Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 27A
Operators, Commutators, Eigenvalues and Eigenvectors

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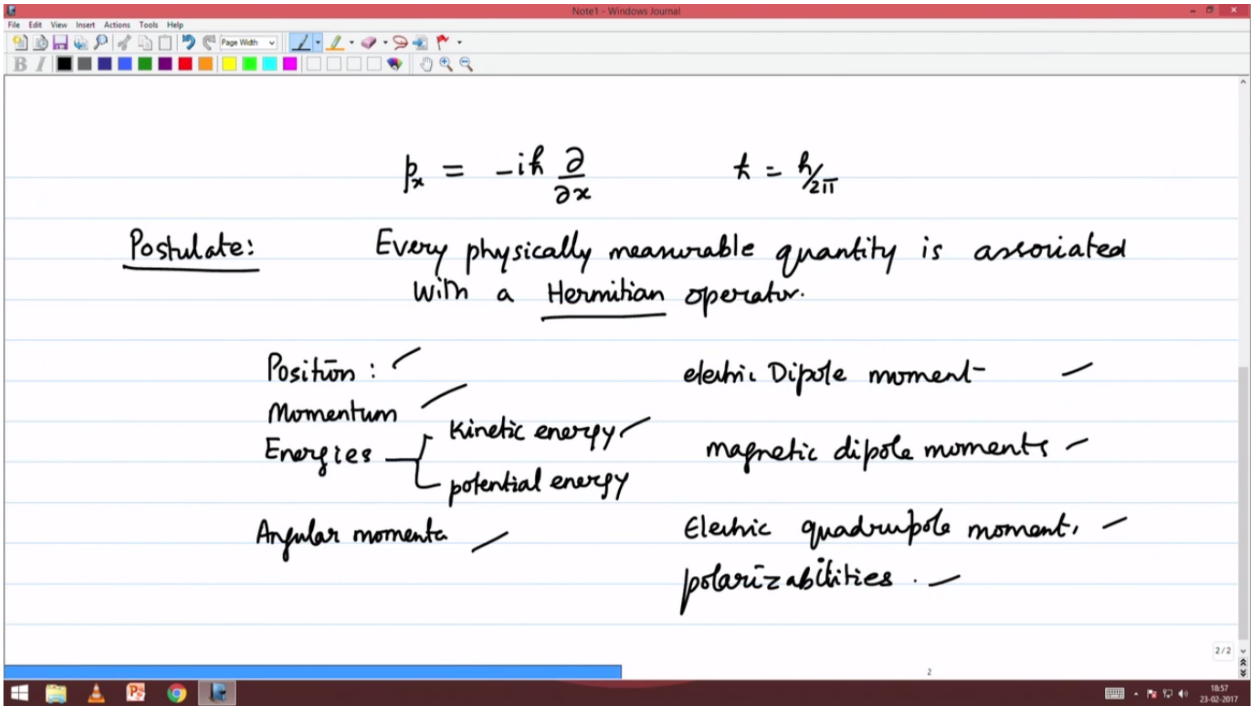
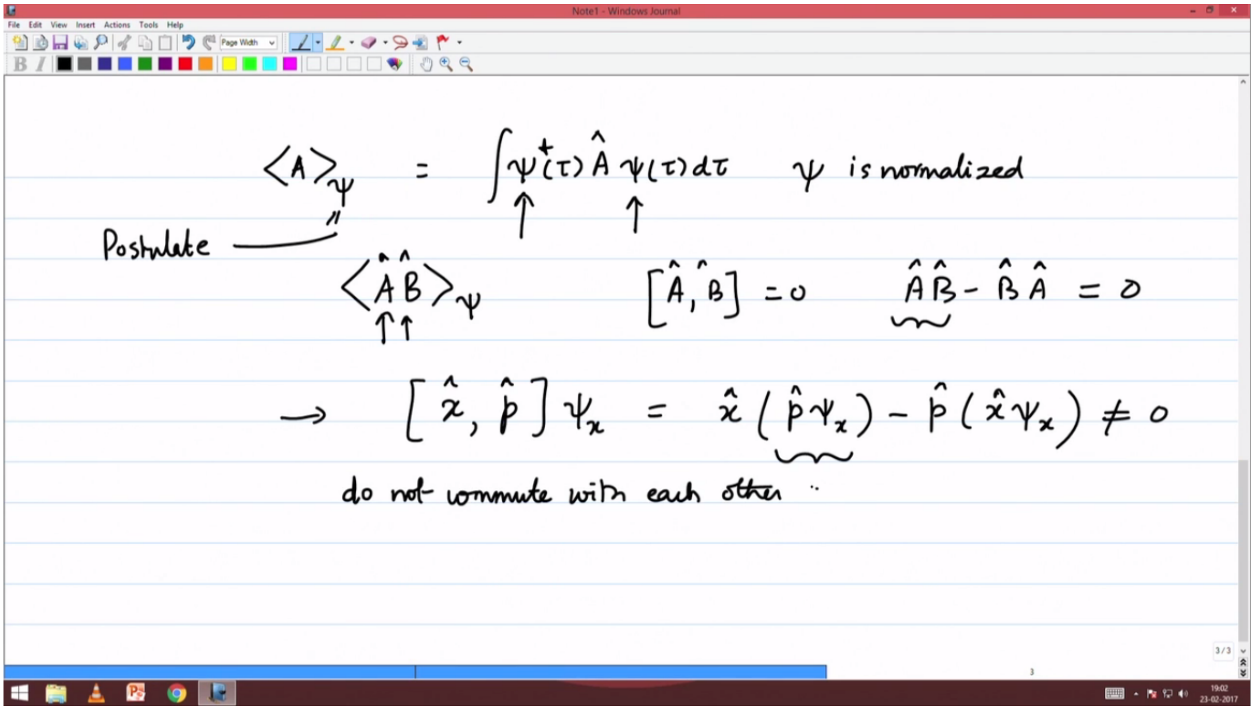
Welcome back to the lectures on introductory quantum chemistry and molecular spectroscopy. This is probably the last lecture on the quantum part quantum chemistry part in this course and the idea for this lecture is to give you some general account of elementary quantum mechanics however, but using the notion of operators, commutators ' and eigenvalues and eigenvectors. You have heard quite often in the course so far mentioning operators and also commutator but I have so far avoided the use of the term eigenvalues and eigenvectors. So towards the second half of this lecture we shall indicate why they are important for the course on quantum mechanics.

