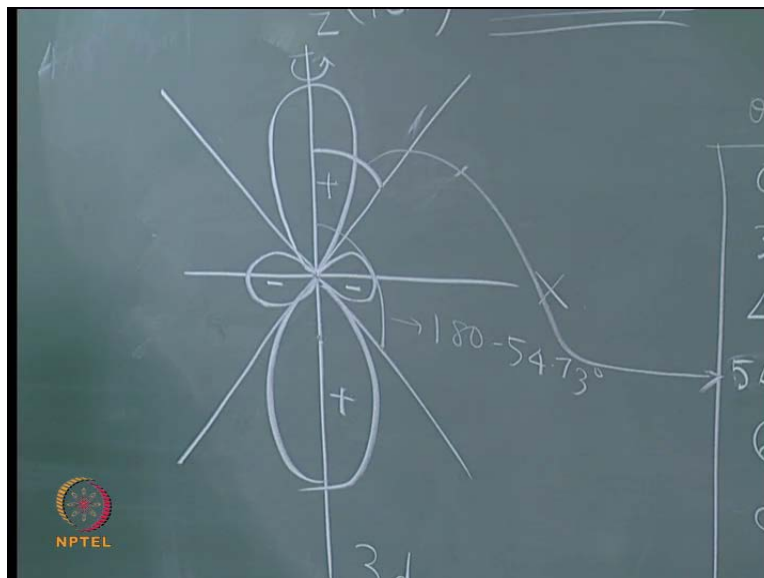


Introductory Quantum Chemistry
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Indian Institute of Science, Bangalore

Lecture - 30
Measurement, Uncertainty Principle

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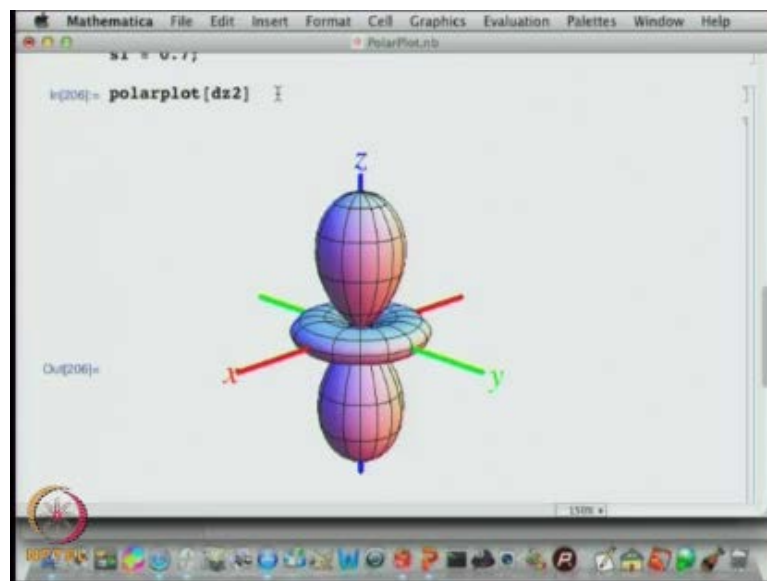
As I told you this is the polar plot in the xz plane, and if you wanted to get the three-dimensional appearance you have to take this figure and rotate it about the z axis. And further I also told you that in the direction with θ equal to $\cos^{-1}(1/\sqrt{3})$, you can actually calculate it; it will turn out to be 54.73 degrees. You will find that the value of the function is 0. So, if you marked that direction in this figure, what you are going to get is z line, along this line such that this angle is equal to 54.73. The value of the function is 0, and similarly along this direction, but why along those two directions only, you think of a direction downward like that over a direction there on the other side, right, such that this angle, this angle is how much? It is actually $180 - 54.7$.

Again you will find that $\cos \theta$ will be equal to $1/\sqrt{3}$. So, when you get the three dimensional appearance by rotating about the z axis, you think of what will happen to these lines. These lines actually will describe a cone something like that, such that the internal angle; this angle of the cone is 54.73 degrees, and similarly these lines will also describe another cone. And you should realize now that for any point lying along the

surfaces of these cones, the angular part of the wave function will be identically equal to 0.

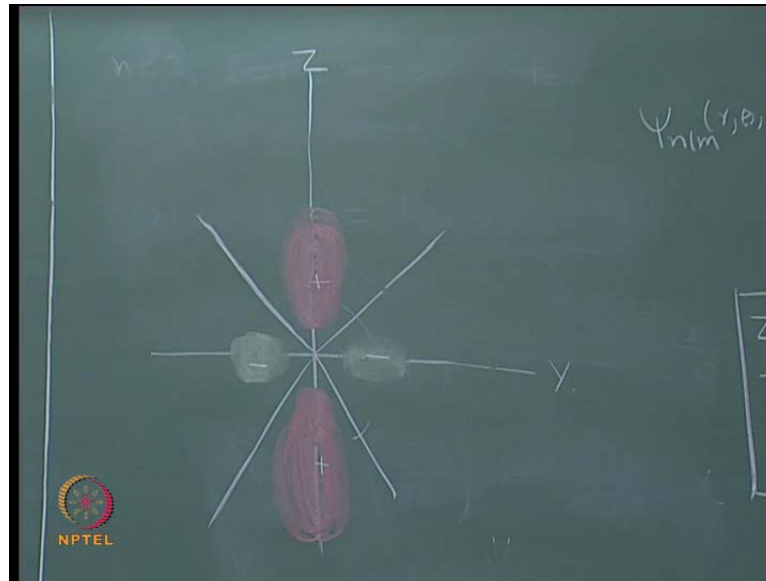
And if the angular part is identically equal to 0, what will happen? The wave function itself will be equal to 0, and therefore if I think of the total wave function, the total wave function has two nodal surfaces; they are surfaces the two nodes, where are they? One is actually along the surface of a cone, right, such that the interior angle this angle within the one is equal to 54.70 degrees, and the vertex of the cone actually is pointing down. And similarly there is another cone whose vertex is pointing up along the surface of that cone also the wave function will be identically equal to 0, and hence we have another nodal surface, okay. So, with this information let me show you a polar plot of this orbital; this is the appearance which is obtained by rotating this figure about the z axis, okay.

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So, these two things actually they are describing something that is a shape like a donut; though not exactly but you can see the appearance from the figure. If you want I can rotate it a little bit. See this is how it would appear, and if you looked from above roughly that is how it looks like, from any angle you can view it. So, this is 3 d is z square orbital; the orbital is referred to as 3 d z square, and you can also make a density plot if you like. So, how will you make the density plot?

