Quantum Chemistry of Atoms and Molecules

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Lecture-23
Angular Momentum…Continued

Here we are in a chemistry course we are writing a lot of mathematical expressions but as we have said in the introductory video itself mathematics is the language of science and we cannot do anything related with quantum mechanics without using math and the math we are using is very simple. And before going further let me just share something with you we are many of us are scared of calculus and I used to be I still am.

And we are writing a lot of equations in like del del y del del 2 del 2 del something 2 so on and so forth. But have you noticed something we have hardly done any calculus so far. What we are doing really is some very simple algebra we are doing algebra with operators which contains derivatives and all ok. So, it is really not as scary as it looks. So, I thought I will just say it once you know so that students we have taken this course with a lot of enthusiasm do not get scared of there is nothing to be scared off.

If you can handle chemistry if you can understand reaction mechanisms if you can work out sequences of organic reactions this should not be difficult for you ok. There is an atrocious joke that I usually say in this context, borrowed from a very senior colleague but since this is going in public domain I will not say that let us just say this there is nothing to be afraid. We are not doing any mathematics that is beyond us. Let us have faith in us and we will be fine ok with that brief message let us continue with what we were doing.

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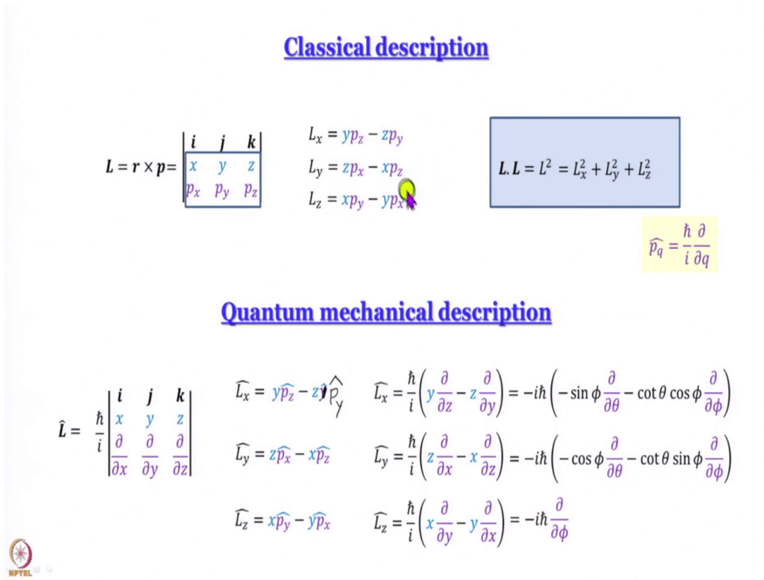

We have written developed the classical description of quantum of angular momentum from there we have built a quantum mechanical description as well ok. And we have written down the expressions oh well we have not really written down the expression of L square operator but we said that it is something in spherical polar coordinates. The operator of be of utmost importance that we will have is this minus ih cross del del Phi which is the L z operator.

And what L square operator is we will see in a moment all right. So, now with this background knowing what angular momentum is and knowing how we handle angular momentum in quantum mechanics let us go ahead and learn some important properties of angular momenta in quantum mechanical systems. Of course remember we are talking about operators so far. So, there must be wave functions also so these operators will operate on those wave functions to give you the value of angular momentum or it is square or one of it is components and so on and so forth.

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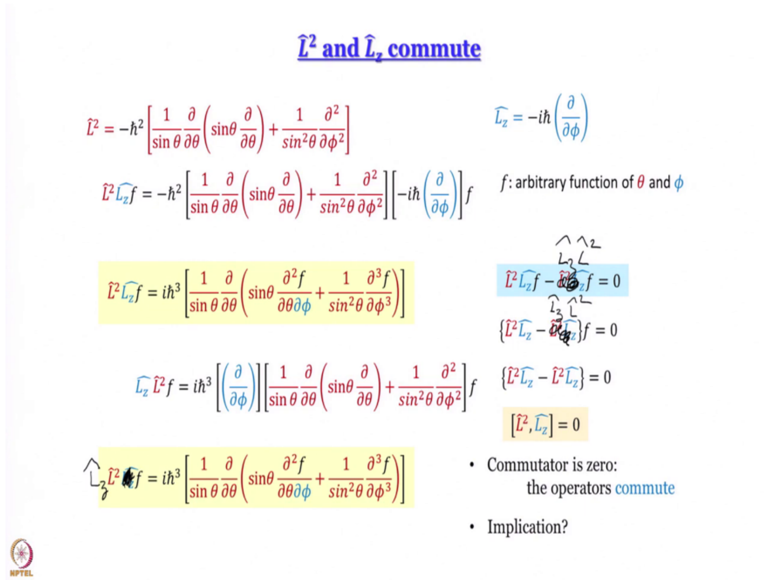

