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

Lecture - 34
Angular Momentum – Continued

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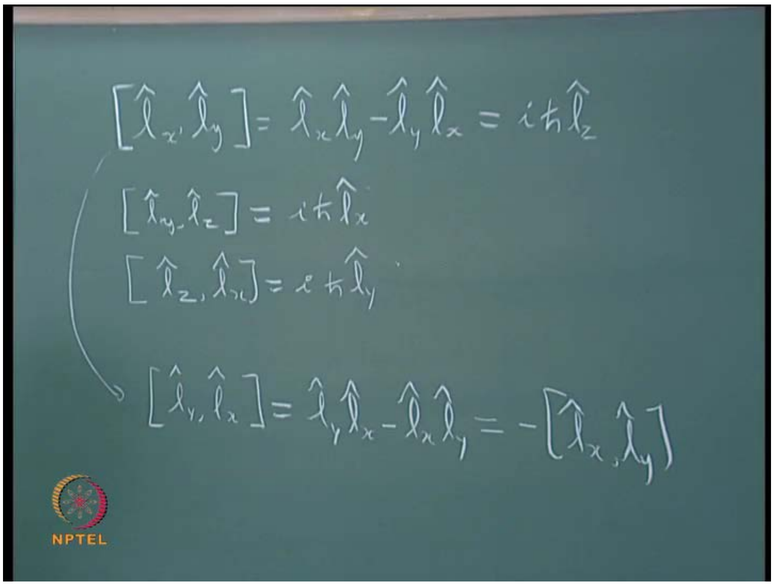

In the last lecture, we successfully derived this expression for the commutator ((Refer Time: 00:20) of l x and l y. We found that this is equal to i h cross l z, and I told you in a similar fashion I can calculate other commutators like l y, l z. This will turn out be i h cross l x, and I can also calculate l z, l x and show that it is equal to i H cross l y. This is not difficult to remember; it is quite easy to remember. I should also tell you that if you instead of writing it like this suppose you had written l y, l x, what would happen? You would have l y, l x minus l x, l y.

This will be the definition of l y, l x; if you had written like this and this obviously is the negative of that. So, therefore, the order in which these things are written is very important, because if you interchange the order the object actually changes sign. So, one has to be careful. So, we find that that l x does not commute with l y neither does l y commute with l z; l z does not commute with l x, right. It is as if it they do not like each other; they do not commute with each other none of them, but interestingly what happens is that if that l square; what is l square?

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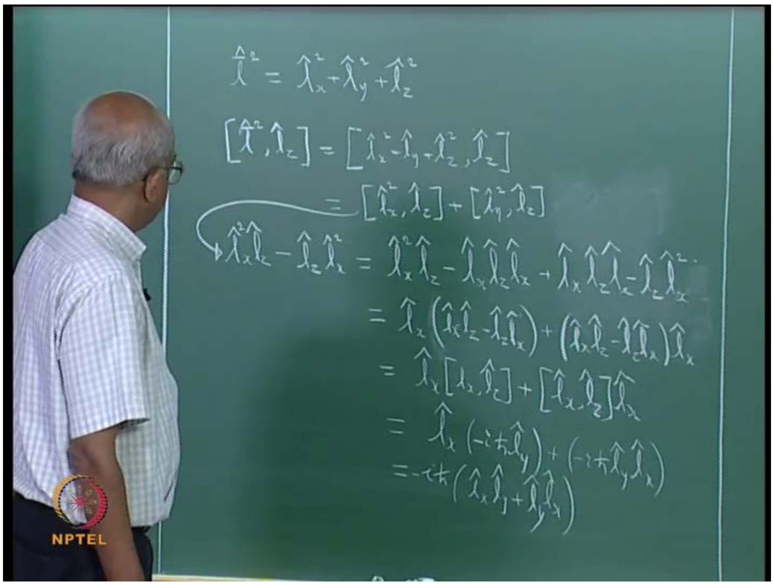

This is l square, and I will now show that l z commutes with this, right, but if l z commutes with this, what would you expect for l x and l y? Well, you see I mean all directions in space are equivalents. So, therefore, if l z commutes with l square, you would expect that l x I mean what is so special about l x? See x, y, and z are things that we choose, right. Now this is our convenience; we have the hydrogen atom. I choose x, y, z; you may choose x, y, z in a different fashion and so on. So, it is really actually no difference between l y, l z and l x in some sense they all have to be having the same kind of properties.