In fact we will realize later that the Schrodinger equation the time independent Schrodinger equation h Ψ is equal to e Ψ is actually an eigenvalue equation. We'll see that and we'll see the connections but let us know collect the ideas which were expressed earlier in this course in several lectures into a coherent form.

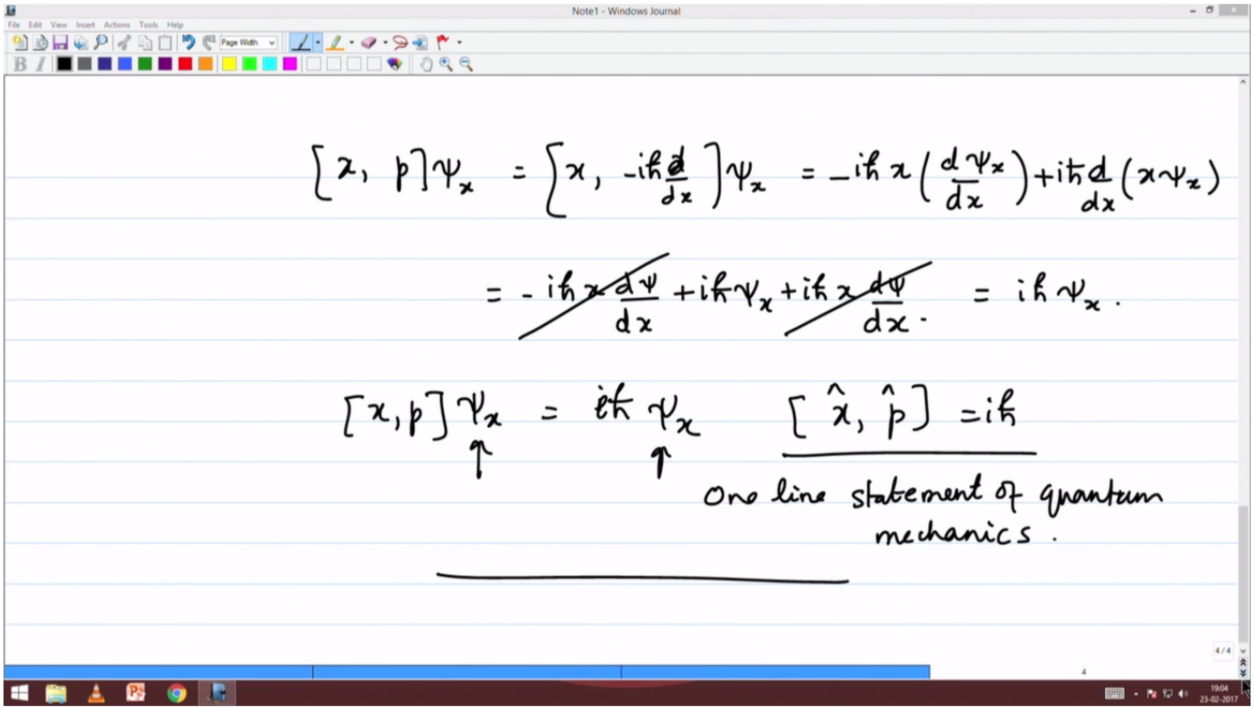
Now let's start with operators. All of you are familiar with the fact that the momentum in one dimension is represented by the derivative operator dou by dou x multiplied by minus ih bar and ih bar is h by 2 pi. It is a postulate in quantum mechanics. One of the postulates in quantum mechanics is that every physically measurable quantity is associated with a Hermitian operator. A stronger statement is physically measurable quantities associated with a self-adjoint operator but we will avoid that and stay with Hermitian and the momentum that p is equal to minus ih bar d by dxX or derivative, a partial derivatives, there is more than one dimension and that is of course the component in that dimension is one postulate. In fact with that you can write pretty much all of quantum mechanics. If you accept that it's possible to rewrite quantum mechanics with this statement.



