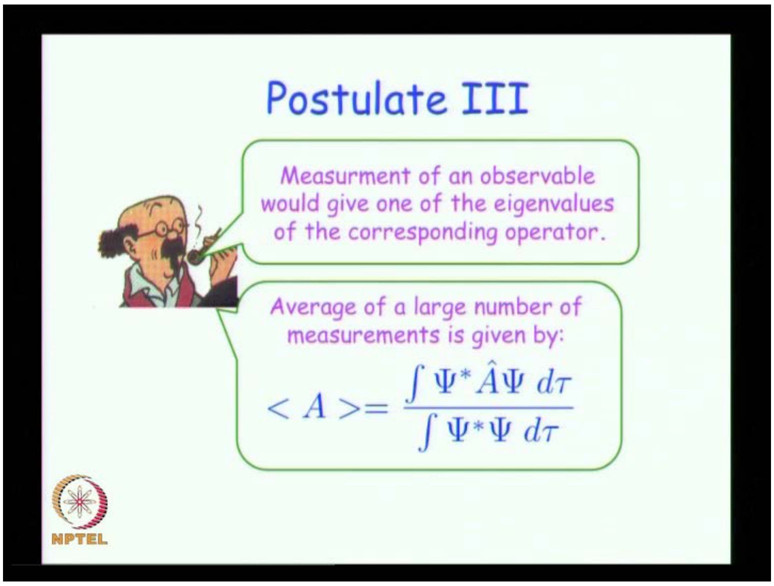
Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 6
Postulates - Part 3

(Refer Slide Time: 00:25)



Postulate III

Measurment of an observable would give one of the eigenvalues of the corresponding operator.

Average of a large number of measurements is given by:

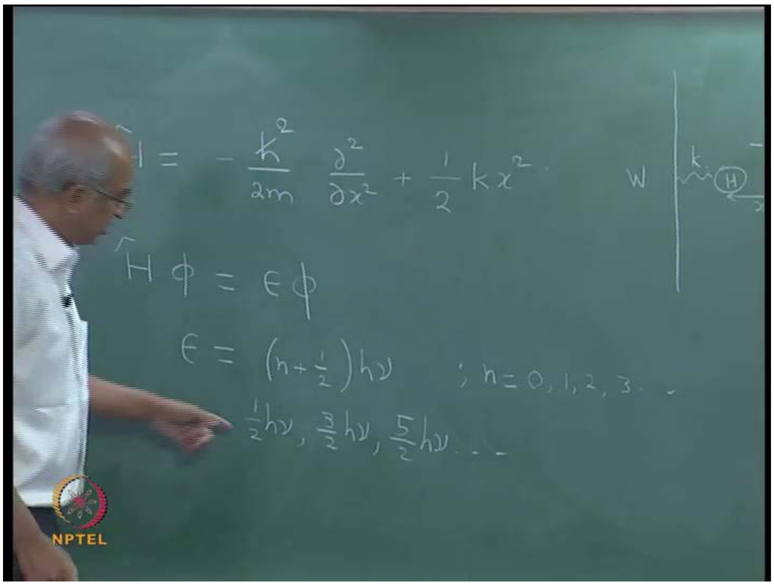
$$< A >= \frac{\int \Psi^* \hat{A} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

Yes, I was telling in my previous lecture the postulate three says, that if you have observable and if you make a measurement of that observable, the answer will be an Eigen value of operator that is associated with these observable.

Now, observables, whenever we make a measurement we will have to get real numbers, right. What this postulate says, that those numbers are Eigen values of the associated operators, therefore it is must that the Eigen values of the operator must be a real number, right. And in our previous postulate we had said, that operators are Hermitian. So, the reason for saying that this operation are Hermitian is that it is possible to prove rigorously, that Hermitian operators have always real Eigen values, ok.

So, that is the reason why the, why the Hermitian occurs in the previous postulate and in fact, when we proceed, sometime during the course I will prove, that Hermitian operators have always Eigen values, which are real; all Eigen values of Hermitian operators can be proven rigorously to be real.

(Refer Slide Time: 01:44)



So, if you think of the Hermitian operator for the harmonic oscillator, the, we show that expression for it is given by minus h cross square by 2 m dou square upon dou x square. This comes from kinetic energy of the particle. And then in addition to that we have the potential energy occurring in the Hermitian operator. And for harmonic oscillator potential energy is actually given by 1 by 2 k x square where k is known as the force constant for the harmonic oscillator. I give you the physical example. This is a hydrogen atom attached on the surface of tungsten and the bond between the hydrogen and tungsten may be thought of as a spring with a force constant k.

Now, what do you mean by that? It means, if you displace this hydrogen from its equilibrium position by a distance x, to a new equilibrium, to new position by distance x, then the bond is going to be stretched and there will be force trying to restore it back to the equilibrium position. And restoring force actually will be proportional to x and the force is actually equal to k times its magnitude equals k times x. That is the meaning saying, that the force constant, this is k and because you see it is in the direction that is opposite to the direction in which x is increasing, we say, that the force is actually minus k x because it is in the opposite direction to the direction in which x is increasing.

