Approximate Methods in Quantum Chemistry
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Lecture 03
Topic - Postulates of Quantum Mechanics - II

Hello students! Welcome to this lecture. In the last lecture we were discussing some postulates of quantum mechanics. We saw what are the experimental results that classical physics could not explain and how and where quantum mechanics came as a saviour to save the day. After the progress of quantum mechanics we decided that we should formulate the language and the basic understanding of quantum mechanics in form of some postulates. This is what we are discussing.

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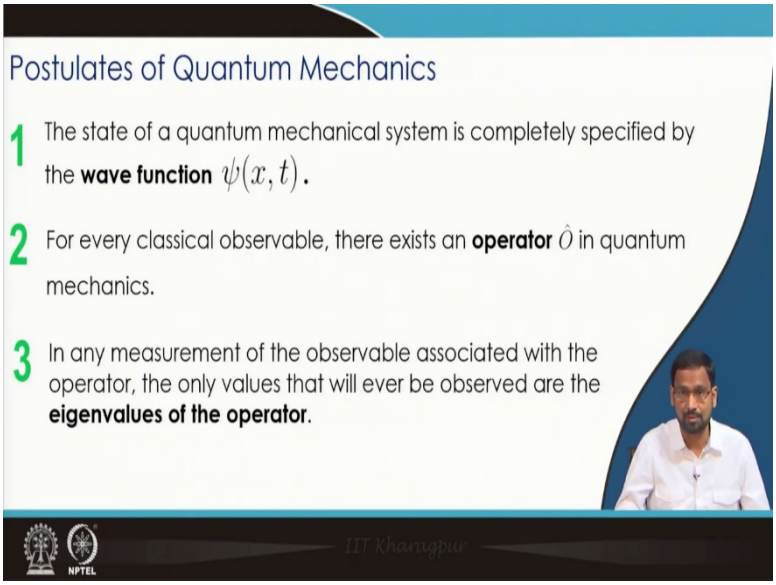

In the last lecture we went through the first three postulates. I will briefly remind you. The first postulate of quantum mechanics suggested that whatever you want to learn about a quantum mechanical system, there exists this so-called wave function, which contains everything that you possibly want to know about the system. We represented the wave function as $\psi(x,t)$, which is a function of the spatial coordinates (x) and temporal coordinate (t).

The first postulate told us about the wave function and the second postulate said that for every classical observable that you were interested in, there exists a quantum mechanical

operator. If you want to observe, say, position or momentum or energy you bring the corresponding quantum mechanical operator. We typically signify an operator with a hat.

The third postulate said while you have the operator and you have the wave function, but what are the observables, what are the outcomes of measurement? That answer is given by the third postulate. It says that whenever you make any measurement corresponding to any observable, that means you are operating the corresponding quantum mechanical operator, the only allowed observables are the eigenvalues of that operator. Hence, it is very important to know the eigenvalues and eigenfunctions of different quantum mechanical operators. The consequence of postulate 3 is that since the outcome of measurement is the eigenvalue of the operator, therefore the quantum mechanical operators must have real eigenvalues.

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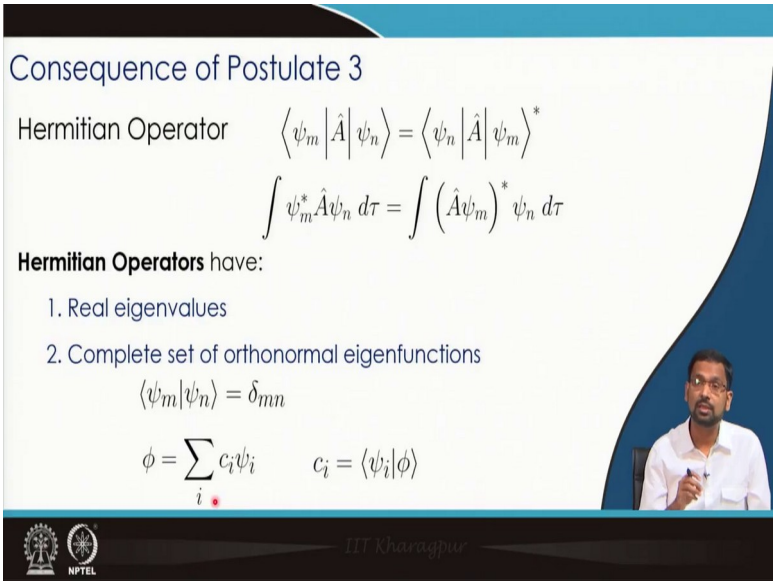

