Introductory Quantum Chemistry

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Lecture - 33
Angular Momentum

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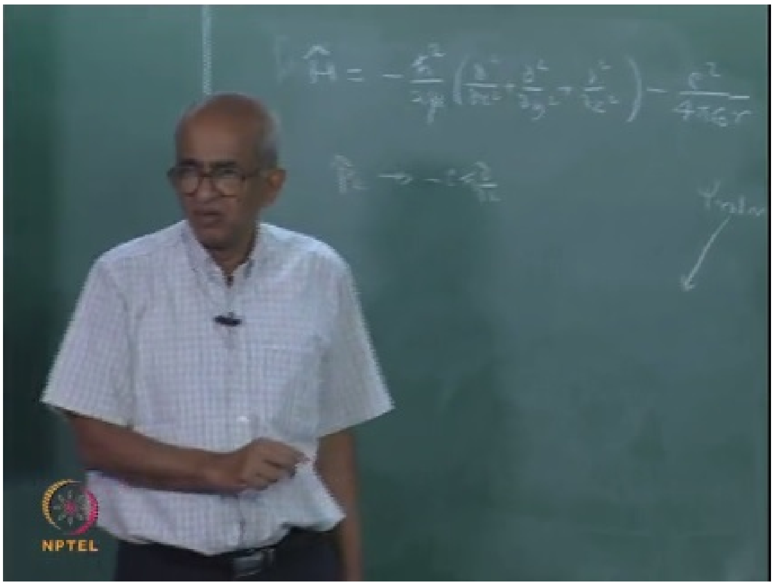

So, let us go back to the case of hydrogen atom. What is the Hamiltonian? The Hamiltonian actually, you can write it in different ways; let me say h cross square by 2 m if you like actually 2 mu dou square upon dou x square plus dou square upon dou y square plus dou square upon dou z square minus e square by four pi epsilon 0 r. This is the Hamiltonian, we have done this earlier. So, you remember that r of course, is the distance of the electron from the nucleus; it will depend upon x, y as well as z.

Now, the question is you see suppose… Will it commute with for example, p x? p x actually is involving differentiation with respect to minus i h cross dou by dou x. Now, it is almost clear. See minus i h cross dou by dou x – actually, it will commute with this; it will commute with that; it will commute with this. It is absolutely no problem with these things, but this operator will never commute with 1 by r, because r is square root of x square plus y square plus z square. And therefore, the commutator of this with the Hamiltonian operator is non zero.

What does that mean? It means that, they cannot have simultaneous eigenfunctions in some sense. Not in some sense; that is a precise statement actually. But, essentially, what it means is that, the uncertainty in energy and uncertainty in momentum cannot be simultaneously 0. That is what it means. Now, when we found the eigenfunctions, these eigenfunctions are states in which the energy is very well-defined. And therefore, there is no uncertainty in energy. Uncertainty in energy is actually 0 for those states. Whenever you measure, you are going to get the same answer.

So, if the uncertainty in energy is 0, can the uncertainty in momentum also be simultaneously 0? It is not possible, because H and p x do not commute. Therefore, for our stationary state that we have found, you see the momentum does not have a precise value; it does not have a precise value. If you can make a measurement; each time you make a measurement, you are going to get different answers; you are not going to get the same answer ever. If you have to get the same answer, what should happen? The momentum holds; the eigenfunction should… The eigenfunctions that we have found should also be an eigenfunction of the momentum operator and that is impossible, because the two operators do not commute.

So, then what is the operator? Is there anything else that is actually commuting with the Hamiltonian operator for the hydrogen atom, is the question that we will ask. In fact, when we solved the Schrodinger equation, we have found the quantum numbers; we found the quantum numbers like n, l and m. But, this n was a quantum number, which just determines the energy of the system. It is just a quantum number that determines the energy of the system. But, there are these other numbers – l and m. What do they mean physically? Do they correspond to some physically observable things? That is a natural question that one should ask.