And actually, if you study the classical mechanics of this, which we will not discuss, what will happen is that the, if you displace this atom and release, it will execute oscillations, it will execute harmonic oscillations. And it will execute the given number of vibrations per unit time and the numbers of vibrations is usually denoted by symbol nu and it is obviously, going to depend upon how strong this bond is and how heavy this atom is. So, therefore, you can expect dependence of this ((Refer Time: 04:12)) vibration on the mass of the atom, as well as, on the force constant then.

In fact, if you study the classical mechanics of the system you will find, the information that it executes, the given number of oscillations per unit time, given number of vibration per unit time refers to as the frequency of the oscillator and frequency is related to the force constant and mass of the particle by this relationship. So, this is number of oscillations that you will, you will execute.

Now, quantum mechanically, suppose you have such a system and you are able to measure its energy, what this postulate says is that answer is going to be an Eigen value of this operator H. So, therefore, you want to know what the Eigen values of this operator are, because if you make a measurement of energy the answer is going be a particular Eigen value of this operator. So, how do you find an Eigen value? The answer is that you will have to allow h to operate upon some function, may be phi, such that what will happen, I am going to say phi is an Eigen function of this operator.

So, what is going to happen is that I am going to get phi back, but multiplied by a constant, multiplied by an Eigen value and that Eigen value I need a notation for it, but this Eigen value is, is eventually going to be energy of the system, right, because the, of the postulates. So, therefore, what I will do is I will denote this by, may be some symbol, which I may denote as epsilon.

So, if you make a measurement of energy, then what is going to happen is that it is going to be an Eigen value of the operator. So, if epsilon is the Eigen value, then the answer could be that epsilon. In fact, in the case of the harmonic oscillator with this Hermitian operator you can actually find the Eigen value, as well as, Eigen function, something that we will do later. So, it is possible to show, that the Eigen values of the harmonic oscillator have the form, which I am going to write. They are of the form n plus half h nu. As I told you, it is possible for an operator to have several different Eigen functions, each having its own Eigen values.

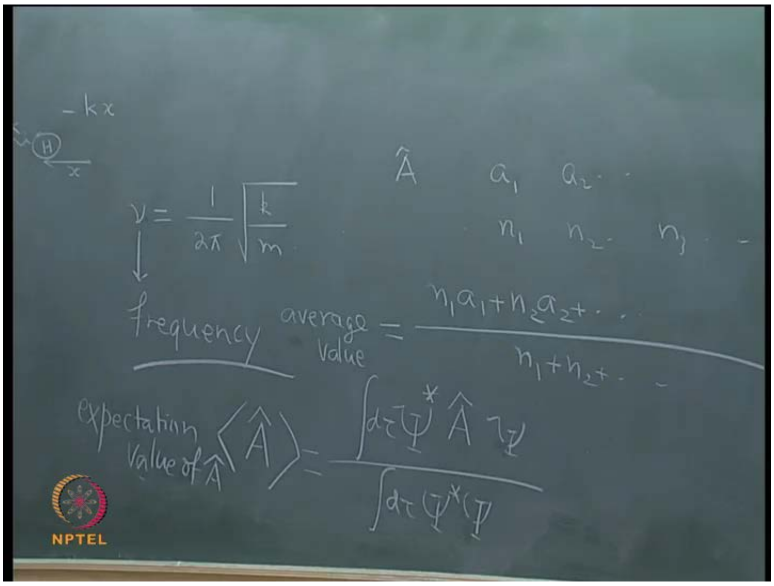
So, therefore, if you ask me a question like, how many Eigen values can an operator have? Normally, the answer will be infinite number of Eigen values. So, this particular operator has an infinite number of Eigen values and they are of the form n plus half nu where n is a number characterizing the Eigen value, which can take the values 0, 1, 2, 3, 4, etcetera. This means, that the different possible Eigen values are obtained by putting these values of n, which are actually half h nu if you put n equal to 0 or 3 by 2 h nu or 5 by 2 h nu, etcetera. These are all different possible Eigen values of this Hermitian operator for the harmonic oscillator.

So, what is means, that if I can measure the energy of the harmonic oscillator, then the answer that I find will be one of these Eigen values and you are not going to another answer that is what this postulate says. One of the Eigen values may be, it may be half h nu or maybe it will be 3 by 2 h nu or may be it can be 5 by 2 h nu and so on. So, the answer is guaranteed according to this postulate to be one of these different Eigen values.

Similarly, if you are making a measurement of the possession what will happen is, that there has to be, the answer has to be an Eigen value of the operator that is associated with possession or if you think of making a measurement of momentum, the answer has to be an Eigen value of the momentum operator, right.

