Chemistry Atomic Structure and Chemical Bonding

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Lecture – 27
Hydrogen Atom: Radial and Angular Solutions and Animations Part II

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.

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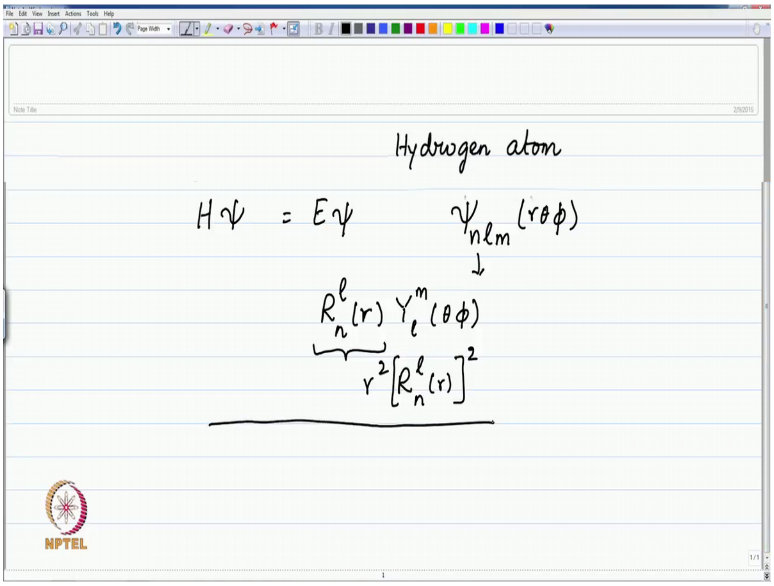

Hydrogen atom

$$H\psi = E\psi \qquad \psi_{nlm}(r\theta\phi)$$

$$\downarrow$$

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

Now, recall that the hydrogen atom wave functions for the Schrodinger equation, that is the solutions have been earlier represented by psi with 3 quantum numbers n l and m. As a function of the 3 coordinates, r theta and phi and this was written as or n l of the radial coordinate or and y l m theta phi.

This phi or phi I seem to have mixing these 2 things, but remember phi or phi in the context I mean they both mean the same thing on this lecture the radial function r in l or and the radial distribution that we will consider in this lecture namely it is r square or n l of r squared or the probability distribution the wave function component and the probability distribution for the radial part ok

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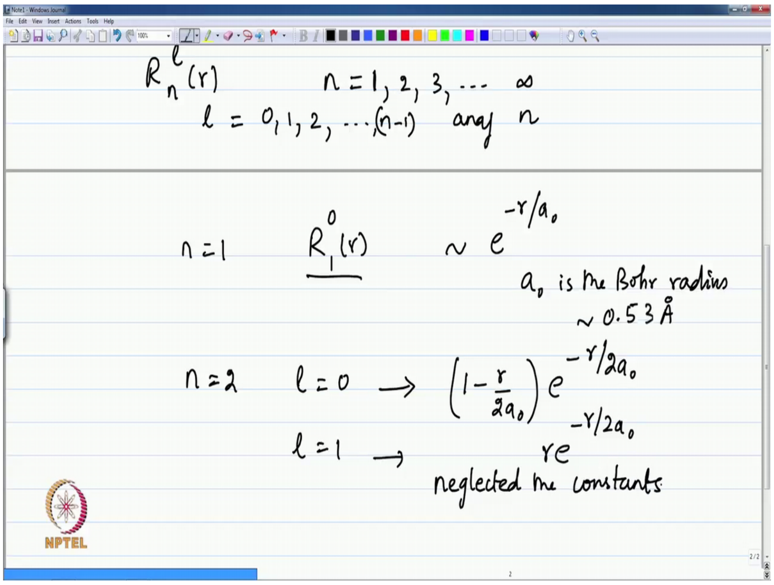

$R_n^l(r)$ $n = 1, 2, 3, \ldots \infty$

$l = 0, 1, 2, \ldots (n-1)$ 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 a earlier other than briefly mentioning that the radial functions have with the quantum number n l m or 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 or 1 0 of r and the solution of the radial Schrodinger equation using the calculus of differential equations. The solutions of differential equation gives us what are known as log n polynomials and the exponentials and this particular function or one or is like exponential minus or by a naught where a naught is the Bohr radius and 0.59 angstroms. For n equal to 2, we have 2 solutions; namely, l equal to 0 and l equal to 1 and the function for l equal to 0 is 1 minus or by 2 e naught times e to the minus or by 2 a naught ok.

For l equal to 1, the radial function happens to be or times e to the minus r by 2 e naught ok. I have neglected the normalization constants of the pre factors constants.

