Chemistry Atomic Structure and Chemical Bonding

Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 45
Video Tutorials on Angular Momentum (Orbital and Spin) and Variational Method
Part –I

Welcome back to the lectures in Chemistry and on the topic of Atomic Structure and Chemical Bonding.

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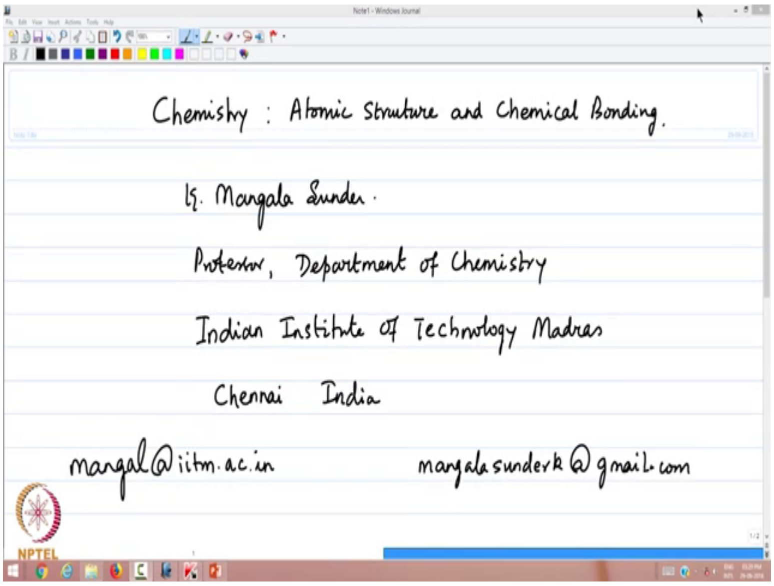

My name is Mangala Sunder; I am from the department of Chemistry, Indian Institute of Technology, Madras. Let us continues to give you a lecture with the tutorial on some of the problems in Angular Momentum and Variational Method; the lectures that were part of the last couple of weeks.

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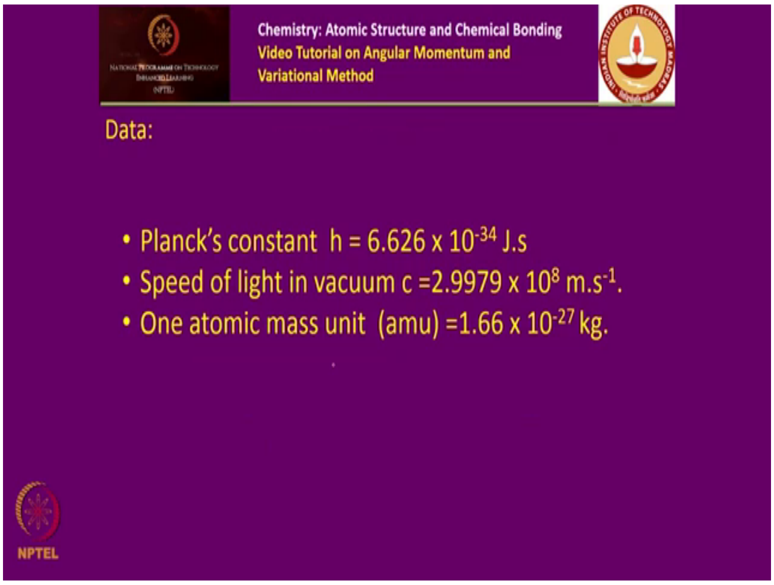

Now, there are 6 or 7 problems from the slide that I have; I have not included spin here, but a lot of questions about spin a half have come in the assign the tutorials that you have online. But we will concentrate on the Angular Momentum Operator; its matrix representation and also some elementary examples on variational principles ok.

The problems are given in the sequence. I shall upload these problem sets before I upload the tutorial, so that those of you who would like to solve these problems on your own without having to look into the answers, we will have some time to check where to do the calculations and then, check the answers with the tutorials here. If you find any mistakes in what I have written down, please feel free to write to me. And you can see that my email co-ordinates are given here; mangal at iitm dot ac dot in and mangala sunder k at gmail dot com.

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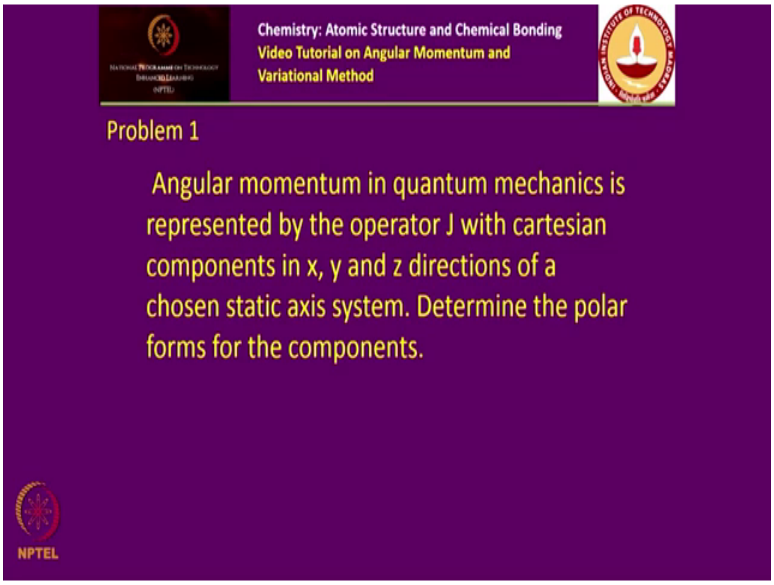

Now, let us go to problem 1. This is a problem of representing angular momentum by Cartesian components is asking you to do the following. Angular momentum in quantum mechanics is represented by the operator J with Cartesian components x, y and z directions of a chosen static access system. Determine the polar forms for the components.

