

Engineering Chemistry - 1

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Module 1: Atoms and Molecules

Lecture - 9

Hydrogen Atom: Part 4

(The Angular Solutions continued)

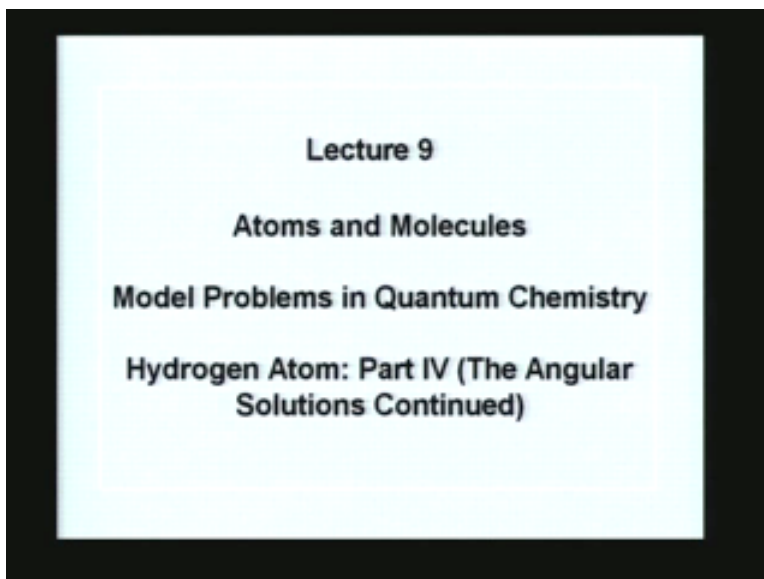
Welcome to the lecture series on chemistry under the National Programme on Technology Enhanced Learning. We have heard a number of lectures on the atoms and molecules from the fundamental point of view namely the quantum chemistry and how we understand them from the principles of quantum mechanics.

This is a continuing series of lectures and today it is 9th lecture. The lecture continues on what we had done earlier that is the Hydrogen atom. The solutions of the Hydrogen atom using the Schrödinger equation are the fundamental equations for matter at the atomic and sub atomic levels just as the Newton equations describe matter at a large scale, at the terrestrial and extra terrestrial scale. We have to follow the solutions of the Schrödinger equation and wherever possible we should also derive the results of the Schrödinger equations.

But considering the limitations on the course as well as the mathematical background required for the students, we are continuing to look at the solutions of the Hydrogen atom. We will continue with that in today's lecture and will hopefully complete the Hydrogen atom part today.

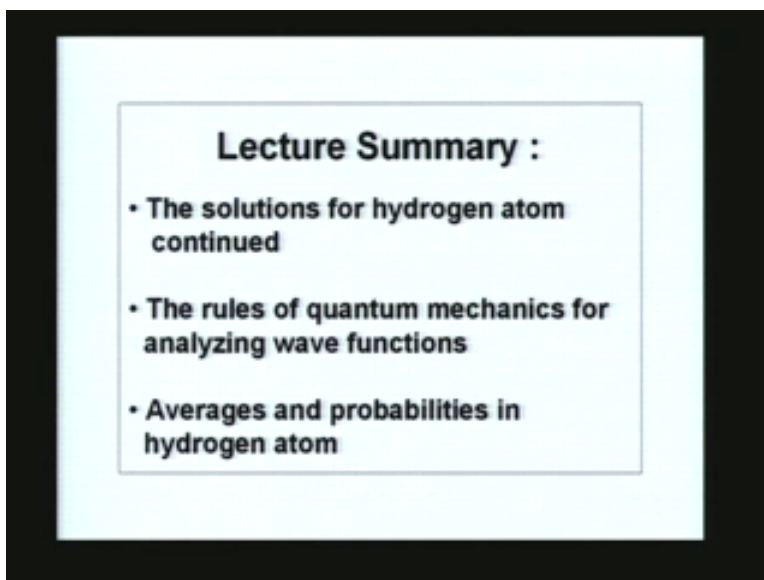
The series is by the support of the National Programme on Technology Enhanced Learning by the Ministry of Human Resource Development and I am in the Department of Chemistry, Indian Institute of Technology Madras.

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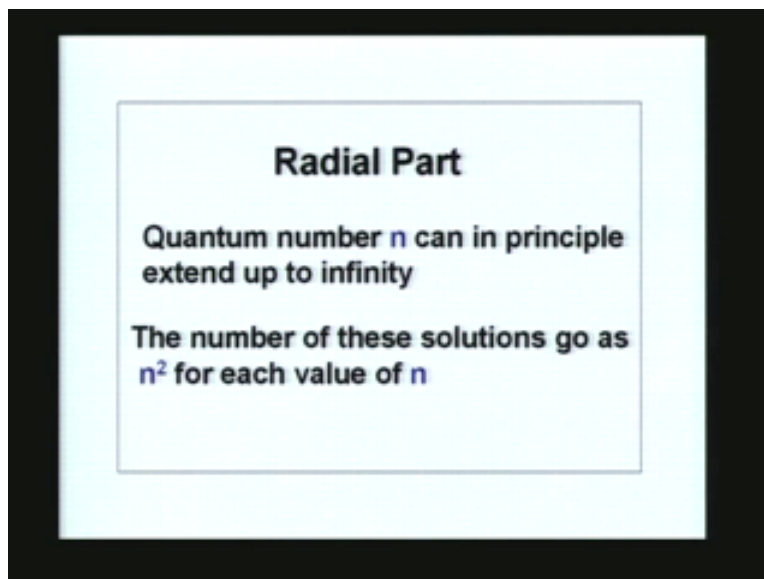
The lecture today continues on model problems in Quantum Chemistry and we look at the angular solutions as well as the overall solutions of the Hydrogen atom today.

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So summarizing the contents of this lecture will give you an overview. We will continue to look at the solutions of the Hydrogen atom. We will go back and look at the rules as given by Quantum Mechanics for analyzing wave functions and if possible we will also indicate the how to calculate the averages and probabilities in Hydrogen atom.

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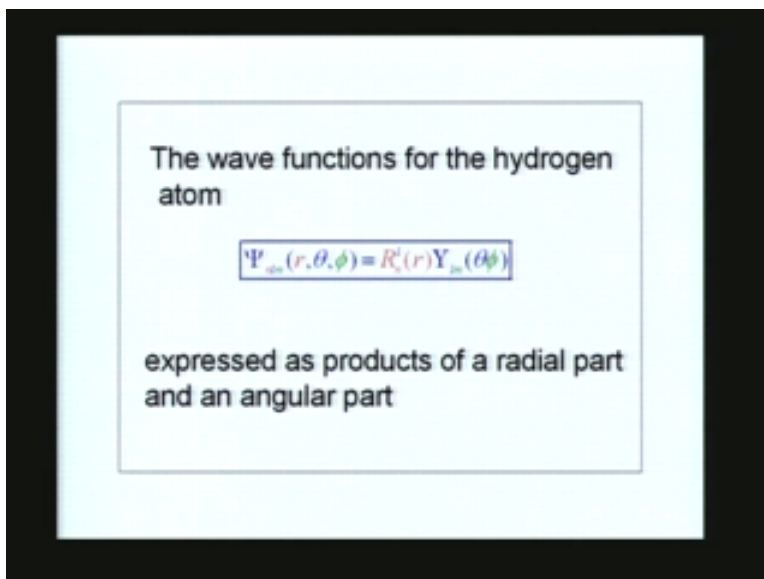
So let us look at the solutions. Let us review the solutions again. We remember that the Hydrogen atom had a wave function which was divided into two parts a radial part and an angular part. The radial part described the distribution of the wave function as a function the radial distance from the nucleus.

The angular part described how the wave function looks like. How the squares of the wave function will be on a sphere of any given radius. Of course any point on the surface of the sphere is described by two angles with reference to the polar axis. So we had the radial coordinate r , we had the θ the angular coordinate as well as the ϕ coordinate.

The radial coordinates and the solution for the radial part gave as a quantum number n and in principle the value of this quantum number can be 1, 2, up to ∞ .

Then number of such radial solutions as we obtain for any given value of n is n^2 for each value of n . This was the summary of the last two lectures with details.

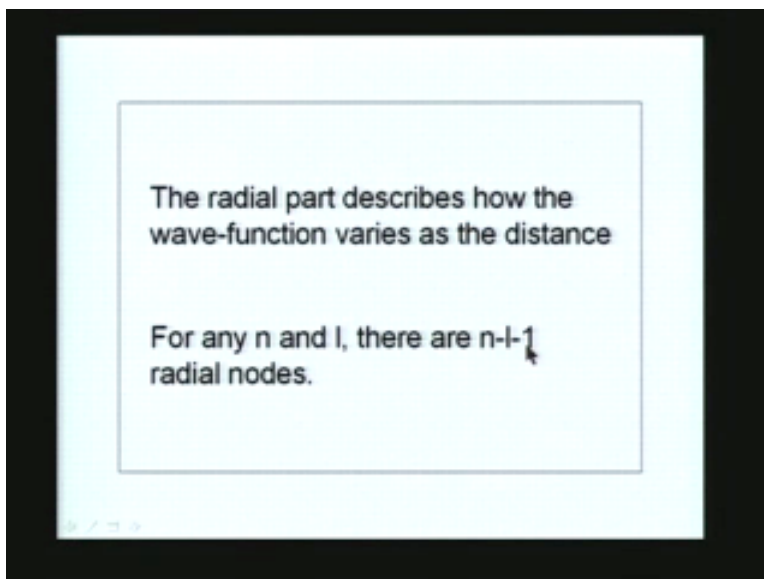
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The wave function for the Hydrogen atom was the product of both the radial and the angular part as you see here. The overall wave function is described by three quantum numbers. The n being the principle quantum number and l and m being the quantum numbers which are the result of the solution of the radial as well as the angular part subject to the constraints and the angular solutions was known as the spherical harmonics the values of m and l were described earlier as l being 0, 1 up to $n - 1$ and m being from $-l$ to $+l$.

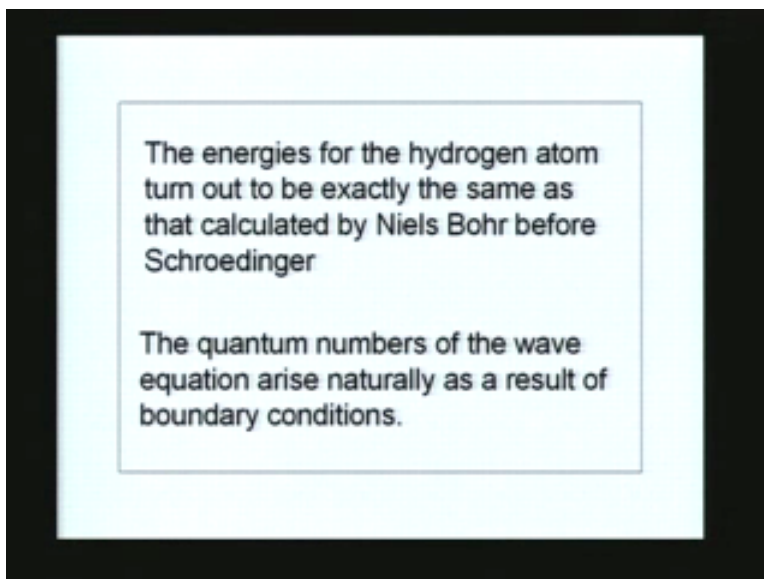
The radial part obviously describes the wave functions as it varies with the distance and the radial function, if you recall from the previous solutions had certain nodes or certain **zero's** and the number of such zero's for the radial solution is $n - l - 1$.

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Thus if you take a 1s orbital the n value is 1, the l value is for the s corresponding to $l = 0$ and therefore there are no radial nodes for the 1s orbital because it is $1 - 0 - 1$. You can compute the radial part the radial nodes using this formula.