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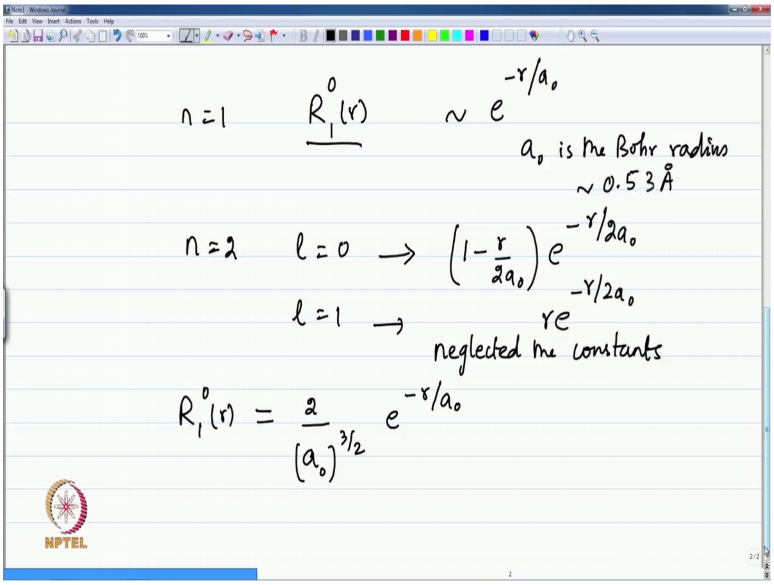

$n = 1 \qquad \underline{R_1^0(r)} \quad \sim e^{-r/a_0}$

a_0 is the Bohr radius ~ 0.53 Å

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

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

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 raise to 3 by 2 e to the minus r by a naught.

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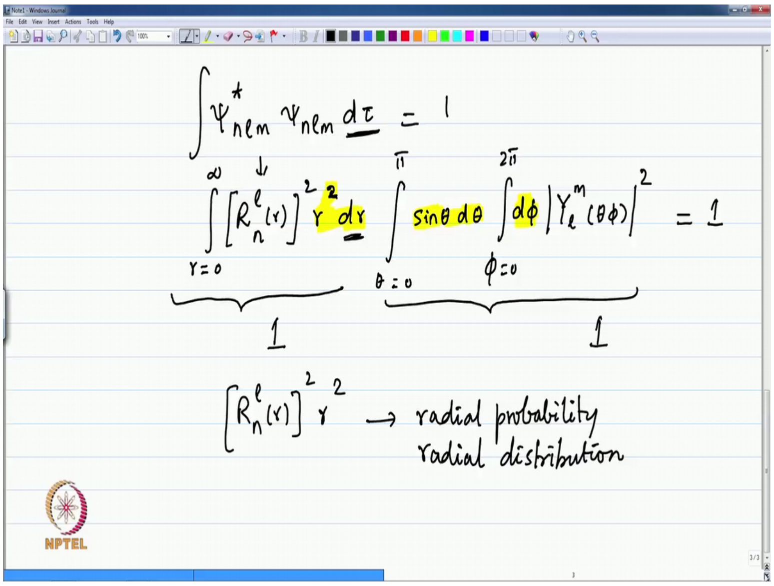

$$\int \psi^*_{nlm} \psi_{nlm} \, \underline{d\tau} = 1$$

$$\downarrow$$

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

$\left[R_n^l(r)\right]^2 r^2 \rightarrow$ 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 the spherical polar coordinates has the following form or equal to 0 to infinity, the radial function n l of or squared because, this is real and r square d r which is the radial part for the d tau. Then, you have theta is equal to 0 2 pi sin theta d theta integral phi is equal to 0 to 2 phi d phi y l m theta phi the absolute square. This has to be 1.

Now, we see that the d tau is essentially r square d r d theta sin theta d phi and 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 work that the definition of y l m y l m's are such that this part is 1 and therefore, the radial part is given by this 1.

And now, you can see immediately y the quantity R n l of r square R square is called the radial probability or radial distribution, radial probability or radial distribution because, this probability when it is calculated for all values of or from 0 to infinity is equal to 1. Therefore, you see the radiant probability in the case of the hydrogen atom is not just the r n l squared, but it is multiplied by the r square and that is important to remember it is not just a square of the function. Let us look at these functions in the pictorial form.

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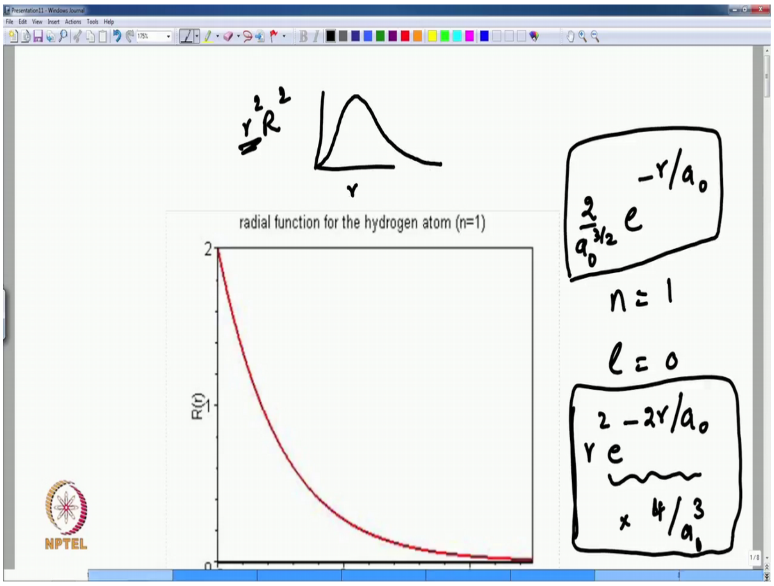