So, therefore, if l z commutes with l square naturally you would expect that l x also will commute, not only l x, l y also will commute. It is just that they do not commute among themselves, but they are going to commute, and this is what you would expect. So, how will I do, how will I show that? Well, it will take a few minutes, but I can prove it. What I want to do is well, this is vector l square. It is an operator; I forgot to write that hat, but it has to be there. So, therefore, this is actually vector l square. What is going to happen is that you will have l x square plus l y square plus l z square l z. This is what you would expect, and what is going to happen is you will have the whole thing plot by l z, right, and then l z followed by the whole thing, correct.

But then you can see individually I can write them. You see this is actually nothing but l x square commutator with l z, right, plus l y square commutator with l z; very easy to verify this if you want to verify, but I would say this is obvious. This is what it is, correct. All that you need to do is if you are not convinced what you do is you write this followed by that; from that you subtract this followed by this expression, and you can see that that is just this object. Now it is not really necessary to do this, but this is convenient, because see this is l z square and l z commutator. Now as far as these things are concerned you see whether I write l z square l z or l z l z square it is all the same, because both of them are equal to l z to the power of 3, both of them and therefore, what will happen? Both of them are equal which means that the commutator is actually equal to zero.

So, this time vanishes and we have to calculate. Well, that is a square missing here. So, let me put that. So, we have to calculate these two commutators. So, let me calculate the first one, l x square l z minus the first commutator is this minus l z l x square, correct. Now what I am going to do is you see all that I know regarding l x l y l z are summarized here. So, I know what these things are. So, I have to somehow use these things that I have to use these things and evaluate that expression which is written there, and how will I do that? A simple trick; you will write this as l x square l z minus l x l z l x. I have subtracted at m; of course, I have to compensate for my subtraction. So, therefore, I will add the same term. So, that everything is fine, right; this and that will cancel. So, I have to just introduce the 0 there and then of course, I will have minus l z l x square.

Now you will see that this is quite useful, because you can now say okay, l x square l z minus l x l z l x. So, what is that? Actually I can take out an l x, and write the remaining term as l x l z minus l z l x. Now you see the advantages, because I know exactly what this is, because this is nothing but the commutator of l x with l z, right. This object is the commutator of l x with l z, and what about the other one? In the other term you see I can take l x to the other side, fine, and this is nothing but l x commutator of l x with l z plus this again is just the same commutator, commutator of l x with l z and l x; this is z.

So, what is the commutator of l x with l z? We have to make use of this last relationship, but l x and this is not exactly that, but obviously, what I have there any one of the commutator there is just the negative of this commutator. So, therefore, what is the answer? This is going to be equal to l x. This object is actually minus i H cross l y, correct. This object is minus i H cross l y, and again this also is minus i H cross l y. So, that what is the answer that I get i H minus i H cross is common. I will take it out minus i

H cross l x l y plus l y l x. So, we have calculated only one; we will calculate the other one, very quickly I will do it.

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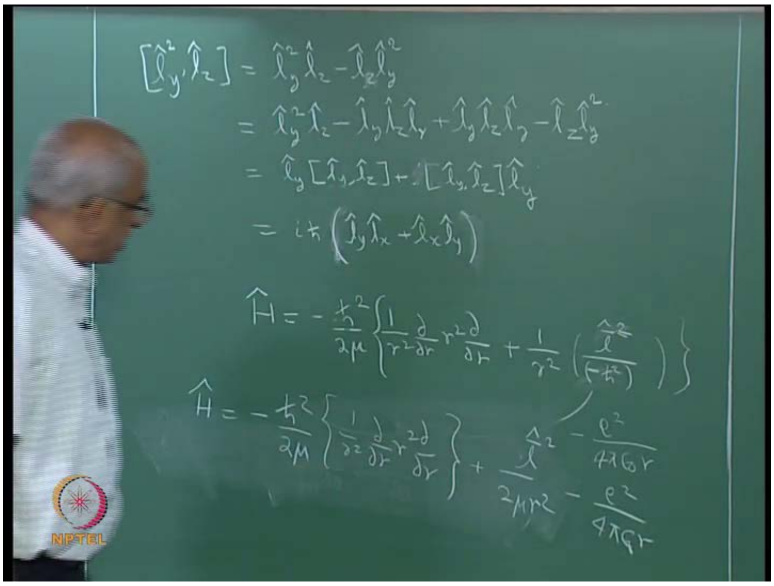

Jump to one step, because we are familiar with this, and what is this? Actually we will find that l y l z commutator is just i H cross l x. So, this becomes i H cross l y l x plus l x l y, and therefore, what do you find? We have evaluated this term; we have evaluated that term, and you find that the second term is nothing but negative of the first, and therefore, what will happen? The net answer is 0 and therefore, my claim that l square commutes with l z is root. In a similar fashion if you like you can easily show that l square commutes with l x; it also commutes with l y. So, l square commutes with everything with l x l y and l z.