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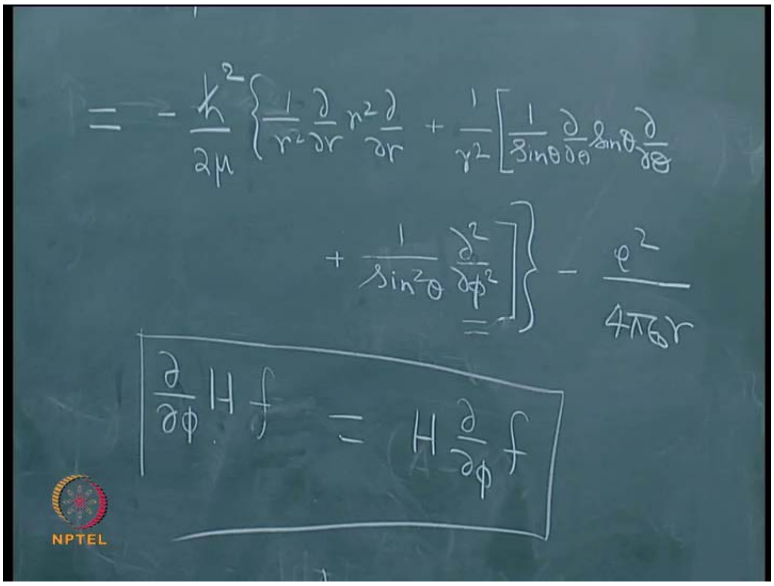

And then I also want to point out you something interesting. This Hamiltonian I can write in the polar coordinates. How will it look like? It will look like minus h cross square by 2 mu. I am going to write a fairly lengthy expression, which we have been using. I have written only part of the Hamiltonian. And this is nothing but the kinetic energy of the electron; nothing more. This is just the kinetic energy of the electron due to its r motion, due to its theta motion and due to the phi motion. And then of course, we have to minus e square by 4 pi epsilon 0 r. This is the Hamiltonian operator. And what I want to look for are operators that might commute with this Hamiltonian operator. Can one think of any operator that will commute with this, is a question that I would like to ask.

And in fact, there are simple operator that will commute with the Hamiltonian operator as you would realize, the operator is just dou by dou phi, because if you think of H followed by dou by dou phi. You see this is partial differentiation with respect to phi. And imagine it is going to operate upon some function; some function; what do I want to call that function? Maybe let me just put an f there. It is a function of r theta phi. When you think of this, you see I am not going to write down, because this is a fairly lengthy expression. But, we imagine dou by dou phi comes from this side. What will happen? It will not affect this, because this is the differentiation with respect to r. It will not affect this, because you have r n theta, but you have the partial differentiation with respect to phi. It will not affect this term. So, directly, what it will do is it will go and simply affect that. Nowhere else it is going to affect. As far as this time is concerned, you will have one more differentiation with respect to phi. Correct?

And, even if you had put dou by dou phi first followed by H, that is all the effect is. Dou by dou phi operating upon H followed f is actually the same as f operated upon by dou by dou phi and then followed with H. This is easy to verify if you are not convinced; simply because you see there is only differentiation with respect to phi sitting here; it is not there anywhere else. So, all that will happen is none of these terms are affected; it will simply come and affect this term if you think about it. And similarly, if you want… I do not have too much time. So, I do not want to do the calculation, but this is definitely true. And therefore, what is going to happen, the commutator to this actually claims that the commutator of H and phi – dou by dou phi is equal to 0. And therefore, what happens is that, the operator dou by dou phi perhaps will correspond an observable, whose value can be precisely known, because you see you think of any particular eigenfunction of H, a stationary state that has a precise value for energy.

And then if you wanted to know precisely the value of anything else, it should correspond to an operator that will commute with the Hamiltonian operator. And dou by dou phi is an operator that will commute with the Hamiltonian operator. And therefore, if there is an observable, which corresponds to dou by dou phi; then that operator, whatever that observable – whatever that observable is; you should be able to think of such an observable. And that will have a precisely known value. Similarly, if you think of this whole thing; not just dou by dou phi, but you just think of this whole thing, which I have enclosed within the bracket; these involve differentiation with respect to theta and phi; nothing else in the Hamiltonian involves differentiation with respect to theta and phi. These things involve differentiation with respect to theta and phi. So, if you now say that, I have this operator; let me just again denote this operator by this symbol. At the moment, it is only a notation, where we will see the physical significance of this in a few minutes.