When we impose this condition that the eigenvalues of the quantum mechanical operators have to be real, then we come to the mathematical formulation that the quantum mechanical operators that correspond to classical observables are Hermitian operator. When we say a Hermitian operator, we should keep in mind that for any Hermitian operator the following rule is followed

$$\langle \psi_m | \hat{A} | \psi_n \rangle = \langle \psi_n | \hat{A} | \psi_m \rangle^*$$
$$\int \psi_m^* \hat{A} \psi_n \, d\tau = \int (\hat{A}\psi_m)^* \psi_n \, d\tau$$

For Hermitian operators, we have got two beautiful properties: the eigenvalues are real, and their eigenfunctions form a complete set of orthonormal eigenfunctions. If I have hundreds of

eigenfunctions of this Hermitian operator, each eigenfunction is going to be orthogonal to every other eigenfunction. A set of eigenfunction ψ_is forms a complete set, when I can express any arbitrary function ϕ,as a linear combination of $\psi_i s$.The coefficients of the linear combination c_i are given by the overlap of function of ψ_i with the arbitrary function ϕ.

If you remember we asked this question, related to postulate 3. We said that postulate 3 says that when you make a measurement, the only allowed value of the observables are the eigenvalues of the operator. That means if the state of the system is an eigenfunction of the operator, of course I understood that the outcome will be the eigenvalue. We can ask, what if the state of the function is not an eigenfunction of this operator, then what?

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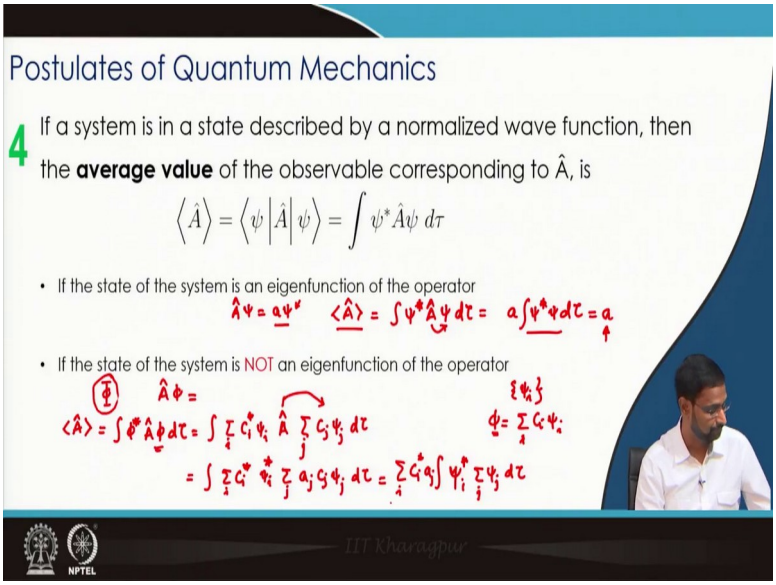

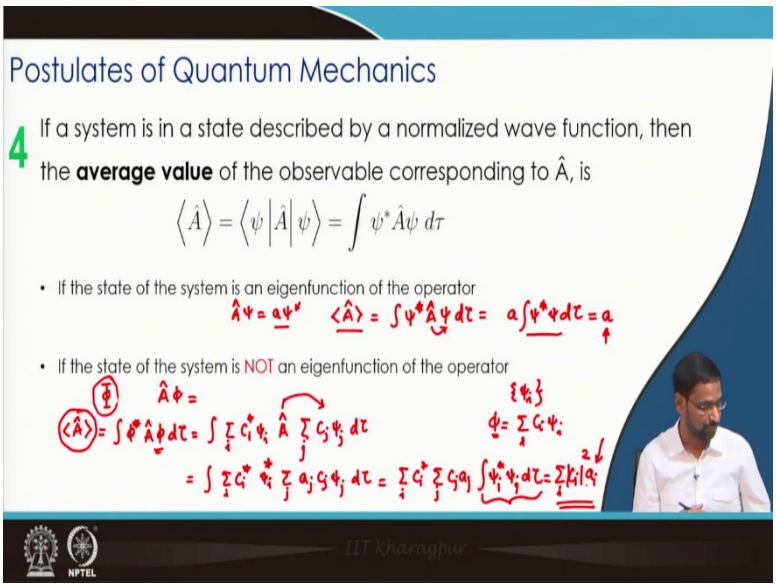

But before that we must equip ourselves with the next postulate, which gives an idea about the expectation value of the measurement or the outcome of a measurement. Postulate 4 tells us that if you have a state of the system, which is described by a normalized wave function in this case it is called ψ, then the average value of this observable corresponding to this operator A is given by,

$$\left\langle \hat{A} \right\rangle = \left\langle \psi \left| \hat{A} \right| \psi \right\rangle = \int \psi^* \hat{A} \psi \, d\tau$$

