Approximate Methods in Quantum Chemistry
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Lecture 02
Topic - Postulates of Quantum Mechanics - I

Hello students! In the last class we discussed about the origin of quantum mechanics. We looked at the experimental results that puzzled the scientist in the late 19th century and early 20th century and the two great theoretical ideas the de Broglie's hypothesis and the Heisenberg's uncertainty principle that led to the discovery of this new field called quantum mechanics. After these major developments, there were many different scientists who contributed in many different ways to further our knowledge in physics and chemistry.

Soon it was felt that we have actually discovered a new field of study: the *quantum mechanics.* At that point it was very important to make some ground rules so that we all can communicate with each other more effectively. This is what we are trying to do in this class. Normally we discuss this in quantum mechanics through the so-called postulates of quantum mechanics, which put forward the ideas and the concepts of quantum mechanics and how we can describe a quantum mechanical system.

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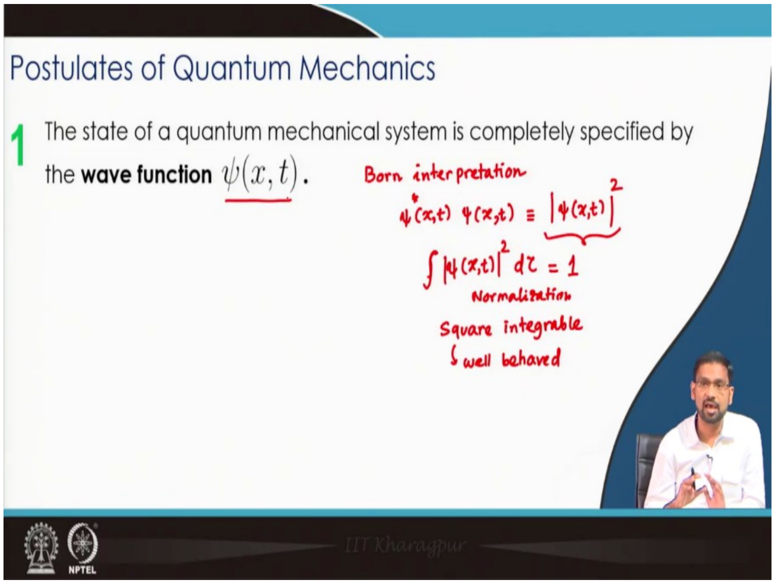


Postulates of Quantum Mechanics

1 The state of a quantum mechanical system is completely specified by the **wave function** $\underline{\psi(x,t)}$.

Born interpretation

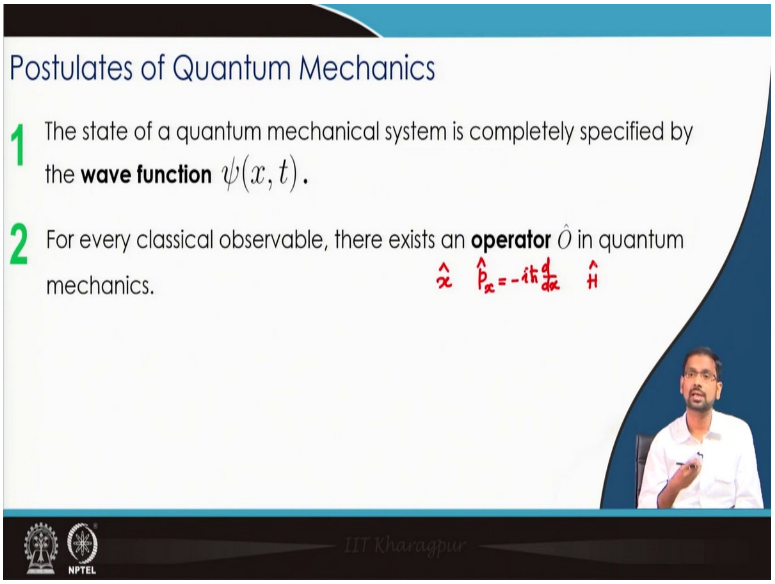
$$\psi^*(x,t)\,\psi(x,t) \equiv \underbrace{|\psi(x,t)|^2}$$

$$\int |\psi(x,t)|^2 \, d\tau = 1$$

Normalization

Square integrable

& well behaved



Postulates of Quantum Mechanics

1. The state of a quantum mechanical system is completely specified by the **wave function** $\psi(x,t)$.
2. For every classical observable, there exists an **operator** $\hat{O}$ in quantum mechanics.

