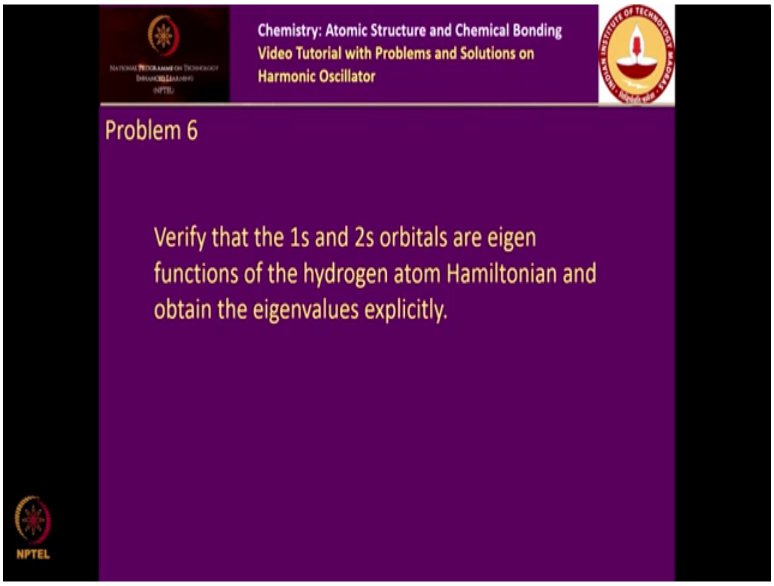
Chemistry Atomic Structure and Chemical Bonding
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 37
Video Tutorials Part 2

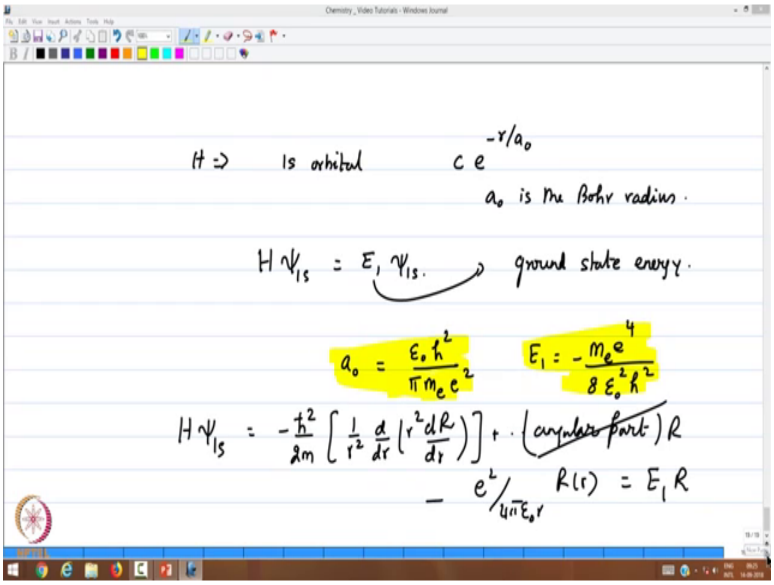
Welcome back to the lectures in Chemistry and on the Atomic Structure and Chemical Bonding. This is the second part of the Video Tutorial which was discussed in the previous lecture; the video tutorial is on the problems and solutions in Hermite polynomials and in hydrogen atom.

(Refer Slide Time: 00:31)



And let me recall that there were nine problems in the tutorial that I have circulated to the course and in the in the course and this is the point where we stopped in the previous exercise. So, this problem is to verify that the 1 s and 2 s orbitals which have been given to you through the lecture nodes and also through the lecture or Eigen functions of the hydrogen atom Hamiltonian and it asks you to obtain the eigenvalues explicitly ok. Let us move to a first page.

(Refer Slide Time: 01:13)



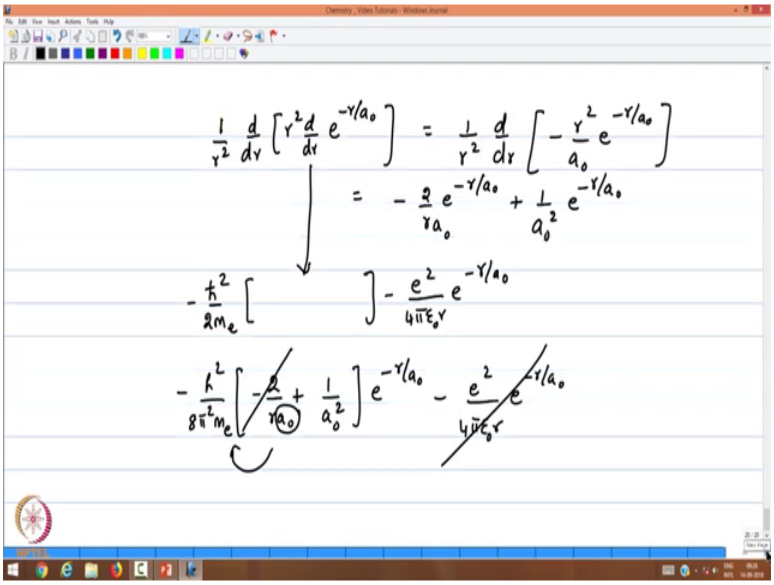
The hydrogen atom Hamiltonian the wave function for the 1 s orbital is normalization constant times an exponential minus r by a naught, a naught is the Bohr radius. And the solution is H psi 1 s is equal to E 1 psi 1 s, that E 1 is the ground state energy ok.

Now the expression for the ground state energy is the same as what Niel's Bohr had given and we should keep that in mind as well as the expression for a naught. Recall that a naught, the Bohr radius is given by the following form, if you recall the hydrogen atom Hamiltonian as minus h bar square by 2 m 1 by r square d by d r r square d radial part.

So, let me write to this a psi 1 s 12 psi 1 s d r, the other is the angular part, which acting on the radial function gives you 0. Therefore, we do not need the component, but then, the potential energy expression is minus a square by 4 pi epsilon naught r times the radial function. This is what we have to show as E 1 times psi 1 s, psi 1 s being the radial function here. Now recall that a naught is from the Bohr's theory and it is still valid it is a definition for the Bohr radius a epsilon naught h square by pi mass of the electron the charge square.

