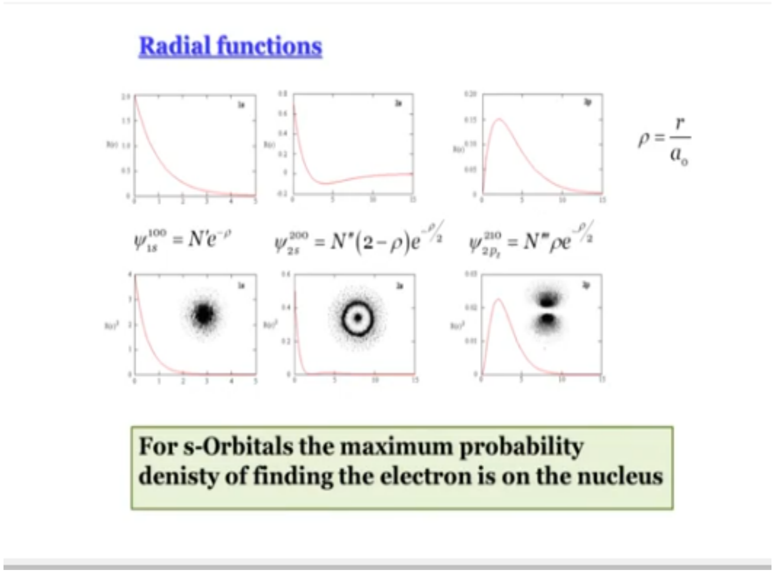
Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology - Bombay

Lecture – 27
Radial Probability Distribution Functions

Okay, we have broken off at this point in the last module, now we will complete the discussion; we were in the middle of the question about probability density and actual probability.

(Refer Slide Time: 00:30)



Radial functions

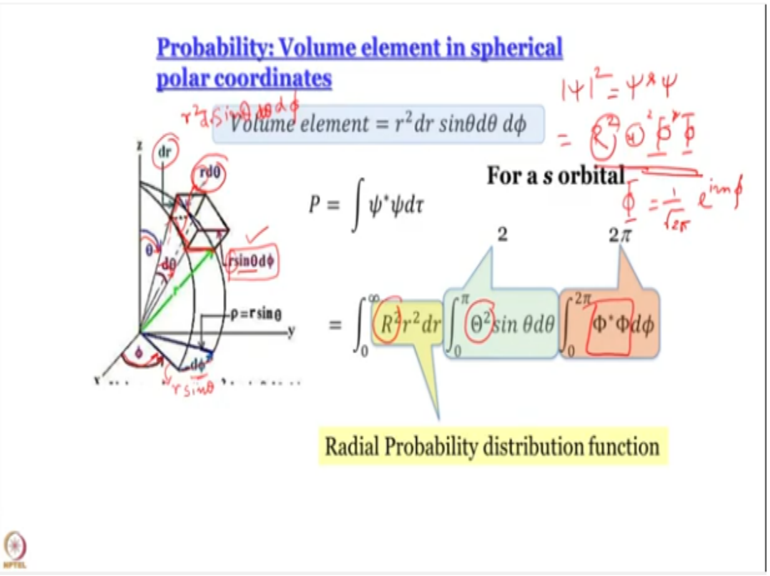
$\rho = \frac{r}{a_0}$

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

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

And we said that it is important to remember that psi, psi star is really probability density, in this case r, r star, okay, so for s orbitals, maximum probability density of finding the electron at the nucleus is probability density is maximum at the nucleus for an s electron, as we will see probability is actually 0, okay, so let us go ahead with that.

(Refer Slide Time: 00:53)



Probability: Volume element in spherical polar coordinates

$r^2 d\sin\theta d\theta d\phi$

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

$|\psi|^2 = \psi^* \psi$

$= R^2 \Theta^2 \Phi^* \Phi$

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

For a s orbital

$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$

2

2π

$$= \int_0^\infty R^2 r^2 dr \int_0^\pi \Theta^2 \sin\theta d\theta \int_0^{2\pi} \Phi^* \Phi d\phi$$

Radial Probability distribution function

And now, I do not remember whether we have done it in the previous module but we will just do it again if required, let us workout an expression for the volume element in spherical polar coordinates, I think we have done it earlier ones but we still do it. See, how do I get a volume element; if it is, if we are talking about x, y, z then it is simple, increase x by a small amount dx, increase y by a small amount dy, increase z by a small amount dz.

So, the volume element would be dx, dy, dz, when we talk about spherical polar coordinates, what we do is; okay, this is one coordinate r, up to here is r, we increase that coordinate by an amount dr, okay so that is one side of our volume element. Next what we do is; next coordinate is theta, so we increase theta, this is your theta by a small amount d theta, so decide that we generate of the volume element there is this section, this one.