But then suppose I make a series of measurement, I am going to have this harmonic oscillator, which is vibrating and I am going to measure its energy again and again and again at different instants of time I make a measurement. Now, may be I will come back tomorrow and again make a measurement, may be next day I will make one more measurement and so on. So, I make a series of measurements. Now, it is not guaranteed, that I should get the same answer. This is one peculiarity of quantum mechanics that I have already spoken about, right, in my previous lectures. It is not necessary, that I should get the same answer.

(Refer Slide Time: 09:28)



So, imagine, I will make a very general statement, imagine that I have an operator A, which is associated with some particular observable and this has different Eigen values. First Eigen value is a 1, second is a 2, third is a 3, etcetera, there are so many Eigen values and what am I going to do is, I am going to make large number of measurements. Now, the first time I make a measurement, maybe I will got the answer a 1, second time it may be a 2, does not have to be same. So, let us say, I make a large number of measurements and what happens is that I shall get, let me say n 1 times, I am going to get, I will get answer a 1; n 2 times, I get the answer a 2; n 3 times, I get the answer a 3 and so on.

So, in given such a situation what do you do? You will make the average of all these numbers that you get. So, how will you define the average? It is going to be n 1 a 1 plus n 2 a 2 plus etcetera until I mean, it goes on divided by the total number of measurements, right. The total number of measurements is n 1 plus n 2 plus n 3, etcetera. So, therefore, this will be the average value of my observable. So, I will say, that the average value of all the measurements, that they have made is equal to so much.

Now, see, if you wanted to find this average, actually it is not necessary to make the measurements, it is possible to calculate these average from quantum mechanics, right. So, therefore, if you want you can calculate the average from quantum mechanics, then make these experimental measurements and find the average and then two are going to match, that is what this postulate is going to say.

So, let me continue this postulate and say that the average of large number of measurements, this average I have given of the experimental definition of average, what is it? You make large number of measurements, the first Eigen value get n 1 times, the second Eigen value get n 2 times, so on and then you calculate average. If you want you do not have to make the measurement, you can just get the average value by doing a calculation. What is a calculation that you have to perform? You take the state function for the system, which as you know, we will denote by psi, allow the operator to operate upon it and then multiply the result by the complex conjugated psi.

Let me repeat, I take the state functions. This is, I know, that my system is in particular stage and state function psi I know. If I know that then I can allow here to operate upon it, multiply the result by complex conjugate of state function, then olium element d 2 and then integrate over the entire space, I will get some number as the answer. And so you calculate this number and divide this by integral of d 2 psi star psi. This is our experimental measurement ((Refer Time: 13:12)), that is what this postulate says.

Now, you may wonder, I mean, if you think of psi star psi d 2 integrate over the entire space, you see, if your wave function is normalized, then this is guaranteed, that part is guaranteed to be equal to 1. So, this expression is evaluated even if the wave function is not normalized. If you, in the case, special case where the wave function is normalized, this is actually going to be equal to 1 and this object in quantum mechanics, it is actually, you should, to denote this itself by the symbol A with that kind of brackets, both the sides and it is referred to as the expectation value of A; expectation value of the operator A. This object is referred to as expectation value of the operator A.

So, what this say, that you see, if you wanted to find the average of your large number of experimental measurements, all that you need to do is just calculate the expectation value of A using your state function. That is enough, that give you average of large number of measurements.

There are a few things that can be proved from here, but I am not going to prove all of them. But what I want is something, which is very important. Suppose it so happens, that your state function is an Eigen function of A; suppose it so happens, that your state function is an Eigen function of A, right. And let me say, that small a is the corresponding Eigen value small a. So, therefore, a operating upon psi is going to give me small a times psi, then what will happen think about it, right. You will have small a times psi. So, maybe I can do it here. This may be replaced with small a times psi. And a, after all, is just a constant, it will not be affected by the integration that you are going to have.

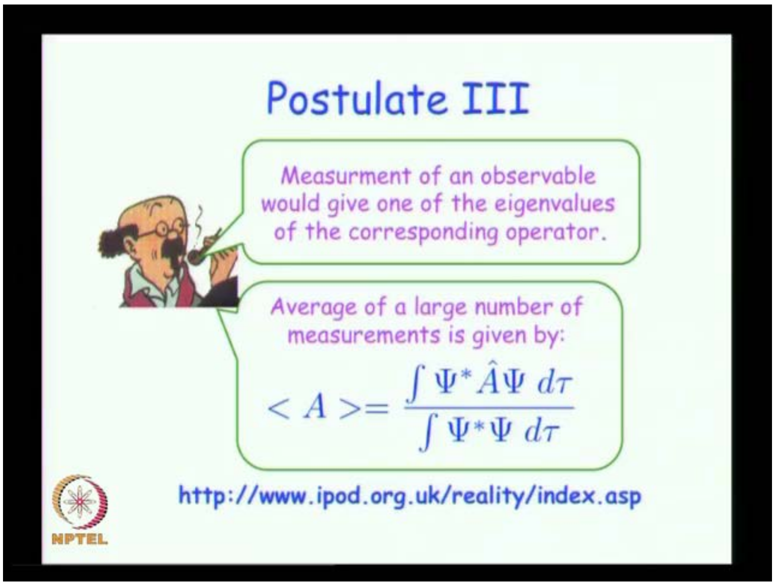
So, this small a can be shifted from there and you can put it here, right, and then you will see that the numerator and the dominator are having common factor. So, you can remove this, right. And therefore, what is it that you find? The answer is very simple. The answer is, that if your state function is an Eigen function of the operator with an Eigen value A, then expectation value is actually nothing but the Eigen value, ok.