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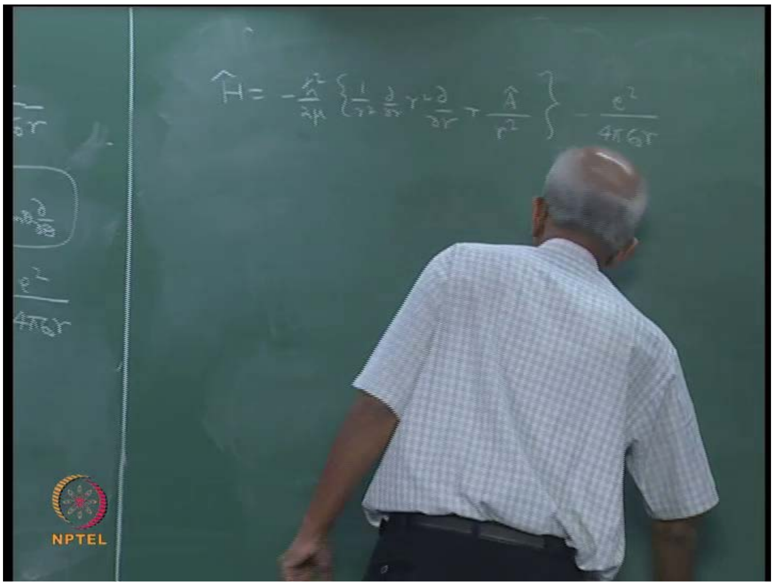

But, if you denote it by this operator, then you will see that, the Hamiltonian operator is nothing but minus h cross square by 2 mu 1 by r square dou by dou r r square dou by dour r plus… I do not want to use this symbol; I will use some other symbol; this is, I have just a shorter notation for some operator. What do I want to call it? Let me call it A. And minus e square divided by 4 pi epsilon 0 r. This A is an operator that depends upon theta and phi; and there is no theta and phi anywhere else. So, it is fairly easy for you to verify that this operator A commutes with the Hamiltonian operator.

And therefore, if you had a physical significance, some physically relevant thing like some physically observable thing, whose operator is A; then that also will have a precise value. When the energy has a precise value, that also can have a precise value. So, with this very brief introduction, let me now think of what is referred to as angular momentum. What actually will happen is that, this operator will actually be related to the z component of angular momentum. That is what we are going to see. And this operator I have removed it; that operator that I have called; it will be a related to the square of the angular momentum of the system. That is the physical meaning. Now, let me therefore, think of angular momentum.

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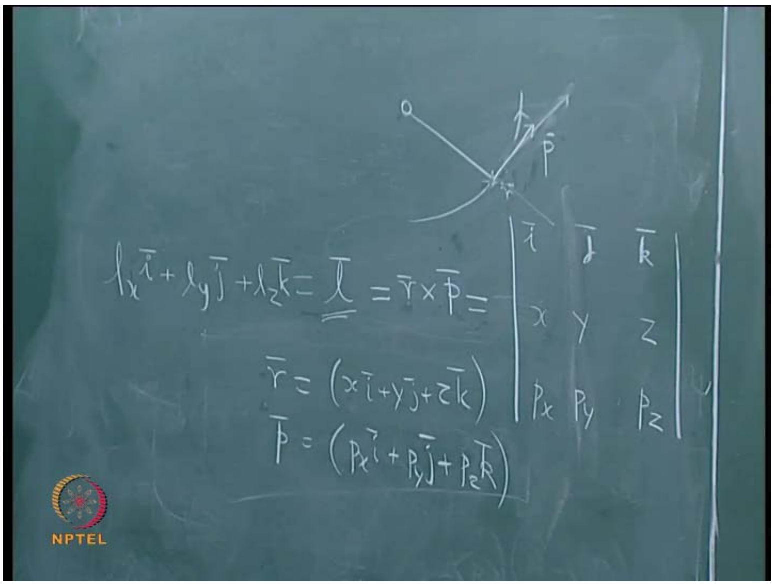

Now, what is the definition of the angular momentum in classical mechanics? If you have a particle; imagine it is moving in 3 dimensional space; to be clear, I can think of a classical system in which I have a nucleus and electron is moving around it; Bohr theory let us say. So, if the electron is moving around it, it will have a momentum p. The electron is moving with a momentum p. And because if it is… classically, it will have a position r – position vector. This is the nucleus and that is the position vector to which the electron is. And if it was following a simple circular orbit like in Bohr theory, then angular momentum is defined to be momentum into the radius of the circle. So, m into v into r. That is the angular momentum – magnitude of the angular momentum.