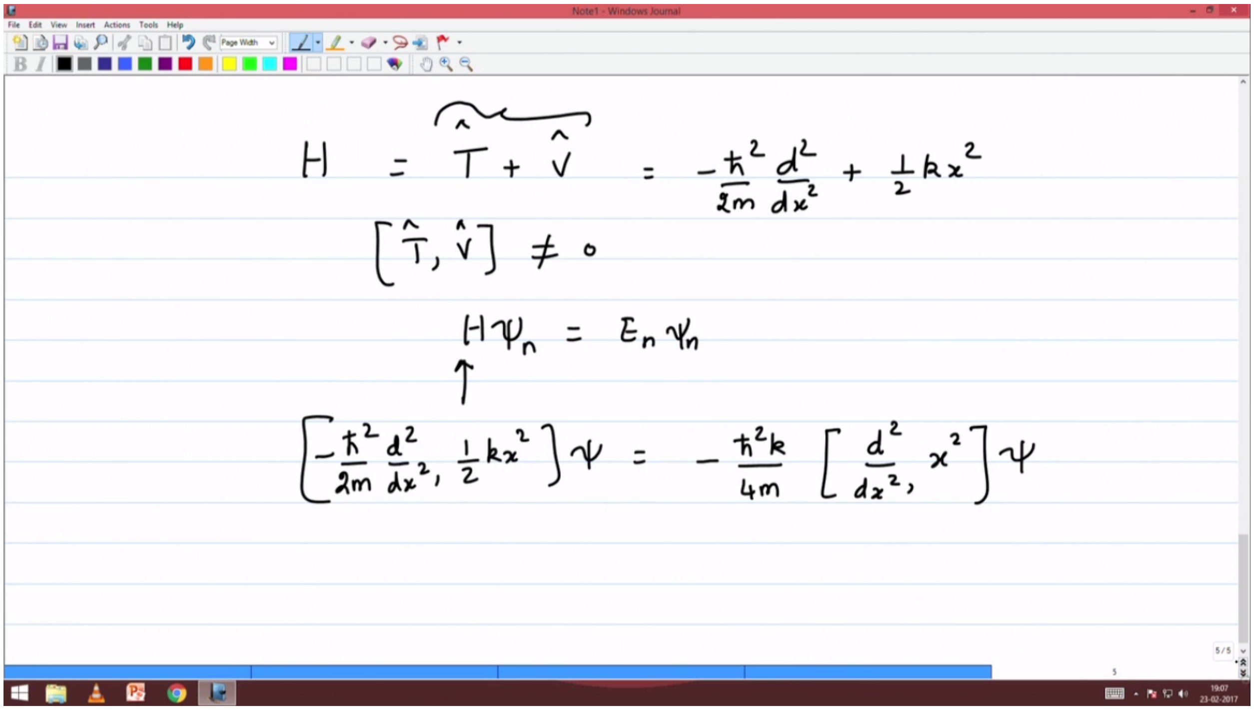
This implies that every quantity that we measure so far we have looked at positions. We have calculated the average values. We have calculated the average values for momentum. We have calculated the average values for the energies. Energies there are two forms the kinetic energy and the potential energy. These are the things we have been concerned with. We have not done much in angular momentum but when we do spectroscopy we will need to know that. Therefore angular momentum. Then molecular properties; dipole moment, electric dipole moment, magnetic dipole moments of nuclei associated with nuclei and electrons. Electric quadrupole moment. It's a multiple moment. Polarizabilities; these are measured in spectroscopy. All of these things and more polarizabilities all these things are represented by operators in quantum mechanics and the expectation value which we have seen before of any operator if the system is in the states Ψ is given by another postulate in quantum mechanics the integral Ψ star tau A Ψ of tau d tau if Ψ is normalized then we don't need the expression in the denominator. Tau is a set of variables. It can be one-dimensional like it's in a particle in the box then it's a position variable and then the limits of the integration are the box limits 0 to L or minus L by 2 to plus L by 2 whatever that is. if it is a particle in the two dimensional box then it's the set of two coordinates X and Y which defined two degrees of freedom for the particle. If it's a hydrogen atom it's a set of three coordinates the [Indiscernible] [00:05:53] are the X,Y,Z as we have done. Harmonic oscillator one coordinate. So tau represents that and the d tau represents the element of integration that's a volume element or the area element or the length element depending on the coordinates and the limits of integration are specified by the boundaries. This is your postulate in quantum mechanics. Now this is a second postulate what is important is that this is the operator that's placed between the two wave functions; the complex conjugate of the wave function and the wave function itself. This is a proposal and it's possible to show that what this is how it should be written but let's assume that as a postulate we have already worked with such things.