But the problem is that l x l y l z do not commute among themselves, and further our Hamiltonian this is something that if I have already told you our Hamiltonian H for the hydrogen atom it is actually minus H cross square by 2 mu 1 by r square dou by dou r. I am writing the expression that I wrote in the morning once more, right. Remember I had written an expression for l square in the morning. Let me write the expression for l square; l square is actually minus H cross square 1 by sin theta dou by dou theta sin theta. Remember I told you that I can express l x l y l z in terms of r theta pi; if you did that this is the expression that you are going to get for l square. And in the Hamiltonian what happens? You get exactly the same operators within there, these operators it is in the Hamiltonian.

If you look into the notes or previous lectures you will find that, and therefore, what I can do is this operator that was sitting there. There is an angle dependent terms sitting there, correct, and then of course, you have the additional term minus e square by 4 pi epsilon 0 or which is the potential energy of the system; that is the full structure of the Hamiltonian, and what is hitting here is nothing but this object without the H cross square; that is what is hitting there, fine. So, therefore, what I can do is I can remove this minus H cross square. I can move it to the other side and say that oaky, after all my Hamiltonian is nothing but l square divided by minus H cross square. That is all, right, because you see in the Hamiltonian this portion was the angle dependent m which is precisely what you find when you actually calculate l square.

So, you can write it in this fashion, and therefore, if you like you can rewrite the Hamiltonian maybe I will write it once more. What it tells me is that is that Hamiltonian is equal to minus H cross square by 2 mu 1 by r square dou by dou r r square dou by dou r which is the kinetic energy term actually. If you remember kinetic energy due to radial motion, something that I have mentioned long ago; this and that together can be written as plus 1 by 2 mu r square. I am combining this with that that is a minus H cross square here, there is a minus H cross square there. So, they will cancel each other, and you are going to get l square here that is occurring in Hamiltonian, right. This together with that will convert into that and then you will have minus e square by 4 pi epsilon.

That is the form of the Hamiltonian, right, and this object what is it actually? If you think about this, this represents the kinetic energy due to angular motion, because that is the only term that depends upon angles; it does it right. None of the other terms it depends upon the angles. So, this actually represents the kinetic energy due to the angular motion, and you can see further that in the Hamiltonian the angles are occurring only here; that is no angle anywhere else, right. So, suppose I asked you what is the commutator of H with l square? L square has only angles in it, right. So, that l square is going to definitely commute with this part, because this has no angle in it. It is also going to commute with that, and the l square will certainly commute with l square. So, therefore, what is the conclusion that I have?

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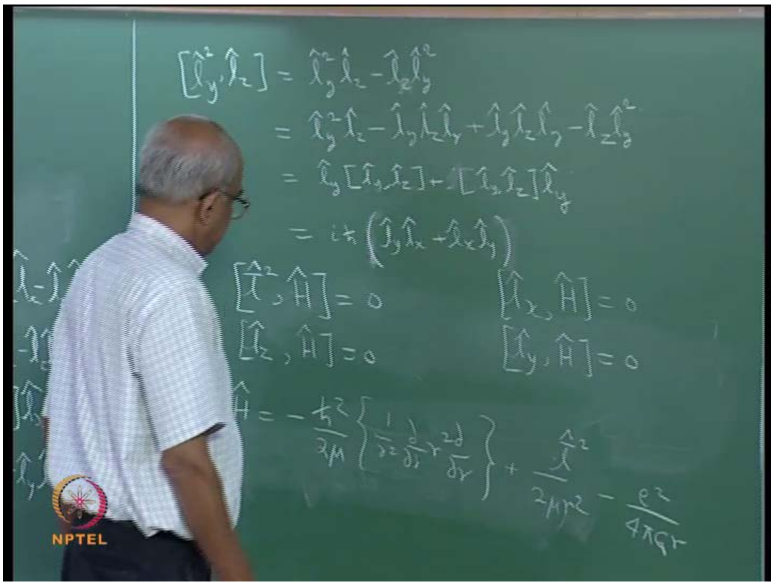

L square actually commutes with my Hamiltonian, right, and then when you think of l z, question is would you commute with the Hamiltonian? Well, the Hamiltonian contains l square that is the only angle dependent term, and we know that l z, something that I mentioned earlier, we know that l z will definitely commute with l square. So, therefore, l z also commutes with the Hamiltonian, and as I told you a few minutes ago there is nothing so special about the z direction. If l z commutes with the Hamiltonian then naturally I would expect l x as well as l y will commute with Hamiltonian; definitely this is something that I would expect to happen.

