

Introductory Quantum Chemistry
Prof. K .L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 5
Postulates - Part 2

Good morning. We... Let me remind you what I did in the last lecture you see, we were discussing the postulates of quantum mechanics. And as I said, there are four postulates.

(Refer Slide Time: 00:27)

Postulate I

The state of a system is specified, as fully as is possible by the state function

$$\Psi(x, y..., t).$$

Probability of finding the system in a volume element $d\tau = dx dy \dots$ is given by

$$\Psi^* \Psi d\tau$$

There he goes!

The first postulate is here. The state of a system is specified as fully as is possible by the state function, which we denote by the symbol capital psi. And then the state function – once you know it, it is possible for you to calculate the probability that the particle may be found for your system; maybe found in a given volume element, which we denote by the symbol d tau. The symbol d tau is here. And I also pointed out that depending upon what the system is, the definition of d tau could be different. It may be dx into dy into dz if it is a particle moving in three dimensions. While if you idealize the particle as something that is moving in one direction, only then the d tau will be just equal to dx.

Now, we will pass on to the... We discussed the consequences of this. We said that the wave function in order for it to be acceptable, the function should at least be a square integrable function. And if it is a square integrable function, we can always carry out the

process of normalization; which means that I shall multiply the function by a suitable constant in such a fashion that the integral of $\psi^* \psi$ over the entire space is equal to 1, and then we said the function is normalized. In addition to that, for physical reasons, we said we expect the wave function or the state function to be a continuous function of position. And further, we also imposed the condition that it should not be multiple-valued function at any particular point, you should have only a single value for the function.

(Refer Slide Time: 02:29)

The slide features a central text box with a speech bubble containing the following text:

Postulate II

Corresponding to every observable, there is a linear, Hermitian operator.

To find the operator, write down the classical mechanical expression for the observable, and make the following replacements:

$$x \rightarrow x$$

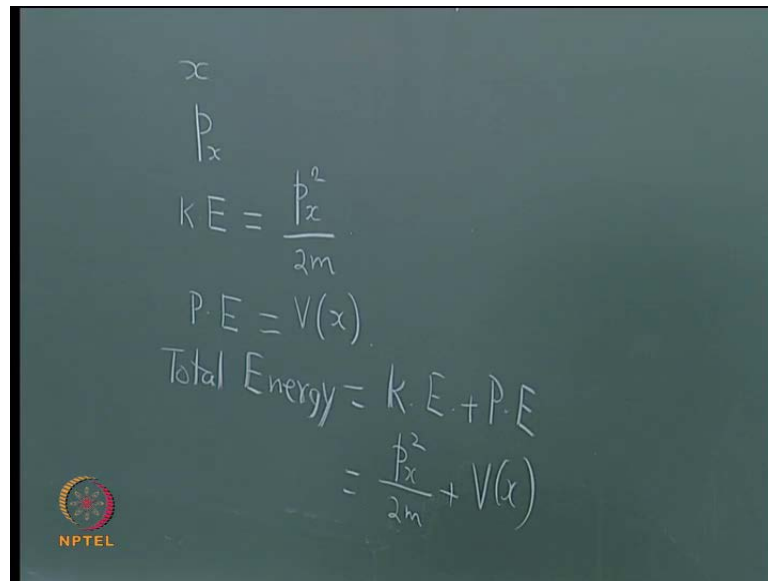
$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$$

The slide also includes a cartoon character on the right, a thought bubble on the left with symbols, and an NPTEL logo at the bottom left.

So, now we come to the second postulates. The second postulate is concerned with observables, because you see after all, in a lab, what we do; we make observations. And therefore, we... Suppose I make a measurement on a quantum system, what would be the result? So, that is the matter of postulates 2 and 3. So, let me introduce the second postulate. It says that, if we have any observable, corresponding to that, in quantum mechanics, there is linear, Hermitian operator. So, there are several words here in this postulate that needs explanation. First of all, what do I mean by an observable?

For our purpose, an observable will be defined by this. We will say that, it is anything that depends upon the position and the momentum of the particle. If I am thinking of one particle system, it is anything... Let me say it is 1 dimensional system. So, it is anything that depends upon x and p ; where, x is the position of the particle and p is the momentum of the particle. If you have a 3 dimensional system, it may be anything that depends upon x, y, z, p_x, p_y, p_z . So, that will be my definition of an observable.