So first we are going to talk about L Square and L z operators. This is the L square operator as promised minus h cross Square 1 by sine theta del del theta operating on sine theta del theta + 1 by sine square theta del 2 del Phi 2 and the moment you see this you will remember perhaps that we have already encountered this when we talked about rigid rotor right. And in fact you would remember that this modified just a little finds it is place in the as the Hamiltonian of the rigid rotor system and else it also is something that we know.

Now we are going to discuss a very interesting and important and perhaps leading to some intriguing discussion of these operators and that is written in the headline. We will see that L square and L z actually come out we are going to show it. What is the meaning of commutation? That means the sequence of operation does not matter ok. You make you take a function make L z operate on it get another function make L square operate on that function you get some answer.

Then go back to that original function make L square operate on it perhaps is best if I write it, not very sure if I written it later but I will write anyway which coloring is to go to this. So, let us say I have some function f I make L z operate on it. So, I will get some function maybe f dash so I make L square operate on it I get say some function f double dash here dash and double dash do not mean first and second derivatives just some function.

So what we have got here is that if double dash is equal to L square L z f. Now what I am saying is that if I reverse it make L square operate on f we get something now I am running out of dashes. So, maybe I will write f subscript dash and now I will make L z operator on this f subscript dash I get say f subscript double dash that is equal to L z this I have written incorrectly actually sorry about that.

So I will just erase this and I will take it from here. So, L z operates on f to give you f dash L square operates on f dash to give you f double dash then we will say f double dash is equal to start from f0 has operated on it first then L square has operated on it so L Square L z f that is f double dashed and here L square operated first on f to give you L z f subscript dash then L z operated on f subscript dash to give you say f subscript double dash, f subscript double dash is start from f this time your L square operates on f first then Lz operates on the new function.

So what we are saying is you will see that f double dash equal to f subscript double dash that means that would mean that they commute. I will erase it because I do not exactly remember where things are going to pop up in the screen. So, this is L z let us see if they commute or not. So, first we will take the this sequence make L z operate on f first then L square will operate on it. So, what do I get you have f, f is a function L z it is minus ih cross del del Phi that operates on f.

Then this L square operator operates on the new function how do I go about it? Well f is a an arbitrary function in theta and Phi. Of course first of all I can take this minus ih cross out because it is a constant so I have one minus sign here another minus sign here they give me minus one sorry they give me plus one minus into minus and the constant I get outside is ih cross cube ih cross cube comes out.

Next what I do is I take f in so here I get del f del Phi now look at the second term this is when I hit L square on the whole thing I am going to get two terms right I left to handle two terms I will take the second term first. Here I have del f del Phi and I am operating it twice with respect to Phi. So, what do I get from here? I will get del three del Phi 3 sorry del 3 f del Phi 3 is it clear here I have del f del Phi I am differentiating it twice with respect to Phi, so I get del 3 f del Phi 3 that is the second term.

And what about the first term this one goes here so basically I have del f del Phi I have to differentiate it with respect to d 2 theta. So, here I am going to get del 2 f del theta del Phi. So, this is what I will get L square operating on L zf gives me ih cube multiplied by 1 by sine theta del del theta sine theta del 2 f del theta del Phi + 1 by sine square theta del 3f del Phi 3. Now I want you to pause the video for a minute and work out the next one.

I want you to work out what L z, L square f will be of course in that case we just altered the sequence of the two operators please do it for yourself and tell me what you get I mean you cannot tell me what you get unfortunately not right now but see for yourself what you get. I hope you have got this answer you took a f in here and there and this del del Phi and del 2 del Phi 2 once again give you del 3 f del Phi 3 in the second term they multiplied by the same 1 by sine square theta and del del Phi of del f del theta is once again del 2 f well del Phi del theta whether you write del 2 f del Phi del theta or whether you write del 2 f del theta del Phi does not matter it is one and the same.

