

Chemistry I – CY1001
Introductory Quantum Mechanics and Spectroscopy
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Lecture – 07

Lecture 4: Part III - Expectation Values and Postulates in Quantum Mechanics

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. 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 is called the postulatory basis and the postulatory basis in quantum mechanics will also be stated in very simple terms. The postulates are mathematical in nature, but we will see simple explanations hopefully.

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Expectation Values and
Postulates in quantum mechanics.

1. $\langle A \rangle = \frac{\sum_{i=1}^n A_i}{n}$

$\begin{cases} A_1 \\ A_2 \\ \vdots \\ A_n \end{cases}$

$A_1 \dots p_1 \text{ times}$
 $A_2 \dots p_2 \text{ ''}$
 \vdots
 $A_n \dots p_n \text{ times}$

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 a standard prescription that if there are n measurements and these things happen with different outcomes for the

measured quantity A with values A 1, A 2, A n for different measurements, then you know that the average is nothing, but the sum over i is equal to 1 to n A i divided by n.

Now on the other hand, suppose you have A 1 occurring n 1 times in an experiment repeated many many times, A 2 occurring n 2 times. Let me change n 1, n 2 to something else which is standard p 1 times, p 2 times and likewise A n and these are the only possible values; let us say these are the only outcomes that you have occurs p n times then the average is calculated by adding all the A 1.

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$$\langle A \rangle = \frac{(A_1 + A_1 + \dots) + (A_2 + \dots + A_2) + \dots + (A_n + \dots + A_n)}{p_1 + p_2 + p_3 + \dots + p_n}$$

$$= A_1 \times \left(\frac{p_1}{P}\right) + A_2 \times \left(\frac{p_2}{P}\right) + \dots + A_n \times \left(\frac{p_n}{P}\right) \quad P = \sum_i p_i$$

$\psi^* \psi \rightarrow \langle A(x) \rangle = \int \psi^* \psi A_x dx$

$$\int \psi^* \psi dx = 1$$

So, the average is calculated by adding all the A 1, p 1 times and adding A 2 which has happened p 2 times and likewise adding all the A n's which have occurred p n times dividing by p 1, p 2, p 3 up to p n. 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 has repeated, what is the probability that that value is repeated and so on.

Now, the same thing can now be written by writing A 1 into p 1 by p; where p is the sum of all of the experiments p i and therefore, p 1 by p gives you the probability that you got A 1 for the measurement of A and likewise A 2 into p 2 by p which is the probability that you have the outcome A 2 and so on. Therefore, you have A n; p n by p, so this is the probability within brackets that a given value occurs and then what is the average when

you do this experiment many many times, this is standard way of representing probabilities in quantum mechanics.

We remember $\psi^* \psi$ represents the probability, density for the system at a given coordinate or at a given momentum the variable x . So, in particular the one dimensional box you talk about the $\psi^* \psi dx$ as the probability that the system is in the space between x and $x + dx$ and in two dimensions $\psi^* \psi; dx dy$ 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 is what it is and for $\psi^* \psi$ is a sort of a probability. And then what we 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 there is an 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 and 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 that would A is defined for each and every value of x . So, what you think is it is like $\psi^* \psi$; which is the probability times the value $A(x)$ that happens into $x; dx$ provided $\psi^* \psi$ represents the probability density which means this integral $\int \psi^* \psi dx$ should be equal to 1.

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The image shows handwritten notes on a whiteboard. At the top, the expectation value $\langle A \rangle$ is defined as $\int \psi^* (A\psi) dx$. Below this, the normalization condition $\int \psi^* \psi dx = 1$ is written. The text 'Physical property' is written below the first equation, and 'Formal definition' is written to the right of the second equation. A bracket groups these two equations with the text 'Mathematical (q.m) representations'. Below this, the momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$ and the energy operator $E = \hat{H}$ are listed. The position operator $\hat{x} = x$ is also listed. To the right, the angular momentum operators are listed as $\hat{L} \Rightarrow L_x, L_y, L_z$, with three upward-pointing arrows below them. The NPTEL logo is visible in the bottom left corner.

