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Chemistry I
Introduction to Quantum Chemistry
And Molecular Spectroscopy

Lecture – 13
Particle in a One-dimensional Box: Part III
Expectation Values and
Postulates in Quantum Mechanics

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Welcome back to the lecture, we continue from what was there in the last lecture on the Heisenberg's uncertainty principle, and I introduced a simple quantity called the average value or the expectation value.
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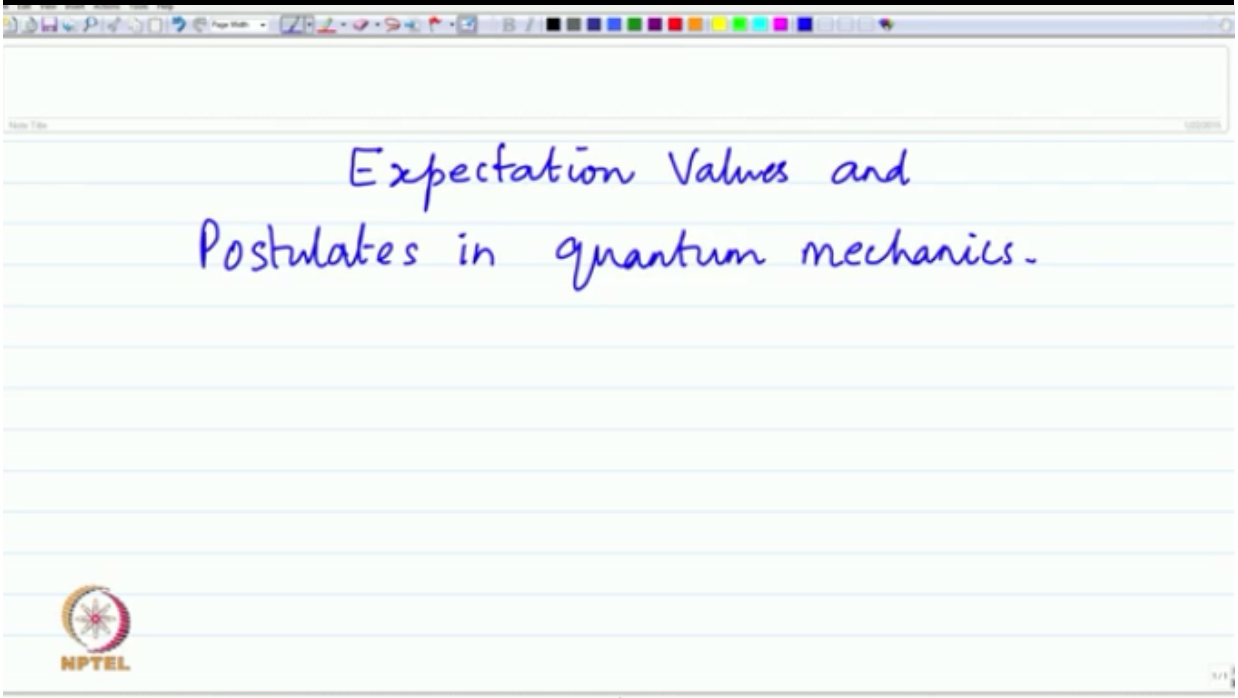

So in this part of the lecture we will consider the formal definition for expectation values in quantum mechanics, and if time permits I shall talk more about the postulatory basis that is basis with which mathematically we can start that, these are the starting points and then quantum mechanics we can build, that's called the postulatory basis, and the postulatory basis in

quantum mechanics will also be stated in very simple terms. The postulates or mathematical in nature, but we will see simple explanations hopefully, okay.

First one is the expectation value, it is denoted by the average value bracket for any quantity, the average value is in general calculated according to the standard prescription that if there are N measurements, and these things happen with different outcomes for the measured quantity A with values A1, A2, AN
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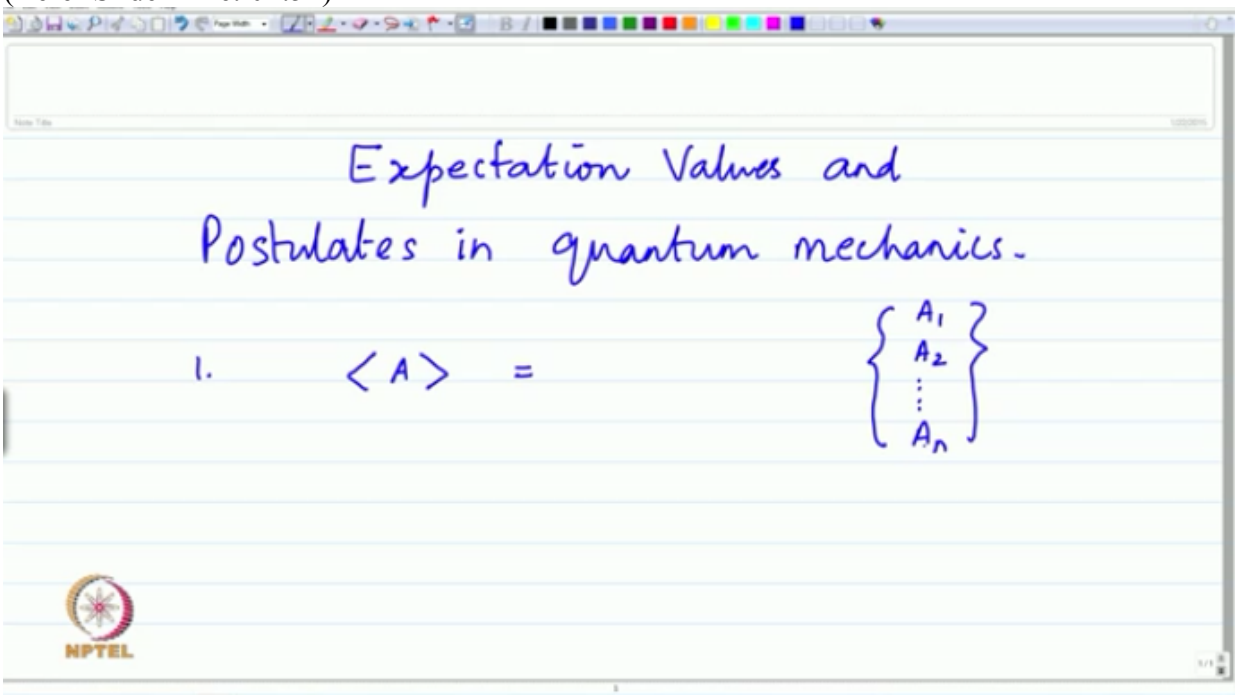

for different measurements then you know that the average is nothing but the sum over I = 1 to N AI divided by N.