Even though I have not actually done any calculations this is what I would expect, and further the way we have found the solution of the Schrodinger equation; we solved the Schrodinger equation for the hydrogen atom, and if you look at the equation obeyed by the angle dependent part, right. You would find that I mean this operator, remember where was it? This operator we had determined all its details and then tried to solve the equation, and when we solved it what did we find?

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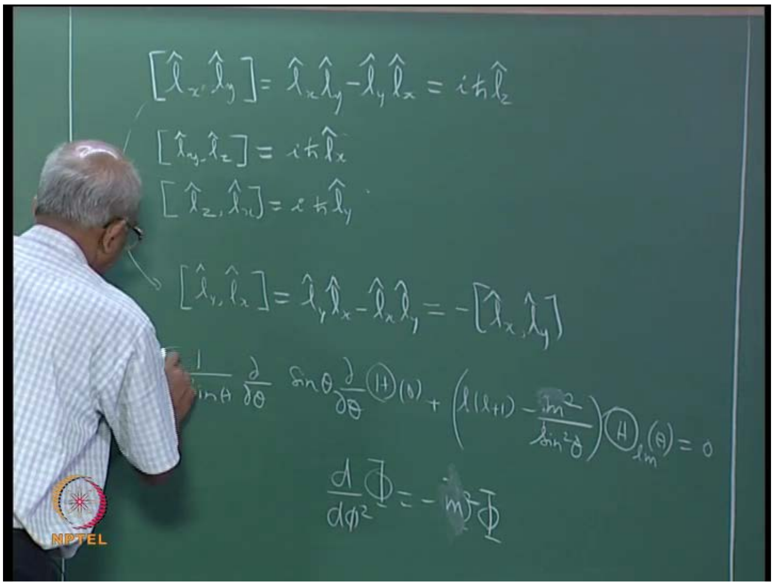

We found that I am just writing the equations that we had actually encountered. This was the equation for capital theta, if you remember this is the equation that we solved; of course, you may say that okay, this was not exactly the way, but there was a beta sitting here, but we found that accept rule solution will occur only if this beta is equal to l in to l plus 1; that is what we find. And therefore, I have put instead of beta l into l plus 1, and further I also know that the capital phi obeys this equation, okay, and the point that I am going to tell you is this. It is possible for me to combine these two equations, and to get an equation that is actually obeyed by the product. See you have in the angle dependent part of my hydrogenic wave function.

You have the angle dependent part which we denote as y l m theta of phi referred to as spherical harmonic, and that was defined to be theta l magnitude of m of small theta capital phi subscript m small phi; this was our definition of y. So, it is actually possible by using these two equations that are written there it is also actually possible to show. Again I will not show it, but fairly simple thing that if l squared operated upon y l m theta phi the answer is actually simple. If l square operated up on these things what is going to happen? L square contains this operator, right, and y contains theta, and l square also contains this kind of operator and y contains phi.

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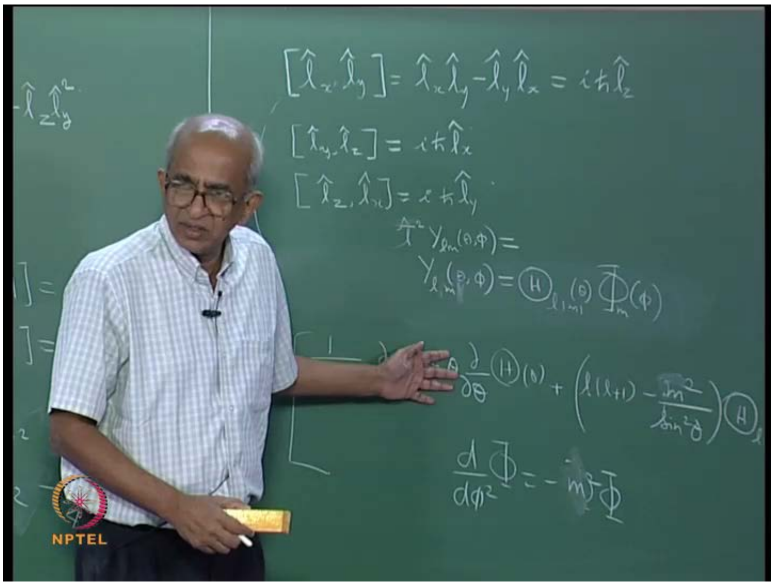

So, therefore, these two equations together can be used to find the result of l square operating upon y l m, and you will find you will be able to show that that is nothing but l in to l plus 1 H cross square y l m; not a difficult result to derive and therefore, I am not going to give it to you to derive this, but this is very easy actually. All that you need to do is just use these two equations; you are going to get that, and further our state function for the hydrogen atom contains our wave function for the hydrogen atom contains.