(Refer Slide Time: 03:20)


$$\begin{aligned}x \\ p_x \\ K.E. &= \frac{p_x^2}{2m} \\ P.E. &= V(x) \\ \text{Total Energy} &= K.E. + P.E. \\ &= \frac{p_x^2}{2m} + V(x)\end{aligned}$$

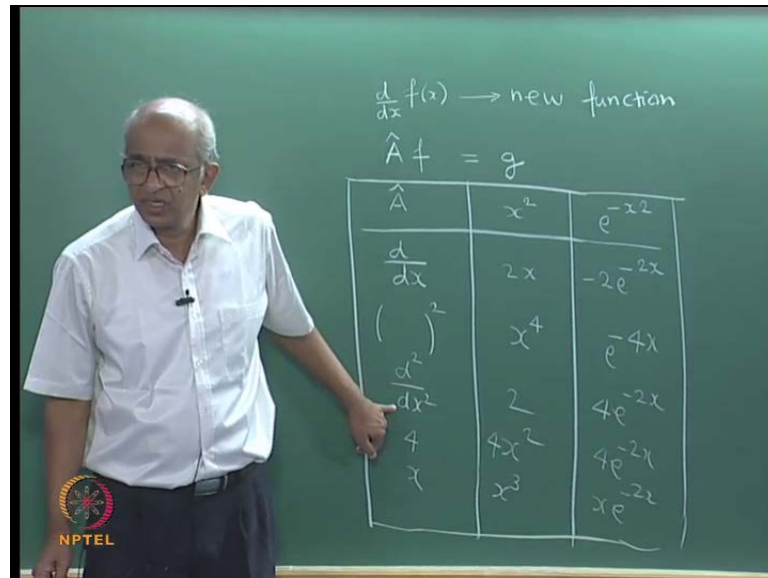
In fact, the symbolized thing is you see if I am making an observation, I may be measuring the position of the particle. Therefore, in that case, observable will be x . Or, I may be measuring the momentum of the particle, which I shall denote by p . It is probably better to put a subscript x , because this is the momentum associated with the particle due to its motion in the x direction.

But, you can think of more complex things. For example, you may think of kinetic energy of the particle. And again for 1 dimensional system, kinetic energy will be p_x square divided by $2m$. Or, if the particle is subjected to a potential energy, it is moving to an external field, which is caused by a potential... We will say there is a potential energy associated with the particle; potential will depend upon the position of the particle. So, potential energy will be a function of x let us say $-V$ of x . And this yet another example for an observable. You may also say total energy. Total energy is just the sum of kinetic and potential energies. So, it is going to p_x square by $2m$, which is kinetic energy plus V of x . This is a function of momentum as well as position. And hence, is another example for an observable.

Then, if you look at the postulate; it also says that, associated with every observable, each one these observables, there is a linear Hermitian operator. So, I have to explain what is meant by a linear Hermitian operator. So, let us start with the definition of an operator; I mean we will adapt the very simplified definition; I mean if you go to the

mathemized department, they will give you more rigorous definitions. But, we are not going to do that; we will have a very practical approach.

(Refer Slide Time: 06:53)



So, the definition or the way in which I am going to define an operator is this. Imagine that, I have a function f of x . And I carry out something with this function; maybe multiply it by let us 4 or maybe differentiate this function maybe. Let me say I am thinking of going to differentiate it. So, what do I do? I carry out the process of differentiation, which we usually denote by this symbol d by dx . And what will be the answer? The answer will be a new function, which is the derivative. Therefore, this gives you a new function, which in this case is nothing but the derivative of the function f of x . So, I will say that...

What is an operator? If you give me any function f , what I will do is; I will perform some operation, which I shall denote by this symbol. So, this is an operator. What does it give me? It gives me a new function, which I shall denote as g . So, this is my definition of an operator. But, then if I write A ; see the fact that it is an operator is not conveyed to you. Therefore, what I will do is I will give it a special hat. So, A with its hat. You should recognize that, it is an operator. So, the simplest example for A will be let me say... I am going to give you a kind of list, which will list different operators. So, d by dx will be let us say a typical operator that I can think of.

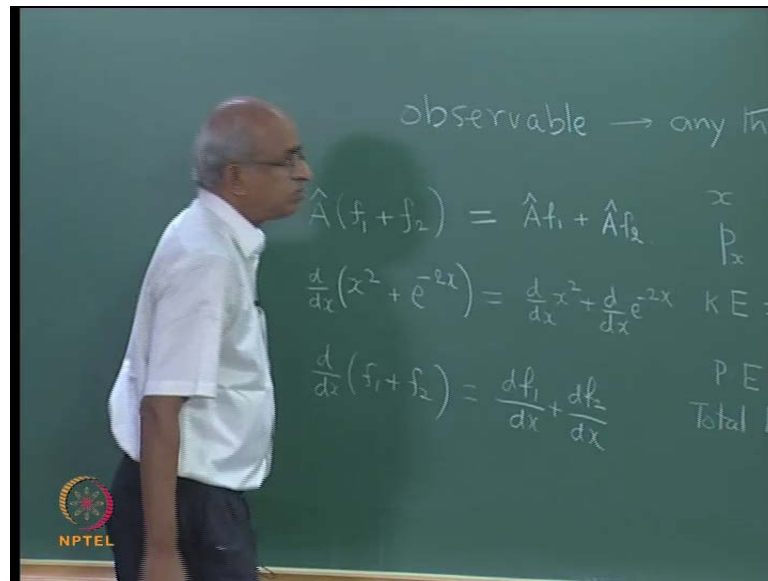
And, let me just for the sake of illustration, let me allow this to operate upon different functions. For example, suppose I have a function like x^2 ; then d/dx operating upon x^2 ; what is the answer? The answer is going to be $2x$. So, this is the new function. From x^2 , I have obtained a new function, which is $2x$. Or, I can also think of an operator like taking the square; which I shall denote by this symbol. So, what it tells me is that, if you give me a function f of x , I will simply take its square.