That means if I prepare millions of copies of my system and make the measurement related to an operator A on each system, and then I took the average value of the outcome, I would get the expectation value given in the above equation. Whenever I am looking for an average value, that means I would see that there is a distribution. For example, let us say that there are three people whose age is 23, 23, and 20. The average age becomes 22. Note, that the average age of these three people's age is 22, although none of them are 22 years old. It is just an arithmetic average. This often appears, that the average value of a measurement may not be an eigenvalue, but each measurement will give one eigenvalue as outcome.

How can we use postulate 3 to answer the question that we asked? For example, there can be two situations: 1. If the state of the system is an eigenfunction of the operator,

$$\left\langle \hat{A} \right\rangle = \left\langle \psi \left| \hat{A} \right| \psi \right\rangle = \left\langle \psi \left| \hat{A}\psi \right. \right\rangle = \langle \psi \, | a\psi \rangle = a \langle \psi \, | \psi \rangle = a$$

I can write down the above equation. So, the expectation value of the operator A would turn out to be a, which is the eigenvalue of A for the normalized eigenfunction ψ. That means expectation value or the average value of my measurement is a, the corresponding eigenvalue.

Since the state of the system is an eigenfunction of this operator, the outcome is the corresponding eigenvalue and I get only one possible value. This is the simple case. Now let us see when the state of the system is not an eigenfunction. Suppose in that case, the state of the system is defined by ϕ, now I know that the state of the this is not an eigenfunction of operator A but I am interested in finding the expectation value.

I know that postulate 4 tells me that you I can express ϕ as a linear combination of the eigenfunctions of A, ψ_is.

$$\begin{aligned}\left\langle \hat{A} \right\rangle &= \left\langle \phi \left| \hat{A} \right| \phi \right\rangle \\ &= \left\langle \sum_i c_i \psi_i \left| \hat{A} \right| \sum_j c_j \psi_j \right\rangle \\ &= \left\langle \sum_i c_i \psi_i \mid \sum_j c_j \hat{A} \psi_j \right\rangle \\ &= \sum_i c_i^* \sum_j c_j \left\langle \psi_i \mid a_j \psi_j \right\rangle \\ &= \sum_i c_i^* \sum_j c_j a_j \delta_{ij} = \sum_i |c_i|^2 a_i\end{aligned}$$

I am expressing the wave function in bra and ket as two expansions with coefficients c_i and c_j. When I evaluate this integral, you see that the operator acts on the ket, which is written as a summation. There are many terms, but it does not matter because each term has psi_1, psi_2, etc. and they are the eigenfunctions of this operator A with eigenvalues a_1, a_2, a_3, etc. We brought all constants, the eigenvalues and the coefficients, out of the integral. Now, we see that this integral is the typical orthonormal condition of the eigenfunction, so therefore this integral will vanish every time i is not equal to j and would survive only when i equals j. So, when I simplify this term, I would find the final result as shown above.

It tells that if the state of the system is not an eigenfunction of the operator then I am still going to get the eigenvalues as the observable. It is only that I get a particular eigenvalue with a certain probability ($|c_i|^2$). That means, if I make 10,000 copies of this system and make 10,000 different experiments corresponding to operator A, I am going to get 10,000 different values, but every time I would get one of these eigenvalues of the operator A. At the end when I calculate the average value, of course I would get the arithmetic average but each individual experiment is going to give me an eigenvalue of the system, and *nothing* other than the eigenvalue.

