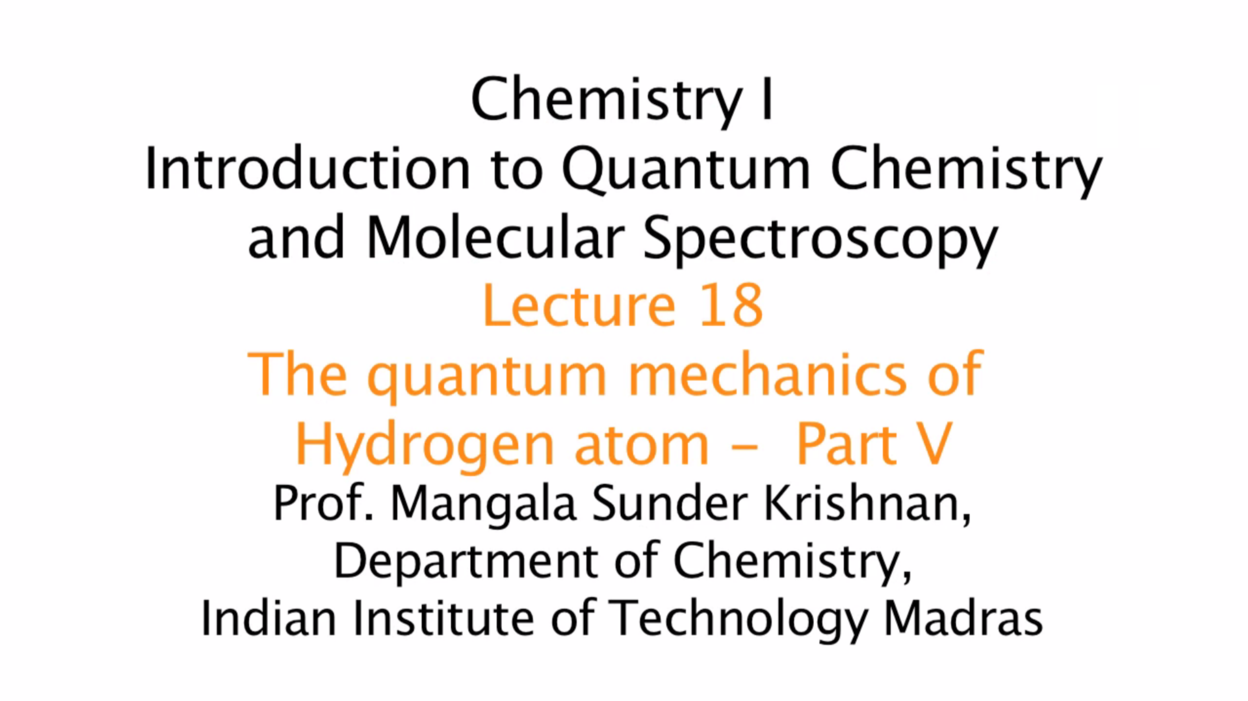
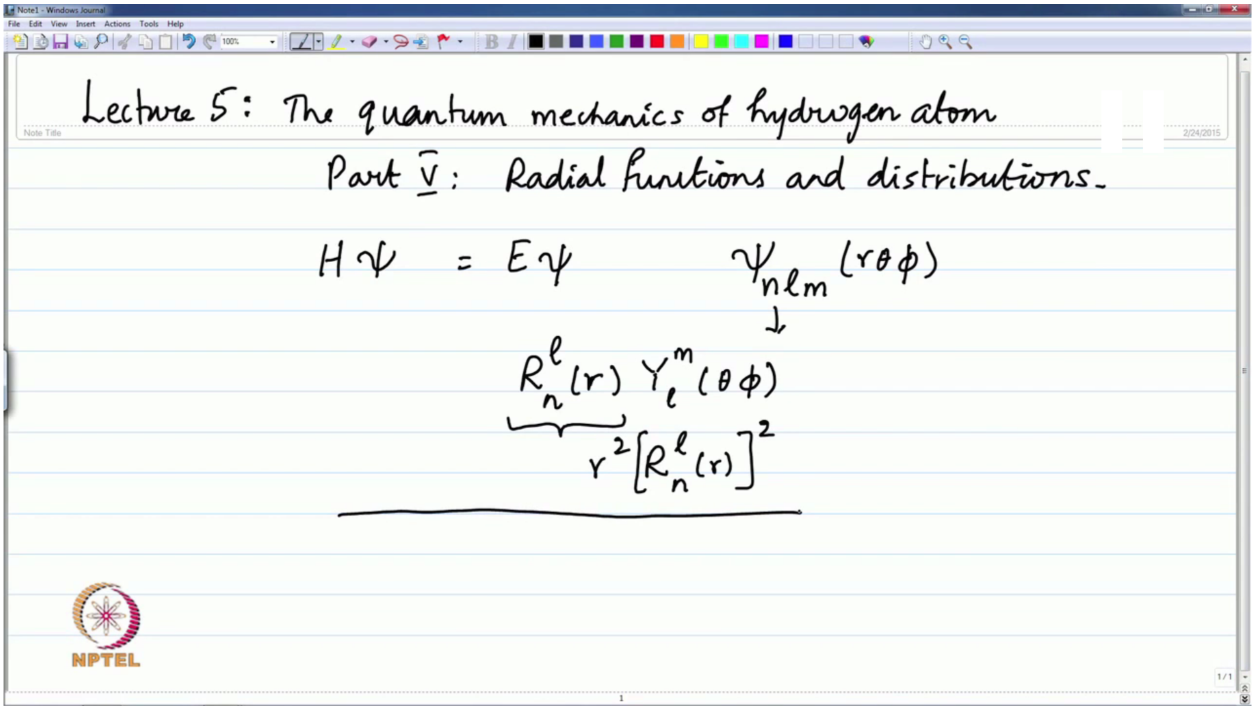


Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 18
The quantum mechanics of Hydrogen atom – Part V

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

Prof. Mangala Sunder Krishnan: Welcome back to the lectures. We will conclude the elementary part of the quantum mechanics of hydrogen atom with this part 5 where I shall give a brief description of radial functions and radial distributions of the hydrogen atom.



Lecture 5: The quantum mechanics of hydrogen atom

Part $\underline{V}$: Radial functions and distributions.