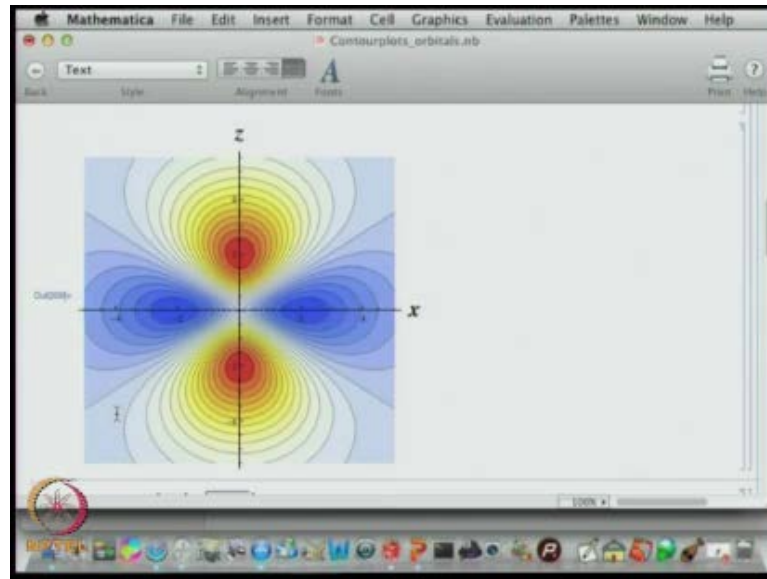
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I can do it here. Well the first thing that I will now do is label the axes; this is let me say the y axis if you like, and this is the z axis. Now in these directions actually the wave function is positive, but then along to a special direction, these are the special directions, along them the wave function is 0, and similarly along these directions also the wave function is zero. So, why do I mark the directions along which the wave function is 0, because you see if the function is positive as soon as I cross this line the function will change sign. So, on this side what will happen? The wave function is going to be negative.

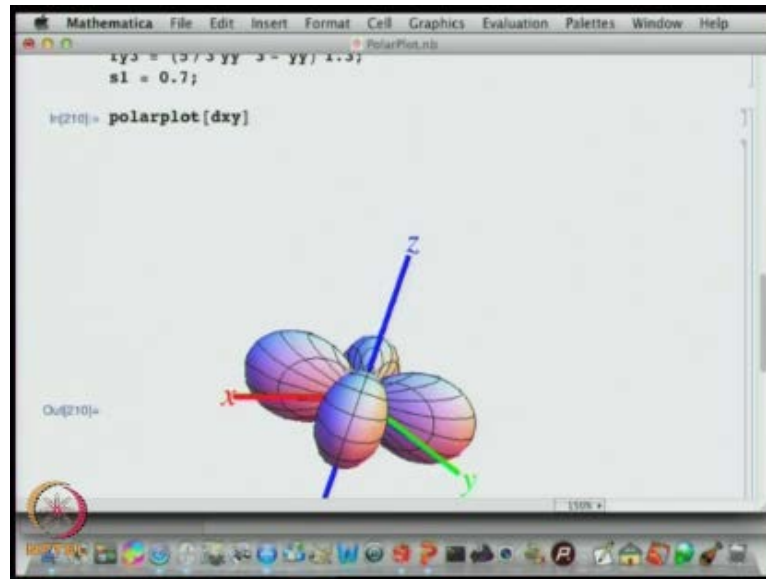
This is positive, and then when again I cross this line what will happen? The function will again change sign. So, therefore, in this region the function will be positive, and then again in this region the function will be negative. So, that is how the appearance of the function would look like; if you made a density plot, this is positive, and that is negative; this is positive, and that is negative. So, using the software Mathematical, I do have a plot of this function a density plot. Let me just draw it.

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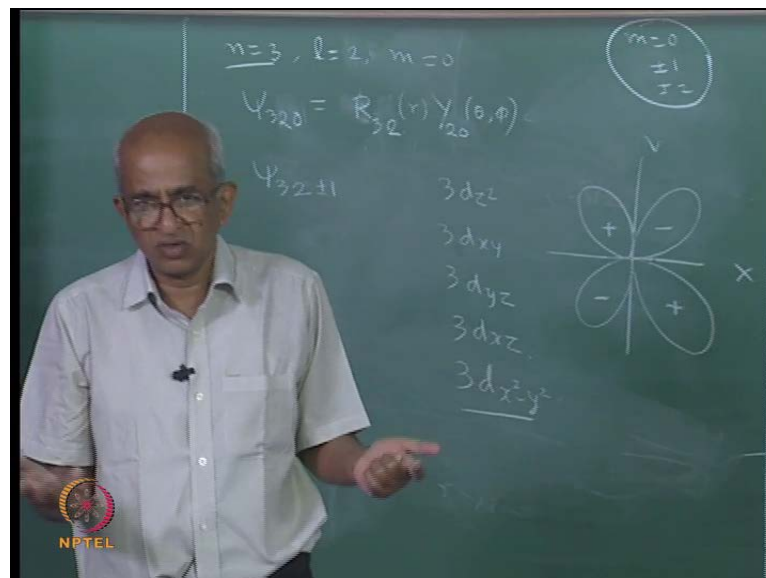
Okay, here it is made in the xz plane, but it does not matter whether it is in the xz plane or whether it is in the yz plane, the appearance will be the same. You will see that in this region the function is positive; in this region the function is negative, sorry again positive. In these blue regions anyway they are represented in these blue regions you can see actually the value is negative. That is clear when I point to one of the lines; you see this is the line along which the value of the function is negative, and it has a value of minus 0.3. So, this is the appearance of the 3 d z square atomic orbital, okay. Then we have to worry about other atomic orbitals. I mean I will not be actually writing down the functions, but perhaps, I can just show you the polar plots of these other functions, and that should be enough.

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Any orbital that you want to see it is easy to make a polar plot. This is actually the orbital that is referred to as a dxy, how will you get them? Either the procedure is just the same as that I have outlined.

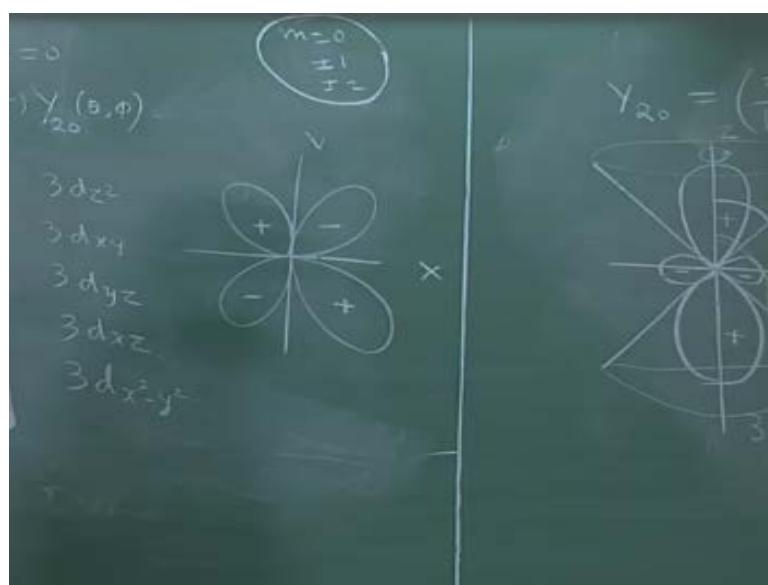
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You have to put other values of m, psi 32 plus or minus 1, but if you put plus or minus 1 the result is going to be complex. So, therefore, you will take either the cosine function or the sin function and then proceed, and the results are actually five orbitals in total, because you have m equal to 0 plus or minus 1 plus or minus 2, you have five orbitals in

