Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 29
Atomic Orbitals – Part four Hermitian Operators

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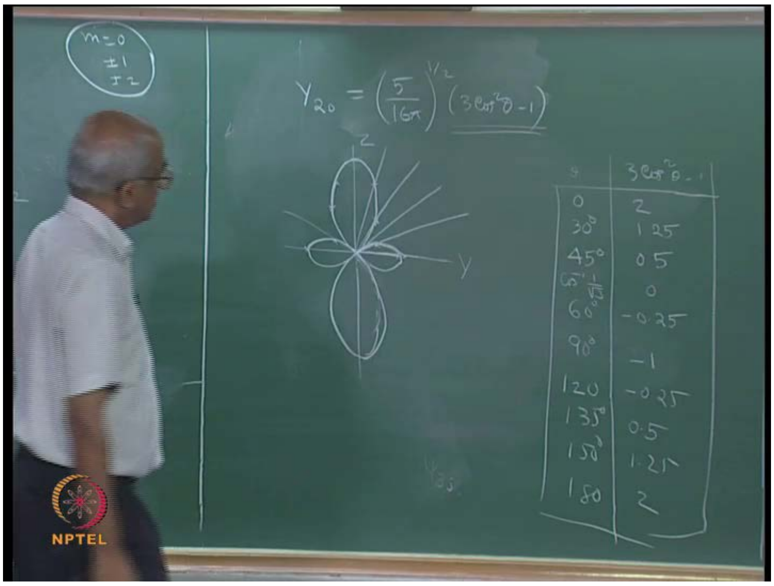

θ	$3\cos^2\theta - 1$
0	2
30°	1.25
45°	0.5
$\cos^{-1}\frac{1}{\sqrt{3}}$	0
60°	−0.25
90°	−1
120	−0.25
135°	0.5
150°	1.25
180	2

We will look at the when we will continue about we were doing, we look at the 3 d z square orbital as I told you this is the polar plot in the x z plane. If you wanted to get the 3 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 theta equal to cos inverse of 1 by root 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 a 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 direction there on the other side such that this angle, this angle is how much it is actually 180 minus 54.7 again you will find that cosine of theta will be equal to 0.

So, whenever when you get the 3 dimensional appearance by rotating about these z axis you think of what will happen to these lines these lines actually I 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 laying along the surfaces of these cones the angular part of the wave function will be identically equal to 0. 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 for 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 such that the interior angle this angle within the cone is equal to 54.73 degrees and the vertex of the cone actually is pointing down. 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.

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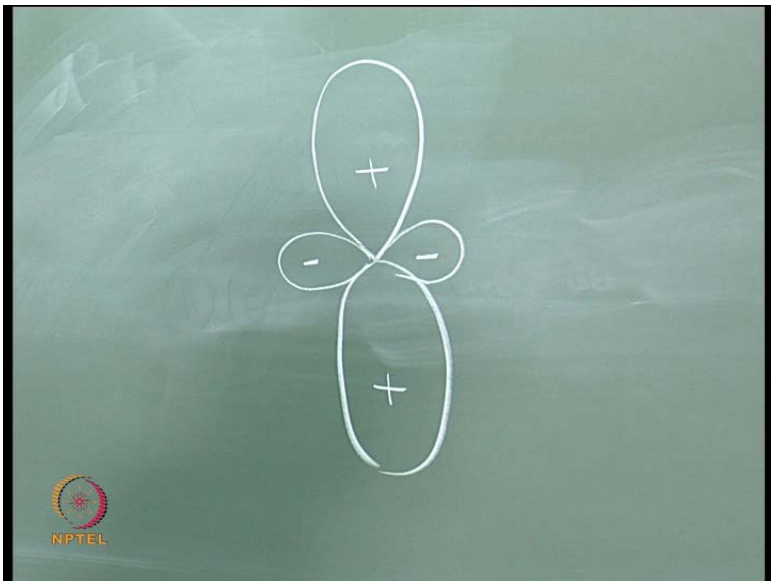

So, with this information let me give show you a polar plot of this orbital, this is the appearance which is obtained by rotating this figure about this z axis. So, these two things actually they are describing something that is to shape like a donor it not exactly. But, you can see the appearance from the figure I can if you want to I can rotate it a little bit see this is how it would appear it look from above roughly that is how it looks like any angle you can move it.