So, this says that if you make a large number of measurements, the answer is going to be that particular Eigen value, that is what they say is, in fact, I have, I have just proved that is the way it is. But then in addition you can prove this is something that I will not prove, that I think you can go on measure a large number of measurements. In this special case where psi is an Eigen function of A, the answer will always be that Eigen value.

See, what I am saying is something stronger. Earlier I said, I make a measurement, it is not necessary that the answer should be the same, but in the case where the state function is an Eigen function of the operator that you are measuring, then the answer will always be the same and it will equal to the same Eigen value. I have not proved it, but it is possible to prove it.

So, therefore I mean, if you, if you want to illustrate, if you want a illustration, imagine you think of ((Refer Time: 17:40)) imagine that it is Eigen, it is in a stage, which is an Eigen function with, it is an Eigen function of H, suppose it is, the state function is an Eigen function of H corresponding to, may be this particular Eigen value phi by 2 h nu, then you can make the measurement of energy any numbers of times, answer will always be phi by 2 h nu. And if the answer is always phi by 2 h nu, what about the average? Average also will be phi by 2 h nu. So, that is what this means.

(Refer Slide Time: 19:13)



Postulate III

Measurment of an observable would give one of the eigenvalues of the corresponding operator.

Average of a large number of measurements is given by:

$$< A > = \frac{\int \Psi^* \hat{A} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

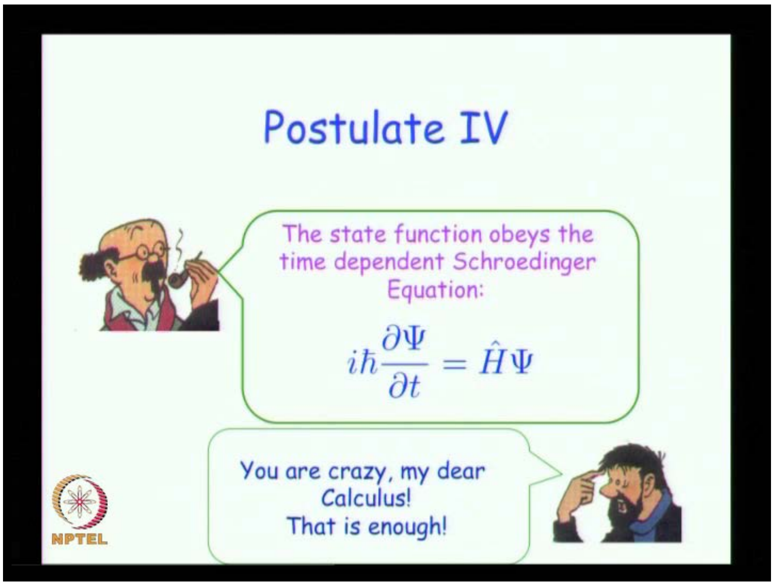
http://www.ipod.org.uk/reality/index.asp

Now, you see, this particular postulate has been subject of many large amount of controversies because people were very unhappy about it. They tried all kinds of things with this postulate and it is a postulate in which research is being done even now, and the subject of this postulate comprises what is referred to as measurement theory, measurement theory and quantum mechanics. And in the last 10 years or so there has been so much progress and if you are interested, you should have looked at this particular website and you will find, that this website has discussions, what is referred to as decoherence.

I am, say, I hope you can see this decoherence. This is concerned with measurement theory essentially. As I said, a lot of research is being done even now on this particular postulate or the subject matter of this postulate. So, if you remember, you see, in the first postulate I said, that the state of the system is characterized by its state function, right. And if you know, the state function, it is possible to calculate the probability of that system may be in any reason or space. That is what the first postulate said.

In the second postulate said, that if I have an observable, then there is an operator associated with it and that operator has to be linear, it has to be hermitian. then we also had a prescription for finding the operator. then in the third postulate, which we have just discussed, it said that if we make the measurement, the answer is guaranteed to be an Eigen value of operator associated with the observable that you are measuring. But you see, I mean, the, you would realize, that knowing the state function is extremely useful, but I, we do not have any procedures for finding the state function and that is the subject of the next postulate, which is postulate number 4, the final postulate.