The first one is like exponential minus r by a naught. This is n is 1, l is 0 and this is a straightforward exponential. The radial function and the integral the square of this function; if you write the normalization constant, also if you write that, remember it is 2 by a naught to the 3 by 2, ok.

Therefore, if you do that, the integral that you have to worry about for radial probability is r square e to the minus 2 or by a naught as 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 a 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 goes like that. It is 0 at r equal to 0 the function 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 the probability distribution is that this is r square R square, the area of this for all that the end of this graph is equal to 1; that is a normalization.

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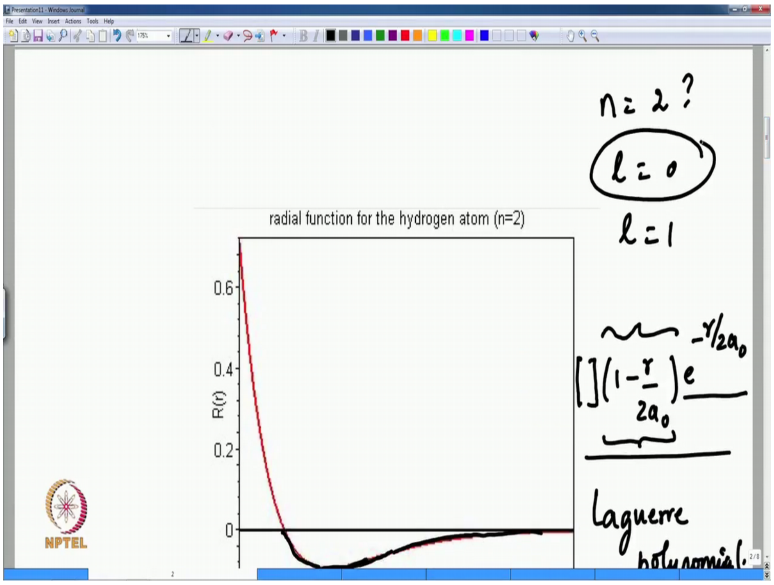

What about the radial function for the hydrogen atom at n equal to 2? There are 2 values l equal to 0 in the n equal to 1. So, if I have to look at to the l equal to 2, the functional form if you remember.

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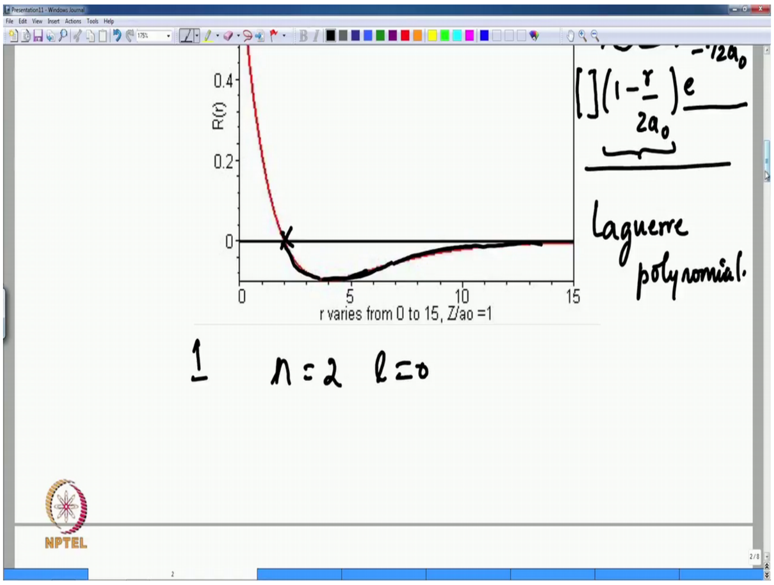

I wrote down is 1 minus r by 2 a naught e to the minus r by 2 a naught. You can see clearly that when r is 0 this is 1. So, you start with some number depending on what the constant in front of is that is a maximum here. But, at r equal to 2 a naught, as r increases from 0 to 2 a naught, you see that the function drops of 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 our greater than 2 a naught. This will increase because, this we 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 the Laguerre polynomial which are solutions for the radial equation ok. For l equal to this is the l equal to 0, I am sorry. This is the function for l equal to 0 and for l equal to 1 l 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; that is the normalization constants.