Now on the other hand suppose you have A1 occurring N1 times in an experiment repeated many many times, A2 occurring N2 times let me change N1, N2 to something else which is standard, okay P1 times P2 times and likewise AN and these are the only possible values,
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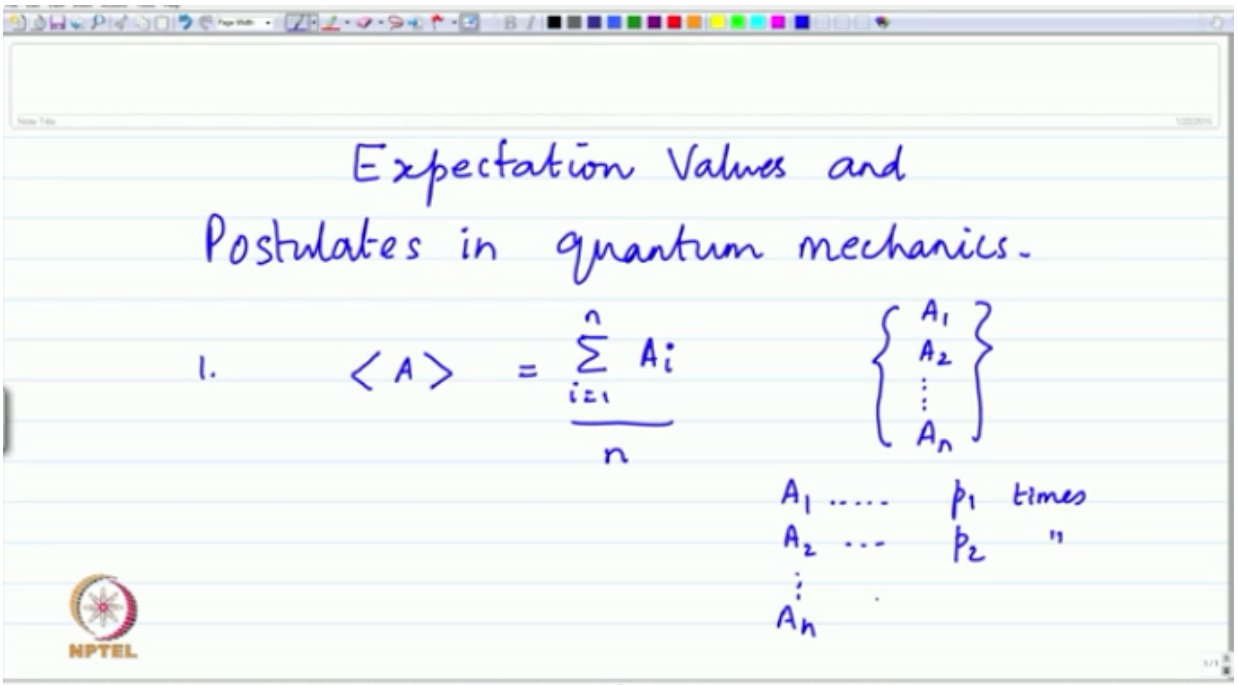

let's see these are the only outcomes that you have occurs PN times, then the average is calculated by adding all the A1,

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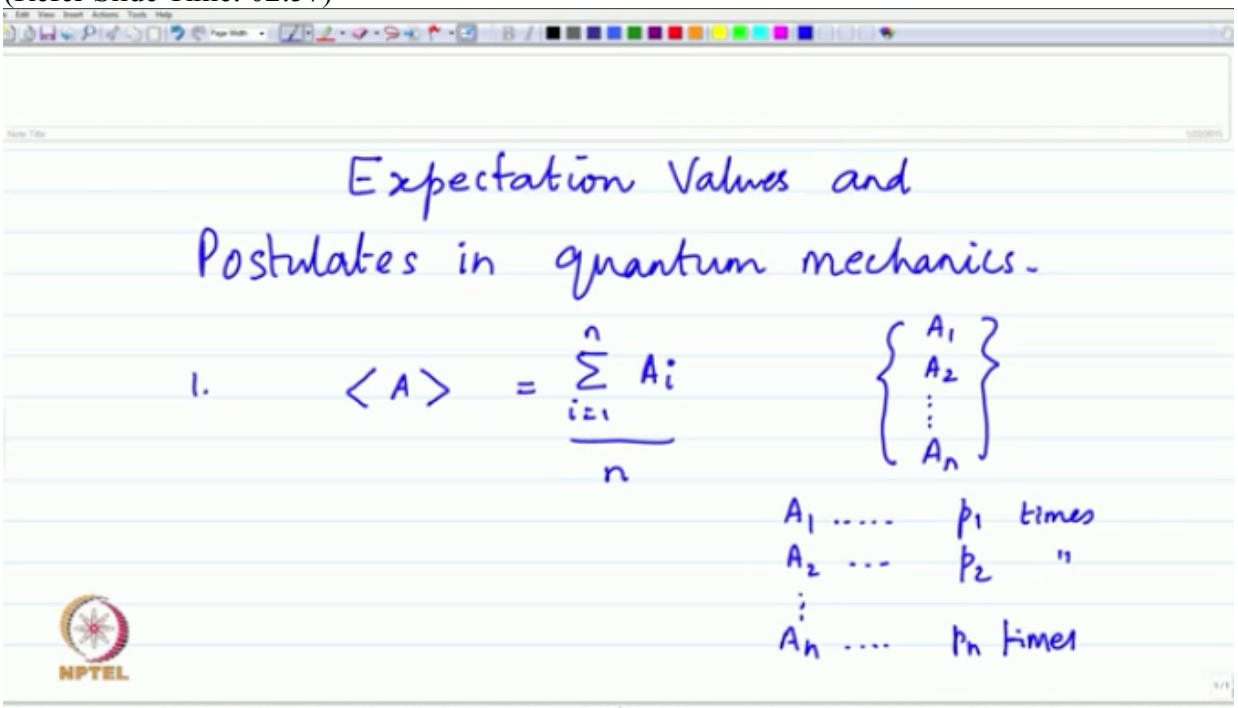

so the average is calculated by adding all the A1, P1 times, and adding A2 which has happened P2 times, and likewise adding all the AN's which have occurred PN times dividing by P1, P2, P3 up to PN okay,