(Refer Slide Time: 20:54)



Postulate IV

The state function obeys the time dependent Schroedinger Equation:

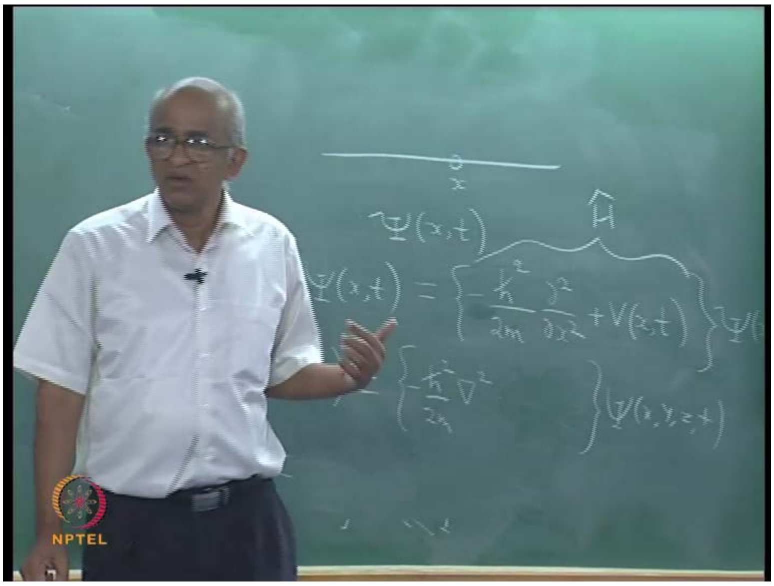
$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

You are crazy, my dear Calculus! That is enough!

So, this is the postulate. It says that the state function obeys the time dependent Schrodinger equation. As I have mentioned earlier, see, we have these four postulates, but instead of that I could have actually started with this path integral approach, introduced that path integral formula that I had as postulate and then try to derive quantum mechanics there from.

If you did that, you see, staring from the path integral formula it is possible to derive this equation. If you assumed, that it is possible to derive this particular equation, which is written here, this equation I have to explain it little bit more, I will do that or if you want, you can assume this particular equation. You can assume this particular equation and derive the path integral formula that I had written in my earlier lecture. So, this equation, let me illustrate it by writing it, may be, for a simple one-dimensional system.

(Refer Slide Time: 22:22)



So, imagine I have a one-dimensional system. I mean, as I always do, I think of illustrating whatever equation that we have in the simplest possible case, which is a one-dimensional system. So, you have a one-dimensional particle moving along a direction and its possession is specified by x, t. So, naturally the state function psi will be a function of x and the time t, that is how it is, that is what the first postulate says.

And we want to determine the state function and how can I do that? The answer is, that I have to worry about this equation, which says, that h cross dou by dou t operating upon psi. In this particular case psi is the function of x and t, just 2 variables, because it is one-dimensional system and that must be equal to h. What is h? Well, h will contain two times, one coming from the kinetic energy of the particle and operate that kinetic energy of the particle, which we know the minus h cross square by 2 m. I note just that because we have two differentiations with respect to that. So, this is the kinetic energy part of the Hamiltonian operator.

And then in addition to that if you denote the potential energy of particle by the symbol v, in general we will depend upon x and may be it can change with time in which case it is the function of both x and t. If you have a potential, which changes with time, then it will be v of x t and this is your total energy for the operator associated with total energy. And what will happen is that this is going to operate upon psi x t. So, this is the equation.

So, what I have, what has been written in this form is rewritten on the board for a simple one-dimensional system. And if you are interested in knowing the state function, what you have to do is, you have to solve this equation. If you are able to solve this equation, you are going to get the state function. For a more complex system, this equation will be more complex naturally, right.

If you had, there is a helium atom in this room, which was moving about in this room, what is going to happen is that you are going to have this equation I h cross dou by dou t, correct. Now, operating upon what you will have a psi, which is the function of x, y and z because you are thinking of your three-dimensional system. So, you will have x, y, z and t and that is going to be equal to minus h cross square by 2 m because your particles are moving in three-dimension.

You will not have just dou square upon dou x square, but you will have dou square upon dou x square plus dou square upon dou y square plus dou square upon dou z square. I mean, that sum if you remember is something that we decided to denote by del square. As I always say, I am lazy, I do not want to do the work of writing dou square upon dou x square plus dou square upon dou y square plus dou square upon dou z square. So, I just write del square.