I am sure you have seen these things again over and again in the last several lectures; but still it is worth doing one exercise on your own particularly calculating the J x operator in the polar coordinate system r theta and phi.

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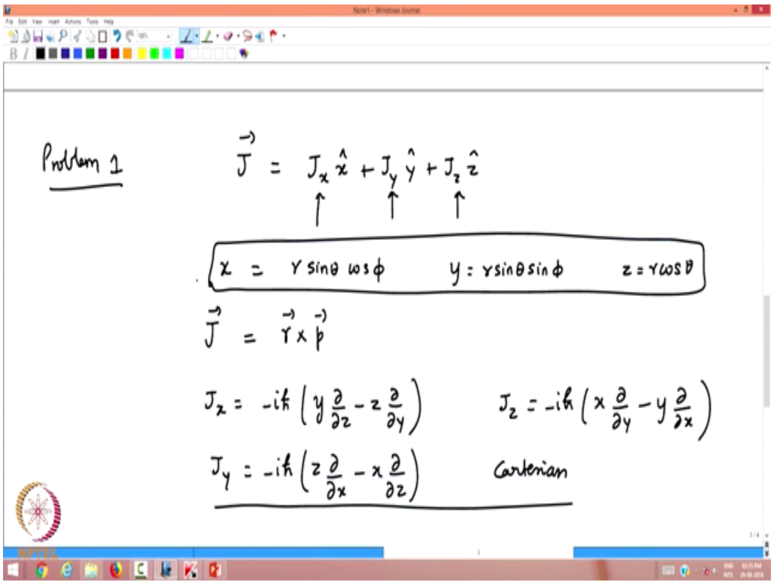

Let us go to the solutions. J represented as a vector in the Cartesian coordinate system; y and J z z. Now, you represent this using spherical polar coordinates which require the transformation to be used, the following transformations r sin theta cos phi y equal to r sin theta sin phi and z equal to r cos theta. You are asked to calculate J which classically is written as r cross p and in quantum mechanics using the x y z coordinate system, J x is written as minus i h bar y dou by dou z minus z dou by dou y.

The minus i h bar dou by dou z is the z component of the momentum linear momentum p. Likewise J y is minus i h bar z dou by dou x minus x dou by dou z and J z the operator is minus i h bar x del y minus y del x ok. So, these are Cartesian representations and you need to write the derivatives also in the polar representation and by now you know the formulae for doing that.

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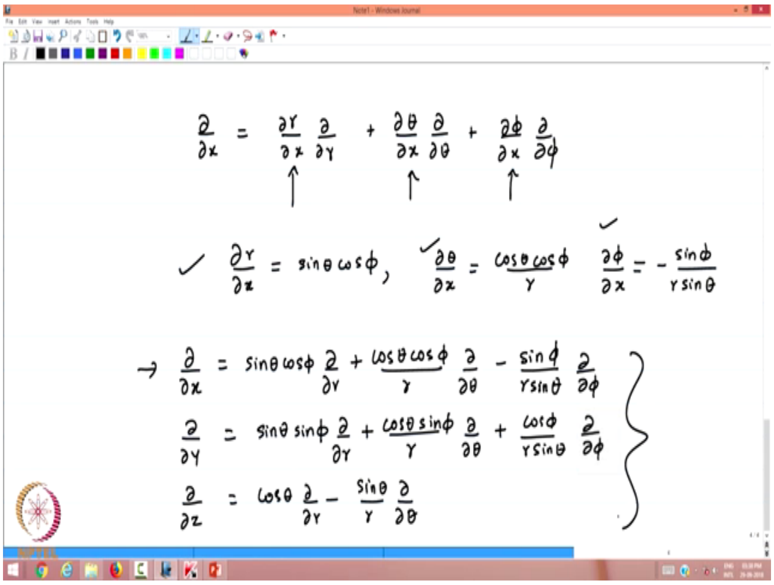

For example, the derivative dou by del x is del r by dou r by dou x into dou by dou r plus dou theta by dou x into dou theta. Then, dou phi by dou x dou by dou phi ok. These things have been calculated in the hydrogen atom earlier and therefore, I would simply copy the answers from the notes that was circulated as part of the course.

The derivatives are dou r by dou x is simply sin theta cos phi and dou theta by dou x is cos theta cos phi by r and dou phi by dou x is minus sin phi by r sin theta ok. They are obtained from the inverse transformation of this ok, when you write r in terms of x square plus y square plus z square under the square root and sin theta likewise theta and phi.