So I hope you have figured out by yourself that you get the same expression L square L z f and L square I made a mistake here peril of copy-paste. So, let me again correct by hand this was L square L zf what I have here is L z operator comes first so you see we can make mistakes while writing too many things please make sure that if there is a mistake you are aware of it and you correct it should not learn something is wrong.

So we got L square L z f and L z L square they are the same expression why do I need f because I mean how do I work with operators unless if they operate on some function that is why so this is what we have got I have done it time and again. So, L square L z f minus just write it all over again L z L square f is equal to 0 which means L square L z - L z L square is equal to 0 just reverse the sequence of operation you get the same answer.

So you subtract the resultant functions you are going to get 0 right because you get the same function no matter whether you make L z operate first or whether you make L square operate first. So, L square L z - L z del square equal to 0. So, remember this is a mistake so L square L z - L z L square equal to 0 this is how you write it this cannot be a mistake fortunately. So, this is how you write it the commutator is equal to 0 commutator means this L Square L z - L z L square it is written as L square hat, L z hat in third bracket that is how you denote commutator in quantum mechanics.

Commutator just means two functions A and B AB minus BA is a commutation you write it as A, B so L square it and L z commutator is equal to 0 right. So, the commutator is 0 the operators commute same one the same thing now the question that is logical to ask after so much of discussion is so what and alright commutator is 0 and how does it matter. To know how it matters we need to go back to the basics of quantum mechanics a little bit.

Take a holiday brief holiday from angular momenta and talk in terms of two general operators and that is what we will do now. Perhaps we should have done it at the beginning but we really wanted to get on with the show without going into too much of nitty-gritty so we will do it now, now that we need it. Now we are going to learn the answer to that question so what if it commutes.

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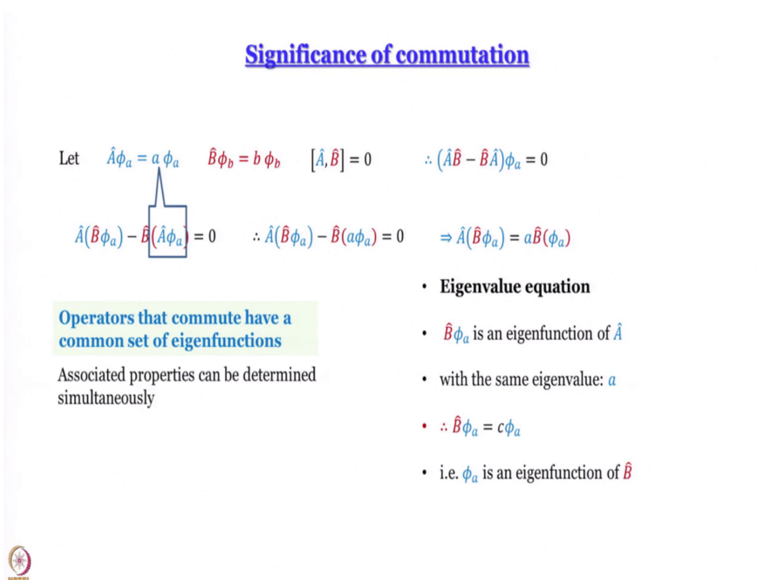

So, to do that let us say a hat is an operator B hat is an operator and Phi A and Phi B are two functions let us say to start with Phi a is a an eigenfunction of a with an eigenvalue of a phi b is an eigen function of b with an eigenvalue of P and let us say that A and B commute right commutator of A and B equal to 0. Now we can write like this AB minus BA operating on Phi a equal to 0 why do you have to write Phi a why not Phi b, you can write Phi b who is stopping you I am writing Phi a you can do the other one.

In fact I encourage you to do the other one and convince yourself that you get the same result. AB - BA operating on Phi a gives you 0. Now we now know the sequence of operations if I read A B phi a that means B operates on Phi first and A operates on the resultant function and if you write B Phi a that means B operates on Phi a first and then B operates on it. So, A operating on B Phi a minus B operating on Phi a gives you 0. Then we already know what Phi a is right, Phi a is the eigenvalue a multiplied by Phi so we can write that Aa operating on B Phi a minus B operating on A Phi a is equal to 0.