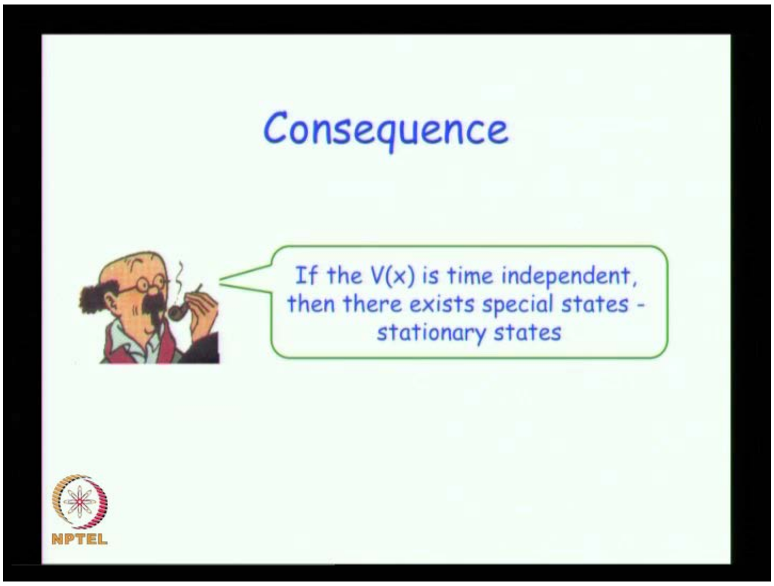
Now, if you had included the gravitational energy, then what will happen? You will actually have a potential energy there, which will be of the form m g z, if you, if you decided to include gravitational energy, but normally it is not important. So, we are not going to do that.

This will be the equation, which will determine the state function if you had included the gravitational energy also, but if you do not include it this stamp will not be there. The gravitational potential energy, I mean, as said, it is not of any importance for most of the problems and so it is not necessary to worry about it. So, this will be how the equation looks like. And if you look at this again, see what it says is, that you see, as time passes the state function is going to change, that is what the equation says.

And the derivative of the state function with respect to the time is determined by what? It is determined by the state function itself, but operated upon by the Hamiltonian operator. So, the Hamiltonian operator determines how the state function evolves in time. How the state function changes in time is determined by the state function itself, operated upon by the Hamiltonian operator.

So, the time evolution or time development of your quantum mechanical system is governed by what? It is governed by the Hamiltonian operator and that is the reason why Hamiltonian operator is of great importance in quantum mechanics because it determines how the state function changes with the time.

(Refer Slide Time: 28:32)



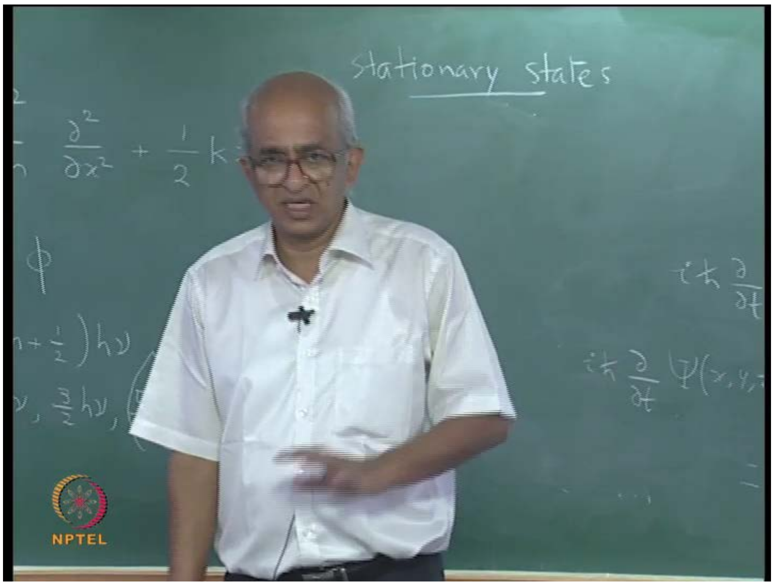
Consequence

If the V(x) is time independent, then there exists special states - stationary states

We have had enough of the postulates and we are now going to look at some consequences of these postulates. Let us, let me tell you ((Refer Time: 28:29) of most important consequences of this postulates. Remember, earlier I was speaking about standing waves.

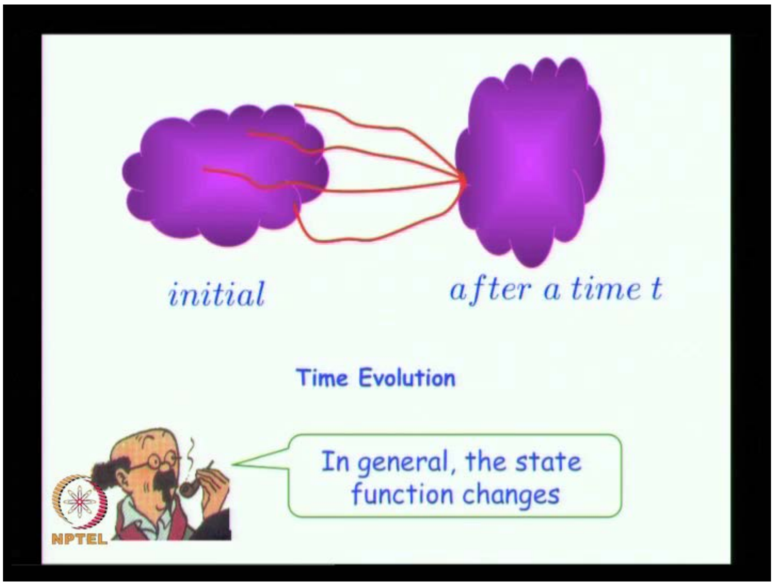
Remember, that I said, that if I had a system in which there are waves, then it is possible for the waves to form standing wave, right. So, you would expect that kind of thing to happen in quantum mechanics because everything is actually determined by waves. So, we, what we want to look for are actually the analogs of these standing patterns and these analogs are actually referred to as stationary states in quantum mechanics.