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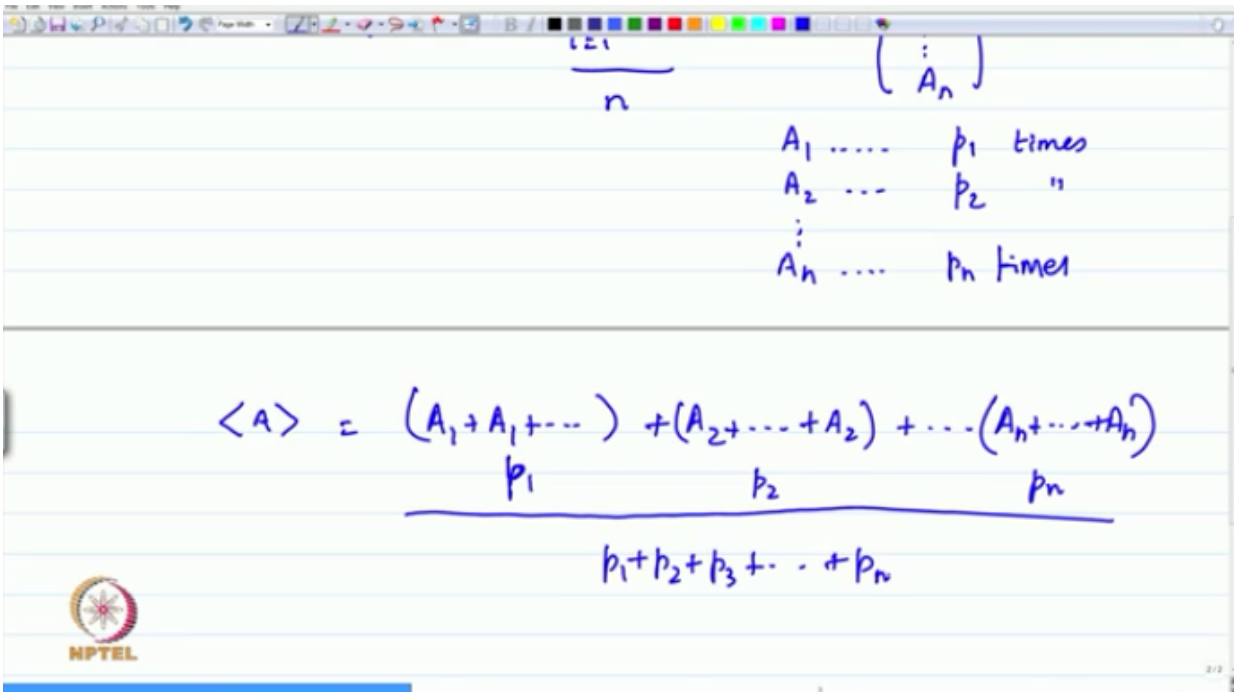

this is also the standard way in which you can calculate the averages if some values repeat many times then you want to find out how many times that it is repeated, what's the probability that that value is repeated and so on.

Now the same thing can now be written by writing A1 x P1/P, okay where P is the sum of all of the experiments PI and therefore P1/P gives you the probability that you got A1 for the measurement of A and likewise A2 x P2/P which is the probability that you have the outcome A2 and so on, therefore you have AN PN/P okay, so this is a probability

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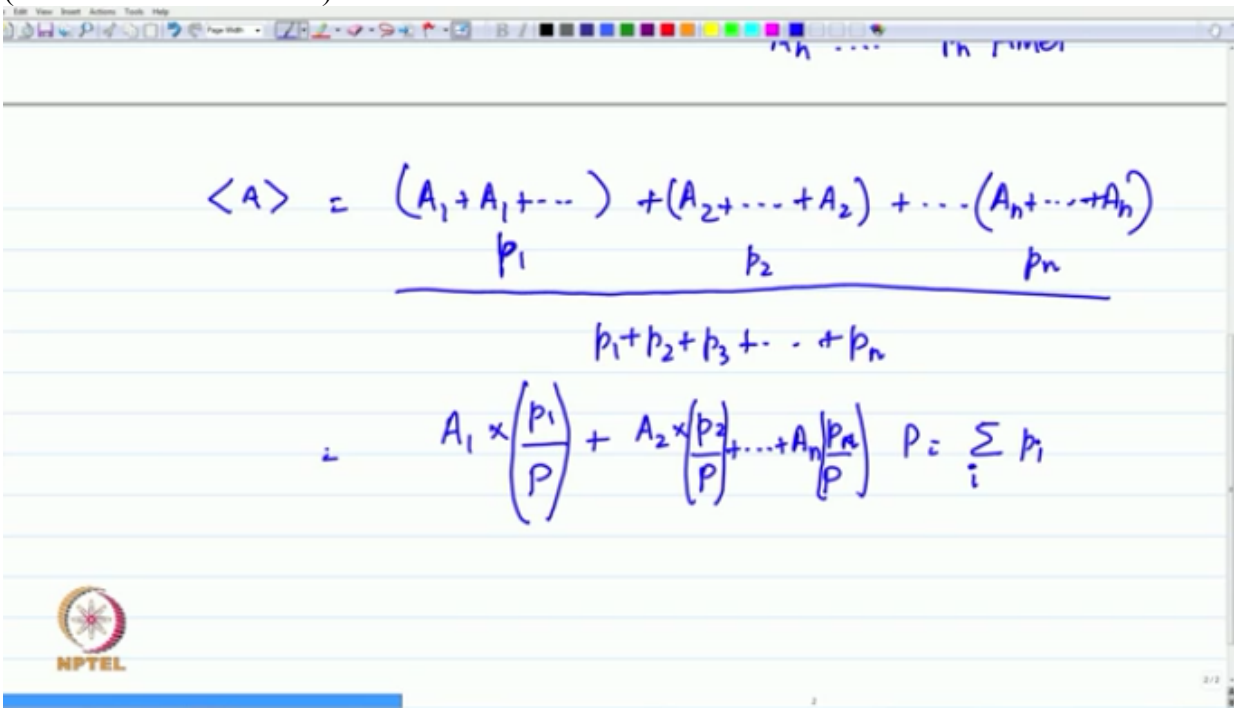

within brackets that a given value occurs and then what's the average when you do this experiment many many times, this is standard way of representing probabilities and in quantum mechanics. you remember sai star sai represents the probability density for the system at a given coordinate or at a given moment on the variable X in particle in a 1 dimensional box you talk about the sai star sai DX as the probability that the system is in the space between X and X + DX.