So, that is its operator. So, taking the square is an operator that can be performed on x^2 . What will be the answer? It is going to be x^4 . You can have other examples; for example, taking the second derivative of the function. What is going to happen is that, if it is operated upon x^2 , the answer will be just 2. Or, you can think of let us say multiplying the function by a constant, which you may denote... Let us say the constant is equal to 4. So, if you give me that any function, what I will do is, I will simply multiply that function by 4 and give you the answer. It is going to be $4x^2$.

Or, another simple thing, which we will often use, is I will take the function; I will simply multiply it by x itself. So, multiplication by x is another example. So, I will just denote that by x . And all that I will do is I will... Given the function, I will multiply it by x . Therefore, the answer here is going to be x^3 . So, these are all examples of operators. And to make it little bit more clearer, maybe I should think of another function; maybe e^{-x} . What is going to happen? Let me put a constant also there; maybe e^{-2x} .

So, d/dx will give me $-2e^{-2x}$; squaring will give me e^{-4x} . Or, taking the secondary derivative, what will it give me? It will give me $4e^{-2x}$. Multiplication by 4; it is going to give me $4e^{-2x}$. And multiplication by x ; what does it give me? It gives me xe^{-2x} . So, it is clear. What we mean by an operator? What is it? I mean you give me a function; I will perform some operation; and the result is going to be a new function. What did I do? Is everything OK? I suppose so. Therefore, having defined an operator, I should tell you what is meant by a linear operator.

(Refer Slide Time: 12:30)



So, imagine I have 2 functions. Imagine I have 2 functions. The first one I will denote by the symbol f_1 or maybe f_1 let me say. And the second function I will denote by the symbol f_2 . So, these are 2 functions. For example, one of them may be x^2 ; the other may be e^{-2x} typically. This may be x^2 ; the other one may be e^{-2x} . And what am I going to do? I am going to add them. So, I have... They do not have to be these; they may be... f_1 and f_2 may be anything, because we are doing quantum mechanics. We will impose the condition; usually that, f_1 and f_2 are acceptable wave functions.

Now, that is what we will do later. But, anyway for the sake of definitions, the f_1 and f_2 can be anything. And imagine that, I have an operator A acting on the sum of these two: the sum of f_1 and f_2 . And I mean I can actually allow A to operate upon f_1 ; and I can also allow A to operate upon f_2 separately. And if it... And then of course, I can sum the two. And if it so happens that, A operating upon the sum of f_1 and f_2 is equal to A operating upon f_1 plus A operating upon f_2 ; if this is satisfied for any arbitrary f_1 and f_2 ; then I can say that, A is a linear operator. But, then you see you may ask a question like is – is not obvious that, this should be always satisfied? And the answer is no. It is not always satisfied. For example, let us say examine this d/dx ; d/dx operating upon f_1 plus f_2 . If you want, we can take this particular example. We can allow d/dx to operate upon x^2 plus e^{-2x} . What will be the answer? We know what the answer is, because we know how to ((Refer Time: 14:50)) a

differentiation of a sum. Differentiation of a sum is... Derivative of a sum is equal to derivative of the first time plus the derivative the second time. So, here it is obvious that, it is actually d by dx operating upon x square plus d by dx operating upon e to the power of minus $2x$. And that is definitely violates with respect to what f_1 and f_2 are. Therefore, in this case, it is clear that, this must be able to $d f_1$ by dx plus $d f_2$ by dx . Therefore, d by dx definitely is a linear operator.

Similarly, if you think of d^2 upon dx^2 ; that also is a linear operator, because second derivative of a sum is actually equal to the sum of the second derivatives. Multiplication by 4 – that is obvious; I mean if you multiply f_1 plus f_2 by 4, it is equivalent to multiplying f_1 by 4 and f_2 by 4 and adding the two. So, this also is a linear operator. Multiplication by x is again another example for a linear operator. But, notice that, I did not discuss this one. What about this operator? Taking the square. So, as an...

(Refer Slide Time: 16:20)

$$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2$$

$$(f_1 + f_2)^2 \neq f_1^2 + f_2^2$$

$$\sqrt{f_1 + f_2} \neq \sqrt{f_1} + \sqrt{f_2}$$

$$\hat{A}f = e^f$$

x
 p_x
 $KE =$
 $P.E =$
 $Total E$

NPTEL

Let us examine whether this is a linear operator. Taking the square, you see you would have f_1 plus f_2 . If this is the sum, you take the square of that. That is the operation. Now, if that operation is performed on f_1 , what will be the answer? You will be taking the square of f_1 . And if you allowed this same operator to operate upon f_2 , the answer will be f_2 square. And then if I sum the two, I am going to get this. Now, the question is whether this is equal to that? And obviously, the two are not equal, because when we

take the square of $f_1 + f_2$, you will get $f_1^2 + f_2^2 + 2f_1f_2$. And therefore, this is not satisfied; and hence, this operator is not linear. All the other operators that I have listed here are linear operators.