$\hat{x}$ $\hat{p}_x = -i\hbar\frac{d}{dx}$ $\hat{H}$

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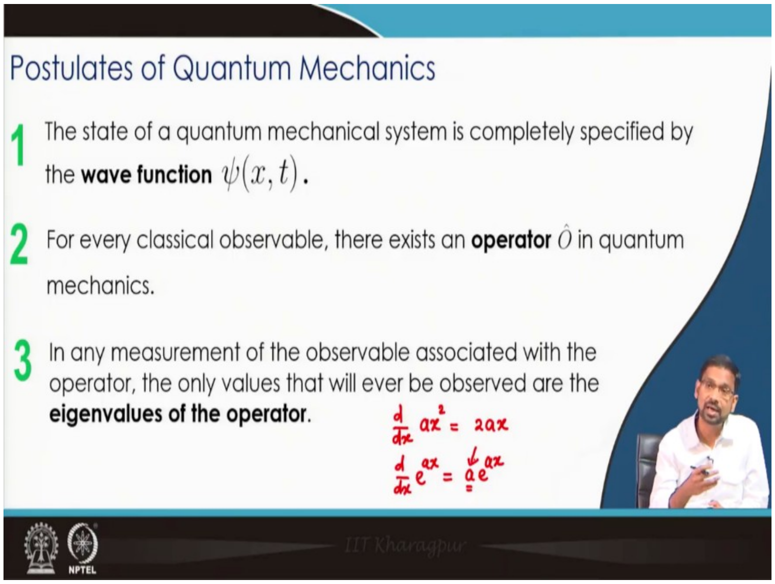

Postulates of Quantum Mechanics

1. The state of a quantum mechanical system is completely specified by the **wave function** $\psi(x,t)$.
2. For every classical observable, there exists an **operator** $\hat{O}$ in quantum mechanics.

3. In any measurement of the observable associated with the operator, the only values that will ever be observed are the **eigenvalues of the operator**.

$$\frac{d}{dx}ax^2 = 2ax$$

$$\frac{d}{dx}e^{ax} = \underline{a}e^{ax}$$

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The first postulate of quantum mechanics says that the *state of a quantum mechanical system is completely specified by the wave function*. Let us, first try to understand what it tries to tell, when I say I want to understand a particular problem quantum mechanically or I want to define a system quantum mechanically, what do I have in mind? I essentially want to obtain some properties of the system. I want to get some information about a particular molecule I have in mind, or a particular chemical reaction that I am studying. Quantum mechanics tells, if you are interested in any system and you want to study it quantum mechanically, there exists something called the wave function that contains all the information that you can possibly think of. Quantum mechanics gives this recipe, that if you want to know something about a particular system: a molecule or a chemical reaction or a biomolecule just have its wave function. What is this wave function? That is the tricky question.

The wave function does not have a physical interpretation. We typically express this wave function with this ψ, which is Greek y. It is a function of position and time $\psi(x,t)$. It has got a spatial dependence (x) and it has got its temporal dependence (t). Since it depends on the location and time, we can also study the time-evolution or how the system evolves in time using quantum mechanics.

This wave function ψ contains all the information about the system that we are interested in, but the wave function itself does not have any physical interpretation. But luckily for us, there exists some other quantity that can be used to obtain some physical idea. This goes by the name *Born interpretation*. Born interpretation suggests that although the wave function itself does not have any physical meaning, what has this physical meaning is $\psi * \psi = |\psi|^2$. This quantity has a physical meaning: a probabilistic interpretation. So, this is also called as Born's probabilistic interpretation, i.e., it gives me the answer to the following question. What is the probability of finding the system at a particular value of x at a particular value of t?

Since we have the wave function square or the mod square has a probabilistic interpretation, we have to make sure that the wave function follows certain conditions. For example, when I say that this has a probabilistic interpretation, normally the next question would be, if I search all over the place, that means from minus infinity to plus infinity, what is the probability of finding the system? Naturally, that would be 1. Because the particle is out there somewhere, I do not know exactly where but it is there somewhere. If you search everywhere you are going to find it somewhere! If I integrate $\psi * \psi$ over all space, I should get 1. This is called normalization of the wave function. As we see, the probabilistic interpretation required that this wave function should be normalizable. That means wave function ψ should be square integrable.

The requirement that the wave function should be square integrable comes from the fact that we are using Born interpretation of the wave function. The square integrability of the function requires that the function should be continuous, single valued, and its first derivative should be continuous. When the function is square integrable we call that function a well-behaved function. So, we impose a condition that our wave function should be well behaved.

The first postulate was simple in its statement: that there exists a quantity the wave function which contains everything that you need to know about the system. That is very reassuring. But the point is I want to know some information, if everything is there what and how can I learn about it?