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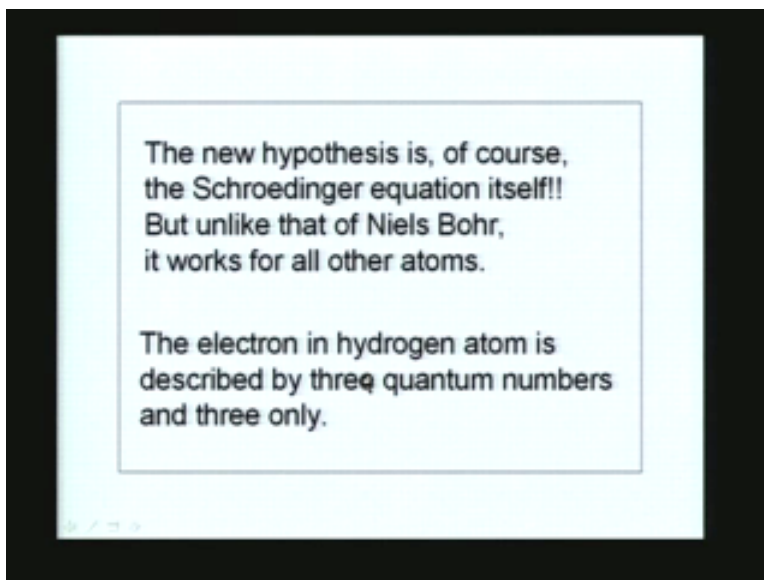


The energies for the Hydrogen atom which is obtained by solving the Schrödinger equation of course comes out to be exactly the same as the energies that were described or that were derived by Neils Bohr without the Schrödinger equation. That is not a surprise because the energies that you obtain as solutions for the Hydrogen atom have to be such that they should satisfy the experimental data obtain in line spectra of the Hydrogen atom.

If you remember the series such as the Lyman series, the Balmer series, the Paschen series, the Brackett series and the Pfund series these series were there as experimental data much before the quantum mechanics described the results. Therefore it is imperative that any new mechanics either that of Neils Bohr or that of Schrödinger or of Heisenberg or any other mechanics accurately accounts for this experimental fact and it is no surprise that the solution of Hydrogen atom given by Schrödinger turned out to be exactly the same as far as the energies are concerned as calculated by the Neils Bohr formula but with one difference.

Neils Bohr had to introduce this as an arbitrary ADHOC facts, I mean he called them as facts as required. These are the assumptions which were required. The assumptions is that the energies of the electron do not vary as long as the electrons are in certain orbit and only when the electron jumps from one or the other orbit either emits or its absorbs radiation. Now this was a constraint proposed by Neils Bohr to describe the overall solution. In the case of Schrödinger equation there is no such artificial constraint you have to believe that the Schrödinger equation works and if it works and if the wave function have to satisfy the boundary conditions as is required for differential equation then the solutions come out naturally and the quantum numbers of this wave equation therefore arise naturally as a result of the boundary conditions.

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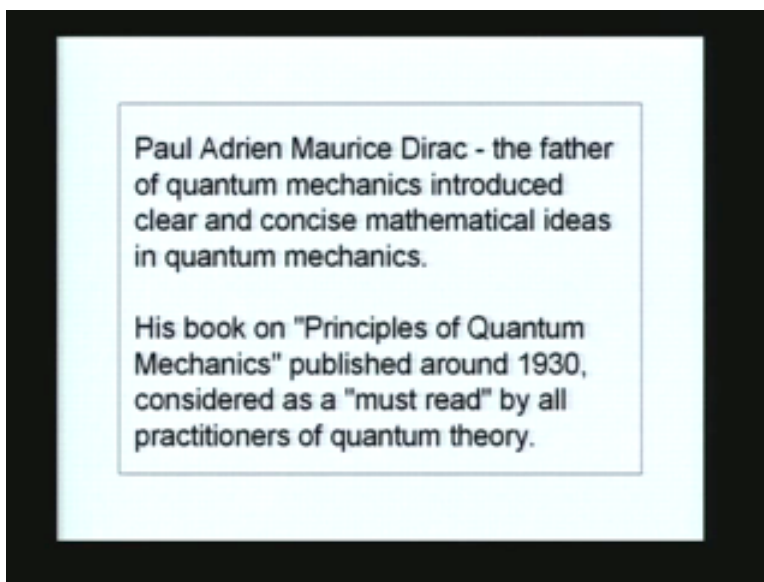
So what is this, in effect it is a new hypothesis. Instead of Neils Bohr condition now we have the Schrödinger hypothesis is, the Schrödinger equation itself. But with a very major difference namely that the Schrödinger equation works for all the other atoms. Neils Bohr formula works for only Hydrogen atom.

The hypothesis is it is still a hypothesis but it is definitely more useful in the sense that it is useful for studying a much larger set of phenomena and in fact all of Chemistry ever since 1927 seem to have centered around the solution of the Schrödinger equation as far as obtaining the

properties of atoms from *an ab initio* that is from the beginning without doing any experiments if you want to calculate them the Schrödinger equation seems to be the equation. The electron in the Hydrogen atom is obviously described by 3 quantum numbers only. And please note here that spin is not a part of the Hydrogen atom model that Schrödinger gave.

The spin was there earlier but it was an ADHOC proposition by [Pauli](#) and spin quantum number is a 4th quantum number that was introduced by [Pauli](#) and with that the Hydrogen atom picture the electron wave function picture is complete. But spin is not part of the Schrödinger equation that was originally used to solve the Hydrogen atom problem.

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[Accounting](#) of the spin into the Schrödinger equation came later by Paul Adrien Maurice Dirac, an English Physicist, Mathematician and he is often considered the father of quantum mechanics. He introduced a very clear and a concise mathematical picture for Quantum Mechanics and it is his work which includes spin which derives the spin as natural 4th quantum number and therefore with the relativistic mechanics that Dirac introduced in the solution of Hydrogen atom equation this process was complete.

It is important to point out here that the book was published by Dirac in 1930 and was revised a little later around 1959 or so. This book is still one of the most important works ever to have been written in Quantum Mechanics or about Quantum Mechanics and the title is “Principles of Quantum Mechanics”. It is very essential for students to read such books.

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How do we identify the hydrogen atom wave functions as

$$\Psi_{nlm}(r, \theta, \phi) = R_l^n(r) Y_l^m(\theta, \phi) \quad ?$$

1. Check for the radial part: The exponential e^{-Zr/na_0} contains **n**. The principal quantum number associated with the wave function is that **n**.

Now let us examine the wave functions a little more closely together. We were looking at the radial part before. We were looking at each one of the angular part before. Now we are going to look at both of them together. So let me rewrite the formula as you have here. (Refer Slide Time: 12:03 min)

The overall wave function as you recall is $\Psi_{nlm}(r, \theta, \phi) = R_l^n(r) Y_l^m(\theta, \phi)$ which is the formula that you see here. Now the radial part contains an $\exp(-Zr/na_0)$ where **n** is the principle quantum number and a_0 is a constant known as the Bohr radius approximate value is 0.53 \AA .

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$$\Psi_{nlm}(r, \theta, \phi) = R_l^n(r) Y_l^m(\theta, \phi)$$

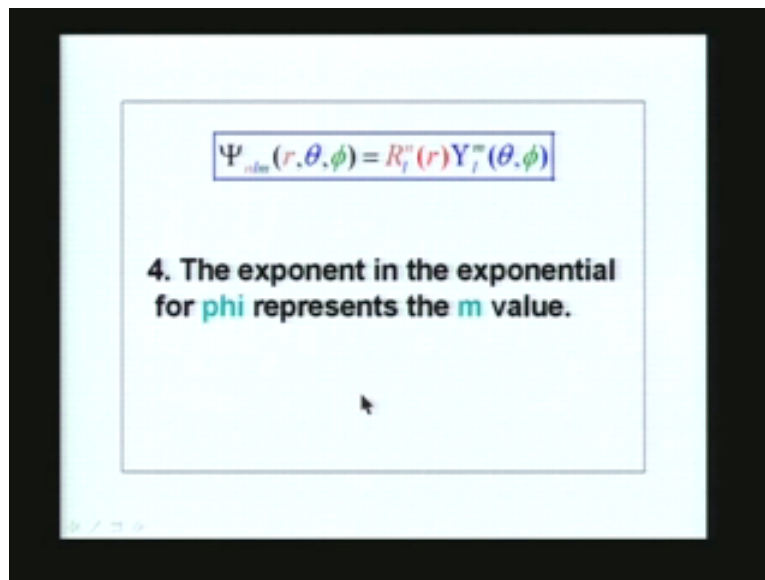
2. If the radial part does not become zero at $r=0$ then it is an **s** function, i. e., **l=0**

3. The radial part has the form $r^l (n-l-1^{\text{th}} \text{ order polynomial in } r)$ then **l=1** means p, **l=2** means d etc.

The $\exp(-Zr/na_0)$ approximate value is 0.53\AA . It contains a quantum number n which is a principle quantum number. The radial part does not become zero at $r = 0$ then it is an s function i.e. $l = 0$ for the s function.

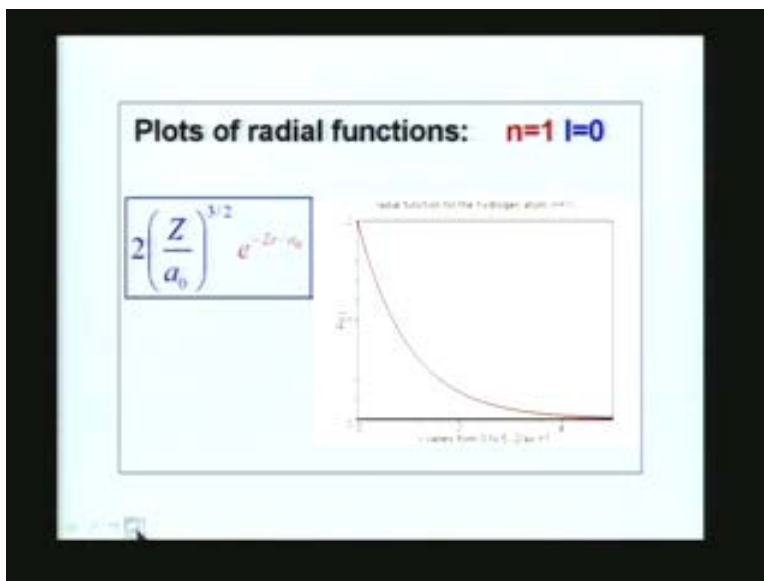
The radial part if it has the formula so that the r raised to some power l where l is the orbital angular momentum quantum number. The r raised to l and multiplied by a polynomial which is $(n - l - 1)^{\text{th}}$ of order then it is a radial function of any specific value n and l . So $l = 1$ means p which means it is r and $n - 2$ the power. When l is 1 this is $n - 2$ is the order of the polynomial multiplied by r that is a p orbital and then $l = 2$ means d orbital and so on.

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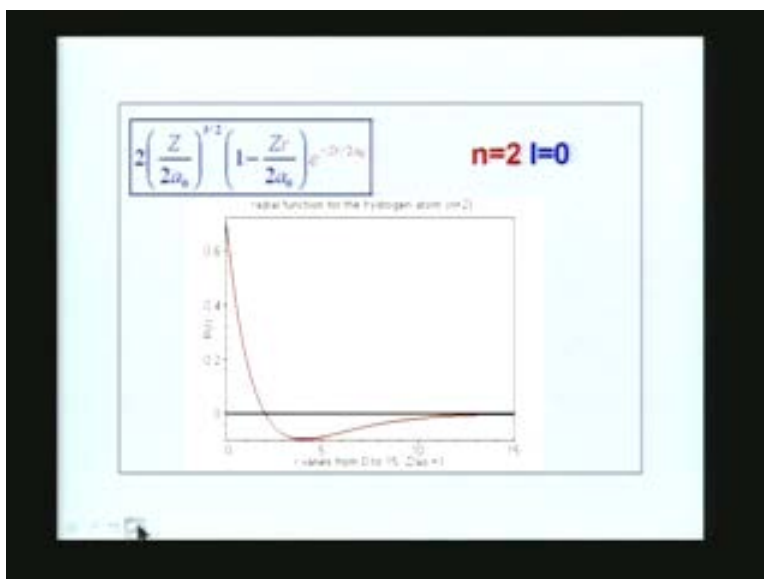
So the functional form of the radial part the functional form of the radial part can be an indication of the quantum number and the type of the orbital that one is interested in.

