Concept of Chemistry for Engineering

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Lecture – 11

Principal Quantum Number

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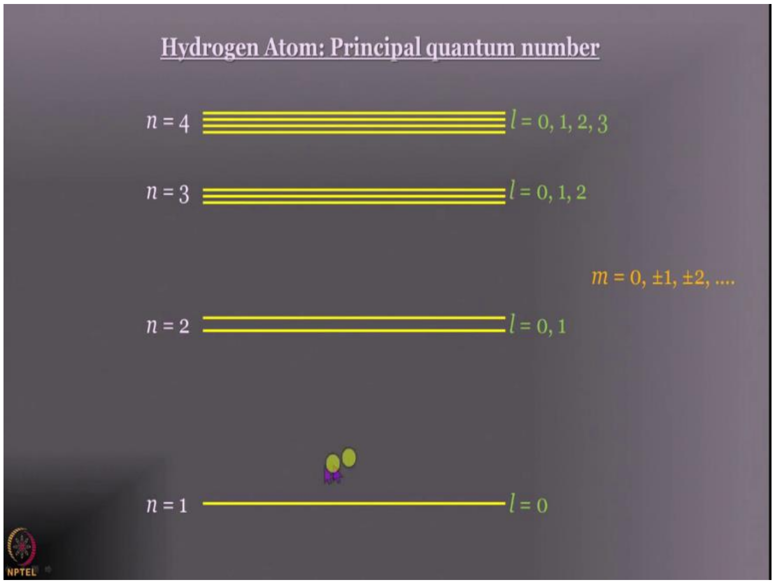

Hydrogen Atom: Principal quantum number

We are going to learn about the principal quantum number finally. It is funny, is not it? When we had learned Bohr theory principal quantum number came first, then came L and then came S and that is how this picture was developed.

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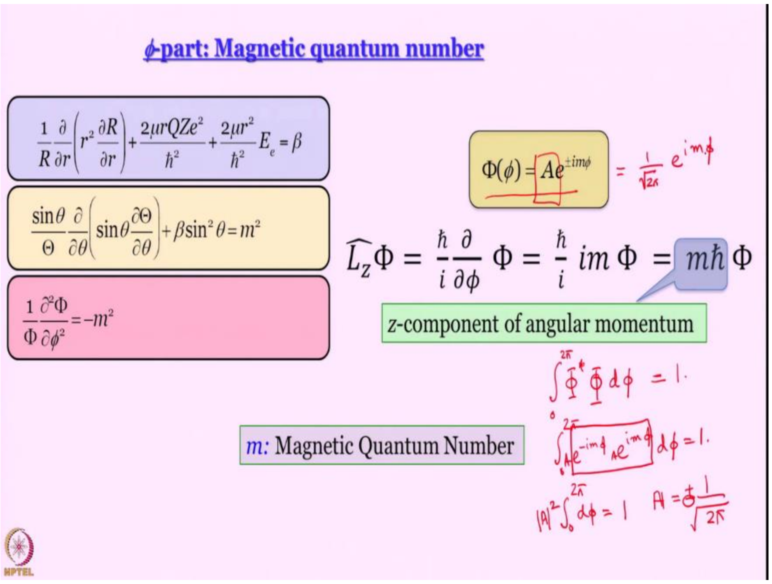

ϕ-part: Magnetic quantum number

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

$$\Phi(\phi)=\boxed{A}e^{\pm im\phi} = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$\widehat{L_z}\Phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi = \frac{\hbar}{i}im\Phi = m\hbar\Phi$$

z-component of angular momentum

m: Magnetic Quantum Number

$$\int_0^{2\pi}\Phi^*\Phi\, d\phi = 1.$$

$$\int_0^{2\pi}\boxed{Ae^{-im\phi}Ae^{im\phi}}\, d\phi = 1.$$

$$|A|^2\int_0^{2\pi}d\phi = 1 \quad A = \pm\frac{1}{\sqrt{2\pi}}$$

What we have got is in exactly opposite sequence. So, if you remember, we have separated the Schrodinger equation for hydrogen atom, well, electron and hydrogen atom into three different parts, r dependent part $\frac{1}{\mathrm{R}}\frac{\partial}{\partial \mathrm{r}}\left(\mathrm{r}^2\frac{\partial \mathrm{R}}{\partial \mathrm{r}}\right)+\frac{2\mu\mathrm{rQZe}^2}{\hbar^2}+\frac{2\mu\mathrm{r}^2}{\hbar^2}\mathrm{E_c} = \beta$,

theta dependent part $\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+ \beta sin^2\theta = m^2$, and phi dependent part $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2$.

We solved the phi part, told you what the solution of theta dependent part is. Today we are going to tell you, not solve what the solution of r dependent part is.

And just to recapitulate, this is the important thing that we have learned so far: $\Phi(\phi) = Ae^{\pm im\phi}$.

One thing I forgot, and you should be able to do yourself. Can you normalize this? Can you try to find out what the value of A will be? That is something that I completely forgot to do, sorry about that. Just remember something, when you try to normalize you have to integrate between the limits of phi.

And the limits of ϕ are 0 and 2π. Maybe I will just do it here, it is a little bit of digression. But let us do it anyway, I want to know what is the value of A if I normalize it. What do I do? I integrate Φ^*, Φ, $d\phi$ between the limits 0 and 2π. And that probability should be equal to 1. $\int_0^{2\pi}\Phi^*\Phi\, d\phi = 1$. So, what is Φ? Let us just say $\Phi = e^{im\phi}$. What is our Φ^* then? $\Phi^* = e^{-im\phi}$. Therefore, $\int_0^{2\pi} e^{-im\phi}e^{im\phi}\, d\phi = 1$, simple. Multiply $e^{-im\phi}e^{im\phi}$, you get 1. So, you get,

$\int_0^{2\pi} d\phi = 1$, but did I miss something? Yes, I missed A. Remember, $\Phi = Ae^{im\phi}$ and $\Phi^* = e^{-im\phi}$. So, I should actually write $|A|^2 \int_0^{2\pi} d\phi = 1$. So, what is A then? A= $\pm \frac{1}{\sqrt{2\pi}}$. It can be plus, it can be minus, we usually do not take the minus sign, plus is good enough.