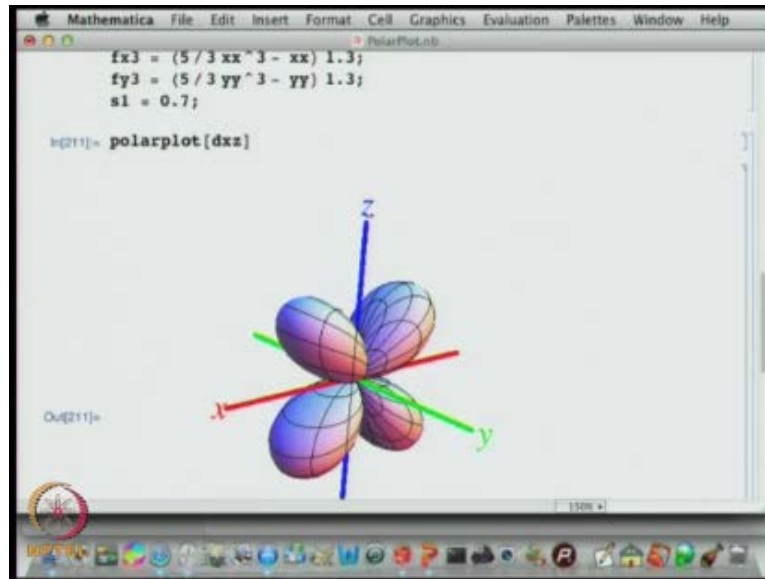
total. And those five orbitals actually the conversion is to label them as $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, then $3d_{z^2}$ I have described, and there is another orbital which is denoted as $3d_{x^2-y^2}$, and you can make polar plots of all these orbitals. So, $3d_{xy}$; xy is the one that we can see here as you will see in the picture. See, this is your z direction; you have the x and y axes, and you can see that these has 4 lobes, right, which are clear in the picture, and these 4 lobes are pointing in between the axis. The important thing is to realize that the orbital is in the xy plane; it is in the xy plane. It is lying in the xy plane, and there are 4 lobes, maybe I can draw this on the board.

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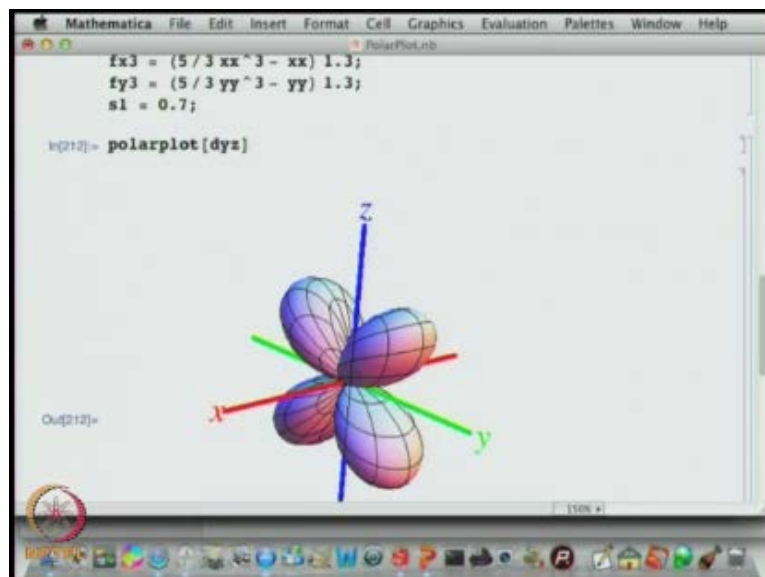
Imagine this is the xy plane. So, you have one lobe here, another one there, another one here, and the fourth one there, and it so happens that this and that are plus; in these directions the wave function is positive, while in these directions the wave function is negative, okay. So, that is how it is. So, $3d_{xz}$ what will happen? The appearance is the same except that it is in the xz plane; the orbital is lying in the xz plane. It is very similar to xy except that the everything is now in the xz plane and of course, this has a two both of these orbitals has two nodal planes; where are the nodal planes? Just to illustrate in the case of this orbital which I have denoted xy , in this case remember the z axis is standing perpendicular to the plane of the board in this fashion.

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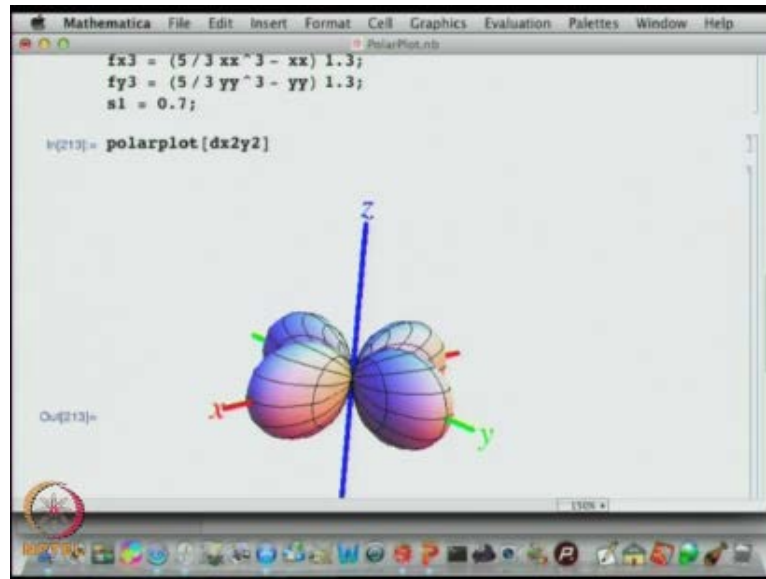


So, if you think of such a plane which is what plane? It is the xz plane, or you think of such a plane which is nothing but the yz plane, then these are actually nodal planes. Similarly, if you think of this orbital you would realize that the xy plane, right, the xy plane is a node, and the yz plane also is a node for this orbital. So, then we have seen xy and xz.

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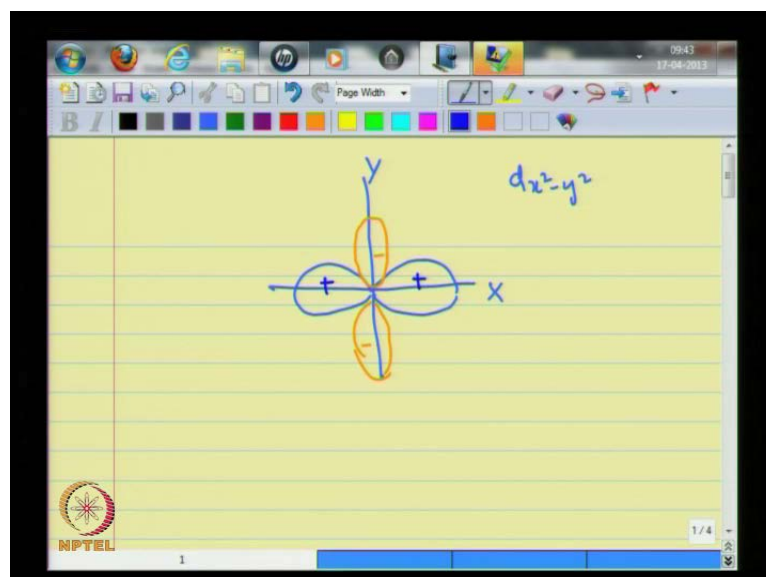