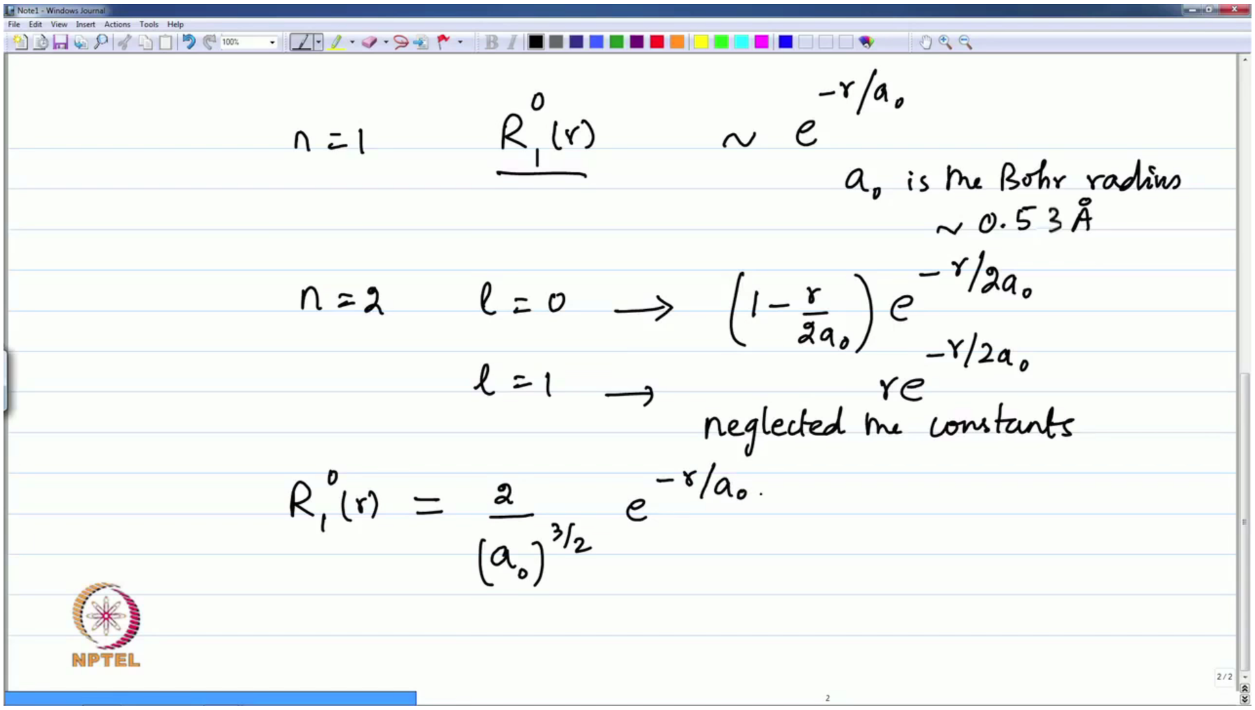
$$H\psi = E\psi \qquad \psi_{n\ell m}(r\theta\phi)$$

$$\downarrow$$

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

Now recall that the hydrogen atom they functions for the Schrodinger equation that is the solutions have been earlier represented by ψ with three quantum numbers n, l and m as a function of the three coordinates r, θ and φ, and this was written as or R n,l of the radial coordinate r and Y l,m (θφ). The φ or φ, I seem to have mixing these two things but remember φ or φ in the context, I mean they both mean the same thing for this lecture.

The radial function or n,l (r) and the radial distribution that we will consider in this lecture, namely it is r^2 [R n,l (r)]^2 are the wave function component and the probability distribution for the radial part.



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

a_0 is the Bohr radius

~ 0.53 Å

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

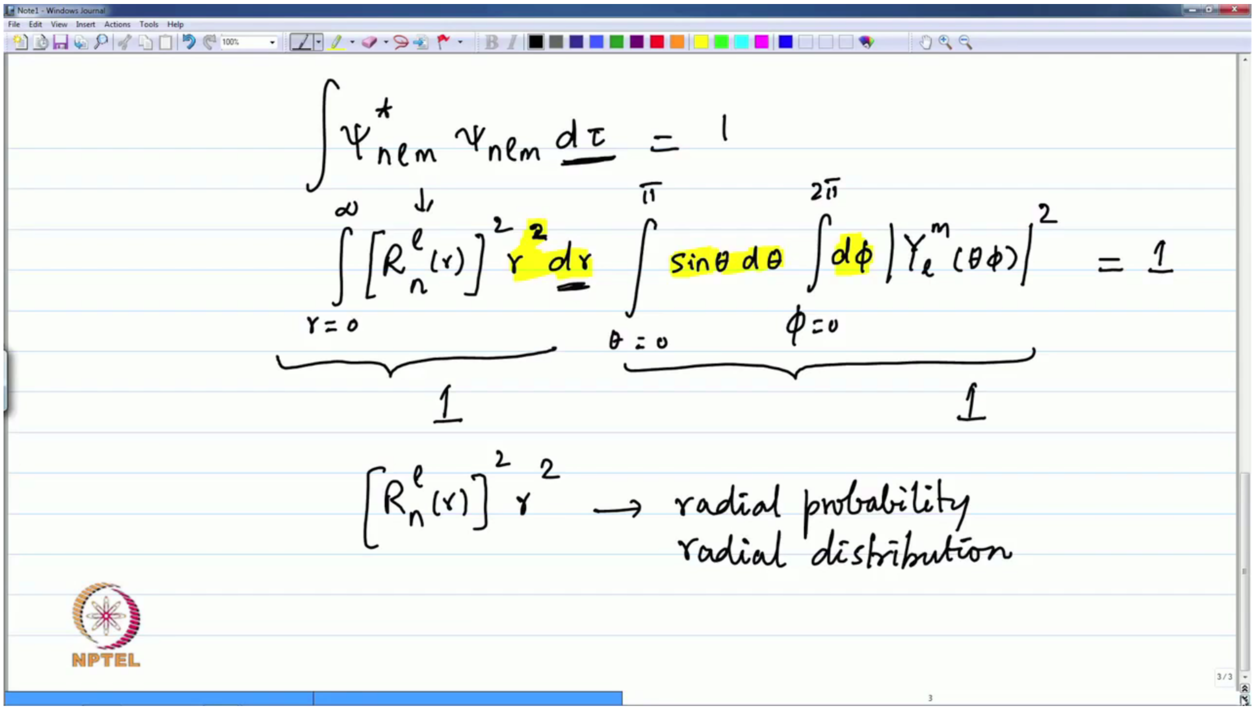
$l = 1 \longrightarrow r e^{-r/2a_0}$

neglected the constants

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

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 (r) have the range for the quantum numbers as n = 1, 2, 3 all the way up to ∞ and l = 0, 1, 2, up to n-1 for any n. Therefore, when n=1 , we have the radial function, which R 1,0 (r) and solution of the radial Schrodinger equation using the calculus of differential equation, the solutions of differential equation, gives us what are known as Laguerre polynomials and the exponentials and this particular function R1 (r) is like e^{-r/a_0} where a_0 is the Bohr radius, and 0.53 Å.

For n=2, we have two solutions, namely l=0 and l=1, and the function for l=0 is (1 - r/2a_0) $e^{-r/2a_0}$, okay. For l=1, the radial function happens to be r $e^{-r/2a_0}$, okay. I have neglected the normalization constants or the P factors constants, but if I don't, if I have to write this exactly then R 1,0 (r) = 2/(a_0)$^{3/2}$ e^{-r/a_0}.