So that can be rearranged to A operating on B Phi a and we take this B hat term on the right hand side so that minus sign goes more over remember we are using linear operators. So, an operator operating on a wave function multiplied by a constant gives you that constant comes out and the operator operates on the wave function well in case you did not understand what I said this is what it means.

It means B operating on A Phi a multiplied by Phi a remember is a constant is equal to a x be operating on Phi a operating on B Phi a is equal to A multiplied by B operating on Phi a. Now will you agree with me that this is an eigenvalue equation, eiganvalue equation in what? Eigenvalue equation in B Phi a. See I can write this B Phi a as Psi this B phi a I can write as Psi what is the equation we have got? We have got a hat operating on Psi has given me a multiplied by Psi.

We have got our good old eigenvalue equation and eigenvalue equation in B Phi a, Psi is equal to B Phi a. So, B Phi a is an eigenfunction of a moreover what is the eigenvalue of B Phi a yeah Psi is equal to B Phi a right. So, eigenvalue is a so B Phi a has the same eigenvalue a for the A hat operator as Phi a what is the eigenvalue of Phi a for A hat operator it is a. What is the eigenvalue of B Phi a that is also equal to a that is what I am saying eigenvalue is the same.

Then we can write that B Phi a is equal to C Phi a. Let me now erase it what I had written earlier because the next thing might actually pop up here. So see A operating on Phi a is equal to A Phi a that we have started with. Now what is a operating on C Phi this is what I was talking about when I said something about linear operators. What is A hat operating on C Phi a that is going to be C multiplied by A hat Phi a right C will come out and now what is A phi a that is again a multiplied by Phi a small a multiplied by Phi a.

So you get C multiplied by Phi a here you can write it as aC multiplied by Phi a. So, you get this since you have the same eigenfunction you see C Phi a has the same eigenfunction as Phi a itself for A hat operator and that is what holds exactly for B hat Phi a that is why it is abundantly clear that B hat Phi a is equal to C Phi a. Problem with quantum mechanics is that sometimes we lose our way while we may end up through so much of mathematical manipulation.

I hope we have not lost our way now your advantage is that you can always go back and replay the video. But what I hope you can see easily is that B Phi a is equal to C Phi a this is again an eigenvalue equation. So, what are we saying here we are saying that Phi a which is actually an eigenvalue of A hat sorry Phi a which is an eigenfunction of A hat is also an eigen function of P hat herein lies the significance of commutation Phi a is an eigenfunction of B hat if A hat and B hat commute.

So this is one of the golden rules of quantum mechanics operators that commute have a common set of eigenfunctions. Please make sure you understand this before going further. As I said it is very important that we do not lose our way in the maze of mathematical manipulation it is very important that at end of the day if we forget all the mathematics the physical insights sync and stay with us ok. What we have learned from this is that for commuting operators there are common sets of eigenfunctions what does that mean?

It means that associated properties the property associated with A and property associated with B can be determined simultaneously. This is the most significant physical outcome of the discussion we have had associated properties with the two operators can be determined simultaneously and that should remind us of something that we have again studied in higher secondary we know that x and px.

Position and momentum cannot be determined simultaneously with any certainty right that is uncertainty principle where does that come from it comes from here x and px actually do not commute I leave it to you to work out to read it by yourself it is there in all standard physical chemistry books x and px do not commute you get something like ih cross. That is why x and px cannot be determined simultaneously.

What is the meaning of determining simultaneously that means you should have a well-defined eigenfunction for A hat operator well-defined eigenfunction of P hat operator. A hat is operator is associated with some property B hat is associated with some property. If they have a common set of eigen functions that means these eigenvalues small a and small b can be determined precisely at the same time from the same functions.

Remember how quantum mechanics works the information whatever information is contained in the wave function can be brought out by applying the appropriate operator the associated with that physical quantity. So, if the wave function knows the answer for the value of that property it will spit it out as the eigenvalue. What we are saying is that if you have a simultaneously if you have a set of eigenfunctions for two different operators that means you have eigenvalues for the two corresponding properties.

