Chemistry Atomic Structure and Chemical Bonding
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Lecture -11
Expectation Values and Postulates in Quantum Mechanics

Hello welcome back to the lectures in Chemistry on the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am a Professor in the Department of Chemistry in the Indian Institute of Technology, Madras. And my email addresses are given here for you to contact me if you need. This lecture is a continuation of some of the calculations we have been doing, namely on the particle in a one dimensional box as well as the expectation values.

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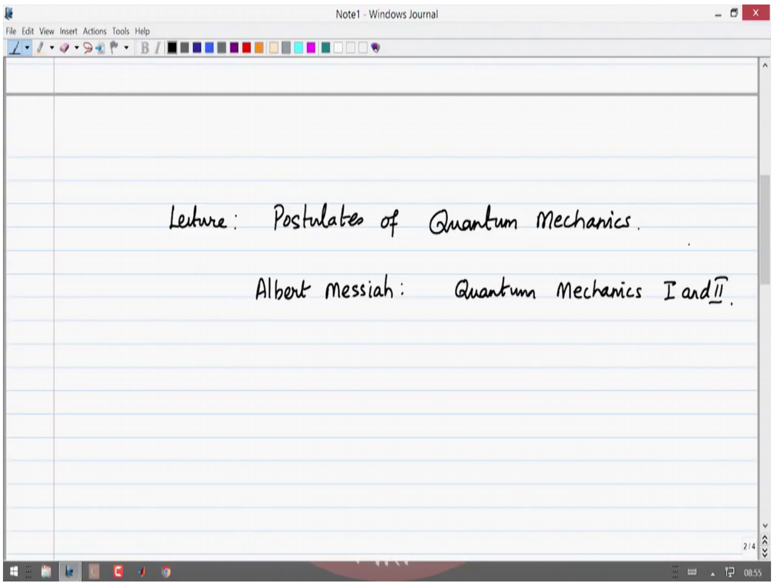

Lecture: Postulates of Quantum Mechanics.

Albert Messiah: Quantum Mechanics I and II.

Go a little bit quicker in the mathematical approach to quantum mechanics or the mathematical methods in quantum mechanics. And let me introduce the postulatory basis of quantum mechanics. And I am helped very much by many text books, but a particular text book that I like a lot, and with which I read and studied quantum mechanics many years ago, as the first topic is the book by Albert Messiah and there are 2 volumes on Quantum Mechanics.

In fact, this is also referred very extensively by another very famous and very thorough, textbook in Quantum Mechanics by Cohen Tannoudji from the from France in quantum mechanics it is a very large volume, and that is of course, if you need to study the topic much more in detail, ok. First few years when quantum mechanics was discussed a lot early 1920s and later. The mathematical basis for quantum mechanics was also studied by many. And one of the developments was to postulate some of the mathematical basis for quantum mechanics, and then apply these postulates also as the fundamental principles of quantum mechanics.

There were 3 or 4 of them postulates which you will find in any textbook, but let me write to them one after the other and explain them in the context of the atomic structure that we are studying now and also using the bracket rotation which I introduced in the mathematics part of this lecture earlier.

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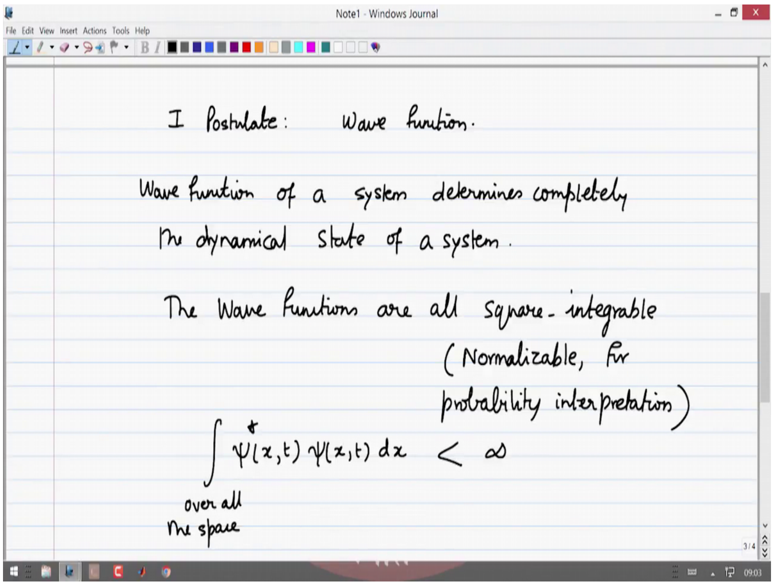

I Postulate: Wave function.

Wave function of a system determines completely the dynamical state of a system.

The Wave functions are all square-integrable (Normalizable, for probability interpretation)

$$\int_{\text{over all the space}} \psi^*(x,t)\,\psi(x,t)\,dx < \infty$$

The first postulate is on wave function. So, the wave function of a system in quantum mechanics, completely describes the dynamics of the system, and the dynamical state of the system. The dynamical state is studied using the equations of motion, but that is another postulate. The wave functions have to have the basic requirement that they are all square integrable or what we are familiar with in terms of the last 2 lectures, they should be normalizable, let me write those things down here.

So, what is meant by this is something that you have already seen; namely, if the wave function is a psi of say x and t it is also time dependent, but we have not talked about the time dependence until now. The x being a representation for all the coordinates that are used to describe the wave function, then this integrals psi star x of t psi x of t dx over all the space available to the system should be finite. This is important in order for the probability interpretation to be meaningful and to be applicable the condition that the square integrable the square of the wave function here being the absolute square of the wave function. Being integrable and giving you a finite value this is what is called the square integrability property.

There are quite a few examples.

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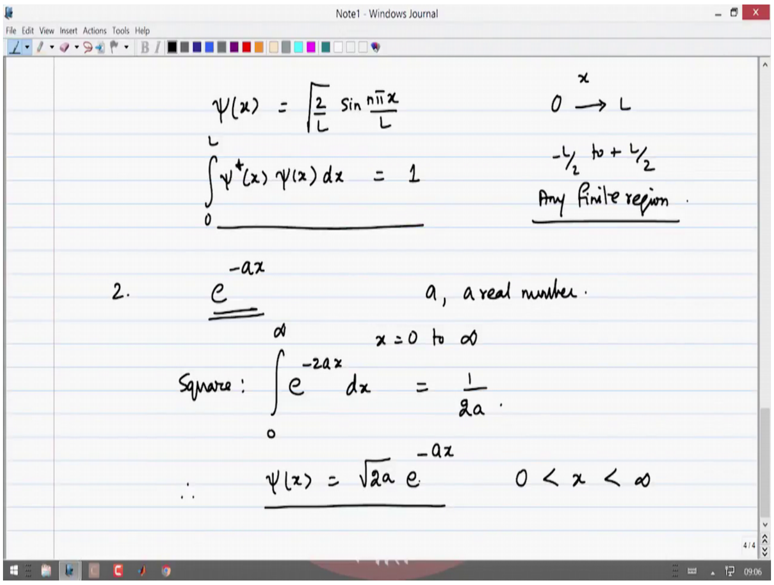

$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$

$\overset{x}{0 \longrightarrow L}$

$\underline{\int_0^L \psi^*(x)\,\psi(x)\,dx = 1}$

$-L/2$ to $+L/2$

Any finite region.