And in two dimensions sai star sai DX DY talks about the probability that the system is in the area DX DY which is enclosed between X and X + DX and Y and Y + DY that's what it is, and therefore sai star sai is a sort of a probability and then what you have is the measured value whatever that you measure, you measure the energy or you measure the position you measure the momentum does not matter some experimentally observable quantity for which the reason operator associated with that in quantum mechanics, the measured value gives you the value with that probability and then the average value is the sum of all of those things, the measured value times the probability that it happens summed over all such possible measured values, therefore technically if you are looking at A as a function of X, because please remember this is a continuous function, therefore A is defined for each and every value of X, so what you think is it's like sai star sai which is the probability times the value AX that happens with the X DX provided sai star sai represents the probability density which means this integral sai star sai DX should be equal to 1, okay, should be equal to 1,

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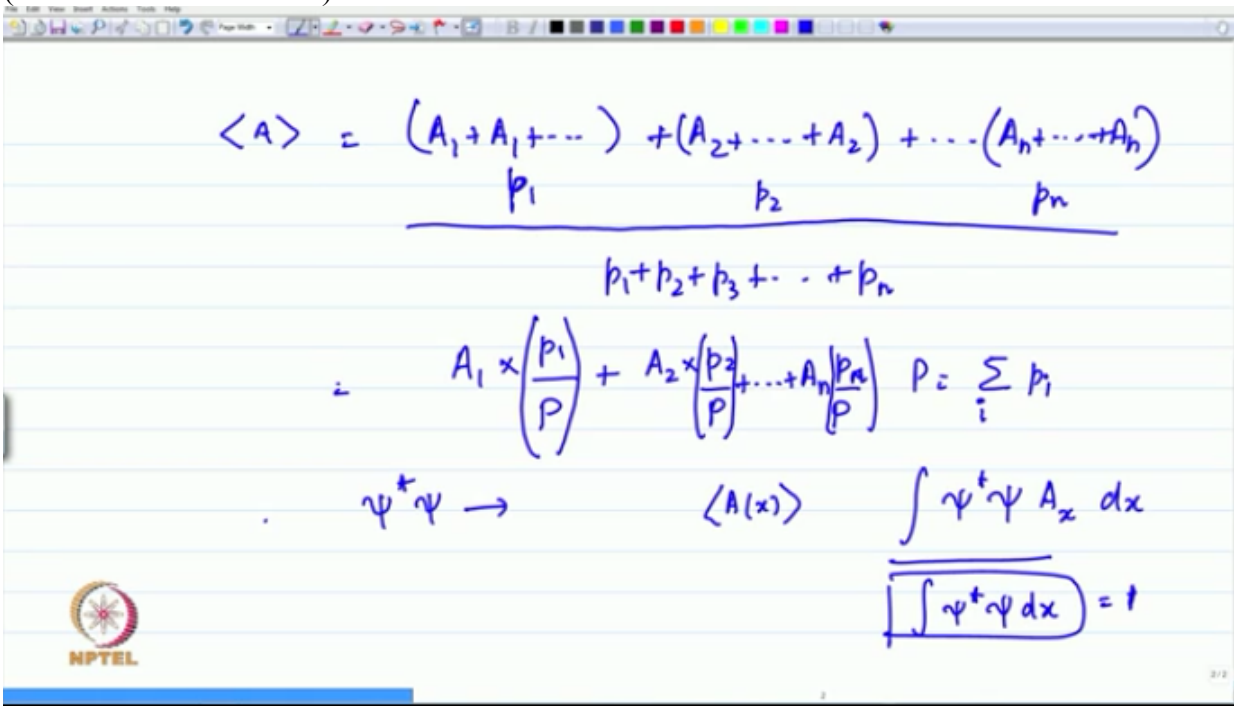

so if you represent this by probability density in quantum mechanics the average value A is the probability times the value that happens with that probability summed over but with one small technical difference namely that the operator corresponding to A acting on sai giving you the measured value, and therefore the measured value times the sai star sai is represented by this quantity divided by integral sai star sai DX, which of course is set to 1 if we think of sai star sai as the probability, so this is the formal definition for the expectation value and this A is the

operator associated with the measured quantity, the physical property called A, this is the physical property.

And this quantity is the mathematical representation or a quantum mechanical representation, quantum mechanical representation of that physical property, okay, you already know because the case of momentum for example the operator associated with P is -IH bar D/DX for one dimension, and what is the operator for the position? It is just the X itself.