So, if you represent this by probability density till 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 ψ . Giving you the measured value and therefore, the measured value times the $\psi^* \psi$ is represented by this quantity divided by integral; $\psi^* \psi dx$ which of course, is set to 1, if we think of $\psi^* \psi$ as the probability. So, this is the formal definition for the expectation value in 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 of that physical property.

You already know because the case of momentum for example, the operator associated with p is $-\hbar i \frac{d}{dx}$ are one dimension and what is the operator for the position? It is just x itself. What is the operator for the energy? We have already seen that it is the Hamiltonian operator that is the operator associated with angular momentum; it is a vector and has three components in three dimensions. So, if you write that in say three dimensions you have three components and each of them is represented by a corresponding operator which is slightly different from the notation that we have here written in 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 the average value is the $\psi^* \psi$, $\psi^* \text{operator} \psi dx$. This is a fundamentally important thing to remember and again when we introduced 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 it turns out to be somewhere right in the middle of the box for a box of length L .

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The image shows a digital whiteboard with handwritten mathematical derivations for the expectation values of position, momentum, and energy for a particle in a one-dimensional box of length \$L\$.

The first derivation is for the position expectation value $\langle x \rangle_{\psi_n}$:

$$\langle x \rangle_{\psi_n} = \int_L \psi_n(x) x \psi_n(x) dx$$

$$= \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx = \frac{L}{2}$$

The second derivation is for the momentum expectation value $\langle p \rangle_{\psi_n}$:

$$\langle p \rangle_{\psi_n} = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

The derivative is shown as $\cos\left(\frac{n\pi x}{L}\right)$, and the integral is simplified to $\int_0^L \sin\left(\frac{2n\pi x}{L}\right) dx = 0$.

The third derivation is for the energy expectation value $\langle E \rangle_{\psi_n}$:

$$\langle E \rangle_{\psi_n} = \frac{\hbar^2 n^2}{8mL^2}$$

The NPTEL logo is visible in the bottom left corner of the whiteboard.

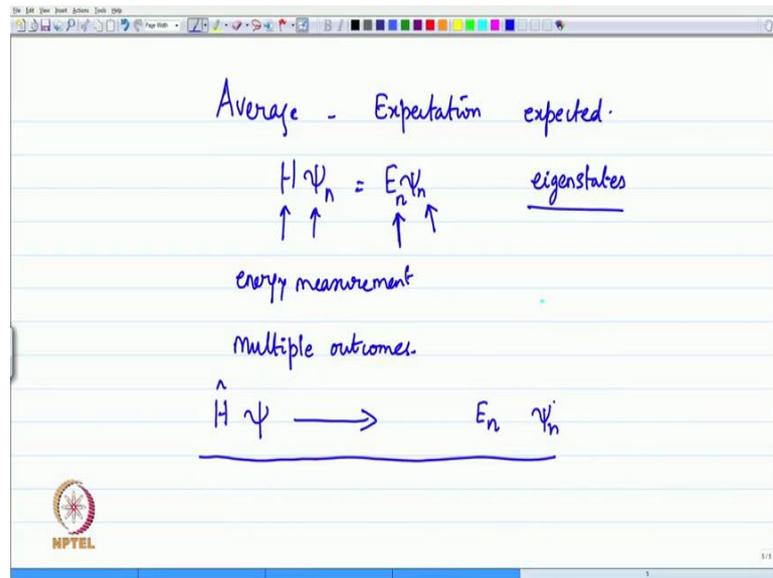
You can calculate for one dimension, the average value x to be ψ_n of x ; if the state of the system is ψ_n then the average value in that state is ψ_n of x , the position operator x and ψ_n of $x - dx$. And ψ_n being normalized to $\sqrt{2}$ by L ; whatever you have that is $\sqrt{2}$ by L times $\sin\left(\frac{n\pi x}{L}\right)$ by L ; you have for the integral 0 to L ; $\sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx$. So, this gives you when you do the integral; this gives you the answer L by 2 . So, very simple integral it is $x \sin^2 x$ and $\sin^2 x$ is of course, you can write it as $\frac{1 - \cos 2x}{2}$ and then you would have you do the simple integral on x and $x \cos x$, it is very easy to do.

Likewise the average value for the momentum, for 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 one dimensional box and that is also easy to verify by writing this down as $\frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{n\pi x}{L}\right) dx$. Now you remember to put the operator in the middle; $i\hbar \frac{d}{dx}$; $\sin\left(\frac{n\pi x}{L}\right)$ by L times dx .