2. $\underline{\underline{e^{-ax}}}$ a, a real number.

$x = 0$ to ∞

Square : $\int_0^\infty e^{-2ax}\,dx = \frac{1}{2a}$.

$\therefore$ $\underline{\psi(x) = \sqrt{2a}\, e^{-ax}}$ $0 < x < \infty$

You have already seen that the particle in a one dimensional box that we have used sin n pi x pi L and we used to the space the finite space of 0 to L for the variable x. So, that is the entire space available to the system x can take all the values between 0 and L. And we found out that when you normalize this to unity you got this particular constant. So, that psi star x psi x overall space namely 0 to L dx is actually 1.

It is a constant, but that constant turns out to be L by 2, if you use only the sin n pi x by L as the wave function, then you divide by the 1 by the square root of the normalizable normalization constant, and we get it therefore, this is a square integrable wave function, ok. You can do that between 0 to L or minus L by 2 to plus L by 2, if you want to be symmetric or any finite region. It is important that you use the finite region of space. You cannot use the entire x axis from minus infinity to infinity and expect to this function to be normalized it does not happen, ok.

Another example of the wave function that we may use from time to time is the function exponential minus ax a real number finite number, between x is equal to 0 to infinity. This function is well defined. And well behaved and you can see that the square integrability here; is e to the minus 2 ax psi star psi, and if you take the integral from 0 to infinity from of e to the minus 2 a x dx if you do this the integral has a value 1 by 2 a. Therefore, therefore, the wave function psi of x is equal to root 2 a e to the minus a x in the interval 0 to infinity. It is a normalized wave function because when you do psi star psi on this you will get.

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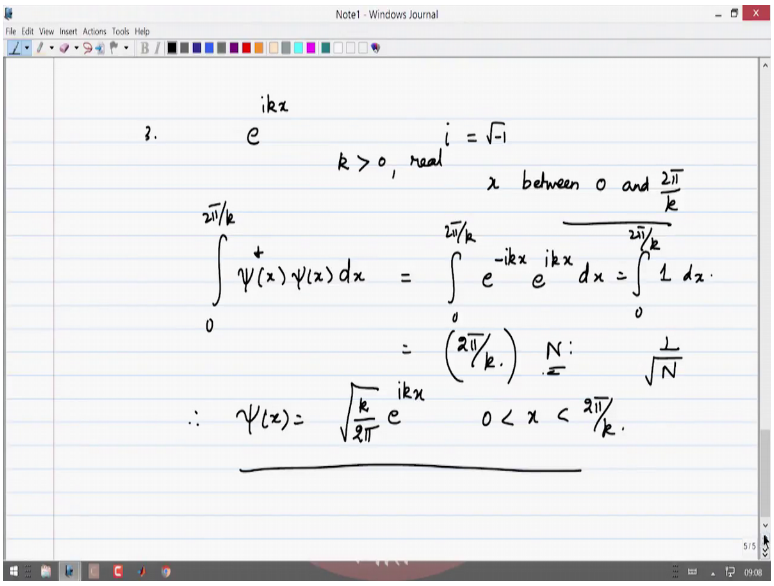

3. e^{ikx} $\quad i = \sqrt{-1}$

$k > 0$, real

x between 0 and $\frac{2\pi}{k}$

$$\int_0^{2\pi/k} \psi^*(x)\,\psi(x)\,dx = \int_0^{2\pi/k} e^{-ikx}\,e^{ikx}\,dx = \int_0^{2\pi/k} 1\,dx.$$

$$= \left(2\pi/k.\right) \qquad \underline{N}: \qquad \frac{1}{\sqrt{N}}$$

$$\therefore \quad \psi(x) = \sqrt{\frac{k}{2\pi}}\,e^{ikx} \qquad 0 < x < 2\pi/k.$$

There is also another important wave function e to the ikx i is square root of minus 1, the imaginary number. And of course, k is a real number greater than 0 and x between 0 and 2 pi by k as a range, because beyond that range this function repeats itself, and you will see this function when you study the particle on a ring. And a solution and the square integrability of this wave function e to the ikx is now carefully to be written with the psi star x psi x dx between 0 and 2 pi by k.

If you do that, then you would see that the answer is 0 to 2 pi by k e to the minus ikx complex conjugate of psi times e to the ikx dx; which is the integral of 1 between 0 and 2 pi by k and the answer is 2 pi by k.

Therefore, the wave function psi of x is equal to square root of k by 2 pi. This is the normalization constant and therefore, the wave function is normalized if you take 1 by root n and you multiply the wave function. So, always that is to be remembered, and then you write e to the ikx in the range 0 x between 2 pi by k is another example of a normalized wave function. And we will see something like that when k is one we will see this as 1 by rho 2 pi.

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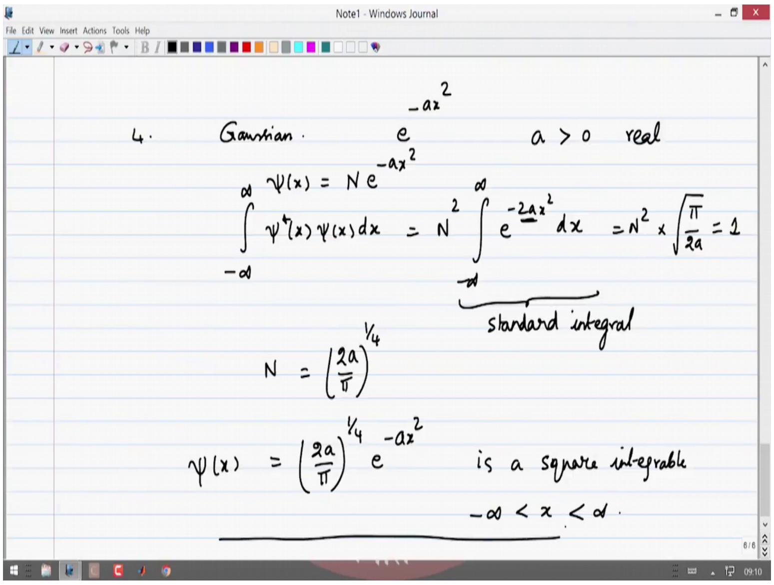

4\. Gaussian. e^{-ax^2} $a > 0$ real

$$\psi(x) = N e^{-ax^2}$$

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = N^2 \underbrace{\int_{-\infty}^{\infty} e^{-2ax^2}\,dx}_{\text{standard integral}} = N^2 \times \sqrt{\frac{\pi}{2a}} = 1$$

$$N = \left(\frac{2a}{\pi}\right)^{1/4}$$

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$$ is a square integrable

$-\infty < x < \infty$.

In the last important example for our problem is the Gaussian wave function, this is the 4th example and the Gaussian wave function is an exponential minus a x square, a is a real constant greater than 0. Then the psi if you write this as the wave function a normalization constant n times e to the minus ax square, then psi star x psi of x d x.

