Quantum Chemistry of Atoms and Molecules
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Lecture – 28
Hydrogen Atom Wavefunctions: s Orbitals

In this module and the next, we are going to have a lot of fun, we have done plenty of mathematics which might have been taxing for some of us but now what we are going to do is we have reached the stage where we can talk about the results of all that mathematics that we have done. Well, as you know we have actually skipped a lot of tedious steps but still now we are in a position to draw these beautiful pictures like the one that is shown here was better still we get to understand what we are talking about.

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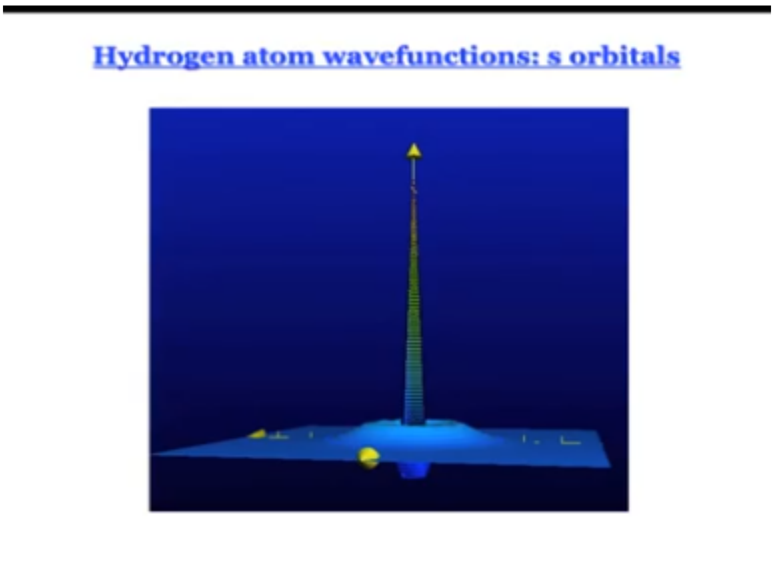

So, we will discuss the acceptable hydrogen atom wave functions as we said earlier, these are called orbitals, so once again let me repeat an orbital is an acceptable solution of Schrodinger equation of a hydrogenic atom, a one electron system okay that is what an orbital is nothing more nothing less, let us get this very, very clear. Hearing this I would expect you to start asking questions right away because if these orbitals are one electron wave functions how is it that we talk about electron configuration of many electron atoms.

How is it that we use them to generate molecular orbitals in molecules, they are not one electron systems, well we will cross those bridges when we come to them right now, let us just see what kind of pictures we can draw, when we consider the functions that the orbitals are.

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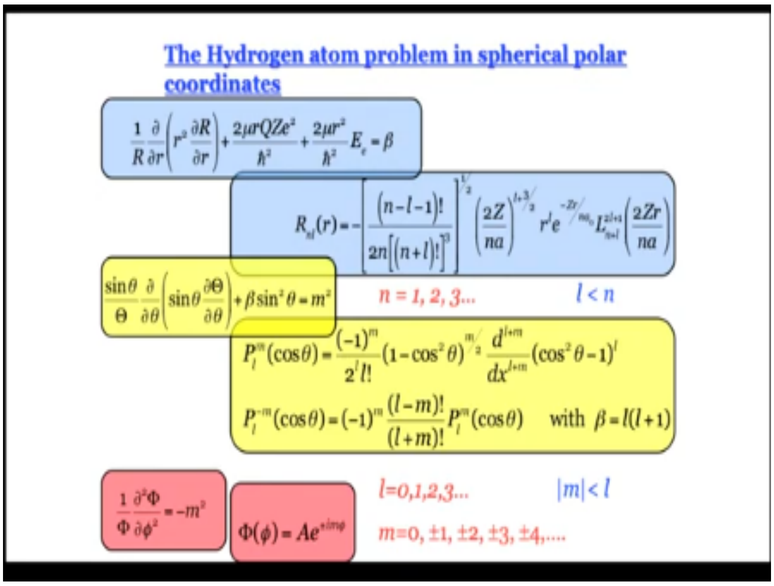

So, we already know what kind of functions they are, we have formulated the hydrogen atom problem in spherical polar coordinates and we have got 3 equations; one in phi, one in theta and the third in r, we have explicitly solved the phi dependent part and we have got a very simple solution, 1 by root over 2pi for whatever reason, I have forgotten to write the normalization constant everywhere, e to the power plus minus im phi, you could just say e to the power im phi because plus minus is incorporated in the values of m themselves.

The theta dependent part we have given you the solution and it is worked out from commutativity of angular momentum component and total angular momentum square, we are actually going to perhaps record those lectures a little later but they might come before the lecture I am presenting now, so at the moment I do not know whether we have done the solution whether you have seen the solution but if you have not, it will come sometime later.

We do plan to do a complete discussion of angular momentum but for now, it is sufficient to know that the solution of the theta part is essentially some polynomials in cos theta and solution well they are characterized by the quantum numbers l; l ranges from 0, 1, 2, 3 so on and so forth and magnitude of m has to be less than l. When we solve the r part we get another series of polynomials, the Laguerre polynomials.

And then by applying the boundary conditions to these wave functions, the r dependent wave functions we get another quantum number, the third quantum number, the principle quantum number n that ranges from 1, 2, 3 so on and so forth and also s has become a pattern by now, from this part we get a limit to the value of l and l always has to be less than n, again this result is something that we have known since perhaps class 11 or class 12. We have said this several times already but before going on to start drawing them, I thought, I will just present them once.