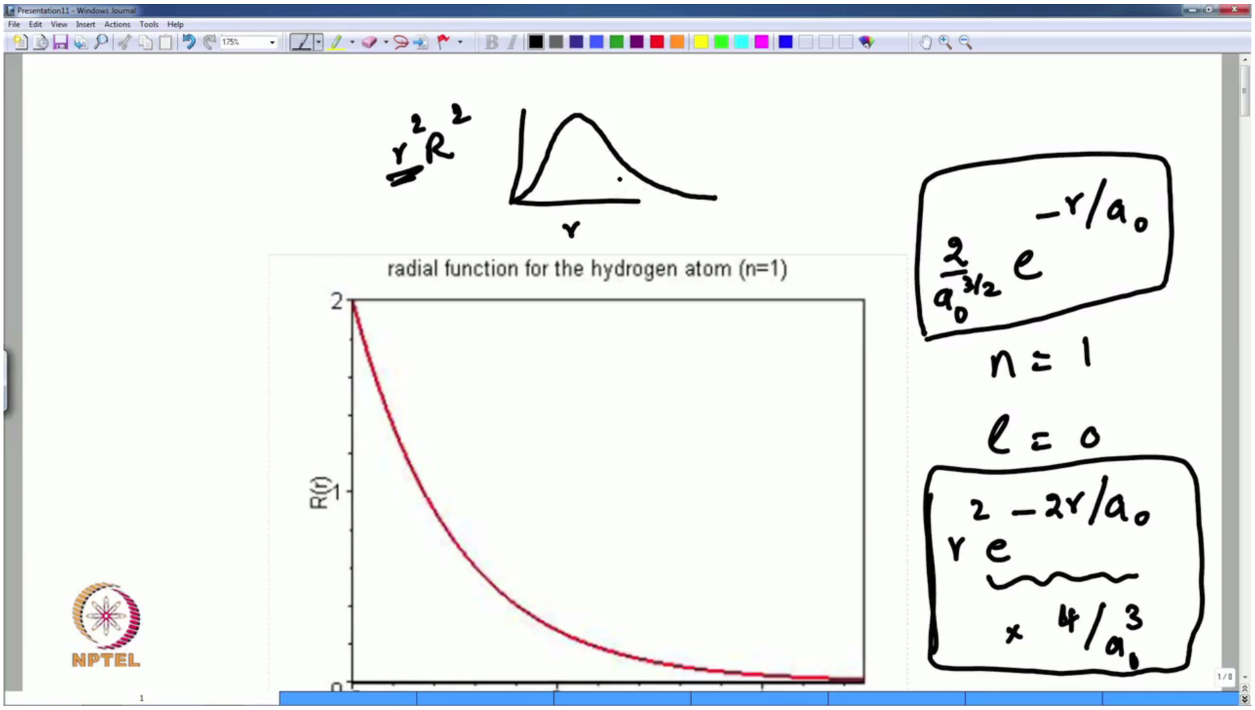
$$\int \overset{\downarrow}{\psi^*_{n\ell m}}\,\psi_{n\ell m}\,\underline{d\tau} = 1$$

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

$$\left[R_n^{\ell}(r)\right]^2 r^2 \rightarrow \text{radial probability}$$
radial distribution

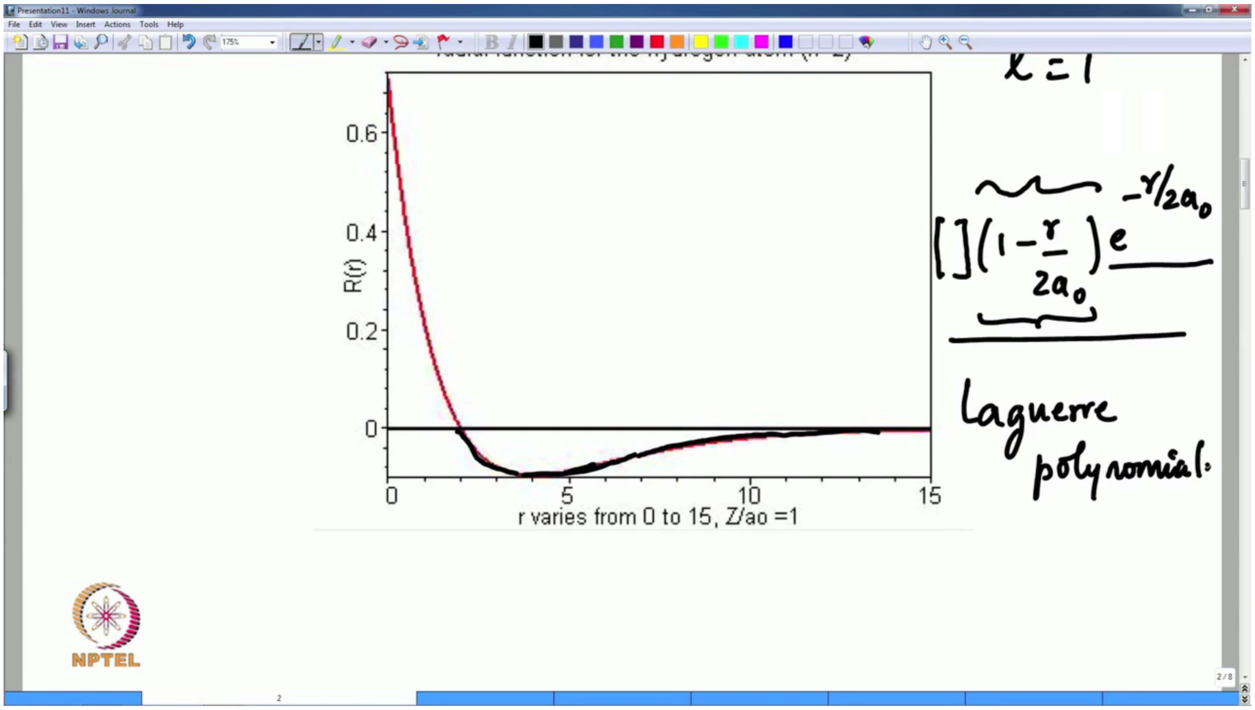
This normalization constant is obtained by the following procedure, namely the ∫ ψ^*_{nlm} ψ_{nlm} dτ = 1, which when we use the spherical polar coordinates has the following form ∫ r=0,∞ [R n,l (r)]^2, because this is real, and r^2 dr, which is the radial part for the dτ, then you have ∫ θ=0,π sinθ dθ ∫ φ=0,2π dφ Y l,m (θφ)|^2 = 1. Now you see that the dτ is essentially r^2 dr dθ sinθ dφ, and the rest of it is ψ^*_{nlm} ψ_{nlm}. Therefore, when you do this integral independently of the θφ integral, note that the definition of Y l,m are such that that this part is 1, and therefore, the radial part is given by this 1.

And now you can see immediately why the quantity [R n,l (r)]^2 is called the radial probability or radial distribution, radial probability or radial distribution, because this probability when it is calculated for all values of r from 0 to ∞ = 1. Therefore, you see the radiant probability in the case of the hydrogen atom is not just the [R n,l]^2 but it is multiplied by the r^2 and that's important to remember. It's not just the square of the function.