It does not matter, whether you say that this direction is plus, that direction is minus for a wave function. So, here we get, $\Phi(\phi) = Ae^{\pm im\phi} = \pm \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$, just a little bit of digression because I had forgotten to do it last time. Better erase this, because I do not know where things are going to pop up. So, this is what it is, the phi dependent part.

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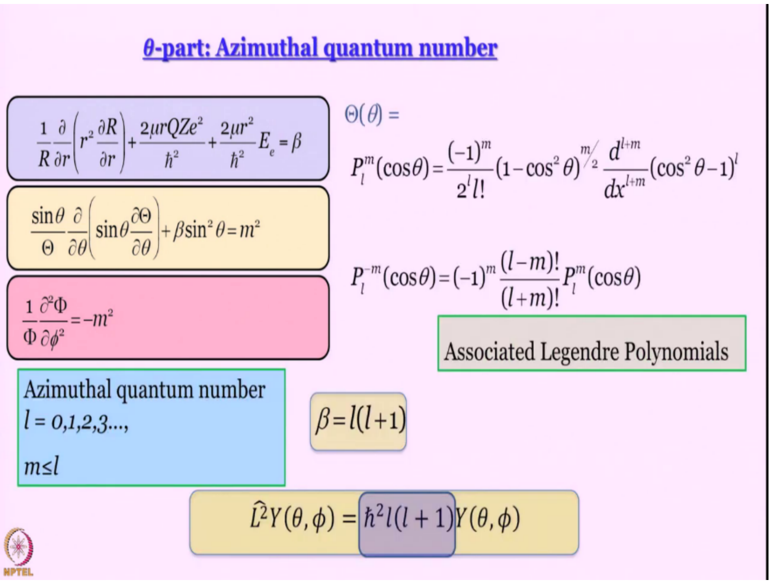

θ-part: Azimuthal quantum number

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

$\Theta(\theta)=$

$$P_l^m(\cos\theta)=\frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(\cos^2\theta-1)^l$$

$$P_l^{-m}(\cos\theta)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)$$

Associated Legendre Polynomials

Azimuthal quantum number
$l = 0,1,2,3\ldots,$
$m \leq l$

$\beta=l(l+1)$

$$\hat{L}^2Y(\theta,\phi)=\boxed{\hbar^2 l(l+1)}Y(\theta,\phi)$$

And from theta dependent part we get an idea of the total angular momentum. And we have discussed why m has an upper limit of l.

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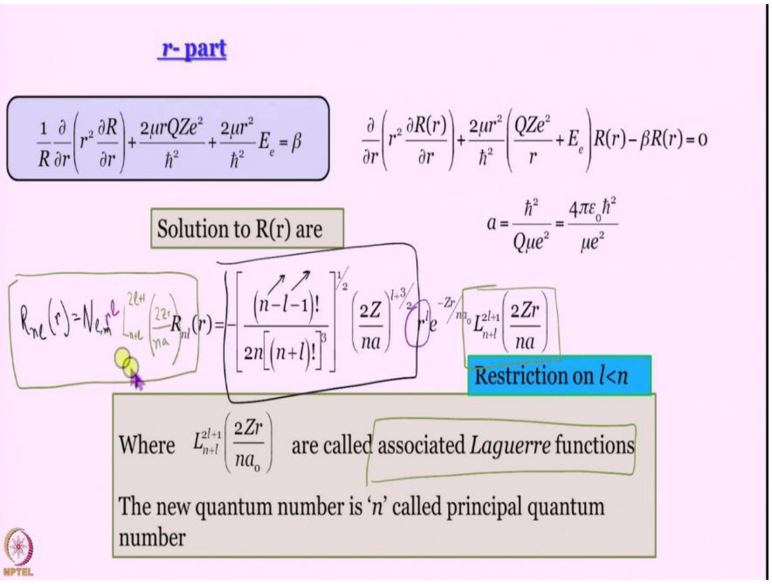

r- part

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r}+E_e\right)R(r)-\beta R(r)=0$$

Solution to R(r) are

$$a=\frac{\hbar^2}{Q\mu e^2}=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$R_{nl}(r)=N_{l,m}r^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

$$R_{nl}(r)=-\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}r^l e^{-Zr/na_0}L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$$

Restriction on $l<n$

Where $L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$ are called associated *Laguerre* functions

The new quantum number is 'n' called principal quantum number

Now, this year, all of a sudden bang on your face is the r dependent part. We are not about to solve this equation, like the theta dependent part, the solution of this was already known when you had this, when this Schrodinger equation was being formulated. So, just use the solution. Let me try to write this in a little more compact, less scary form. So, what am I trying to write here? I am trying to write, what is $R_{nl}(r)$, which is a function of small r. What will it be?

$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2} r^l e^{-Zr/na_o} L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$. The first thing that I have here, $-\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2Z}{na}\right)^{l+3/2}$, it is a constant. And it is a constant that depends on the quantum number n as well as quantum number l. So, let me write $R_{nl}(r) = N_{l,m}$. Now I will change the color. What do I have next? I have this r^l, (())(05:02) write it as such, that is not scary. What do I have next? I have this, $L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$, a polynomial L_{n+l}^{2l+1}, which depends on $(n+l)$ as well as $(2l+1)$.

And this polynomial is in $\left(\frac{2Zr}{na}\right)$. And these polynomials are called associated Laguerre functions. So, $R_{nl}(r) = N_{l,m}\, r^l\, L_{n+l}^{2l+1}\left(\frac{2Zr}{na}\right)$ is the functional form that we need to know, I am saying you need to know this, because there is something important. r^l and a polynomial, we are going to see, what kind of polynomials we have. But, it is important because that is what gives shape to the radial part of the wave function. No need to read, the need to remember this nl all these things, if you can remember, it is good enough.