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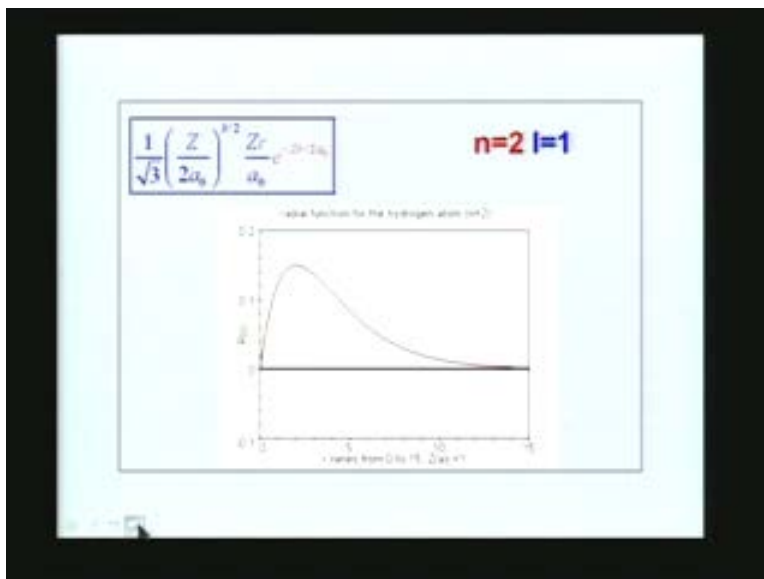
Let us look at the radial function one after the other and then we will look at the radial function square. First let us plot the radial functions for the several values of $n = 1, 2, 3$ etc with the appropriate values of l . The ground state or the state with the least amount of energy, $n = 1$ is the first state and then $l = 0$ is the only possible value. The radial part is exponential $-Zr/a_0$ times the constant. If you plot this as a function of r , this is nothing other than an e^{-r} . It is an exponential which drops off to zero as r goes to infinity. But the point to remember is that the function is not zero at $r = 0$.

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The next one, when you plot this at $n = 2$ and $l = 0$ you see that there is a $(1 - Zr/2a_0)$ which is a monomial and then $\exp(-Zr/2a_0)$. When you plot this function at $r = 0$ this function is again nonzero you start from somewhere and it goes to 0 when this part becomes 0 that is $Zr/2a_0 = 1$ that value of r is given by that and for any value of r greater than that this function is negative but it keeps on going and you see that it is brought back to 0 by the exponential. So this is the radial function for $n = 2, l = 0$.

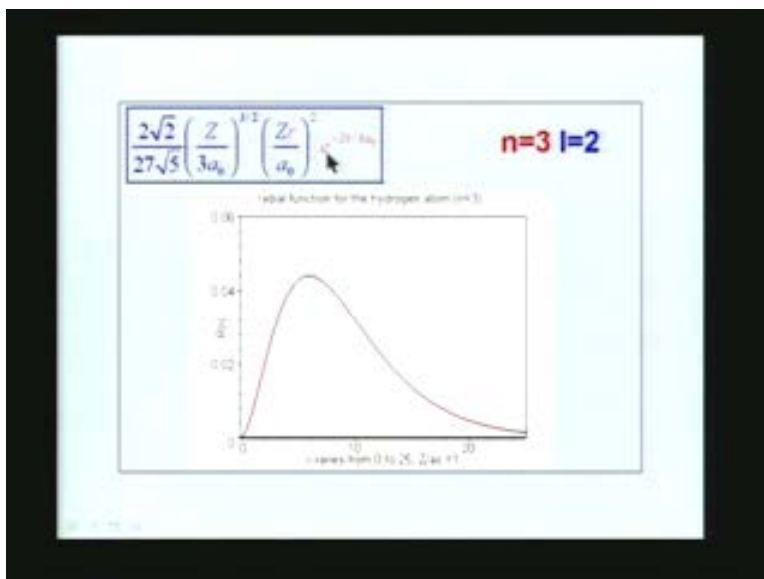
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Likewise for $n = 2$ and $l = 1$ you have r^1 which is $l = 1$ here so it is r^1 and the polynomial goes to 0 because l is 2 and n is 1 so $n - l - 1$ is 0. Therefore there is no polynomial here only r and the $\exp(-Zr/2a_0)$ and you see that this has a simple function that r increases then exponential decreases. So there is a competition and after a maximum the exponential brings everything back to 0. This is the radial function for $n = 2, l = 1$ for 2p type of orbitals.

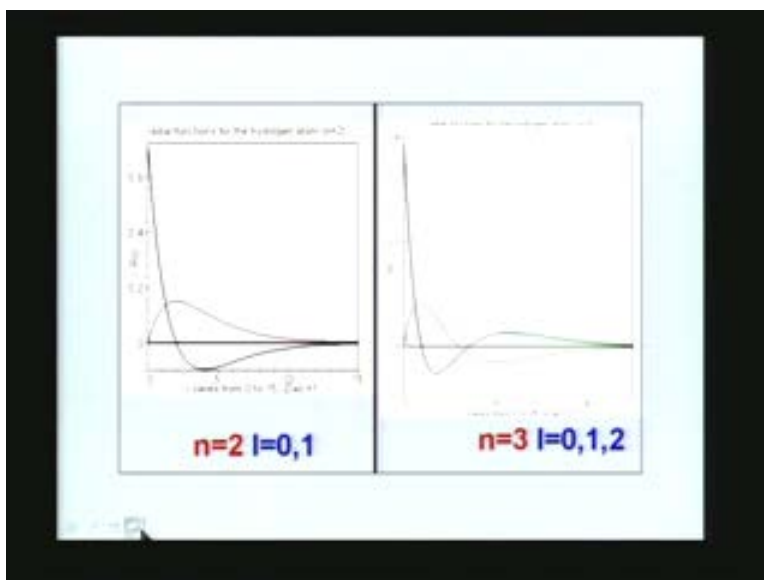
When $n = 3, l = 0$, it is 3s orbital and you see that r raised to 1 and l is 0 there is a quadratic function here which is a constant times r and an r^2 and an exponential. (Refer Slide Time: 16:46 min). This quadratic has two zero's, two roots where the function goes to 0. Those two roots are the two points when you plot them. When you put $r = 0$ this is nonzero you start again from a nonzero value for the radial function and then the exponential. These two roots and then the function goes to 0 because of the exponential. So you see that there is an alternating sign for this wave function. Will do just two more of them are $n = 3$ and $l = 1$ corresponding to 3p that is r^1 and then $n - l - 1$ which is obviously a polynomial of degree 1. The $\exp(-Zr/3a_0)$ and you see that this goes to 0 only once and this never goes to zero except that infinity. So you have one node the radial node is 1 node for $n = 3, l = 1$ and the function goes like this.

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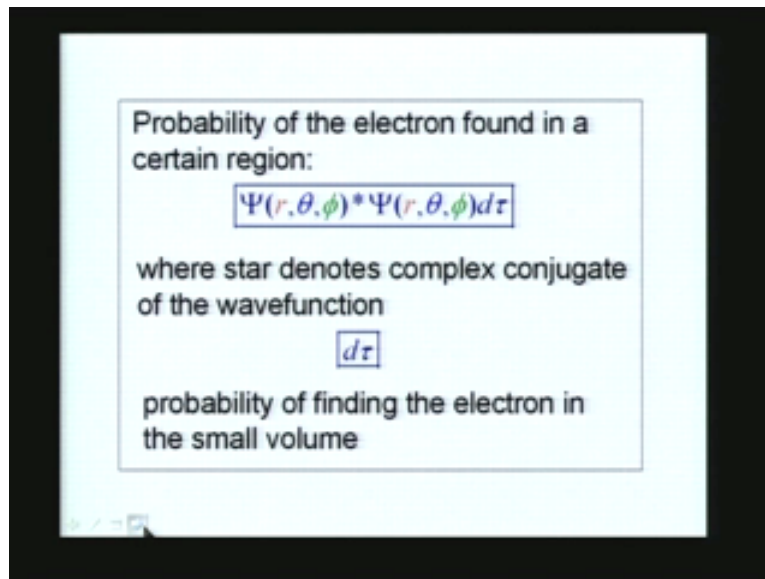
The last one $n = 3$ and $l = 2$ the expression is $r^2 \exp(-Zr/3a_0)$. It never goes to 0. It starts with a zero and you see that this is a straight forward plot of the $r^2 \exp(-Zr/3a_0)$.

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So if you put all these plots together for a given value of n you see that there is a radial function which is this is a 2s and this is a 2p. The curve with two radial nodes is a 3s, the curve with one radial node is a 3p and a curve with no radial node is a 3d. You have to remember that the radial nodes decrease as you go from s to p to d etc. because it is $n - l - 1$. So as l increases the number $n - l - 1$ keeps on decreasing until it becomes zero. So the picture also tells you where the radial nodes are for a given value of n relative to each other. Now all of this is for the radial function.

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Then we also know that the wave function itself does not have an interpretation. There is no physical interpretation for the wave function. It has to be because otherwise we have a problem. You have a wave function which starts off with a nonzero value at $r = 0$. What does it mean? That means the electron **is** has a finite I mean some function at the nucleus. It does not make sense. The wave function is not to be interpreted but it is the absolute square of the wave function which is to be interpreted as a probability density. So what is exactly is the formula. For this wave function what is the probability interpretation.

The function $[\Psi_{nml}^*(r, \theta, \phi) \Psi_{nml}(r, \theta, \phi)]$ This is for any value of n, l, m since n, l, m same ones r, θ, ϕ product that is the function and its complex conjugate multiplied or the absolute square of the wave function \times over a small interval of space let me call them $d\tau$ here, gives you the probability of finding the electron in that space $d\tau$ where this $d\tau$ is sent at some value of (r, θ, ϕ) . It is $r + dr, \theta + d\theta$ and $\phi + d\phi$ in the small region.

What is the probability of finding the electron **in that small region** is the only interpretation that can be given by the presences of this wave function by the solution of the Schrödinger equation and this **'*'** is extremely important here because you remember that the spherical harmonics which part of the Hydrogen atom solution has complex quantities in them. Therefore if you forget the **'*'** you are going to make mistakes. Any real number can be obtained from a complex number by taking the absolute square of the complex number and here probabilities are real can be measured. Therefore they have to be interpreted and this interpretation was due to Max Born and in fact Schrödinger himself did not make such an interpretation for the wave function but it was Max Born who did that several year later. Now with that sort of an interpretation what is the $d\tau$.

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A digital blackboard with a white border and a toolbar at the top. The equation
$$\left[\psi_{nlm}^*(r\theta\phi) \psi_{nlm}(r\theta\phi) \right] \times d\tau$$
 is written in white. The term $d\tau$ is circled.

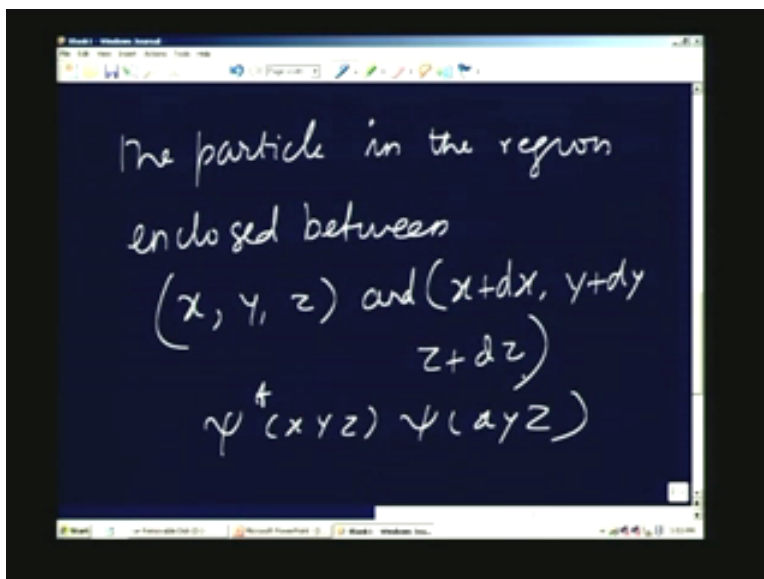
Supposing we were to write the wave function as $\psi^*(x y z) \psi(x y z)$ Then it is very clear to us that what is $d\tau$. You recall the particle in a 1D and the 2D box. The $d\tau$ was something like a dx . Let me write $d\tau$ here and $d\tau$ is like a $dx dy dz$ which is a volume element.