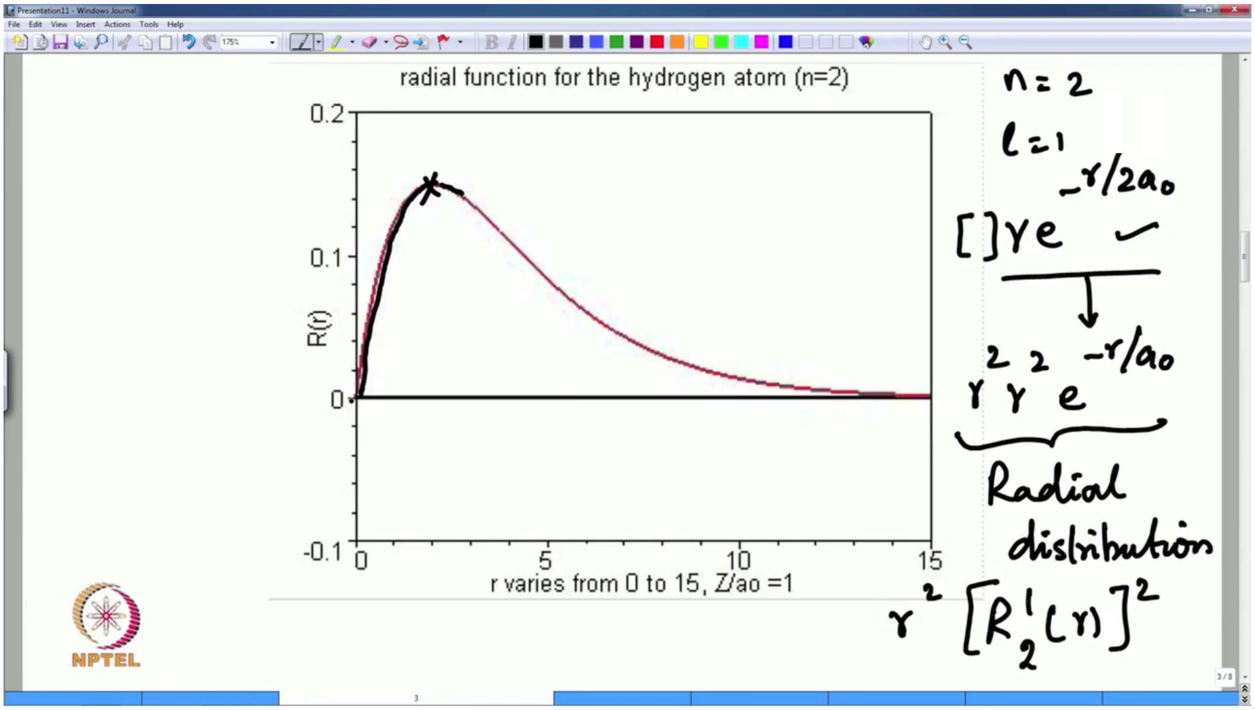


Let us look at these functions in the pictorial form. The first one is like e^{-r/a_0}. This n=1, l=0, and this is the straightforward exponential, the radial function, and the integral, the square of this function -- if you write the normalization constant also, if you write that, remember it is $2/a_0^{3/2}$, okay. Therefore, if you do that, the integral that you have to worry about for radial probability is $r^2 e^{-2r/a_0}$, as this is the square of the radial function and then you have the multiplied by $4/a_0^3$, okay. So this is the radial probability, this is the radial function, okay.

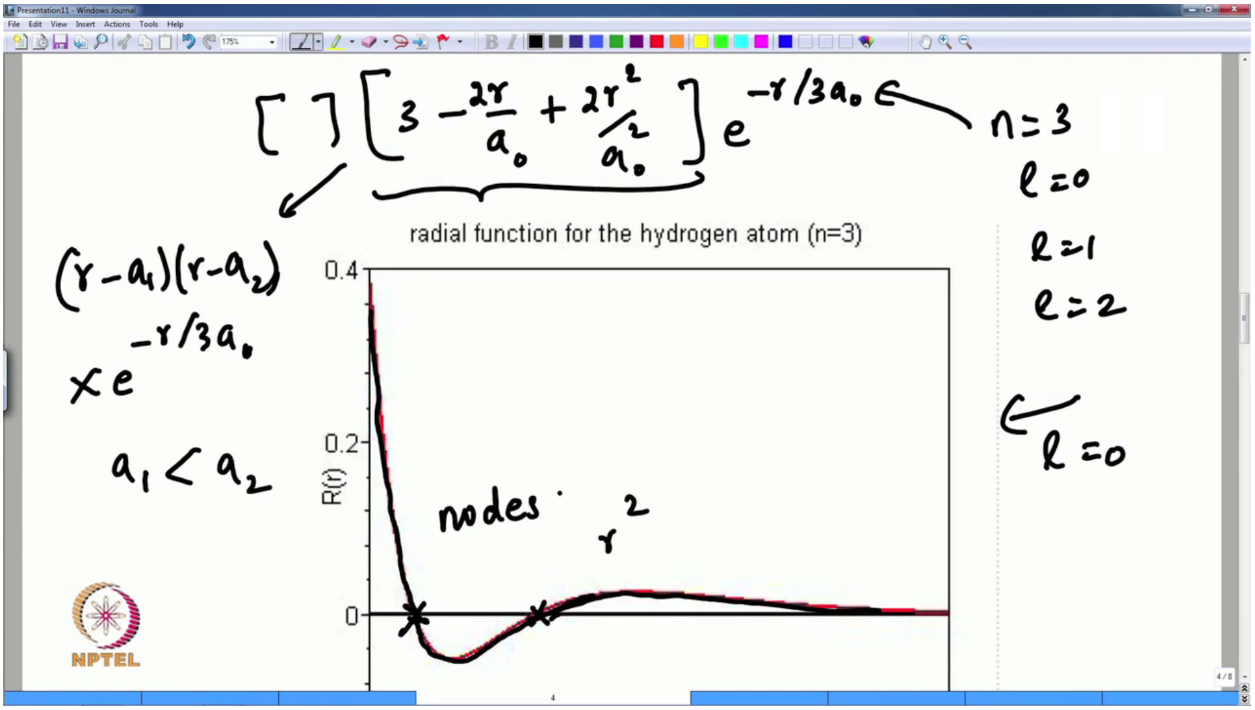
The radial function is given like this and the radial probability, if you have to plot it, if I have to make a brief plot of this, I don't have it in the screen here. If I do the plotting for as a function of r, if I do the R^2, the radial probability goes like that. It is 0 at R=0, the function, radial function, itself is not 0 at R=0, but the radial probability, because of this r^2, is always 0 at the nucleus as the value, the probability -- density is 0 and the probability distribution is that. This is r^2 R^2. The area of this for the end of this graph is equal to 1. That's a normalization.



What about the radial function for the hydrogen atom at n=2? There are two values l=0 and l=1. So if I have to look at to the l=2, the functional form if you remember I wrote down as $(1 - r/2a_0)\ e^{-r/2a_0}$. You can see clearly that when r=0, this is 1, so you start with some number depending on what the constant in front of A is, that's a maximum here but at or equal to $2a_0$, as r increases from 0 to $2a_0$, you see that the function drops off while the exponential is also $-r/2a_0$. So you see that this function goes down, but for all values of $r > 2a_0$, this will increase, because this will increase but the exponential will decrease, therefore after some time, the function goes such that the exponential tapers it off. So this initial increase is due to this. This is the part of what is known as Laguerre polynomial, which are solutions for the radial equation, okay.