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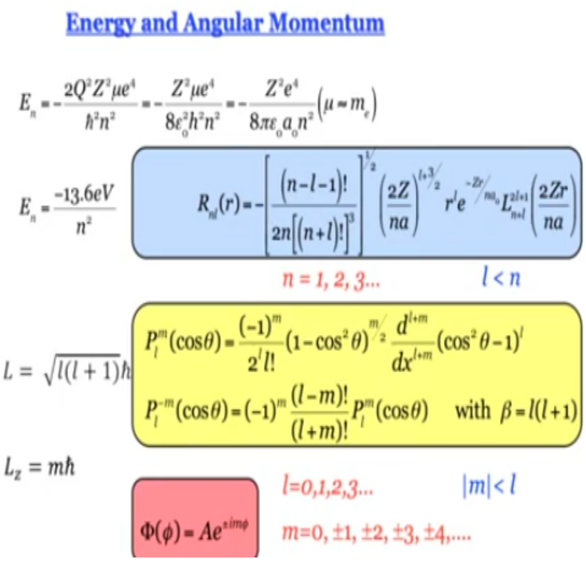

And also what you have learnt is that from these wave functions, we can find out the energy from the r dependent part and you can find out total angular momentum from the theta dependent part, you can find out the z component of angular momentum from the phi dependent part, these are the information's contained in each of these parts of the wave function.

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Radial and angular parts

$$\psi(r,\theta,\phi) = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi) = R_{n,l}(r)Y_l^m(\theta,\phi)$$

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

$n = 1, 2, 3\ldots$ $\quad l < n$

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

$l = 0,1,2,3\ldots$ $\quad |m| < l$

$m = 0, \pm1, \pm2, \pm3, \pm4, \ldots$

So, here it is r, R multiplied by capital theta multiplied by capital phi and you can also put theta and phi dependent parts together and you can write this as a spherical harmonics because after all in spherical polar coordinates you have 1 radius which is a length and you have 2 angles, so theta and phi are coordinates of a kind, so usually they are put together and they are called spherical harmonics.

And you can write it as the radial part multiplied by this spherical harmonics, what we are going to do in the next couple of modules is that we are going to try to plot them one by one and we are going to try to see what they look like. Of course, naturally a question that will arise is that what happens when m is non-zero, then you will have an imaginary function, how do you plot an imaginary function, we will see, right.

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Radial Functions of Hydrogen Atom

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

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

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

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

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

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

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

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

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

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

Number of radial nodes = $n-l-1$

We have already talked about this radial functions, I will not repeat them once again, number of radial nodes as we know is n - l – 1.

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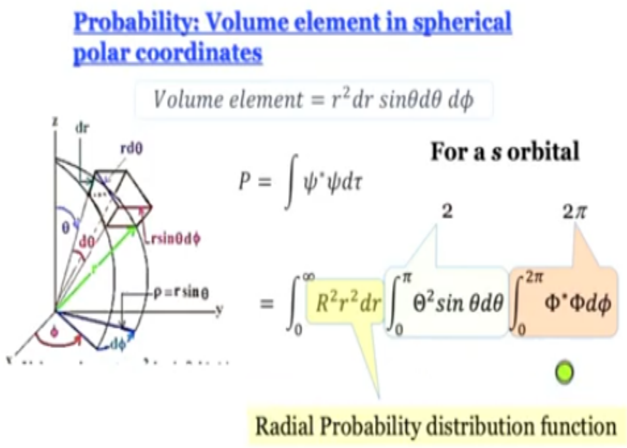

And a very important concept that we have discussed is that of radial probability density, we have said that it is important to consider the volume of the volume element written in spherical polar coordinates, if you want to talk about probability distribution, so from there we have realized that it is not enough to talk just about R square, you must talk about R square multiplied by r square, if you are going to understand what kind of probability density is there across, well along a radius.

They will be modulated by the theta and phi dependent parts, we will come to them one by one, in this module we only want to talk about s orbitals which do not really have any contribution from the theta and phi dependent parts, so it is enough if you consider this part to start with, when we talk about p orbitals then of course, we cannot not consider the angular part as well, alright.

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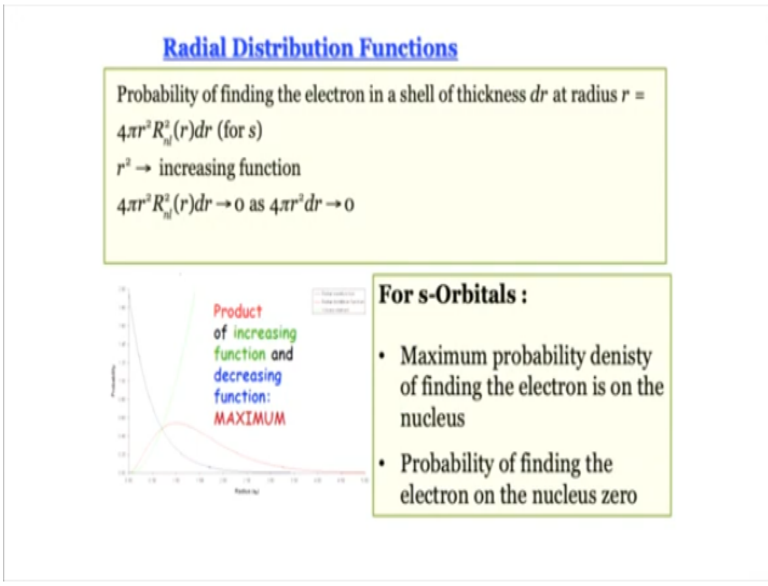

So, this is the radial distribution function, we will actually plot them one by one.

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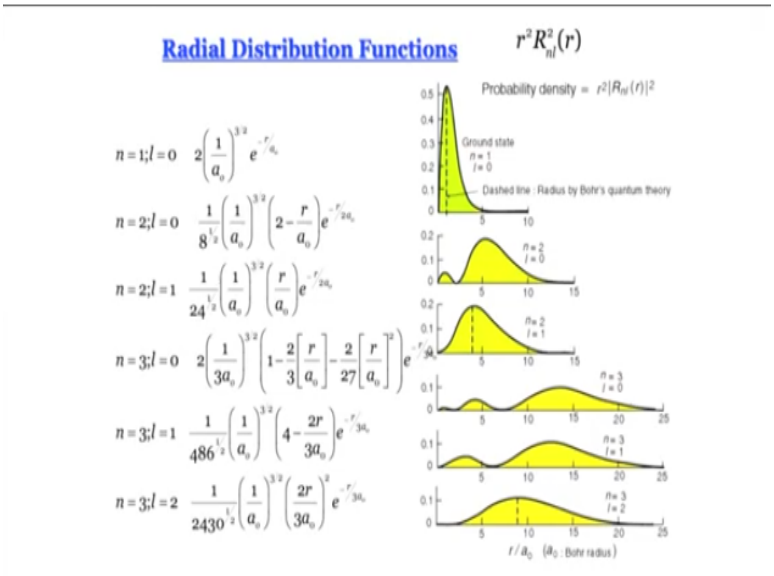

We have already shown you the result today; we will plot them in front of you and see how we get this, okay.