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A digital blackboard with a white border and a toolbar at the top. The equation
$$\psi_{nlm}^*(x y z) \psi_{nlm}(x y z) d\tau$$
 is written in white. Below it, the definition
$$d\tau = dx dy dz$$
 is written, with $d\tau$ circled.

What exactly does this mean? This means the probability of finding the particle in the region enclosed between x, y, z and $x + dx, y + dy$ and $z + dz$. That is if you draw a small rectangular volume element from x to $x + dx, y$ to $y + dy, z$ to $z + dz$ as the appropriate sides. The probability of finding the particle in that volume element is given by $\psi^* \psi$ that is the only interpretation given.

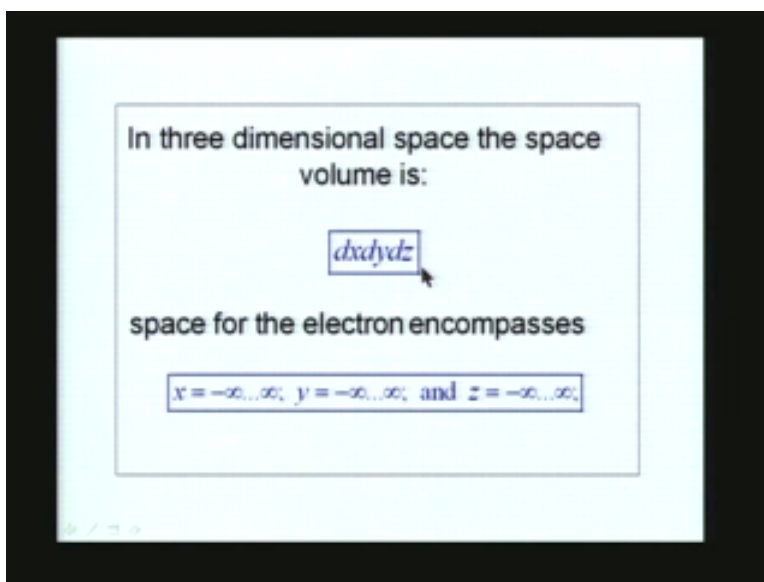
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Now, in Cartesian coordinates the volume elements are easy to write. The $d\tau$ is as I wrote $dx\,dy\,dz$. But in the case of spherical coordinates the $d\tau$ is not the $dx\,dy\,dz$ but elementary mathematics tells us that it is $r^2 dr\, \sin\theta\, d\theta\, d\phi$. This is the volume element in spherical coordinate system.

It is $r^2 dr\, \sin\theta\, d\theta\, d\phi$ but it is not $r^2 \sin\theta\, dr\, d\theta\, d\phi$. Please remember this. Now this r^2 will play a critical role in our interpretation of the radial function in terms of the probability density. So let us look at the slide. (Refer Slide Time: 22:52 min) I have said that the '*' denotes the complex conjugates. So $\psi^*\psi$ is the probability of finding the electron in the region $d\tau$ and in 3D space I also said that $dx\,dy\,dz$ is the volume element.

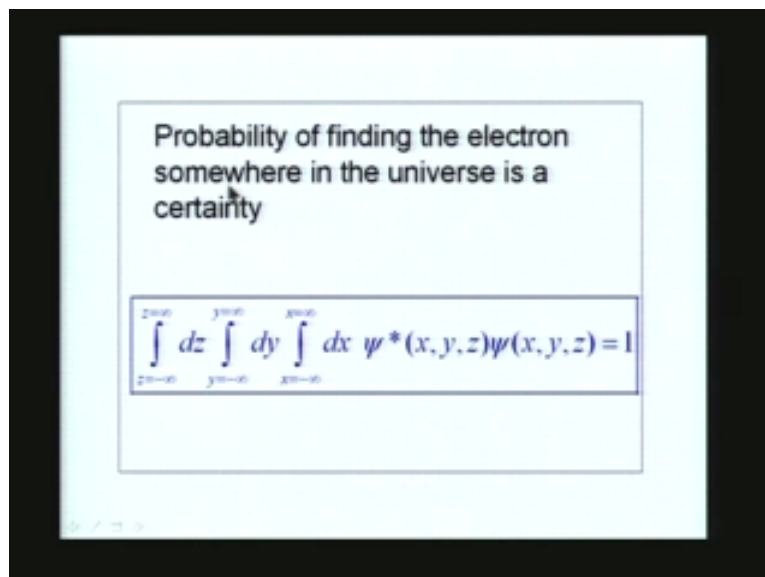
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What is the space for the **electron**? It is all the way from $-\infty$ to $+\infty$ for the x, y and z. That is entire universe but however if the entire Universe does not really make sense for us because you remember that there is a fundamental unit which governs the exponentials. The exponentials are $\exp(-r/a_0)$ where a_0 is the bore radius 0.53\AA . Therefore if r is about $5a_0$ that is five times the bore radius the factor is e^{-5} , and this e^{-5} decreases, it's pretty close to zero and e^{-10} is even closer to 0. Therefore even though this mathematical limit is required for us to do the interpretation of the electron probabilities in consistent to the mathematical description We do not really need large values of x, y, z because of the fact that the exponential is tapered of by the values of a_0 the bore radius.

Therefore the universe the electron can be anywhere in the universe but it is likelihood of being far away from the Hydrogen atom. If that electron where to be near of the Hydrogen atom and if it is to be far away from the Hydrogen atom the probabilities in these two cases will be quite drastically different i.e., anything more than 10 atomic radii. We do not have to worry about the electron as electron belonging to that atom or to that nucleus. But this mathematical limit is something that you have to keep in mind. **It is a sort of not an arbitrary limit**. It is required to do the algebra but it is not very meaningful in practical interpretation.

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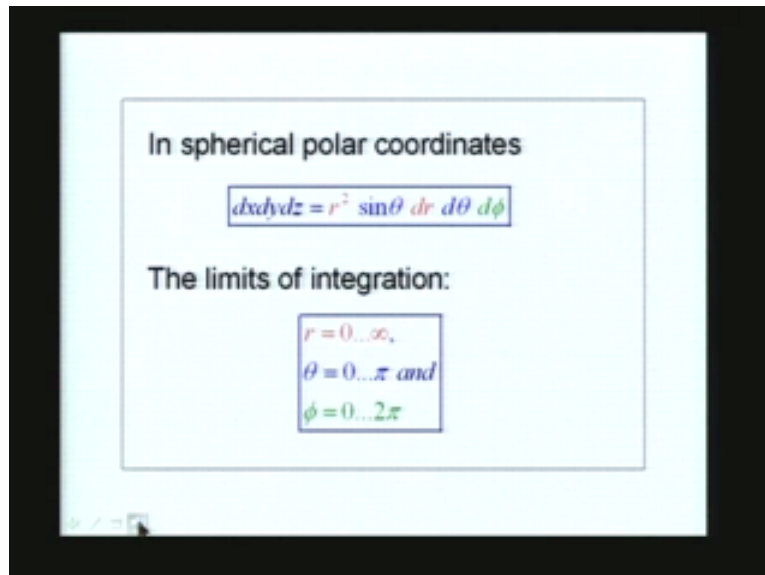
Probability of finding the electron somewhere in the universe is a certainty

$$\int_{z=-\infty}^{z=\infty} \int_{y=-\infty}^{y=\infty} \int_{x=-\infty}^{x=\infty} \psi^*(x, y, z) \psi(x, y, z) = 1$$

What is the probability of finding the electron anywhere in the **Universe**? Obviously you know if the electron was there with the Hydrogen atom to begin with, it's going to be in the universe all the time somewhere. Therefore the overall probability is when you say the integrals $\int dz \int dy \int dx$, all these means is that you are adding this probabilities for every possible values of x, y and z. (Refer Slide Time: 26:23 min) Integration means addition for continuous variables x, y and z. Therefore when you add all these probabilities it has to be 1. So this is the conservation of the total number of electron with the Hydrogen atom. The electron and the nucleus were to be

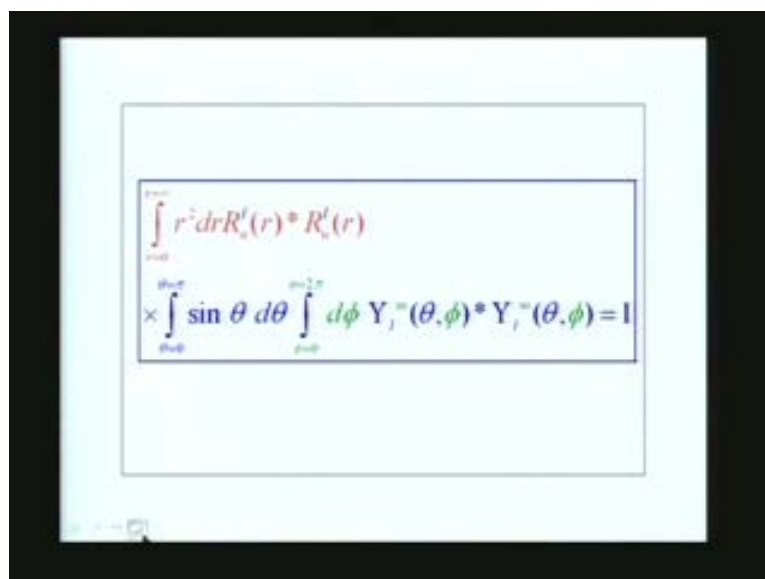
studied in the beginning the electron remains through out. The total probability of finding the electron anywhere in the universe is a certainty or is 1.

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In spherical polar coordinates as I told you that integration now takes a different form. The $dx \, dy \, dz$ is now replaced by $r^2 dr \sin \theta \, d\theta \, d\phi$ and the limits of integration are now for the radial coordinate r is between 0 and ∞ , it refers to the sphere and the θ coordinate is between 0 and π and the ϕ coordinate is between 0 and 2π . Therefore we can easily rewrite this mathematical statement namely the integrals $\int dz \int dy \int dx \, \psi^*(x \, y \, z) \, \psi(x \, y \, z)$ in between $-\infty$ to $+\infty$ in all these 3 cases is equal to 1 using spherical polar coordinates namely.

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We will write it in this form. Let us write this slowly using this formula for $d\tau$ we can write the integral $\iiint \psi^* \psi d\tau$ as $\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \psi^*(x, y, z) \psi(x, y, z)$ where r goes from 0 to ∞ and θ goes from 0 to π and ϕ goes from 0 to 2π

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$$\iiint \psi^* \psi d\tau$$

$$\Rightarrow \int_{r=0}^{\infty} r^2 dr \int_{\theta=0}^{\pi} \sin\theta d\theta \int_{\phi=0}^{2\pi} d\phi$$

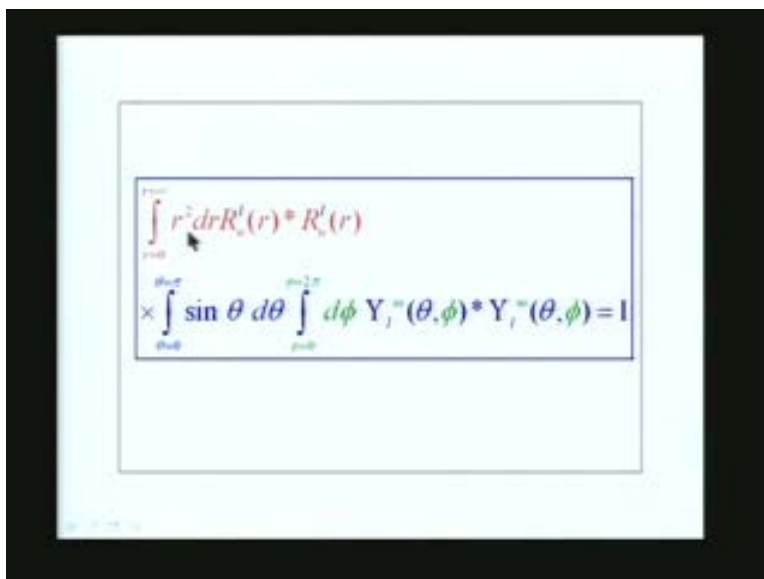
This is the probability interpretation in spherical coordinates and the probabilities because we are calculating over the entire universal universe and this is equal to 1. Now you see that we are able to write the integral as a dr , $d\theta$ and $d\phi$ and we know the functional forms for the ψ^* and ψ in terms of the r and θ and ϕ . You know this is given by the radial function and this is given by the angular function spherical harmonics. (Refer Slide Time: 29:09 min) Therefore it is possible to these integrals fairly easily. So let me just complete this part by writing $\psi_{n l m}$ as $R_n^l(r)$ of the radial coordinate and $Y_l^m(\theta, \phi)$ as the angular coordinate therefore the overall triple integral that you had is written as an integral involving a radial part and an integral involving the angular part which you can write as r goes from 0 to ∞ now you have to take $\psi^* \psi$ which means $[R_n^l(r)]^* [R_n^l(r)]$, so this is the radial part of the integral $\int r^2 dr \psi^* \psi$ but containing only the radial part. This is everything that depends on the radial coordinate. Therefore this is the integral that we need to evaluate as far as the radius coordinate r is concerned.