The other thing is not two operators if you are trying to make measurements of two operators in the same state then there are conditions associated with these two operators. The operators A and B must commute or the quantity A B minus B A that is the measurement in the sequence of B first and A next must give you the same result as the measurement of A first and B next that's what this means. The difference between the two should be zero. A better way or a more comfortable way to understand this is that suppose we have a position operator for the position of the particle and we have the momentum operator for the momentum of the particle and if the state of the system is given as Ψ of x then what this commutator essentially means is it is x, p on Ψ of x minus p on x Ψ of x. Please remember this is the measurement of p on the wavefunction leading to something and that will be again used for measuring the x and likewise the sequence here. It's a measurement of x on the wave function and the result of that is used to make a measurement of the momentum p. The difference between the two in this case of course is not zero. Therefore the order in which you do the measurements is going to be very critical. That's one reason why we say that the x and p do not commute or x and p cannot be simultaneously accurately determined. So the operators here are not – do not commute with each other. We have never explicitly done this calculation but now we will do that. What's the result x,p on Ψ of x is x, minus ih bar d by dx on Ψ of x and that is equal to minus ih bar which is a number. It's a constant therefore that can be taken out. What you have is x and d Ψ of x by dx minus there is also a minus therefore it's a plus ih bar d by dx on x of Ψ of x which will give you minus ih bar x d Ψ by dx plus ih bar d by dx acting on x will give you 1 so it gives you Ψ of x and the other would be ih bar x d Ψ by dx. These two cancel therefore what is left over is ih bar Ψ of x. So what you see is x,p the operation of xp minus px on Ψ of x gives you ih bar times the Ψ of x it's independent of what Ψ of x is. Therefore we say that the commutator of x and p is ih bar. In fact this is the one line statement of quantum mechanics. So here clearly the operators don't commute with each other.