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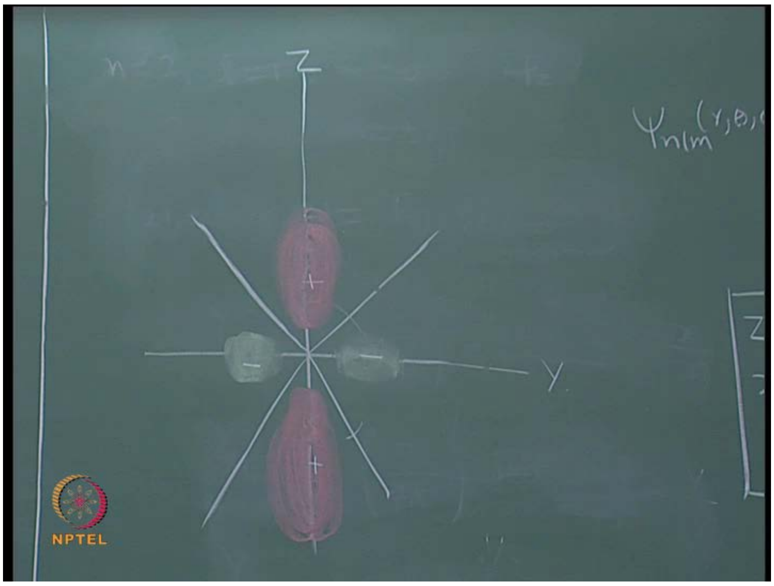

So, this is a 3 d z square orbital the orbital is referred as 3 d z square and you can also make a density plot if you like, so how will you make the density plot I can do it here. So, in the first thing that I will now do is the label the axis this is let me say the y axis if you like and this is the z axis, now in this direction actually the wave function is positive. But, then along that then it was special directions these are the special directions along them the wave function is 0 and similarly along these directions also the wave function is 0.

So, why do I mark the line directions along which the wave function is 0 because you see if the function is positive as soon as I cross the line the function will change sign? So, the 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 signs.

Therefore, in this region the function will be positive and then again this region of 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 this of shore mathematics yes I do have a plot of this function a density plot let me just draw it here it is made in the x z plane. But, it does not matter whether it is at the x z plane over by it is in the y z 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 they are represented in these blue regions you can see actually the value is negative that is clear. When I point one of the lines you see this is the line along which the value 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 then we have to worry about other atomic orbital I can I mean I will not, we are actually writing down the functions. But, I have, so I can just show you the polar plots of these other functions and that should be enough 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 d x y.

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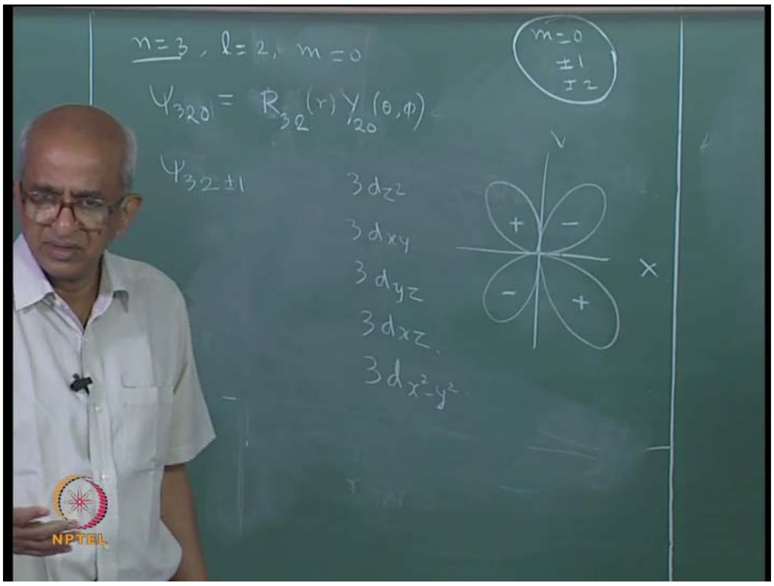

How will you get them my procedure is just same as that I have outlined to have to put other values of m psi 3 2 plus or minus 1, but if you put plus or minus 1 the result is going to be complex. Therefore, you will take either the cosine function or the sine function and then proceed and the results are actually 5 orbitals in total because you have m equal to 0 plus or minus 1 plus or minus 2, you have 5 orbitals in total.