But, even if it is not following a circular path; I mean it is not necessary that when you have a two-particle system, the second particle should be following a circular path. If you think of the earth going around the sun, it is not following a circular path, but an elliptical path. So, if you had such a situation, what is the angular momentum? The angular momentum will be given by angular momentum… Let us say as far the electron is concerned, I can have a general definition of angular momentum, which will be defined to be r cross p. So, position vector, momentum vector – you have to take the cross product of the two; and that is defined to be angular momentum. The reason why angular momentum is important is, if you have problems in which you have spherical symmetry like what you have in the case of the hydrogen atom; then what happen is that, the angular momentum in classical mechanics is a constant of motion.

What do you mean by the constant of motion? The position is changing. The position is changing and momentum also may be changing. But, this object will not change; it will remain a constant. So, wherever… the motion will be such that, this object will be a constant. This of course, is a vector object. So, when I say it is a constant, it actually means that, 3 numbers are constants: the x component, the y component, and the z component. That is the importance of this object if you are doing the classical mechanics. So, now, let us think of the hydrogen atom. We are defining angular momentum to be the cross product of r and p. And how do you calculate a cross product? I hope you remember the vector algebra. If I was doing classical mechanics, what I would do is, I would have the unit vector i in the x direction, unit vector j in the y direction, and unit vector k in the z. Then this r is the position vector; or, it may be written in terms of i, j, k as x i plus y j plus z k. These are x, y and z components of the position vector.

And similarly, p may be written as p x – x component of momentum, y component momentum, and z component of momentum, multiplied by the corresponding unit vectors. So, this is the definition of momentum. This is the definition of position vector. And these components may be used to calculate the cross product of r with p. And what will happen is that, you will have x, y, z, p x, p y, p z. And also, what you should remember is that, this is the position vector; this is the direction of motion at that particular point.

As the particle moves, you see this direction of motion will normally change. So, at this particular position, that is the position of motion. And when you say r cross p, what is it actually? When you again… Let me remind you what it is. What is the cross product of two vectors? It is a third vector, which is perpendicular to both of them. Therefore, if this is the way it was; if this is the particle… Let me say precisely; this is the electron; I am just at the moment, imagining everything is obeying classical mechanics. So, this is the electron; that is the nucleus. The electron is going around it if the electron is at a position or it is moving with a momentum p; and the motion takes place in the plane of the board. Then what is r cross p? r cross p is a vector perpendicular to both of them; that means the vector is actually perpendicular to the plane of the board. And not only that, r cross p – this is the way I have drawn it; it is defined in such a fashion that it is pointing towards you. That is how it is.

When this has… The direction is determined by – as you know, what is referred to as the right-hand screw rule; should be familiar to you from vector algebra. So, the way it is drawn, r cross p will be a vector, which is pointing towards you, because the r is a vector in this direction; p is a vector in that direction; and you take the cross product; you get the vector in this direction. And what about that magnitude of r cross p? Again, this is only reminder of vector algebra; it will be equal to the magnitude of r into magnitude of p multiplied by the sign of the angle between r and p; only to remind you. All these things are of course contained in this determinantal formula, which I have written down here. So, this is angular momentum in classical mechanics.