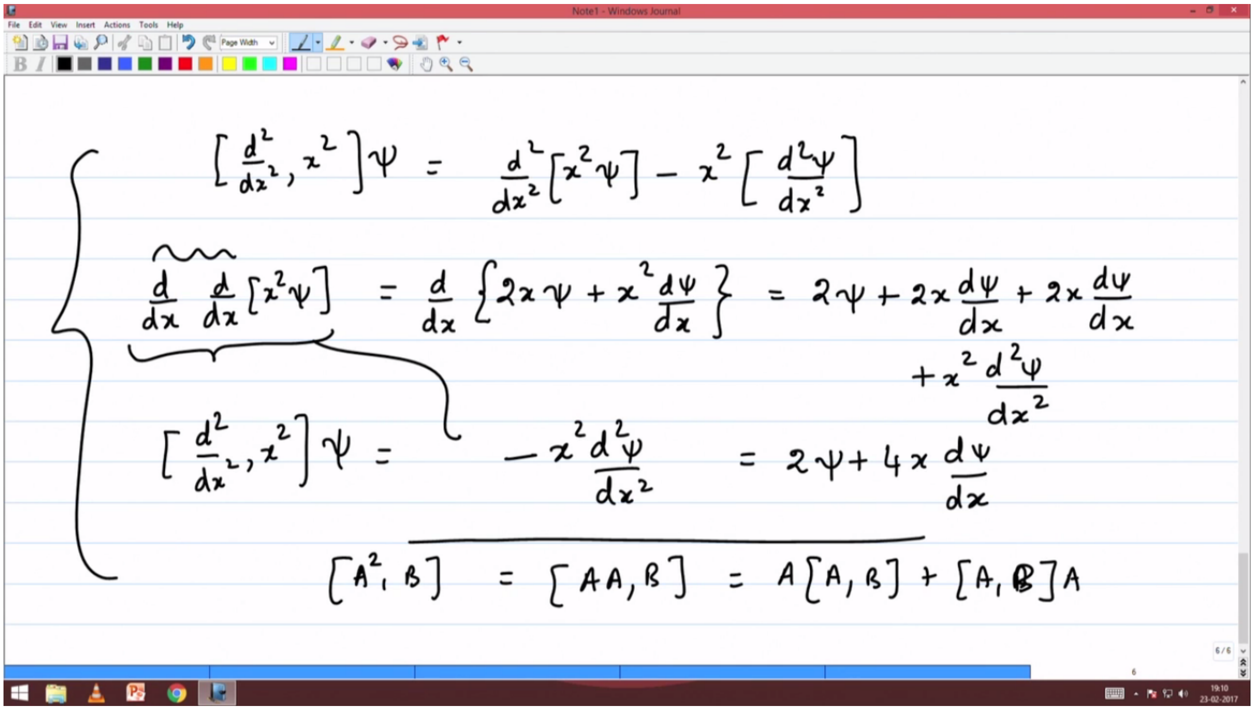


Now let's go back to the say Harmonic oscillator. The Harmonic oscillator Hamiltonian has two operators the kinetic energy operator T and the potential energy operator V and the kinetic energy operator is minus h bar square by 2m d square by the dx square and the potential energy is 1/2 kx square. The commutator of T and V is not zero. Therefore T and V cannot be simultaneously measured independently but when you solve this equation h Ψ of n is equal to En of Ψ n you are obviously finding the eigenfunction for the overall Hamiltonian which is the sum of the two and the sum of the two, the eigenfunction for that is not the same as the sum of the T acting on an eigenfunction then V acting on the same eigenfunction. In fact scientist Ψ n will not be simultaneously eigenfunction for both T and V. Therefore the non-communiting property of the operators essentially mean that the kinetic