(Refer Slide Time: 29:17)



So, what we will actually rigorously show is, that if you have a situation where the potential energy does not change with time, right. Here, if you look at the equation, the way the equation is written, we can be a function of the time. But imagine that you have a situation where the potential energy does not change with time, then it is possible to show, that there can be states, which are referred to as stationary states. Maybe, I can illustrate this better. See, this is a pictorial presentation, that I adopted something that is wavy. This, let me say, is the wave function and what this equation says is, that as time passes this wave function is going to be changed. That is what it means.

(Refer Slide Time: 30:19)


initial *after a time t*

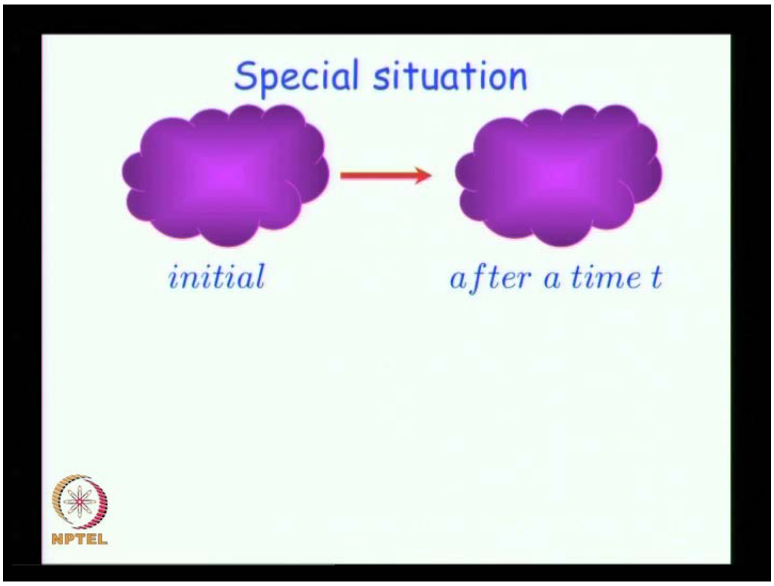
Time Evolution

In general, the state function changes

So, suppose, as time passes what will happen? You see, your state function is going to change and that change I have just indicated by drawing some lines. And what happens, you see, this is, this is my state function at the initial time, this is after some time. So, you can see that the shape of these wave functions has changed in general.

This is what happens in general, but there are certain special situations, where what happens is that even though this system evolves in time, the shape does not change. So, those are the states that we are referred to as stationary states and we want to find them. And the question is how do we find them.

(Refer Slide Time: 31:38)

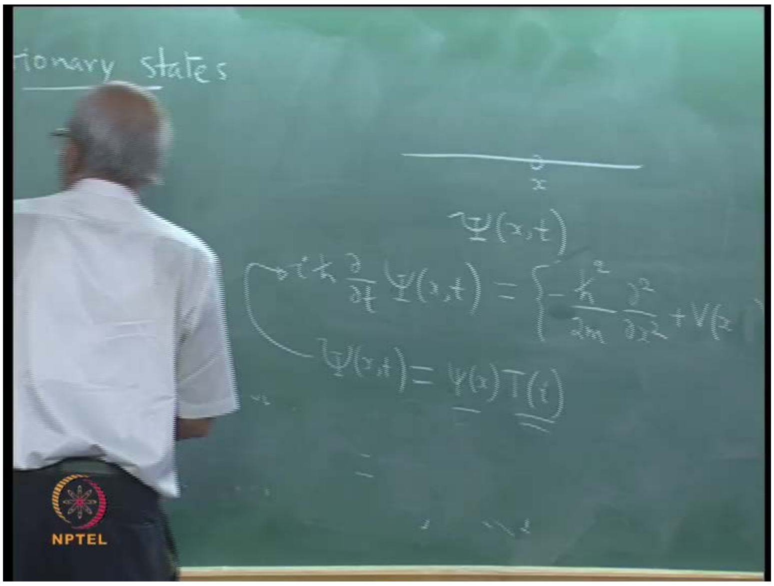


Special situation

So, in general, as we see, as professor calculus says in general, the state function actually changes, but it is possible to think of special situations where even though the time is passing, the shape of the wave function does not change.