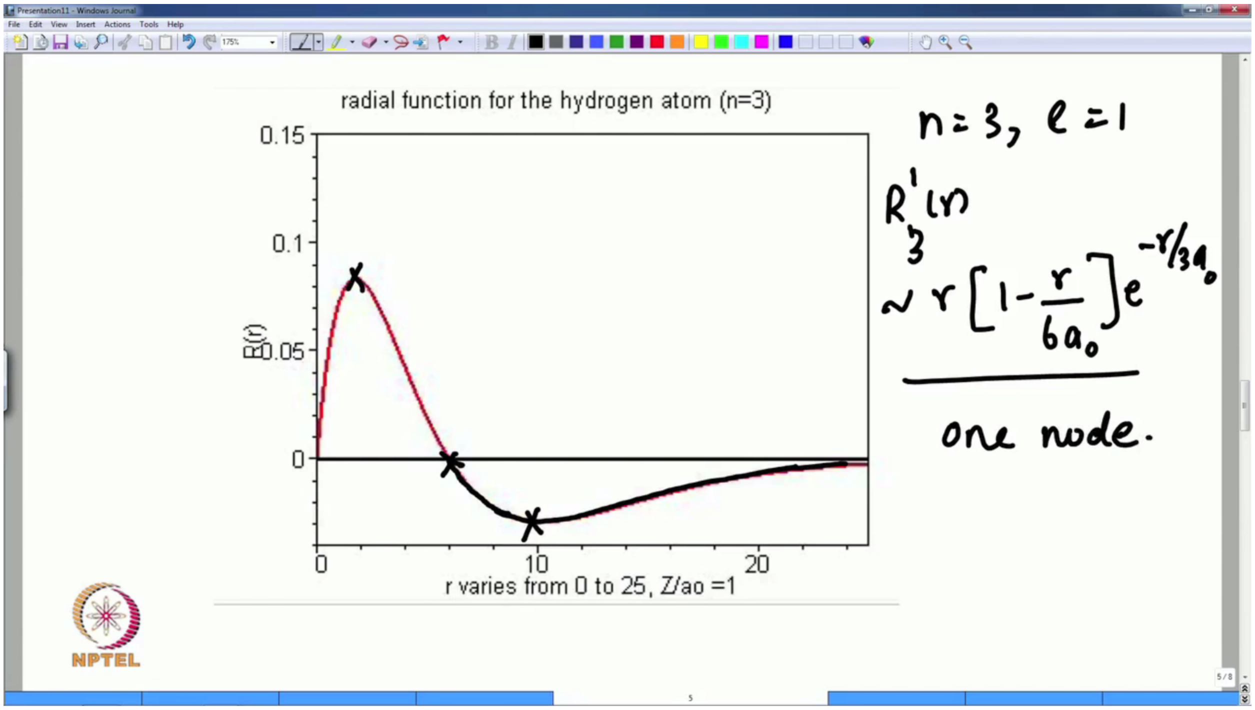


For l= -- this is l=0, this is the function for l=0 and for l=1, n=2, the radial function that you have is r $e^{-r/2a_0}$ with again some pre-factors that is the normalization constants. You can see that this function is 0 at r=0, as r increases, this increases, but this decreases. So there is a competition between the increasing r up to a point, there 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 to 0 for large values of r. This is the radial function for n=2, l=1 and the radial distribution is r^2 multiplied by square of this function, which is again another r^2 e^{-r/a_0}. This is the radial distribution. This $[R\ 2,1\ (r)]^2$ multiplied by r^2. So again the maximum that happens is quite far away from the 0.



n=3 has three possible functions, namely l=0, l=1 and l=2. This one is l=0. The form of the radial function is essentially $[3 - er/a_0 + 2r^2/a_0]^2$. This is the quadratic in front of the function multiplied by $e^{-r/3a_0}$, n=3, okay. The quadratic has two solutions, both of which are positive, and you can see that those two solutions are these. That is a quadratic goes to 0 for these two values of r. If you factor this out, this quadratic with the two roots, these are the two roots, and you can see that when r=0, the function is positive, it's non-zero because of the 3 and the pre-factor in front of it, the normalization factor in front of it. It's somewhere here. And then as r increases, if you write this as the two roots quadratic $(r-a_1)$ $(r-a_2)$ $e^{-r/3a_0}$ and if $a_1<a_2$, you can see for $r<a_1$, r is also less than a_2, therefore, this product is positive and the exponential is always positive, but 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 $r>a_1$ but $r<a_2$, the function is negative, but it's also multiplied by $e^{-r/3a_0}$, and for $r>a_2$, this is positive so the function tends to increase as r^2. However, $e^{-r/3a_0}$ eventually brings it down to 0, okay. So it has two roots called nodes.



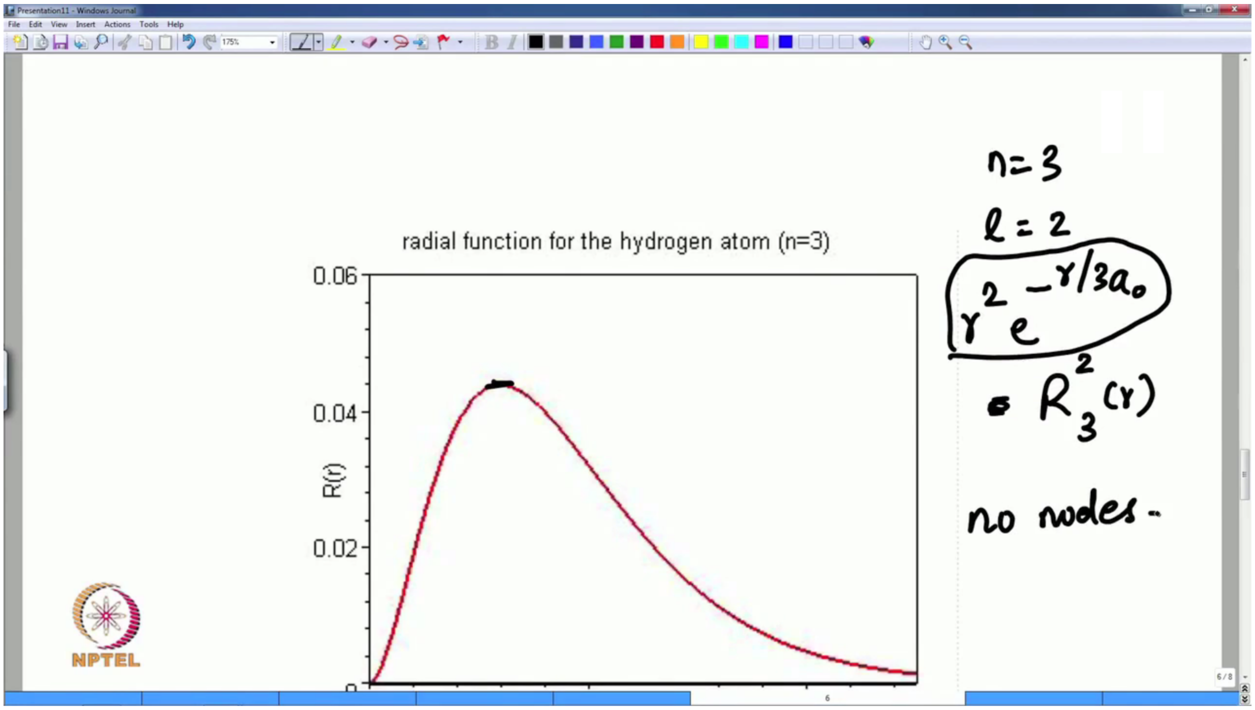
$n=3,\ \ell=1$

$R_3^1(r)$

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

one node.