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Information from the radial part

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 as you said the information you get from radial part are average value of radius and most probable value of radius.

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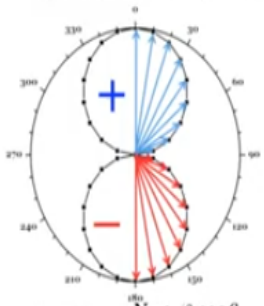
Angular Distribution Functions

p-Orbitals

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}\cos\theta \quad m = 0 \text{ case}$$

Angular part: Polar plot of $2p_z$ --- $\cos\theta$



θ	cosθ
0	1.000
10	0.985
20	0.940
30	0.866
40	0.766
50	0.643
60	0.500
70	0.342
80	0.174
90	0.000
120	-0.500
150	-0.866
180	-1.000

$$\psi_{210} = \psi_{2p_z} = N\rho e^{-\rho/2}\cos\theta$$

In addition, of course, the most important energy and when we go to the angular part, we will talk about angular distribution function as well okay.

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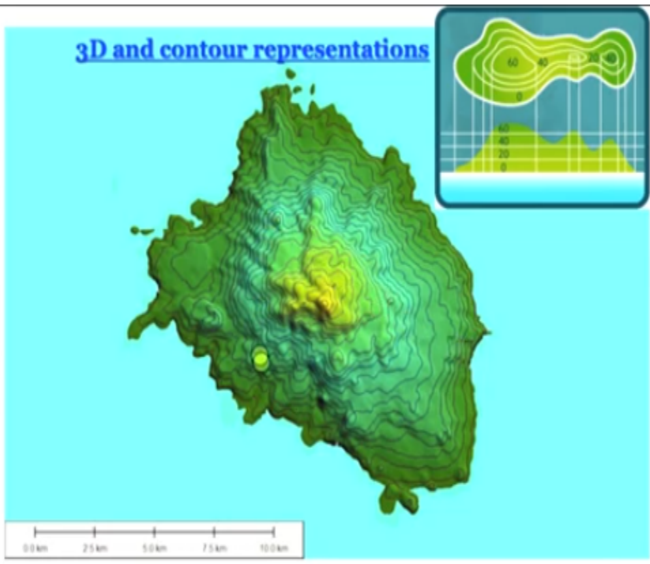

Now, the way we represent this is by using 3 dimensions, 3 dimensional representation and since we cannot represent unless we draw a model, if you want to draw on paper, the most convenient way of doing it is to use contours, those who have studied geography to some extent or those who are interested in maps will have seen maps like this, what you see here is the map of an island, right.

So, here the island is shown in relief, looking at the colour coding, you can see that this is the peak and then this is a ridge and as you go down, well as you go in this direction or this direction or this direction radially out, the height decreases and these small lines that are there these are the contour lines, contour lines essentially join all the parts, all the points that have the same height as far as an island is concerned okay.

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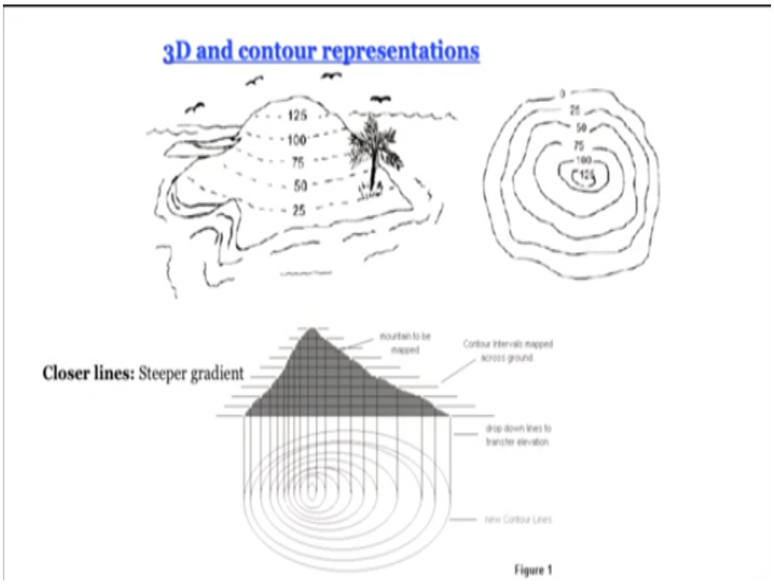

So, maybe we will go to the next slide and show it because it is more of a sketch, all this is from internet, I have not drawn this, so let us say this is the island, if you take a section of the island this is what it looks like. This side is steep, this side has a more gentle slope, so what you do is first of all you look at all the points, connect all the points that have the same height.

So, one way one analogy we can use is that suppose, the sea level keeps rising and let us say the sea level rises to this side, let us say this is 10 meter or something, then if you look from the top from a helicopter, what will you see; you will see this out, right now what you see is this zero line that is the outline of the island that is the zeroth contour line. Suppose, the sea rose 25 meters, then you would see this line that is marked 25, is not it.

Then if it rose to 50 meters, you would see this line, this would be the outline of the island okay and that is what we draw here okay, so essentially what you do is you take a section and you draw perpendiculars and then you join all the points that you get such, these are the contour lines. Contour lines denote the same height we are going to demonstrate with wave functions shortly.

Now, see one thing that is very important to remember is that wherever the lines are close together on this side for example, the slope is steeper wherever the lines are far apart, the slope is gentler because the slope is essentially the vertical displacement between 2 contour lines divided by the horizontal distance. Now, generally contour lines are drawn in such a way that the vertical displacement between successive lines is same, so 0, 25, 50, 75, and so on and so forth.

But then if the horizontal separation is more between 2 successive contour lines of course, it will be far apart from each other, if the horizontal separation is not much like here they will be close to each other, this is how one reads contour maps of course, one problem that we face once again is that in our case if you want to draw contour maps for wave functions, wave functions do not always have plus sign.