What's the operator for the energy? You have already seen that it is the Hamiltonian operator or C operator associated with angular momentum it's a vector and has 3 components in 3 dimensions or in N components in N dimensions so if you write to that in say 3 dimensions you have 3 components and each one of them is represented by a corresponding operator which is
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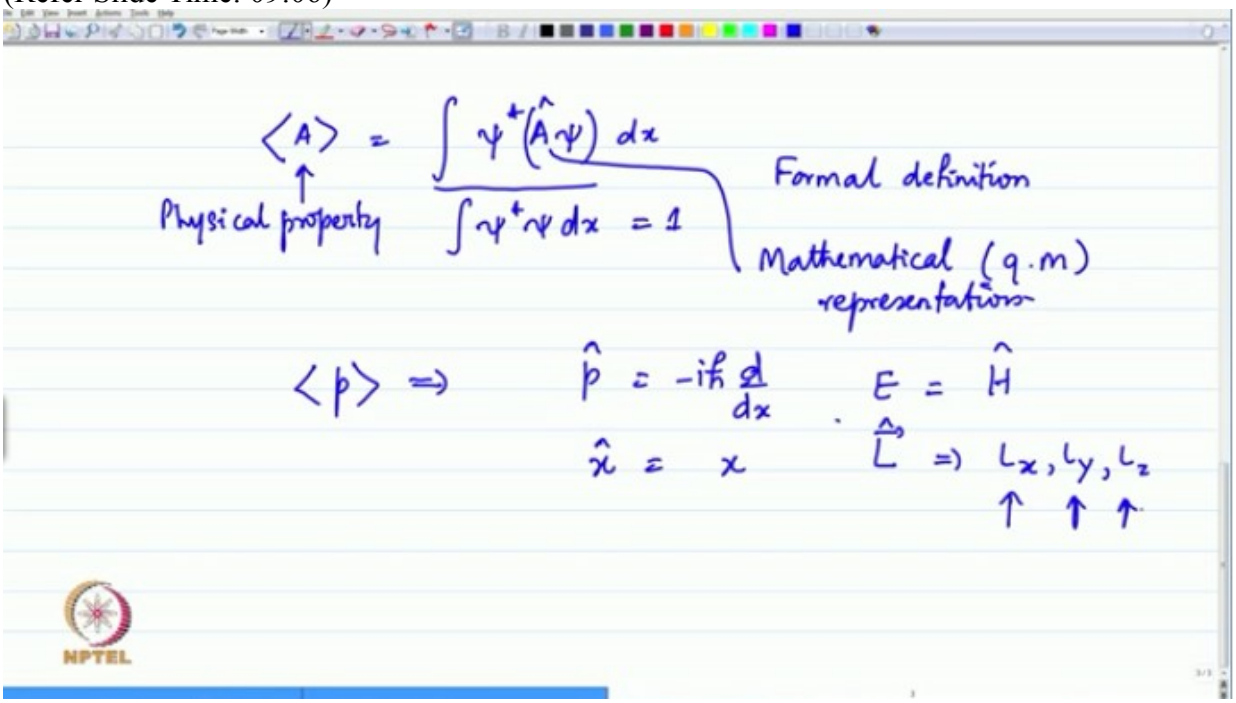

slightly different from the notation that we have here it will be all the derivatives, so the point is every measured quantity has a mathematical representation in quantum mechanics, and the average value that we expect by definition, the average being, the average of an infinitely large number of measurements, the average value that we expect of that system that you see here,
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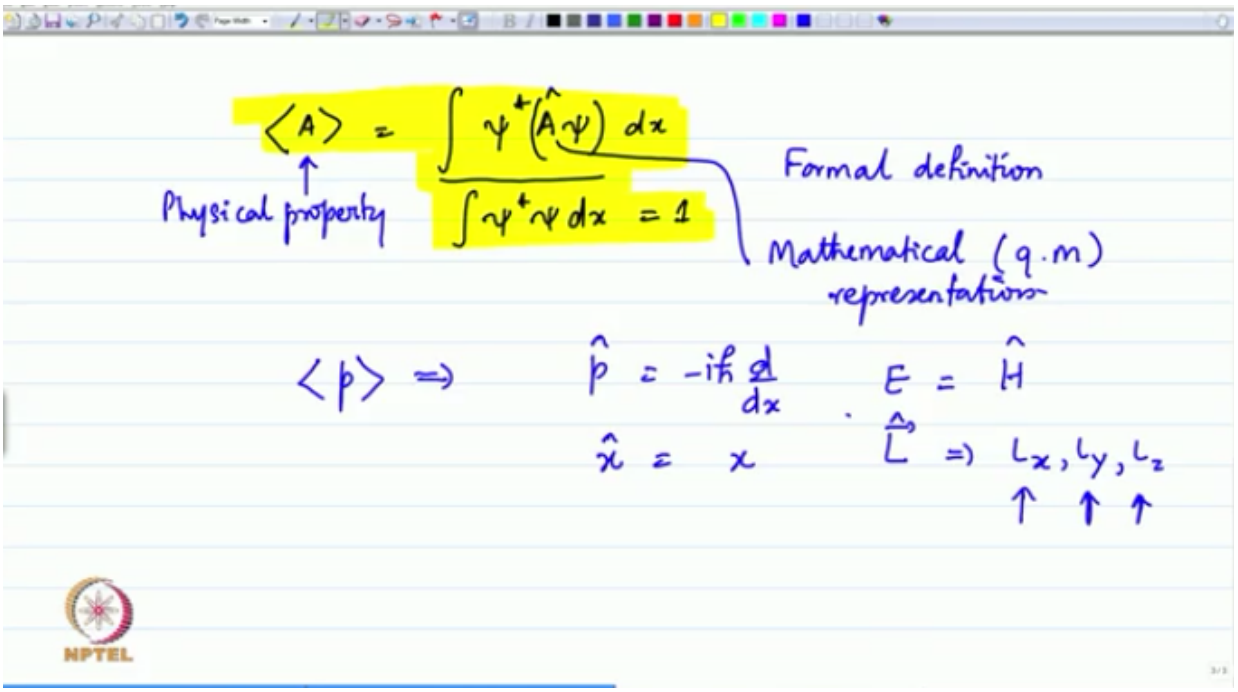

the average value is the sai star sai, sai star operator sai DX this is a fundamentally important thing to remember and again when we introduce the postulates of quantum mechanics this will be introduced as one of the postulates of quantum mechanics itself.

Therefore in the last lecture when I said that the average value of the position logically turns out to be somewhere right in the middle of the box for a box of length Y L you can calculate for one dimension, the average value X to be sai N(x) if the state of the system is sai N then the average value in that state is sai N(x), the position operator X and sine(x) DX. And sai N being normalized to root 2/L whatever you have that is root 2/L times sine N pi X/L, you have for the integral 0 to L sine N pi X/L, X sine N pi X/L DX okay, so this gives you when you do the integral this gives you the answer L/2,