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The image shows a digital screen with handwritten mathematical equations. The first equation is $\Psi_{nlm} = R_n^l(r) Y_l^m(\theta, \phi)$, where $R_n^l(r)$ and $Y_l^m(\theta, \phi)$ are circled. Below this, an arrow points to the integral $\int \int \int r^2 [R_n^l(r)]^* [R_n^l(r)] dr$, with the lower limit of the r integral set to $r=0$.

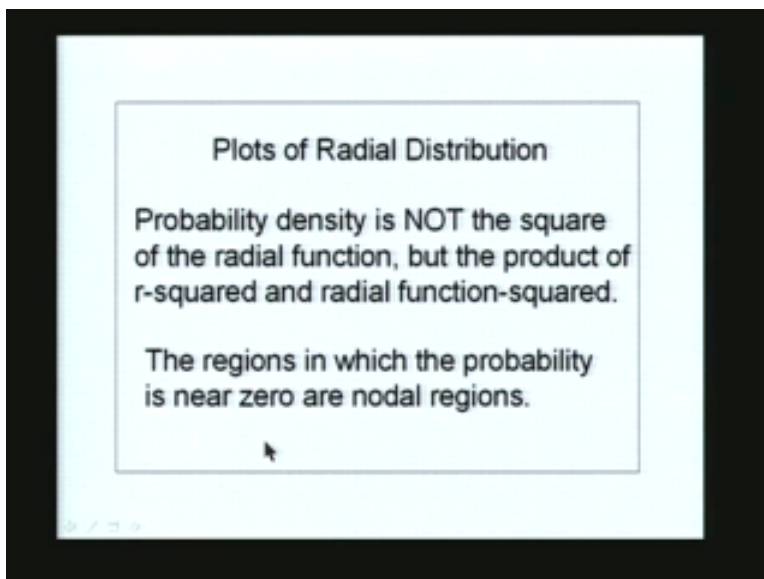
What are the theta phi parts and then θ and ϕ parts are multiplied to the radial part by where θ is equal to $\int \sin\theta d\theta$ with in 0 to π and ϕ is equal to $\int d\phi$ with in 0 to 2π the integral theta is equal to 0 to $\pi \sin\theta d\theta$. Let us also do this $\phi = 0$ to $2\pi d\phi$. Now we have got the θ, ϕ dependent angular function which is $Y_l^m(\theta, \phi)^*$ multiplied by $Y_l^m(\theta, \phi)$ Y_l^m theta phi star multiplied by Y_l^m theta phi itself. This is the angular part. So you see the angular part integration as that containing the θ, ϕ integration and then the radial part integration containing the r integration now the interpretation for the probability is now meaningful when you include this r^2 as part of the radial probability distribution. Now let us go back to the slide.

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$$\int_{r=0}^{\infty} r^2 dr R_n^l(r) * R_n^l(r) \times \int_{\theta=0}^{\pi} \sin \theta d\theta \int_{\phi=0}^{2\pi} d\phi Y_l^m(\theta, \phi) * Y_l^m(\theta, \phi) = 1$$

So what I have done is to write this radial part $\int r^2 dr R_n^l(r) * R_n^l(r)$ the radial integral and then there is the angular integral multiplied to it and if it is taken over all the limits for the all the 3 variables and then this is equal to 1.

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Plots of Radial Distribution

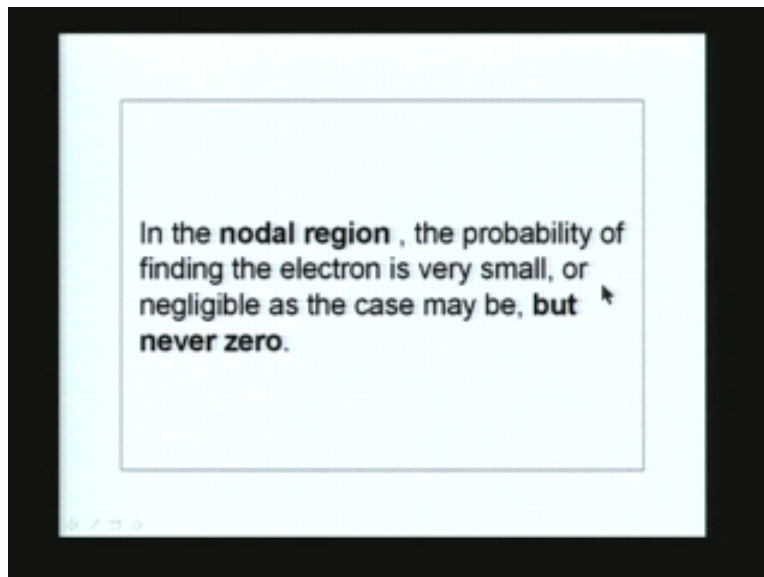
Probability density is NOT the square of the radial function, but the product of r-squared and radial function-squared.

The regions in which the probability is near zero are nodal regions.

Therefore you see the probability density when we talk about the radial distribution is no longer simply the R squared but it is also the product of the r squared and the radial function squared. That is, it is this part r squared, one R and the other R . Together it is called the radial probability distribution function and this has definitely a meaningful interpretation as far as the likelihood of finding the electron away from the nucleus is concerned. Now the regions in which the

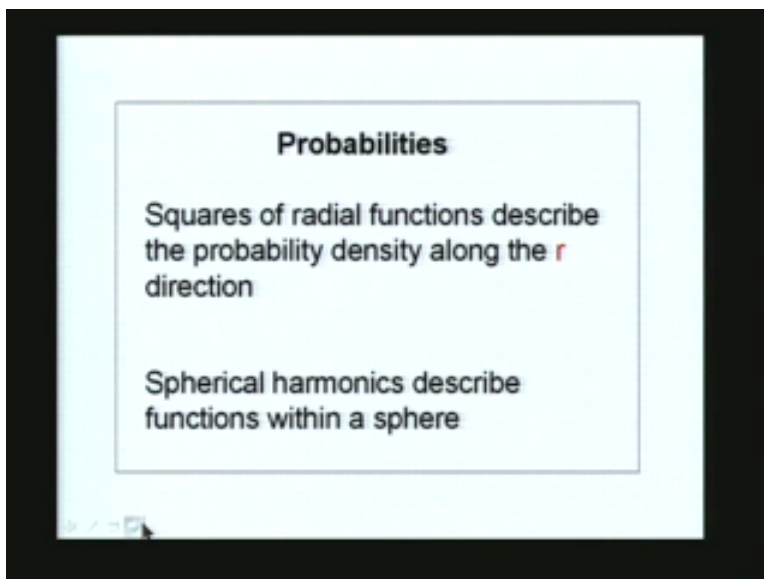
probability is near zero are called the nodal regions and the point at which the probability is **zero** is nothing called the probability of finding the electron at this point is **zero** or at that point is **zero**, no. There is no such interpretation like finding the probability at a particular point. These are all continuous variables. Therefore we can only talk about a probability density and the probability density can be zero but the probability itself is meaningful only when you talk about a small region of space. Therefore whenever you have a small region of space the probability is never **zero**. May be extremely small but it is never ever zero. The regions in which the probability is near zero are called nodal regions.

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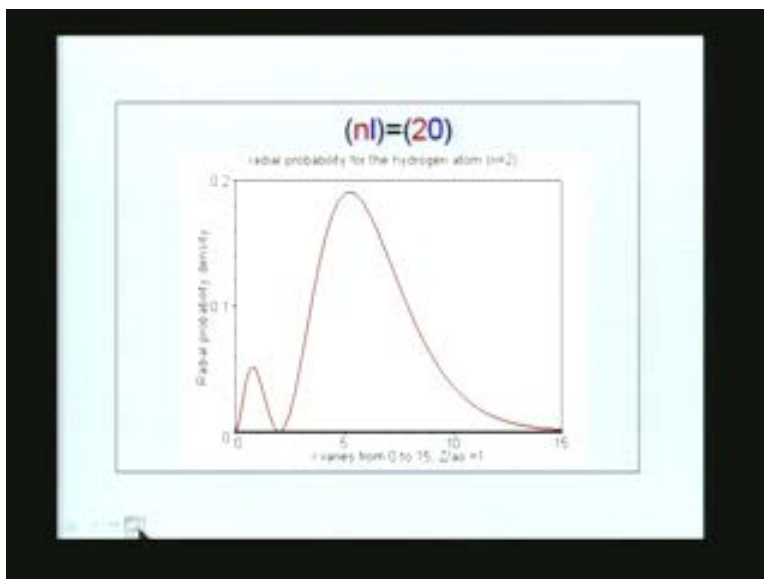
The probability of finding the electron is very small or negligible but never **zero** because we do not talk about the probability densities but we do talk about the probabilities as themselves.

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Let us now plot the squares of the radial functions along with the r . So let us go back now look at the $n=1$ and $l=0$. This plot has to be contrasted with the earlier plot of the radial function r . The radial function if you remember was a simple exponential. The radial function was a simple exponential. $R(r)$ versus r which was from the previous plot. Now you look at the radial probability function which is multiplied by r^2 and the R^2 . See now it is rightly **zero** at the nucleus and it increases to a maximum value and then it goes down. So in this region the likelihood of finding the electron is in this value of r . The corresponding value of r is the corresponding value of r is um somewhere between **0.53** and **0.7**. Finding the electron in this region the probabilities is the maximum and then the as you go farther away the likelihood of finding the electron also becomes very small. This is for the $n=1, l=0$ case so this is the $1s$ orbital. Therefore for $1s$ orbital the electron probability is very near the nucleus maximum.

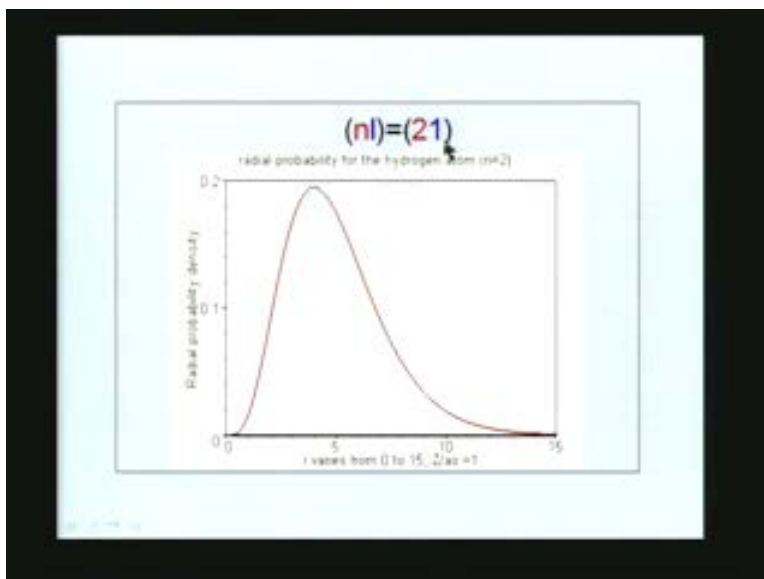
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Let us go to 2s where $n = 2$, $l = 0$. For 2s you see that the probability of finding the electron is maximum slightly farther away from the nucleus but there is a small region where the probability is also a local maximum and then it increases to much larger value slightly far away. That means the 2s orbital is extended in space with a likelihood of finding the electron near the nucleus for some value but most of its probability is farther away from the nucleus farther away from the 1s region. That is the 2s orbital which is the outer orbital when you compare the language of Neils Bohr where $n = 1$ is the first shell and $n = 2$ is the second shell.