When we talk about islands they only have plus heights, there is no minus, so it is a little simpler in case of wave functions, we will have troughs as well, so how do you designate troughs; well you can write - 25, - 50 and so on and so forth or you can use contour lines of different colour generally, as we are going to show contour lines and colour shading together gives us very beautiful pictures, right.

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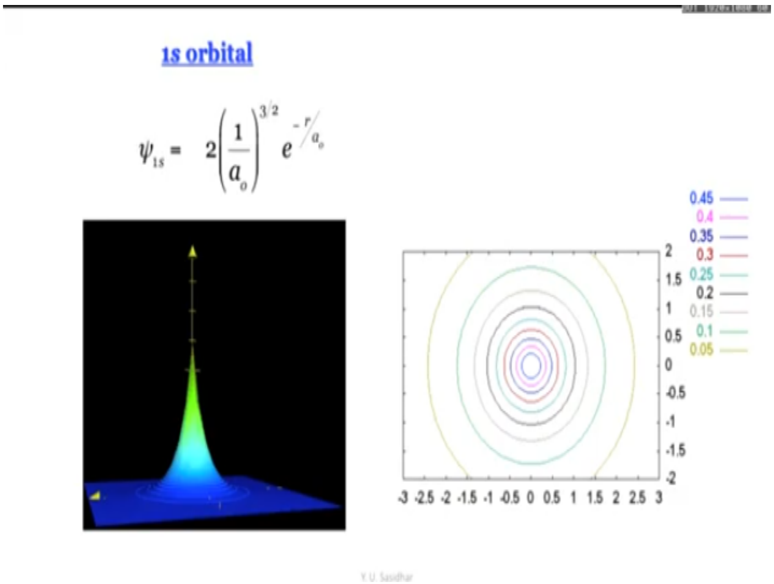

So, let us go ahead, first picture that I show and I drop a bombshell on you right away is 1s orbital, this is my depiction of 1s orbital but it is important to understand what I have drawn here, to understand that let us have a look at the function first. This is the simplest possible function one can get some constant multiplied by an exponential decay in r e to the power - r by a0. So, if you draw in 2 dimensions what will you get; you will just get an exponential decay, is not it, so why do not I just draw it, let me draw the function and let us see what we get.

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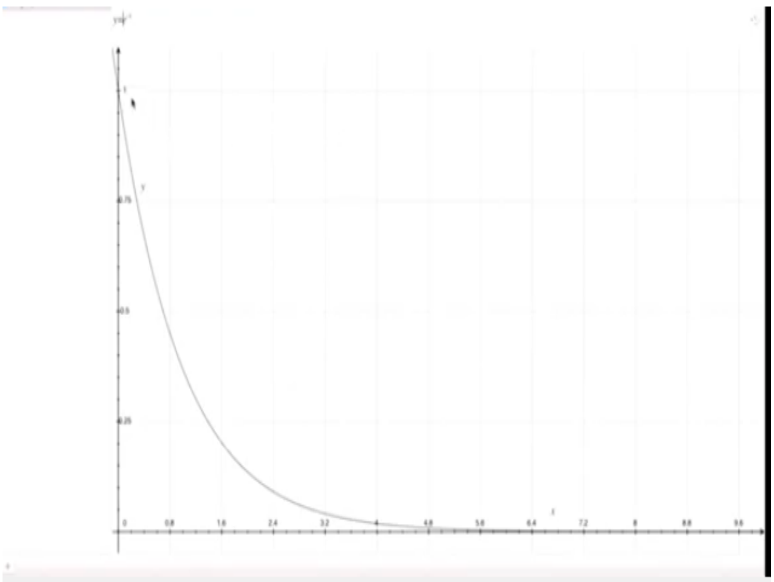

Okay, I have given you the preview of an even better looking function but we will come to that eventually, so let me just plot it, I want to plot e to the power - x that is all, so I will plot x into e to the power - x and I strongly encourage you to do this yourself, it is a lot of fun, I am using, I have a macbook, so I am using grapher but you can use any graph plotting software of your choice and you can play around like I am doing right now, okay here goes, so exponential decay.

One thing to remember is that this function for you, when you plot it is going to have values for plus x and minus x but in case of wave function remember x axis is really r, so there is no minus r, r if you remember goes from 0 to infinity, so we will just neglect since I do not know how to restrict my picture to your only positive values of x, we will just neglect the negative one.

So, let me change this frame limits, - 0.1 to 10 is fine it is just that the maximum will definitely go beyond 1, so we will go to 1, so I will make it 1.1 okay, please neglect the one that goes this side, this is a simple exponential decay okay. Now, this is a very drab one dimensional plot, is not it, we want to make it a little more interesting, so we can think like this that we have r and this r is independent of phi.

So, for all values of phi we can draw plot like this, what is the picture you get, take this exponential decay and turn it around by 360 degrees, whatever you get is your 1s orbital but remember when we plot this 1s orbital, one axis is r, fine, second axis what we are saying is phi, third axis is psi itself or r itself in case of 1s orbital, well in case of s orbitals, r and psi are one and the same.

So but we are not considering theta, theta does not have an effect here but these 3 dimensions are really not the 3 physical dimensions, 2 are physical dimensions r and phi, the third one is psi, so how to go from there to drawing a picture of an orbital in real space, we will come to that eventually but for now let me show this nice 3d picture also, instead of destroying that let me just open a new graph.