So the two properties can be determined simultaneously very, very important and profound quantum mechanical concept something that is very central to quantum mechanics. So, we are very happy that L Square and L z commute.

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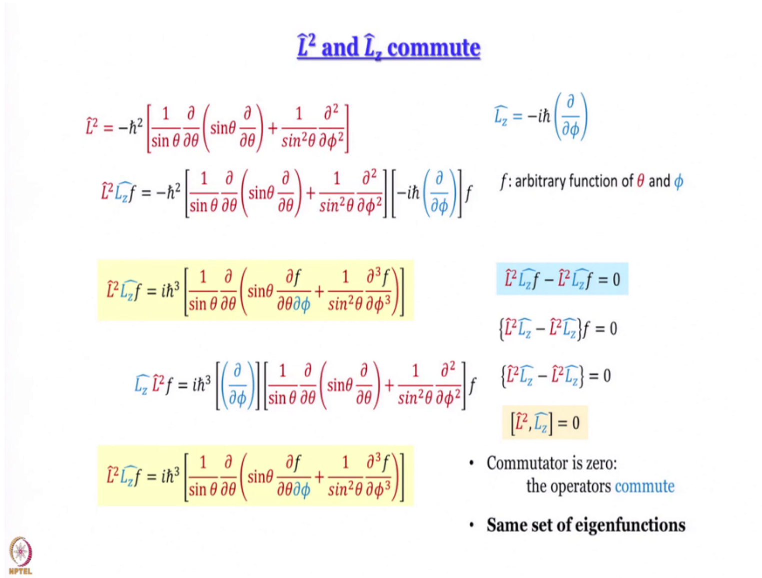

So, L Square and L z can be determined together is not it we have same set of eigenfunctions we said so we can determine L squared and L z together. Now think what we have done in rigid rotors. We have always talked about the total momentum from L Square and we have talked about z component of angular momentum why? Because we have we can determine these two together because L square hat and L z hat are commuting operators they commute ok.

This is a very important take-home message and this sort of tells us why is it that; we always talk about L z and L together.

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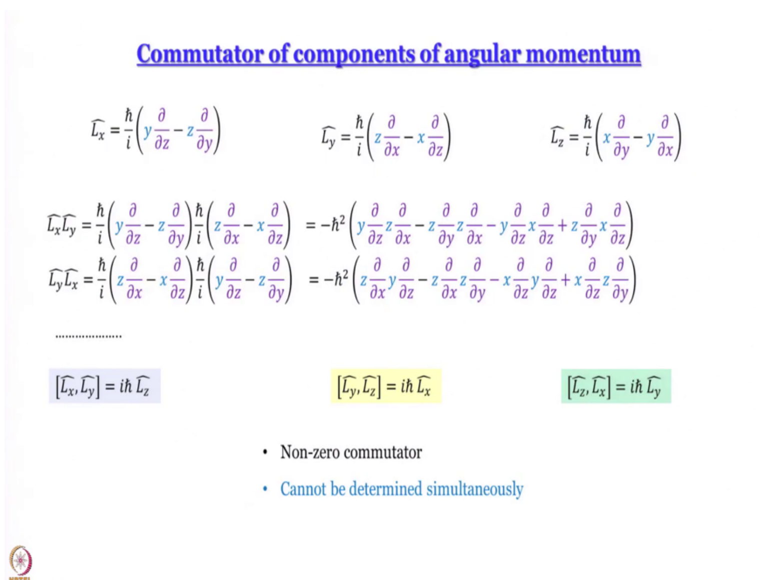

The corollary that should come out is that why do we not about L x and L y we know L we know L z will be so nice if we can find out L x and L y as well actually we cannot that is the uncertainty sets in because I have not worked it out myself it is worked out in Pillar's book to some extent. And you can work it out yourself now with a little it is a little tedious that is all but just believe me when I say that L x and L y, L y and L z, L z and L x do not commute.

So L x and L y commutator is ih cross L z that is very beautiful result right because this is what is used in things like NMR spectroscopy to find out the different components of electrons nuclear spin. L y and L z commutator is ih cross into L x, L z and L x commutator is ih cross L y. So, you cannot determine the x component and y component together. If you try to do that I mean you will not get anything. So, a corollary to corollary question that can arise is that we understand that.