But, of course, we are not doing classical mechanics; we are doing quantum mechanics. And whenever you have something in classical mechanics – some observable in classical mechanics, you will have a corresponding operator in quantum mechanics. And the question is, how do I find that operator? Answer is extremely simple. You look at the expression for the observable. So, here what is the observable? The observable is actually angular momentum, which is a vector. So, because it is a vector, I have three components to it. So, I could say that, I have 3 observables: one is the x component of the angular momentum; the other is the y component of the angular momentum; and the third is the z component of the angular momentum. Therefore, this vector l is actually equal to l x into i plus l y into j plus l z into k. So, for example, what will be…

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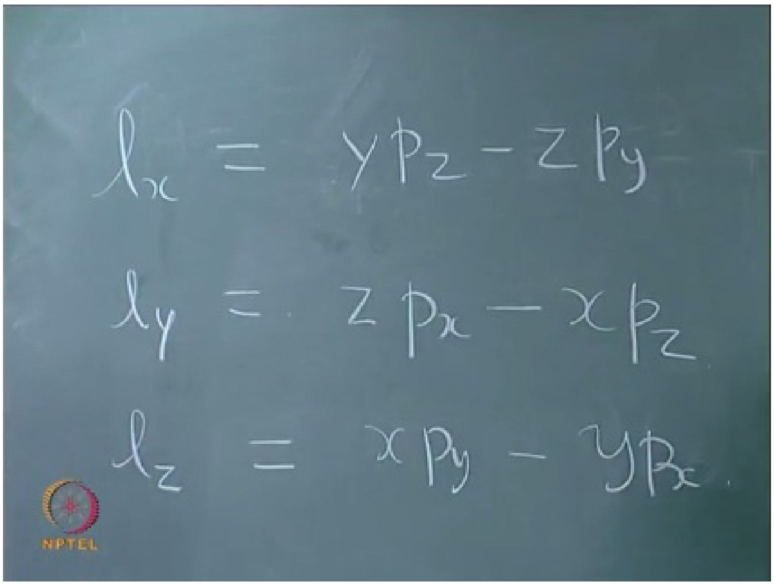

This again is classically speaking. So, what will be the l x – the observable l x. If you use this formula; I hope you remember how to expand a determinant. All that you need to do is you have to expand this determinant and take the coefficient of this vector i. And that you will find is nothing but y into p z minus z into p y. Correct? This again is just classical mechanics. What will be l y? It is fairly simple actually; I mean what you can do is, you can say it is z into p x minus x into p z; and l z – x into p y minus y into p x. that is ((Refer Time: 21:11)). So, these are the classical mechanical expressions for the observables: l x, l y and l z, which are nothing but the components of the angular momentum.

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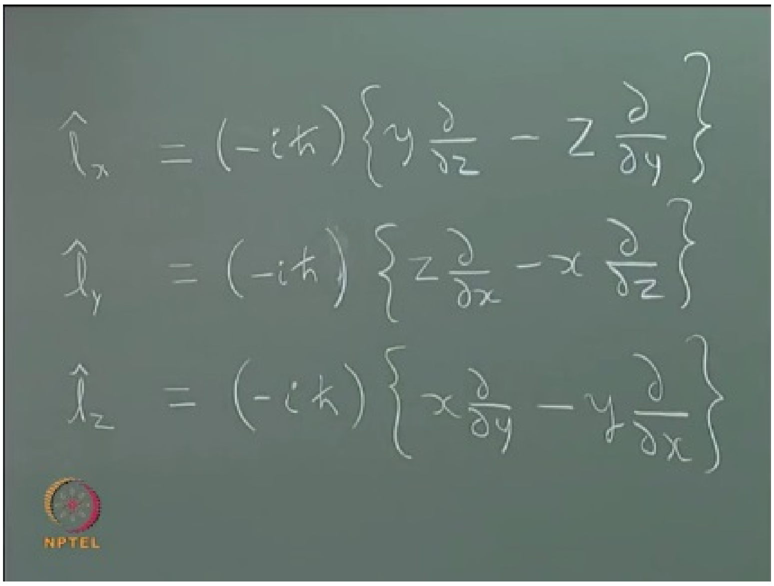

But, as I said, in quantum mechanics, what will happen; corresponding to each one of them, you are going to have an operator. So, corresponding to l x, you will have an operator, which we will denote by this symbol; and operator associated with l y; and yet another operator associated with l z. And how will you find them? The answer is as we have already seen the answer, wherever p x, p y, p z occur, you will replace them with minus i h cross dou by dou x minus i h cross dou by dou y and minus i h cross dou by dou z. So, if you followed that prescription, what will be the expression for l x? You will have minus i h cross. And then you will have y dou by dou z. This p z is replaced with minus i h cross dou by dou z; and that is how I obtained this expression – minus. If you did the same thing, you are going to get e z dou by dou y. So, this is the expression for l x. Then expression for l y will be similar. You will get minus i h cross z dou by dou x minus x dou by dou z. And the expression for the l z will be minus i h cross x dou by dou y minus y dou by dou x. So, these are the expressions.