The previous one has one node n=2, l=0. When n=2 l=1, no nodes. When n=3 l=0, there are two nodes. When n=3 and l=1, the radial function turns out to be 3,1 (r) turns out to be barring the normalization constant, it is r [1 - r/6a$_0$] $e^{-r/3a_0}$. So you can see that this is 0 when r=0 and then r=6a$_0$. So between 0 and 6a$_0$, the function increases, and at r-6a$_0$, it goes to 0, okay. And for all values of r>6a$_0$, this whole thing is negative and you can see that the function will decrease r^2, okay, but the $e^{-r/3a_0}$, eventually brings it back to 0. So here is the maximum and then the function goes to 0, but only one node.



$n = 3$

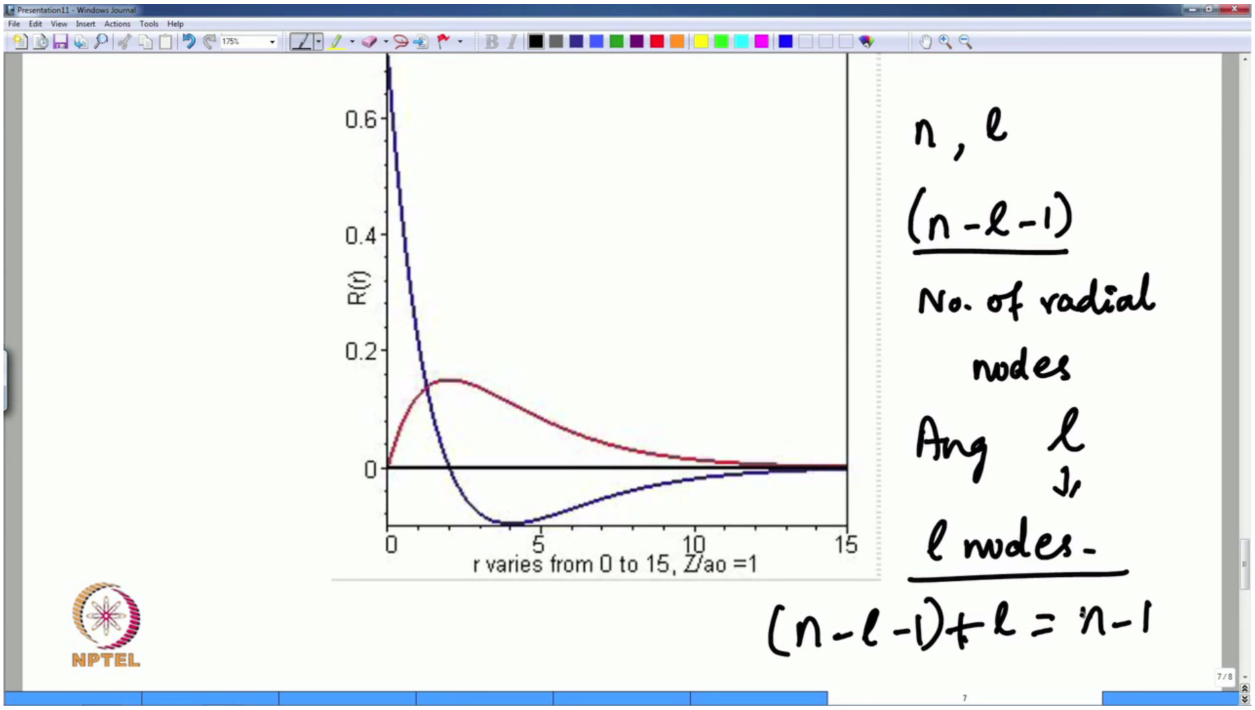
$l = 2$

$\boxed{r^2 e^{-r/3a_0}}$

$= R_3^2(r)$

no nodes.

And the last one when you look at n=3 l=2, the function is $r^2 e^{-r/3a_0}$. This is like the radial function R 3,2 (r). I mean I have not put in the normalization constant, but that's what it is, and the r^2 has only 1 maximum and then the exponential eventually goes to 0, no nodes.



n, l

$\underline{(n-l-1)}$

No. of radial nodes

Ang l

$\downarrow$

l nodes.

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

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

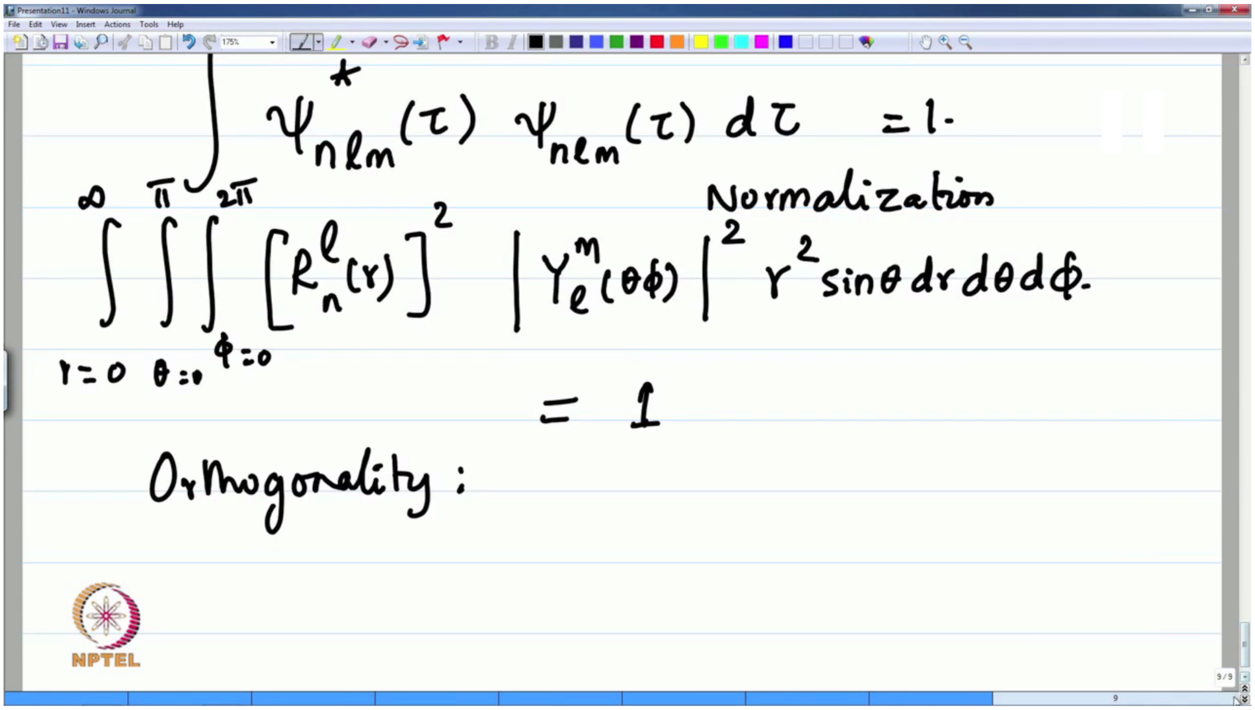
And for angular functions, we saw already for any l has l nodes. So the total number of radial plus angular nodes for any function is (n-l-1) + l = n-1. These formulas are somewhat familiar to you from the elementary school introduction of the hydrogen atom functions as pictorial functions, but you can see that the radial functions are like this and the radial probability is the square of the radial function multiplied by r^2.