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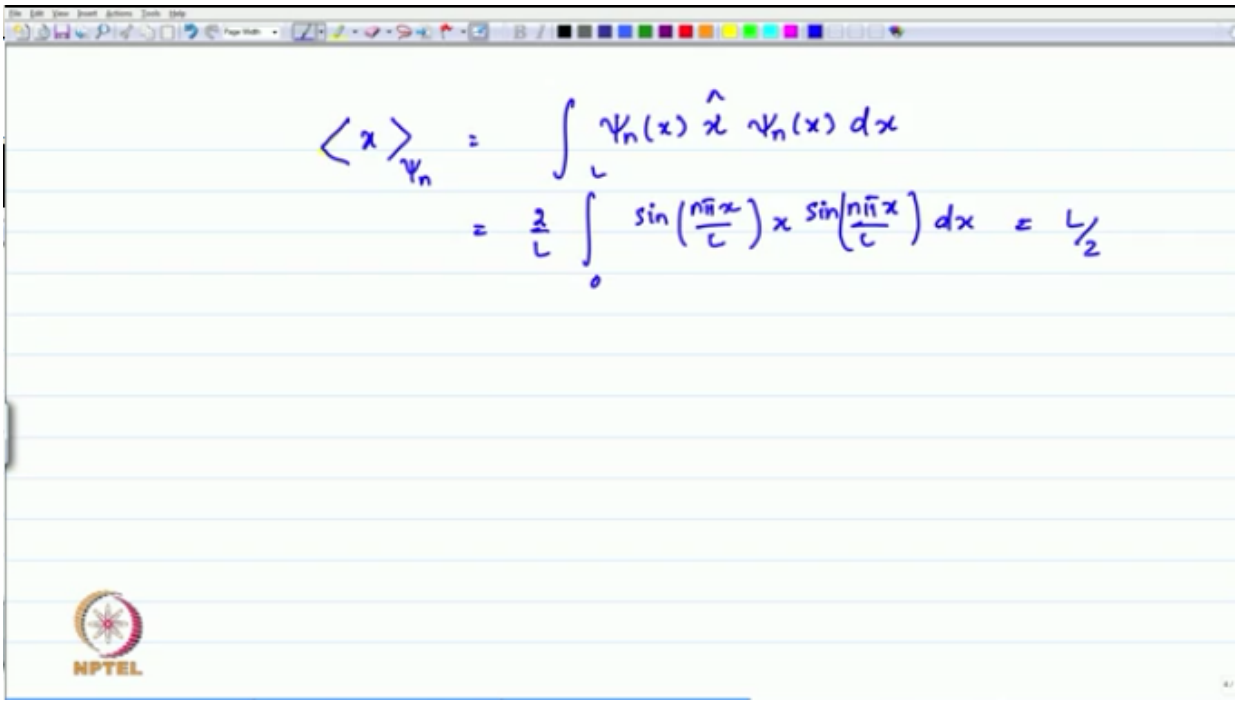

so very simple integral it is X sine square X, and the sine square X is of course you can write it as 1 - cos 2X/2, and then you do the simple integral on X and X cos X it's very easy to do.

Likewise the average value for the momentum or the particle was also argued out to be 0 based on the fact that the momentum is a vector and therefore it has a positive or a definite negative direction at any point in space, if you do that the average value of the momentum will turn out to be 0 for the particle in a 1 dimensional box and that's also easy to verify by writing this down as 2/L sine N pi X/L.

Now you remember to put the operator in the middle IH bar D/DX sine N pi X/L times DX, okay, now the derivative of the sine will give you a cosine N pi X/L, you can see mathematically and the sine cosine will give you a sine 2N pi X/L times 1/2, but that integral between 0 to L is a full sine wave and therefore that goes to 0 okay DX,
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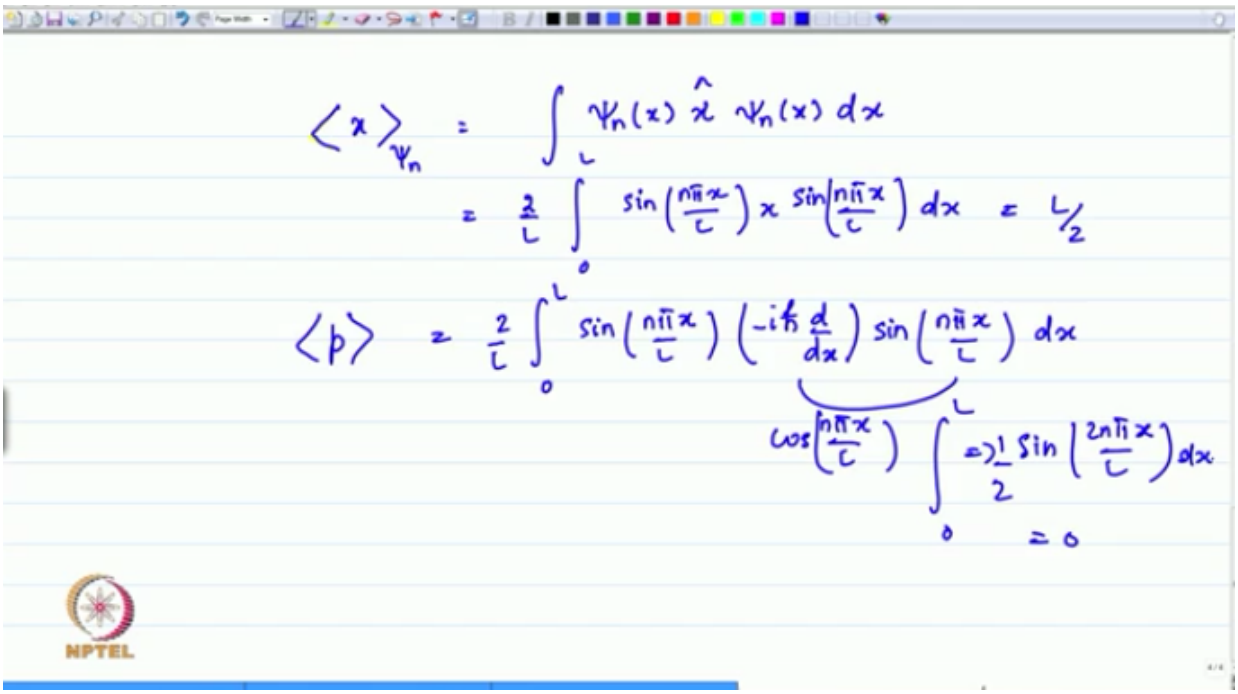

so it's easy to verify simple relations like the expectation values for position, expectation values for momentum and these are the two things that you can think about, and if you have the kinetic energy you already know that the particle in the box is only kinetic energy inside the box, therefore the total energy is the same as that of the kinetic energy and you can see that the average value E for the particle in the state sai N is H square N square/8ML square that also comes out. So these are simple prescriptions for doing calculations for the average values based on quantum mechanics.