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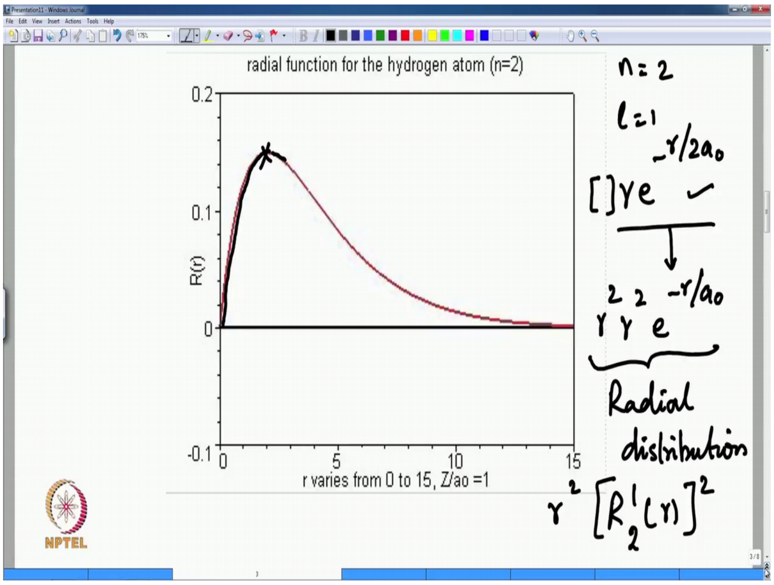

$n = 2$

$l = 1$

$[\ ]\, r e^{-r/2a_0}$ ✓

$$\downarrow$$

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

$r^2 [R_2^1(r)]^2$

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 or up to a point, there is a maximum and then the function is reducing due to the exponentially even though r is increasing, the exponential dominates. And therefore, the function goes back to goes to 0. What large values of r?

This is the radial function for n equal to 2 l equal to 1 and the radial distribution is r square multiplied by 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.

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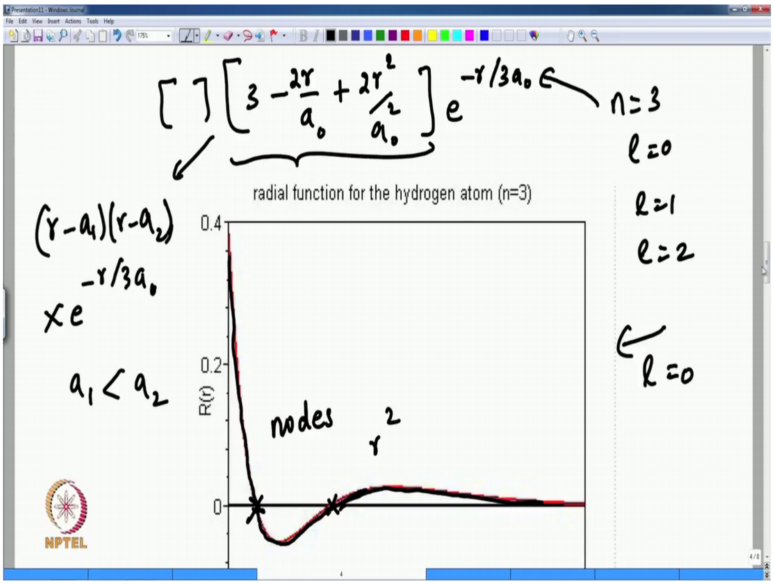

$$[\ ]\left[3-\frac{2r}{a_0}+\frac{2r^2}{a_0^2}\right]e^{-r/3a_0}$$

$n=3$

$l=0$

$l=1$

$l=2$

$l=0$

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

$a_1<a_2$

So, again the maximum that happens is quite far away from the 0, n is equal to 3 has 3 possible functions; namely l equal to 0, l equal to 1 and l equal to 2. This 1 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 square 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 ok.

The quadratic has 2 solutions both of which are positive and you can see that those 2 solutions are these; that is a quadratic goes to 0 for these 2 values of r. If you factor this out, this quadratic with the 2 roots, these are the 2 roots and you can see that when r is 0, the function is positive. It is non zero because of the 3 and the pre factor in front of with the normalization factor in front of it. It is somewhere here.

And then, as r increases, if you write this as the 2 roots, quadratic r minus a 1 times r minus a 2 times e to the minus r by 3 a naught and if a 1 is less than a 2, you can see 4 r less than a 1 or 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 of all, 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 by 3 a naught and for r greater than a 2 this is positive.

So, the function tends to increase as r square. However, e to the minus r by 3 naught eventually brings it down to 0, ok. So, it has 2 roots called nodes. Now, previous 1 has 1 node n equal to 2 l equal to 0.