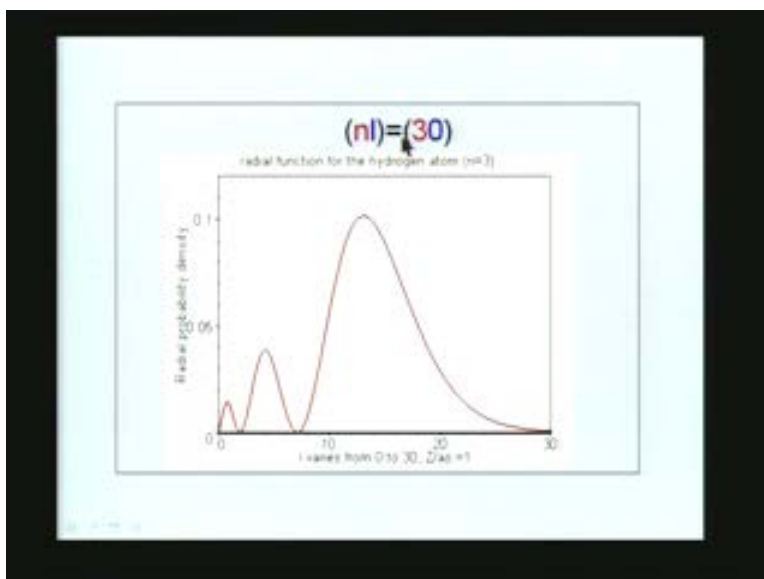
The 2s is now, you no longer talk about a shell or an orbital but you talk about a region of space where the probability of finding the electron is high and the 2s orbital gives you the concepts and this value is roughly close to the value of the radius that Neils Bohr derived. Therefore there is a one to one correspondence between the particulate model that Neils Bohr had and the wave function model that Schrödinger equation proposes that you replace the electron dot by an electron cloud such that the density of finding the cloud in that region is the maximum.

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This is for 2p where $n = 2$, $l = 1$. The radial probability density is now you see there is a maximum and this maximum also is very near the maximum of 2s. You look at the values here for 2s. This is Z/a_0 , there is an r value. This is scaled to this bore radius a_0 . So what you have here is approximately around 5 and for 2p is also approximately around that region. So you see that the 2s and 2p nearly occupy the same region but slightly different of course.

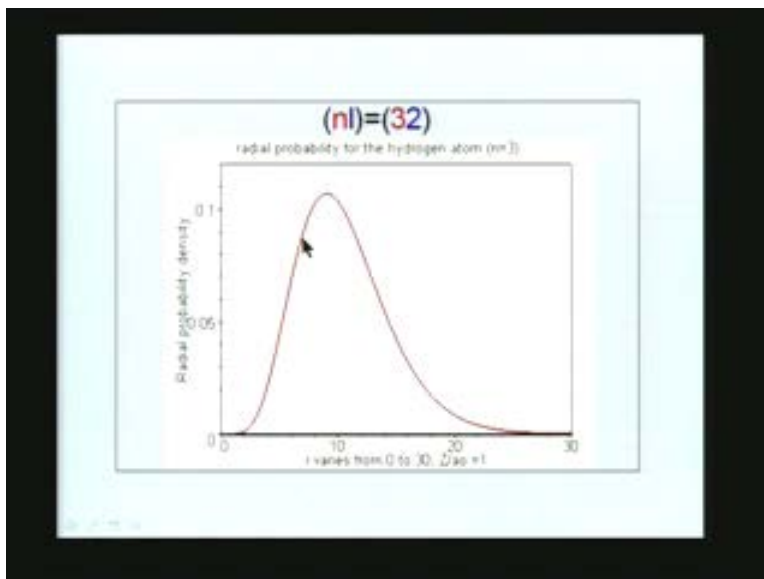
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Go to the $n = 3$, $l = 0$ which is the 3s orbital and now the density of finding the probability density or the likelihood of finding the electron is farther away from the nucleus is more. But you see 1, 2 there are two nodal regions corresponding to this value zero and zero here. The

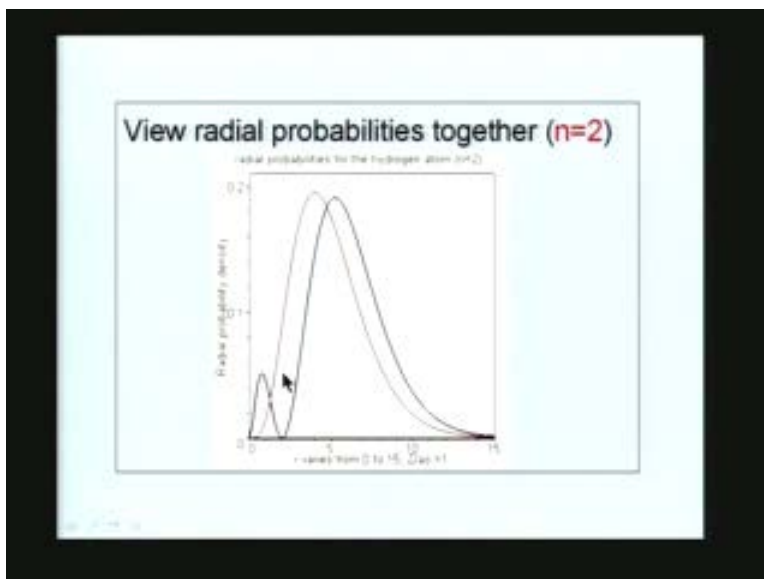
probability is zero of course at the nucleus or probability density is **zero** at the nucleus. And then you have these two nodes and then there is a likelihood of finding the electron. The 3s orbital is extended in space farther from the 2s orbital. This is the 3p orbital which has 1 node and the region of space where the bulk of the likelihood of finding the electron is in quite far away from the nucleus compared to the 2s. This is the 3d corresponding to $n = 3$ and $l = 2$ and again there is no node so the region is reasonably flat and the likelihood is again farther way from the nucleus.

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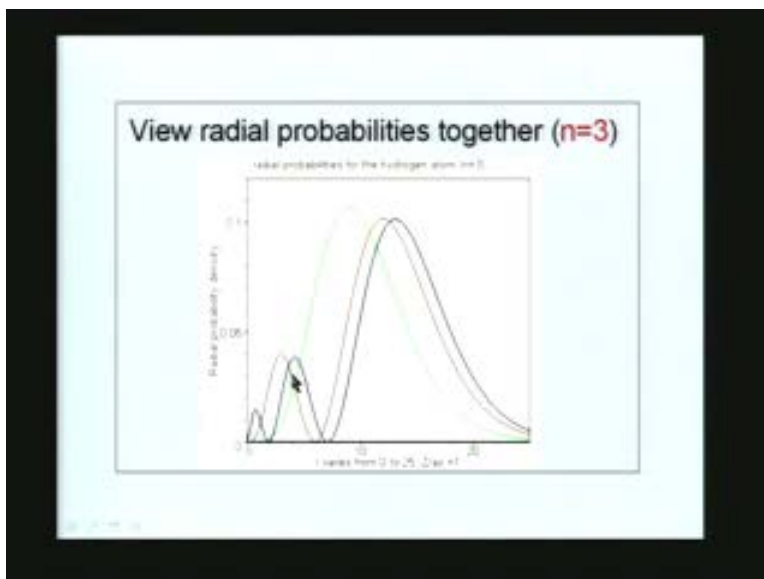
Therefore if the radial functions are plotted they only tell you approximately the values for which the radial probability density is 0 or high. But you have to remember that the radial probability distribution as an additional factor of the r^2 . That r^2 comes from the volume element in spherical polar coordinates and that volume element ensures that there is a reasonably correct interpretation for the distribution of the electron probability as one **move** away from the nucleus.

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If you put the probabilities together for the $n = 2$ case. You see this is the one with a node is $2s$ and the one without the node the red line The line that you see here without the node is $2p$ radial probabilities

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and if you put all the three orbitals $n = 3$ orbitals and the 1 with the 2 nodes. The blue curve has 2 nodes. These 2 with the 2 max 3 maxima that is a $3s$. The red curve which has 1 node is a $3p$ and the green curve which has no nodes is the $3d$ and you see the maxima are roughly close to each other. They are not very far away but they are considerably far away from that of the $n = 2$ case

as you see here. The $n = 2$ case as you see they are quite far away. The $n = 3$ case is somewhere in this region.

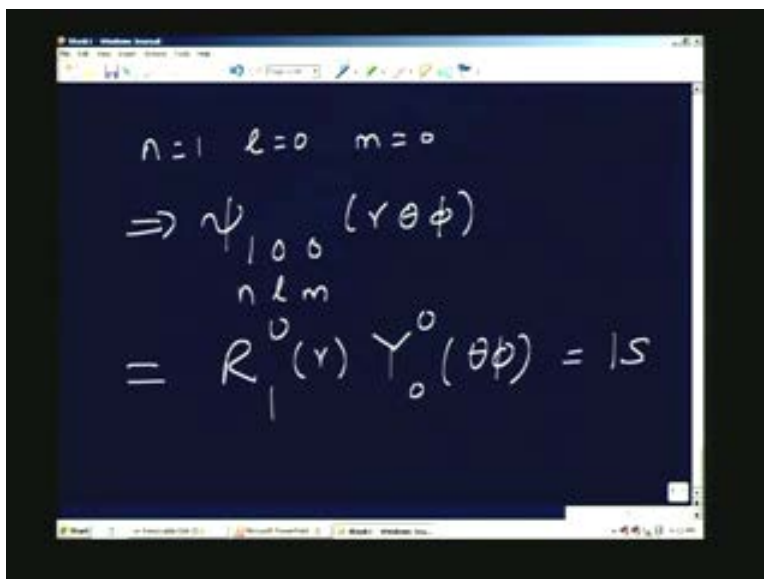
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$n = 1$	$l = 0$	1s(1)
$n = 2$	$l = 0$	2s(1)
$n = 2$	$l = 1$	2p(3)
$n = 3$	$l = 0$	3s(1)
$n = 3$	$l = 1$	3p(3)
$n = 3$	$l = 2$	3d(5)
$n = 4$	$l = 0$	4s(1)
$n = 4$	$l = 1$	4p(3)
$n = 4$	$l = 2$	4d(5)
$n = 4$	$l = 3$	4f(7)

So the concept of the bore radius and the bore shell $n = 1$, $n = 2$, $n = 3$ is now reinterpreted in terms of the probability densities as the regions where the likelihood of finding the electron is maximum.

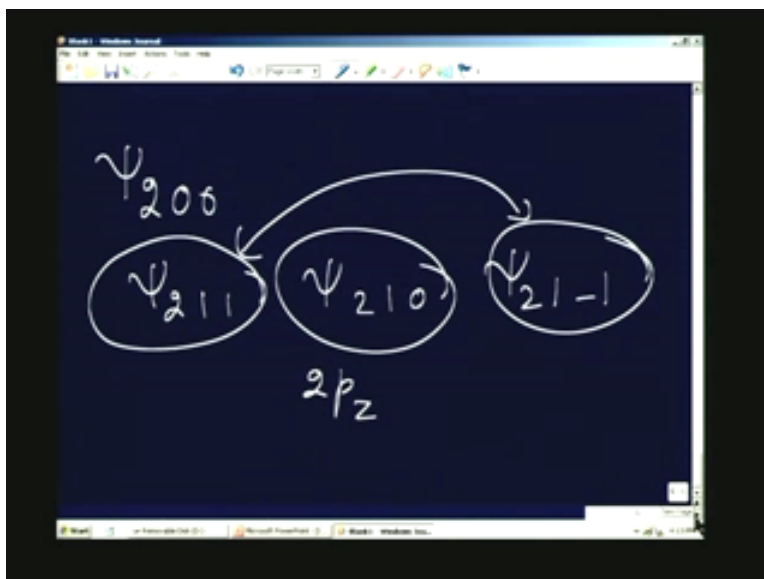
Let us see how many such orbitals are there for given value of n . I told you that it is n^2 . We will now substitute that numbers and see that that's what we get. For $n = 1$, $l = 0$ is the only possible value. There is no $m = 0$. Therefore there is only one such solution 1s. Let me write the solutions in the indexed form. $n = 1$, $l = 0$. Therefore m is 0. The wave function is $\psi_{100}(r, \theta, \phi)$ this is $\psi_{nlm}(r, \theta, \phi)$. Let me write it clear r theta si is obviously $R_1^0(r) Y_0^0(\theta, \phi)$ where n is 1, l is 0 and m is 0 this is 1s orbital.