Now, it is easy to think of operators, which are not linear. For example, instead of taking the square, suppose you had taken the square root. This square root of $f_1 + f_2$ is not equal to square root of f_1 plus square root of f_2 . Therefore, this is another example for an operator, which is not a linear operator. Or, if you like, you can think of another operation, which is taking the exponential. See for example, if I say that, A operating upon f ... Where should I write? Let me define a new operator – A operating upon f ; I say it is equal to e to the power of f . If you give me any function, I will just take the exponential of that function. Very easy to convince yourself that, this is not a linear operator; it is an operator that is non-linear. So, this is enough as far as the linearity is concerned.

(Refer Slide Time: 02:29)

The slide features a light green background with a black border. At the top center, the title "Postulate II" is written in blue. Below the title, two speech bubbles contain text. The first bubble says "Corresponding to every observable, there is a linear, Hermitian operator." The second bubble says "To find the operator, write down the classical mechanical expression for the observable, and make the following replacements:" followed by two mathematical expressions: $x \rightarrow \hat{x}$ and $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$. On the right side, a cartoon character with a beard and glasses is shown speaking. On the left side, there is a small cartoon character with a thought bubble containing various symbols, and a logo for NPTEL at the bottom left.

Now, we have another way. See here in the postulate, which says Hermitian operator. So, what do you mean by Hermitian operator?

(Refer Slide Time: 18:43)

Hermitian Operator \rightarrow eigenvalues

ψ ϕ

$$\int d\tau \phi^* \hat{A} \psi = \left(\int d\tau \psi^* \hat{A} \phi \right)^*$$
$$\int_{-\infty}^{\infty} dx \phi^*(x) \frac{d}{dx} \psi(x)$$

NPTEL

Let me imagine that I have two acceptable state functions. Let me denote them by the symbol psi and phi. This of course means that, you see they can be normalized. So, they are square integrable functions; they are continuous; they are single valued. Now, suppose I allow an operator. I allow an operator A to operate upon the wave function psi or the state function psi. And then what will I do is I will multiply this result. This of course is a new function. If you allow A to operate upon psi, the answer is a new function; I am going to multiply the result by the complex conjugate of phi. What is the result? It will be something new – some new thing. And what I will I do is I will multiply the whole thing by the volume element d tau and integrate over the entire space

Now, if you need an example, this is... This is written in a general notation. For example, if you say that, A is d by dx and psi is a function of x alone; that means that I am thinking of a particle, which is moving in one dimension. And this phi is a function of x. And I will take its complex conjugate. And if it is a 1 dimensional system, what I am really talking about is this integral over the entire space; over the entire space means that, I have to integrate from minus infinity to plus infinity. So, if you are thinking of a 1 dimensional system, this object actually means that. But, if you are thinking of a 3 dimensional system, what is going to happen is that, psi will be a function of xyz. Operator A may be perhaps differentiation with respect to x alone; and phi will again be a function of xyz. So, this is the special case of a 1 dimensional system. But, this is this notation as it is written is very general; it can apply to 1 dimension or 3 dimension or

maybe higher dimensional systems. So, what is going to happen is that, once you have performed an integration over the entire space, the answer is going to be some number.

Now, what I can do is instead of doing things in this fashion, I can allow A first to operate upon ψ . But, here notice I am allowing A to operate upon ψ . But, instead of that, suppose I allow A to operate upon ψ , multiply the result by ψ^* and then by the volume element $d\tau$ and integrate over the entire space. So, what will happen? I shall get some number there. And if it so happens that, the number that I obtained here; I take it and take its complex conjugates. And if it so happens that, after complex conjugation, it is equal to this number. Then I say that, A is a Hermitian operator. It is a Hermitian operator, not a...

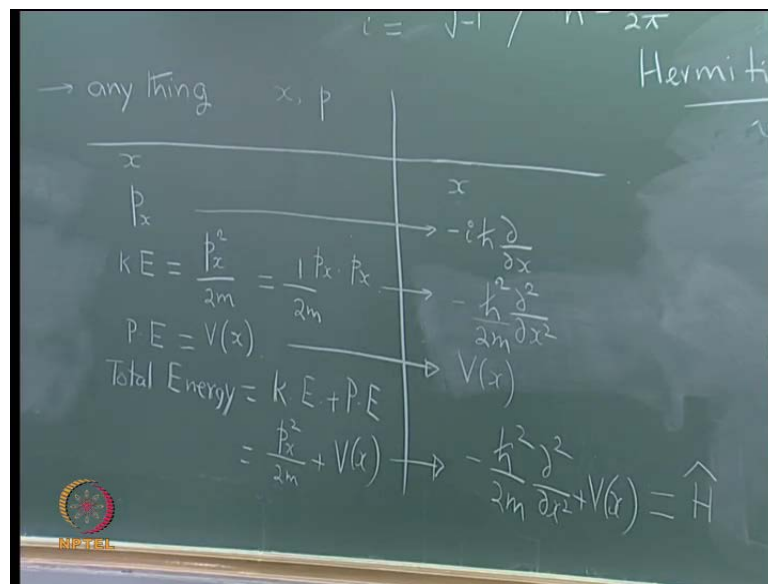
So, this is how a Hermitian operator is defined. Now, this definition actually sounds a little bit abstract. And there is a reason why operators that occur in quantum mechanics have to be Hermitian. The reason is that, the eigenvalues of Hermitian operators – we will come to eigenvalues in the next postulate – are guaranteed to be real. That is a special property of Hermitian operators. I have not defined what is meant by eigenvalues. But, I will do that. But, it is possible to show that, if an operator is Hermitian, then all its eigenvalues are real. And as I said, the reason for this postulate will become clearer when I discuss the next postulates.