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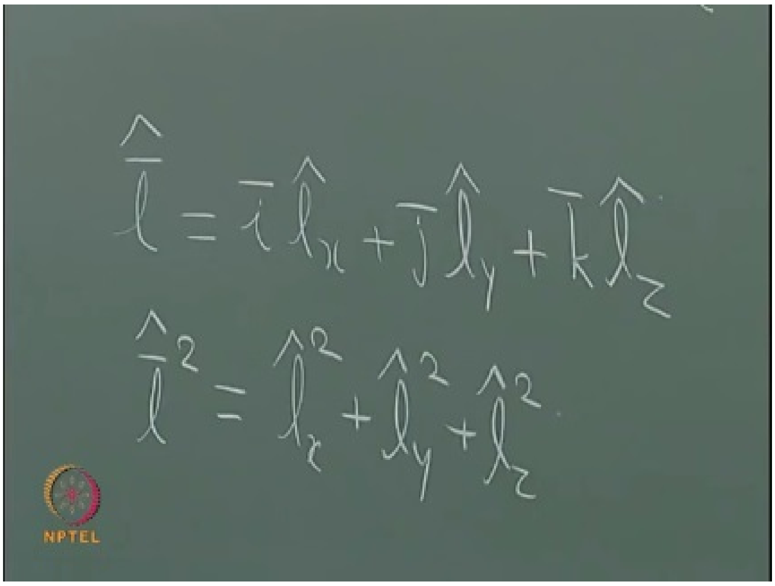

And, further if you wanted to find the operator associated with the angular momentum vector itself, what will that operator be? You will have to write it as l vector, but it is going to be an operator. Therefore, I will put a hat on top of it. And that is actually going to be equal to i into this operator, which is l x; that means you see you will have to substitute this whole expression in here plus j into l y plus k into l z. So, this will be the operator associated with the angular momentum vector. And in a similar fashion, if you are interested in the square of the angular momentum vector, it will be again an operator, which may be written as l square with an operator symbol on top of it. And it is obvious; I mean if you had a vector with the components l x, l y, l z, what will be the square of the vector? It is going to l x square plus l y square plus l z square.

But, then we have this question – these operators – do they commute with one another? For example, I can ask the question whether l x will commute with l y and whether l y will commute with l z and so on. So, in order to answer that question, I am actually going to calculate the commutator of l x with l y. And once I have calculated that, I can actually guess what is going to be the commutator of l y with l z as well as the commutator of l z with l x. So, let us try to do that calculation.

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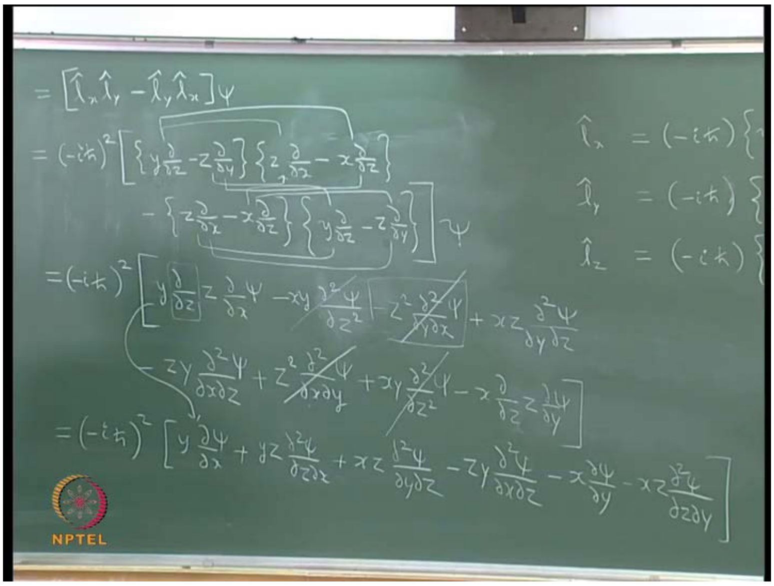