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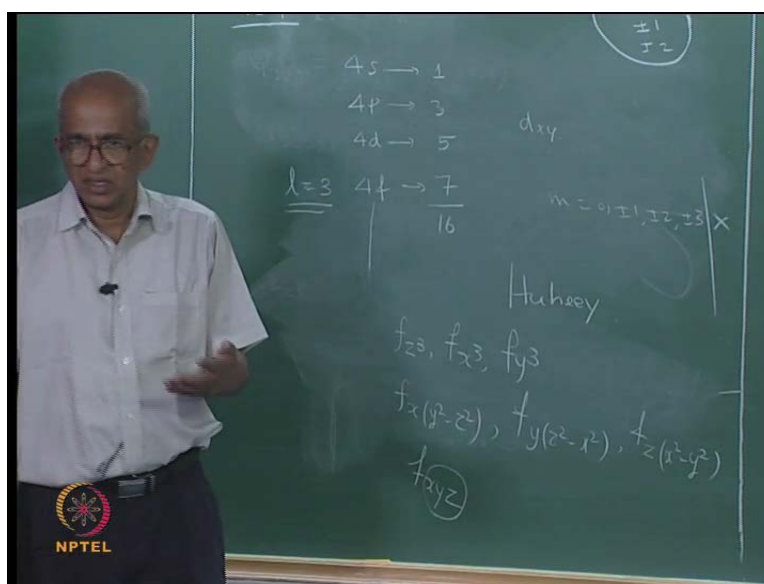
We should also see yz ; almost the same except that this is now in the yz plane, okay. Then we have only one more orbital left, what is that? It is actually the orbital that is called $x^2 - y^2$, this one; how does it appear? You can see that this is the appearance. The important thing is to notice that these are not lying in between the axes, but if you look at it you would see that these are actually lying along the x ; these are lying along the x and the y axis, right. Then now draw the $x^2 - y^2$ orbital showing you clearly the positive and the negative lobes of this orbital.

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So, these are my axes x and y, and the orbital that I am drawing is $d_{x^2 - y^2}$; it will have a positive lobe like this and another one in exactly opposite direction, and it also has two negative lobes. One is like that, and the other one is like this, and let me put the signs of these orbitals, signs of these lobes; there is a negative sign here, negative sign there. These are negative regions for the wave function, and you have a positive lobe here, another positive lobe there. And the important thing is to notice that if you performed the operation of inversion the orbital would remain unchanged, and people normally say that this is an orbital that is symmetric under the inversion operation. So, that is what, that is what regarding these orbitals. So, how many of them? In total you have five of them corresponding to m equal to 0 plus or minus 1 plus or minus 2. Then when you think of n equal to 4 again I am not going to describe n equal to 4 in all its details.

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When n is equal to 4 you would have the 4 s atomic orbital; I am not going to describe it. You will have 4 p whereas atomic orbital there is only one 4 p, there are 3 of them; they will be 4 p x for p y and 4 p z, okay. Then we will have l equal to 2 you will have 4 d; that will be five of them. Their appearance everything is similar to the to the 3 d orbitals that we have just now described, why? Because the angular part of the wave function is just the same, but then when you have 4 f this actually will correspond to l equal to 3. When l is equal to 3 you have the 4 f orbitals; there are how many of them? There are actually seven of them, why? Because m can take on the values 0 plus or minus 1 plus or

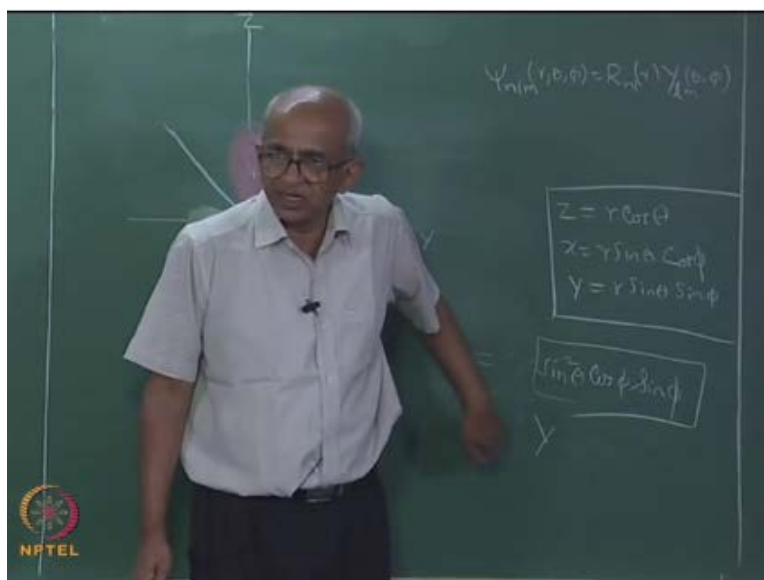
minus 2 and plus or minus 3. So, there are seven atomic orbitals; all of them have precisely the same energy.

In fact, in the case of the hydrogen atom all these orbitals are precisely the same energy, and if you counted them how many are there? 7 f orbitals, 5 d orbitals, 3 p orbitals and 1 s orbital; so the total number is sixteen which is actually equal to n^2 where n is the principle quantum number, n in this case is 4. So, if you have n particular value then there are n^2 orbitals having precisely the same energy. Then what about the 4 f orbitals; what about their shapes? Well, the shapes are actually given in many a text books; I can use Mathematica and show you the shapes of these seven f orbitals. I will show you the shape of one particular set of the seven f orbitals; I mean if you look into a book the text book like the book by Huheey on inorganic chemistry you will find that he gives you two different sets of f orbitals.

So, people have I mean two sets of f orbitals, one set of seven and another set of seven. These are actually not independent of each other, because one can be expressed in terms of the other. So, what I am going to show you is referred to as the cubic sets. So, the cubic set actually consists of these seven orbitals which I will list first, and then show you how their shapes are? They are actually written as fz^3 , fx^3 , fy^3 . Then the next orbitals are $fx^2y - y^2z^2$, $fy^2z - z^2x^2$ and $fz^2x - x^2y^2$, three of them and then finally, $fxyz$.

So, these are the seven orbitals that I will show to you, but before I show it to you that actually you may ask, why do you use these symbols? For example, in the case of d_{xy} why do I write the orbital as d_{xy} , right? That is a natural question that one would have. The answer is actually very simple. What you should do is you should take x^2 is given by this expression, and y is given by that expression you multiply the two.