Now, see this postulate is actually saying that, if you give me any observable like position or momentum or kinetic energy, there is actually an operator that is associated with this. But, the question is how does one find the operator? The postulate also gives you the prescription for that. So, we continue this postulate. And the second part of this postulate actually gives you a prescription for finding the operator. So, what it says is if you wanted to find the operator, what you have to do is you have to write the classical mechanical expression for the observable. Now, we have actually written down a few observables here x , p_x ; kinetic energy given by $p_x^2/2m$; potential energy given by $V(x)$; total energy given by this expression.

So, these are actually classical mechanical expressions for these observables. Classical mechanical expression for a position is x . Then momentum p_x ; kinetic energy – it is actually given by $p_x^2/2m$. So, we have actually done it for a few observables on the board. And then we follow the prescription. What does it say? You look at the

expression; you look at the classical mechanical expression and you have to make these replacements. What are the replacements that the postulates says? If you have x , that is, position occurring; then do not do anything; $x \dots$ The arrow shows x goes to x ; that means, do not do anything; you do not do anything with position; they remain unchanged. But, if we have p_x occurring in the expression, what you have to do is you have to replace p_x with minus $i \hbar$ cross dou by dou x .

(Refer Slide Time: 25:48)



Minus i is actually equal to minus of square root of minus 1; or, i is actually square root of minus 1. And \hbar cross... Let me just remind you; I am sure you are all familiar with it. But, \hbar cross is equal to \hbar divided by 2π ; where, \hbar is Planck's constant. So, let us follow this prescription and illustrate the postulate by doing these things, doing those replacements for all these things that are written here. So, here is the classical observables. These are the observables. And what are the associated operators? If you are thinking of x , you do not do anything. This is therefore, the operator associated with position for a 1 dimensional system; it is just x itself. What does this means? This means that, if you have a function; if you have any wave function or anything, I will just multiply that function by x . That is the meaning of saying that, x is a operator associated with position.

Similarly, if you say you have momentum, then what you will do is you will have the associated operator, which is going to be minus $i \hbar$ cross dou by dou x . Then if you have

kinetic energy actually; kinetic energy is interesting, because it has p^2 . So, if you like, you can say p^2 is equal to $p \cdot p$; that is what it is anyway – divided by $2m$. And then it is clear. What we should do? We have $2 p$'s in this expression. So, we will have 2 minus $i \hbar$ cross $\frac{d}{dx}$; one $i \hbar$ cross $\frac{d}{dx}$ followed by the other.

So, what this actually means is you see if you have any function on which this operator is going to operate; I will allow this operator to operate on it first; that means if this is operating upon ψ of x ; if this is operating upon ψ of x , the answer will be minus $i \hbar$ cross $\frac{d}{dx}$; that means I am calculating the derivatives of ψ . But, then I have to do the same operation once more. So, that means I would have differentiate this once more and then multiplied that by minus $i \hbar$ cross once more. So, effectively, what I have is I have minus $i \hbar$ cross; multiplication 2 times; I am going to get square of that. And the differentiation I am going to do is again 2 times. Therefore, I would be evaluating the second derivative. Therefore...

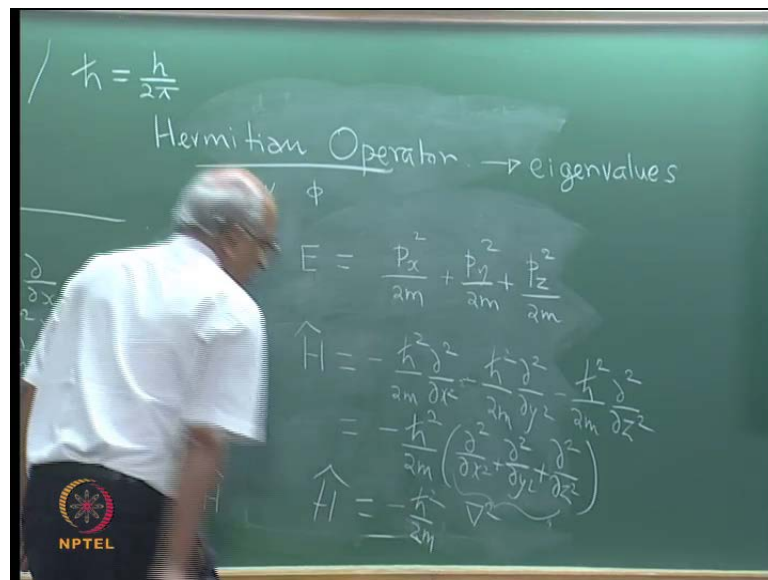
Let me just remove this, because there is no enough space in the table that I am writing. This turns out to be equivalent to taking the second derivative of any function that you have; and then multiplying that by minus $i \hbar$ cross the whole square. So, when you take the minus $i \hbar$ cross actually, it is going to be equal to $i^2 \hbar^2$; and i^2 is minus 1. Therefore, this is actually going to be minus \hbar^2 cross square. And then of course, I should not forget this 1 by $2m$. So, naturally, it will be 1 by $2m$ sitting there.