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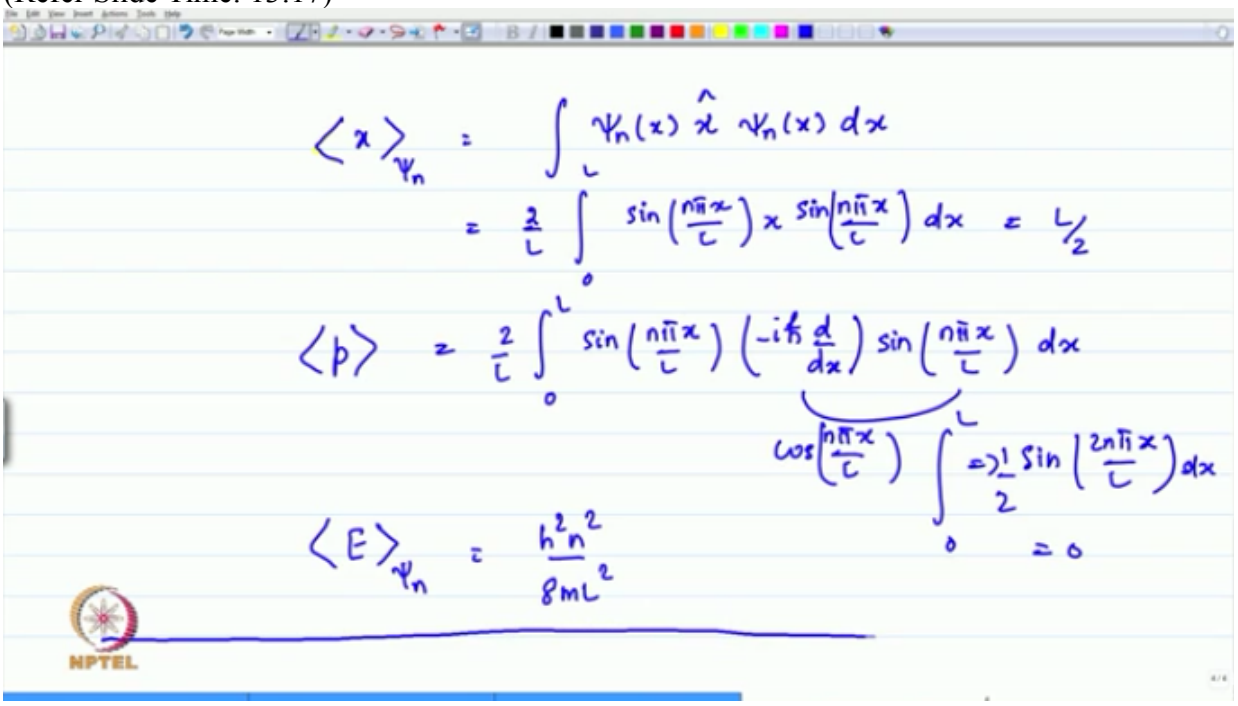

Now please remember these are average values, expectation values that is these are what are expected when you do many, many measurements, but if I do a single experiment what value will I get? Is there a prescription in quantum mechanics? That's what this equation tells you, okay, if the state of the system is in this function, is in this state sai N for the particle in the one dimensional box it doesn't matter, how many times I make measurements on that state for the energy, doesn't matter all the times I will get only one answer namely E sai N(x), it's like the simple analogy you have a dye at 6 phases and you print only one dot on all the 6 phases therefore the dye has only one state namely with an outcome of a single dot, no matter how many times you throw the dye, you get only one dot as the answer because that's how you prepared the state of the system, such states are called eigen states in quantum mechanics, okay.

In the case of a dye you have 6 possible things that you have for a single dye 1 dot, 2 dot, 3 dot, 4 dot, 5 dot, and 6 dots, therefore you have 6 possible outcomes. In the case of a particle in the box if I make a measurement and I do not know what the state of the system is, what result can I expect for a single measurement, I've already told you what the result we can expect for a very large number of measurements and then what's the average, that's what we did before what is it for a single measurement if you ask that question the answer is one of the eigenvalues of the system.

In case of the dye which is a normal dye or a regular dye which has 6 different phases with 1, 2, 3, 4, 5, 6 dots there are 6 possible outcomes, multiple outcomes, therefore in a single experiment of throwing the dye we get a dot, or 2 dot or 3 dot all with identical probabilities 1/ 6 if the dye is a perfect cube, because the dye is not prepared in any other way.

Likewise in quantum mechanics if the probabilities for all outcomes are uniform, then in a single measurement one of these energies will be the outcome, for the particle in the box if you measure the energy only one of the EN's is possible. Which of the EN? Statistics, Einstein was very unhappy he said God doesn't play dice, and Niels Bohr told him don't tell god what to do okay, but there is an inherent statistical character built in the measurement outcomes according to what is called the Copenhagen School or the Niels Bohr School of quantum mechanics which is still practiced by most of us, a single measurement will give you one of the eigenvalues and will result in the state of the system being one of that eigen state, the eigen state corresponding to that eigenvalue therefore if we make a measurement for a particle in a one dimensional box in an arbitrary state that we do not know what it is, the result that we will get out is only one result and that result the measurement will give you an eigenvalue EN and the state of the system will become sai N.