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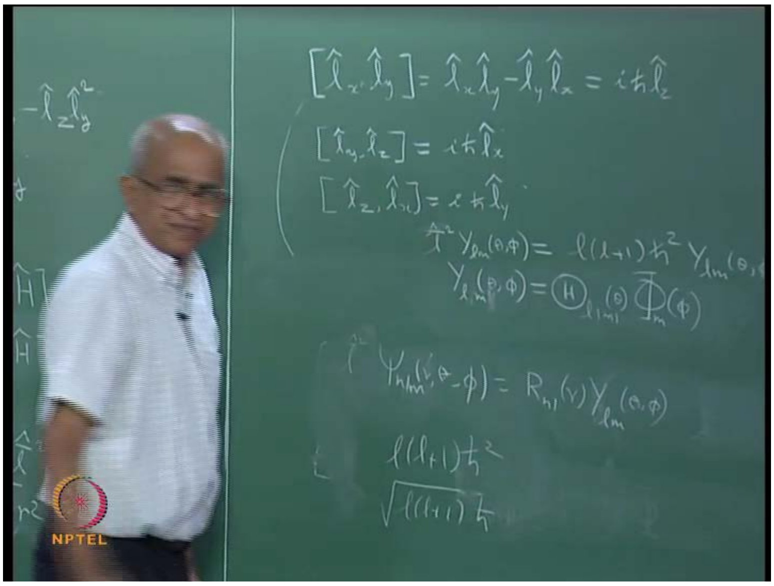

What was the form of the wave function? Psi n l m theta phi r theta phi is actually equal to r n l small r multiplied by y l m of theta phi; this was our wave function. Now I know that y l m satisfies these equations. So, therefore, if I had operated here with l square, l square remember it operates only up on the angles. So, directly it will go and operate upon capital y, and what would be the result? The result would be nothing but l into l plus 1 H cross square times that function itself. So, why am I saying this? The answer is very simple. If l square operated upon your Eigen function psi n l m, what you get? You get psi n l m back and if you get it back but multiplied by l into l plus 1 in to H cross square.

So, this actually means that the functions that we have found are Eigen functions of the operator l square, and therefore, if I am able to measure l square. The answer that I get will be equal to l into l plus 1 in to H cross square. This actually means that the magnitude of the angular momentum, right, the magnitude of the angular momentum is such that its square is equal to l in to l plus 1 H cross square, and remember l is a quantum number; it cannot have arbitrary values. So, therefore, and what are the values? The values are actually l equal to 0, 1, 2, 3, etcetera. So, therefore, you find that the square of the angular momentum vector can have only values of the form l in to l plus 1 H cross square with l equal to 0, 1, 2, 3, etcetera, or you can say that the length should be length of this vector should be l into square root of l into l plus 1 into H cross, right.

This is the only possibly. I mean I should not say only possibility it is the square root of l in to l plus 1 H cross with l taking the values 0, 1, 2, 3, etcetera. So, for example, if you are in an s orbital, what will happen? L is 0, and the magnitude of the angular momentum vector would be equal to 0. And if you are in a p orbital which has l equal to 1 then you will have root 2 times H cross; then the next possibility is root 6 H cross, okay, then root 12, etcetera. First possibility of course, I should list with this 0 times H cross. Now this is actually somewhat different from what happens, not somewhat very different from what happens in classical mechanics. Imagine I have the nucleus and say the electron is moving around it; let us say in a classical orbit.

Classically see the size of the orbit can be anything, radius can be anything; there is no condition actually. I mean the speed has to adjust; if there the radius is large it can go slow. Well, if the radius is small it has to go fast so that it stays in that orbit, okay. So, therefore, if that is the way it is angular momentum vector can have any magnitude. In fact, any magnitude inference simply starting from 0 to infinity is possible, okay. So, therefore, classically speaking you see there is no quantization of angular momentum nothing but quantum mechanics as we know is different.

It does not allow everything; it allows only certain values for the magnitude of the angular momentum vector, and these are the only values, right, and the states that we are found this is psi and l m. They have a precise value for the energy. They have a precise value for this square of the angular momentum vector also, why? Why do they have a precise value? The answer is that l square and the Hamiltonian they commute, because they commute you can have precise values for both, right, and then we are going to look at l z.