So, this is the operator associated with kinetic energy. And if you think of potential energy again, what is going to happen is you see V of x . You look at the expression; there is no momentum occurring in this expression; only x is occurring. Therefore, what do you do? You do not do anything, because it is just a function of x alone. Then as far as total energy concerned, things are quite straight forward now, after we have seen these examples. You have p^2 . So, p^2 is going to be replaced; p^2 is going to be replaced with this object. And V of x is not going to change. Therefore, you are going to get minus \hbar^2 cross square divided by $2m$ $\frac{d^2}{dx^2}$ plus V of x as the operator associated with total energy of the system.

Now, in our discussions, the operator associated with total energy is very very very important. It is going to occur in the Schrodinger equation, which I will introduce later.

And therefore, it is given a special symbol. It is usually denoted by the symbol h with a hat on top of it to indicate that it is an operator and it is referred to as the Hamiltonian operator. The reason is that, you see in classical mechanics, this object is referred to as the Hamiltonian of the system; p square by $2m$ plus V of x is the Hamiltonian. And therefore, this is referred to as the Hamiltonian operator; and it is going to be important. Maybe I can illustrate the way the things proceed by taking a 3 dimensional system. Imagine you have a helium atom moving in this room. You have a helium atom in this room; something that I talked about yesterday; you say that, this room is completely empty except for one helium atom; something that we cannot attain, but it does not matter.

(Refer Slide Time: 32:00)



As an example to think of; and if you are thinking of let us say the total energy of helium atom; as I said, I am only interested in the helium atom as a particle; I am not going to think of the internal structure. Therefore, in this room, you see the potential energy... There is gravitational potential energy, but we will not worry about that, because it is very small for our purpose. So, the helium atom will be executing translational motion. And because of translational motion, what is going to happen is that, the total energy of the system will be given by... Its momentum has a component in the x-direction, a component in the y-direction as well as a component in the z-direction. So, because of its motion in the x-direction, the energy will be p_x square by $2m$; kinetic energy will be so much. Then you will have of course p_y square by $2m$. This is total energy that I am

talking about. And then p_z^2 by $2m$. So, this will be the classical mechanical expression for the total energy.

The total energy... Notice I have taken the potential energy to be 0. And this is the kinetic energy. And then what will be the Hamiltonian operator, which will describe the helium atom? Hamiltonian operator is the operator associated with total energy. And what is going to happen? You will make these replacements. You see you have p_x^2 . So, I am going to get minus \hbar^2 over $2m$ times the second derivative with respect to x . Then the next time, you have p_y^2 ... p_y is going to be replaced with minus $i\hbar$ times the derivative with respect to y . So, you are going to get minus \hbar^2 over $2m$ times the second derivative with respect to y . This means partial differentiation with respect to y . Then this is going to be replaced with minus \hbar^2 over $2m$ times the second derivative with respect to z . So, this is the operator that is associated with total energy. And it is obvious that, this may be written as minus \hbar^2 over $2m$ times the sum of the second derivatives with respect to x , y , and z .

Now, it is obvious that you see this is rather tedious to write. And therefore, people have invented clever ways of writing these things. Instead of writing this whole thing, it is usual to write that as ∇^2 . Therefore, the Hamiltonian will be minus \hbar^2 over $2m$ times ∇^2 . So, when you write ∇^2 , it actually means this sum – sum of these second derivative operators. Now, suppose for some reason, you wanted to include the gravitational potential energy also, you can easily do that. All that will happen is that, you will have to say, energy is given by the sum of these plus the potential energy, gravitational potential energy; as you know, will depend upon the mass of the particle. It will also depend upon g – the acceleration due to the gravity; and then of course, it will depend upon the height at which the particle is.

So, you can say the way it is z coordinate, measures the height of the particles let us say from the floor. Therefore, what will happen? If that was the way it was, you will say gravitational energy would be $m g z$. But, as I said, in most of the things, gravitation is not at all important; most of our atomic and molecular physics, gravitation does not play any role, because... It essentially because you see we do not cover that much distance in space or that much height in space. But, if you wanted to include that, what will happen is that, this will be the modification that you will have to do. That is just to illustrate the point.