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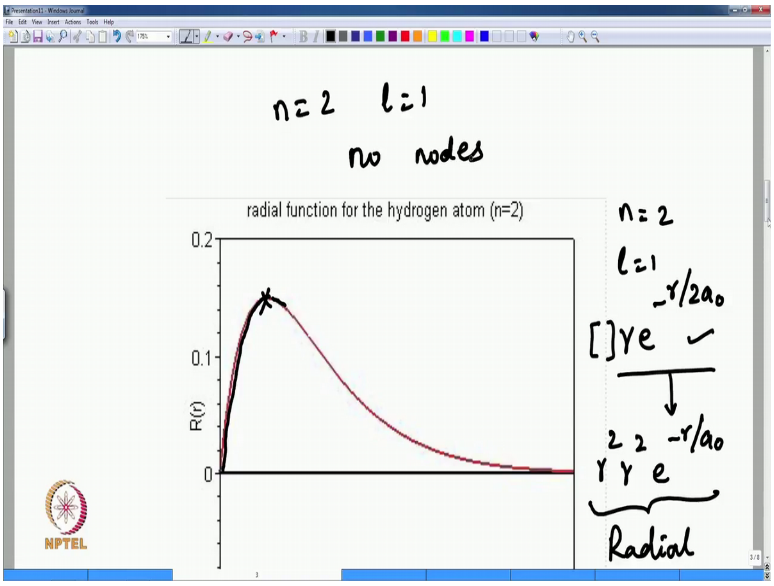

When n equal to 2 l equal to 1, no nodes.

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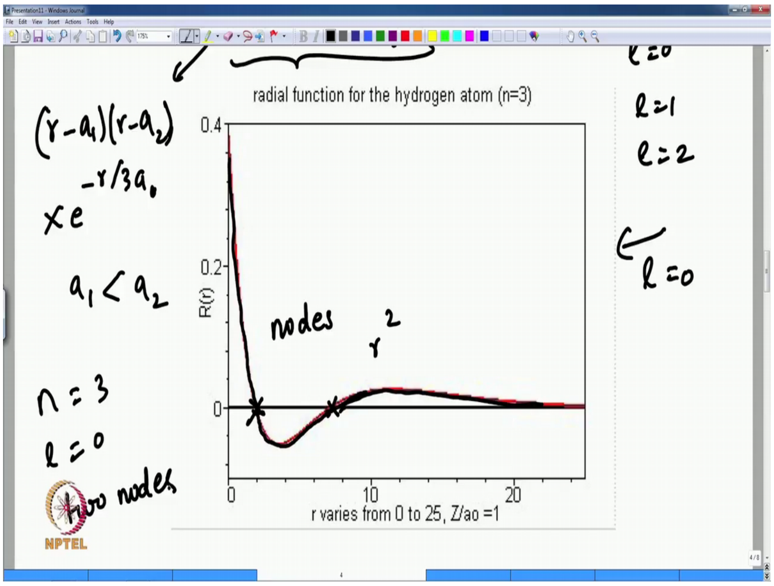

When m is 3 l is 0, there are 2 nodes.

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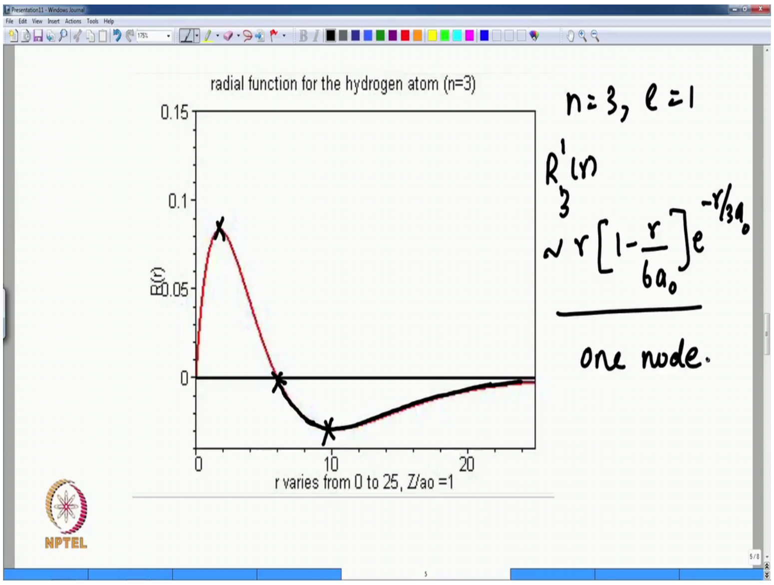

$n=3,\ l=1$

$R_3^1(r)$

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

one node.

When n is 3 and l is 1, the radial function turns out to be 3 1 of r turns out to be boring. The proportion, the normalization constant it is r times 1 minus or 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 when r is 6 a naught. So, between 0 and 6 a naught, the function increases we and at r equal to 6 a naught. It goes to 0.