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=2, the two functions are l=0 and l=1 gives you an idea that the larger part or the maximum value of these functions are slightly farther from the maximum values that you would see for n=1. This is a statement that the 2s orbital is more extended than the 1s orbital, the maximum for the 2s orbital or the probabilities for the electron in the 2s orbital are maximum when it is slightly farther away compared to the electron being in the 1s orbital where the maximum is closer to the Bohr radius, okay.

And the same thing happens for n=3. The maximum is even shifted further and there are two nodes. So if you look at the radial square functions, namely the r^2 [R 3,0 if you square, if you look at that function, the radial probability will look like this quantity here. The radial probability will look somewhat like that with the two nodes, corresponding to the points where this polynomial, the radial function goes to 0, okay. And then for 3,1, you will have two maxima and for 3,2 only one maxima, but the maximas are all towards the farther side, meaning that the 3s orbital is much more extended in space than the 2s orbital, than the 1s orbital, and the maximum of the 3s orbital is quite far away compared to that of the 2s orbital, and that is also far away compared to that of the 1s orbital.

So this picture of Bohr having 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, but then the only question that I would not be able to answer, why Schrodinger equation. We don't know the answer, okay.



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

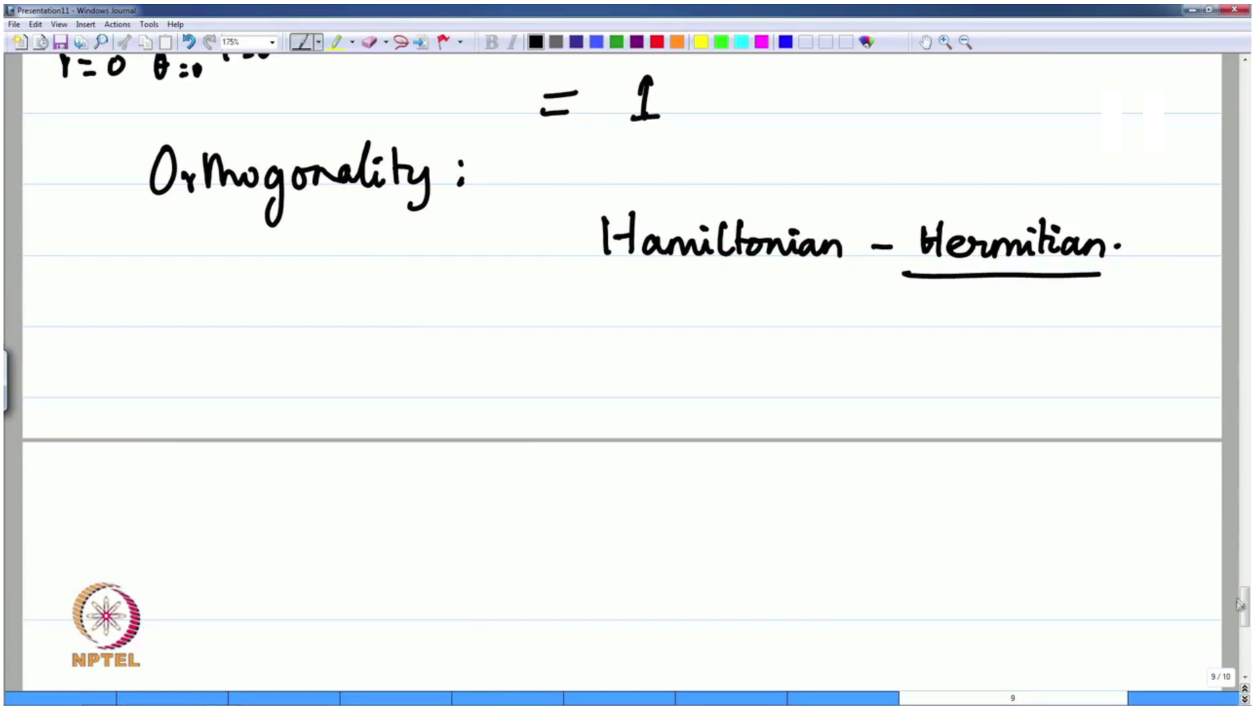
Normalization

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left[R_n^{\ell}(r)\right]^2 \left|Y_{\ell}^{m}(\theta\phi)\right|^2 r^2 \sin\theta\,dr\,d\theta\,d\phi.$$

$$= 1$$

Orthogonality :

Let me conclude this lecture with a note on the statements probability distributions. The wave functions ψ_{nlm} are chosen to be normalized wave functions, so if I put all the three coordinates by the abbreviated symbol τ, then it is $\psi^*_{nlm}\,\psi_{nlm}\,\tau\,d\tau$, the integral is equal to 1. This is normalization. From the functions given in the lecture notes for the individual R n,l (r) and the Y l,m the integral note takes the specific representation as a triple integral $r=0$ to ∞, $\theta=0$ to π and $\varphi=0$ to 2π, is of radial function square, you have the absolute value of the spherical harmonics $(\theta\varphi)|^2$ absolute value multiplied by the $d\tau$, which is $r^2 \sin\theta dr d\theta d\varphi$, okay. That's equal to 1, and the orthogonality of these wave functions as being solutions of a Hamiltonian which is a Hermitian Hamiltonian.