Those 5 orbitals actually whether convention is to double them as 3 d x y, 3 d y z, 3 d x z then 3 d z square I have described and there is other orbital which is we denoted as 3 d x square minus y square. You can make a polar plots of all these orbitals, so 3 d x y, x y is the one that you can see here as you will see in the picture see this is your z direction is there you have the x and y axis and you can see that these has four lobes which are clear in the picture.

These 4 lobes are pointing in between the axis the important thing is to realize that the orbital is in the x y plane, it is in the x y plane, it is lying in the x y plane and there are 4 lobes maybe I can draw this on the board imagine this is the x y plane. So, you have one lobe here another one there, another one here and 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. So, it is how it is, so 3 d x z what will happen the appearance is the same except that it is in the, it is in the x z plane the orbital is lying in the x z plane. It is very similar to x y except that everything is now in the x, x z plane and of course this has two both of these orbitals has 2 nodal planes.

Where are the nodal planes just to illustrate in the case of this orbital which I have denoted x y in this case remember this z axis is standing perpendicular to that plane of the board in this fashion. So, if you think of such a plane which is what plane it is the x z plane or you think of such a plane which is nothing. But, the y z planes then these are actually nodal planes, similarly if you think of this orbital you would realize that the x y plane the x y plane is a node and the y z plane also is a node for this orbital. So, then we have seen x y and x z we should also see y z almost the same except that this is now in the y z plane then we have only one more orbital left what is that it is actually the orbital that is called x square minus y square d x square minus y square.

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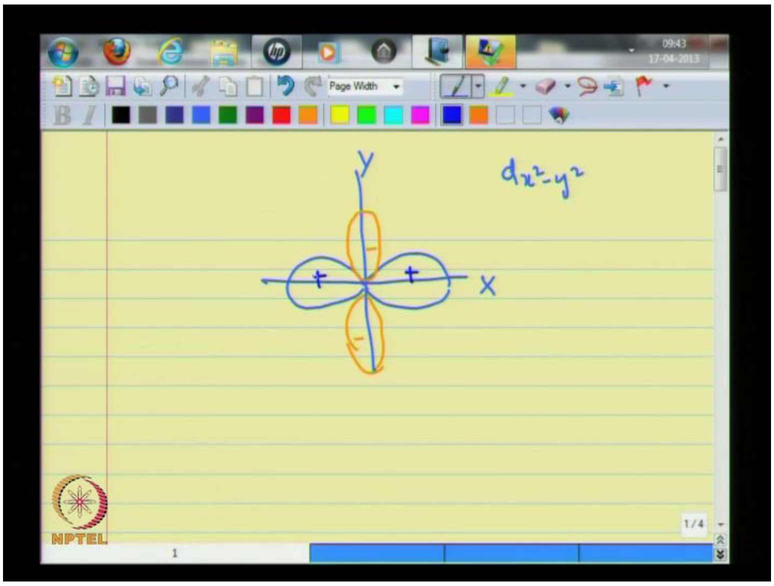

This one how does it appear you can see that this is the appearance the important thing is to notice that that these are not lying in between the axis. But, if you look at it you would see that these are actually lying along the x, these are lying along the x and the y axis. Now, draw the d x square minus y square orbital showing you clearly the positive and the negative lobes of this orbital.

So, these are my axis x and y and the orbital that I am drawing d x square minus y square it will have a positive lobe like this and another one in exactly opposite direction. It also has 2 negative lobes one is like that and the other one is like this and let me put the signs of this orbitals signs of this lobes. There is 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.