Once you have them, you can calculate the derivatives as you have here. Therefore, dou by dou x is sin theta cos phi dou y dou r plus cos theta cos phi by r dou by dou theta minus sin theta by r sin sin phi by r sin theta r sin theta dou by dou phi phi. This is the derivative dou by dou x, likewise you need to know the derivative dou by dou y and derivative dou by dou z. In order to calculate the x component of the angular momentum given by this formula y y dou by dou z minus and dou by dou y and so on the others.

Therefore, the first thing is to write to these derivatives and let me just copy the other derivatives from your lecture sets earlier. Dou by dou y is given by sin theta; sin phi dou by dou r plus cos theta sin phi by r dou by dou theta plus cos phi by r sin theta dou by dou phi and the last one, dou by dou z is cos theta dou by dou r minus sin theta by r dou by dou theta ok.

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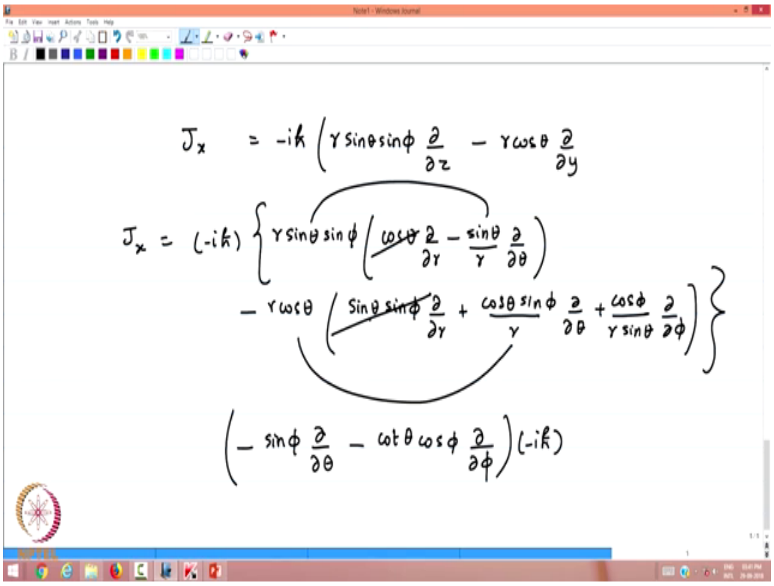

So, these 3 need to be substituted into the expression for the corresponding angular momentum operators, namely J x if you have to write that it is given by y which is r sin theta sin phi times dou by dou z minus z which is r cos theta dou by dou y. So, let me just do the J x and in a similar way, you can do the other things.

So, if you have to write this its minus i h bar, the derivative that you have to worry about is the derivative dou by dou z which is given as cos theta dou by dou r minus sin theta by r dou by dou theta. And, the other expression is the z which is minus r cos theta sin theta sin phi dou by dou r plus cos theta sin phi by r dou by dou theta plus cos phi by r sin theta dou by dou phi.

You can see that the first term cancels with this one, r sin theta sin phi cos theta r sin theta sin phi cos theta. Therefore, these 2 terms disappear and this term is sin square theta r sin phi and the r goes away. So, this is minus sin square theta dou by dou theta times sin phi and this term is cos square theta minus sin phi dou by dou theta. Therefore, these 2 will give you minus sin phi dou by dou theta.

And the last term that you have is of course, there is no other term is the only one. So, this is given as minus sin theta by r minus sin phi, you have seen that. There is a minus sin here. So, you get minus cos theta by sin theta is cot cotangent theta and the r goes away and you have cos phi dou by dou phi times minus i h bar.

So, the algebra is very clear that the first thing you need to know is to get these derivatives. The second is a simple substitution of these derivatives in this expression for the x component and the y component and the z component and then, the canceling of the terms and simplifying them and that is all.

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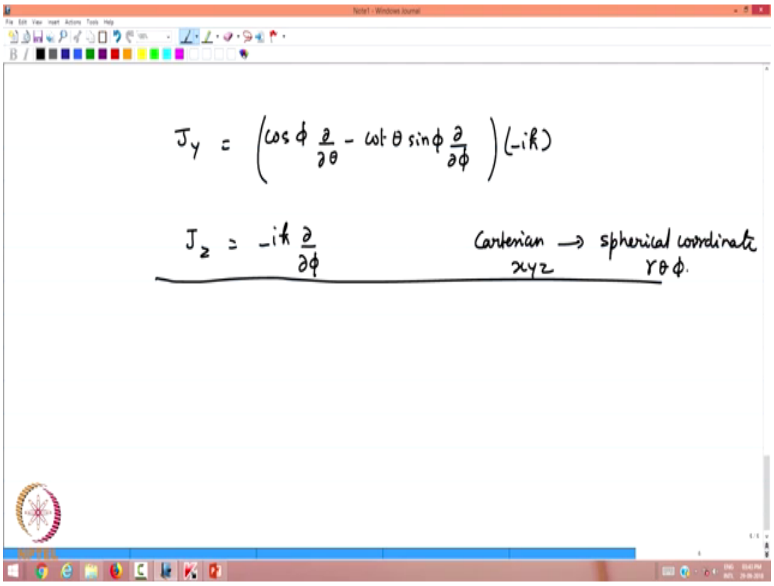

So, therefore, the algebra is simple enough for me to write down the corresponding J y components and J z component for you to verify that the J y turns out to be cos phi dou by dou theta minus cot theta sin phi dou by dou phi multiplied by minus i h bar.