So, let me highlight to this is one expression we should remember and the other one is the expression for the E 1 which is minus the mass of the electron times the charge raise to the power 4 divided by 8 epsilon square h square the Planck's constant. These two we will come out from the Hamiltonian when we apply the differential operator ok.

(Refer Slide Time: 04:39)



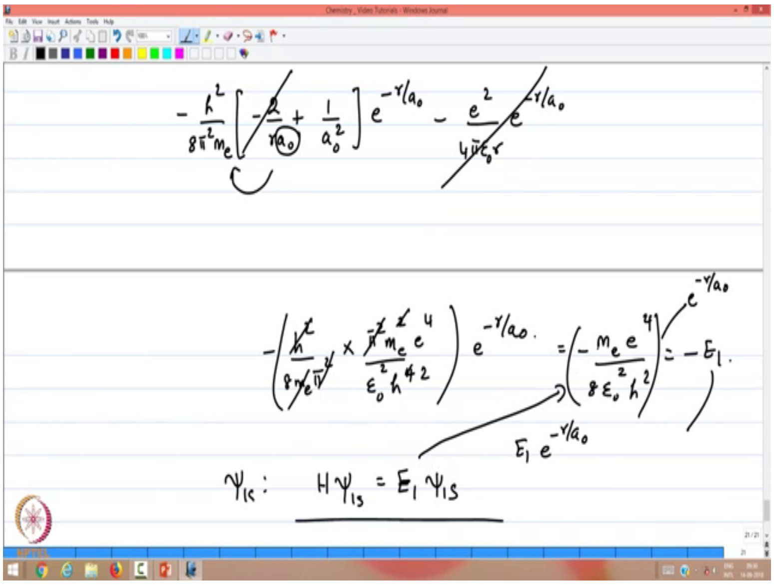
First 1 by r square d by dr r square d by d r of exponential minus r by a naught, if you look at that it is 1 by r square d by d r minus r square by a naught exponential minus r by a naught ok. Which is minus 2 pi r e to the minus r by a naught times a naught, plus r square will cancel out, you have 1 by a naught square e to the minus r by a naught.

Hamiltonian is of course, minus h bar square by 2 m e times all of this, all of these. Therefore, what you have is you have minus h bar square by 2 m e sorry, the Hamiltonian also has the potential term minus e square by 4 pi epsilon naught r e to the minus r by a naught ok.

And if we substitute that n, we have minus h square by 8 pi square m e times minus 2 by r plus r a naught plus 1 by a naught square exponential minus r by a naught minus e square by 4 pi epsilon naught r e to the minus r by a naught ok. Substitute for a naught in this expression, you will see that this is exactly this is positive and this is exactly the same as this term except for the psi.

Therefore, this term can be cancelled to this term with this term, what is left over? You have to substitute for a naught using the expression for a naught given here, epsilon h square by pi m e e square ok, you will see that these two terms cancel out.

(Refer Slide Time: 07:39)

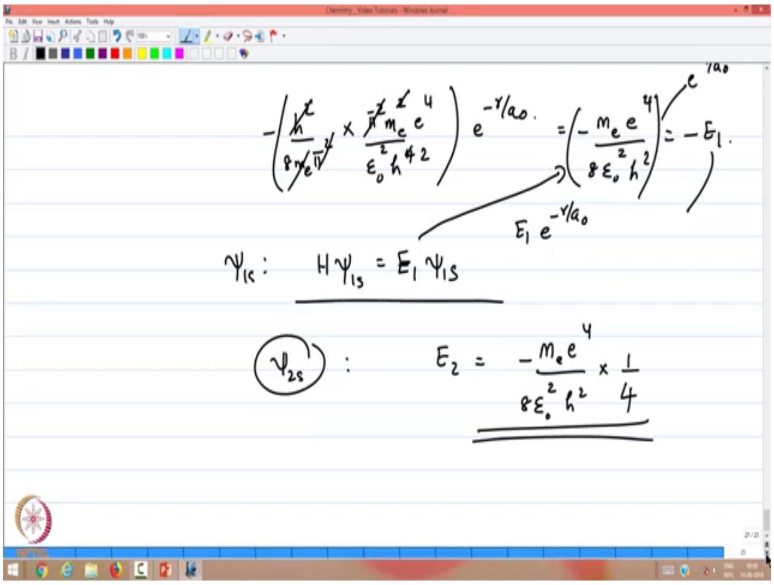


So, what is left over would be minus h square by 8 pi square m e times 1 by a naught square. And a naught square 1 by a naught square is pi square m e whole square e raise to 4 divided by epsilon square h raise to 4 times e to the minus r by a naught.

So, you can cancel off common terms. So, what you will get? Is after canceling all the terms you will get minus m e, there is an m e here there is an e raise to 4 here. And there is an 8 epsilon square, epsilon naught square and h square and that is exactly E 1 times gives you minus E 1 times e to the minus r by a naught ok, here also the reason e to the minus r by a naught multiply.

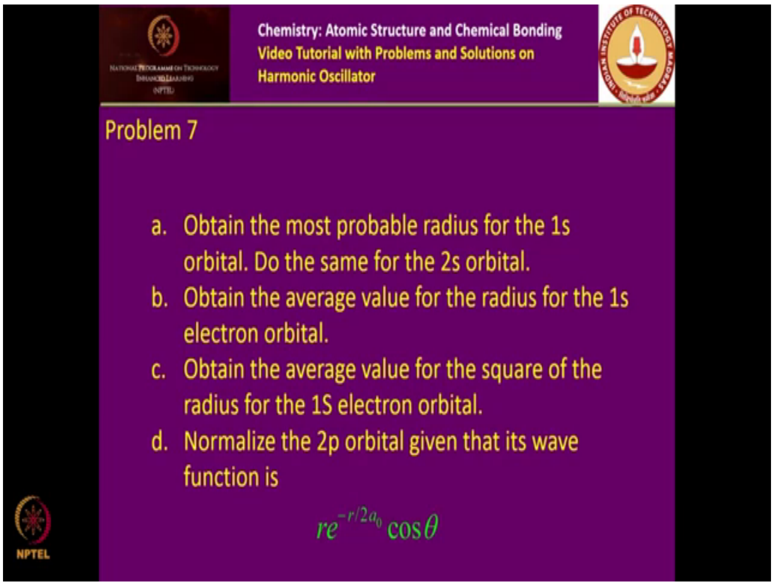
So, psi 1 s gives you the energy h 1 s is equal to minus E 1 ok, this is minus sign of course, because this is a ground state energy E 1 psi 1 s or if you write it as E 1 you simply write this as E 1. And E 1 contains I think this is consistent to what we had done earlier, but E 1 itself is this expression with the minus psi ok.