Between minus infinity to plus infinity, the entire range of x over the real axis is permissible now and you have the integral e to the minus 2 a x square, dx between minus infinity to plus infinity, and you know this is a standard integral given in textbooks. And it is something that you might also have to memorize for this course is this integral is 2 pi by 2 a whatever is the constant here.

And therefore, and that should be set to one for normalization, and therefore, n is squared 2 a by pi to 1 by 4, ok. So, the wave function psi of x is equal to 2 a by pi to 1 by 4 e to the minus a x square is a square integrable wave function over the entire x axis the real axis minus infinity x plus infinity. So, these are some examples of the normalized or normalizable or square integrable wave function. And in the quantum mechanics that we would be studying in this course, we would confine ourselves to wave functions which can always be normalized to 1.

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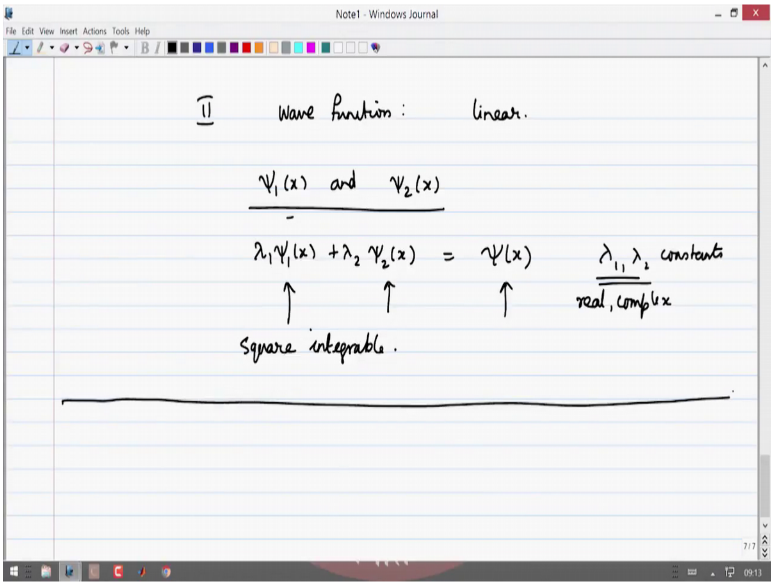

II Wave function : linear.

$\psi_1(x)$ and $\psi_2(x)$

$\lambda_1\psi_1(x) + \lambda_2\psi_2(x) = \psi(x)$ λ_1, λ_2 constants

real, complex

Square integrable.

Second property it is related to the wave function itself the second property for the wave function is it is linear. That is if psi 1 of x and psi 2 of x are 2 solutions to the dynamical equation. Any combination linear combination lambda 1 psi 1 of x plus lambda 2 psi 2 of x will also be your wave function that can be used.

This is linearly combining the 2 wave functions or for that matter not just to any number of them. But they have to be combined as linear, but lambda 1 and lambda 2 as constants. They can be real or complex it does not matter. They have a specific interpretation when we try to normalize this wave function overall, and attribute specific properties to these wave functions as Eigen functions of the operator whatever Hamiltonian or any operator that we deal with. But if the vector space in which we are working mathematically, the vector space contains to any for any 2 functions psi 1 and psi 2 x, it also contains all linear combinations of the 2 wave functions and likewise for infinitely many.

Theses these are also square integrable as long as lambda 1 and lambda 2 are finite. So, this is regarding the postulate of the wave function.

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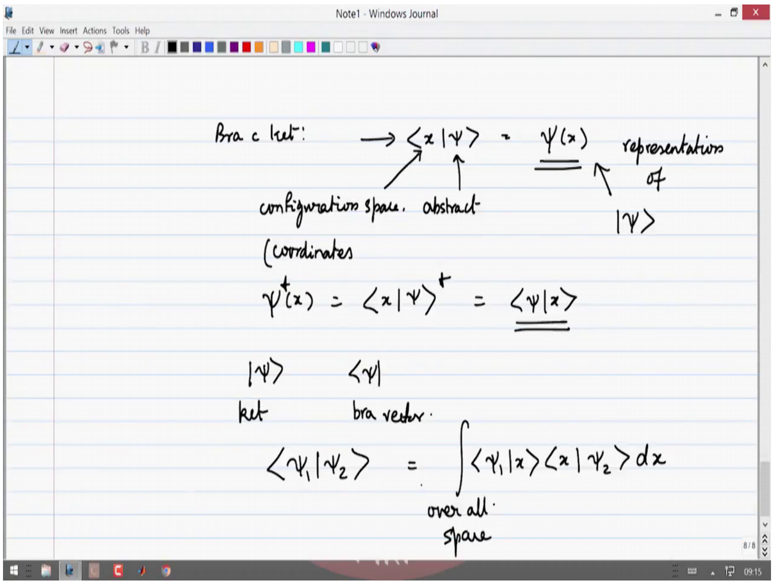

Bra c ket: $\longrightarrow \langle x|\psi\rangle = \underline{\underline{\psi(x)}}$ representation of $|\psi\rangle$

configuration space. abstract

(coordinates

$\psi^{+}(x) = \langle x|\psi\rangle^{+} = \underline{\underline{\langle\psi|x\rangle}}$

$|\psi\rangle$ ket $\quad \langle\psi|$ bra vector.

$$\langle\psi_1|\psi_2\rangle = \int_{\text{over all space}} \langle\psi_1|x\rangle\langle x|\psi_2\rangle\, dx$$

Now, before we move on to the second postulate, that is write down these things using the notation that we are familiar with the bracket notation. The wave function psi of x is actually a number. It is a projection of the abstract vector psi into what is known as the configuration space x; meaning coordinates length position whatever you talk about so, these are coordinates. So, it is the projection of the abstract psi onto the coordinate axis which gives you the wave function psi of x. And we have been working with these wave function still now, but this is the notation for psi of x using the bracket. And psi star of x is quite; obviously, the complex conjugate of this. So, if you want to write the x psi star the complex conjugate is psi x with the bracket reversed.

This is obviously, if this is a ket vector, then you know this is a bra vector. And therefore, if you want to talk about the scalar product of 2 vectors psi 1 and psi 2, in the space of x in which we represent to these wave function. So, you can also call psi 1 of x is a representation of the ket psi, ok. And if you want to take the scalar product of 2 such vectors abstract vectors, they are written using the operator space, that we have earlier introduced except now we are using continuous vector space therefore, what we will have is psi 1 of x x psi 2 dx over all space available.

So, this is the coordinate representation scalar product, and you can recall immediately that this is psi 1 star x, and this one is psi 2 x dx.