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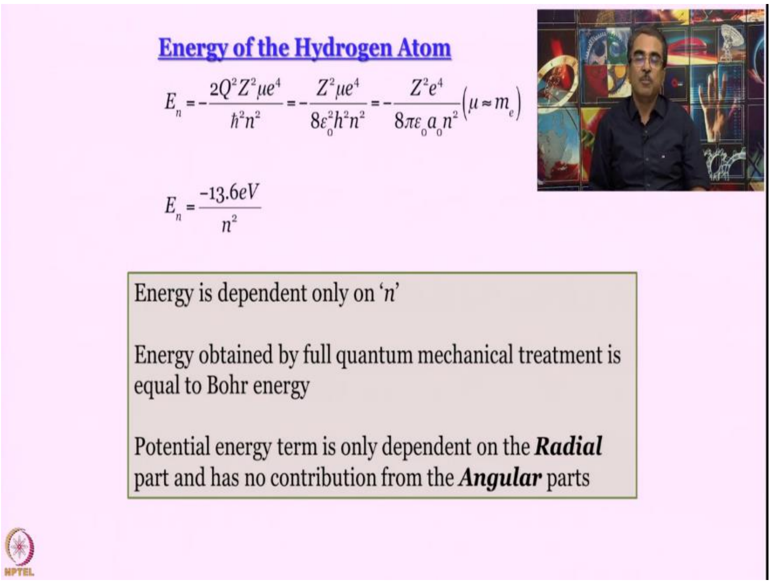

Energy of the Hydrogen Atom

$$E_n = -\frac{2Q^2Z^2\mu e^4}{\hbar^2 n^2} = -\frac{Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_0 a_0 n^2}\left(\mu \approx m_e\right)$$

$$E_n = \frac{-13.6eV}{n^2}$$

Energy is dependent only on '*n*'

Energy obtained by full quantum mechanical treatment is equal to Bohr energy

Potential energy term is only dependent on the ***Radial*** part and has no contribution from the ***Angular*** parts

You cannot remember that also is fine. One thing that we need to see is that, see if you go back to these three equations, you will see that energy appears only in the r dependent part. So, it tells us essentially, that for a hydrogen atom energy does not depend on the subsidiary quantum number L, or the magnetic quantum number M. Is that right? Is that wrong? Well, it is right, it is fine. Why is it that you get a different, why do you get the fine structure?

Actually, fine structure is obtained for other atoms. And for other atoms, this degeneracy is lifted, we are not going to talk about that in this course. But what I am saying is the expression of E that comes out is this, $E_n = -\frac{2Q^2Z^2\mu e^4}{\hbar^2 n^2}$ = - $\frac{Z^2\mu e^4}{8\varepsilon_o^2\, h^2 n^2}$ $= -\frac{Z^2 e^4}{8\pi\varepsilon_o a_o n^2}$ $(\mu \approx m_e)$, as the Eigen value. And it is exactly the same expression as that in Bohr theory $E_n = \frac{-13.6\ eV}{n^2}$. So, the strength of Bohr theories is retained here. The strength of Bohr theories was that, it could give you the right value of energy.

Remember, it could determine, it could give you the theoretical value of Rydberg constant correct to many, many places of decimals. And it turns out to be $\frac{-13.6\ eV}{n^2}$, -13.6 eV is another number that we should know. It is like A B C D as far as quantum mechanics is concerned. It is ionization potential of hydrogen atom. So, as you go higher up the energy ladder, as you go higher up in n, what happens to this number?

E_n becomes, well n becomes larger. So, the magnitude becomes smaller, and E_n becomes therefore larger. Why does it become larger? Because a negative quantity, it goes more and more and more towards 0, that is all. When energy is equal to 0 that means, the electron has left the atom. It no longer experiences the potential energy due to the nucleus. So, that is what it is. So, the energy depends only on the radial part, which is in agreement with Bohr theory, this is a very important take home message.

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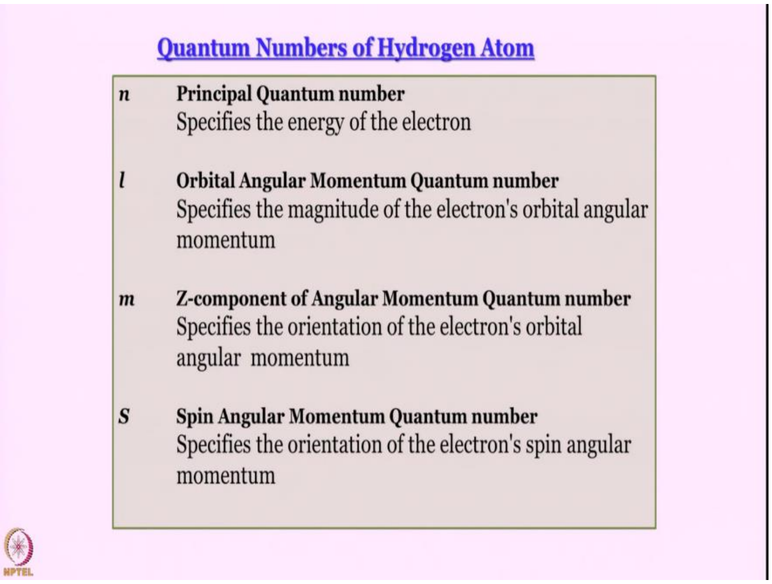

Quantum Numbers of Hydrogen Atom

n	**Principal Quantum number** Specifies the energy of the electron
l	**Orbital Angular Momentum Quantum number** Specifies the magnitude of the electron's orbital angular momentum
m	**Z-component of Angular Momentum Quantum number** Specifies the orientation of the electron's orbital angular momentum
S	**Spin Angular Momentum Quantum number** Specifies the orientation of the electron's spin angular momentum

So, we have got three of the four quantum numbers that we know. What we have not got is S, spin angular momentum quantum number. Spin angular momentum quantum number, well, spin quantum number comes from direct statement, which is very different, we are not going to talk about spin at all in this course, I think, maybe a little bit when we talk about bonding, maybe not. So, n l and m are obtained. And they make sense, when we get them using this Schrodinger's treatment of the hydrogen atom problem.