(Refer Slide Time: 09:34)



Exactly the same thing can be done for psi 2 s, the E 2 that you should get should be minus me e raise to 4 by epsilon 8 epsilon naught square h square times 1 by 4 ok. This is what you should get? If you use the psi 2 s orbital and do the differentials as indicated in the problem here.

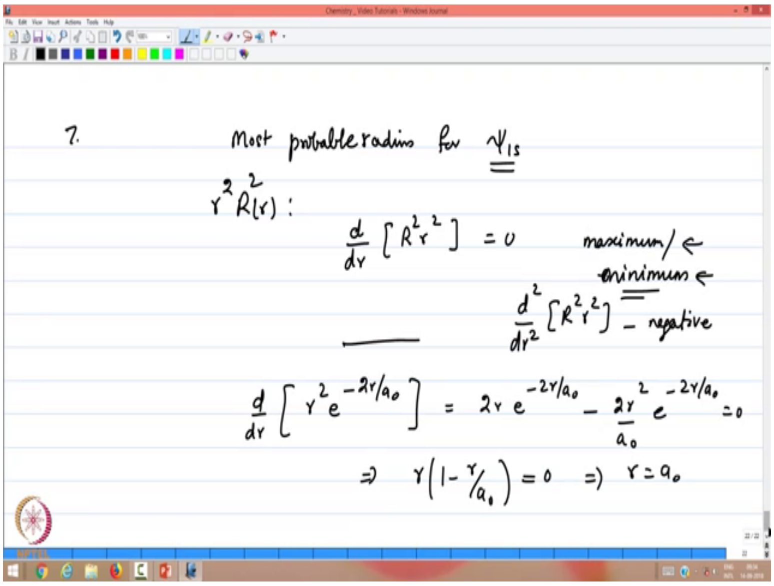
(Refer Slide Time: 10:00)



The next problem is on again some of the aspects of the radial functions, the first part is to obtain the most probable radius for the 1 s orbital and also do the same calculation for the 2 s orbital. The second part to the problem is the value the average value for the radius for the 1 s electron orbital.

And the third part is of course, to get the square of the radius the average value for that for the 1 s electron. We do 1 s electron because, it does not it is a simplest radial function, but the calculations involving 2 s and 3 s or all the others is exactly the same as the calculations done for 1 s. And the last is of course, to give you an idea how to normalize an angular part by taking into account to the non zero angular part in a 2 p orbital and obtain the normalization constant.

(Refer Slide Time: 11:11)



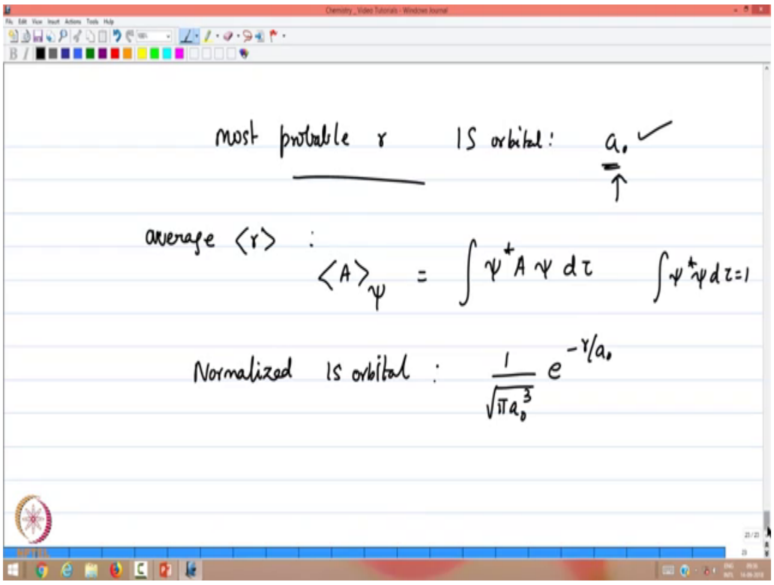
So, let us do 1 by 1, first it is the most probable radius for psi 1 s orbital, this is problem 7, most probable radius for psi 1 s. What it means is that? The radial distribution is r square radial function square, there is also a radial that is a numerical constant, but we will not worry so much about that.

So, the most probable radius is to find out the maximum value namely d by dr of R square r square said it equal to 0, which gives you either a maximum or a minimum it gives you an extremum. And then from the value of that r calculate the second derivative of the same function and find out for which of these this is negative, that value of r is the one for which we have the most probable radius ok.

So, the derivative is very simple d by dr, leaving out the numerical constant or the normalization constant it is r square e to the minus 2 r by a naught because, it is a square of the radial function and that is given as 2 r e to the minus 2 r by a naught minus r 2 r square by a naught e to the minus 2 r by a naught that is equal to 0.

Since, the exponential is never 0 except for infinite value of infinite value of r, what you have is r into 1 minus r by a naught that is equal to 0, which gives you r is equal a naught which is the Bohr radius.

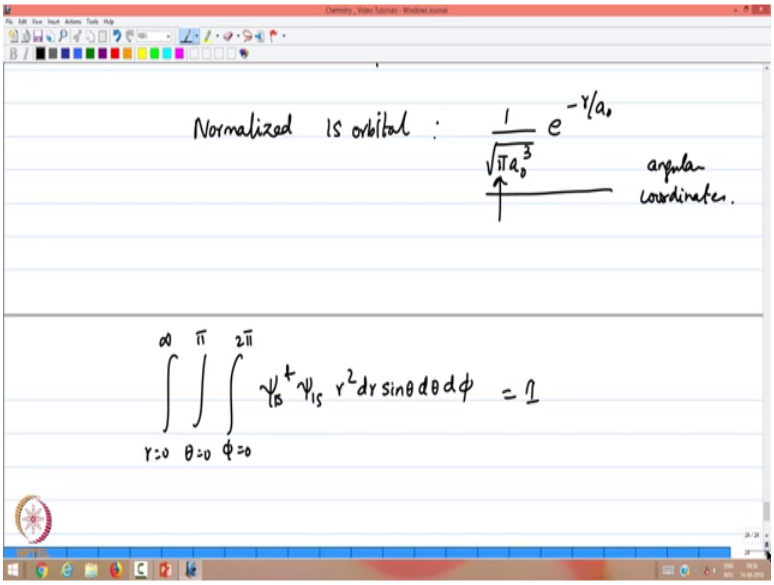
(Refer Slide Time: 13:17)



The most probable r for 1 s orbital is the Bohr radius a naught, talks about the insight; that means, Bohr had 15 20 years before all these things happened. And it is a fundamental, it is also an extremely important constant in the quantum chemistry and the all of atomic physics a naught.