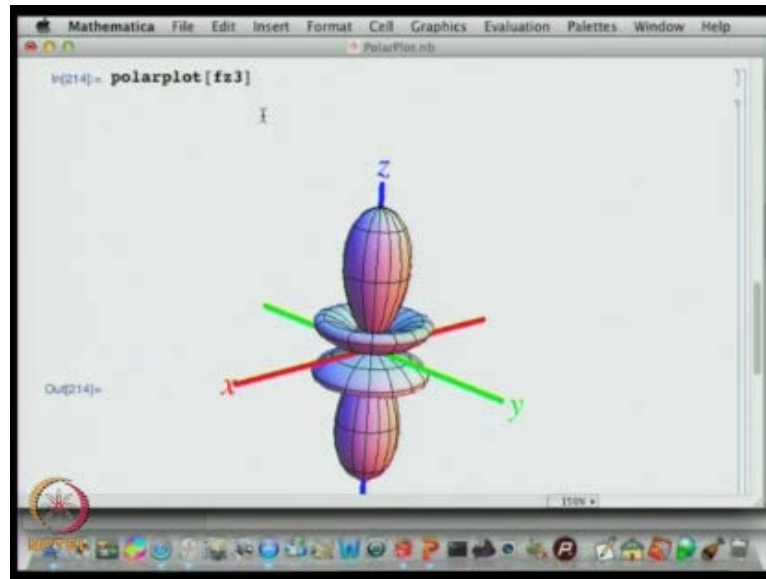
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So, what will be $x^2 y$, x^2 into y ? It is actually going to be equal to $r^2 \sin^2 \theta \cos \phi \sin \phi$. That is the result, and you just look at the angular dependence of this product $x^2 y$. The angular dependence is $\sin^2 \theta \cos \phi \sin \phi$ and that precisely is the y function. Remember any orbital would have a y part, and this is just the y part of this orbital. So, when you write d_{xy} actually you are implying that you take the expression for x , you take the expression for y , multiply the two, and remove the radial dependence; you will get the spherical harmonic corresponding to that function.

So, when you see a symbol like d_{xyz} it is actually very simple if you wanted to find out the angular dependence of this function; all that you need to do is multiply these things, right, and then throw out the r dependence, what is left is the angle dependence of the function. Now this is actually useful for this one, it is useful for this one, but with this it is a little bit more complex. See what I have told you does not give you that; it is not applicable for d_{z^2} also, it is not applicable for d_{z^2} , but it is applicable for other orbitals, for all the other orbitals this is what I have told you is applicable. So, let me now look at the f orbitals.

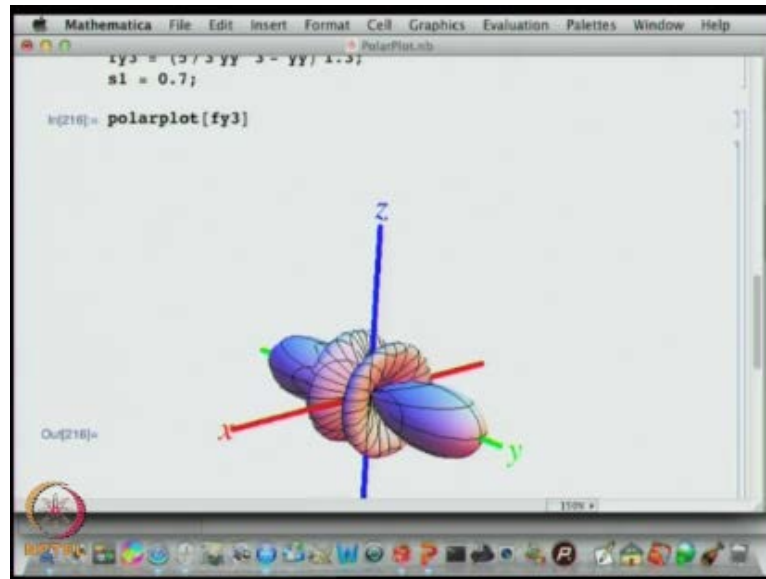
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First I will plot $f z$ cube; I have to execute the command. So, you will see that this is $f z$ cube. It is similar to your $d z$ square, but there are also differences. What are the differences? You can say well, this lobe will be positive if you like this is going to be; what about this one? If this is positive this I would assume is negative and so somewhere in between is a cone on the surface of which the wave function will be 0. Then if this is negative the next one will be positive; again in between there will be a surface on which the function will be 0, and that in this case is very simple. It is nothing but the $x y$ plane, right, and then if this is positive, what will happen? This other thing will be, well, let me repeat plus this is plus, this is minus, that is plus, and the last one will be negative, correct, and so how many nodal surfaces?

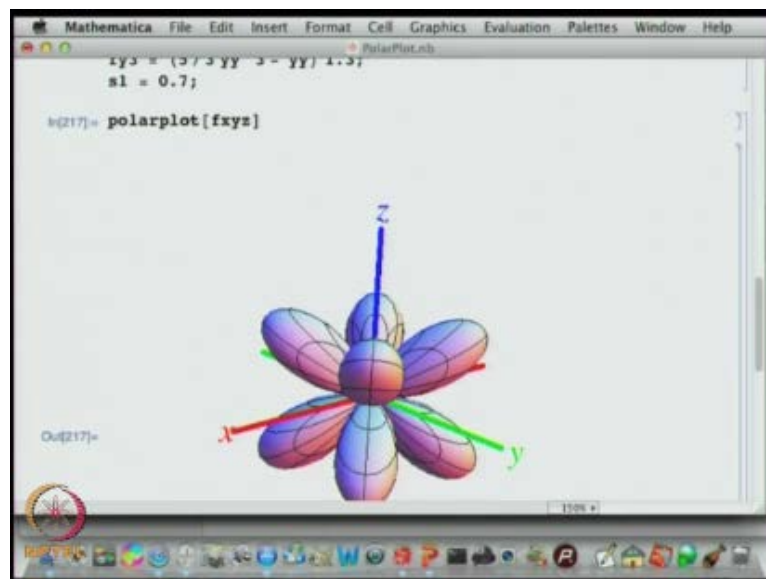
Well, the answer is one here, another one in between these two, and third one between those two; so therefore, three nodal surfaces. So, this is the appearance of the $f z$ cube. Notice that it is oriented along the z direction, right. So, if I put x cube there all that will happen is that the appearance is going to be similar except for the fact that it is oriented along the x direction, and that is what you are going to see. This is oriented along the x direction.

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Then you can have f y cube. This would be oriented along the y direction.