energy and the potential energy cannot be independently determined at the same time exactly but the overall energy can be determined. Therefore the statement is that the kinetic energy operator and the potential energy operator do not commute with each other.



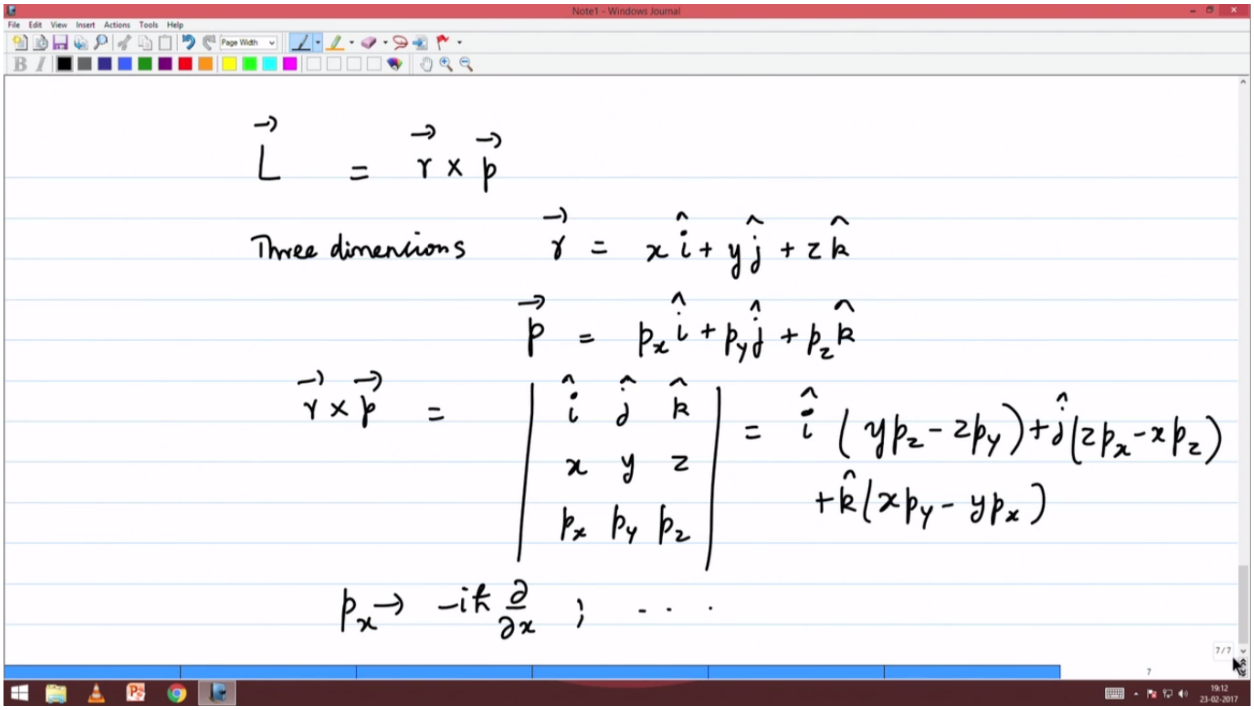
Now what's the result? What's the commutator? Remember it's h bar square by 2m d square by dx square and the other one is 1/2 kx square acting on some Ψ. Let's look at what that it is. So that gives you minus h bar square k by 4m it gives you the commutator d square by dx square, x square acting on Ψ. Let's look at what that commutator is d square by dx square, x square on Ψ is d square by dx square acting on x square Ψ minus x square acting on d square Ψ by dx square. Now this is a derivative so first you have to do d by dx acting on x square Ψ and then it's followed by d by dx that's what is the d square by dx square.