The important thing is to notice that if you performed the operation of inversion the orbital would remain and changed and people normally say that this is an orbital that is symmetric under the inversion operation. So, that is what the result regarding these orbitals, so how many has them in total you have 5 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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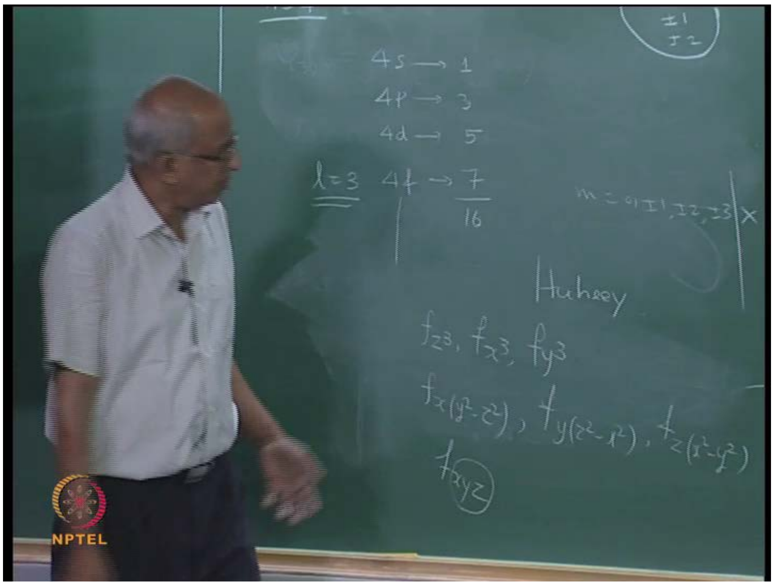

When n is equal to 4 you would have with the 4 s atomic orbital I am not going to describe it you will have 4 p 4 s atomic lobe, there is only one 4 p, there are 3 of them.

They will be 4 p x, 4 p y and 4 p z then we will have l equal to 2, you will have 4 d that the 5 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 your 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 7 of them why because m can taken the values 0 plus or minus 1 plus or minus 2 and plus or minus 3. So, there are 7 atomic orbitals all of them have precisely the same energy in fact in the case of the hydrogen atom all these are orbitals are precisely the same energy and if you counted them how many are there seven f orbitals 5 d orbitals 3 p orbitals and 1 s orbital.

So, the total number is 16 which is actually equal to n square, where n is the principle quantum number n in this case is 4, so if you have n a particular value then there are n square orbitals having precisely the same energy. Then what about the 4 f orbitals what about their shapes well the shapes are actually give an in many textbooks I can use mathematics and show you the shapes of these 7 f orbitals I will show you the shape of one particular set of the 7 f orbitals. Now, I mean if you look into your book your textbook like the book by Huheey on inorganic chemistry you will find that he gives you two different sets of f orbitals.

So, people have to two sets of f orbitals one set of 7 and another set of 7 these are actually not independent of each other because one can be expressed in times of the other. So, what I am going to show you is referred to as the cubic set, 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 f z cube, f x cube, f y cube.

Then next orbitals are f x into y square minus z square f y into z square minus x square and f z into x square minus y square, three of them and then finally f x y z. So, these are the 7 orbitals that I will show to you, but before I show it you that actually you may ask why do you have why do you use these symbols for example in the case of d x y why do I write the orbital as d x y.

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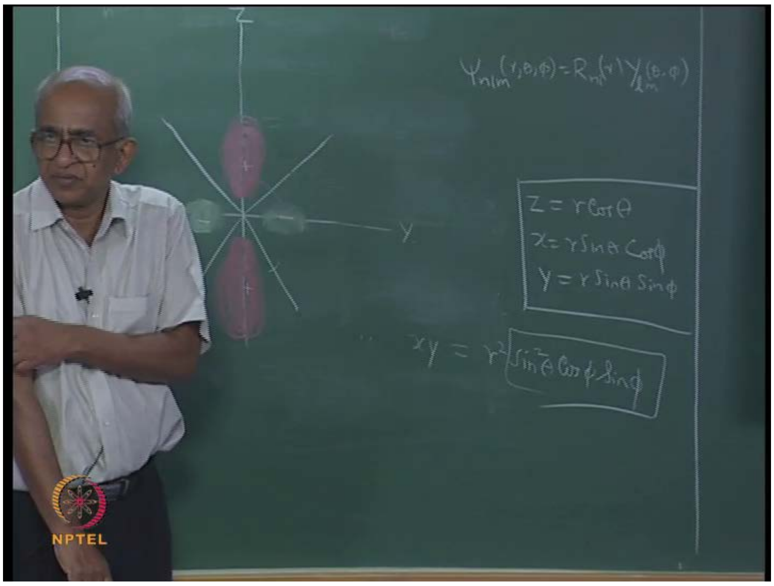