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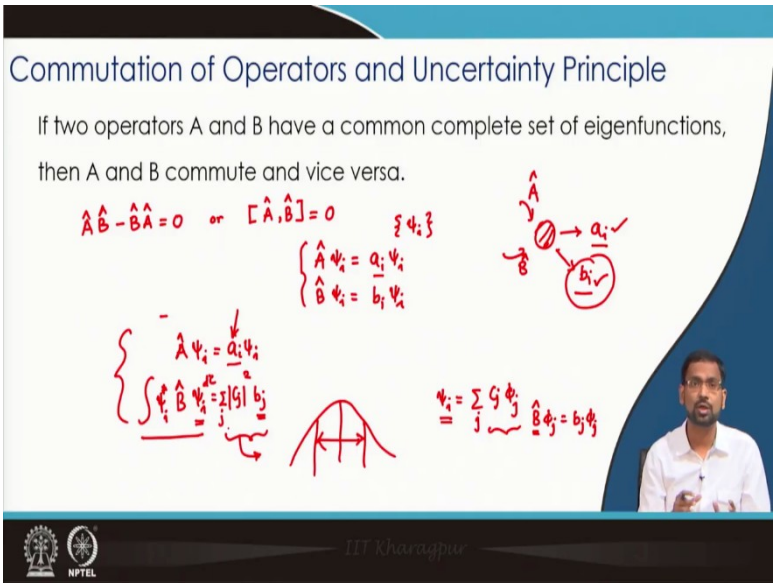

Now, let us go ahead with our discussion with a very interesting property of operators, i.e., the commutation of two operators. Let us state this general statement that if two operators A and B have a *common complete* set of eigenfunctions then the operators A and B commute.

Mathematically when I say two operators commute I simply say that $AB = BA$, i.e., the order of operation of action of operators A and B does not matter. And if commutation of A and B is not equal to 0 then in that case the two operators do not commute. Now, the theorem states that if there are two operators who commute then they have a common complete set of eigenfunctions. We have already understood what is a complete set of eigenfunction, i.e., with a complete set of eigenfunction I can express any arbitrary function as a linear combination of this complete set of eigenfunctions. The new phrase is *common.* That means the *same* complete set of eigenfunction is now simultaneously eigenfunction of operator A and of operator B. When is that possible? That is possible when A and B commute.

Let us consider this example when they actually commute. They have common complete set of eigenfunctions. So, suppose $\{\psi_i\}$ form a complete set of eigenfunctions. If operator A acts on one of these eigenfunctions ψ_i I will get a_i, since the state of the system is an eigenfunction of the operator A. Therefore, the outcome of this measurement is going to be one eigenvalue, there is no distribution here. Now, since A and B commute, therefore ψ_i is also an eigenfunction of operator B. So, when I act B on ψ_i I get b_i as the eigenvalue corresponding to operator B. This is simple case because both the operators commute, so therefore they have common complete set of eigenfunction. If I operate A I get exact value a_i, if I operate B I get exact value b_i.

Now, come to the situation where A and B do not commute, in that case let us say I prepared my system ψ_i, which happens to be an eigenfunction of operator A. Hence, when I act operator A I get the result as a_i. When A and B do not commute, if I operate operator B on this ψ_i what should I get? Remember, ψ_i is not an eigenfunction operator B.

There is no problem because I know I can express this ψ_i(an arbitrary function) as a linear combination of the eigenfunction of operator B. So, now what I am saying do not worry if operator B does not commute with A. The eigenfunctions of A are not the eigenfunction of operator B, but operator B can have its own eigenfunctions, call them ϕ_j and since the operator B is a Hermitian operator, ϕ_j also form a complete set of eigenfunctions. And we can express $\psi_i$as a linear combination of $\{\phi_j\}$.

When such a situation occurs, what would be the result? We already know, the outcome is going to be b_j, since every measurement will give one of the eigenvalues. But what would be the probability of observing this?

$$\left\langle \hat{B} \right\rangle = \left\langle \psi_i \left| \hat{B} \right| \psi_i \right\rangle = \left\langle \sum_j c_j \phi_j \left| \hat{B} \right| \sum_k c_k \phi_k \right\rangle = \sum_j |c_j|^2 b_j$$

Now, you see when I make operation A on this system the outcome is simple a_i. But when I make measurement corresponding to B, I do not have this simple case of observing a single eigenvalue rather I have this complicated situation where I get many possible values b1, b2, …., with different probability. Instead of getting a single value, I am going to get a distribution of values. Now, when I get a distribution of value, then you can imagine that I can have an average value, I can have a most probable value, I can also have a standard deviation. Hence, there is an *uncertainty* in the outcome of this measurement. Now, you would see that if two operators A and B commute, then there is no uncertainty, because in both cases I get a single eigenvalue (a_i and b_i), both A and B operator have precise values.