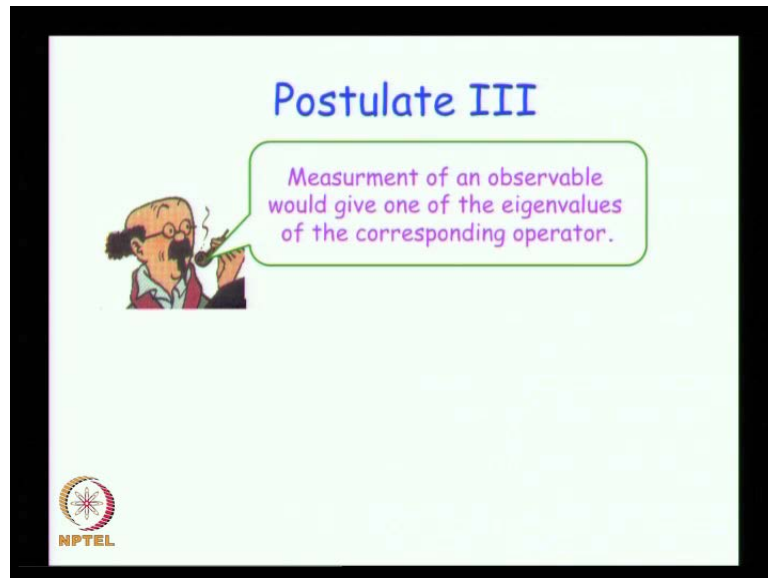
Now, if I was interested in the internal structure of helium atom – something that I talked about in my previous lectures; then what I will imagine is that, I have the nucleus, for example, at the origin; and then I will have the 2 electrons. I can say the 2 electrons will be moving about. And then as I will have a kinetic energy, they will also have potential energy because of their interaction with the nucleus, because electrons are negatively charged, the nucleus is positively charged. Therefore, the expressions will get little more complex. We will see such expressions later on in the course.

(Refer Slide Time: 02:29)

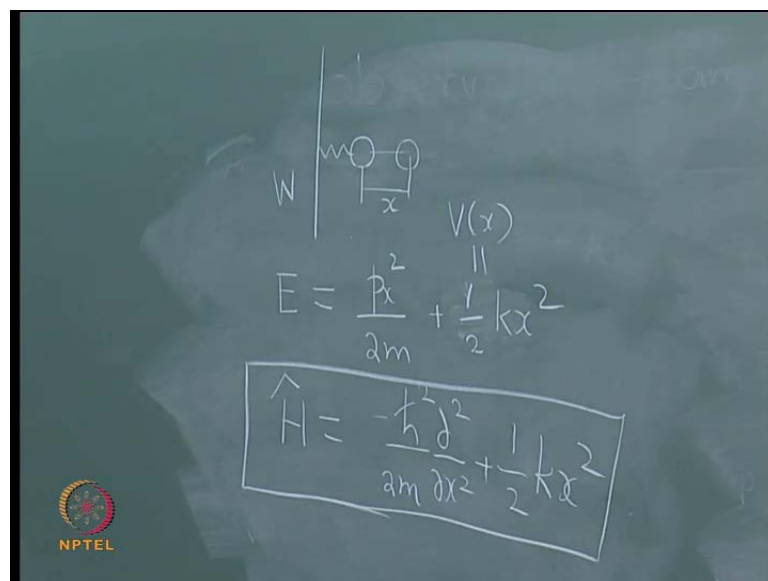
The slide is titled "Postulate II" in blue text. It contains two main text boxes with a light green background. The first box says: "Corresponding to every observable, there is a linear, Hermitian operator." The second box says: "To find the operator, write down the classical mechanical expression for the observable, and make the following replacements:" followed by two equations: $x \rightarrow x$ and $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$. The slide also features a cartoon character on the right, a thought bubble on the left containing physics symbols, and an NPTEL logo at the bottom left.

Now, this is the second postulate. What it has said is that, if we have any observable, there is an operator. But, then you see in the lab, what do we do? We make a measurement. And so we have the next postulate. It talks about measurement. So, it says that, suppose you make a measurement of a particular observable; then what it says is that, the answer will be always an eigenvalue of the corresponding operator. This is the postulate. To make it clearer, let me consider a specific example.

(Refer Slide Time: 38:16)



(Refer Slide Time: 39:08)



The example will be the hydrogen atom. Remember in one of my earlier lectures, I spoke about the hydrogen atom, which is adsorbed on the surface of tungsten; and imagine that you displace the hydrogen atom in this direction and release it; then it will execute vibrational motion. So, as far as this system is concerned, what is going to happen is that, the total energy – if you assume that it obeys classical mechanics, the total energy will be given by $p \times \text{square by } 2m$. This is the kinetic energy. And then you will have to add to that the potential energy of the system. The system has now a potential energy. Why? Because if I take the hydrogen and move it; and what will happen is that, this ((Refer

Time: 40:10)) which I have shown as a spring will get stretched. And the stretching means that, you see you are storing potential energy into that boat. Therefore, you see if you denote the displacement of this atom from its equilibrium position; from here, suppose you displace it to a new position by displacing it by an amount x from the equilibrium position. Then what will happen is that, the potential energy of the function, that is, the potential energy of the particle will be dependent upon x ; it will depend upon how much you have displaced the particle. Therefore, you will have V , which is a function of x .