So if you do this it's d by dx acting on 2x Ψ plus x square d Ψ by dx and that gives you again when you do this operation gives you 2 times Ψ plus 2x d Ψ by dx then d by dx acting on x square gives you 2x d Ψ by dx and the last term is x square giving you d square Ψ by dx square. This is the action of d square by dx square acting on x square Ψ and minus if you want to look at the commutator it's d square by dx square, x square Ψ and that you want to write it as this minus x square d square Ψ by dx square and so what you get you get to Ψ plus 2x, sorry 4x, 4x d Ψ by dx. The other gets canceled.



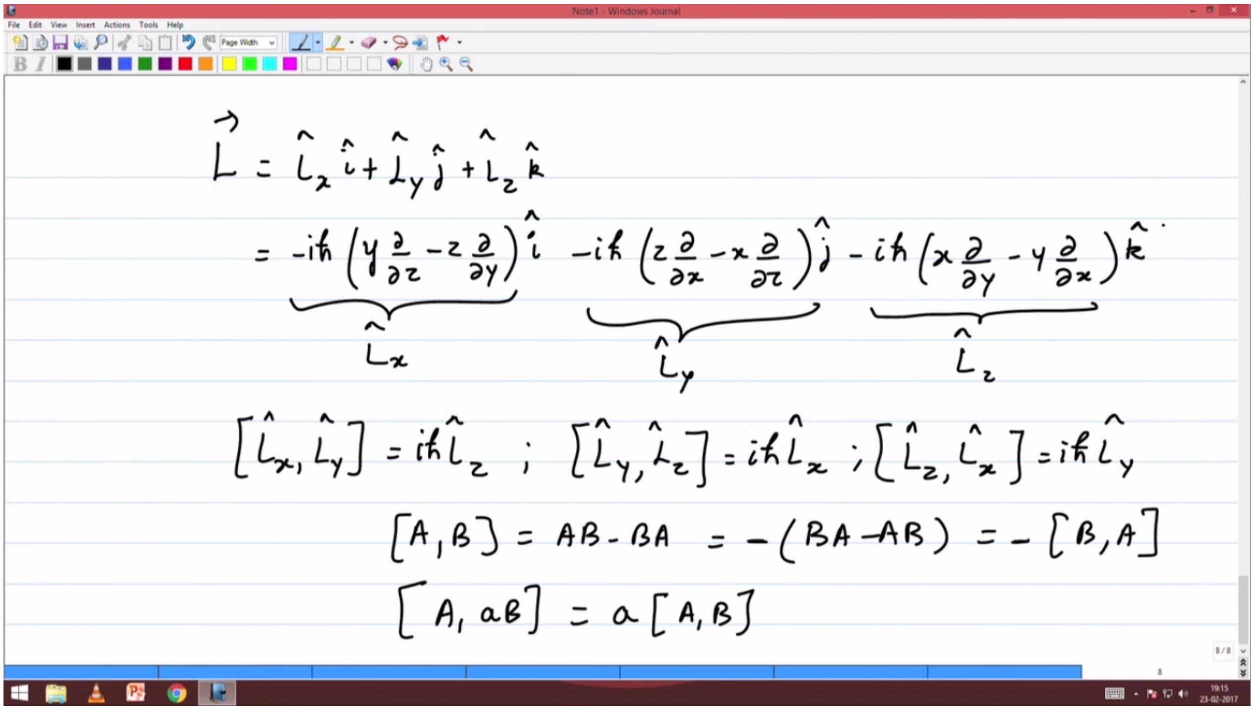
There is an easier way to do such commutators but in the next course you might see how to do the commutator involving A square, B as as writing it as A A,B and then finding that this is equivalent to A on A,B plus A, B on A we will not do that but the idea is that the square of the potential energy term the 1/2 kx square and the momentum the kinetic energy term d square by dx square multiplied by minus h bar square by 2m they don't commute and therefore the non commutation of operators is very important in our understanding of what is measurable, what is assignable as a property to the system and so on. So that was the purpose for giving you this quantity, this definition.