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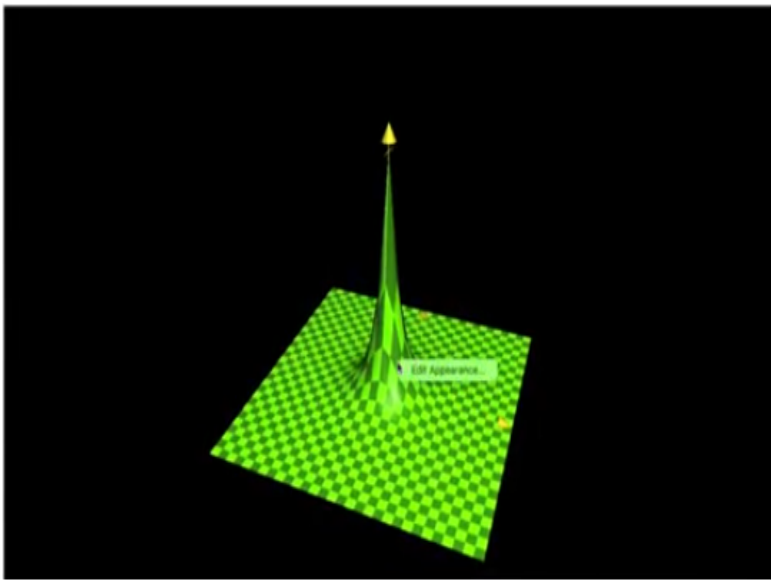

I want to plot a 3D plot, I want to make a 3D plot and here z we have to write is sorry; e to the power minus, I want r right and here it is written as x and y, z axis is psi and x and y, so I have to convert x and y to r, so in 2 dimensions r square equal to x square + y square, so instead of r, I am going to write e to the power - square root of x square, did I say minus then I was wrong; x square + y square actually, is not it, x square + y square okay.

Let me have a look at it for a minute just in case I am wrong, z equal to e to the power - square root of x square + y square okay, this is the plot that I get, I will make it a little more good looking, so that we see it better frame limits, I think we went to 10 up to there, so this I will make - 10 to + 10, so y will also be - 10 to + 10, these are all arbitrary values, please do not worry about the actual values here.

Look at the picture, I do not have anything in the negative side, so I will just make it 0.2 or something, positive side I do not have anything beyond 1 actually, so I will just make it 1.1 okay, so this is your 1s orbital, it started looking like it but I will make it look better and the reason why I am doing all this is that you should have an idea of how these pictures are generated.

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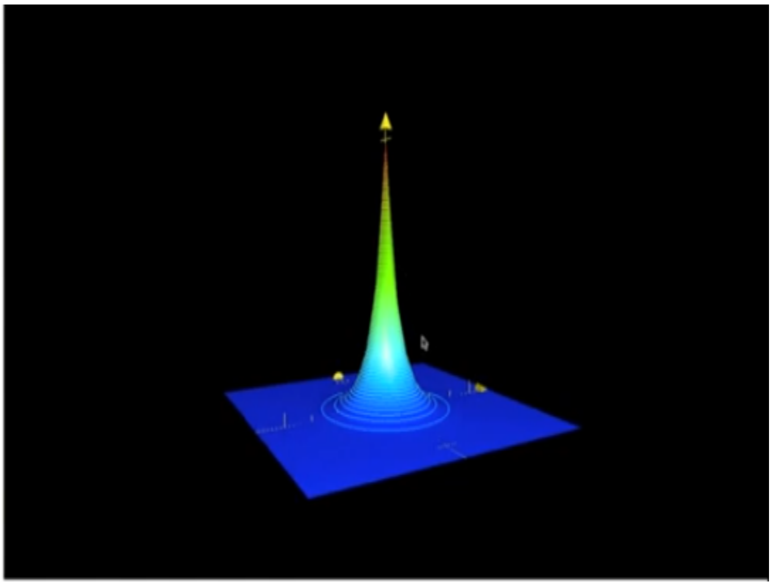

So, see what I am doing; I am colouring this picture of mine according to height, so this colour unfortunately, I have colour line, so I will not take the risk of saying that this is blue and this is red but I hope that is correct, you can figure out which colour it is, or you can say is that it is going from this end to that end of the spectrum as height increases and also to make us understand what contours are, I will turn contours on.

You see this, this circle here this is one contour line, it joins all the points that let us say 0, this one joins all the points that are at some particular height, same for all the contours and fortunately, I can play around with this, I will just increase the number of lines, yes this is what I have, so this here is my depiction of 1s orbital in a 3 dimensional plane that is the diagram that we have in the slides.

And the good thing about this software is that you can play around with it, you turn it around and look inside it, it basically looks like a cone now, I will turn it around like this, do you see what you get. Now, if you look from the top remember when we talked about the island example, we talked about a helicopter on top of the island looking down on the hill and then you see a picture like this, so it is like a 2 dimensional projection of a 3 dimensional object that is what we have drawn okay.

This here is the contour lines, this n allows us to represent a 3 dimensional feature in 2 dimensional paper or screen okay, so this is essentially what you have and then of course, there is no node here, the wave function is always positive or always negative depending on how you define it okay, so this is 1s orbital for you, we will go back to the presentation, so this is the picture that I showed you perhaps with different limits and these are the contour lines.

Well, I have created this picture but the contour lines were created many, many years ago by my senior colleague YU. Sasidhar, I am immensely grateful to him for having created these pictures before when I had means to actually plot them like this, so you will see his name on many slides in this presentation and the next okay, so these are the contour lines that represent 1s orbital and for good measure we usually write a plus sign here okay.

So, remember these are contour lines and remember the z axis that is pointing towards you is psi, it is not the Cartesian z axis, it is very important to understand this, it is a common source of confusion among students right, so this is 1s orbital for you.

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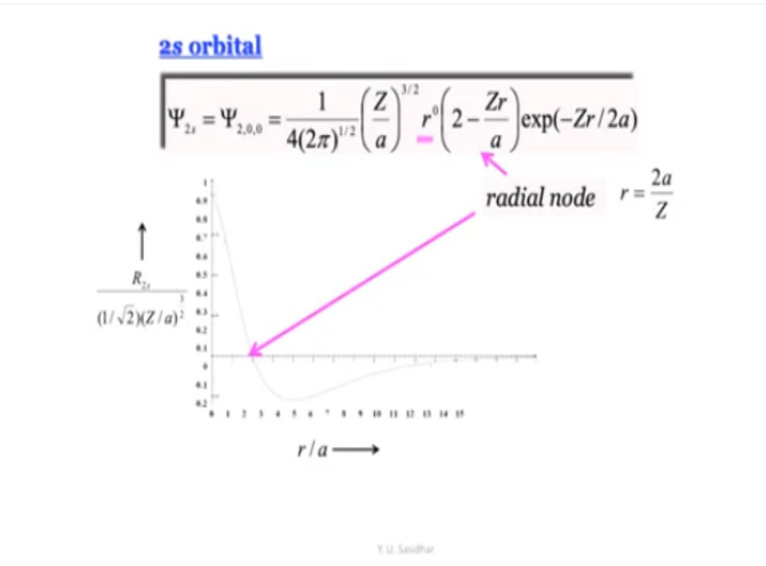

Let us go over to the 2s orbital; in 2s orbital what you have is; you have r to the power 0, it is fine, 2 - Zr by a, a polynomial of first order multiplied by the exponential term, the difference between this exponential term and the earlier one is that here in the denominator, you have 2, right so the falloff is supposed to be faster. So, what do we have here; we have a fall off and then this function as we discussed earlier can become 0 at some value at which value; r equal to 2a by Z that is where we will get a node and that is where the wave function will change sign, right.