And J z turns out to be even simpler and you have already seen the J z in the particle on a ring as well as in the hydrogen atom and that turns out to be simply minus i h bar dou by dou phi or phi ok. So, this is how you do the 3 components of angular momentum in spherical polar coordinates using Cartesian to spherical coordinate transformation variables x y z to r theta phi.

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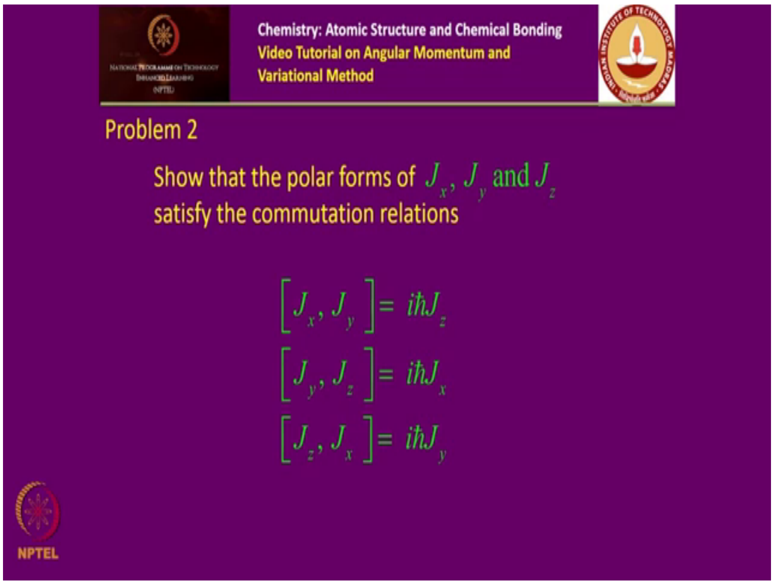

So, that is the first problem, the second one is to show that the corresponding polar forms of the angular momentum operation J x, J y and J z satisfy the commutation relations in exactly the same way that they do in Cartesian coordinates.

I mean it is not a surprise it is just algebraic exercise for you. But you know how these commutation relations between J x and J y and J y and J z were obtained in the first place.

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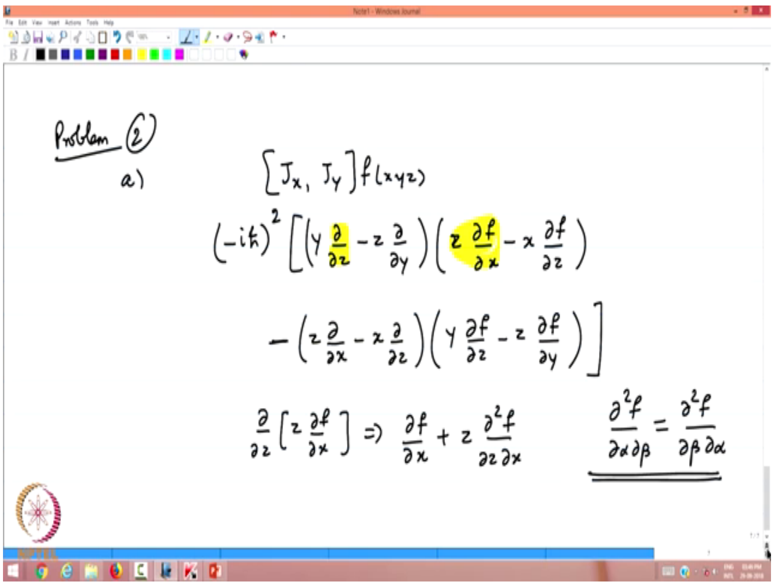

So, if you recall that the problem 2, part a, if you have to write J x J y then the commutator is you usually work with a function and then later; I mean at least until you become very familiar with these operations, I would write this as operating on a function of x y z and you know that J x J y both contain a minus i h bar. Therefore, I would write this as y dou by dou z minus z dou by dou y.

Acting on this quantity z dou f by dou x minus x dou f by dou z that is J x J y and J y J x is minus z dou by dou x minus x dou by dou z. Acting on this quantity which is y dou f by dou z minus z dou f by dou y. This is what you have to do and you can see that the derivative dou by dou z sorry, the derivative dou by dou z acting on this gives you, it is a product of functions here because f is a function of x y z.

Therefore, this derivative will also contain x y z and that is also f z. So, the only thing that you have to be careful about is in writing this term that dou by dou z acting on z dou f by dou x is to give you dou f by dou x because, that is left over then the derivative x on z or x derivative of z. And, the other term is that z dou square f by dou z dou x and you must know that dou square f tau alpha tau beta is for a well behaved function dou square f by dou beta dou alpha. The order of differentiation is irrelevant and we would consider only those functions.