So, what I will calculate is the commutator of l x with l y, which we usually denote by this. And the way we will calculate this is, actually, we will allow this thing to operate upon a function psi and ask, what the answer is going to be. And by definition, I know that, this is defined to be l x l y minus l y l x operating upon psi. So, this is the definition of the commutator. But, then you see we have these two expressions for l x and l y; I will have to take these expressions and put them in there and then do the calculation. So, let us do that. You know that, there is minus i h cross here; there is another minus i h cross there. So, these two i's will combine.

And, I am going to get minus i h cross the whole square. And then within square brackets, let me say I would have the operators; the first of ((Refer Time: 26:36)) comes from l x; and that is going to be y dou by dou z minus z dou by dou y. And the second part comes from l y; and it is going to be this part. Let me write that. And from this, we have to subtract… Exactly the same two operators, but put in the reverse order. So, this will come here; z dou by dou x minus x dou by dou z followed by y dou by dou z minus z dou by dou y. And these things together they are going to operate upon the function psi.

And, now, it is a fairly simple calculation, though it requires calculating all these terms; but not very difficult. So, let me go ahead and do the calculation. I would have minus i h cross the whole square. Then you see we have to multiple this term and that term. Let me write that term; it is going to be y dou by dou z operating upon z dou by dou x. And this whole thing is actually going to operate upon this into operating on that, is going operate upon psi. So, I shall write this psi also. Then this actually is going to operate upon that which is followed by operating upon that. So, that term will be actually… It will occur by the negative sign, because there is a negative sign here; it is going to operate upon that. So, that is going to be minus y dou by dou z followed by x dou by dou z operating upon psi.

Now, if you compare these two terms, you see here dou by dou z is going to operate upon this z as well as that dou psi by dou x. So, from here, I am going to actually get 2 terms. But, this dou by dou z – you see it is going to operate upon x dou psi by dou z; but this x – remember this is a partial differentiation with respect to z. And because it is partial differentiation with respect to z ((Refer Time: 29:18)) is taken to be a constant. So, this is not going to affect x. And therefore, I can take that x outside. I can put the x here, so that it will become x into y. And then we have second differentiation – 2 differentiations with respect to z. Therefore, I can simply write this term as dou square psi by dou z square. This kind of simplification I will be making as I write down. So, this is the second term.

And then the third term will be obtained by allowing this to operate upon that. So, what will be the third term? You are going to have minus dou by dou y is not going to affect z. So, it will go past z. So, you will get minus z square. So, this z can be taken and combined with that z; you will get minus z square – second derivative with respect to y and x operating upon psi. And then this is going to be combined with that. That will occur with a positive sign; dou by dou y does not affect x. Therefore, I can combine x and z to get plus xz dou square by dou z dou y operating upon psi. So, these are the first 4 terms.

And now, let me write the next four terms. The first term will be obtained by combining these two. And what would that be? z dou by dou x and y dou by dou z. So, that is actually going to be z y dou square upon dou x dou z. And because of this negative sign, this is going to occur with a negative sign. Then the next term will be this combining with that. And that again is going to… That will occur with a positive sign minus… There is a minus sign here. So, it will occur with a net positive sign. It is going to be plus z square dou square upon dou x dou y operating upon psi. Here I had forgotten to put the psi. So, there is a psi there as well as there. Then the next term is going to be this combining with that. And that actually will turn out to be plus x y dou square upon dou z square operating upon psi. And finally, you will have this combining with that. And that will occur with a negative sign. It is going to be x dou by dou z z dou by dou y operating upon psi.

But, then when I look at this, you would realize that, it is possible to make simplifications. For example, there is a minus x y dou square psi by dou z square. Here there is a term exactly like that, but with opposite sign here. So, I can cancel these two. And further, if you look at this term; this is second differentiation with respect to x and y. Here again you have second differentiation with respect to x and y. As far as second derivatives are concerned, you see it does not matter; the order in which we carry out the differentiation. Whether you carry out the differentiation with respect to x first; follow it by differentiation with respect to y; or, if we read it in the reverse order, the derivatives are the same. So, this term and that term will also cancel.