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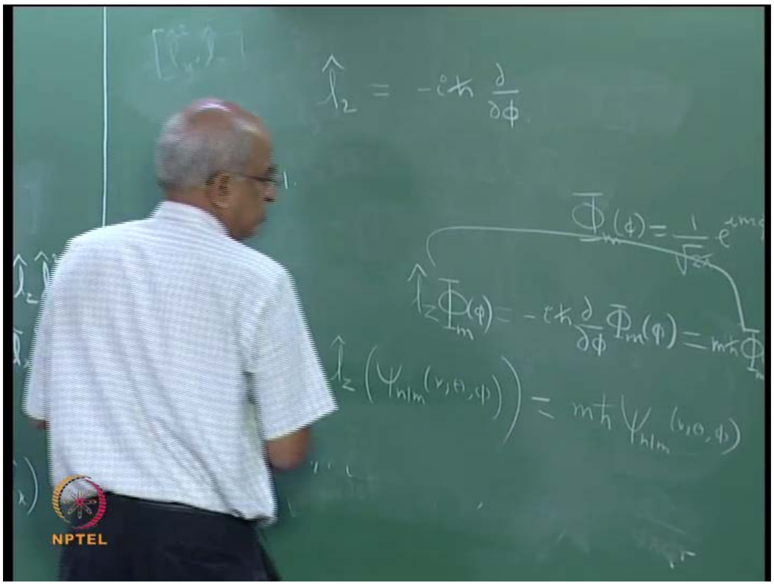

L z I told you the expression for l z in terms of Cartesian coordinates. I also told you that if I expressed it in terms of polar coordinates, the answer will be minus H cross dou by dou phi, right. And if you remember the object y l m actually contains capital phi, and capital phi what was the form? Capital phi had the form I mean I can choose it to be 1 by square root of 2 pi e to the power of i m phi, right. I can choose it to be this with m taking the value 0, plus or minus 1 plus or minus 2, plus or minus 3, etcetera. There is also another possibility which I did not mention; for example, if m is equal to 1 or minus 1 you can say okay, I will have e to the power of plus i phi. I will also have e to the power of minus i phi, but they are complex, and therefore, we can combine them, and that is the way we obtained our p x and p y atomic orbitals.

We did it, right, in one of the earlier lectures, but suppose I say this is the function. Then I have this very nice feature; allow minus i H cross dou by dou phi to operate upon phi m. What would be the result? This is nothing but the operator l z. Well, when you differentiate with respect to phi then what happens is that this i m will come down from the exponent, right, an i m will come down, and then that i m and this minus i m will make into plus m H cross into capital phi, correct, and what does this mean? This means that this particular function capital phi subscript m is an Eigen function of l z, right, because you allow l z to operate upon phi m. The answer is equal to m H cross times phi m, but then if that is the way it is I can say okay, l z suppose it operates upon psi n l m, what is going to happen? You see the psi n l m depends upon phi only through capital phi; the other parts do not depend upon phi.

So, therefore, this effectively l z will operate only upon that, and then that will give back capital phi itself, and therefore, what happens? You get m H cross times psi n l m. So, therefore, the Eigen function where we have found they are Eigen functions of l z also, right, and what does it say? If you measure the value of l z the z component of the angular momentum vector, you will get only certain values. You will get only values which are of the form m H cross, right; you do not have any other value. Now this again is quite different from what happens in classical mechanics. You see in classical mechanics if I have an angular momentum vector okay, let us say this is the angular momentum vector.

As I told you in classical mechanics the angular momentum vector can have any length; that is absolutely no problem, any length is allowed why? Because the particle maybe moving slowly or maybe moving fast depending upon which the angular momentum vector can have any magnitude, right, and not only that this vector you see it can be oriented in any direction in space. There is no condition on the way it is oriented; therefore, its z component if you think it may be having a value 0 maybe or maybe the z component is positive or maybe this subcomponent is negative.

It all depends upon how this vector is oriented in space, and it can be oriented to any directions. So, therefore, the z component of the angular momentum in classical mechanics can have any value, but here what is it that we find? We find that first of all the length of the angular momentum vector can have only certain values, right, and not only that its z component is constrained to have only certain values which are of the form m H cross. So, let us look at a specific ate sample; let us say that I have l equal to 1.