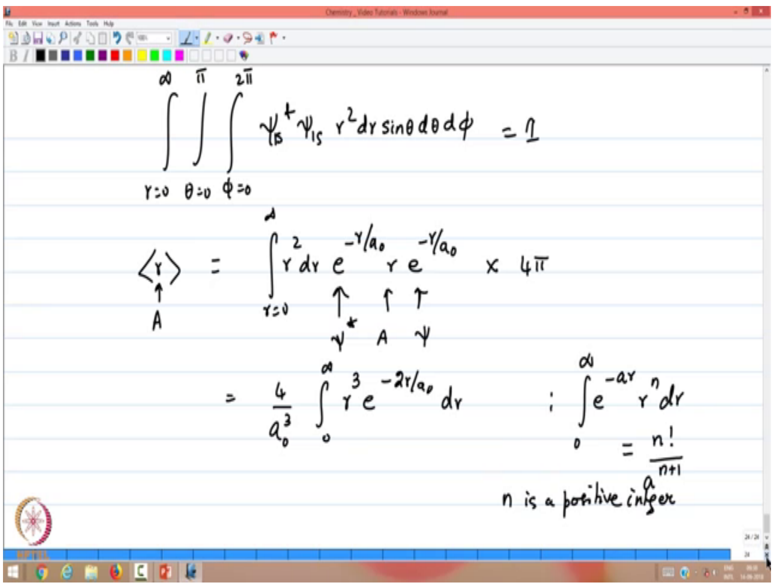
Second problem, if I look at it is the average value for the radius for the 1 s electron orbital. So, we need to calculate the average value for the expectation value or you recall the average value A for any quantum's system in the quantum state psi is given by psi star A psi d tau provided psi is normalized is 1. Therefore, here we will use the normalized 1 s orbital, which is 1 by square root of pi a naught cube exponential minus r by a naught.

(Refer Slide Time: 14:53)



Remember the normalization here is done using angular coordinates also the pi is clearly there. So, what is meant by the psi s normalization 1 s psi star 1 s r square d r sin theta d theta d phi between the three integrals r equal to 0, to infinity theta is equal to 0 2 pi and phi is equal to 0 to 2 pi this is 1 and this is what gives you that constant 1 by square root of pi a naught cube.

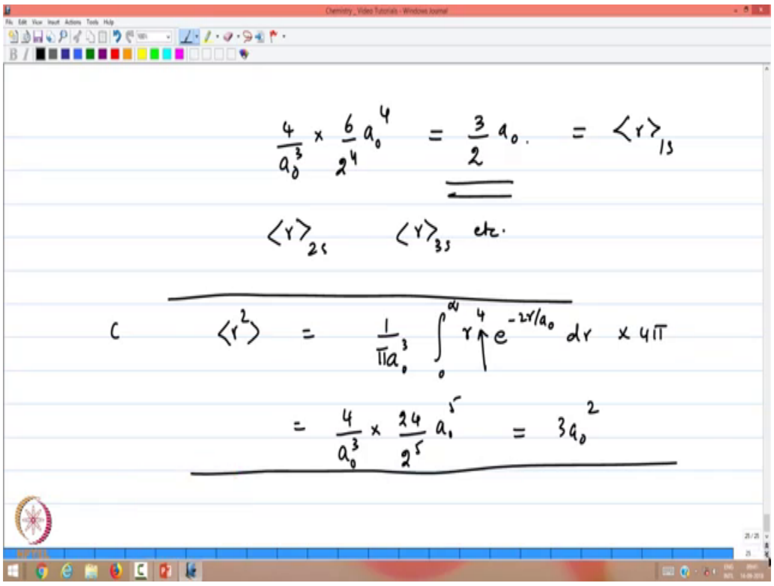
(Refer Slide Time: 15:42)



Therefore, when you calculate the average value r you have to do exactly the same thing namely r is equal to 0 to infinity r square dr and exponential minus r by a naught r exponential minus r by a naught. So, this is psi a psi and write it as psi star so, if this is the operator A, ok.

And then of course, there is no other angular part. So, the angular integral will give you anyway 4 pi ok. So, what you are calculating is essentially, 4 by a naught cube cancelling of the pi's, the integral 0 to infinity r cube e to the minus 2 r by a naught dr. Recall simple standard integral e to the minus a r r raise to n d r 0 to infinity the standard integral is n factorial divided by a raise to n plus 1 where n is an integer and it is a positive integer.

(Refer Slide Time: 17:04)



Therefore, we can easily see that the integral gives you 4 by a naught cube into n is 3 therefore, it is 3 factorial is 6 and the other is a naught by the constant a is 2 by a naught and it is in the denominator.

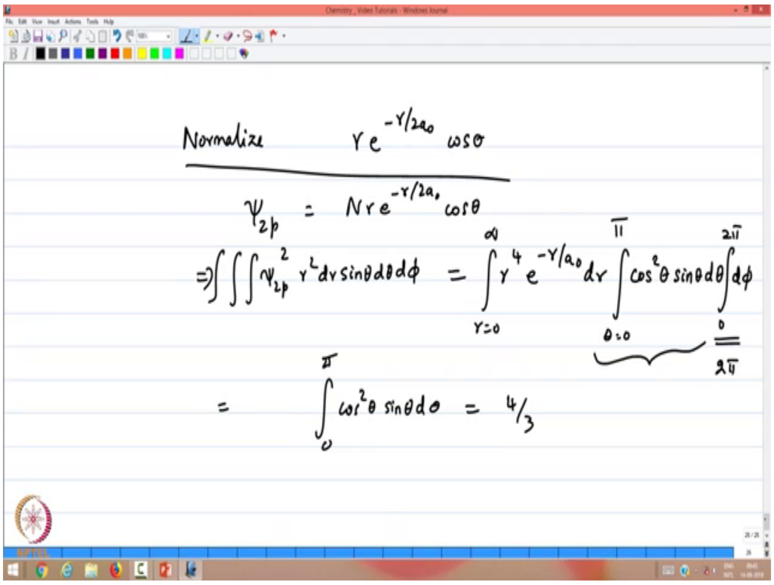
Therefore, you have divided by 2 raise to 4, a naught raise to 4 which gives you 3 by 2 a naught this is the average value for the radius ok. In the 1 s orbital likewise the average value for the radius in the 2 s orbital, 3 s orbital etcetera, they will all be larger than this and you can see that they correspond roughly to what Niel's Bohr had a picture as an orbit of the electron.