And, the simplest thing to say that, this V is given by a quadratic function of x . So, it is equal to half k square. This is the simplest model that you can use to describe such a system. This essentially says that, if you displace the particle to one side and release it to execute harmonic oscillations, it would behave like an oscillator oscillating with a particular frequency. See if you say that, this harmonic model... We will study this in detail later. But, let us say that, I will say V of x in this case is very well-approximated by a quadratic function of x .

Then, what will happen is that, the total energy will be given by $p^2 x^2$ by $2m$ plus half $k x^2$ square; where, half $k x^2$ square is the potential energy of the system; k being a constant, which essentially characterizes how stiff the bond is between the hydrogen and transcend surface. So, if you say this is the total energy of the system, then you can ask, what is the corresponding operator? The corresponding operator will be denoted by the symbol \hat{H} . And if I follow the prescription that we saw in the previous postulates, what will happen? This is going to be given by minus \hbar^2 cross square by $2m$ dou square upon dou x^2 square plus half $k x^2$ square. So, this will be the Hamiltonian operator for the system.

Now, suppose you look at postulate 3 and ask, suppose I make a measurement of the energy of the system; what this postulate says is that; the answer is going to be an eigenvalue of the operator that is associated with energy. And the operator that is associated with energy is the Hamiltonian operator. It is given by this. Therefore, what it says is that, if you make a measurement of the energy of the system, the answer is going to an eigenvalue of this Hamiltonian operator. But, then of course, I should explain to you what is meant by an eigenvalue, which I have not done yet. So, let me define what is

meant by... Let me tell you what is meant by an eigenvalue. Again, I shall illustrate with this with examples.

(Refer Slide Time: 43:51)

$$\frac{d}{dx} x^3 = 3x^2$$
$$\frac{d}{dx} e^{i3x} = (i3)e^{i3x}$$
$$\hat{A} \phi = a \phi$$

eigenvalue → a
eigenfunction → ϕ

Let me think of the operator d by $d x$. And you know that, d by $d x$ operating upon maybe x cube gives me the answer $3x$ square. What happens is that, it operates upon x cube and gives me a totally different new function. But, suppose it... What d by $d x$ does is; suppose I allow it to operate upon a function, which I will write as e to the power of $i 3x$. So, what is the answer? It is obvious; if you know how to differentiate, you know what the answer is. The answer is just e to the power of $i 3x$ itself, but multiplied by i into 3 .

See you compare the two cases. In the first case, you got a totally new function. But, in the second case, what is happening is that, you do not get a totally new function; what is happening is that, you get the original function itself, but multiplied by a constant, which is i into 3 . Therefore, we say that, as far as this operator is concerned; as far as this operator is concerned, this function is special. Why is it special? Because the effect of this operator on this function is just to multiply it by a constant. So, such a function is referred to as an eigenfunction of the operator.

So, we can generalize this and say, imagine I have an operator A ; and suppose when it operates upon a function ϕ , what happens? I do not get a completely new function, but I get the same function back, but multiplied by a constant. And that constant I shall

denote by the symbol small a . Therefore, A operator upon a ϕ gives me ϕ back, but multiplied by the constant a . Then I say that, this ϕ is special; and it is an eigenfunction of the operator A . And small a I will refer to as the associated eigenvalue. So, this is eigenfunction; and small a is the eigenvalue. A given operator may have several different Eigen functions.

For example, I could have said e to the power of $i 4 x$. That also is an eigenfunction of the operator d by dx . So, e to the power of $i 5 x$ again is an eigenfunction. So, it is possible for a given operator to have a large number of eigenfunctions; and each eigenfunction has its own associated eigenvalue. In this case, of course, you see eigenvalue is actually a complex number. In this particular case, the eigenvalue is actually i into 3 or maybe i into 4 or i into 5 depending upon which function you consider; and the eigenvalue happens to be actually a complex numbers; strictly speaking, it happens to be a purely imaginary number.

Now, suppose I think of the operator d^2 upon $d^2 x^2$; and imagine that, it operates upon a function, which I may denote as $\sin kx$. it is very easy to carry out two differentiations of the sine function. To carry out two differentiations, what will be the answer? I hope I can just write it as it is. The answer is going to be minus $k^2 \sin kx$. Maybe I can remove this. So, this makes you realize that, $\sin kx$ is an eigenfunction of the operator d^2 upon $d^2 x^2$. And the associated eigenvalue in this case is minus k^2 . And it is also obvious that, you can have... k can have any value; maybe it is 0 or 1, 1.5; it does not matter what its value is; always $\sin kx$ is an eigenfunction of d^2 upon $d^2 x^2$. I think I will stop here and continue in the next lecture.

Thank you for listening.