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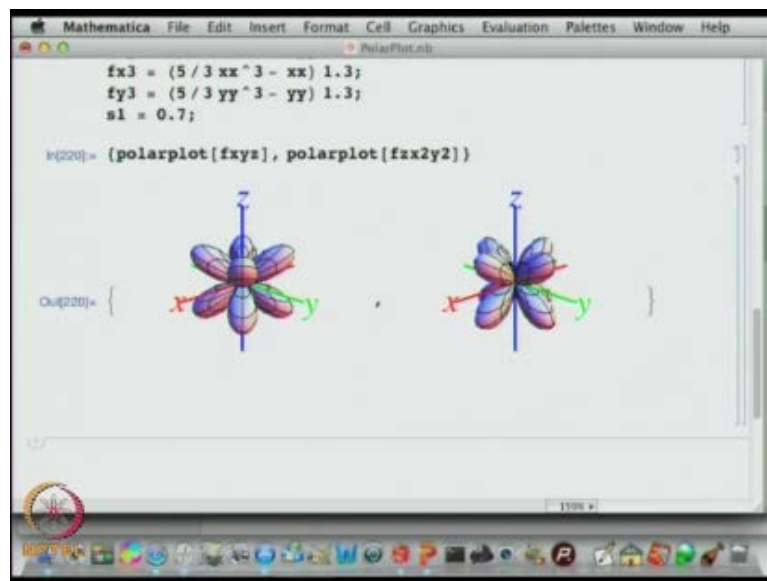


Then let us look at f xyz, interesting shape. Well, it is actually an interesting question to ask how many nodal planes are there. It has three nodal planes; where are they? You can see if you think of the x z plane, x z plane it is a nodal plane. If you think of the y z plane again you would realize that it is a nodal plane, and similarly the x y plane also is a nodal plane. So, that is how this orbital is; I mean if you are not convinced actually I can rotate it in any direction I like say for example, here I am looking down along the z axis, right;

you are just looking down along the z axis. So, there are actually eight lobes for this orbital, and four lobes are sitting on top of the other four lobes, and therefore, you can see only four lobes essentially, and you will see that along this direction, right, remember red color actually denotes the x axis; blue color is the z axis.

So, this is actually the blue color along with this x direction is actually the x z plane, and you can see that the function vanishes. Similarly this is the y axis the green color. So, that is the y axis, and again the z and the y axes together they form a nodal plane. So, similarly I can rotate it in any direction, and you would realize that there are three nodal planes. So, let us now look at another orbital which may be what we want to call it let us say $f x y^2 - z^2$. Maybe what I will do is instead of this I will first plot another one.

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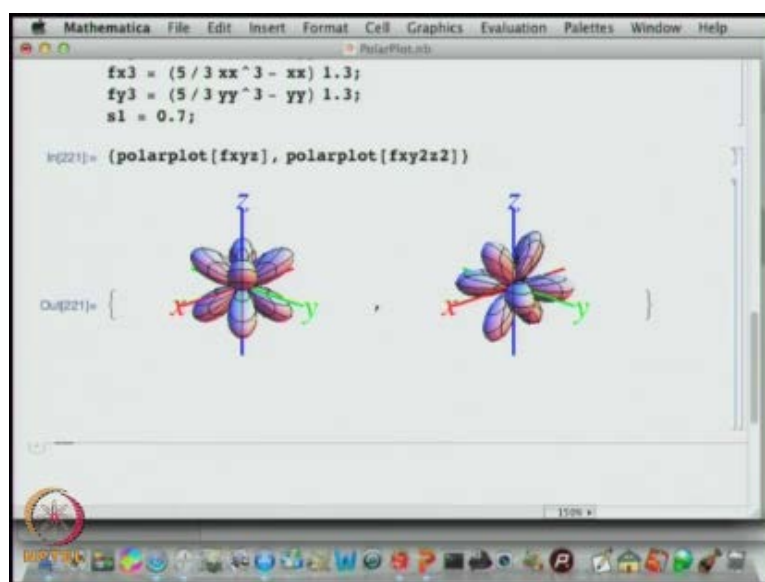


See if we look at this figure this is your $f xyz$ which we have looked at and understood, and this is the other orbital which I am plotting now; what is it? You have $f z$, the orbital is $f z x^2 - y^2$; that is the orbital that is being plotted, and if you looked at the two orbitals what you should realize is that the appearances are roughly the same. In fact, if you inspect it closely you would realize that this second orbital can be obtained from the first if you like how? By rotating this orbital about the z axis you just take this orbital rotate it about the z axis by 45 degrees it might need some time to realize that, but

all that you need to do is take this orbital, rotate it by 45 degrees about the z axis, you are going to get this orbit, okay. That is how this was.

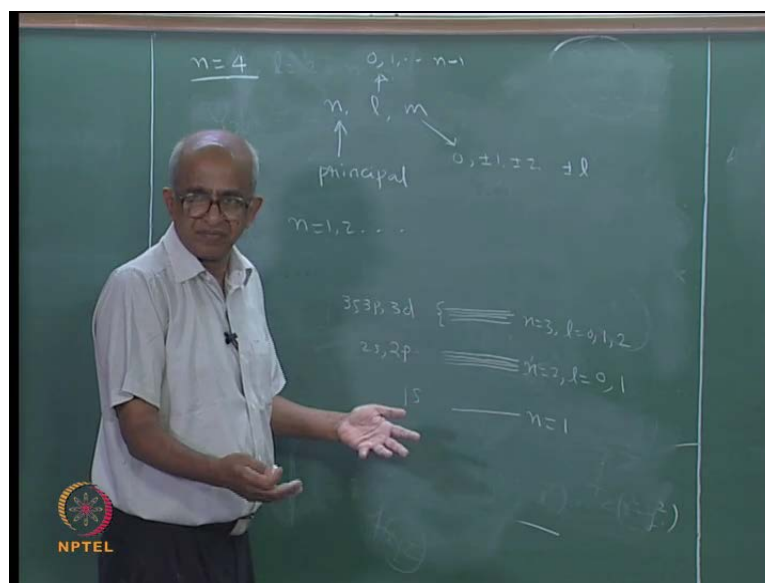
Therefore, the shapes everything is the same except that one is obtained from the other by rotating by 45 degrees about the z axis. Similarly if you took this orbital and rotated it about the y axis by 45 degrees, you will get this orbital. If you rotate about the y axis by 45 degrees you will get this orbital; while if you rotated it about the x axis by 45 degrees you are going to get this orbit, okay. I mean if you want to see I can obviously show them.

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Again I will show just one of them f_x ; that means I am rotating by the x axis. So, that is how these orbitals are. So, there are seven of them. So, you have seen once I have told you what is referred to as the cubic set of f orbitals according to the book by Huheey; the book is inorganic chemistry by Huheey, okay. Let me summarize what I have told you regarding the hydrogen atom. We have completely solved the Schrodinger equation for the hydrogen atom, and we found that there were three quantum numbers arising in the process of solution.

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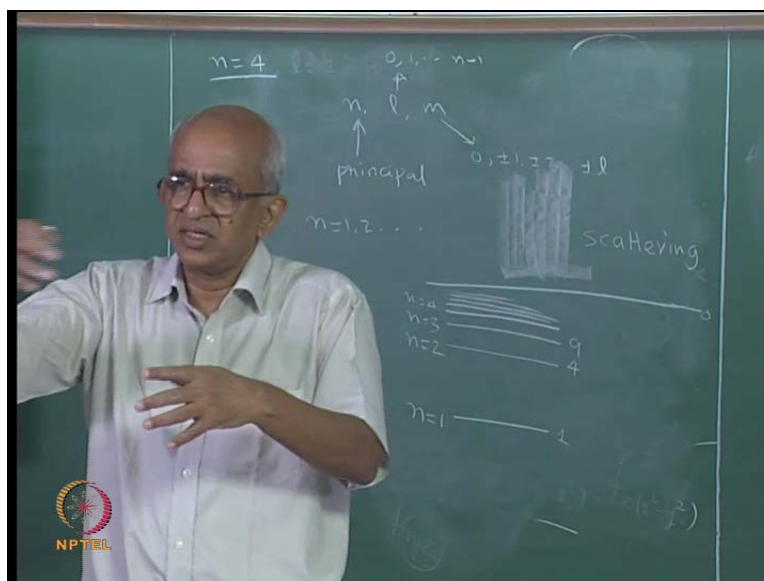


There were three quantum arising in the process of solution. They are actually the quantum numbers that are referred to as the n , l and m ; n is referred to as the principle quantum number. It can take values like n is equal to 1, 2, 3, 4, etcetera, right. The other quantum number is l ; it is referred to as the Azimuthal quantum number. It can take the values 0, 1, 2, 3, etcetera up to n minus 1. This condition actually arose automatically when we try to solve the equation, and the third quantum number is m referred to as the magnetic quantum number. It can take the values 0 plus or minus 1, plus or minus 2, etcetera and to the maximum value actually will be plus or minus l , the last possibilities either plus l or minus l .