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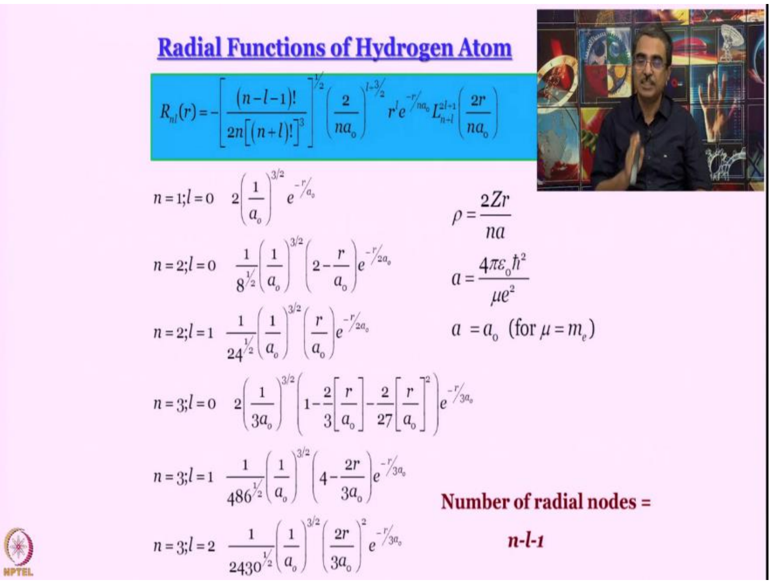

Radial Functions of Hydrogen Atom

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} L_{n-l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$n=1; l=0$ $\quad 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$n=2; l=0$ $\quad \frac{1}{8^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=2; l=1$ $\quad \frac{1}{24^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$

$n=3; l=0$ $\quad 2\left(\frac{1}{3a_0}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_0}\right]-\frac{2}{27}\left[\frac{r}{a_0}\right]^2\right)e^{-r/3a_0}$

$n=3; l=1$ $\quad \frac{1}{486^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(4-\frac{2r}{3a_0}\right)e^{-r/3a_0}$

$n=3; l=2$ $\quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{2r}{3a_0}\right)^2 e^{-r/3a_0}$

$$\rho = \frac{2Zr}{na}$$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$a = a_0$ (for $\mu = m_e$)

Number of radial nodes = n-l-1

Now, that being said, let us have a look at the radial functions. So, this is what it is.

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2}{na_o}\right)^{l+3/2} r^l e^{-r/na_o} L_{n+l}^{2l+1}\left(\frac{2r}{na}\right)$$

Remember, some constant $-\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2}{na_o}\right)^{l+3/2}$ multiplied by $r^l\, e^{-r/na_o}$. Did I write that in the previous part? Perhaps not so sorry about that, e^{-r/na_o} is required, because the function has to vanish, vanish at infinity. If you just write r^l multiplied by this function will not be right.

So, there was a typo in the previous slide, e^{-r/na_o} is very much there. So, these are the wave functions. Please do not try to find out the numbers here from this $\frac{(n-l-1)!}{2n[(n+1)!]^3}$ and all that. Because this, to do that, you will need to know what these Laguerre polynomials L_{n+l}^{2l+1} are, because they also have some constants, which get multiplied with $-\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2}{na_o}\right)^{l+3/2}$ to get, give you the constants that you see here. But let us have a look at the wave functions, n = 1; l = 0, 1s.

That is a, decay in terms of e^{-r/a_o}, n = 2; l = 0 has the same decay multiplied by $\left(2-\frac{r}{a_o}\right)$, n = 2; l =1. Again, there is no polynomial here, it is just $\left(\frac{r}{a_o}\right)$ multiplied by e^{-r/a_o}. Where is that r^l term here for n = 2; l = 0? Well l = 0. So, r^0 is l. What about here, n = 2; l = 1? So, see, $\left(\frac{r}{a_o}\right)$ is there. For n = 3, l = 0, now you have a polynomial of second order. n = 3; l = 1 has a polynomial of first order, $\left(4-\frac{2r}{3a_o}\right)$, so on and so forth. And we will see how that determines the shapes of these wave functions. What are nodes? I think you are familiar with radial nodes and angular nodes and all that. Radial nodes are points, where the radial part of the wave function goes through 0 and changes sign. Please remember and changes sign part of it. So, how do you get the number of radial nodes?

Well, it, it is $n-l-1$ as you know. Where does it come from? It comes from, what is the degree of this polynomial $-\left[\frac{(n-l-1)!}{2n[(n+1)!]^3}\right]^{1/2}\left(\frac{2}{na_o}\right)^{l+3/2} r^l$. As you see, when n = 1; l = 0, what is the degree of that polynomial, $1-0-1$, that is 0. So, that polynomial is not there, when n = 2; l =

0, 2 − 0 – 1 = 1. So, this is, this polynomial $\left(2-\frac{r}{a_o}\right)$ is of order one. What about n = 3, l = 0? 3 – 0 − 1, that is 2, you have polynomial of order two $\left(1-\frac{2}{3}\left[\frac{r}{a_o}\right]-\frac{2}{27}\left[\frac{r}{a_o}\right]^2\right)$, so on and so forth.

So, number of radial nodes comes from equating these radial parts of the wave function to 0. So, higher the degree of polynomial, more nodes you get. So, if I want to know what the, where the, where are the nodes, you just equate these functions to 0. And you get a quadratic equation in case of n = 3, l = 0, you get a linear equation for n = 2; l = 0 case and solutions of r give you the position of nodes.

One question that students often ask us here, is that how do you know that when this part, e.g. $\left(1-\frac{2}{3}\left[\frac{r}{a_o}\right]-\frac{2}{27}\left[\frac{r}{a_o}\right]^2\right)$ is equated to 0 you are going to get real roots? Well, we know because these are not just any polynomials, they are Laguerre functions. Laguerre functions are such that when they are equated to 0, you do get real roots only, you do not get imaginary roots, that is the saving grace.

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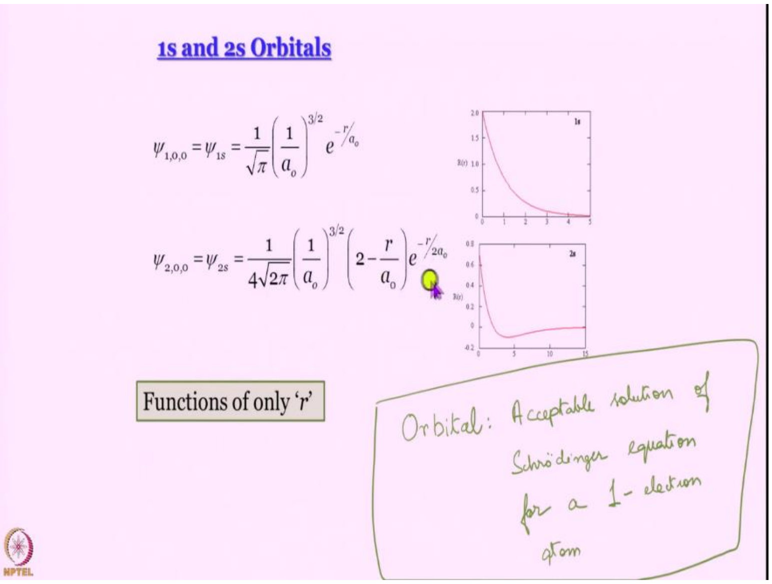

1s and 2s Orbitals

$$\psi_{1,0,0} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$$

$$\psi_{2,0,0} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right) e^{-r/2a_o}$$

Functions of only 'r'

Orbital: Acceptable solution of Schrödinger equation for a 1- electron atom

Now, let us take a closer look at the orbitals. Now, before that, let me formally say what an orbital is. What is an orbital? Many of you believe that, an orbital is a region of space in which probability of finding the electron is maximum, that definition is wrong. An orbital is an acceptable solution of Schrodinger equation for a 1 electron atom, that is what an orbital is. So, orbital is a wave function, not just any wave function. A wave function that you get by solving Schrodinger equation for a hydrogenic atom.