Now what about angular momentum? Remember in classical mechanics angular momentum is expressed as a cross product of the position vector and the momentum vector and in three dimensions r is expressed as x times the unit vector, sorry, x is the coordinate in the unit vector direction i plus y times j if you want to write these as unit vectors and z times k and p is given by px, the x component of the momentum along i plus the y component of the momentum along j and the z component of the momentum along k and therefore r cross p if you recall the determinant notation for the cross product if you write this as ijk you have xyz, you have px py pz and that is expressed as i times y pz minus zpy. It does not matter whether you write ypz or pzy because they commute with each other. The z component of the momentum and the y component of the particles positions they are independent of each other. Therefore you can write it this way ij xpy minus ypx and k unit vectors xp sorry this one is wrong. Y, this one is zpx minus xpz and then you have k xpy minus ypx.



Now in quantum mechanics ps are given by the partial derivative px is minus ih bar dou by dou x and likewise for the others. Therefore if you have to write the angular momentum in terms of the components in Lxi plus Lyi these are operators now and this is i is of course is a unit vector so you have to be – you have to remember the difference between the two Lz the operator and this is the unit vector k and this is minus ih bar y dou by dou z minus z dou by dou y of the unit vector i minus ih bar z dou by dou x minus x dou by dou z the unit vector j minus ih bar x dou by dou y minus y dou by dou x the unit vector k.

So now you can see that this is Lx the operator. This is Ly the operator and this is Lz the operator. A relation which I would leave it to you to prove is that an Lx, Ly the commutator of it is equal to ih bar Lz, are they operators? And likewise, Ly, Lz the operator is ih bar Lx and Lz Lx the commutator of that is ih bar Ly. Also remember when you write a commutator A,B this is AB - BA which is minus of BA minus AB and therefore this is minus of the commutator B and A. I have already used the fact if A a constant times B if you take the commutator the constant is outside it's simply the commutator A,B multiplied by the constant.



So these are properties and using this and the definition that the postulate that x,px is ih bar y, py is ih bar, z, pz is ih bar these are all the operators. Therefore the ih bar is actually multiplied by the identity operator if you have to write it carefully. This is the identity operator. This is the identity operator. So with these and with the zero result, x,py that commutator is zero x,pz that commutator is zero and likewise y,px is zero y, pz is zero and z, px is zero. Z, py is zero. With this set you can prove the angular momentum relation I mentioned here namely the relation Lx, Ly the commutator between the two is the commutator of the two is ih bar Lz. The commutator of Ly and Lz gives you ih bar Lx and the commutator of Lz and Lx gives you ih bar Ly. So this is the angular momentum commutation relation.

These are important in spectroscopy in quantum mechanics in the study of scattering phenomena, chemical reactions, rotationally induced chemical dissociation, rotational phenomena; in pretty much all of molecular quantum mechanics. We need to know the angular momentum and the commutation relations between the angular momentum well. We should be able to use them. So in microwave spectroscopy lecture I will say more about it.

$$\left\{\begin{array}{l} [\hat{x}, \hat{p}_x] = i\hbar\hat{1}, \quad [\hat{y}, \hat{p}_y] = i\hbar\hat{1}, \quad [\hat{z}, \hat{p}_z] = i\hbar\hat{1} \\ [\hat{x}, \hat{p}_y] = 0, \quad [\hat{x}, \hat{p}_z] = 0 \\ [\hat{y}, \hat{p}_x] = 0, \quad [\hat{y}, \hat{p}_z] = 0 \quad \text{and} \\ [\hat{z}, p_x] = 0, \quad [\hat{z}, p_y] = 0 \end{array}\right.$$

So these are what I would like to call as the basic what are called algebraic quantities that you should have in mind. The second part to this lecture is eigenvalues and eigenvectors. Let me continue this in the next part.