But when A and B do not commute, if I decide to get operator A outcome precisely, the action of operator B on the system will give me a distribution of b_j's. That means, I will get a range of eigenvalues. So, there will be a distribution and there will be uncertainty. When two operators do not commute, they do not have common complete set of eigenfunctions. The consequence of that is that there is an uncertainty in measuring both the operators simultaneously and precisely.

Since, $[x, p_x] \neq 0$, there is the famous position momentum uncertainty. If two operators commute, then there is no such uncertainty relation.

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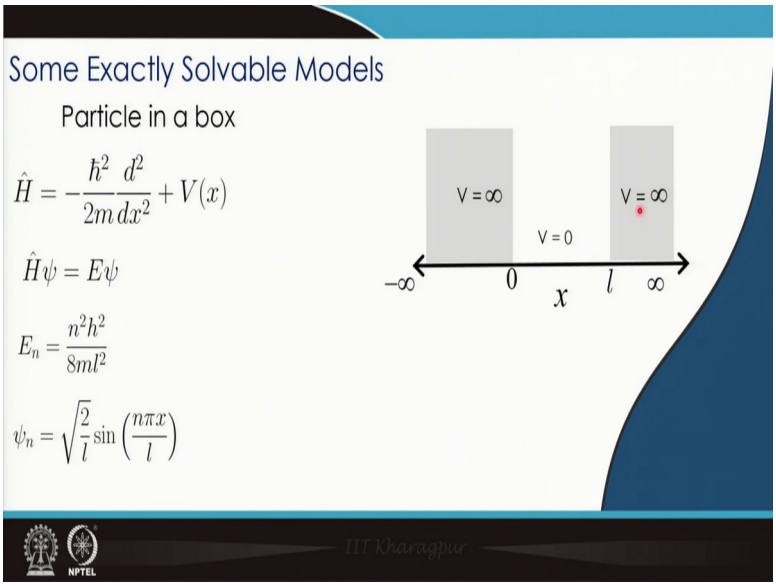

So far, we have looked at some of the postulates and the principles of quantum mechanics. Now, we will use this knowledge to discuss some exactly solvable models. Remember, we said that there are only a few simple systems that we can exactly solve. Most systems that are of chemical relevance are too difficult for an exact solution of its Schrodinger equation. So, let us now first try to understand what are these exactly solvable models. We will not do the derivation of the results rather we will just discuss the results of those models.

The first system is a particle in a box. A particle in a box is a widely used model that has got great chemical relevance. A particle in a box model in chemistry can represent a molecule. A molecule is composed of many electrons that are confined to the nuclear environment of the molecule. So, if a molecule exists at one place, all electrons of this molecule exist somewhere within the nuclear framework of that molecule. We can also say that the electron of these molecule is certainly not present at a far-off place. Why? That is because the electrons cannot simply escape the molecular environment (unless of course we ionize the molecule). But if I have a sample system, I know that the electrons are confined to their molecular environment that means the electrons (or particles) are experiencing a huge potential that they cannot easily escape, as if they are in a box. Hence, particle in a box. The box is the molecular

environment. Within the molecule, of course the electrons can get delocalized. If we consider conjugated pi-systems, then the electron delocalization is very facile.

In this case the electron can perhaps move around the molecular environment, but it can never escape. So, as if electron is experiencing an infinitely high barrier to escape the molecular environment. But this barrier is not necessarily always infinitely high. For example, we know if two reactants are brought together, they react and they form a product. When the reaction occurs, there can be a transfer of electron. In those situations, the electron can move away from its molecular environment. Here, the electron experiences a finite barrier to escape the molecular environment (particle in a potential well). This barrier can be made infinite, that is an ideal system, where it can never escape or this barrier can be made zero, in the sense that there is no barrier and the electron is a free particle (an ionized electron).

So, now by playing with different values of V the barrier for the electron to escape this box we can have particle in an infinitely high wall or we can have particle trapped by a finite barrier or we can have a free particle.

Whenever we have a quantum mechanical problem the first step of the solution is to write down the operator, in this case the Hamiltonian. The Hamiltonian operator, which is the operator for energy can have contribution from kinetic energy or potential energy. I have got a particle with certain mass and it has got its kinetic energy, given by $/2m$. In addition, it would also have the potential energy (V), which can be a function of x, the dimension of the box. We consider that the particle experiences 0 potential within the box, between length 0 and l, and it experiences infinite potential outside the box.

We have written down the Hamiltonian and we will discuss the results of this problem in our next class. Thank you for your attention.