Hydrogenic means, only one electron is there, z can be whatever. One electron is there, so He^+ would be hydrogenic atom. What you get from there is an orbital. Li^{2+}, same. Please remember, an orbital is an acceptable solution of Schrodinger equation for a 1 electron atom. So, now let us look at these 1s and 2s orbitals. Exponential decay in r, this is what it looks like. For $\psi_{2,0,0}$, where is this $\left(2-\frac{r}{a_o}\right)$ going to become 0? $\left(2-\frac{r}{a_o}\right) = 0$, so $r = 2a_o$. So, at $r = 2a_o$, we have a node, what is a_o? The Bohr radius.

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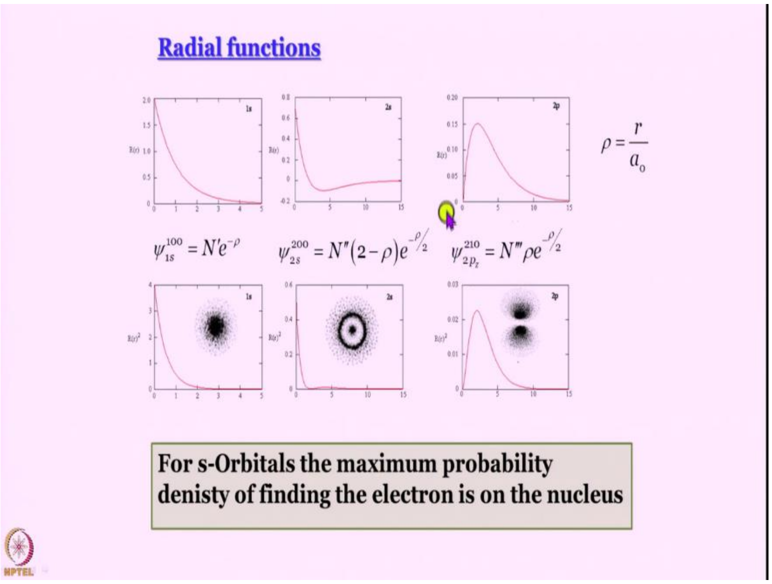
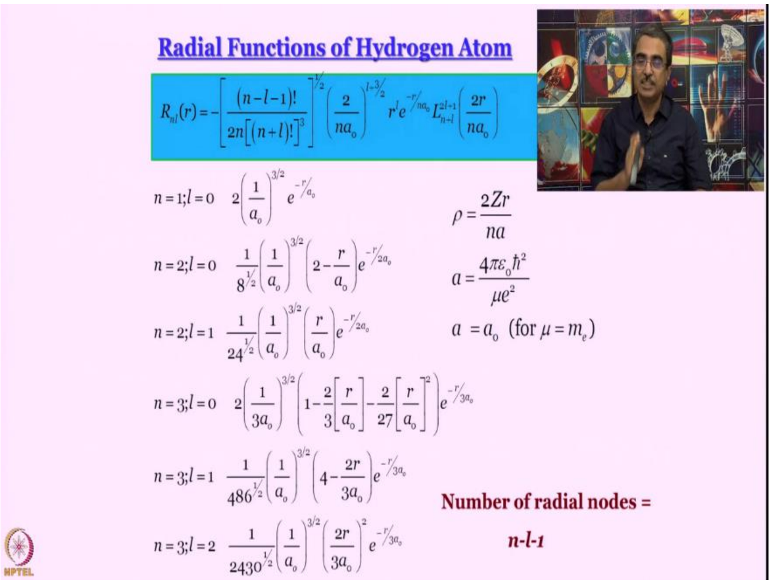


Radial functions

$$\rho = \frac{r}{a_o}$$

$$\psi_{1s}^{100} = N' e^{-\rho} \qquad \psi_{2s}^{200} = N''(2-\rho)e^{-\rho/2} \qquad \psi_{2p_z}^{210} = N''' \rho e^{-\rho/2}$$

For s-Orbitals the maximum probability denisty of finding the electron is on the nucleus



Radial Functions of Hydrogen Atom

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \left(\frac{2}{na_o}\right)^{l+3/2} r^l e^{-r/na_o} L_{n+l}^{2l+1}\left(\frac{2r}{na_o}\right)$$

$n=1; l=0 \quad 2\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$

$n=2; l=0 \quad \frac{1}{8^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$

$n=2; l=1 \quad \frac{1}{24^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}$

$n=3; l=0 \quad 2\left(\frac{1}{3a_o}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_o}\right]-\frac{2}{27}\left[\frac{r}{a_o}\right]^2\right)e^{-r/3a_o}$

$n=3; l=1 \quad \frac{1}{486^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(4-\frac{2r}{3a_o}\right)e^{-r/3a_o}$

$n=3; l=2 \quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{2r}{3a_o}\right)^2 e^{-r/3a_o}$

$$\rho = \frac{2Zr}{na}$$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$a = a_o$ (for $\mu = m_e$)

Number of radial nodes =

n-l-1

Now, here we show you the three radial parts, $\psi_{1s}^{100} = N' e^{-\rho}$ (1s), $\psi_{2s}^{200} = N''^{(2-\rho)e^{-\rho/2}}$ (2s) and $\psi_{2p_z}^{210} = N'''\,\rho e^{-\rho/2}$ (2p). As you see, this 2p goes through a maximum. We will come back to this later also. But if we just go back to the equations, I think you can see it very clearly. Where is 2p? $n = 2;\ l = 0$ is 2s, $n = 2;\ l = 1,$ this is your 2p. What do I have in 2p? I have $\left(\frac{r}{a_o}\right)$ multiplied by $e^{-r/2a_o}$. So, $\left(\frac{r}{a_o}\right)$ increases with r naturally, $e^{-r/2a_o}$ decreases with r.