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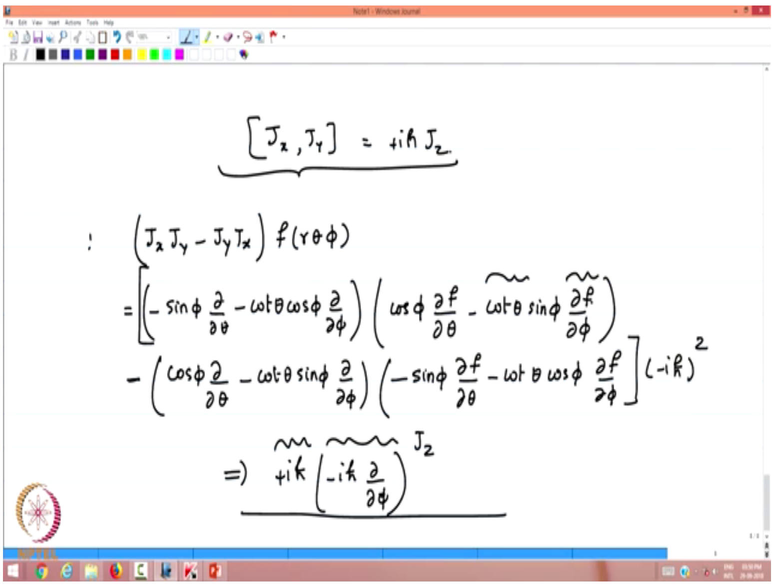

This is how one obtains J x J y is minus sorry plus i h bar J z. Now we are supposed to verify this using the polar form. Therefore, I do not think there should be any problem.

But let me write one step and leave the rest of it for you have to do the same way. So, J y let us first do the term J x J y minus J y J x on a function of r theta and phi.

And then, we will neglect have been removes the function at the end of the calculations. What you see here is minus sin phi dou by dou theta minus cot theta cos phi dou by dou phi. All of this is J x and J y is cos phi dou f by dou theta minus cot theta sin phi dou f by dou phi. This is J x J y on f minus J y J x on f is obviously, cos phi dou by dou theta minus cot theta sin phi dou by dou phi; acting on the function obtained through the differentiation dou f by dou theta minus cot theta cos phi dou f by dou phi. This is all that you have to calculate; of course, the whole thing is multiplied by minus i h bar square.

So, if you go through the algebra, keeping in mind that dou by dou theta acting on this term; obviously, gives you only dou square f by dou theta square because, cos phi is not affected by it. But dou by dou theta acting on cot theta and dou f by dou phi will give 2 terms and likewise, dou by dou phi on each one of these will give you 2 terms; one being the action on cos phi, the other being the action on dou f by dou theta which is a function of phi.

And likewise here, the action on sin phi and the action on dou f by dou phi. You have to do in a similar way and this will give you the result actually i h bar ok. Let us say i h bar and you know what is dou J z. J z will be minus i h bar dou by dou phi. This is what you should get.

This is i h bar this is J z because J x J y gives you that ok. It is a fair enough, it is a somewhat lengthy, but a lengthy calculation, but when you are doing it for the first time, it is what sitting down and doing this algebra for yourself and convince that you do not leave any holes behind your approach and your learning process. So, this is a fairly straightforward problem for you.

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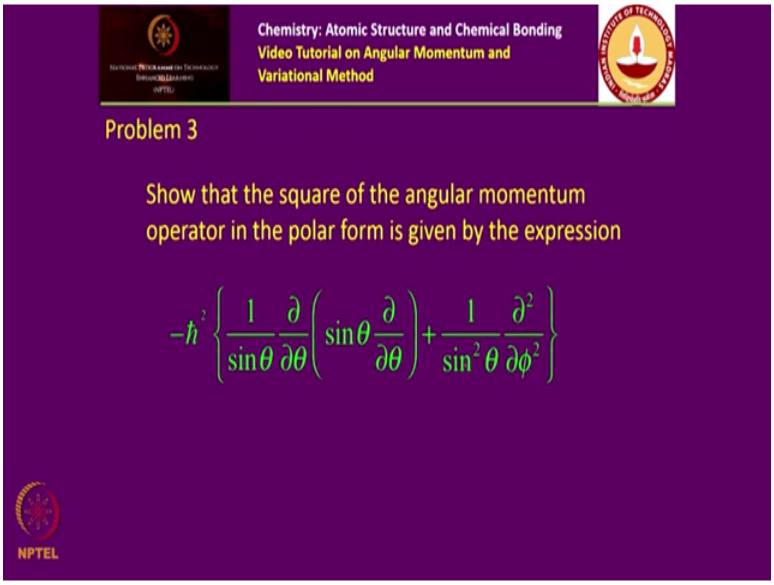

Let us go to the next problem. The next problem is to show that the square of the angular momentum operator in the polar form is given by the expression minus h bar square 1 by sin theta dou by dou theta sin theta dou by dou theta plus 1 by sin square theta dou square by dou phi square. All that you have to do is obviously; repeat the calculation that you have done from the angular momentum operator by using this operator; J x square plus J y square plus J z square.