And therefore, the classical or the semi or the pre quantum description the Niel's Bohr gave using quantization of angular momentum on an ad hoc basis. And using classical mechanics to get approximate values for the orbits, the Schrodinger's wave equation provides a mathematically clear and as we know today the correct picture, using the wave functions and the probabilities ok.

Third problem c is if I recall the average value for the square of the radius or square of course the integral is extremely simple and straightforward. So, all you have to do is again for the 1 s electron it is 1 by pi a naught cube 0 to infinity for r square. Therefore, you have to write r raise to 4 e to the minus 2 r by a naught d r times 4 pi. This 4 is because, you have r square d r as part of the integral the element the radiant element.

Therefore, this is also fairly straightforward, you can write this as 4 by a naught cube into 4 factorial which is 24 divided by 2 raise to 5 a naught raise to 5, which gives you 3 a naught square right. So, these are simple calculations involving the radial quantities and now let us do a little bit using the radial and the angular quantities in the next problem, namely, let us normalize the 2 p orbital or I think the orbital list r e raise to minus r by 2 a naught cos theta yeah cos theta.

(Refer Slide Time: 19:55)

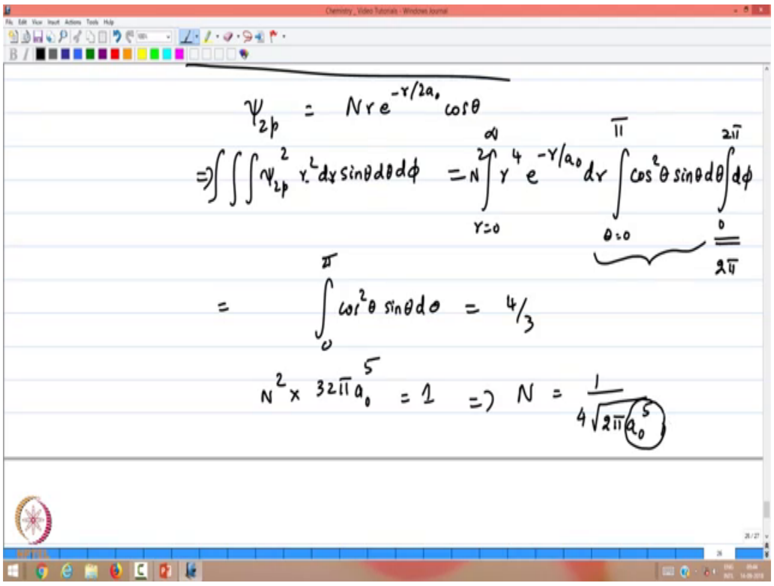


The 2 p orbital or I think the orbital list r e raise to minus r by 2 a naught cos theta yeah cos theta. So, the normalization now involves the angular integration also. So, if we call this a psi as 2 p as n r e to the minus r by 2 a naught cos theta, then the integral psi 2 p square r square dr sin theta d theta d phi.

The corresponding integration with the limits if you do that it is r equal to 0 to infinity r square and there is also an r square here. Therefore, this will be r raise to the 4 power 4 e raise to minus r by a naught the square of this function d r that is a radial integral and the corresponding angular integral is 0 theta is equal to 0 2 pi you have cos square theta.

And then, you have sin theta d theta and then you have the d phi 0 to 2 phi which will give you 2 pi ok. Therefore, the integral is pretty straightforward, we have already done this integral earlier, the integral cos square theta sin theta d theta either in the problem or as a lecture node and this you know is 4 by 3.

(Refer Slide Time: 22:01)



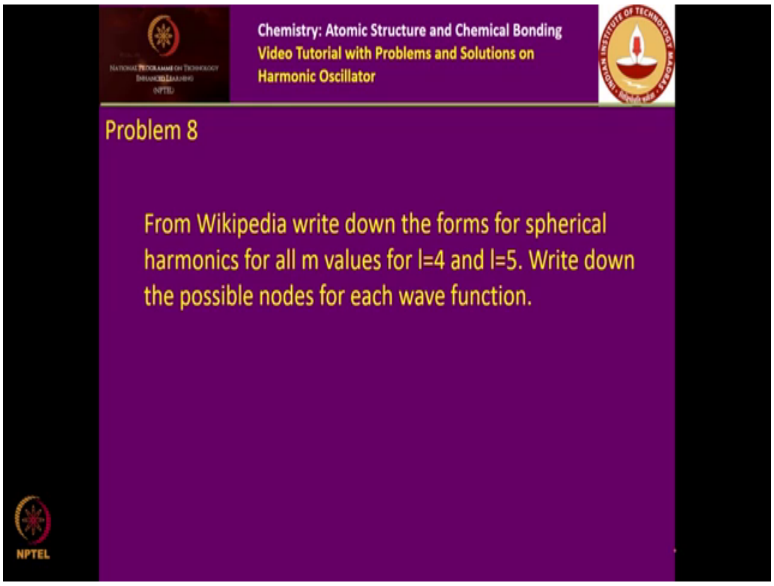
Therefore, you can calculate this integral very quickly using the general formula for the exponential you will get n square times 32 pi a naught raise to 5 is equal to 1, which will give you in the constant N is equal to so, there is an n square here s.

So, this will give you N is equal to 1 by 4 square root of 2 pi a naught 5, the normalization constant involves a naught raise to the power 5 that is important to recall because, you remember the wave function has the radius and therefore, length coordinate. And the integral contain r square dr therefore, the wave function square we will contain the length square and the r square dr we will contain a length cube. Therefore, the whole integral will have the dimension of length raise to 5 unless you have a normalization constant which takes the length raise to 5.