So, these actually arose out of our solution, but the energy depended only up on the principle quantum number. It does not depend up on the values of l and m ; it simply depends only up on the value of n . And this is actually the case with the hydrogen atom, okay, and then if I represented the allowed energy levels n is equal to 1 has the lowest possible energy that is the ground state. This will give me the 1 s atomic orbital, n is equal to 2 there are four allowed orbitals corresponding to l being 0 and l being 1; this is n is equal to 2, four orbitals. The next one is n is equal to 3; you can have l equal to 0 or 1 or 2, and correspondingly how many orbitals do you have? In total you have nine orbitals. So, I should represent that by drawing nine lines very close to each other that is difficult.

So, I will not do it, but there are nine orbitals; what are they? They are actually the 3 s 3 p and 3 d orbitals. In the case n is equal to 2 you will have 2 s and 2 p orbitals, and when n is equal to 4 you have 4 s 4 p 4 d and 4 f, sixteen orbitals, right; they are all degenerate. So, typically I mean if I do not represent the degeneracy the way I would represent this let me not worry about the degeneracy because that is difficult to represent. This is n is equal to 1, this is n is equal to 2; that is n is equal to 2, then n equal to 3, may be I am not drawing it correctly, because the energy separation has to be realistic.

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So, let me draw one more figure. This is n is equal to 1, then I have n equal to 2. This is one fold degenerate which means it is non-degenerate. This is four fold degenerate; then I have n equal to 3 nine fold degenerate, n equal to 4 sixteen fold degenerate, then n is equal to 5, 6, 7, 8. As you go up the separation between the energy levels gets closer and closer and closer. In the limit n tends to infinity the separation becomes 0. So, therefore, somewhere here is energy 0, right; here the energy is 0. We found only these solutions. Remember in our analysis we said that the total energy of the system is negative, but then you may ask what will happen if the total energy is positive, okay? So, the answer is actually extremely simple.

If we have actually taken a situation where we have the proton and if the electron is at infinite distance there is no interaction between the two and the energy of the system is 0, okay. Now how can I have an energy which is greater than 0? The answer is that the

electron has to move with some energy. Then it will have nonzero energy, right. It has to move from infinity suppose I just push it then it will move. It will have some kinetic energy and the kinetic energy of the electron suppose the electron is at infinity I just give it some kinetic energy, it will come and it will be sit.

So, to say or it will collide, or it will get scattered by the proton and after the scattering what will happen? It will go away, and the amount of kinetic energy that I can give is decided by me; I can give it any kinetic energy and therefore, I can solve the Schrodinger equation with the electron having some kinetic energy starting with; it starts at infinity with some kinetic energy comes near the proton, and it goes away, and as I have told you the kinetic energy that of the electron initially is determined by me. So, I can choose it to have any energy and therefore, above this 0 actually you can give the electron any energy, and the energy levels are not quantized. It is possible to have any energy starting from 0 to infinity. These are what are referred to as the scattering states in which the electron is simply scattered from the proton.

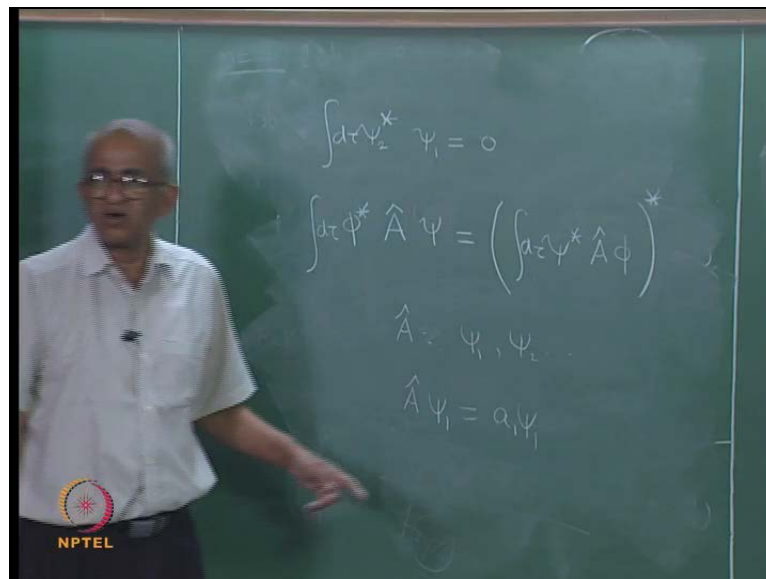
It comes hits the proton; it spends some time in the vicinity of the proton and goes away. So, this is how the allowed energy levels of the hydrogen atom are, okay, and again I should also remind you that we have just spoken of the bound states and the scattering states. But in addition to this you have the hydrogen and the proton. Suppose they form the bound state which is what is referred to as the hydrogen atom then the hydrogen atom can execute translational motion as a whole, right. That is something that we have not worried too much, but that also is there just to remind you. But then of course, you see you have already studied something about the nature of the hydrogen atom, and you would know the three quantum numbers are not enough to describe the state of the hydrogen atom.

I mean in the case of hydrogen atom three quantum numbers are not enough, you actually need four quantum numbers, and this fourth quantum number arises from the idea of spin. Something that I will describe later, but before I do that I want to do some general things, because we now have enough background to do a few general things. Now you see we have solved the Schrodinger equation for which system. So, particle in a box we have solved the Schrodinger equation for the harmonic oscillator. We now have solved the Schrodinger equation for the hydrogen atom. In all the cases if you remember

it was possible to normalize the wave function; wherever we had the solution we can normalize it; that was not difficult.

Then further in the case of the particle in a one dimensional box I did demonstrate you that any two wave functions, right. They are orthogonal to one another, and I demonstrated that for the harmonic oscillator also; for the hydrogen atom I have not demonstrated it, but it is possible to show that you give me a 1 s atomic orbital, this 1 s atomic orbital will always be orthogonal to the 2 s, it will be orthogonal to the 2 p, right. So, therefore, if you give me any two wave functions which are solutions of the Schrodinger equation.