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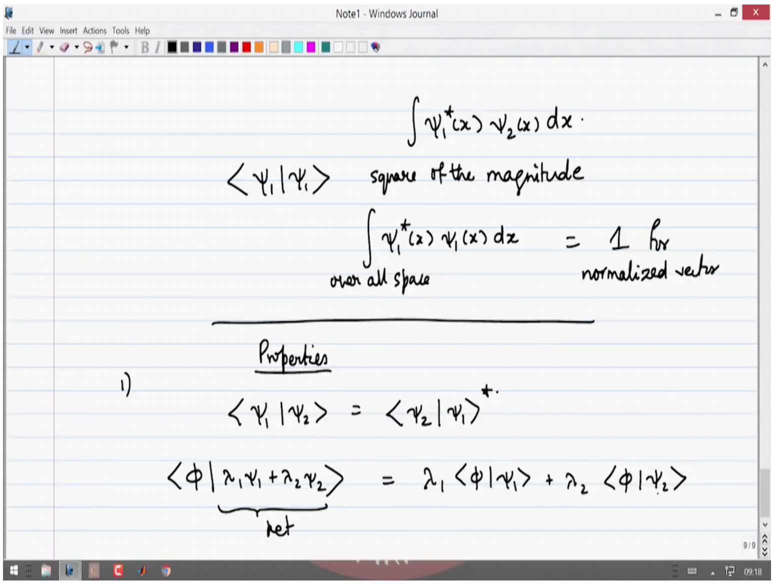

$$\int \psi_1^*(x)\, \psi_2(x)\, dx .$$

$\langle \psi_1 | \psi_1 \rangle$ square of the magnitude

$$\underbrace{\int}_{\text{over all space}} \psi_1^*(x)\, \psi_1(x)\, dx = 1 \text{ for normalized vector}$$

Properties

1) $\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle^* .$

$$\langle \phi | \underbrace{\lambda_1 \psi_1 + \lambda_2 \psi_2}_{\text{ket}} \rangle = \lambda_1 \langle \phi | \psi_1 \rangle + \lambda_2 \langle \phi | \psi_2 \rangle$$

Therefore, the normalization property is now represented by psi 1 psi 1, and this is the square of the magnitude of psi. And if this is normalized, then what it means is that psi 1 star x psi 1 of x dx over all space is 1 for normalized vector.

It is important that you get to use the standard notations of the vector space quantities the vectors the wave functions, in configuration space in momentum space on in any other coordinate space that we have; therefore, the x is a symbolic representation of the space in which we consider the wave functions, but the wave functions are basically ket vectors in an abstract space known as the Hilbert space, but we will not worry so much about that, but this notation is important to keep in mind,.

Now, we will move on to the second postulate, ok before that a few properties of this needs to be looked at. So, let us write them down properties. The first one is something you have already seen namely psi 1 psi 2, also defines the complex conjugate of this psi 2 psi 1 star. Likewise, the scalar product of any linear combination lambda 1 psi 1 plus lambda 2 psi 2, if you write that, and if this is a ket vector the linear product linear combination leads to the scalar product lambda 1 phi psi 1 plus lambda 2 phi psi 2, ok.

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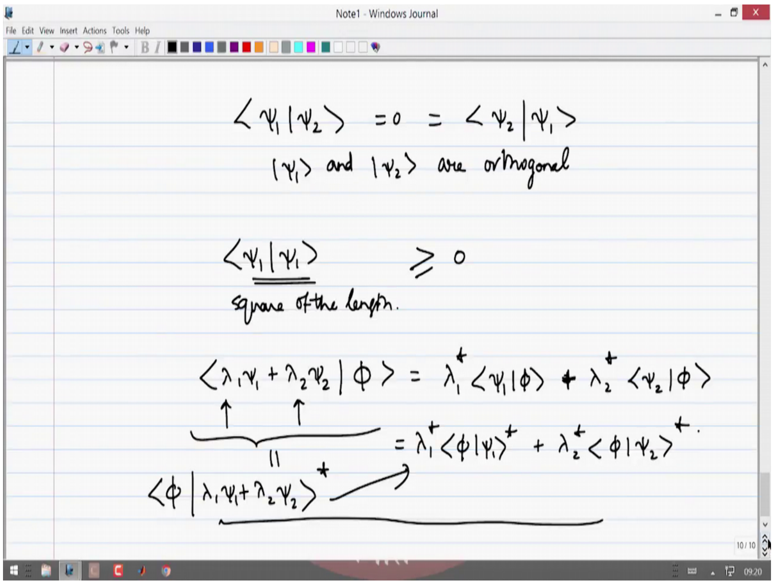

$$\langle \psi_1 | \psi_2 \rangle = 0 = \langle \psi_2 | \psi_1 \rangle$$

$|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal

$$\underline{\underline{\langle \psi_1 | \psi_1 \rangle}} \geq 0$$

square of the length.

$$\underbrace{\langle \underset{\uparrow}{\lambda_1 \psi_1} + \underset{\uparrow}{\lambda_2 \psi_2} | \phi \rangle}_{\parallel} = \lambda_1^{\dagger} \langle \psi_1 | \phi \rangle + \lambda_2^{\dagger} \langle \psi_2 | \phi \rangle$$

$$= \lambda_1^{\dagger} \langle \phi | \psi_1 \rangle^{\dagger} + \lambda_2^{\dagger} \langle \phi | \psi_2 \rangle^{\dagger}.$$

$$\underline{\langle \phi | \lambda_1 \psi_1 + \lambda_2 \psi_2 \rangle^{\dagger} \nearrow}$$

If 2 vectors psi 1 and psi 2 or such that that this is 0 and therefore, the complex conjugate is also 0, then vectors psi 1 and psi 2 are orthogonal. The scalar product or the norm of a vector this is a square of the length or the magnitude as you call it is always greater than or equal to 0 if the vectors are the same.

Now, another important property is what if the linear combination is a bra vector, if you do that the coefficients or the bra vector if you recall the postulates the bracket notation earlier the coefficients come out as complex conjugates lambda 1 star then you have psi 1 phi plus lambda 2 star psi 2 or phi ok.

And you know this is nothing other than lambda 1 star, phi psi 1 star plus lambda 2 star phi psi 2 star. And you know this is the complex conjugate of this product lambda 1 psi 1 plus lambda 2 psi 2 star. These 2 are equal, and you can see therefore, this is the same thing as taking the lambda 1-star psi 1-star phi psi 1 star and likewise. So, these are properties which are important when we calculate the wave functions they are normalization constants they are orthogonal properties and so on, ok.

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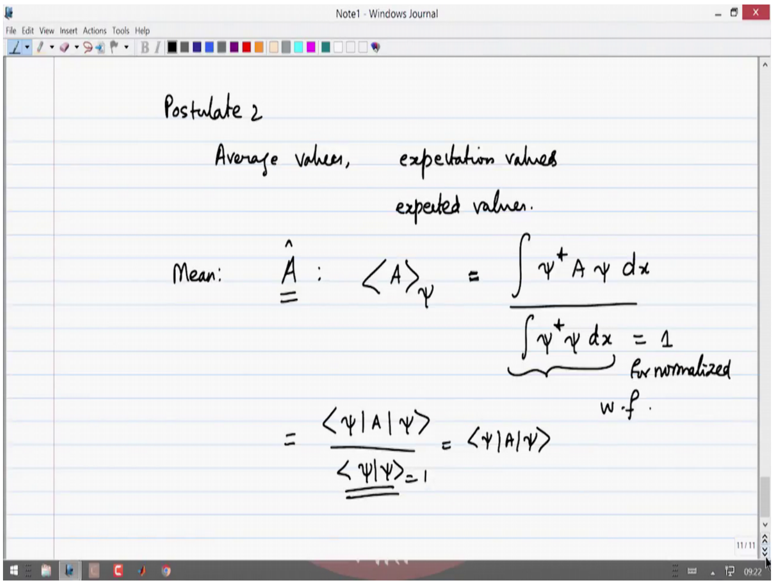

Postulate 2

Average values, expectation values

expected values.