And gets and cancels it in order to make this integral a probability and therefore, a dimensionless number equal to 1. Therefore, you see this is clearly to be checked every time you look at the radial function, if you do a 3 s orbital you will see that the radial part is r square essentially.

So, it means that if you take the square of the function it is r raise to 4 and then the r square d r will also give you three more I mean length cube. So, the wave function for psi 3 p should have in the denominator square root of a raise to 7 and so on, I think dimensions are very important. So, these problems are not only to do the algebra, but to check consistencies in your results between the starting point and the end point ok. Therefore, the normalization constant for this function can be easily obtained by doing the angular integral, but of course, we have some more in the next two problems ok.

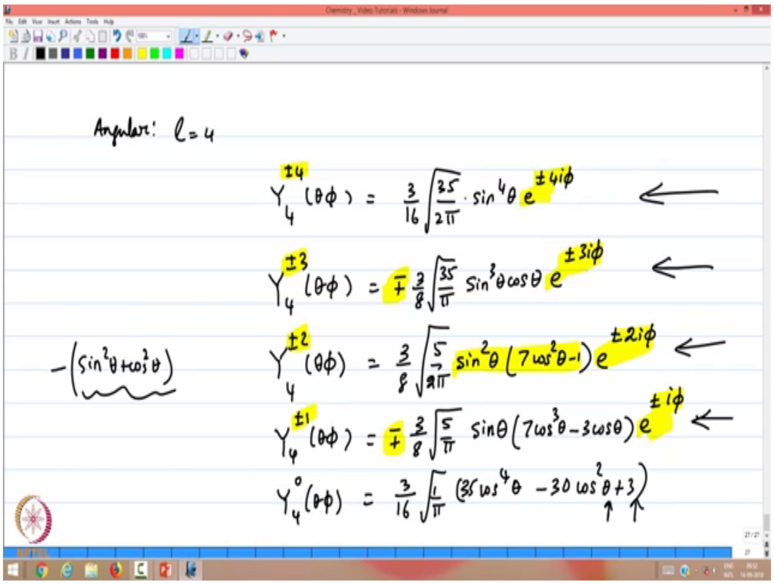
(Refer Slide Time: 24:28)



Let us go to the next problem, it says from Wikipedia write down the forms for spherical harmonics for all m values for l equal to 4 and l equal to 5, I mean I use that source because I found that particular table to be very useful for my classes. And; the table goes on for larger values of l l equal to 7 8 and so on. And you also have to write down the possible nodes for each wave function, recall that an angular function represented by ylm where l is the angular quantum number and m is the projection quantum number, the angular function has l angular nodes.

Therefore, if you are writing the ylm for l equal to 4, every one of those functions will have 4 angular nodes; every one of the functions yl m with the l equal to 5 will have 5 angular nodes. So, let me just give you the table which I have copied from and then discuss the angular nodes using that table you can also get this from the internet ok.

(Refer Slide Time: 25:40)



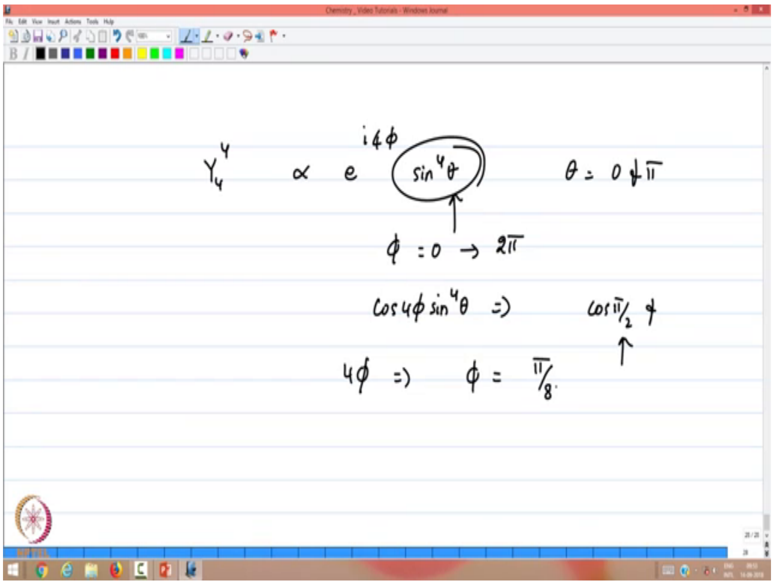
So, in the screen you see the angular functions for l equal to 4, there are 9 4 functions Y plus minus 4, m equal to plus minus 4, m equal to plus minus 3 plus minus 2 plus minus 1 and 0. First thing, when you see m equal to plus minus 4 the exponentials, you can see that they all take the m value this is the m value plus minus 3 plus minus 3 plus minus 2 plus minus 2, plus minus 1 e to the plus minus I phi and m equal to 0 is of course, this is 1. Second thing is when l m if m is odd you will also see that between the plus m and the minus m there is a sign change here.

These are all standard throughout these spherical harmonics these patterns are there. And the other important thing is that every function in theta is a homogeneous fourth order polynomial. For example, sin raised to 4 theta no problem this is sin cube theta cos theta so, the homogeneous order 4 in sin and cos theta.

Now, this looks like it is not there is a minus 1, but I have told you this is the earlier there minus 1 is nothing other than sin square theta plus cos square theta in the minus sign minus 1. Therefore, you can see that this is 6 cos square theta minus sin square theta multiplied by sin square theta it is homogeneous in order 4 with power 4.

And likewise 3 cos theta you multiply this by cos square theta plus sin square theta you will also get that this is a fourth order polynomial and likewise the fourth order homogeneous polynomial here by having this and this both multiplied by the unity ok. It is just I mean this is to tell you that there are patterns.