As and for all values of r greater than 6 a naught, this whole thing is negative and you can see that the function will decrease r square ok, but the exponential of minus r by 3 a naught eventually brings it back to 0 ok. So, here is the maximum and then the function goes to 0 or, but only 1 node.

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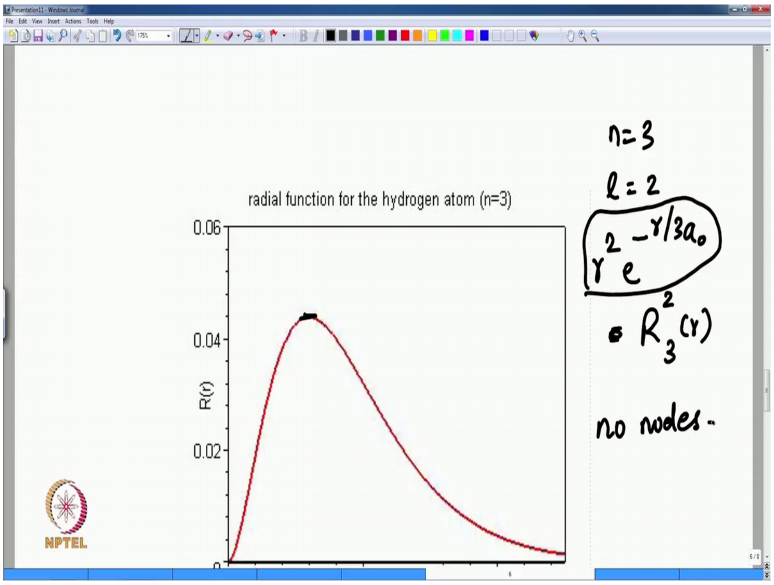

$n=3$

$l=2$

$$\boxed{r^2 e^{-r/3a_0}} = R_3^2(r)$$

no nodes.

And the last one when you look at n 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 mean, I have not put in the normalization constant. But, that is what it is and the r square has only 1 maximum and then the exponential eventually goes to 0, no nodes.

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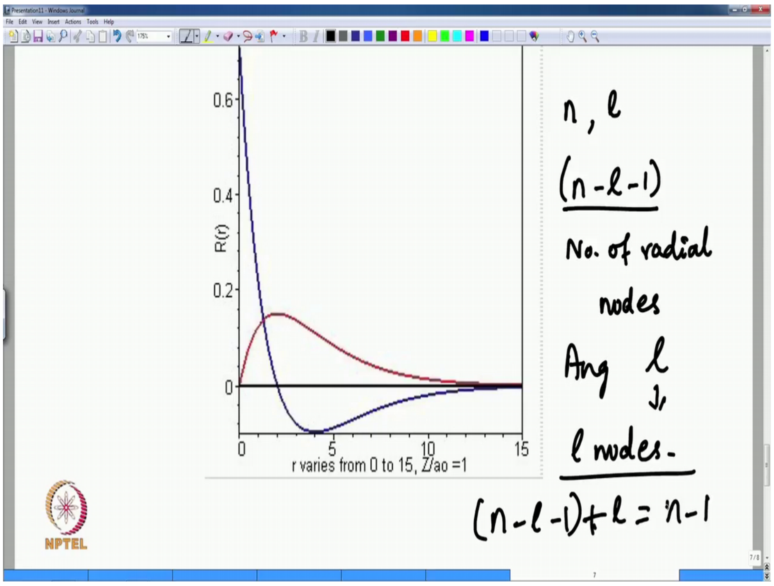

n, l

$(n-l-1)$

No. of radial nodes

Ang l

$\downarrow$

l nodes.

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

Therefore, the Laguerre polynomials which are therefore, for various values of n and l or 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 the when n is 1, n is 0, there are no roots, no nodes. When n is 2 l is 0; that is 1 node, no node. Then 2 1 0 then, n is 4, you have 3 2 0 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 minus l minus 1 plus l which is n minus 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 square.

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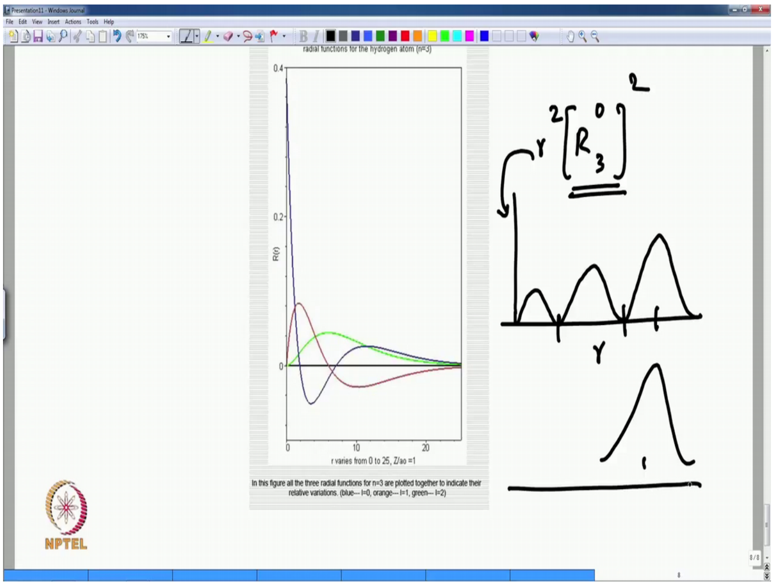