That is a natural question that one would have the answer is actually very simple what you should do is you should take x, x is given by this expression and y is given by that expression you multiplied the two. So, what will be x y x into y it is actually going to be equal to r square sine theta or sine square theta actually cos phi sine phi that is the result. You just look at the angular dependence of this product x y the angular dependence is sin square theta cos phi sine 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 x y actually you are implying that you take the take the expression for x you take the expression for y multiply the two. To remove the radial dependence, you will get the spherical harmonic corresponding to that function, so when you see a symbol like d f x y z 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 and then throughout the r dependence what is left is the angle dependence of the function. Now, this is actually useful for this one, it is so useful for this one, but with this it is a little bit more complex that what I told you does not give you that it is not applicable for d z square also. It is not applicable for d z square, but it is applicable for other orbitals for all the other orbitals this, what I have told is applicable, so, let me, now look at the f orbitals first I will plot f z cube see at the command.

So, you will see that this is f z cube it is similar to your d z square, but there is there are also differences what are the differences I 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 somewhere in between z 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 one which the function will be 0 and that in this case is very simple it is nothing but the x y plane and then if this is positive what will happen.

This other thing will be let me repeat plus this is plus this is minus that is plus and the last one will be negative correct. So, how many nodal surfaces well the answer is 1, here another one between these two and third one between those two therefore 3 nodal surfaces. So, this is the appearance of the f z, f z cube notice that it is oriented along the z direction, 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 is oriented along the x direction. That is what you are going to see this is oriented along the x direction then you can have f y cube this would be oriented along the y direction.

Then let us look at f x y z interesting shape well it is actually a interesting question to ask how many nodal planes are there, it has 3 nodal planes where are they you can see the if you think of the x z plane, x z plane. It is a nodal plane 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 that mean if you are not convinced actually I can rotate in any direction I like see for example, here I am looking down along the z axis see if you are just looking down along the z axis. So, there are actually 8 lobes for this orbital and the 4 lobes are sitting on top of the other four lobes.

Therefore, I can have only 4 lobes essentially and you will see that along this direction, remember red color actually denotes the x, 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 taken the z axis to the y axis together they have form a nodal plane, so similarly I can rotate it is in any direction and you would realize that there are 3 nodal planes. So, let us now look at another orbital which may be what do you want to call it let us the f x y square minus z square may be what I will do is instead of this I will first plot another one.

See if you look at this figure this is your f x y z which we have look that 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, z f square minus y square. That is the orbital that is being plotted and if you look at look at that the two orbitals what you should realize is that the appearance 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 we will 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 this z axis we are going to get this, that is how this was. Therefore, the shapes everything is the same except that one is obtain from the other by rotating by 90 degrees above sorry not 90, but 45 degrees about the z axis. Similarly, if you took this orbital and rotate it about the y axis by 45 degrees you will get this orbital you will get this orbital, if you rotate about the y axis by 45 degrees you will get this orbital.