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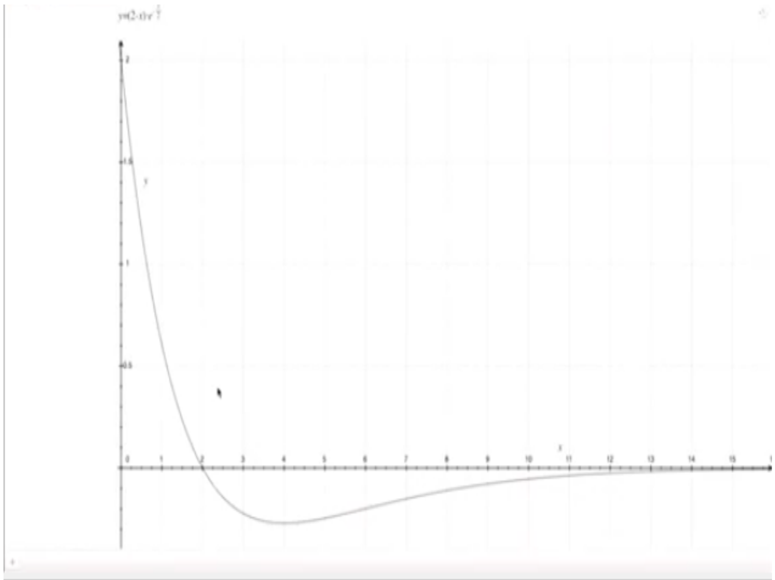

So, once again we will just plot it for you and we will make it a little interesting, so let us do that, we will go to the 2d plot here, so we have the exponential function already but now I want to divide it by 2, I hope you understand what I am doing here , I am setting Z to 1 and I am drawing these functions in terms of Bohr radius a0, so a0 is also essentially set to 1 and I am not really considering the normalization constants, all the normalization constant would do is just multiply everything, it will not change the shape.

Right now, I am not interested in values, I am interested in shape, so remember what we had earlier we had factor, a polynomial that polynomial was 2 - r by a or something like that, so I will just make it 2 – x, so x is going to be 2, x equal to 2 is going to be the node right, so here goes let us see what the function looks like, we will have to change the frame limits, this one is fine, x we have make it a little bigger, maybe I make it 16.

Remember arbitrary units do not forget, this one we will need a little more, this one will be I think 4 or something like that let us see okay that is too much and this is too little okay, this is 2 actually, so I will make it 0.4 and I will make it 2.1, now we see it, this here is your 2s wave function, okay. So, the 2s wave function does have a radial node, we will go back and we will show it once again on the slides.

But here you can see the node clearly, wave function goes from positive values to negative values through a value of 0, here it is showing 2, actually it is going to be 2a0, remember I have plotted this in terms of your a0, we will come back to this and we will see what the radial probability distribution function turns out to be from here but before that let me show you the more beautiful picture.

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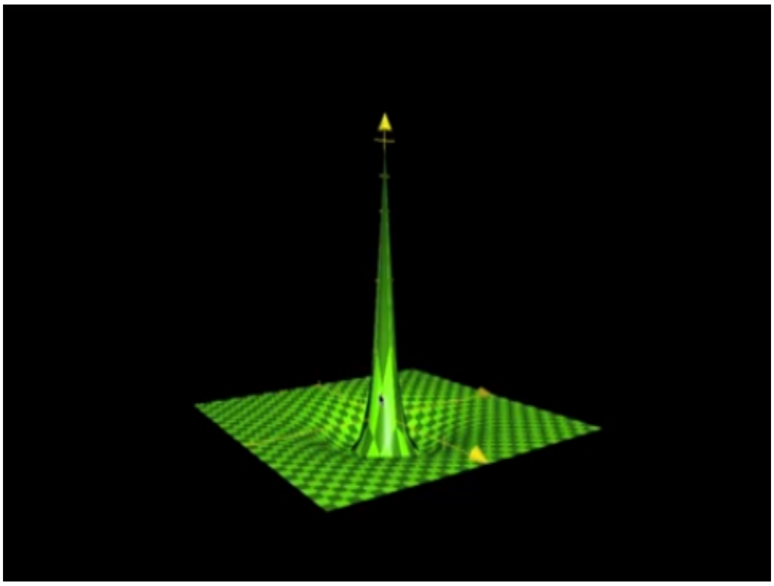

Let me show you the 3d picture here, so what I need to do is okay, this is divided by 2 that seems to be correct and this has to be multiplied by if you remember 2 - r once again, r is essentially root over x square + y square, if you are talking about a 2 dimensional situation, the third dimension is psi, so let us see what we get; this is what we get. We have to change the limits once again remember what we had done.

We had set this to 16 if I remember correctly in the 2D plot, this will be plus 16, y has to be the same thing otherwise it will be distorted and this one I think we had made it 0.4 and this one was 2.1 or something, no harm if I say 2.2, this is your 2s orbital in 3D, I think you can already see the depression.