Now, the derivative of the \sin will give you a cosine $\frac{n\pi x}{L}$, you can see mathematically and the $\sin \cos$ will give you a $\sin\left(\frac{2n\pi x}{L}\right)$ times $\frac{1}{2}$, but that integral between 0 to L is a full \sin wave and therefore, that goes to 0 dx . So, it is 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 a 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 ψ_n is $h^2 n^2 / 8mL^2$ 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 is what this equation tells you. If the state of the system is in this function; is in this state ψ_n for the particle in one dimensional box, it does not matter - how many times I make measurements on that state for the energy does not matter; all the times I will get only one answer namely E_n of ψ_n ; it is like the simple analogy you have a die with six faces and you print only one dot on all the six faces.

Therefore, the die has only one state namely with an outcome of a single dot, no matter how many times you throw the die, you get only one dot as the answer because that is how you prepared the state of the system; such states are called Eigenstates in quantum mechanics. In the case of a die, you have six possible things that you have for a single die 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 a 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 have already told you what result we can expect for a very large number of measurements and then what is the average; that is what we did before. What is it for a single measurement if you ask a question; the answer is one of the eigen values of the system.

In case of the die, which is a normal die or a regular die which has 6 different phases with 1, 2, 3, 4, 5, 6 dots there are 6 possible outcomes; multiple outcomes. Therefore, in a singled experiment of throwing the die, we get a dot or 2 dot or 3 dot all with identical probabilities $1/6$ if the die is a perfect cube because the die 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 a box if you measure the energy only one of the E_n 's is possible which of the E_n ? Statistics, Einstein was very unhappy, he said God does not play dice and Niels Bohr told him do not tell God what to do. But there is an inherent statistical character built in the measurement outcomes according to what is called the Le 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 eigen values and will result in the state of the system being one of that eigen state, the eigen state corresponding to that eigen value. Therefore, if we make a measurement for a particle in A 1 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 eigen value; E_n and the state of the system will become ψ_n . This is fundamental in quantum mechanics 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 eigen value.

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The image shows a digital whiteboard with a blue border and a toolbar at the top. The whiteboard contains handwritten mathematical equations in blue ink. The first equation is $\langle E \rangle_{\psi_n} = \int_0^L \psi_n \hat{H} \psi_n dx$. Below the integrand, there is a wavy line under $\hat{H} \psi_n$ and the text $E_n \psi_n$ written below it. The second equation is $= \left(\int_0^L \psi_n \psi_n dx \right) E_n = E_n$. A bracket under the integral in the second equation is labeled $= 1$. In the bottom left corner of the whiteboard, there is a logo for NPTEL (National Programme on Technology Enhanced Learning) featuring a stylized sun or star symbol.

That is why I mean, I wrote the average value for E in the last slide or a few minutes ago if I go back to the screen, I have written that already here. If the state of the system is psi n; the measurement of energy every time will give you the same value h square n square by 8mL square and since it is a same value in all measurements the average is also the same as the single measurement.

If you know the state on the system very precisely that is what it is, if you do not know the state of the system to be an eigen state, but an arbitrary psi this system is (Refer Time: 18:48) for an arbitrary psi. Now let me write down the tab psi here that if the system is in the state psi a measurement of the quantity physically will give you psi star a psi dx integrated over the domains completely available to the system and for particle in an one dimensional box is between 0 to L that is the whole space available to the system; therefore, you take the average by adding all the probabilities.

It is very easy to see that the same one is what you get because if you write E of psi n, which is an eigen state of the Hamiltonian operator, then you see that this relation is psi n h; psi n d x and you know between 0 to L, you know that h psi n is E n psi n and you know that psi n is normalized therefore, the answer is 0 to L psi n, psi n dx and with E n and this is equal to 1 and therefore, the average value is the same as the eigen value for E n.

Let me stop here and we will continue these discussions over the next few weeks on various aspects, but it is important for us to remember that the expectation value is a fundamentally important quantity and the fact that that involves a wave function and its complex conjugate is a very meaningful reason in a very important way, 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 is very important and very useful for calculating average values, calculating other quantities called the 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 will continue this in the next lecture.

Thank you.