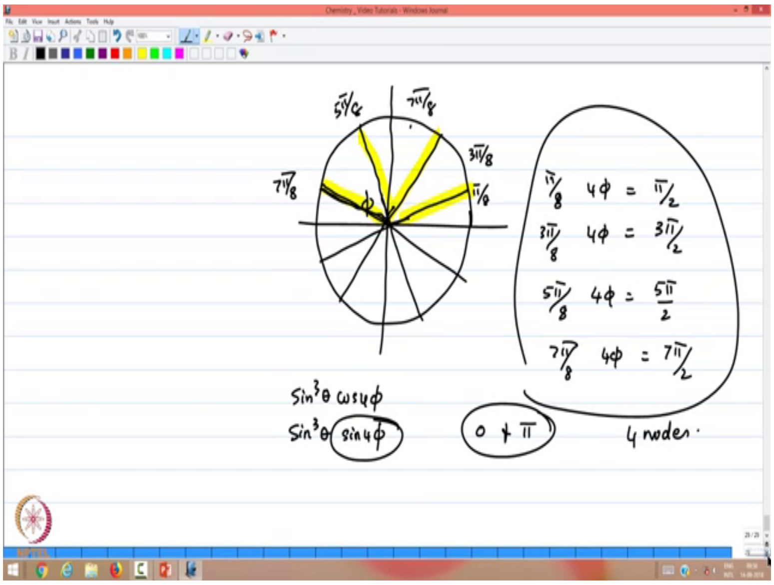
(Refer Slide Time: 27:56)



Now what about the nodes for these functions? The first one let us take the function exponential Y 4 4 proportional to exponential i 4 phi to 4 phi sin 4 theta. Theta is between 0 and phi sin theta does not go to 0, that therefore, no angular node is due to theta, but exponential i 4 phi for the value of phi is equal to 0 to 2 pi as nodes in the following.

Please remember, when we plot the cos and sin there are 4 nodes, if we take the cosine 4 pi sin 4 theta the real part will have at cos pi by 2 and cos 3 pi by 2 or the 2 places, 2 values of theta for which the function is 0. But, cos pi by 2 is the same line as cos three pi by 2 therefore, we do not have that assuming one node.

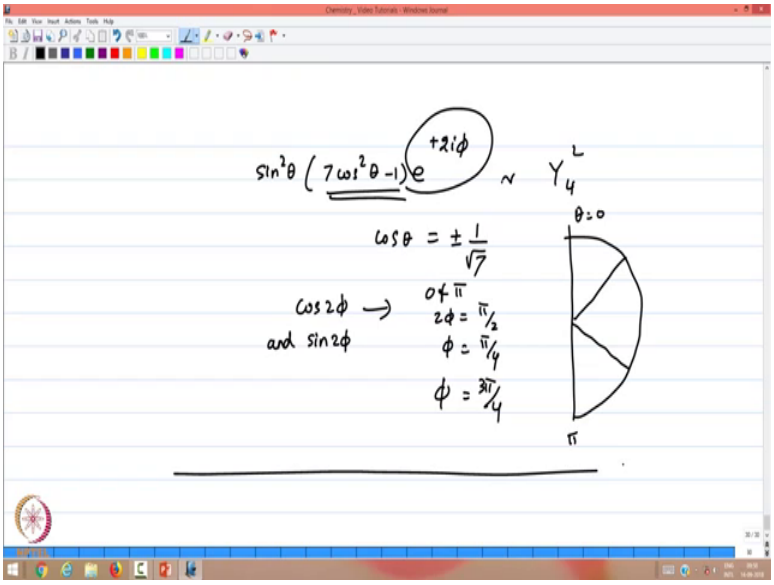
(Refer Slide Time: 29:17)



And now its 4 phi therefore, we have phi is equal to pi by 8 in the circle if we have to write, this is the phi ok. At phi is equal to pi by 8, 3 pi by 8, this is 5 pi by 8 and this is 7 pi by 8. Of course, this axis extends here, this axis extends here therefore, this is all the angular node so, all you need is only the 4 angular node the first 4, this one, this one, this one and this one, this is not the node this is just the 90 degree axis.

So, there is the last node that we have is seven pi by 8 4 phi is 7 pi by 2. All the or integral pi by 2 up to this point, the other nodes are the same as these nodes that therefore, there are only four values of the angle ok. This is for sin cube theta cos 4 phi and exactly, the same thing that you can do for sin cube theta sin 4 phi which is 0, the real part is 0 for the values 0 and pi between 0 and pi there are 4 values of sin 4 phi which would be 0 ok. So, those are the 4 nodes.

(Refer Slide Time: 31:03)

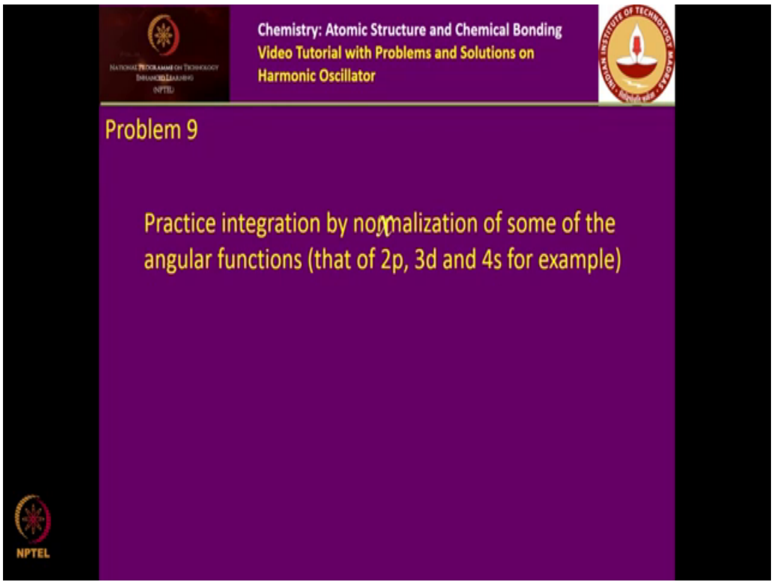


What about the nodes for; again one more example I will do, the example of sin square theta 7 cos square theta minus 1 e to the plus 2 i phi, this is Y 4 2 ok. Now 7 cos square theta minus 1 goes to 0, when cos theta is plus or minus 1 by root 7. Therefore, those are the angular nodes in the radial coordinate theta 0 to pi. So, the value is of plus minus 1 by root 7, so, somewhere here and the corresponding minus 2 nodes.

These are the nodes due to the theta, the nodes due to the value of phi or cos 2 phi and sin 2 phi 1 of them cos 2 phi has a angular node between 0 and pi at 2 phi is equal to pi by 2 r phi is equal to pi by 4 exponential 2 i phi corresponds to that phi distribution. Therefore, there are 4 lobes and phi is equal to pi by 4 and phi is equal to 3 pi by 4 are the 2 values for which the real and the imaginary parts that the real part goes to 0, and then the imaginary part goes to 0 for corresponding other values.