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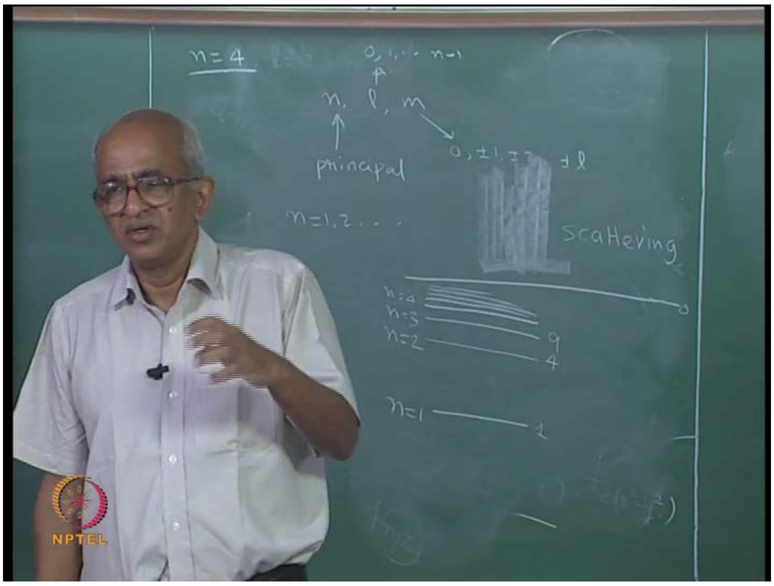

While if you rotated it is about the x axis by 45 degrees you are going to get this orbital I mean if you want to see them I can obviously show them again I will show just one of them you have x that means I am rotating by the x axis. So, that is how these orbitals also there are 7 of them, so you have seen was I have told you what I referred to as the cubic set of f orbitals according to the to the book by Huheey, the book is inorganic chemistry by Huheey.

Let me summarize what I have told you regarding the hydrogen atom, we have completely solved the Schrodinger equation for the hydrogen atom. We found that there were three quantum numbers arising in the process of solution, there were three quantum numbers arising in the process of solution. They are actually the quantum numbers that are referred to as n l and m n is referred to as the principle quantum number you can take values like n is equal to 1, 2, 3, 4 etcetera rights the other quantum number is l.

It is referred to as the azimuthal quantum number you 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. 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 the maximum value actually will be plus or minus value the last possibility is a plus l or minus l.

So, this is actually arisen out of our solution, but the energy depended only upon the principle quantum number it does not depend up on the values of l. Then it simply depends only up on the value of n and this is actually the case with the hydrogen atom 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 one being 0 and one 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, 1 over 2 and correspondingly how many orbitals do you have in total you have 9 orbitals. So, I should represent that by drawing 9 lines very close to each other that is typical. So, I will not do it up to 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 then n is equal to 4, you have 4 s, 4 p, 4 d and 4 f, 16 orbitals, they are all degenerates. So, typically I am if I do not represent the degeneracy the way I would represent this let not worry about degeneracy because that is typical to represent this is n is equal to 1, this is n is equal to 1 that is n is equal to 2 then n equal to 3.

If I am not drawing it correctly because the energy separation has to be really takes, so let me draw one more figure this is n is equal to 1. Then I have n equal to 2 this is the one fold degenerates which means it is not 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 closer and closer and closer in the limit ten times to infinity their separation becomes 0. Therefore, somewhere here is energy 0, here the energy is 0 then we find only these solutions, so 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, so the answer is actually extremely simple if we are we have actually taken a situation where we have the proton. If the electronic is at infinite distance there is no interaction between the two and the energy of the system is 0, now how can I have a energy which is greater than 0. The answer is that the electron has to move with some energy then it will have a non 0 energy, it has to move from infinity suppose I just push it then it will move it will have some kinetic energy. The kinetic energy of the electron if we suppose at the electronics at infinity I just give it some kinetic energy it will come and it will be sit.

So, to say or it will colloid or it will gets scatted by the proton and after this 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. Therefore, I can solve the Schrodinger equation with the electron having some kinetic energy is starting with its starts at infinity with some kinetic energy comes near the proton and it goes away. As I told you the kinetic energy that the electron initially has this determine by me, so I can choose it have any energy and therefore above this 0 actually you can give the electron any energy.

The energy levels are not quantized this possible to have any energy starting from 0 to infinity these are what are referred to as these scattering states in which the electron is simply scattered from the proton it comes. It is the proton it spend some time in the vicinity of the proton and goes away, so this is how the allowed energy levels of the hydrogen atom r and again I should also remained 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 in which is what is referred to as the hydrogen atom.