Then quantum mechanics answers that question by saying, if you want to know something about a quantum mechanical system, there is a way. The way is to first ask this question, what do I want to know about this system? Which classical observable am I interested in it? Am I interested in the momentum? Am I interested in position? Am I interested in the energy? Because the answer lies in the question that I ask. If I am interested in position, then I must bring the so-called position operator. The second postulate tells that *for every classical observable there exists an operator in quantum mechanics*. If my classical observable is position, the operator that I must bring is the operator for position. If my classical observable is momentum, I must bring my momentum operator.

In quantum mechanics the operator is typical usually shown with a hat which signifies that I am talking about an operator. If I am looking for a momentum as the classical observable I must bring momentum operator or p_x whose form is given as minus $p_x = -i\hbar \frac{d}{dx}$. Similarly, if I am interested in kinetic energy, the operator is $\frac{p^2}{2m}$. If I am interested in the energy of the system, I would bring the Hamiltonian operator. Hamiltonian is the name of the operator whose classical observable is energy.

We said that we have to get this operator to get the answer. But then after getting this operator what answer am I going to get? The answer to that question lies in the third postulate. The third postulate says that, when I do the measurement for any classical observable, the only values that I only values that I will ever observe are the eigenvalues of the operator. Therefore, the eigenvalues and eigenfunctions are extremely important quantities in quantum mechanics. The result of my experiment is going to be the eigenvalues of the operator and only the eigenvalues of the operator, nothing other than the eigenvalues of the operator are going to be allowed as outcome from my experiment.

Consider this operator $\frac{d}{dx}$, which appears in the momentum operator.

$$\frac{d}{dx} a x^2 = 2ax \left(a x^2 \, not\ an\, eigenfunction \right)$$

$$\frac{d}{dx} e^{ax} = e^{ax} \left(e^{ax} \, is\, an\ eigenfunction \right)$$

The postulate 3 describes the second case, that only allowed observables are the eigenvalues of that operator. So, if I doing the measurement corresponding to the position, I am going to get the eigenvalues of the position operator, if I am making the measurement corresponding to the energy I will get the eigenvalues corresponding to the Hamiltonian operator, not the position operator, but the Hamiltonian operator because I am trying to measure the energy.

Now, you might be wondering what about the first case? What if the system is not an eigenfunction? What would I get? The answer is going back to postulate 3, postulate 3 tells no matter what only values that will ever be observed are the eigenvalues of that operator. You would still get the eigenvalues of the operators as outcomes and how that would happen we will come to that, but before that we get one interesting consequence of this third postulate.

Since the third postulate says that the eigenvalues are the observables of the experiment, the eigenvalues should be real and not imaginary. If the quantum mechanical operator corresponds to a classical observable, then the eigenvalues of the quantum mechanical operator is real.

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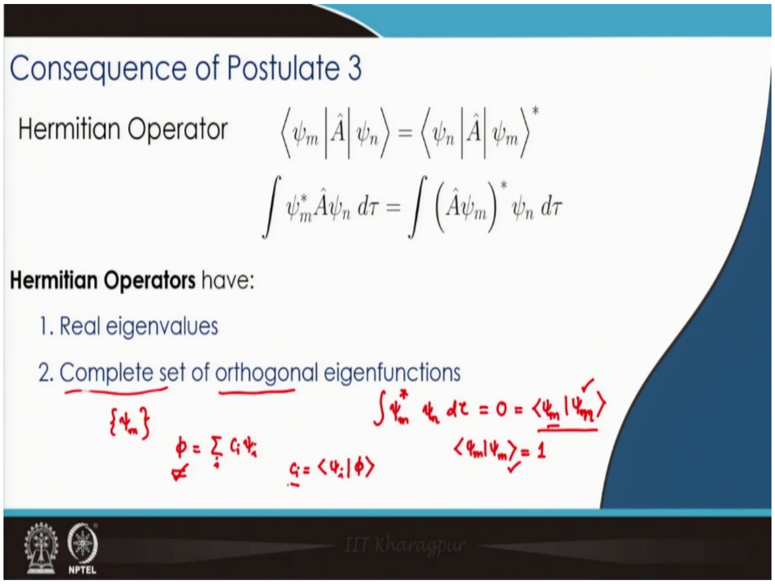

Consequence of Postulate 3

Hermitian Operator $\left\langle \psi_m \middle| \hat{A} \middle| \psi_n \right\rangle = \left\langle \psi_n \middle| \hat{A} \middle| \psi_m \right\rangle^*$

$$\int \psi_m^* \hat{A} \psi_n \, d\tau = \int \left(\hat{A}\psi_m\right)^* \psi_n \, d\tau$$

Hermitian Operators have:

1. Real eigenvalues
2. Complete set of orthogonal eigenfunctions

$\{\psi_m\}$

$\phi = \sum_i c_i \psi_i$

$c_i = \langle \psi_i | \phi \rangle$

$\int \psi_m^* \psi_n \, d\tau = 0 = \langle \psi_m | \psi_n \rangle$

$\langle \psi_m | \psi_m \rangle = 1$

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Now, this is a very interesting observation, because it has got great consequence. The consequence of postulate 3 is that if we impose this condition that the eigenvalues of the quantum mechanical operator is real and then if we do little bit of algebra will come to this equation

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

First, let us try to understand the second equation which is written in the integral form. $\psi_m^{¿}, \psi_n$ are two different functions, *A* is a quantum mechanical operator corresponding to some classical observable, therefore the eigenvalues of operator *A* are going to be real. Look how this left-hand side and right-hand side are different. In the left-hand side, the operator *A* acts on ψ_n. On the right-hand side, you see there is a turn-over, the operator *A* does not act on ψ_n rather it acts on ψ_m . This is a beautiful mathematical form that would help us obtain many interesting results. When an operator satisfies this relation, we call this operator a *Hermitian* operator. I am sure in your basic quantum mechanics course you have learnt how to show, the momentum, kinetic energy operators, etc. as Hermitian operators. If not, you please go back and try to do that.

The first equation (see above) is a reformulation of the second equation, by using the so-called Dirac's bra-ket form of writing the integral. There are three places in bra-ket, the left-hand side, the central, and the right-hand side. The left-hand side is called bra, the right-hand side is called ket. So, I have ψ_m in the bra, ψ_n in the ket and the middle part is the place for the operator. The operator acts on the ket giving rise to a function, which is then multiplied with the function in the bra. When a function is in the bra, and you open this bra-ket notation to write it in integral form, the function is written as its complex conjugate ($\psi_m^{¿}¿$, star is the indicates it is the complex conjugate of this function. Dirac's bra-ket formulation is quite convenient to write long equations and also to express the results in matrix form.

One consequence of the postulate 3 is that, all quantum mechanical operators that correspond to some classical observable are Hermitian operator. Now, what is so great about it? The great thing about this is that the Hermitian operators have some special properties.

First, they have real eigenvalues that we have already discussed. The second property is that, the eigenfunctions of a Hermitian operator form a *complete set of orthogonal functions.* There are two keywords here: orthogonal and complete set. First let us understand orthogonal. So, suppose I say that this Hermitian operator *A* has got two eigenfunctions, $\psi_m^{\square} \wedge \psi_{n.}$ Now, when I say they are orthogonal to each other I have the following in my mind. If I evaluate $\int \psi_m^{¿} \psi_n d\tau$, I should get 0. that would mean that they are orthogonal to each other. In bra-ket form this is shown as, $\langle \psi_m | \psi_n \rangle = 0. \psi_m^{¿}$is simply replaced by having $\psi_m^{\square}$ in the bra. This relation shows that the overlap of $\psi_m^{\square} \wedge \psi_{n,}$ which are two eigenfunctions of the same Hermitian operator *A* the overlap of these two functions is 0, that means they are orthogonal to each other. And of course, the wave function itself can be normalized (Born interpretation), $\langle \psi_m | \psi_m \rangle = 1$. Together, normalized and orthogonal functions are called orthonormal, $\langle \psi_m | \psi_n \rangle = \delta_{mn}$, which is 1 when $m = n$ and 0, otherwise. If I have, say, 10 eigenfunctions of a Hermitian operator each eigenfunction is going to be orthogonal to every other eigenfunction.

Now, what is a complete set? A complete set is even more interesting or has got even more significance. Suppose I have this eigenfunction ψ_m of the operator *A*. Just like ψ_m, I can have other eigenfunctions, $\psi_m, \psi_n, \psi_o \cdots$. I call them a complete set of eigenfunctions when I would be able to express any other arbitrary function (let us call it ϕ) as a linear combination of these eigenfunctions, i.e.,

$$\phi = \sum_i c_i \psi_i$$

If I have any arbitrary function ϕ, I would be able to express this arbitrary function of the complete set of eigenfunctions ψ_i. When I can do this, then I would say that the eigenfunctions form a complete set. Now, what is this c_i? The values of c_i are given as simply $c_i = \langle \psi_i | \phi \rangle$, which is

the overlap of ψ_i, that is one of these eigenfunctions, with the arbitrary function ϕ. In other words, c_i shows how similar ψ_i is to the arbitrary function ϕ. Hermitian operators have got these two beautiful properties: real eigenvalues and they form a complete set of orthogonal eigenfunctions.

In this lecture we discussed about three postulates of quantum mechanics and the consequence of this third postulate in so far as describing the Hermitian operator and how Hermitian operator have these beautiful properties which we would be using in the next class and discuss our quantum mechanical systems further. Thank you for your attention.