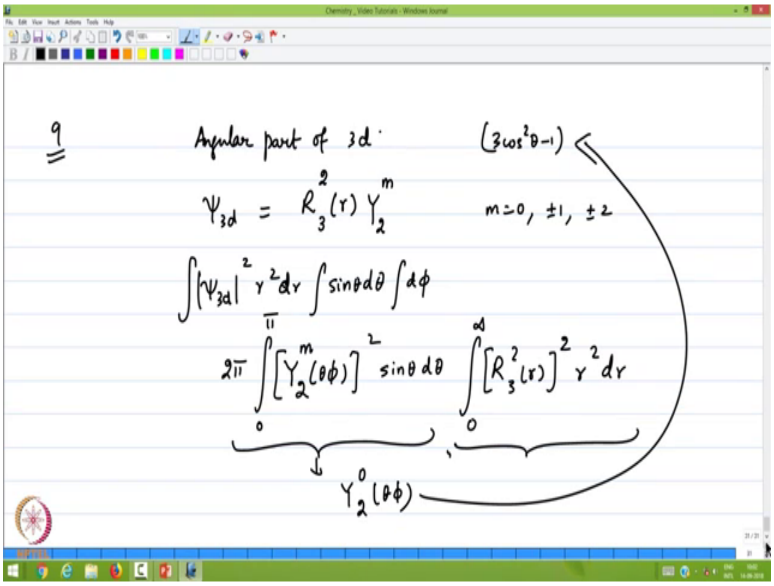
So, those are the 4 angular nodes, with respect to the Y lm l equal to 4 and m equal to 2. So, likewise you can calculate all the other the angular nodes for the problem. Last problem is of course, I have not said anything about l equal to 5 in this problem, exactly what has been done I have grouped them into five categories of functions plus minus 4 plus minus 3 plus minus 2 plus minus 1 and 0 in the case of l equal to 5 you will have 6 of these and you can see again 5 4 3 2 1 0 or 6 functions. Totally there are 11 spherical harmonic functions and they will be grouped into the pattern which I explained l equal to 4. So, you can do that yourself.

(Refer Slide Time: 31:36)



Now, the last problem is to practice integration by a normalization of some of the angular functions 2 p three d and 4 s. So, I shall indicate simple steps and I think the algebra is something that you can do yourself.

(Refer Slide Time: 31:56)

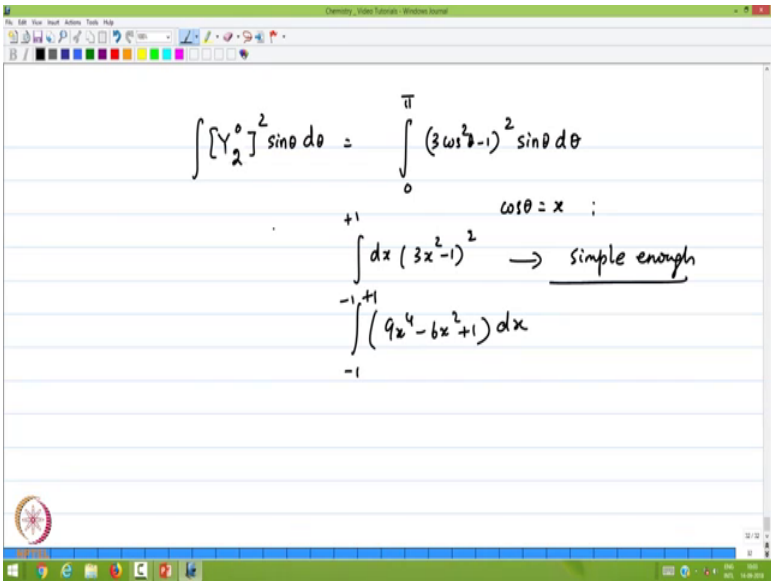


Let us do 3d, the angular part of 3 d easy enough this problem 9 ok. Angular part of 3 d s 3 cos square theta minus 1 ok, we remember the psi 3 d contains a radial part with the n equal to 3 and l equal to 2 or and the l equal to 2 and m there are 5 of these m equal to 0 plus minus 1 plus minus 2.

Therefore, the normalization essentially means psi 3 d square absolute square, I think that is important, now because, the functions can be complex. Then you have r square dr then you have sin theta d theta and d phi. So, if you take the absolute square the exponential parts go away so, it becomes 2 pi the m disappears and what is left over is? The spherical harmonics Y 4 m theta phi square 0 2 pi sin theta d theta which can be separately normalized.

And the other being the radial function R n l n is 3 you see n is 3 l is 2 radial part R square and you have r square dr between 0 and infinity. This can be separately normalized as the radial function and we will just concentrate on one of this corresponding to Y 2 sorry, this is not 4, this is 2 Y 2 0 theta phi which is 3 cos square theta minus 1 ok.

(Refer Slide Time: 36:16)



Therefore, the integral Y 2 0 square sin theta d theta is the integral 0 to pi 3 cos square theta minus 1 whole square the sin theta d theta. You can easily do the change of variables cos theta is equal to x and follow up all those things. So, you will get from minus 1 to plus 1 d x you get 3 x square minus 1 whole square.

Simply enough integral and I would let you finish that by yourself, 9 x raise to 4 minus 6 x square plus 1 dx between the limits minus 1 to plus 1 please do this. But all of the algebra that I have mentioned in the video tutorial; is only to give you a feeling that you can do the algebra yourself, if you spend sufficient amount of time to sit down and learn what is the purpose? The purpose is of course, to make you more comfortable with the whole mathematical framework.

However elementary it may be with the chemistry, the quantum chemistry part of it, but even more importantly, all these things are the basis and the idea of the linear combination of atomic orbitals etcetera or based on our understanding of the hydrogen atom orbitals. And the way that the electronic structure an approximate electronic structure of the atom is organized by the principle of the Huns multi maximum multiplicity involves this fundamental idea of the hydrogen atomic orbitals.

Therefore, familiarity as well as a fairly complete understanding of the hydrogen atom problem in quantum chemistry is fundamental to understanding all of quantum chemistry ok that is the reason why this tutorial has so many algebraic calculations. I have not given any numerical results in this particular tutorial many of that can be found in several textbooks ok. We will continue with the lectures in the next step and we will find out about the general principle of the linear combination of atomic orbitals and others in the succeeding lectures until then.

Thank you very much.