Mean: $$\underset{=}{\hat{A}} : \langle A \rangle_{\psi} = \frac{\int \psi^{*} A \psi \, dx}{\underbrace{\int \psi^{*} \psi \, dx} = 1}$$

for normalized w.f.

$$= \frac{\langle \psi | A | \psi \rangle}{\underline{\underline{\langle \psi | \psi \rangle}} = 1} = \langle \psi | A | \psi \rangle$$

So, let us move on to postulate 2. Postulate 2 is on the average values or what are known as the expectation values or expected values. So, the mean value or what is called the average value of any quantity which is measurable in quantum mechanics experimentally is represented by an operator a such that the measurement of that property in the state psi of that system is given by this definition psi star A psi dx I am writing dx as for the integral over all the configurational space quantities divided by psi star psi dx. And if the wave function is normalized this is usually 1 for normalized wave function.

So, to write this in the bracket notation this will be psi A psi divided by psi psi; which is psi A of psi, as long as this is normalized unit.

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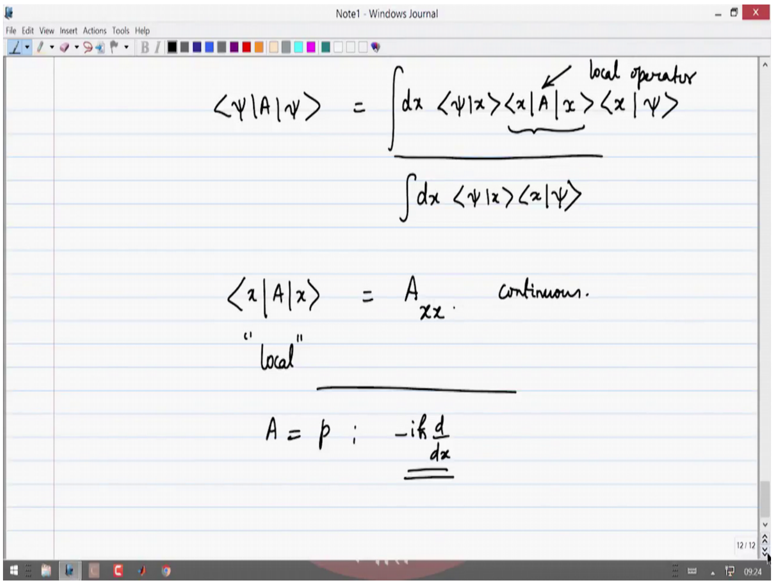

$$\langle\psi|A|\psi\rangle = \frac{\int dx\, \langle\psi|x\rangle \underbrace{\langle x|A|x\rangle}_{} \langle x|\psi\rangle}{\int dx\, \langle\psi|x\rangle\langle x|\psi\rangle}$$

local operator

$$\langle x|A|x\rangle = A_{xx} .$$

continuous.

"local"

$$A = p \; ; \quad \underline{\underline{-i\hbar \frac{d}{dx}}}$$

So now, you can see immediately that if we write this quantity psi A psi using our notation of the configuration space this integral is dx psi x x A x x psi divided by integral dx psi x x psi,. These operators are called local operators position, momentum, all these things that we study the dipole moment and all the properties that we normally represent physical properties for a molecular system or on atomic system. They are usually considered to be local operators. And therefore, if you recall this is like the matrix element of the operator A is the matrix element A x x; with a slight difference that x can take any values therefore, the matrix is not only infinite dimensional, but it is also the labels like 1 2 3 4 for columns and rows is A is a bit difficult.

So, this is a continuous space, these are all generalizations. So, this is called the local property local operators, and there are non-local operators, but we will not concern ourselves. Therefore, when you write the integral for example, for A is equal to p the integral is written using minus ih bar d by dx; which is the operator representation.

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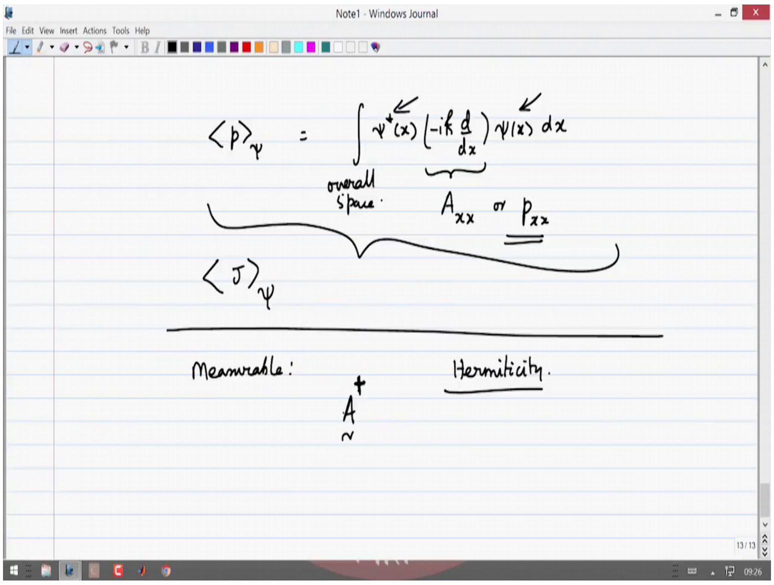

$$\langle p \rangle_{\psi} = \underset{\text{overall space.}}{\int} \psi^{*}(x) \underbrace{\left(-i\hbar \frac{d}{dx}\right)}_{A_{xx} \text{ or } \underline{\underline{P_{xx}}}} \psi(x)\, dx$$

$$\langle J \rangle_{\psi}$$

Measurable :

$$\underset{\sim}{A}^{+}$$

Hermiticity.

Therefore, if you expect if you calculate the expectation value of p of psi, it should be psi star of x minus ih bar d by dx psi of x dx between overall space.

Now, recall that this is the equivalent of A x x or P x x this is the local property, ok. Now, for the examples of the particle in a one dimensional box we saw that this answer is 0, but if you have to calculate instead of momentum you calculate the angular moment for the particle on a ring. You will see that for certain wave functions this number is not 0, it is a very precise value. Therefore, depending on the form of the wave function psi of x, it is possible for us to have an average value for the momentum of the particle which means that the momentum is nonzero.

But for the one dimensional 2 dimensional box problems and also for the harmonic oscillator that we will study, we will see that the linear momentum for eigenfunctions of the Hamiltonian is always 0. But this is the general representation for the matrix element or the calculations of the expectation values of the operator, ok. Since we consider only measurable quantities, the operators all have a specific property known as Hermiticity, ok. Let us first define the Hermitian adjoint of an operator A dagger by the following.