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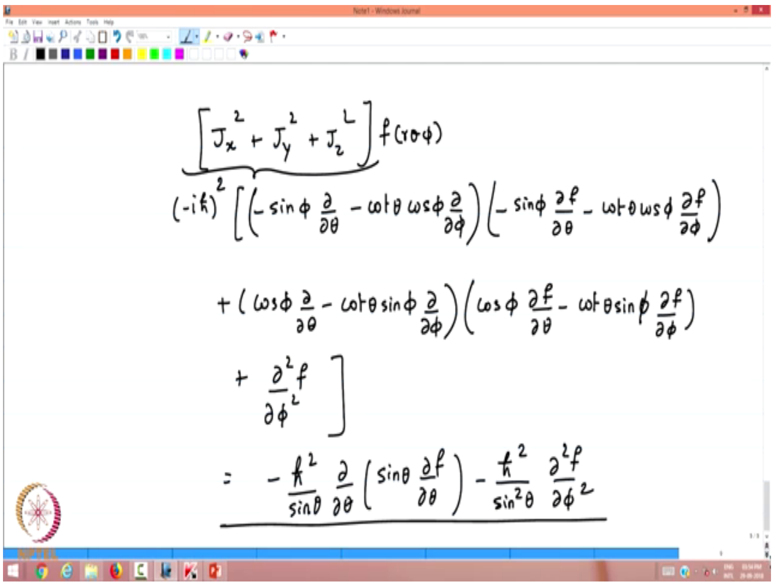

So, the J x square term is of course, you know if you have to write this it is minus i h bar square times minus sin phi dou by dou theta minus cot theta cos phi dou by dou phi; acting on itself, if you want to write a function here on r theta and phi is acting on this function minus sin phi dou f by dou theta minus cot theta cos phi dou f by dou phi.

This is J x square and likewise for J y square you will come plus cos phi dou by dou theta minus cot theta sin phi dou by dou phi, acting on this function cos phi dou f by dou theta minus cot theta sin phi dou f by dou phi and the last one, is of course, you have taken the minus i h bar whole square. Therefore, it is simply dou square by dou phi square of f.

And then, of course, when you get the simplified expression, you will see that the f is an arbitrary function. Therefore, the identity is between this operator and the corresponding operator form; which of course, will turn out to be minus h bar square by sin theta sorry, dou by dou theta sin theta dou by dou theta of f. And we will have minus h bar square by sin square theta dou square f by dou phi square.

I think that is what you have here, minus h bar square by sin theta dou by dou theta sin theta dou f and then, 1 by sin square theta with the minus h bar square. So, you get that ok. Again it is a simple repeated application of these derivatives to each other and then, simplifying algebraically.

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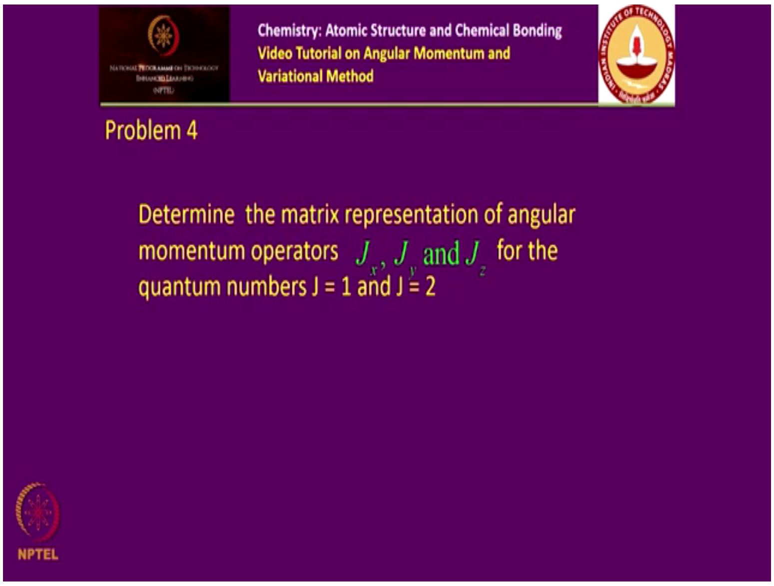

Now, the next problem is a fairly simple problem. It says determine the matrix representations of angular momentum operators J x J y and J z for the quantum numbers J is equal to 1 and 2 ok. I think all you need to do is to recall the action of the angular momentum operator on the basis set for each J value. But J, any J integral value the basis set will contain 2 J plus 1 basis functions J m or J k or whatever label that you put in.

If you remove the dimensions out of J, usually we write it in the form of i x and i y and i z; does not matter now. What matters is that you are the basis functions which are only 2 J plus 1 in number for h J value and therefore, for J is equal to 1; there are 3 basis functions and for J is equal to 2; there are 5 basis functions.

Therefore, the operators for the basis set corresponding to J equal to 1, they will all be 3 by 3 matrices and the operators for J is equal to 2 will all be 5 by 5 matrices, that is one thing you need to know. The second is of course, immediate recalling this result, you must know the 3 operational properties, J plus on J m is given by h bar square root of J minus m into J plus m plus 1 changing the basis set to J m plus 1.