Take a product, you are going to get a function that goes through a maximum and we will have more to talk about that. What are these? These are square of capital R, R$(r)^2$. This is what your square of 1s orbital is, again a fall which is a little steeper. And for 2s orbital what do you get? It falls off becomes 0, then increases again and tapers to 0 later on. For 3s orbital sorry, rather for 2p orbital, what is it? We take square, again it is a curve that looks like this.

What are these figures that are shown in inset? We will take a rain check on that. We will talk about it later. But let me ask you a question. What I see is that, R$(r)^2$ is maximum at $r = 0$, that is a nucleus for s orbitals, does that mean that probability of finding the 1s electron or 2s electron at the nucleus is maximum? Because if it is, then we are back to square 1, we are back to the Rutherford model, what have we gained?

So, here it is important to remember what Born interpretation is, what is $\psi\,\psi^*$ or $R\,R^*$ in this case, well no R^* is there, R^2 r is a real function anyway. Please remember that R^2 or $\psi\,\psi^*$ is probability density, is not probability. So, it is absolutely okay to say that for s orbitals the maximum probability density, and after all these years, I noticed that density spelling is wrong here, maximum probability density is at the nucleus, fine. Probability density, not probability. What am I talking about? You will see what I am talking about.

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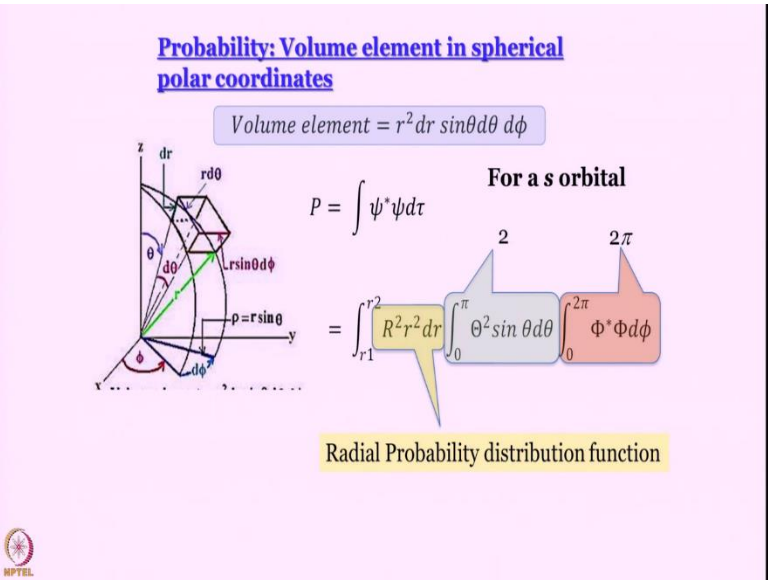

Probability: Volume element in spherical polar coordinates

$Volume\ element = r^2 dr\ sin\theta d\theta\ d\phi$

For a s orbital

$$P = \int \psi^* \psi d\tau$$

$$= \int_{r1}^{r2} R^2 r^2 dr \int_0^{\pi} \Theta^2 sin\,\theta d\theta \int_0^{2\pi} \Phi^* \Phi d\phi$$

2

2π

Radial Probability distribution function

So, remember what probability is? Probability density is defined at a point, you cannot talk about probability of a point. You have to define a volume element about that point. And you can talk about probability in that small volume element. And the volume element, as we had established earlier is $r^2\, dr sin\theta d\theta d\phi$. So, if you want probability, you need to integrate $\psi^*\, \psi$ with respect to this $d\tau$. So, this is what it is going to be. $P = \int \psi^*\, \psi\, d\tau$ = $\int_{r1}^{r2} R^2 r^2 dr\ \int_0^{\pi} \Theta^2 sin\theta d\theta\ \int_0^{2\pi} \Phi^*\, \Phi d\phi$

Suppose I want to know what is the probability of finding the electron between some r1 and r2. Even if r1 is 0, I have to write some value of r 2 there. That is going to be $\int_{r1}^{r2} R^2 r^2 dr\ \int_0^{\pi} \Theta^2 sin\theta d\theta\ \int_0^{2\pi} \Phi^*\, \Phi\, d\phi$. For s orbitals, what happens is in fact, I do not even need to know for the discussion that we are going to do later. If you understand that, these two integrals $\int_0^{\pi} \Theta^2 sin\theta d\theta\ \int_0^{2\pi} \Phi^*\, \Phi\, d\phi$ would be some constant that is enough. Because for an s orbital, and s orbital only. For s orbital, what happens is that there is no theta phi dependence. So, these integrals naturally will be some constant. So, $R^2 r^2 dr$ is called the radial probability distribution function.

So, it tells you how, what is the probability of finding the electron at some distance r? Well, it means what is the probability of finding the electron between r and $r + dr$. For s orbital, there is no theta phi dependence. So, $\int_0^{\pi} \Theta^2 sin\theta d\theta$ becomes 2 and $\int_0^{2\pi} \phi^*\, \phi\, d\phi$ becomes 2π. I recommend that you read this part from Atkins physical chemistry book, it is discussed very, very nicely there.

So, if it is not an s orbital, you only work with $R^2 r^2 dr$. If it is an s orbital, and if you want to find out some probability, you need to work with $4\pi R^2 r^2 dr$. But it does not matter for the discussion we are performing. If you remember capital R squared, small r square that is enough. What does it now mean for an s orbital especially?