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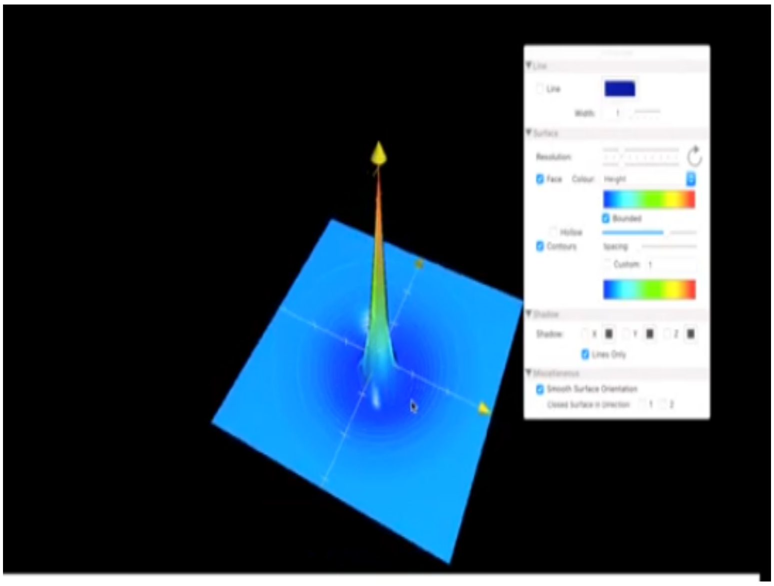

But as usual we are going to colour it according to height and we are also going to get the contours. Now, we got the picture that should be easy to understand, I will turn it around, what do we have in the immediate vicinity of the nucleus is a large positive value or large negative value if you choose to be later on when we talk about hybridization, will actually make this negative, it does not matter.

Because the sine of wave function is only relative and then do you see the depression; this is the region where it has gone below the xy plane, so it has negative values and then it gradually recovers and becomes 0 at infinity asymptotically, it never crosses 0, so there is we do not have a second node, we do have that in 3s orbital we will see but let me turn around this is the view that I really like, you see the negative part and the positive part.

This is plus inside, outside this is the negative basin and again you can look at inside and you can see, do you see these contour lines, these are all negative okay, this one at best is 0, these are all minus whatever you have inside is plus, so a sharp peak in the middle followed by a basin that is negative and it becomes 0 asymptotically at r equal to infinity okay, this is the 2s wave function for you.

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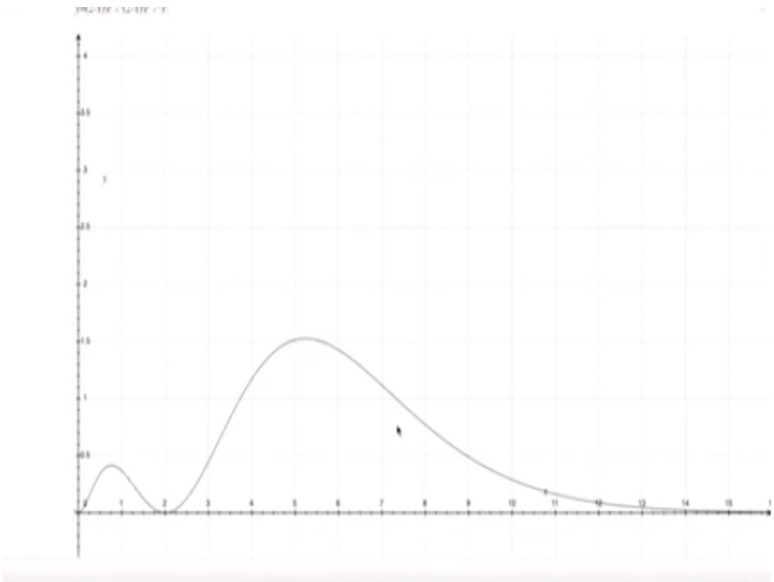

I really like it that we can make this rotate and it can sort of entertain us while we learn something beautiful, so this is 2s orbital for you, so as promised let us go back once to the 2d picture and let us see what r square multiplied by R square is; you already know the answer but I think if I plot it and if you see it evolving in front of your eyes, I think you will understand better.

So, I want r square, so I can be a little lazy and just copy paste the same function once again and I have to multiply it by do not forget by r square in this case, x is r, this is what we get, see this is what, this is a picture that we had shown you earlier is not it, this is your radial probability distribution function okay and in case you miss something, I will just repeat the show for you.

For now, I will remove x square or r square remember where r square came from; it came from the volume element, so if I just remove it, what I have is we have psi 2s square, psi 2s multiplied by psi 2s square of the wave function, this is what the square of the wave function looks like okay. Where is the maximum, where is the minimum; I have to change the frame limit once again.

Earlier it was 2.1, so now it should be 4.2 or something, see this is psi square for the 2s orbital near the nucleus the wave function and therefore square of the wave function is huge, remember square of wave function is probability density not probability, the outer lobe that we have here is actually very, very small and this is positive because I have taken square okay.

But the moment I multiply it by the volume element low and behold, this small apparently small probability density region turns out to be the region with much greater probability, so this is what we have been trying to emphasize probability density is not the be all and end all, probability really depends on the volume element as well of course, it depends upon probability density but not just probability density okay.

So, let us entertain you a little bit and repeat the same thing here, let us see what it looks like in 3 dimensions, please do not forget here, the third dimension is actually, the wave function itself, here I have to write 12, here I have to write simply x square + y square, why; because in 2 dimensions, radius of a circle is given by what; r square equal to x square + y square, this radius is the coordinate, do not forget.

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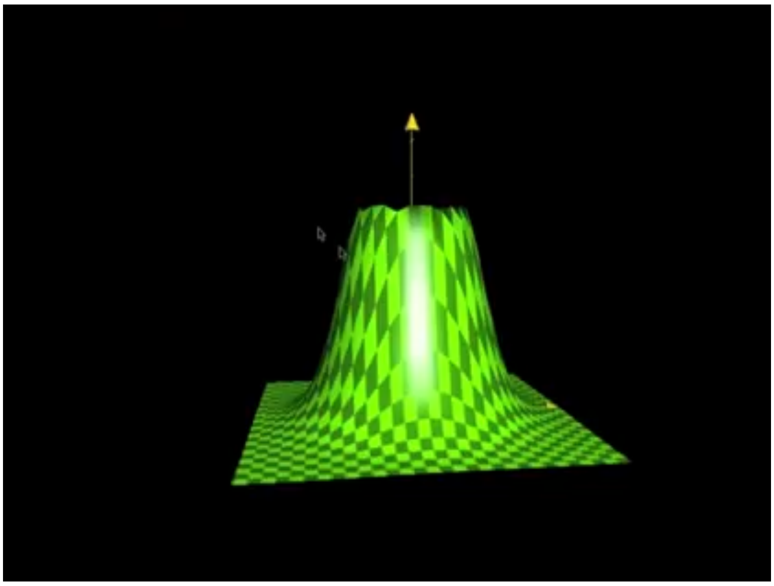

Here we go, looks good, does not it, go back to our usual way of doing things, more contour noise maybe alright.