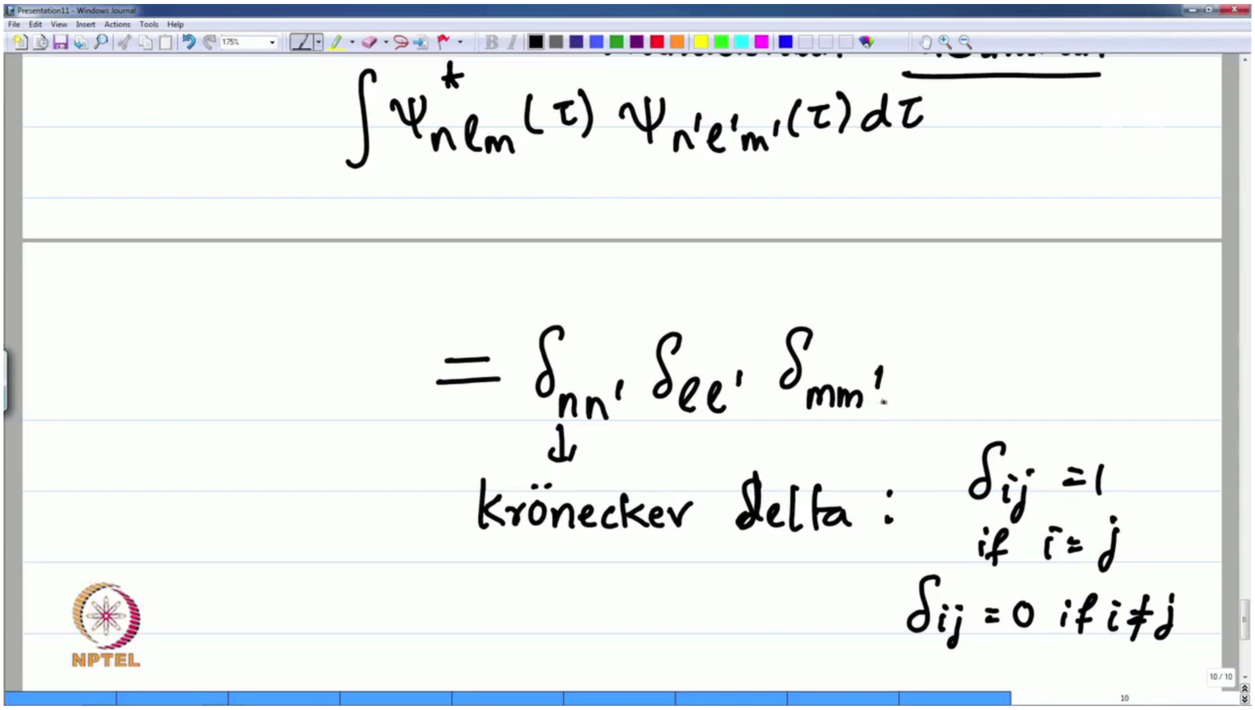
$r = 0 \quad \theta = 0$

$= 1$

Orthogonality :

Hamiltonian – Hermitian.

I've again introduced a new term called the Hamiltonian as a Hermitian operator, which has real eigenvalues for -- all the eigenvalues are real.



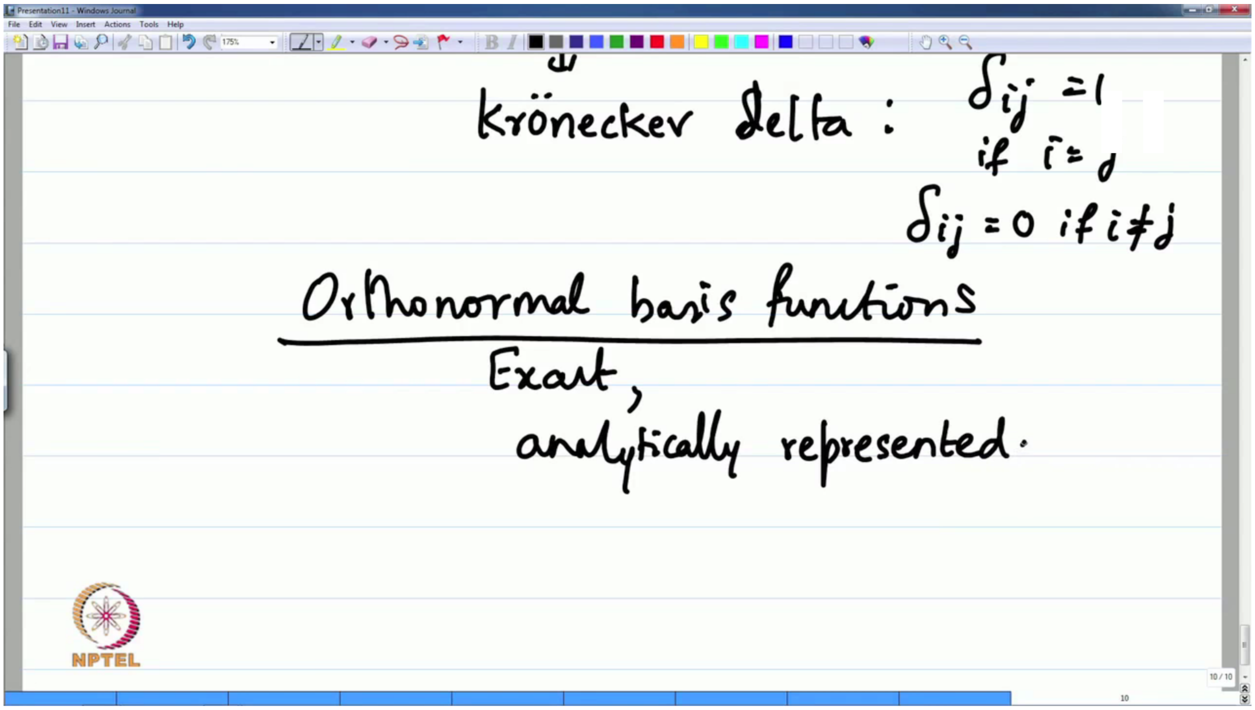
$$\int \psi^*_{n\ell m}(\tau)\, \psi_{n'\ell' m'}(\tau)\, d\tau$$

$$= \underset{\substack{\downarrow \\ \text{Kronecker delta}}}{\delta_{nn'}}\, \delta_{\ell\ell'}\, \delta_{mm'}$$

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

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

The Hamiltonian operator, the wave functions $\psi_{nlm}(\tau)$ $\psi^*_{n'l'm'}(\tau)$ $d\tau$. These functions are orthogonal to each other and if I have to write that in the integral notation, the answer is the $\delta_{nn'}$, $\delta_{ll'}$, $\delta_{mm'}$. This is Kronecker delta, meaning delta $\delta_{ij} = 1$ if i=j, $\delta_{ij}=0$ if i is not equal to j. Therefore, if the n is not equal to n', if l is not equal to l', if m is not equal to m', any one of them, any pair of them if they are not equal, the wave function is -- the wave functions are orthogonal.



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

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

Orthonormal basis functions

Exact,

analytically represented.

Therefore, the wave functions being already normalized are thus known as orthonormal basis functions for all other problems of atoms. If we need to, we can always use the hydrogen atom wave functions as the basis functions, orthonormal basis functions, representing the wave functions for any other atom or any other system of nuclei and electrons together, we wish to. I mean we would 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 atom 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's usually given in a higher or a 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 mathematicians and physicists and have been shown to be exact. Hydrogen atom is an extremely important problem in the understanding of the quantum mechanics of 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 don't have exact solutions for the differential equations. We use approximation methods known as perturbation methods or variational methods, but those will form part of a lot of course, and as far as this elementary introduction to hydrogen atom is concerned, I will leave the hydrogen atom at this point and move on to looking at the harmonic oscillator in the next set of lectures. Until then, thank you very much.