Then the hydrogen atom can execute translational motion as a hold that is something that we have not worried too much, but that also is there just remain. But, then of course you see view we have already studied something about the nature of the hydrogen atom and you would know the three quantum numbers are not to enough to describe the state of the hydrogen atom. In the case of, I mean in the case of hydrogen atom three quantum numbers are not enough you actually need four quantum numbers and these four quantum numbers 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 some a few general things. Now, you see we have solve the Schrodinger equation for which system say particle in a box we have solve the Schrodinger equation for the harmonic oscillator. Now, we 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 the solution, we can normalize it that was not difficult. Then further in the case of the particle in 1 dimensional book I did demonstrate you that any two wave functions they are orthogonal to one another.

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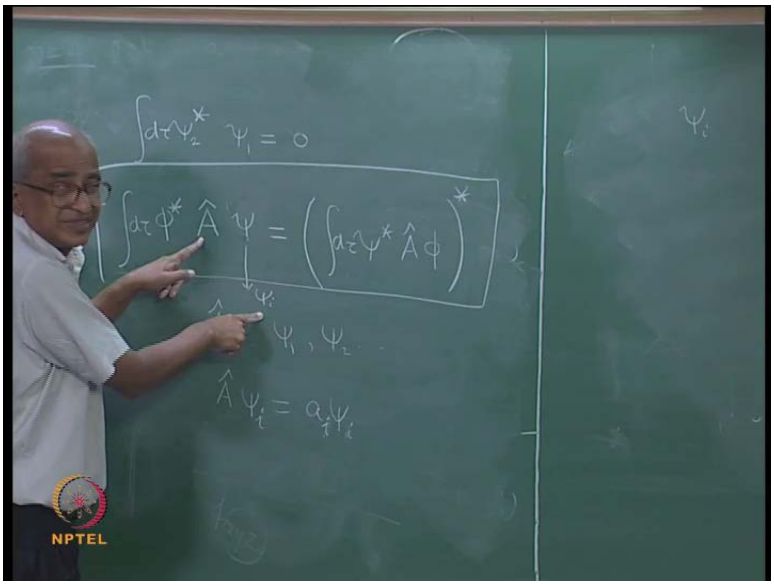

So, I demonstrated that for the harmonic oscillator for the hydrogen atom I have not demonstrated it, but it is possible to show that you give me 1 s atomic orbital. This 1 s atomic orbital will always be orthogonal to the 2 s, it be orthogonal to the 2 p therefore if you give me any two wave functions which are solutions of the Schrodinger equation then I take.

The first one which I am a denote as may be psi 1 I will take the second one I may denote it as psi 2 for example it is may be with this 1 s atomic orbital this may be the 2 s or it may be the 2 p it does not matter. Let take another atomic orbital multiply the two together and by the volume element d 2 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 you made that postulates and in the postulates this is actually a part of the postulates. So, what is a hermitian operator the hermitian operator is an operator let me say for which what I will do is I will allow this two operators upon an acceptable wave function like psi which I denote as psi. Multiplied by the complex conjugate of another acceptable wave function which I denote as phi and then integrate over the entire space because I have done integration over the entire space the answer is going to be a number the number may be complex.

Now, suppose instead of doing this I take a allow it to operate on phi instead of operating on psi and then multiplied by the complex conjugate of psi and integrate over the entire space. If it so happens I am in or if it is, so that this number and that numbers are complex conjugates one another for any acceptable psi and phi then I define a as a hermitian operator. This was how the definition of a hermitian operator and what are the properties of hermitian operators that are of interest to as the most important thing is that there Eigen values are always real.

Now, I am going to prove that if I have a hermitian operator then any give Eigen value of that hermitian operator has to be a real number that is what I am going to proof. Now, I mean I could have done the proof earlier, but I thought it is best to do at this point because you do have some familiarity with orthogonality normalization and the related things. So, it will not appear as obstruct has it would have appeared earlier if I had done it, so let me say that I have an Eigen function well may be I mean that this operator, a would have several I mean in principle and infinite number of Eigen functions.