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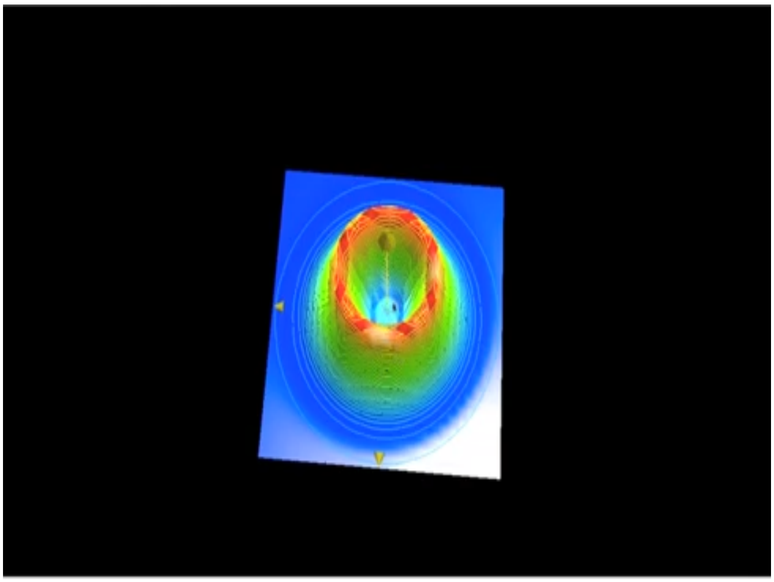

So see what is this; this is the r value for which the probability of finding the 2s electron is maximum okay, you get it by differentiating r square multiplied by R square with respect to r and equating it to 0. What do you have inside; it is a little difficult to see, looks like the crater of a volcano, does not it and our vision is a little messed up by this arrow head that is part of the software, let us not bother about it.

But inside the crater like that lava down below, do you see the second peak, this is the inner peak that you have for r square multiplied by R square and that is much smaller than the outer maximum that we have, this is a maximum of the inner one at r equal to 0 much smaller compared to this. Even though the wave function itself if we just plot the wave function itself, the square of a function, here are your contour lines do you see it well, oh that was bad, very dark, okay, I do not know if that helped, maybe I will just stick to this.

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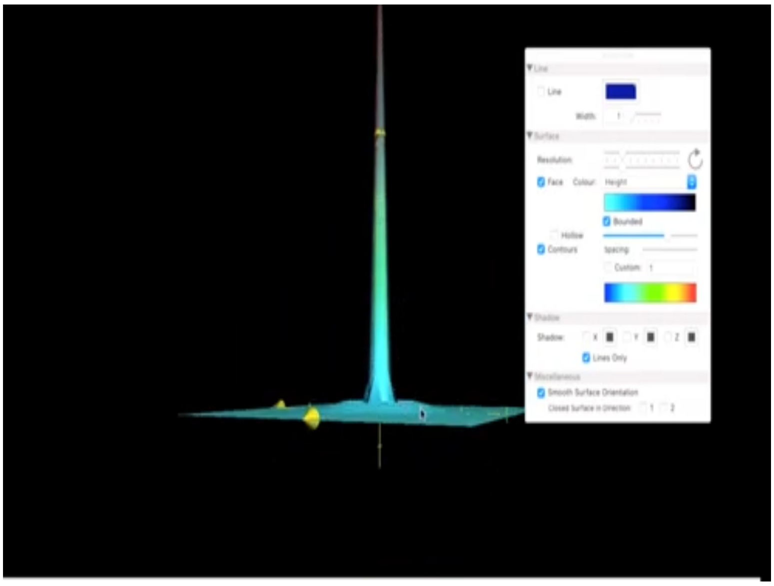

Do you see it now, if you just take psi, psi star or psi square in this case, you see the peak inside, the one that is close to the nucleus is so much bigger, you do not even see the outer one, you even see the outer one, this is the outer one right, very, very small compared to this peak.

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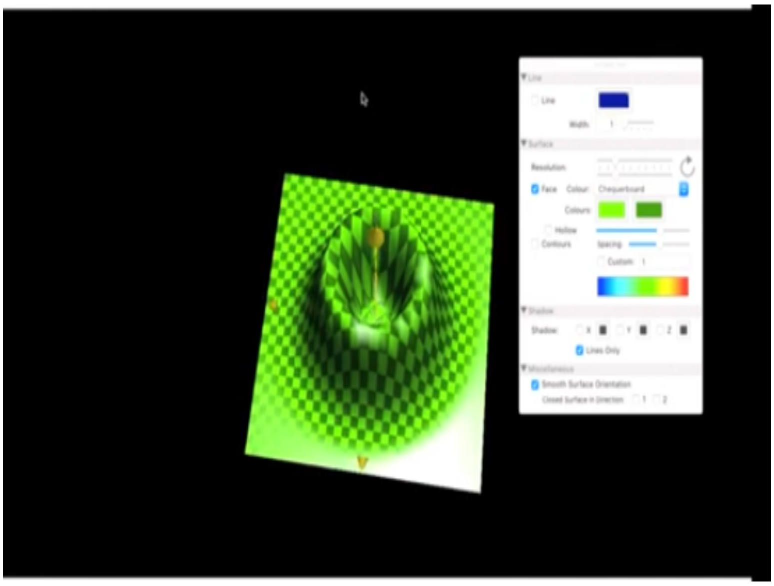

But just multiplied by r square the entire shape changes, so it is important now, I am doing, multiplied by r square, the entire shape changes and the maximum; the small band of psi, psi star actually turns out to be associated with a greater probability okay, so we will close this module here and we will come back with the next one continuing from here.