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$$\begin{aligned} n=1 \quad l=0 \quad m=0 \\ \Rightarrow \psi_{100}(r, \theta, \phi) \\ \quad \quad \quad \begin{matrix} n & l & m \end{matrix} \\ = R_1^0(r) Y_0^0(\theta, \phi) = 1s \end{aligned}$$

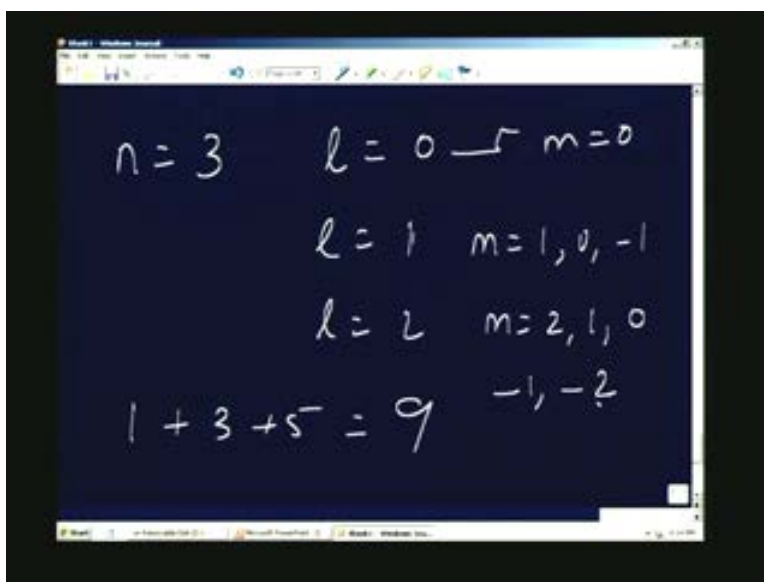
It is not just the angular part. It is a radial and the angular part put together. Next $n = 2$, there are 2 possibilities for the l . The $l = 0$ is one choice and $l = 1$ is other choice. For $l = 0$ then m is 0. For $l = 1$ you have got 3 choices namely $m = 1$, $m = 0$ and $m = -1$. So what are the 3 the four wave functions that you have is. This is also $n = 2$ here. So the 4 possible wave function that you talk about are ψ_{200} , ψ_{211} , ψ_{210} and ψ_{21-1} . This ψ_{210} is the $2p_z$ orbital. This the real part or the imaginary part of these give you the $2p_x$ and the $2p_y$ orbital. (Refer Slide Time: 42:27 min) This function is complex but you have to take linear combination of this function and its complex conjugate to get the p_x and the p_y . But there are 3 such p orbitals and 1 therefore there is a total of 4 orbitals.

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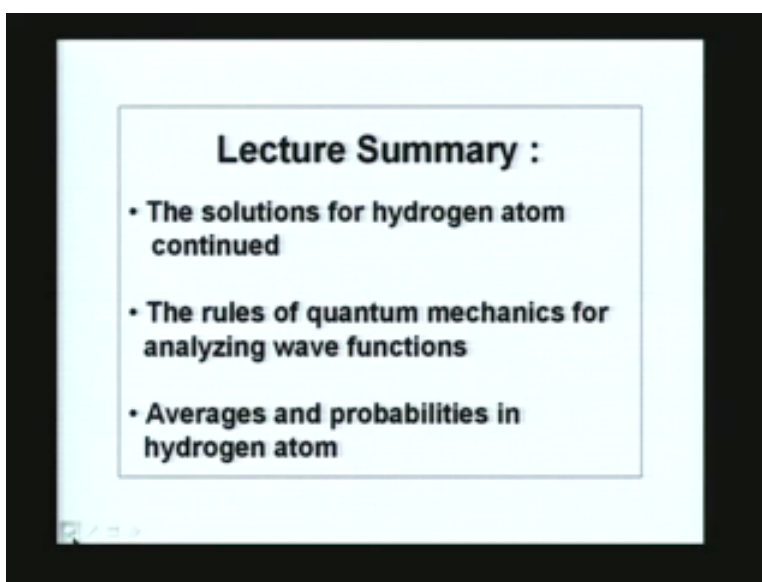
Now we look at the n quantum number for $n = 3$ the 3 possible values $l = 0$, $l = 1$ and $l = 2$. For $l = 0$ you have got $m = 0$. For $l = 1$ you have got $m = 1, 0, -1$ and for $l = 2$ you have got $m = 2, 1, 0, -1, -2$ so you have got 5 functions so you have got $1 + 3 + 5$ a total of 9 functions for $n = 3$ and these 9 wave functions are the 9 orbitals. But you have to remember when it comes to d orbitals and p orbitals we do not take the m values as they are but we take linear combinations of them.

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For example, for $m = 2$ and -2 if we take the linear combinations as I said in the last lecture you get the $d_{x^2 - y^2}$ orbital or you get the d_{xy} orbital. But the point is there are 5d orbitals. There are 3p orbitals and there is one s orbital for the $n = 3$ case. So there is a total of 9. So this is the table which gives you that number. So $n = 2, l = 0$ 2s(1) orbital and then 2p(3) orbital. For $n = 3, l = 0$ is 3s(1) orbital and $n = 3, l = 1$ is 3p(3) orbitals and $n = 3, l = 2$ gives you 3d(5) orbitals. So that is, the total is $1 + 3 + 5$ is for the $n = 3$ case, nine of them and for $n = 4$ you can likewise show a 1s orbital 3p orbitals 5d orbitals and 7f orbitals leading to a total of 16. Therefore for any given value of n there are n^2 orbitals as you have studied them in the earlier chemistry courses except that now you know what those wave functions are and what the products of the angular and radial parts of them turn out to be.

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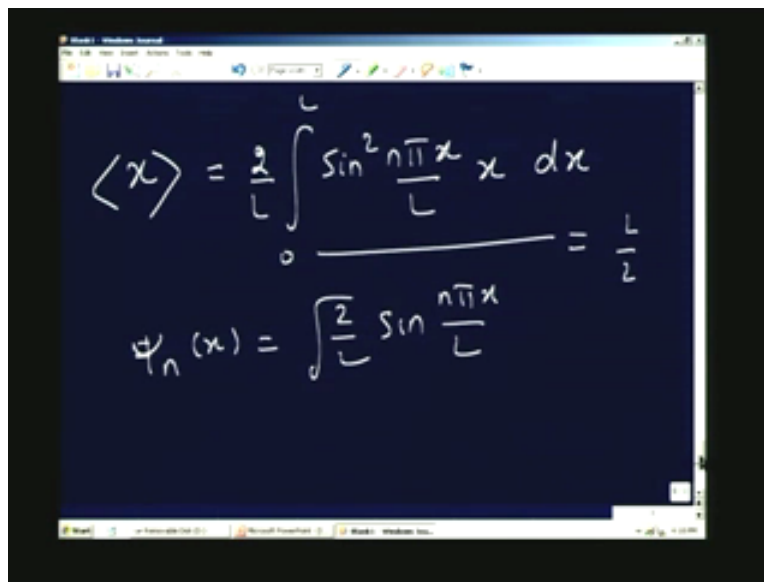
So the solutions for the Hydrogen atom we have done so far in this lecture is to look at the solutions from the radial part and the angular part and then bring them together and determine what are called the radial probabilities the radial wave functions as they are. And then the square of the radial function multiplied by the r^2 gives you what is called the radial probability distribution. Let us look at the basic rules. The averages and probabilities of Hydrogen atom let me indicate to you. The calculations are somewhat tedious but you must know how to do the calculations. So let me do that process and we will go through formal algebra here. Please recall that the expectation value of any observable in quantum mechanics from the previous lecture I have given as the integral with the operator corresponding to the expectation the value.

The observable operator between the two wave functions $\int \psi^* A \psi d\tau / \int \psi^* \psi d\tau$. This is a postulate. This is a postulate in quantum mechanics. We will have to take this as given and we have to work with it and feel comfortable about how to manipulate this for various cases. We have already done this for a particle in a one dimensional box. If you remember, the average

value for the position for a particle in a 1D box was calculated as $L/2$ and this was a few lectures ago.

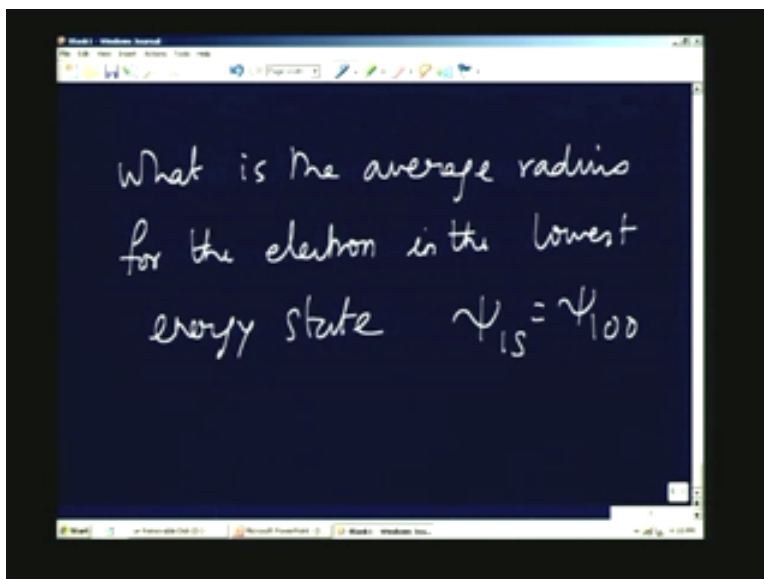
As now $\frac{2}{L} \int \sin^2(n \pi x/L) x dx$ between 0 and L came out because you have the wave function as $\psi_n(x) = \sqrt{2/L} \sin(n \pi x/L)$. This was the wave function. So, if you put this in here put the x in here and put the wave function again. You will get this result and you calculated this to be $L/2$ the average value of x this was already done. Now except that in the case of Hydrogen atom you have got 3 variables to take care of and therefore we got these 3 functions to worry about in taking the average values.

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$$\langle x \rangle = \frac{2}{L} \int_0^L \sin^2 \frac{n\pi x}{L} x dx = \frac{L}{2}$$
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

So even in the simplest case of calculating what is the average radius for the electron in the ground state that is in the lowest energy state in the lowest energy state corresponding to ψ_{1s} or ψ_{100} .

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Here the principle quantum number is 1. The l value is 0 and the m value is 0. What is the average value for this radius? Even this will be somewhat a long expression but it is doable because it involves simply exponential. So what you have to do is what the average value for the radius r is. If you do this question the answer to that is $\langle r \rangle = \iiint \psi_{100}^*(r, \theta, \phi) r \psi_{100}(r, \theta, \phi) r^2 dr d\theta \sin\theta d\phi$ where dr is now $r^2 dr d\theta \sin\theta d\phi$. So it is a triple integral. This is what you have to calculate but you see that this is involving only the value r and you remember that the ground state wave function has a spherical harmonic Y_0^0 corresponding to this. The Y_0^0 is independent of the functions. If you recall $Y_0^0(\theta, \phi)$ was $1/\sqrt{4\pi}$.