And so what am I left with? Let me write the terms that I am left with; minus i h cross the whole square; within bracket… You have this term; let me calculate that term. See you have here differentiation with respect to z and there is an z dou by dou x operating upon psi. See if we carried out this differentiation, what will be the answer? This derivative is going to operate upon z; it is also going to operate upon that. So, you are going to get two terms. What are those two terms? The first term is going to be y dou psi by dou x; and the second term is going to be plus y z dou square psi by dou z dou x. Hope I have not made any mistake; let me just check. First term is that and the second term is this.

And then we have that term – plus x z dou square psi by dou y dou z. This term I have written. Then we have this term, which is minus z y dou square psi by dou x dou z. And lastly, we have this term, which also I will calculate. This term – you see again there is a differentiation with respect to z; and that operation is to be done on z into dou psi by dou y. Let me calculate the terms that arise. There are two terms: the first term is going to be minus x dou psi by dou y; and the second term is going to be minus x z dou square psi by dou z dou y. And if you look at this, you will see that, this term and that term – they will cancel each other. So, let me remove these two. And in exactly similar fashion, this term and that term will also cancels. So, what is the answer that I am left with?

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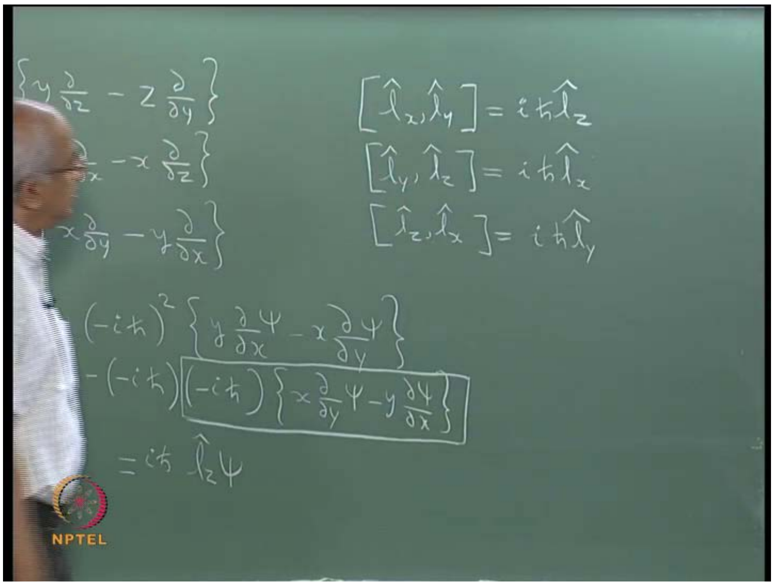

The answer that I am left with let me continue write here. It is going to be minus i h cross the whole square into y dou psi by dou x minus x dou psi by dou y. So, that is the answer that I am left with. And if you look at the answer, you can already see that, it is actually resembling this operator l z. So, let me rewrite this in a slightly different fashion. What I will do is, I will I will introduce a minus sign here. So, I will have minus of minus i h cross. This minus i h cross I will write it two times. And once I have introduced the negative sign here, I can reverse the order of these two things. So, I will have x dou by dou y operating upon psi minus y dou psi by dou x.

And, if you look at this expression; why did I write this expression in this fashion? If you look at this expression, you would realize that, this object is nothing but l z operating upon psi. And if that is l z operating upon psi, you have this minus sign; you have that minus. So, the two may be combined together and you are going to get i h cross as the result. And therefore, the answer is that thing that is written there namely, i h cross l z psi. So, what is it that we have proven? We have shown that, the commutator of l x and l y operating upon any function psi; commutator of l x and l y operating upon any function psi is equivalent to i h cross l z operating upon psi. And therefore, this means that, the commutator of l x and l y, which we normally write this is equal to i h cross l z. And in a similar fashion, it is possible for you to calculate other commutators that are of interest. And if we calculated l y, l z, you will find that, it is equal to i h cross l x. And if you calculated l z commutator with l x; again, you will find that, it is equal to i h cross l y. So, these are the computational relationships involving the operators – l x, l y, and l z.

Thank you for listening.