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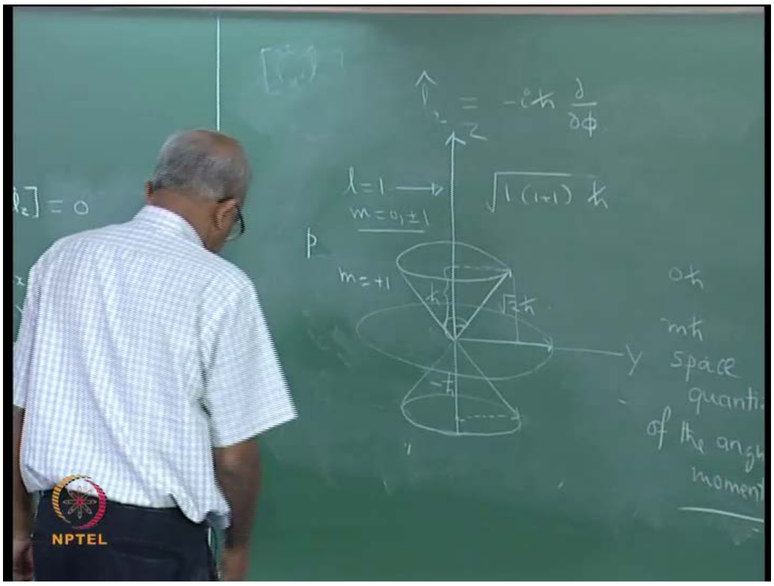

If l is equal 1 actually why I am thinking of a state that we will normally refer to as p. It is the p orbital that we are thinking of l is equal to 1, and for such a state what is the value of angular momentum vector? You will say it is okay, it is nothing but square root of 1 into 1 plus 1 h cross. So, this is the value of the angular momentum vector the length, okay. So, if I say I can say this is my origin, and then I will draw an angular momentum vector like this such that the length is actually root 2 times H cross. Now if l is equal 1 I know that m can have three values 0 plus or minus 1. These are the three possible values, and if you think of physical significance of this I have told you the physical significance; m actually specifies the z component of the angular momentum vector.

So, for example, if you say m is equal to zero; that means the z component of the angular momentum vector is actually 0 times H cross, right, and how will I represent that? Maybe I can draw a line like this. This is my angular momentum vector; length is root 2 times H cross. It is oriented in such a fashion that it is perpendicular to the z direction. This is my z direction, and if my angular momentum vector is oriented perpendicular to the z axis. Then naturally its z component is going to be 0 which is what I want. So, therefore, if you say l is equal to 1 and m is equal to 0, then it just means that the angular momentum vector is oriented in a direction that is perpendicular to the z axis. What are the other possibilities? M is equal to plus 1 means that the angular momentum vector is oriented in such a fashion that its z component is plus H cross.

So, what does that mean? It just means that this angle is such that the projection of this vector on the z axis is equal to H cross, correct, and if you say m is equal to minus 1; what does it mean? This is actually meaning that it is pointed downwards such that the z component of the angular momentum vector is now minus H cross. So, therefore, if you think about it you see what it says is that the three states that I have; for l equal to 1 I have three different possible states characterized by different values of m, right, and what are the different in? They are having the same value for the length of the angular momentum vector, correct, and therefore, if you thought of kinetic energy for angular motion they will have precisely the same value, because the length of the angular momentum vector is the same.

So, that means kinetic energy has to be the same, and therefore, while you see why the total energy of all the systems all these states are the same; if you remember these are degenerate states, right. That is because you see the kinetic energy for angular motion is the same for all the three states, and what are they different in? They are different in the fact that the angular momentum vector is oriented in different directions in space that is all. There is no other difference; I mean qualitatively speaking that is the main difference. Then the other thing that you have to understand is that if I drew a picture like this; this picture actually says that well, this is my let me say my y axis, this is my z axis, and the way things are drawn, this is my x axis, okay; this is my x axis.

If I drew such a figure actually it means that the value of l y I know precisely what it is. That is what it means if I drew such a vector, but then I know that l y and l z they do not commute and therefore, they cannot simultaneously have precise values. So, if we have specified the value of l z that means the value of l y should be uncertain; I cannot specify exactly what its value will be, right. So, therefore, here actually what happens is that that the value of l y can be anything and therefore, you can only specify the value of l z; you can also specify the length of the vector. Unfortunately it is not possible to specify the value of l y, neither is it possible to specify the values in it; you cannot do, why? Because the operators are not commuting; if they commuted there would not be any problem, but they are not commuting.