In this figure all the three radial functions for n=3 are plotted together to indicate their relative variations. (blue--- l=0, orange--- l=1, green--- l=2)

So, let me conclude by putting all these functions together for each value of n. So, this is for n equal to 2, the 2 functions are this is n equal to 0 and l equal to 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 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 or 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 closer to the Bohr radius ok. And the same thing happens for n equal to 3. The maximum is even shifted further and there are 2 nodes.

So, if you look at the radial square functions, namely the r square times 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 2 nodes corresponding to the points where this polynomial the radial function goes to 0.

And then, for 3 1, you will have 2 maxima and for 3 3 3 2 only 1 maxima, but the maxima's are all towards the farther side meaning that, the 3 s orbital is much more extended in space than the 2 s orbital. Then, 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 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 do not know the answer.

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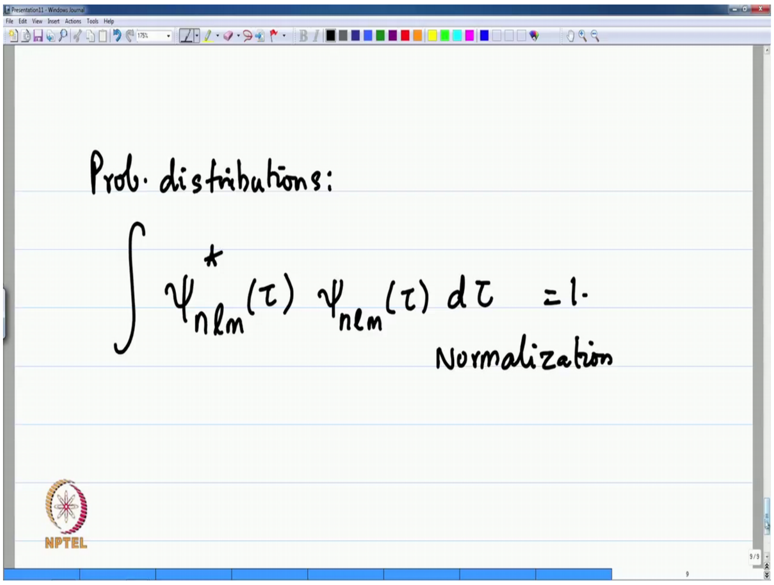

Prob. distributions:

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

Normalization

Let me conclude this lecture with a note on the probability statements. Probability distributions the wave function psi n l m's are chosen to be normalized wave functions. So, if I put all the 3 coordinates by the abbreviated symbol tau, then it is psi star n l m psi n l m tau d tau. The integral is equal to 1, this is normalization.

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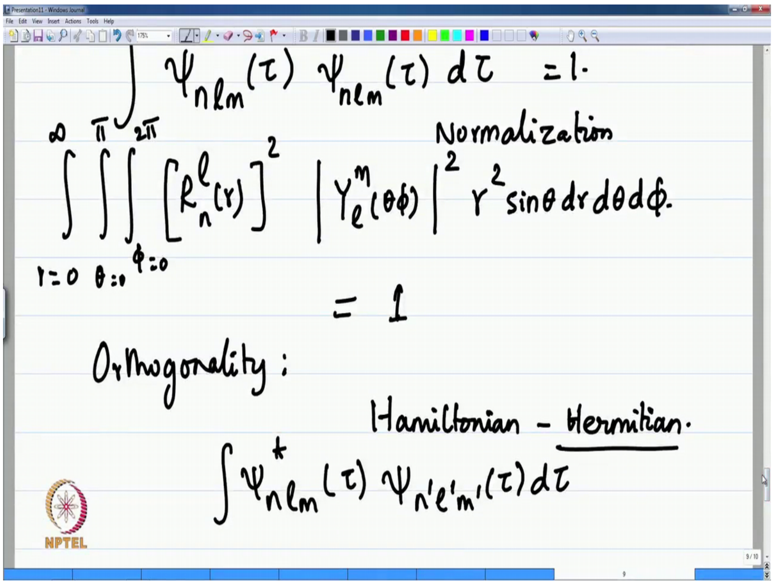

$$\int \psi_{nlm}(\tau)\, \psi_{nlm}(\tau)\, d\tau = 1.$$

Normalization

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

$$= 1$$

Orthogonality :

Hamiltonian - Hermitian.