So we understand that you can determine total angular momentum and z component of angular momentum simultaneously. We also understand that you cannot determine x component of angular momentum and z component of angular momentum simultaneously but can we determine L Square and L x simultaneously. Can we determine L Square and L z simultaneously the answer is yes we can L Square and L x actually commute, L x square and L y actually community L x and L y do not commute with each other L y and L z do not commute with each other.

So first point we can determine any of the components and total angular momentum together but the moment we do that the other two components are not defined. Remember L square capital L squared is equal to L x square + L y squared + L z square. So, if you have determined say L y square then you also know L x square + L z square but from there you cannot find L x square or you cannot find L x or L y separately do not be able to separate it out that is from uncertainty principle.

Because L x and L y themselves do not come out and that you can replace x by y, y by z answer will remain the same. Why do we always talk about z first it is convention we always like to define z as a unique axis second is it makes our life so much simpler. You have seen that the operator in spherical polar coordinates for L z is so simple and for L x and L y it is quite complicated. So, our life is simpler if we do this right that is why.

So this is what we have that you cannot determine the components two components of angular momentum simultaneously you can determine the total angular momentum and one of the components simultaneously great.

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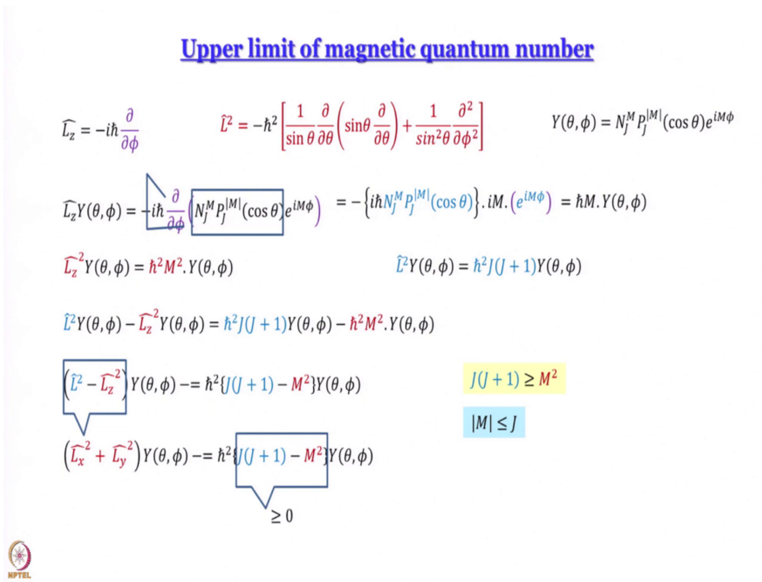

Now with that understanding let us conclude this part of the discussion with something really nice and something that we sort of skipped giving a hand waving argument while talking about rigid rotor. I am talking about why is it there an upper limit of magnetic quantum number. To do that let us work with L z operator L square operator and the spherical harmonics. The wave function for rigid rotor will get the same wave function for hydrogen atom later on.

So now we know that these two operators commute right so why do not we do this we will make L z operate on the spherical harmonics this is what we get and of course del del Phi will operate only on a to the power i M Phi and will give me i and i give you minus 1 minus 1 minus 1 + 1 here we will be left with Mh cross we know this and what we can do of course is we can before we do that we can bring this polynomial in cos theta and normalization constant out because as far as Phi is concerned these are all constants.

So this is what we get yeah ih cross NJ P MJ cos theta comes out multiplied by iM multiplied by i M phi that finally gives me h cross M multiplied by the spherical harmonics. Now we are familiar with this, this is the eigenvalue equation for L z ok we know this already. Now let us make L x square operate on it L z square let us find out what L z square is? What is L z square I do not have to need an operator for it because I know the eigenvalue.

So just square the eigenvalue that is what I will get do I square the wave function as well no, please do not, it is not as if you are squaring both the sides when I write L z square I means I make L z operator operate on the wave function twice. So, this is your wave function you take this and make the L z operator operate on it once again what do you get you get another h cross multiplied by M right M here remember is magnetic quantum number so you get h cross square M square.