And what is a length of this r, well r multiplied by d theta, right, d theta is a small angle, remember, so since it is a small angle, it is going to be this r multiplied by d theta, this is again something that we learned in very simple 3 dimensional coordinate geometry in 11, 12, okay, the expression for the length of an arc, okay r d theta. So, 2 sides of the volume element are defined now, the third side is this one.

To get this volume element, what we should do is; we should go down to the xy plane because that is where phi is defined, this here, this angle is phi, the angle between the projection of the position operator in the xy plane with the x axis, so increase that angle by a small amount d phi, remember this length, what is this length; this is r sin theta. So, what will the length of this arc be; r sin theta d phi.

And essentially what we do is; this is the length of the arc, it is not taking back okay, the length of this arc is equal to the length of this arc, it is the same value r sin theta d phi, what then is the volume element; you have 1r from here, another r from here, so even though it is written later on, I will just write it, we will get r square, then let us write everything in theta, we get a sin theta from here, so sin theta, I will just write d theta and anything else in phi, no, okay I should write dr may be, r square dr sin theta d theta d phi.

This is the volume of the volume element, okay and this is what is going to lead to our answer, what is this volume element for r equal to 0. So, r equal to 0, see r square multiplied by we do not care what else is there, r is equal to 0 means r square equal to 0, so volume element for r equal to 0 is equal to 0, so no matter how high psi square might be since the volume is 0, the probability which is a product of probability density and the volume is equal to 0, okay.

You take the heaviest thing in the universe, if its volume is 0, it is not even there, so mass is 0, similarly probability is a product of volume and probability density, if the volume itself is 0, then even for a high probability; for high probability density, probability will be equal to 0, okay, so this is the reason, volume element is r square dr sin theta d theta d phi. Now, let us actually do a little more rigorous calculation of the expression for probability.

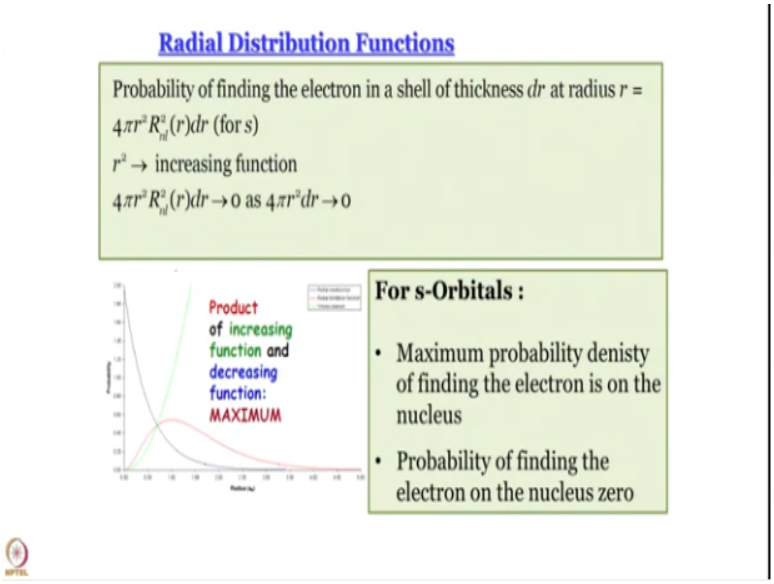
P of course is equal to integral psi, psi star d theta within the required limits, so let us write this out, so we get; what is psi; psi is R into capital theta into capital phi, and you might remember that R is your; R is real, capital phi is also real, sorry capital theta is also real, capital phi is an imaginary quantity. So, when we write mod psi square that is psi star psi that boils down to R square capital theta square capital phi star multiplied by capital phi, okay.

Of course, what I have written here is essentially what you have here is R square, R square, capital theta square here, capital phi star capital phi is here and you might remember what capital phi is; capital phi is 1 by root over 2 pi e to the power im phi, so you can figure out what capital phi star is going to be, right. Now, let us simplify this a little bit; so this here R square into r square into dr is called the radial probability distribution function, I will come back to this dr quantity a little later.

We will see why we should consider that also, the second one is capital theta square sin theta d theta. For s orbital, we know that this; these do not make any contribution, okay, so capital theta square you can take as 1, so that is the case then integral 0 to pi sin theta d theta, what will it be; minus cos theta d theta, cos theta is equal to 1 for theta equal to 0, -1 for theta equal to pi, so we are going to get 1 - - 1 that is equal to 2.