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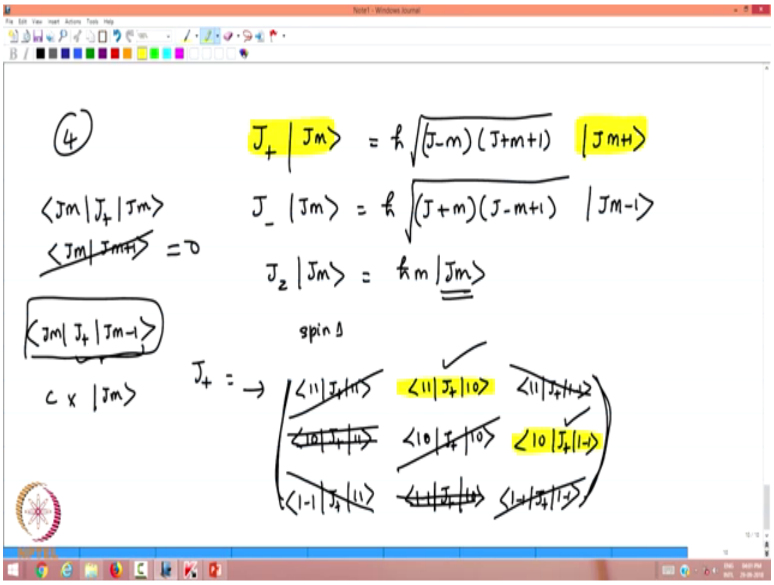

And therefore, in a similar way J minus on J m is given by h bar square root of J plus m J minus m plus 1 and giving you the basis function J m minus 1 and the last one is the J z on J m giving you h bar m J m. This is an eigen function for the z operator. But it is not an eigen function for the plus or minus operators.

Therefore, the J plus matrix element, if you have to do this for spin 1, the matrix will be given by these 3 by 3 matrix quantities. 1 1 J plus 1 1 1 1 J plus 1 0 and 1 1 J plus 1 minus 1 and this is the basis function 1 1, the row is along 1 1 and the columns all contain different basis functions.

So, next one is 1 0 J plus on 1 1 and 1 0 J plus on 1 0 and 1 0 J plus on 1 minus 1 and likewise 1 minus 1 J plus on 1 1 1 minus 1 J plus on 1 0 and 1 minus 1 J plus on 1 minus 1. Now, looking at the 3 equations that you have here, J plus on J m giving you J m plus 1 and therefore, if I do the matrix element calculation that J m J plus on J m, I know that the result will be J m J m plus 1 ok. Therefore, that is orthogonal this is 0.

So, you can see immediately that the 3 diagonal elements are 0 and the second is that J m and J m on the side m plus 1, the difference between the 2 is only 1 plus 1 or minus 1. In the case of J plus operator, it is always plus 1 from left. If you have J m on the left, the right hand side can only contain J m minus 1 because, if you look at J plus on J m minus 1 that will give you the basis function J m and some constant.

Let us say a constant given by this formula. Therefore, you can see that the orthogonality of the basis set in angular momentum is such that this is the only non-zero matrix element for J plus. Therefore, every time you are going to do this for the spectroscopy for the angular momentum calculations in quantum mechanics for space fixed angular momentum operators, you would see J plus is connecting m minus 1 state to the m 2 state. Therefore, this is non-zero m minus 1 to m 2 state this is non-zero. This is that the states different by 2 values of m.

This is m minus m is minus 1. Therefore, this is m plus 2. Therefore, this is 0 and this is also 0. Here, we do not even have a problem. J plus on 1 1 is anyway 0 because this is the maximum value; you remember when m is equal to J this goes to 0. Therefore, this is 0 and likewise, J plus this we have already looked at and you can see that this is also 1 0 will actually move it to 1 plus 1 and therefore, this is also 0 ok. So, you are essentially left with calculating only 2 matrix elements for J plus in the spin 1 state; this one and this one. What about J minus?

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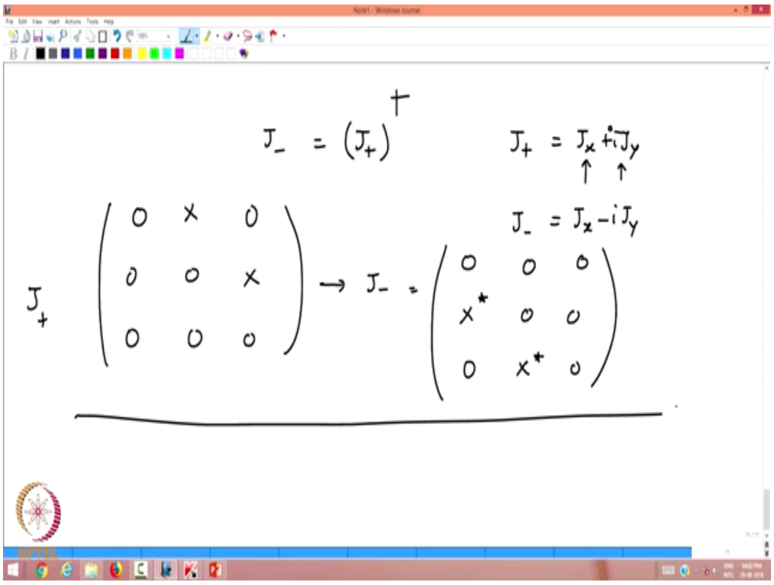

No problem, J minus is J plus Hermitian adjoint. Remember J plus operator is J x plus i J y and the operators J x and J y all Hermitian. Therefore, J minus is the Hermitian adjoint of J plus. Therefore, if you have a matrix with 2 non-zero elements here and everything else is 0, then if this is J plus; then, the corresponding matrix for J minus would be the transpose Hermitian conjugate.