So, I need some notation let me say that psi 1, psi 2 etcetera I mean this is a least it goes to infinity these are Eigen functions of the operator a. What it means is that if a operator upon psi 1 the answer is going to be psi 1 itself multiplied by the corresponding Eigen value which I will denote by the symbol small a 1. If it operate upon psi 2 the answer is going to be a 2 times psi 2 or I can generalize and say if a operated upon psi i, the i-th Eigen function the answer is going to a subscript i multiplied by psi i. This is how the Eigen value equation would look like and what is 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, will I prove it the answer is actually extremely simple well I what I am going to do is you see in this equation that I have this is guaranteed if the operator a hermitian this is guaranteed. 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, I am going to put it as psi subscript i because what do I want to have I want to have a operating upon psi i. 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.

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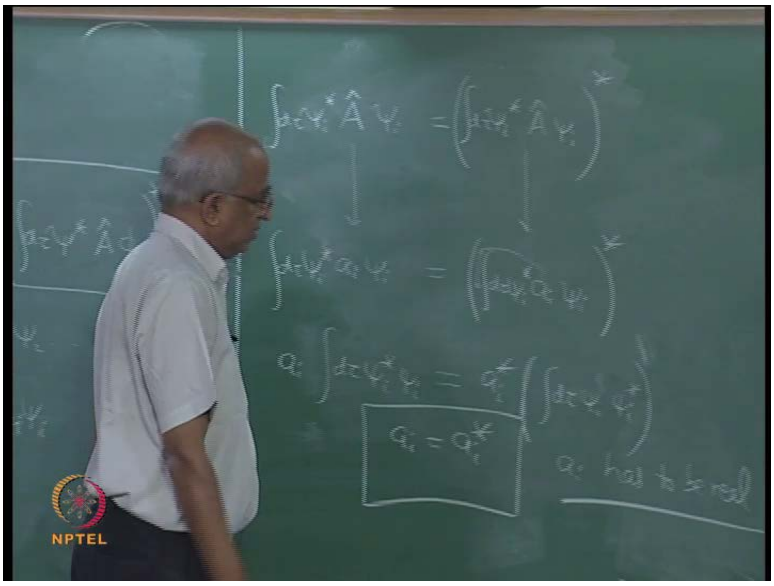

Then I would have the volume element d 2 and I have to integrate over the entire space and the fact that a is a hermitian operator implies that I can do the same thing here on the right hand side. so, instead phi what would i have, i would have a operating upon psi i because phi is identified with psi i and this psi is identified with psi i itself.

So, I would have psi i is star and then the volume element d two integrate over the entire space and then I will have the star. So, all that I am doing is this is satisfied by a hermitian operator for arbitrarily as suitable psi and phi I just say that these are both the psi and phi are both the same Eigen function of that operator that Eigen function being psi i. So, if that is the way it is what will happen to the left hand side a operating upon psi i is going to give you they are corresponding Eigen value which is small a, i which is a just a number multiplied by psi i then i have to multiply by psi i star d 2 integral.

That is the left hand sides and what will happen to the right hand sides there is a star this a operating upon psi i is going to do exactly the same thing I am going to get a i then psi i then psi i star volume element d 2 integrated over the entire space. But, now you look at this is just a number therefore you see here I have integration with respect to position coordinates and so on. But, a number does not depend up on precession coordinates, so I can just move it out and therefore what will happen i will have a, i coming outside then integral d 2 psi i star, psi i.

If your wave function is, if your Eigen function is normalized then this will actually be equal to unit a, at the moment I will not say it is normalized because I do not need it. What will happened 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 and then I have to take complex conjugates. So, what will happen the i will have a i star and do i have left i would have to left integral d 2 psi i star psi i the whole thing complex conjugated. This complex conjugation I can take it inside if I like, so if you took it inside what will happen I will have psi i star, star double star, double star is equivalent to doing no staring.

Therefore, this start and that star I can remove, but when I take this star it is going to get here, so that is what happens and then when you look at is you would realize that this integral, that integral they are the same. 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 star 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. If a i is a complex number this will not satisfied therefore any given Eigen value a i has to be real, so that is a very general result and to this is the reason why in postulate number 3 in it was in postulate number 2.

In postulate number 2 we said that the operator has to be hermitian because the Eigen value is guaranteed should be real, in postulate number 3 we talked about measurements. We said that if I make a measurement the answer has to be an Eigen value of the corresponding operator and we know that when we make measurements the answer is that we get a real number it is right. 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.