And what will I get here to integrate this, we will get from the normalisation constant, we will get 2 pi, so what we get is 4pi square, so for an s orbital, the radial probability distribution function that we work with is 4pi square multiplied by R square into r square dr, for others we just work with R square into r square dr, this part you can study from some basic book like Atkins physical chemistry, okay.

(Refer Slide Time: 08:58)



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 :

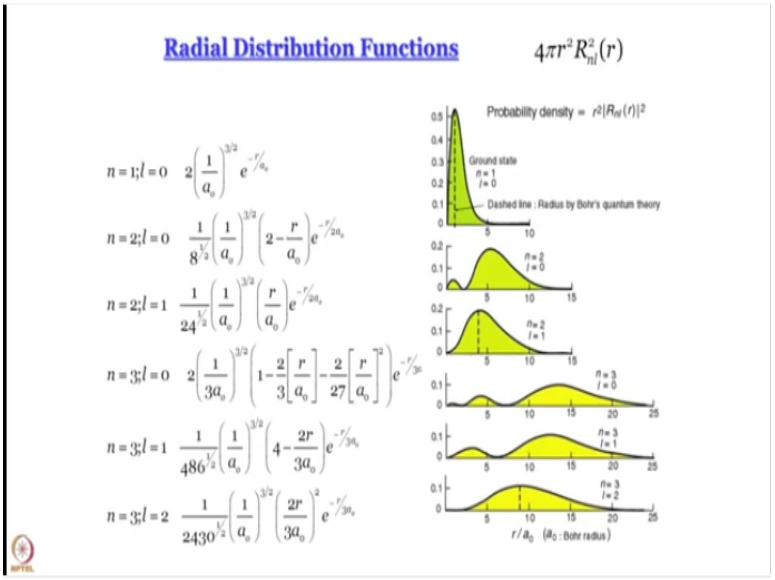
- Maximum probability denisty of finding the electron is on the nucleus
- Probability of finding the electron on the nucleus zero

So, now what you want to do is; we want to find the probability of finding the electron in a shell of thickness dr at radius r, this is what is boils down to. So, what we are saying is that let us consider a shell of uniform thickness dr at different values of r, okay; 4pi r square into R square into dr; dr is a constant, so this is for s orbital right, for others this 4pi will not come, r square is of course a parabolic increasing function in r and what about this R; R for s orbital is maximum at r equal to 0, then it becomes 0 asymptotically.

So, now see since r square is; r square is equal to 0 at r equal to 0, this product 4pi r square R square dr becomes 0 as 4pi r square dr becomes 0 at r equal to 0, so this is what we get. So, actually the maximum is somewhere in the middle, maximum probability would be somewhere in the middle for 1s orbital, for 2s orbital we are going to get a little more interesting plot. For s orbitals, maximum probability density of finding the electron is on the nucleus, no doubt.

But probability of finding the electron on the nucleus is actually 0, why; because the volume element, volume of that element is actually equal to 0, okay, so it does not matter how high the value of r square or psi, psi star s for r equal to 0, this is what gives an answer to the apparently problematic question of why is it that the electron, 1s electron, why is it that it does not reside at the nucleus most of the time, okay.

(Refer Slide Time: 11:02)



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

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

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

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

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

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

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

So, here we are, these are the different wave functions what we have said now, if you work out this radial distribution function, radial probability functions what we will get for 1s orbital, we already know what we are going to get, will go through a maximum, for 2s orbital, it has to go through 2 maxima, now remember that okay may be I will show you the answers first, this is the answer, let us go through the pictures one by one.

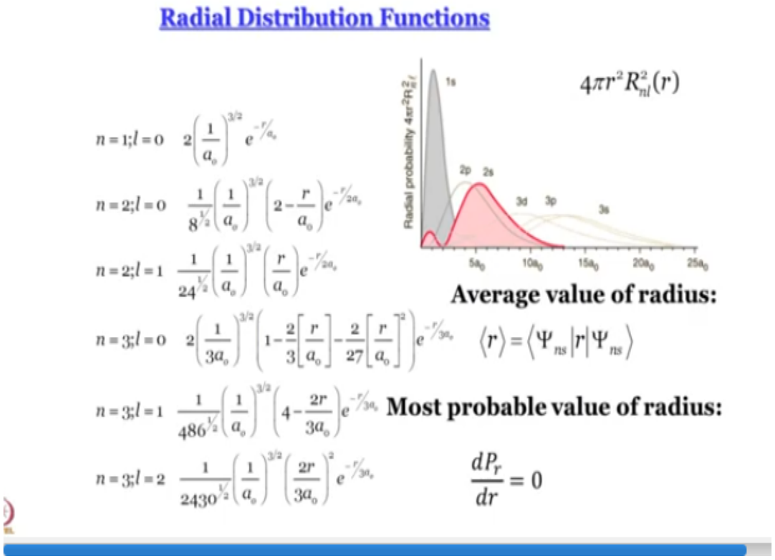
For 1s orbital, we have discussed it already, somewhere it is going to be maximum, the probability density is r square R square, okay now for 2s orbital remember, if you just look at psi, for psi square, the inner lobe is much bigger but when you look at the probability distribution along radius, you see the outer lobe becomes the major lobe, why; because you are multiplying by r square, as you go out, r increases, r square increases as its second power.