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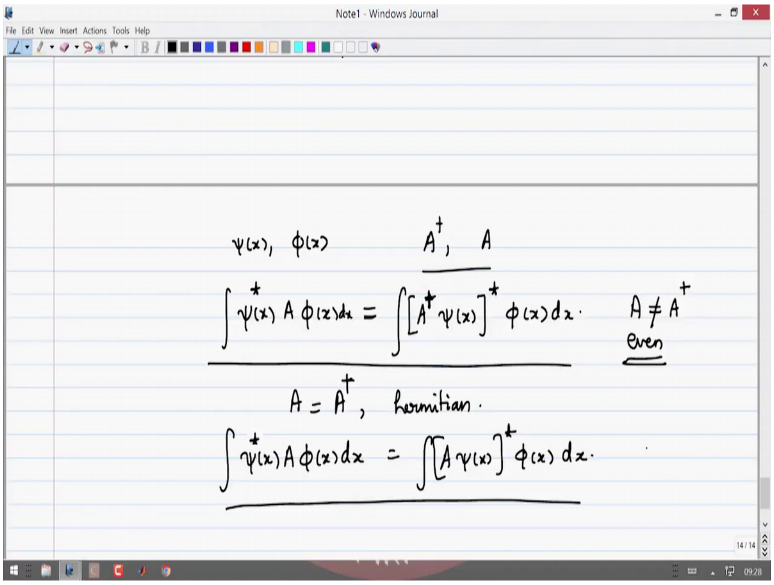

$\psi(x), \quad \phi(x) \qquad \underline{A^{\dagger}, \quad A}$

$$\underline{\int \psi^{*}(x)\, A\, \phi(x)\, dx = \int \left[A^{\dagger}\psi(x)\right]^{*} \phi(x)\, dx.} \qquad A \neq A^{\dagger} \ \underline{\text{even}}$$

$$A = A^{\dagger}, \ \text{hermitian}.$$

$$\underline{\int \psi^{*}(x)\, A\, \phi(x)\, dx = \int \left[A\,\psi(x)\right]^{*} \phi(x)\, dx.}$$

For any 2 wave functions psi of x phi of x which is permissible within the space that we are studying, the Hermitian adjoint of the operator A dagger A is defined as follows. Psi of star x A phi of x is always equal to A dagger psi of x star phi of x dx dx.

This is always true even if the operator is not Hermitian, ok. This is the definition of the Hermitian adjoint. The operator sandwiched between 2 wave functions psi and phi on the left hand side, and the Hermitian adjoint is acting on the wave function the left wave function, but the product is taken as a complex conjugate multiplied by the right hand wave function phi of x dx, this is now 2 operators a and A dagger or equal Hermitian if the following were true namely psi of x A phi of x dx is A psi of x star phi of x dx.

Therefore, A dagger is now replaced by A this definition holds and then we say that the operator is Hermitian. And all quantum mechanical measurable quantities like position momentum, angular momentum, dipole moment, electric quadrupole moment the polarizability in spectroscopy; practically all the quantities that you calculate in quantum mechanics, for the atomic and molecular properties electron density everything is a Hermitian operator is represented by a Hermitian operator.

Therefore, the Hermitian operator is something that you have to be very clear. It is easy to understand the Hermitian operator from the matrix viewpoint, because what you have seen is the definition of A.

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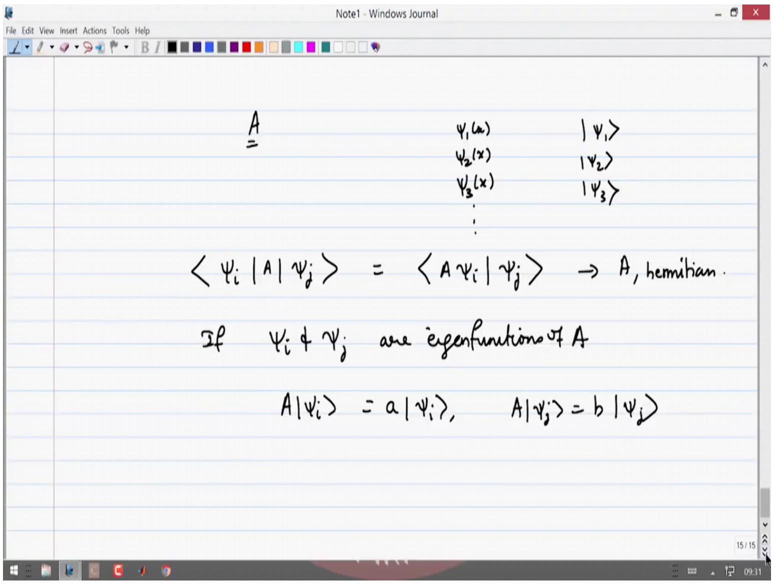

$\underset{=}{A}$

$\psi_1(x)$ $|\psi_1\rangle$

$\psi_2(x)$ $|\psi_2\rangle$

$\psi_3(x)$ $|\psi_3\rangle$

$\vdots$

$\langle \psi_i | A | \psi_j \rangle = \langle A\psi_i | \psi_j \rangle \rightarrow A$, hermitian.

If ψ_i & ψ_j are eigenfunctions of A

$A|\psi_i\rangle = a|\psi_i\rangle, \quad A|\psi_j\rangle = b|\psi_j\rangle$

If you go back in the basis psi phi 2 different labels therefore, if you have many basis functions, psi 1 of x psi 2 of x psi 3 of x, or in the vector notation psi 1 psi 2 psi 3 and so on, then the Hermitian operator is given by this property phi. So, sorry we have psi so, let us write them is using psi i A psi j is now A psi i psi j.

If psi i and psi j are eigenfunctions, if are eigenfunctions of A this is for a Hermitian. Then what we have is A psi i gives you some eigenvalue times psi i A psi j gives you some another eigenvalue b times psi j.

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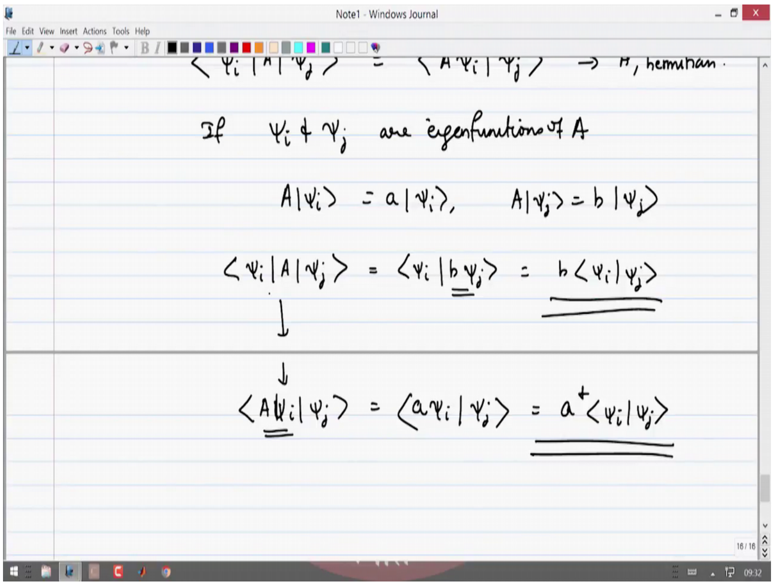

$\langle \psi_i | A | \psi_j \rangle = \langle A\psi_i | \psi_j \rangle \rightarrow A$, hermitian.