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

From the functions given in the lecture notes, for the individual or n l's r's and the y l m the integral now takes the specific representation. As a triple integral or equal to 0 to infinity, theta is equal to 0 2 pi and phi is equal to 0 to 2 pi. You have the radial function square you have the absolute value of the spherical harmonics theta e squared absolute value multiplied by the detail which is r square sin theta d r d theta d phi, ok.

That is equal to 1 and the orthogonality of these wave functions as being solutions of a Hamiltonian which is a Hermitian. Hamiltonian, I have again introduced a new term called the Hamiltonian; as a Hermitian operator, which have real eigenvalues for all of all the eigenvalues are real, the Hamiltonian operator.

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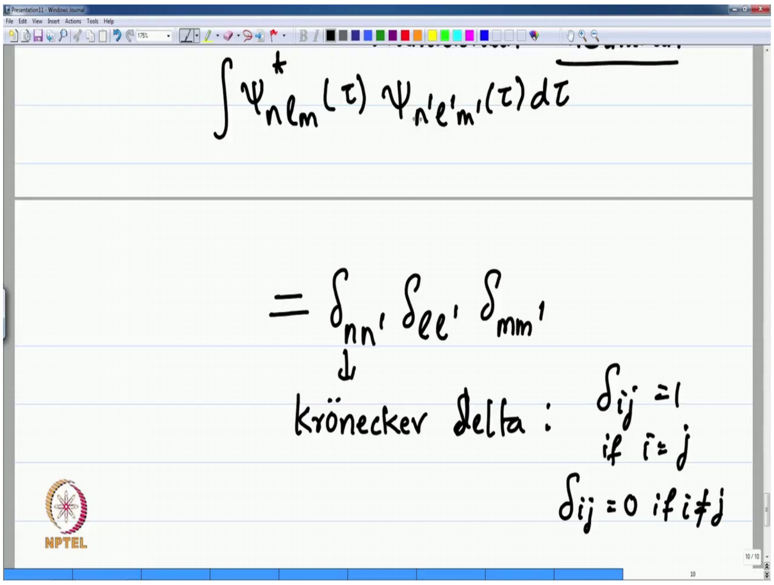

$$\int \psi^{*}_{nlm}(\tau)\,\psi_{n'l'm'}(\tau)\,d\tau$$

$$= \delta_{nn'}\,\delta_{ll'}\,\delta_{mm'}$$

$\downarrow$

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

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

The wave functions psi n l m tau psi is tau 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 n prime. This is kronecker delta.

Meaning, delta i j is 1 if i is equal to j delta i j is 0 if i is not equal to j. Therefore, if n is not equal to n prime, if l is not equal to n prime, if m is not equal to n prime any one of them any pair of them, if they are not equal the wave function is they are wave functions are orthogonal.

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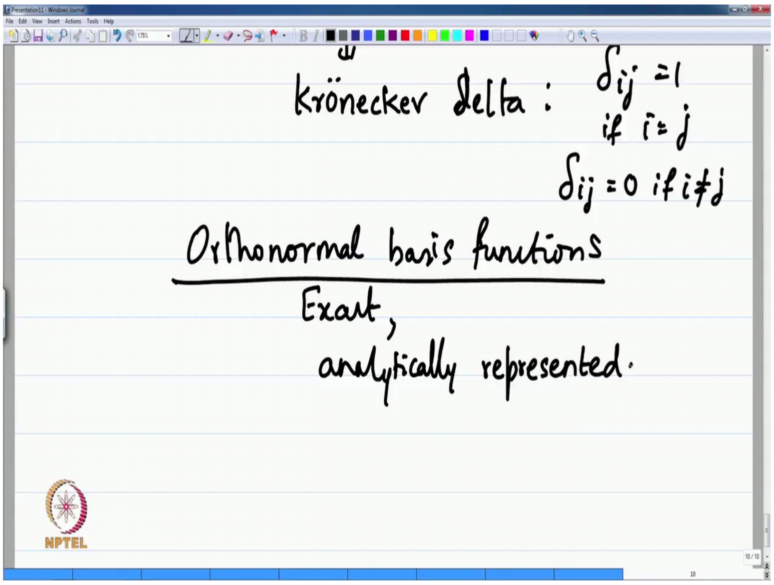

Kröneckev delta : $\delta_{ij} = 1$ if $i = j$

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

Orthonormal basis functions

Exact,

analytically represented.

And therefore, the wave functions being already normalized or thus known as orthonormal basis functions or 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, as representing the wave functions for any other atom or any other system of nuclei 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 atom which has more than 1 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 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 probability is the radial distributions. All these things enhance one's capability in using similar mathematical techniques and tools in the understanding of atoms that 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 far as this elementary introduction to hydrogen atom is concerned, until then.

Thank you very much.