So, even though the value of the wave function itself or its square is very small at say 5 or 10 units of r, the value of r square multiplied by R square, r square multiplied by R square blows up because this r increases as second order of r, that is why as far as probability is concern, the outer lobe is the major lobe, right. Similarly, for 3s orbital, you have only 1 maximum, for 3p orbital, this is what you get, okay, now sorry, I think this is 2p orbital not 3s sorry, I would carry away little bit.

For 2p orbital, there is only 1 maximum, no node for this one, for 3s orbital there are 2 nodes, remember and if you just look at psi square it will be something like this, it will decay but since you are multiplying it by r square, the innermost band is smallest followed by the next one, the biggest one is on the outside. So, when we draw this what we are really drawing is the plot of finding the electron along; plot of probability of finding the electron along the radius, as r increases how does the probability of finding the nucleus change, okay.

This is what we are generating using the orbital, in this case R and right now we are only working with r, we have not work with theta, phi and this is how we can generate those regions of; maximum regions of maximum probability of occurrence of the electron by using the orbitals, okay.

(Refer Slide Time: 14:03)



Radial Distribution Functions

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

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

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

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

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

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

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

Average value of radius:

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

Most probable value of radius:

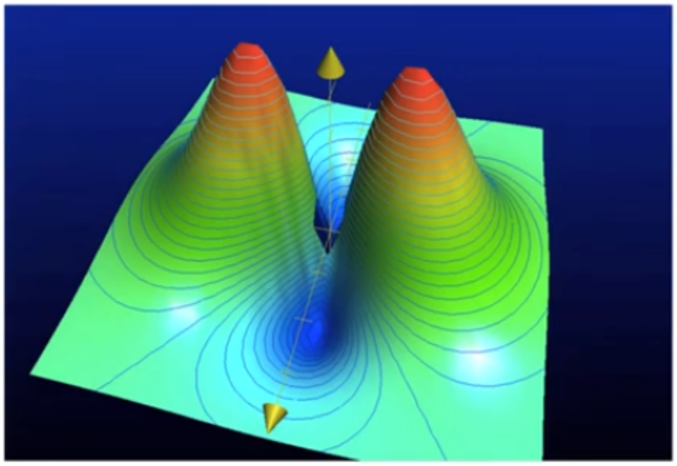
$$\frac{dP_r}{dr} = 0$$

And then if you just overlay all of them this is the kind of a figures that we get, this is where maximum probability of finding 1s, 2s, interestingly 2p has a maximum at a smaller value of r compared to 2s, then again 3s of course is the maximum that is at a much larger r compared to 2s but 3p has a maximum for a smaller value than 3s, 3d has a maximum for a smaller value than 3p, these become very important when we talk about multi electron atoms and when we consider phenomena like shielding, okay.

But then how do we find where these are, how do we know what is the probability, where the probability is maximum, these are 2 very important things, we can find out the average value of radius in the usual way by calculating the expectation value okay, of course here the expression means that we are working with the normalised wave functions and also we can find the most probable value by differentiating the probability with respect to r and equating it to 0 that will give us maxima, okay. So, this is; these are things that we can do using the radial part of the wave function and this is what we will do in our assignments as well so, we close this discussion.

(Refer Slide Time: 15:31)

Coming next: Put them all together



What comes up next is very interesting, we have talked about phi, theta, r dependent parts separately, now we are going to learn what happens when we put them together and when we put them together we generate beautiful pictures like this, what is this picture; this axis is actually the wave function, these are the other axis, so of course the problem here is that we have r theta phi and we have psi.

So, if I have to draw a picture of psi as a function of r theta phi, all together, then I need 4 dimensional space but I only have access to 3 in fact, when I draw on a paper I only have access to 2, so how do we handle this problem, how do you represent the orbitals which seemed to be a 4 dimensional which seem to require 4 dimensional space to depict, how do we depict them in 3 dimensions or 2 dimensions, do we take sections, do we use some other trick, how do we generate figures like this, that is what we are going to discuss in the next couple of modules.