If ψ_i & ψ_j are eigenfunctions of A

$A|\psi_i\rangle = a|\psi_i\rangle, \quad A|\psi_j\rangle = b|\psi_j\rangle$

$\langle \psi_i | A | \psi_j \rangle = \langle \psi_i | \underline{\underline{b}}\psi_j \rangle = \underline{\underline{b\langle \psi_i | \psi_j \rangle}}$

$\downarrow$

$\langle \underline{\underline{A\psi}}_i | \psi_j \rangle = \langle a\psi_i | \psi_j \rangle = \underline{\underline{a^{+}\langle \psi_i | \psi_j \rangle}}$

And then you can see immediately that psi i A psi j is given by psi i with the constant A sorry this is a b b psi j, and since this is a constant we can take it out and it is on the ket therefore, we can take the constant as this b psi i psi j.

Now, if the operator is Hermitian then this is A psi i psi j, these 2 are equal, ok. And that gives you a psi i psi j. Because the eigenfunction psi i for the operator a has the eigenvalue a and therefore, this is a star, psi i psi j. These are some examples of how to manipulate the wave functions and hermiticity property of an operator using the ket bra notation.

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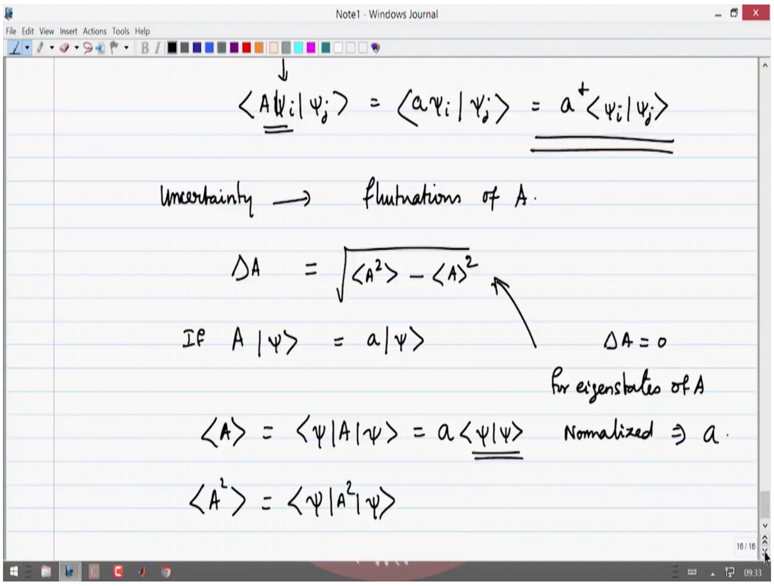

$$\langle A\underline{\underline{\psi_i}}|\psi_j\rangle = \langle a\psi_i|\psi_j\rangle = \underline{\underline{a^{+}\langle\psi_i|\psi_j\rangle}}$$

Uncertainty → fluctuations of A.

$$\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}$$

If $A|\psi\rangle = a|\psi\rangle$

$\Delta A = 0$

for eigenstates of A

$$\langle A\rangle = \langle\psi|A|\psi\rangle = a\underline{\underline{\langle\psi|\psi\rangle}}$$

Normalized ⇒ a.

$$\langle A^2\rangle = \langle\psi|A^2|\psi\rangle$$

Now the last thing regarding the operator is what is known as the uncertainty in the measurement, or what are known as fluctuations in the values for A ok.

The uncertainty delta A is given by the square the average of the square of the operator minus the square of the average; however, if psi is an eigenfunction of the operator A giving you an eigenvalue A psi, then you can see immediately the following delta a goes to 0, for eigenstates of A. It is easy to calculate, because you know what is the average value? A is psi A psi, and this is the constant a times psi, psi and let us assume that this is normalized and therefore, the answer is a a. What is the A square average? A square average is psi A square psi.

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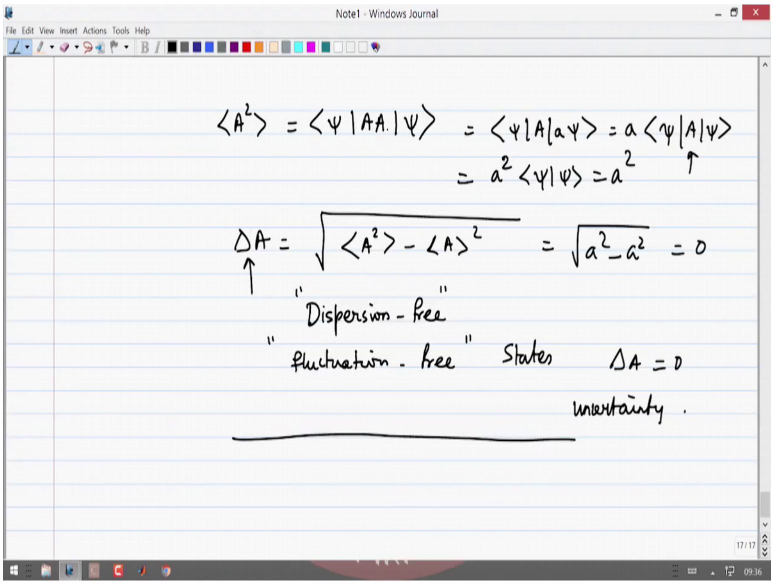

$$\langle A^2 \rangle = \langle \psi | AA | \psi \rangle = \langle \psi | A | a\psi \rangle = a \langle \psi | A | \psi \rangle \uparrow$$

$$= a^2 \langle \psi | \psi \rangle = a^2$$

$$\underset{\uparrow}{\Delta A} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} = \sqrt{a^2 - a^2} = 0$$

"Dispersion - free"

"fluctuation - free" States $\Delta A = 0$

uncertainty.

And that is easy to see immediately that if you write to this A square as psi A A psi as you have done with the p square operator. You remember minus ih bar d by dx, minus ih bar d by dx for the particle in a one dimensional box was written as minus h bar square d square by dx square. The kinetic energy times 2 m the mass.

So, if you write this then you see immediately that this is psi A A psi and that is taken out to give you psi A psi. And this will give you one more a therefore, it gives you a square psi. And therefore, it is equal to a square.

So, it is immediate therefore, to see that the delta A which is the difference between the A square average and the average of the squared is A square minus A square, therefore this is 0. Therefore, the eigenstates of any operator are such that the uncertainty in the measurement of the eigenvalue delta A is always 0, ok. These are called dispersion free states or fluctuation free states fluctuation free states.