And therefore, what can you say? Then well, you can say that I have only these two things known. One, length of the vector, two, it is z component, right, and therefore, I am forced to now say that okay, the angular momentum vector can be oriented in any direction along the surface of such a cone. All that I can say is that this interior angle of the cone must be such that the z component of the angular momentum has a value plus H cross; that is all that I can say. I cannot say anything more. I cannot say anything about l x and l y, right, because they are uncertain, and similarly in this case I cannot say that this vector is lying in the y plane, but I will have to say that it is oriented somewhere along the surface of such a cone, and the orientation is such that the cone is such that the z component of the angular momentum vector is minus h cross.

Now in the third case in this case, right, in this case again I can say well, the angular momentum vector is in the x y plane, but in which direction that I cannot say. So, it may be oriented in any direction along the surface along the periphery of a circle of that radius. So, the condition actually that the z component of the angular momentum can have only values which are of the form m H cross. This is usually referred to as a space quantization of the angular momentum vector. Now this is for well, I realize this figure is not very nice.

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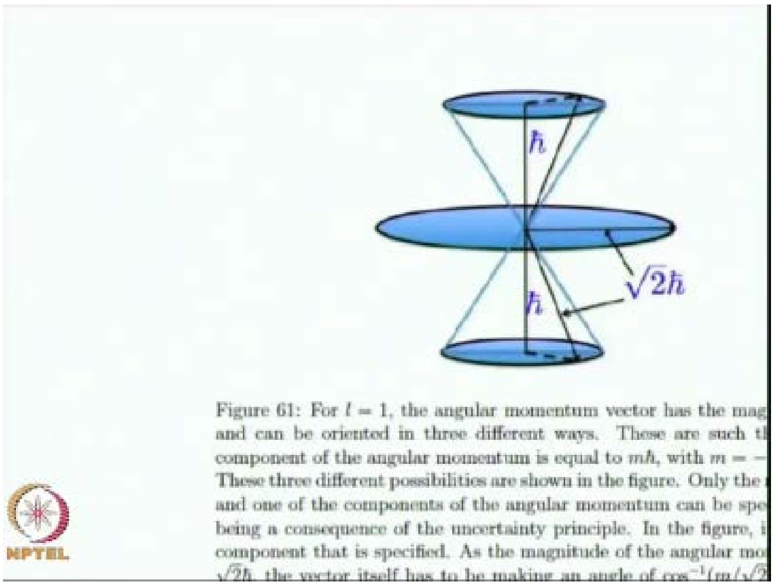

So, the different orientations are shown in this picture. Similarly if you like you can worry about other states with l equal to 2. Suppose you had l equal to 2, what will happen? It is quite simple.

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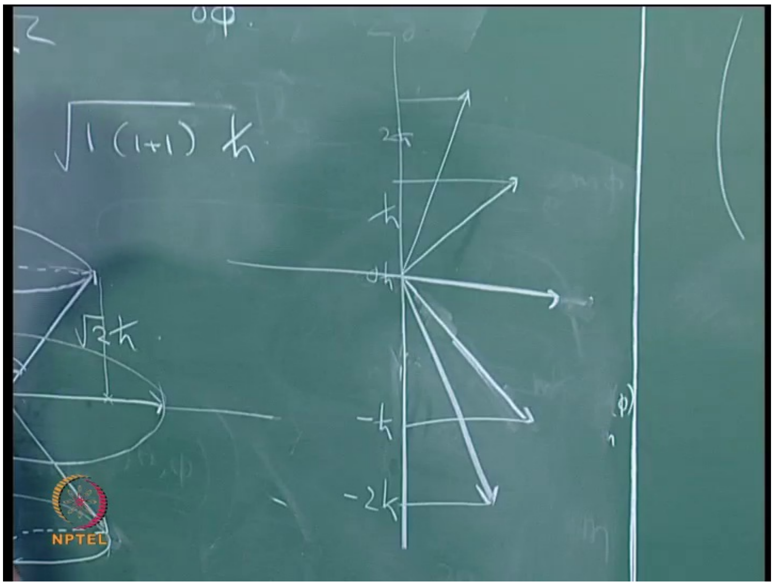

If l is equal to 2 let me draw another figure very very quickly length of the angular momentum vector will be root 6 times H cross; if l is equal to 2 the value is of m can be 0 plus or minus 1 plus or minus 2 five different values. So, I could have five different orientations. So, let me draw the first one, the second one, the third one, fourth and fifth, right. This is actually how much? 2 H cross 1 H cross 0 H cross minus 1 H cross, and finally minus 2 H cross. Unfortunately the way I have drawn this does not appear to be I mean the scale is not correct actually, but I am sure you can understand. So, this is how the orientation could be, five different orientations. Okay I think I will stop here, and continue later.

Thank you for listening.