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Then I take the first one which I may denote as may be psi 1; I will take the second one I may denote it as psi 2. For example, this may be the 1 s atomic orbital, this may be the 2 s, or it may be the 2 p; it does not matter. Take another atomic orbital; multiply the two together and by the volume element d tau integrate over the entire space. The answer is going to be 0, and we say that these two functions are orthogonal. We have already seen this. We have also in our postulates we have said that any operator that occurs in quantum mechanics has to be a Hermitian operator. We made that postulates; I mean in the postulates this was actually a part of the postulate.

So, what is a Hermitian operator? The Hermitian operator is an operator let me say A for which what I will do is I will allow this to operate up on A an acceptable wave function

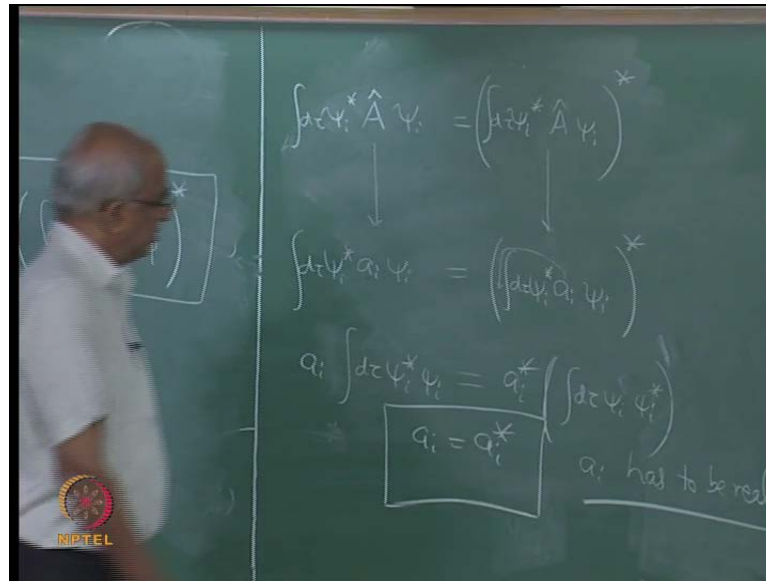
like ψ which I denote as ψ ; multiply it by the complex conjugate of another acceptable wave function which I denote as ϕ , and then integrate over the entire space. Because I have done integration about the entire space the answer is going to be a number; the number may be complex, okay. Now suppose instead of doing this I take A , allow it to operate on ϕ instead of operating on ψ and then multiply it by the complex conjugate of ψ and integrate over the entire space.

If it so happens I mean or if it is so that this number and that number are complex conjugates of one another for any acceptable ψ and ϕ , then I define A as a Hermitian operator. This was our definition of a Hermitian operator, okay, and what are the properties of Hermitian operators that are of interest to us? The most important thing is that their Eigen values are always real. Now I am going to prove that if I have a Hermitian operator then any given Eigen value of that Hermitian operator has to be a real number; that is what I am going to prove now, right. I mean I could have done the proof earlier, but I thought it is best to do it at this point, because you do have some familiarity with orthogonality, normalization and related things.

So, it will not appear as abstract as it would have appeared earlier if I had done it. So, let me say that I have an Eigen function; well, maybe I mean this operator A would have several I mean in principle an infinite number of Eigen functions. So, I need some notation. Let me say that ψ_1 , ψ_2 , etcetera; this is a least it goes to infinity. These are Eigen functions of the operator A . What it means is that if A operate up on ψ_1 the answer is going to be ψ_1 itself multiplied by the corresponding Eigen value which I will denote by the symbol a_1 , and if it operate up on ψ_2 the answer is going to be a_2 times ψ_2 , or I can generalize and say okay, if A operated up on ψ_i the i th Eigen function, the answer is going to be a_i multiplied by ψ_i , right.

This is how the Eigen value equation would look like and what is it that I want to prove? I want to prove that all a_i 's are real numbers. They cannot be complex; that is what I want to prove. So, how will I prove it? The answer is actually extremely simple, okay. Well, what I am going to do is you see in this equation that I have this is guaranteed if the operator A is Hermitian this is guaranteed.

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So, in this equation what I am going to put is this psi I am going to put it as psi subscript I; this psi I am going to put it as psi subscript I, because what do I want to have? I want to have A operating up on psi i, right, and this phi also I am going to identify with psi i. suppose I did that, what will happen? This psi is going to be identified with psi i then I will have A operating on it, and then here I will have psi i star, right, and then I would have the volume element d tau, and I have to integrate over the entire space. And the fact that A is the Hermitian operator implies that I can do the same thing here on the right hand side. So, instead of phi what would I have? I would have A operating up on psi I, because phi is identified with psi i and this psi is identified with psi i itself.

So, I would have psi I star, and then the volume element d tau integrate over the entire space, and then I will have the star, right. So, all that I am doing is this is satisfied by a Hermitian operator for arbitrarily acceptable psi and phi. If I just say that these are both this psi and phi is both the same Eigen function of that operator that Eigen function being psi I, right. So, if that is the way it is what will happen to the left hand side? A operating up on psi I is going to give you the corresponding Eigen value which is small a i which is just a number multiplied by psi i. Then I have to multiply by psi I star d tau integral, right; that is the left hand side, and what will happen to the right hand side? There is this star. This A operating up on psi i is going to do exactly the same thing.

I am going to get a I , then ψ_i , then ψ_i^* , volume element $d\tau$ integrated over the entire space, but now you look at this? This is just a number. So, therefore, you see here I have integration with respect to position coordinates and so on. But a number does not depend up on position coordinate. So, I can just move it out, and therefore, what will happen? I will have a i coming outside, then $\int d\tau \psi_i^* \psi_i I$, right, and if your wave function is if your Eigen function is normalized then this will actually be equal to unity. At the moment I will not say it is normalized, because I do not need it, okay, and what will happen to the right hand side? See this a i is a number. So, I can just move it out of the integral sign; I will have it here, but then I have to take the complex conjugate.

So, what will happen? Then I will have a i^* , and what do I have left? I would have left $\int d\tau \psi_i^* \psi_i I$ the whole thing complex conjugated, right, and this complex conjugation I can take it inside if I like. So, if we took it inside, what will happen? I will have $\psi_i^* \psi_i$, double star; double star is equivalent to doing no starring. So, therefore, this star and that star I can remove, but when I take the star inside it is going to get here. So, that is what happens, and then when you look at this, then would realize that this integral and that integral they are the same, right. If they are the same I can just remove them, and so what is the result? I get the result that a i is equal to a i^* . What does that mean? Any given Eigen value is equal to its own complex conjugate, and this can be valid only if a i is a real number, right. If a i is a complex number this will not be satisfied.

So, therefore, any given Eigen value a i has to be real. So, that is a very general result, and this is the reason why in postulate number two we said that the operator has to be Hermitian, because the Eigen value is guaranteed to be a real, right. In postulate number three we talked about measurements, and we said that if I make a measurement the answer has to be an Eigen value of the corresponding operator, right, and we know that when we make measurements, the answer is that we get our real numbers, right, and therefore, it is necessary that the Eigen values should be real, and for a Hermitian operator the Eigen values are guaranteed to be real. So, this is a general result; I will prove one more general result later.

Thank you for listening.