The uncertainty delta A is 0, this is only true for the eigenstates of any operator. Therefore, if you take 2 operators delta a and a and b, and if you calculate the uncertainties of delta a and delta b and take the product delta a will be 0, and delta b will be 0 only if a and b both have the same eigenfunctions. Therefore, it is important that the uncertainty principle in general can be generalized to operators which do not have simultaneously the same eigenstates. We will see more of those things as we go along, but I have already introduced to this idea that uncertainty can be generalized using what is known as the non-commutation between the 2 operators and such relations are quite unknown, ok.

But for the present discussion these definitions and the introduction of the postulates is what you have to keep in mind.

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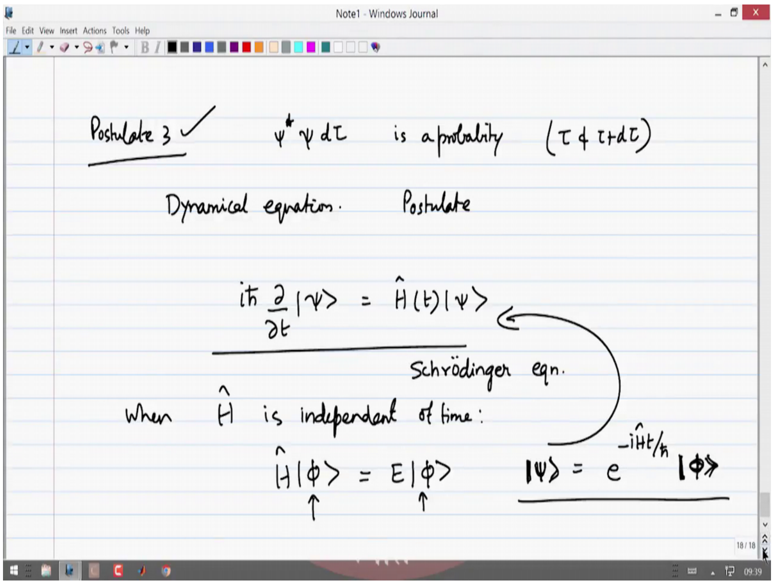

Postulate 3 ✓ $\psi^* \psi \, d\tau$ is a probality $(\tau \,\&\, \tau + d\tau)$

Dynamical equation. Postulate

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H}(t) |\psi\rangle$$

Schrödinger eqn.

When $\hat{H}$ is independant of time:

$$\underset{\uparrow}{\hat{H}} |\phi\rangle = \underset{\uparrow}{E} |\phi\rangle \qquad |\psi\rangle = e^{-i\hat{H}t/\hbar} |\phi\rangle$$

The third postulate is something that you already know, the definition of the wave function entails that psi star psi d tau is a probability. For finding the system between tau and tau plus d tau of the system, ok. This is actually postulate one in the definition of the wave function, the wave function is defined such that psi star psi dx must be a probability, but it is also sometimes the represented as a separate postulate.

But the more the last one the most important postulate is the dynamical equation. This is an extremely useful postulate. We will not solve this equation, but the dynamical equation for the wave function for any system with the Hamiltonian H is given by d psi by dt. Well, to be precise I should write the partial derivative dou by dou t of psi is the Hamiltonian which may or may not depend on time; when H is independent of time, we have seen this earlier also that we study the equation h some wave function phi is equal to e of that wave function phi.

So, that the phis or eigenvalues of the Hamiltonian operator with the eigenvalues E and the connection between psi and phi in such case is the operator e to the minus iht by h bar, acting on phi gives you the time dependent solution that you have for this problem.

These 2 are not the same wave functions, ok. The wave function here depends on the time the wave function phi does not depend on the time, but it has the factor associated with it which is obtained by putting in the eigenvalues of the Hamiltonian in here. And we have probably even an assignment problem that you have solved earlier; that this is nothing other than psi.

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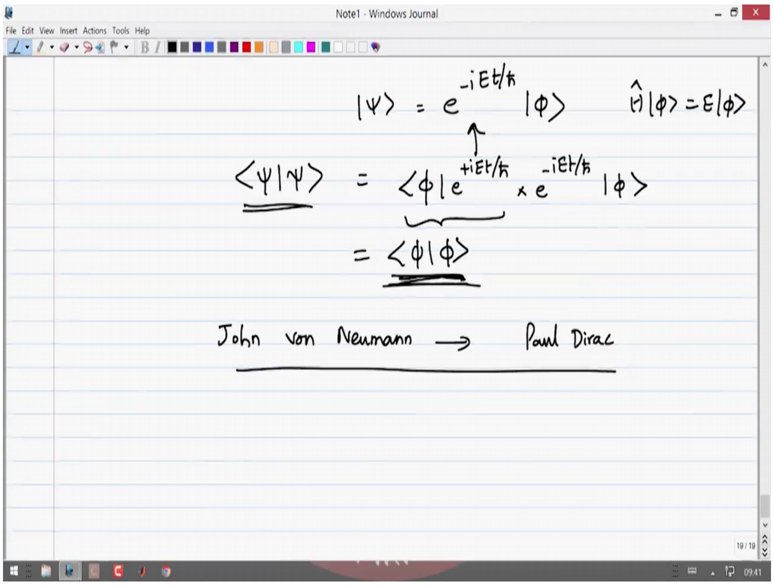

$$|\psi\rangle = e^{-iEt/\hbar}|\phi\rangle \qquad \hat{H}|\phi\rangle = E|\phi\rangle$$

$$\underline{\underline{\langle\psi|\psi\rangle}} = \langle\phi|\underbrace{e^{+iEt/\hbar} \times e^{-iEt/\hbar}}|\phi\rangle$$

$$= \underline{\underline{\langle\phi|\phi\rangle}}$$

John Von Neumann → Paul Dirac

This is nothing other than e to the minus i e t by h bar of phi, provided that h on phi gives you e on phi.

So, there is a time dependent factor; however, if you calculate to the probability density or the normalization factor psi, you will see that the ket is e to the plus i t by h bar, because this is a complex conjugate. And then you have the bra this is the bra state and the ket state is e to the minus iet by h bar phi. And so, you can see that this is nothing but phi. Therefore, for time independent Hamiltonians the probability density and the normalization factor do not depend on time, they are both given by the same normalization factor m.

So, these postulates are important to keep in mind. You will have to go back to these things as the fundamental mathematical basis. This is a very preliminary non descriptive, I mean mathematically it is not a very descriptive form it is more in English words. The postulatory basis is often invoked in the mathematics of the linear vector spaces the mathematics of the operators, that is a whole branch of mathematics which builds on the foundations of quantum mechanics, which was first put forward by 2 very famous people.

Professor Von John Von Neumann, and in a lot of this mathematical basis is also found in the book by Paul Dirac. These are 2 of the most illustrious founding fathers of quantum mechanics and who provided a considerably detailed mathematical representations for the wave functions quantum mechanics.

I only introduce this to you in a brief form. We will stop this we will not look at it, but remember the bracket notation is something that we will use quite often in the later lectures. So, please keep this in mind, we will meet again with the next week's assignment. Until then,

Thank you very much.