Please do not think that I have squared it like some number or something. Square of operator means operating twice, so we have L z square and we already know what L square is, so what we will do is we are going to subtract this L z square from L y square from L square I will subtract this L z square from L square where L is total angular momentum this is what we get so you can simplify this a little bit.

We can write L square - L z square operating on y function of Theta Phi gives me this minus you can neglect there is a typo again h cross square multiplied by J into J + 1 minus M square multiplied by y Theta Phi again an eigenvalue equation. However I got this eigenvalue equation by taking the eigenvalue equations of L square and L z square subtracting them from one another that has led to another eigenvalue equation in which the operator is L square - L z square eigenvalue is h cross square multiplied by J into J + 1 - M square.

Now see what is this operator L square - L z square we briefly mentioned this a little while ago will you agree with me. If I say that this operator is L x square + L y square because a total angular momentum operator L square we had said this at the beginning of our discussion previous module this is actually L square + y square. So, L square + y square operator has an eigenvalue of h cross square multiplied by this.

Now we come to 1 again simple but important to understand concept. Can L x square whatever the value is can it ever be negative? No right because square of the x component of angular momentum we may not be able to determine it but it is a real quantity. So, it is square will always be a positive number. What about y component? Same thing, so we agree with me if I say that L x square operator L x square + L y square operator must have a positive eigenvalue real positive eigenvalue right yeah because it is a sum of two positive quantities.

L x square can never give you negative quantity because L x it iself is a real quantity it is not an imaginary quantity. So, this has to be greater than equal to 0. You see that we are there which means J into J + 1 has to be greater than equal to M square or I can simply say that mod M has to be less than equal to J. I can just neglect this J this one to get this get rid of this square. Here we now understand why is it that there is an upper cap to the modulus of magnetic quantum number M mod M is less than or equal to J this is where it comes from.

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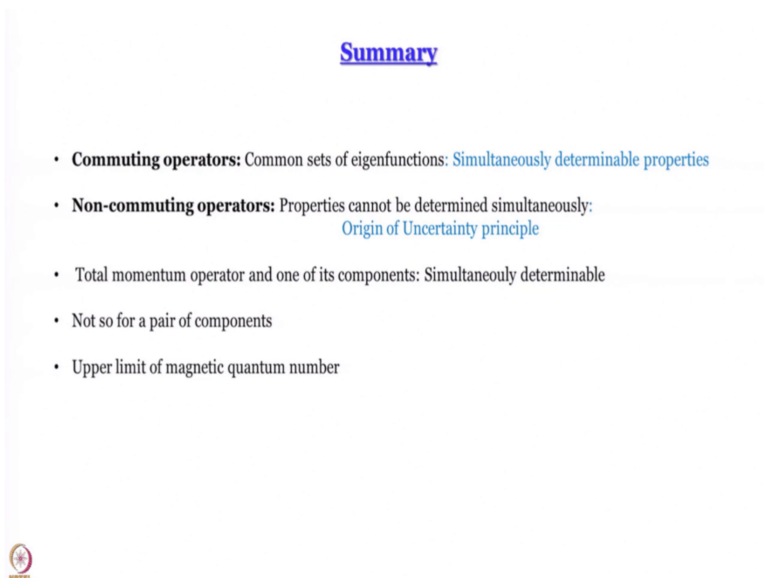

So, to summarize we have learnt that if operators commute then the properties that they stand for can be determined simultaneously. What we have not done is that this non commuting operators which have properties that cannot be determined simultaneously that leads to uncertainty principle that I have left for you to do as self-study. We have learned that total more angular moment total angular momentum operator sorry I may say the crucial angular word here and one of it is component these are these operators are commuting.

So these properties are determinable simultaneously but if you take a pair of components they are not determinable simultaneously. And finally we have learned how this leads to an upper limit of magnetic quantum number. I hope you have found this discussion on angular momentum very interesting and fruitful. There is more to angular momentum but once again we do not want to lose our way before in all this maze of what seems like mathematical manipulation.

So we will take another holiday from angular momentum after this we will go on and discuss something that we are familiar with that is hydrogen atom. Then while talking about multi-electron atoms perhaps if you feel it is required we might discuss about angular momentum in a little more detail. I really have not made up my mind about that but we will see. But next in my agenda coming up is hydrogen atom.