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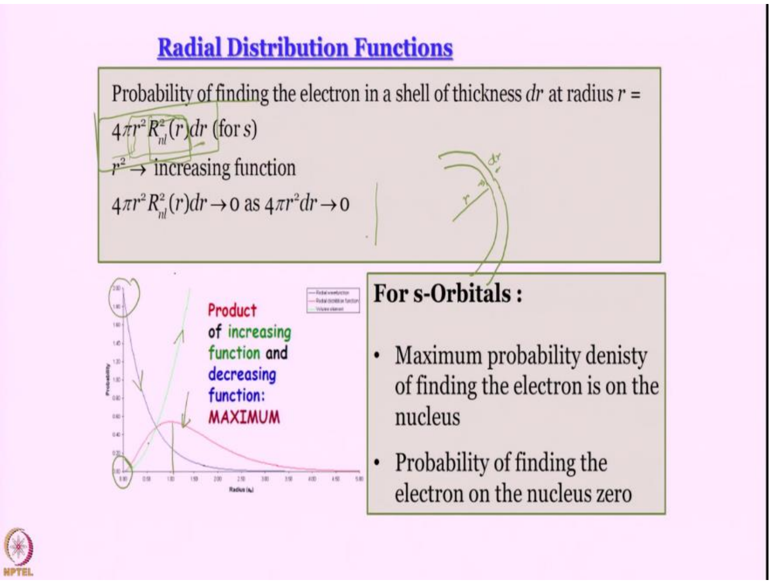

Radial Distribution Functions

Probability of finding the electron in a shell of thickness dr at radius r =

$4\pi r^2 R_{nl}^2(r)dr$ (for s)

$r^2 \rightarrow$ increasing function

$4\pi r^2 R_{nl}^2(r)dr \rightarrow 0$ as $4\pi r^2 dr \rightarrow 0$

Product of increasing function and decreasing function: MAXIMUM

For s-Orbitals :

- Maximum probability denisty of finding the electron is on the nucleus
- Probability of finding the electron on the nucleus zero

What it means is that, if I want to find out the probability of finding the electron, s electron in a shell of thickness dr at radius r. So, this is small r. This is let us say, when I write like this, it means the separation between these two arrows is dr. So, what is the locus of this point, a circle, what is the locus of this point? Actually, a sphere, not even a circle. So, what I get is a spherical shell. So, probability of finding the electron in a shell of thickness dr is actually $4\pi r^2 R_{nl}^2(r)dr$.

$r^2 R_{nl}^2(r)$ is density. And volume of the sphere is 4 pi r square, well sorry, what am I saying. $R_{nl}^2(r)$ is the density, probability density, and $4\pi r^2 dr$, that is your volume of the shell. That is what gives us the probability. Now, what happens? For, s orbital probability density is very high at small r equal to 0. But remember that it is not being multiplied by small r square, so for the product, the value at small r equal to 0 is actually 0.

So, you are multiplying r^2 which is an increasing function of r, by R_{nl}^2, which is a decreasing function in r. I am talking about s orbitals, what will the product be? The product will be something that goes through a maximum. So, maximum probability of finding the s electron is somewhere here, wherever this curve becomes maximum. It is not at r equal to 0. So, this discussion brings about a very important understanding, that probability density and probability are not one and the same.

Probability density is one thing, but if the volume element is very small, then probability will be 0. So, probability density is like your intelligence or competence or smartness. And this r squared dr, this is like the amount of work you put in. So, if you are super smart, but you do not work, you are not going to do well. So, that total probability of doing well is 0. So, something similar to that, let us say this is just an analogy. Do not take it too far. But that is what it means. It is not sufficient to have high probability density, your volume element must also play a very, very important role.

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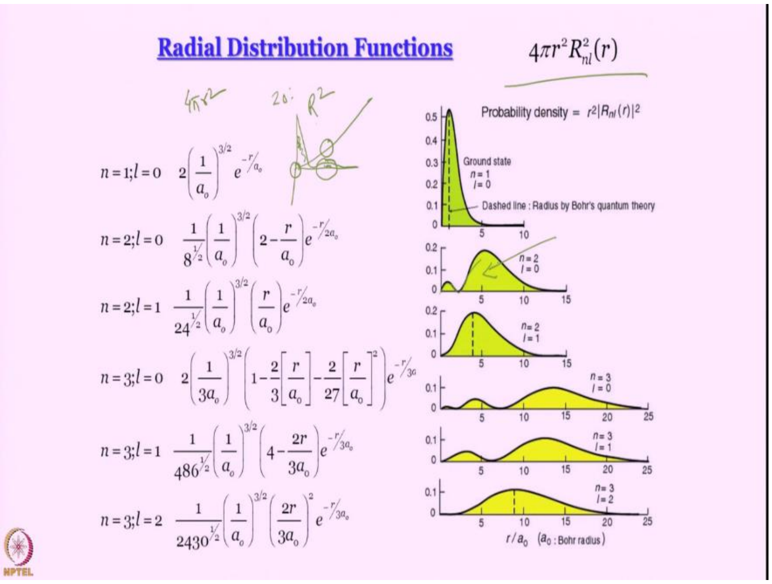


Radial Distribution Functions

$4\pi r^2 R_{nl}^2(r)$

4πr²

2s: R²

$n=1; l=0 \quad 2\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$

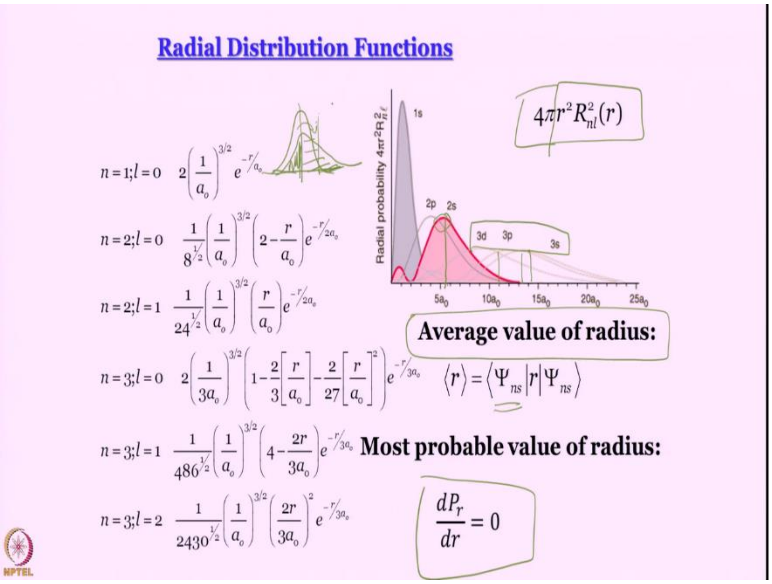
$n=2; l=0 \quad \frac{1}{8^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$

$n=2; l=1 \quad \frac{1}{24^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}$

$n=3; l=0 \quad 2\left(\frac{1}{3a_o}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_o}\right]-\frac{2}{27}\left[\frac{r}{a_o}\right]^2\right)e^{-r/3a_o}$