Of course, you have to take into account and that will turn out to be 0 x star 0 and 0 0 x star, then you have 0 0 0 ok. Therefore, this is how you calculate the matrix elements of J plus and J minus.

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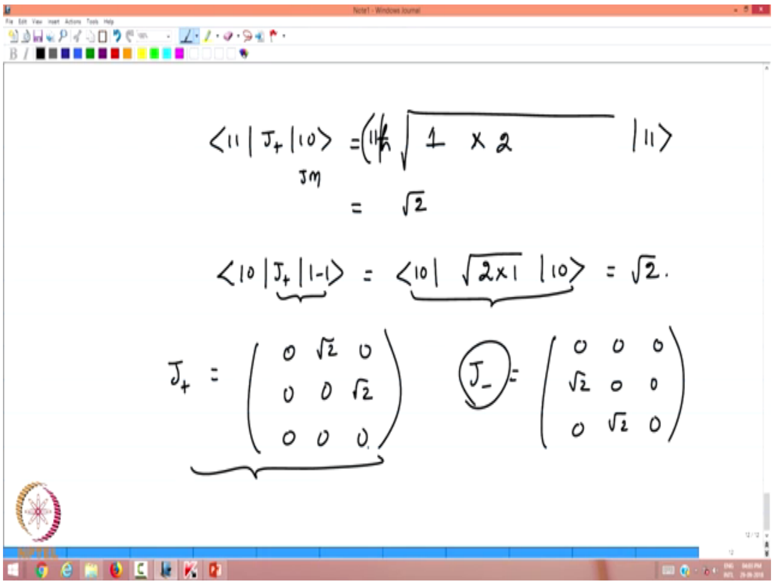

So, let us see the 2 elements that we have to calculate. 1 1 J plus 1 0 is obviously, h bar J minus m which is 1 this is J m J plus m plus 1 which is 2 and the state is 1 1. Now, it is taken as a scalar product with the state 1 1 that would the answer is root 2.

Likewise 1 0 J plus on 1 minus 1 is 1 0 and this action J plus 1 J m J minus m will give you square root 2 and J plus m plus 1 is 1 and state will be 1 0. Therefore, these 2 normalize each other to give you again a root 2. Therefore, the matrix form of J plus is 0 root 2 0 0 sorry 0 0 root 2 0 0 0. So, what about J minus? J minus is 0 root 2 0 0 0 root 2 0 0 0 because this is the adjoint or transpose complex conjugate of this matrix.

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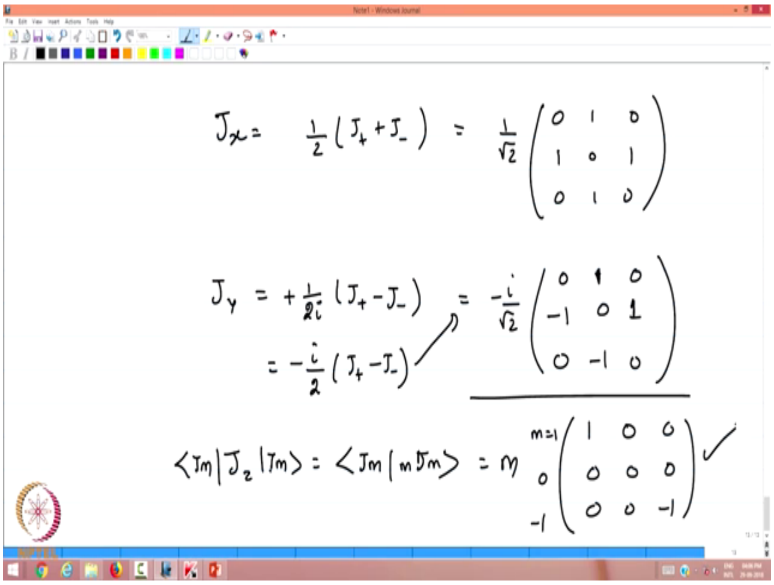

Now, you know the answer for J x. J x is 1 by 2 times J plus plus J minus and therefore, if you add these 2 matrices, the result that you will get is 1 by root 2 0 1 0 1 0 1 0 1 0. J y if you have to calculate, it will be minus 1 by 2 i sorry it is 1 by 2 i J plus minus J minus and you see that the J minus comes with. Therefore, if you write to this, this is minus i by 2 J plus minus J minus.

And this you can write it as minus i by root 2. Since, the operator J minus comes at a negative sign, you have to be careful. This is the operator for J plus and the operator for J minus comes with a minus sign. Therefore, this is the operator for J minus and the sum of the 2 gives you that with the minus sign by root 2.

This is the J y and J z on J m is of course, is diagonal, it gives you m times J m. Therefore, the only matrix element that will be non-zero is if you do J m on this, if you take the scalar product of this; then, what you have is the scalar product of J m on m J m and that is m.

Therefore, you have 1 0 0 0 0 0 0 0 minus 1 because m is 1 in this column, 0 in this column and minus 1 sorry 1 in this row, 0 in this row, minus 1 in this row and therefore, this is the J z operator. So, in a similar way, we can do the angular momentum J is equal to 2, but let us have a small break here.

And then, continue with the angular momentum 2 representation of all these operators and also the remaining 2 problems; 2 or 3 problems that we have in this video tutorial ok. We will pause for a short break.

Thank you.