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$$\langle r \rangle = \iiint \psi_{100}^*(r, \theta, \phi) r \psi_{100}(r, \theta, \phi) \times r^2 dr d\theta \sin\theta d\phi$$
$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

What is the origin of that? It is a normalization constant for the function Y_0^0 . If it is independent of θ and ϕ , the angular part is $d\theta \sin\theta d\phi$ between the integrals. So let me do this calculation now. You have the radial function $\int R_1^0(r) r R_1^0(r)$ and again the radial function $1/r$. It is a real function so '*' is not needed. Then there is $r^2 dr$ multiplied by the integrals $\int [Y_0^0(\theta\phi)]^2 \sin\theta d\theta d\phi$. This is how you calculate the expectation values of quantities for the Hydrogen atom and here the expectation value that we calculate is the average value for the radius of the electron. I mean how far away it is from the nucleus, the average value you cannot locate the electron in to particular point because Quantum Mechanics the wave function model precludes such a description. But on the average where are we likely to find the electron the value is given by this expression and you have $R_1^0(r)$ times the r and this integral. The calculation times this integral.

The calculation of this is very straight forward. This is straight away one can do this. You remember that $Y_0^0(\theta\phi)$ was $1/\sqrt{4\pi}$. Therefore the square of this is $1/4\pi$ and it is independent of θ and ϕ and r . Therefore the integral for θ and ϕ can be done as $1/4\pi \int_0^\pi \int_0^{2\pi} \sin\theta d\theta d\phi$ this integral is between 0 to π for $d\theta$ and 0 to 2π for $d\phi$.

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$$= \int R_1^0(r) r R_1^0(r) r^2 dr \times \left[\int_0^\pi \int_0^{2\pi} [Y_0^0(\theta\phi)]^2 \sin\theta d\theta d\phi \right]$$

$$\frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \sin\theta d\theta d\phi$$

You can show that the angular part whole thing is 1, the angular part. Let me write this again. This whole integral $1/4\pi \int \sin\theta d\theta \int d\phi = 1$ between $\theta = 0 \rightarrow \pi$ and $\phi = 0 \rightarrow 2\pi$. This integral is 1. Therefore the radial part the average value r is essentially integral where r goes from 0 to ∞ is $\int r^2 dr R_1^0(r) r R_1^0(r)$ here you have got the radial function $R_1^0(r)$. The operator corresponding to the radial is the radius and $R_1^0(r)$. This is the only integral that you need to calculate.

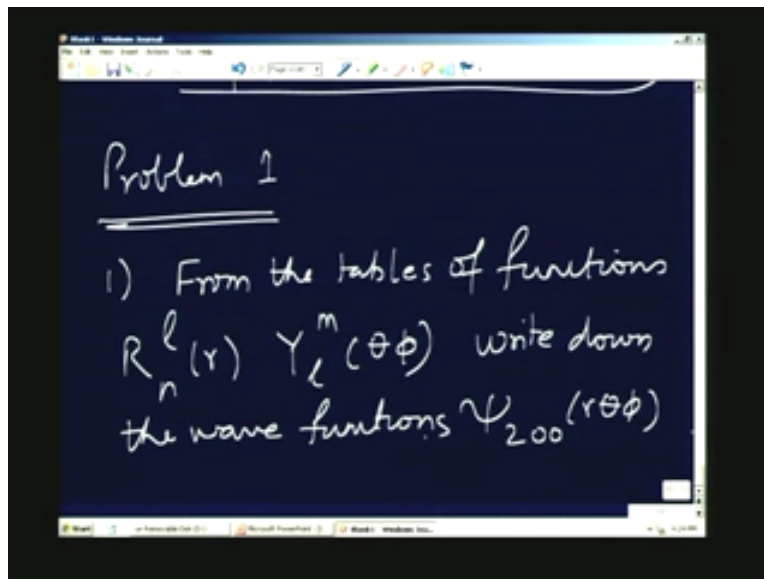
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$$\frac{1}{4\pi} \int_{\theta=0}^{\pi} \sin\theta d\theta \int_{\phi=0}^{2\pi} d\phi = 1$$

$$\langle r \rangle = \int_{r=0}^{\infty} r^2 dr R_l^0(r) r R_l^0(r)$$

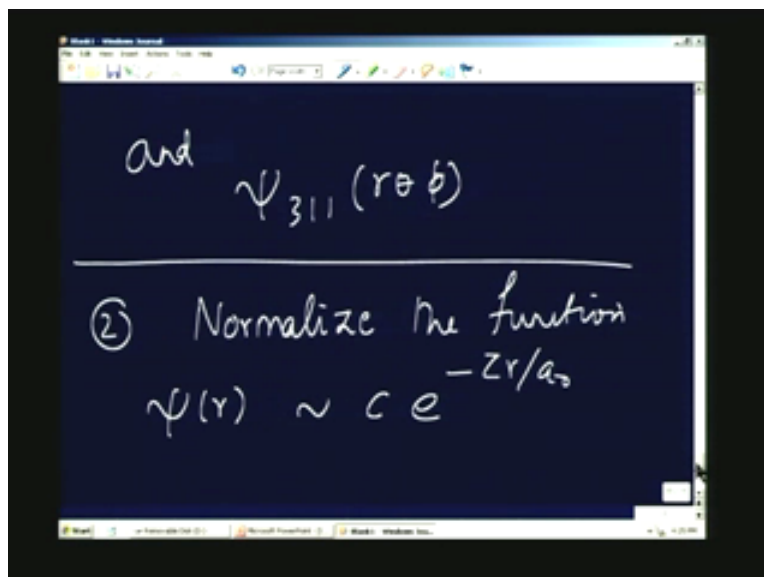
Now you see that the separation of the variables in terms of spherical polar coordinates [has](#) its advantages. When you calculate the properties of the electron what are the average values of the radius of the electron. What is the average value for the momentum of the electron. So, if you want to calculate every such average all you need to know is the corresponding operator associated with the property that you want to measure and then put the operator between the two wave functions and calculate the integral. So let me conclude this lecture with the following 2 or 3 problems for the Hydrogen atom. This covers the last 3 or 4 lectures. So let me write the first problem as 1: [From the tables of functions given as \$R_n^l\(r\)\$ \$Y_l^m\(\theta, \phi\)\$](#) . Write down the wave function [\$\psi_{200}\(r, \theta, \phi\)\$](#) wave functions and [\$\psi_{311}\(r, \theta, \phi\)\$](#) wave functions.

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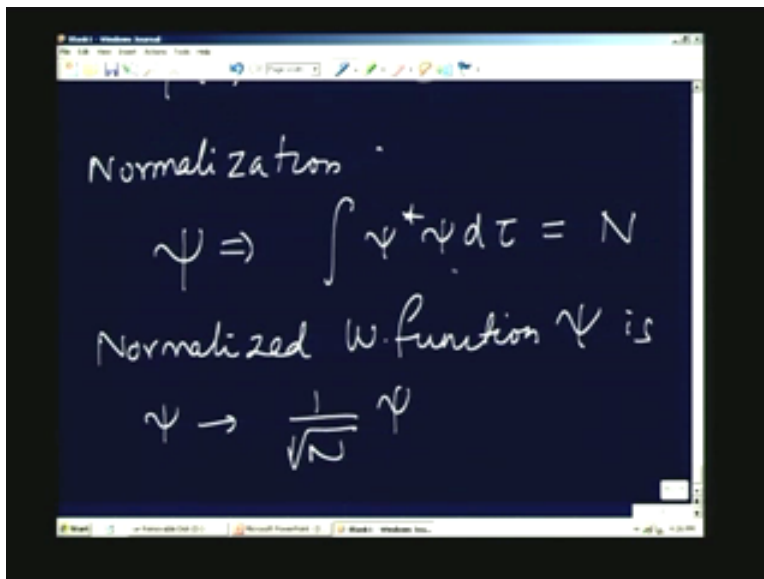
This is a straight forward multiplication but please do this exercise by writing the individual wave functions. Second one: normalize the function $\psi(r)$ given by a constant c times an $\exp(-Zr/a_0)$. If I do not give you this constant how would you get the normalization constant of this wave function.

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Remember the normalization constant is obtained by the following method. If the wave function is given as ψ the normalization means that the $\int \psi^* \psi d\tau$. If it gives you a value of N , the normalized wave function ψ is given by, you replace the ψ by $1/\sqrt{N}\psi$.

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Normalization

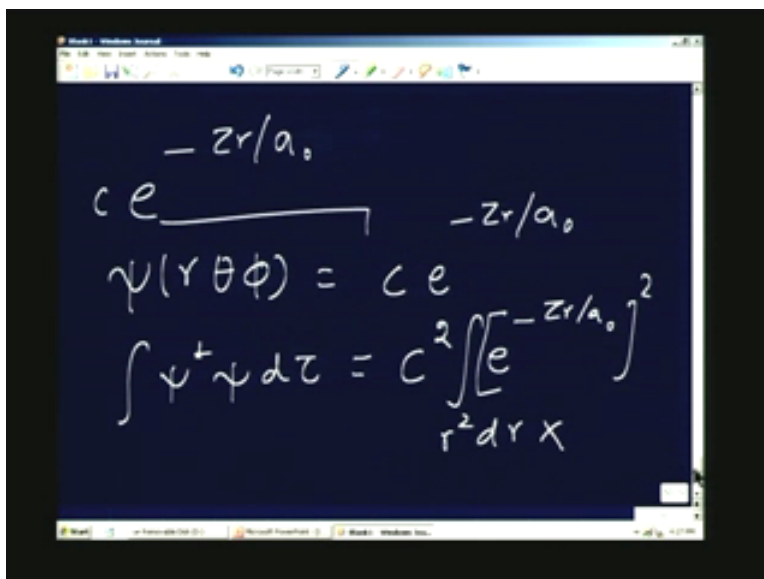
$$\psi \Rightarrow \int \psi^* \psi d\tau = N$$

Normalized W. function ψ is

$$\psi \rightarrow \frac{1}{\sqrt{N}} \psi$$

Then the wave function is said to normalize. So this is the normalization constant which is obtained by taking the square of the absolute square of the wave function and integrating over the space that is available. The only tricky part that you have to remember in this problem with respect to $\exp(-Zr/a_0)$ and c is that $\psi(r)$ is given as $\psi(r, \theta, \phi)$ as nothing but $c \exp(-Zr/a_0)$. There is no (θ, ϕ) part. It is independent of that. Therefore what is meant by normalization when you write $\int \psi^* \psi d\tau$? The normalization means that you calculate $c^2 \int [\exp(-Zr/a_0)]^2 r^2 dr$. You must remember that this is the radial part you have to consider with respect to the wave function.

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$-Zr/a_0$

$$\psi(r, \theta, \phi) = c e^{-Zr/a_0}$$
$$\int \psi^* \psi d\tau = c^2 \int [e^{-Zr/a_0}]^2 r^2 dr d\Omega$$

It is not enough. Also this is multiplied by the corresponding angular part. The angular part is simply there is $\int d\theta \sin\theta \int d\phi$. So all that we have done is the integral $d\tau$ in this case is a triple integral corresponding to the fact that it is $r^2 dr d\theta \sin\theta$. The function that you are asked to normalize does not depend on θ and ϕ . Therefore this is taken out and this you know the value of this. If you calculate using simple integral it is 4π and all you need to do is to calculate the integral this c^2 times and you should set this is equal to 1 to calculate the value of c .

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$$\psi(r, \theta, \phi) = c e^{-zr/a_0}$$

$$\iiint \psi^* \psi d\tau = c^2 \int_0^\infty e^{-2zr/a_0} r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$\left[\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \right] = 4\pi$$

$$\Rightarrow 1$$

This is somewhat difficult but it gives you a little bit of Mathematics involved in handling the wave functions. So let me summarize the purpose of going through the Hydrogen atom in all these details. We have not solved the Schrödinger equation for Hydrogen atom but we have looked at the solutions of the Hydrogen atom and try to analyze them.

The important part is that. Remember that it is done in a spherical coordinate system and it is split into variables which can be handled independently and the description of the wave function in terms of the probabilities involves a radial probability and an angular probability. The visualizations of these functions the angular part of this gives you a mental picture about the likelihood of the distributions of these wave functions and so on. Hydrogen atoms and wave functions are fundamentally important in the study of the Chemistry of the atoms and molecules. In fact all the energy levels of the atoms are based on the classification of the energy levels of the Hydrogen atoms. We will continue this in next lecture. Thank you