$n=3; l=1 \quad \frac{1}{486^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(4-\frac{2r}{3a_o}\right)e^{-r/3a_o}$

$n=3; l=2 \quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{2r}{3a_o}\right)^2 e^{-r/3a_o}$



Radial Distribution Functions

$4\pi r^2 R_{nl}^2(r)$

$n=1; l=0 \quad 2\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$

$n=2; l=0 \quad \frac{1}{8^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$

$n=2; l=1 \quad \frac{1}{24^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}$

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$n=3; l=2 \quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{2r}{3a_o}\right)^2 e^{-r/3a_o}$

Average value of radius:

$\langle r\rangle = \langle \Psi_{ns}|r|\Psi_{ns}\rangle$

Most probable value of radius:

$$\frac{dP_r}{dr} = 0$$

So now, let us see what this $4\pi r^2 R_{nl}^2(r)$ is, for different orbitals. This is what they look like. For 1s orbital, it goes through a maximum. For 2s orbital, well if you just take square of it, what will you get? Again, if you search Anindya Dutta quantum in YouTube, you will get a lecture series. And in that series, they are actually plotted in front of your eyes, and shown how these functions arise.

I will not do it here, I encourage you to do it, use any graph plotting software of your preference, and please work out, it is a lot of fun. So, what is capital R square for 2s? Starts from a high value, goes down to 0. It is not a straight line, increases and then tapers off to 0 at a long long r. So, see, this volume is so much more than this volume, is not it? So, if you just look at R^2, that is what it is. It is much higher in the vicinity of the nucleus.

But do not forget you have to multiply it by $4\pi r^2$ in order to get this radial distribution function. And $4\pi r^2$ what will it look like? It will be something like this, that is why when you multiply a small value of R^2 by a large value of $4\pi r^2$, the outer portion actually blows up.

And in the vicinity of the nucleus, since r is equal to 0 or very small value, this becomes very small. That is how you get this kind of a distribution. Two humps, the one close to the nucleus is small, the outer one is much much larger. Similarly, these are the shapes that you get for 3s, 3p and 3d radial parts. And if I just plot them all together, you see, we will talk about two quantities here, quickly. Average value of radius $\langle r \rangle = \langle \Psi_{ns} | r | \Psi_{ns} \rangle$ and most probable value of radius $\frac{dP_r}{dr} = 0$. What is the most probable value of radius?

It is essentially the radius at which, at which these curves become maximum. How do I find it? Just take dPr and differentiate with respect to dr, $\frac{dP_r}{dr}$. Please remember what dPr is, please remember, you have to take $r^2 R_{nl}^2(r)$. Does the 4π matter? Not in this discussion, because you are equating to 0. It does not matter whether it is 4, 4 pi or whether it is 400 pi.

You are equating it to 0 anyway. So, when you equate, when you differentiate $r^2 R_{nl}^2(r)$, equate to 0, for whichever value, this becomes 0, that gives you the R value at which you get a maximum in the curve, that is called the most probable radius or most probable value of radius. And see this, if you can compare 3p, well, 3s 3p and 3d, the most probable radius of 3s is actually larger than that of 3p, which is much larger than that of 3d.

This is something that I guess we have learned in the high school. And it has been said that d orbitals are attracted more towards the nucleus, because they are more diffuse. We do not even have to go that in, into that in that course. In this course, please remember that, well do not, you do not even have to remember this. I am just showing you here, that the most probable radius of 3s is more than that of 3p more than that of 3d. That is one quantity.

And what is the average value of radius? That you know very well, since I am working with normalized wave function, this is sufficient expression for average value of radius. When will they be same? When will they not be same? Well, if you have a distribution that looks like this, a symmetric distribution, then the average value and the most probable value will be one and the same. Most probable value is just the modal value.

However, when the distribution is skewed something like this, then what will happen? This will be average value, but look at the areas, the area on the left hand side of average value is so much less than the area on the right hand side of the average value. So, the average value, not average value sorry, most probable value. So, the average value will actually be larger than the most probable value here.

You can just work this out to satisfy yourself taking some numbers, you will see that average and most probable values need not be same unless you have a perfectly symmetric distribution. Which one is important? Both are important for different things.

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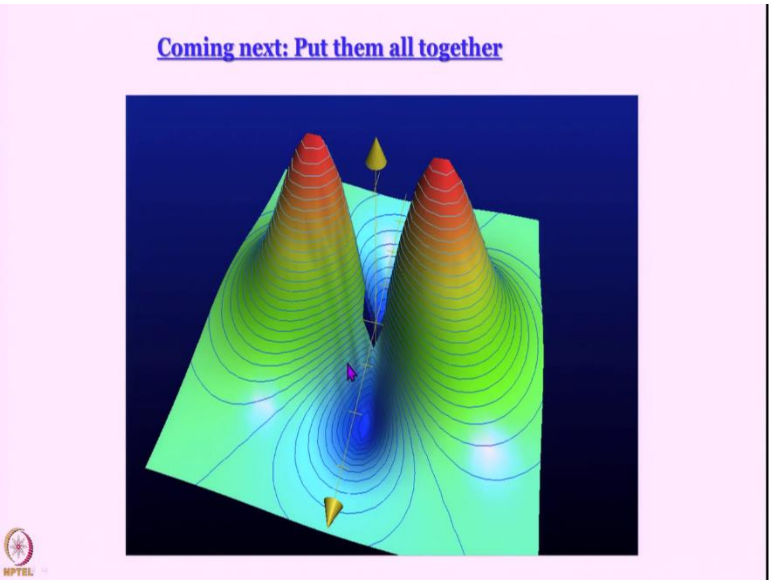

Coming next: Put them all together

So, we have performed a discussion of r dependent, theta dependent, phi dependent parts separately. Now, to get those beautiful pictures that I had shown you earlier, we need to put them all together. That is what we will do in the next lecture. And we will see what kind of pictures that we get. And that is what gives us what we call, shapes of orbitals. And using these orbitals, we will be actually able to generate the, we will be able to work out the regions of space, where probability of finding the electron is 90 percent or 95 percent, 98 percent or something.

So, what you see here is a depiction of the wave function. The z axis, vertical axis is actually a wave function. The other two axis can be x and y or whatever. And you will see how we arrive at this kind of shapes for the orbitals, that we are going to study in the next lecture.