This is fundamental in quantum mechanics,
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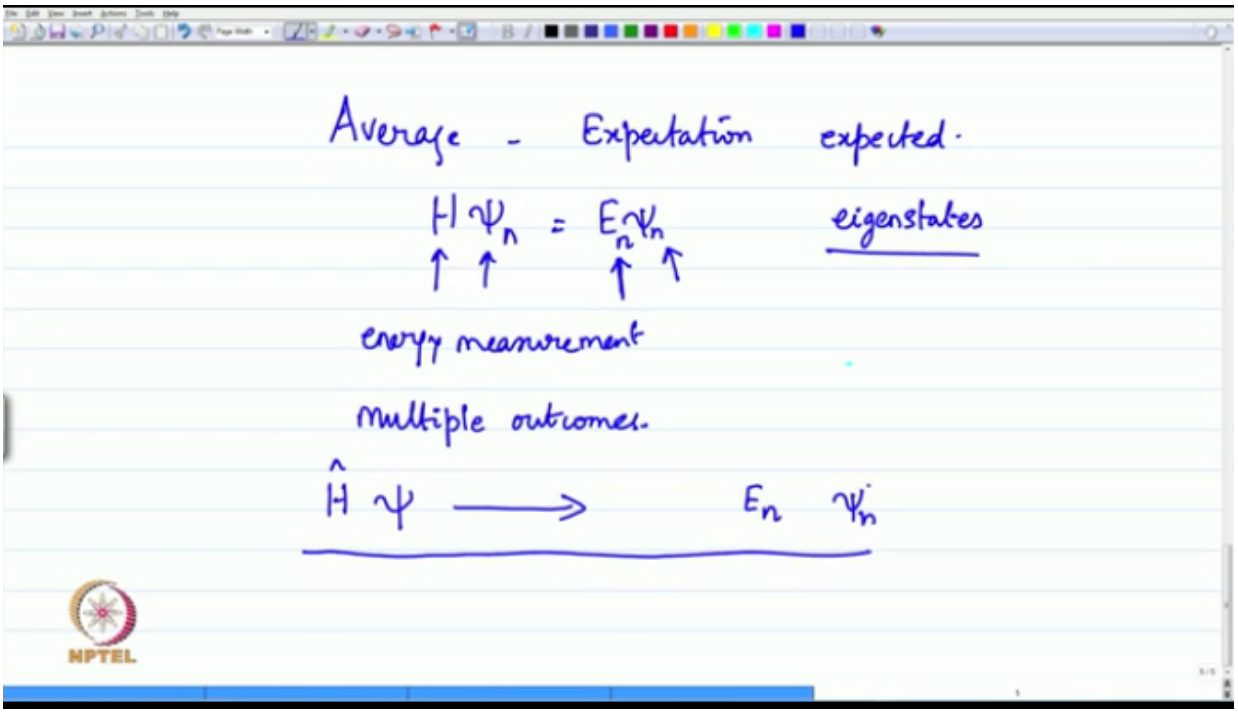

and if the state is already an eigen state then no matter how many times you make copies of that state and how many times you make the measurements you will always get the eigenvalue, that is why I mean I wrote the average value for E in the last slide or the few minutes ago if I go back to the screen I've written that already here, if the state of the system is sai N, the measurement of energy every time will give you the same value H square N square/8 ML square, and since it's the same value in all measurements the average is also the same as the single measurement, if you know the state of the system very precisely that's what it is, if you don't know the state of the system to be an eigen state but an arbitrary sai, okay, this is the result for an arbitrary sai, now let me write down the tab sai here that if the system is in the state sai a measurement of a quantity, physically will give you sai star A sai DX integrated over the domains completely available to the system and for particle in a one dimensional box it's between 0 to L, that's the whole space available to the system therefore you take the average by adding all the probabilities, it's very easy to see that the same one is what you get because if you write E(sai N) which is an eigen state of the Hamiltonian operator then you see that this relation is sai N H sai N DX and you know between 0 to L, you know that H sai N is EN sai N, and you know that sai N is normalized therefore the answer is 0 to L sai N sai N DX and with EN this is equal to 1, and therefore the average value is the same as the eigen value for EN.

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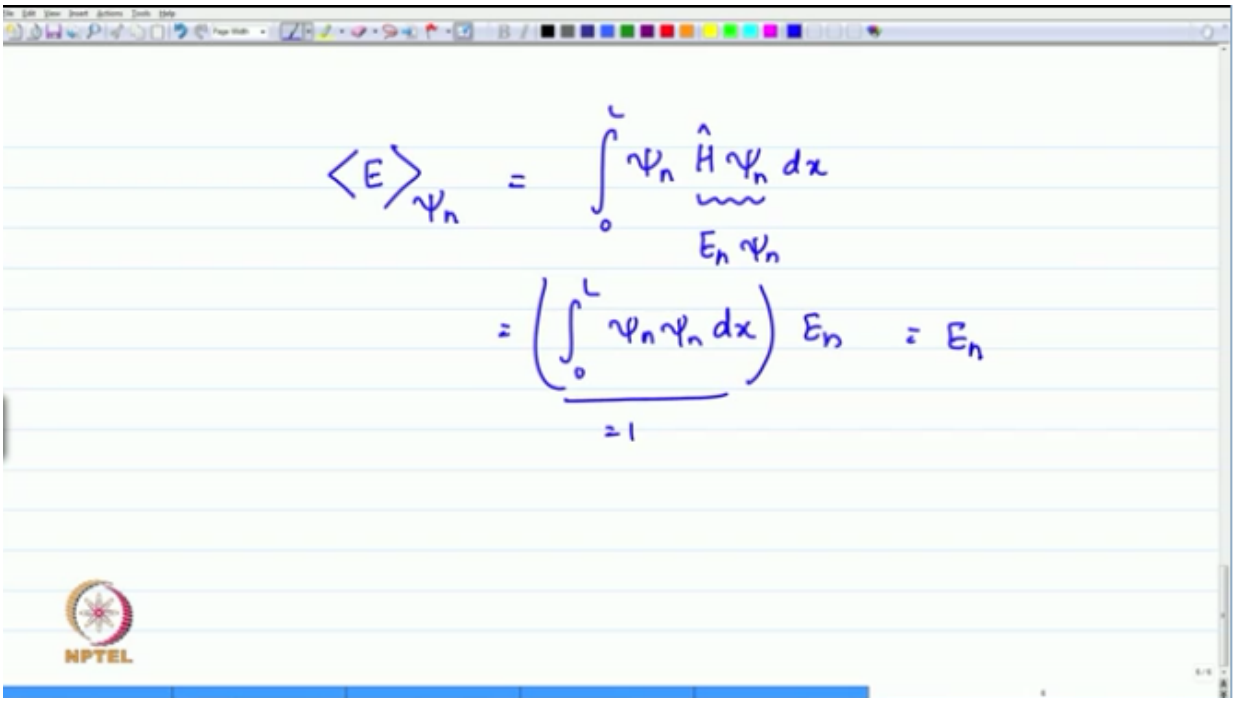

Let me stop here and we will continue these discussions over the next few weeks on various aspects, but it's important for us to remember that the expectation value is a fundamentally important quantity, and the fact that involves the wave function and it's complex conjugate is a very meaningful reason, it's a very important reason why one is always interested in solving the Schrodinger equation to get the wave function first, that the wave function has an interpretation due to probability is one thing but the wave function is extremely important in the actual calculation for the expectation values and the measurements, and therefore you have a function which you cannot physically explain or visualize but it's very important and very useful for calculating average values as calculating other quantities called matrix elements, calculating the average values through various processes and so on, therefore the wave function has come to stay with all of us. We'll continue this in the next lecture, thank you.

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