So, how do we how does one find that the answer is the following. First of all we imagine that the potential energy does not change with time. That means, in this equation, I mean, we will think of your one-dimensional system, but whatever proof I am going to give you, can be generalized very easily to any number of dimensions, whether it is three-dimensional or bigger dimensional system. Whatever proof I am going to give you is generally applicable. The only condition is that the potential energy should not depend upon time.

(Refer Slide Time: 32:13)

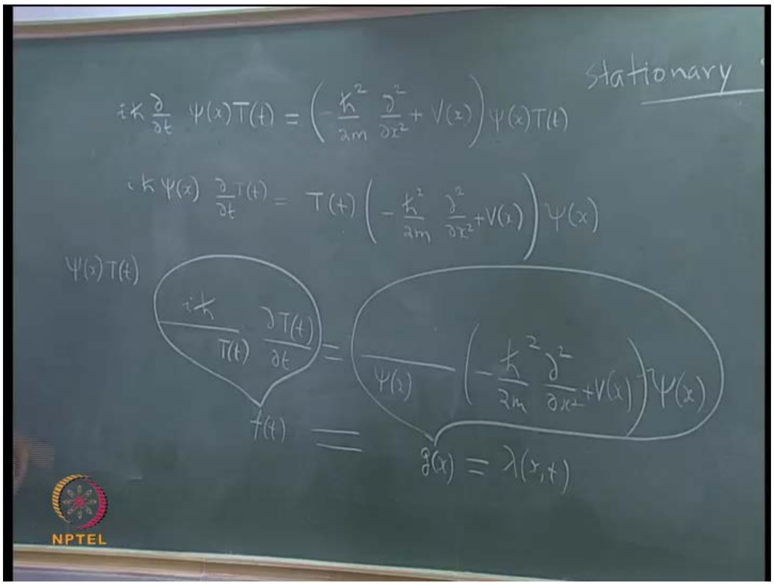


So, suppose potential energy does not depend on time, then what will happen? There is no time there, and you want to solve this equation, so how do you solve the equation? Well, if you look at this equation you will realize that it is the partial differential equation. There is the partial differentiation with respect to time here; partial differentiation with respect to possession.

So, you want to solve this equation and when ordinary differential equations can be difficult to solve, so in such a situation how do we find solutions? Well, what we adopt is the method of divide and concur. So, this psi, which is the function of x and t, imagine that we have a solution, which is of the form psi of x into capital T of t. See, what we are saying is this capital psi is a function of x and t, but now I am going to say ok, let me think of only those cases where capital psi can be written as a product of two functions, the first one I will call small psi, the symbol, we look at the way it is written, this is the capital psi and that is small psi. And small psi I will assume, that it depends only upon x and then there is another function here, which I will denote by the symbol capital T and that I am going to say will depend only upon the time t. So, I have split my total wave function, which I actually depend upon x and t into two separate parts. So, I have divided it in two separate parts, first part only depends upon x, other depends only upon the time t, right.

Now, obviously, you see, this is, this will not happen in general. So, this is something special. This assumption, it does not have, will not have general validity. We are actually finding some special solutions of the equation for which this kind of separation can be done, right. So, then the question is, I want just a small psi and capital T. That means, I want to choose small psi and capital T in such a fashion that the product will obey this equation that is what I want to do. I want to choose small psi and capital T in such a fashion that the product will obey this equation.

(Refer Slide Time: 35:40)



Stationary

$$i\hbar\frac{\partial}{\partial t}\psi(x)T(t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)T(t)$$

$$i\hbar\psi(x)\frac{\partial}{\partial t}T(t) = T(t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)$$

$\psi(x)T(t)$

$$\underbrace{\frac{i\hbar}{T(t)}\frac{\partial T(t)}{\partial t}}_{f(t)} = \underbrace{\frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)}_{g(x)}$$

$$f(t) = g(x) = \lambda(x,t)$$

So, let us see what happens if I took this assumption. This is actually an assumption. I take this assumption and put it back into the original equation, which I want to be satisfied. So, if you do that, you are going to get i h cross dou by dou t operating upon capital psi, but capital psi, I have assumed is given by this expression. So, psi of x capital T of t is equal to minus h cross square by 2 m dou square upon dou x square plus v of x operating upon psi of x capital T of t, right. This is what happens if you took this assumption and put it back to the original equation.

But then if you look at the left hand-side of this equation, you have partial differentiation with respect to t. Now, when you are partial differentiating with respect to t, that means, you are not allowing x to change. So, as far as this definition is concerned, psi of x is a constant. So, it is not affected. So, this partial derivatives are going to affect only capital

T. So, therefore, I can write this as i h cross psi of x dou by dou t operating upon capital T of t and that is equal to the right hand side.

On right hand side you have partial differentiation with respect to x. So, this is going to affect only psi, it is not going to affect capital T. So, this capital T is completely unaffected by whatever is there in this operator because there is no time anywhere in this operator. So, we can take this capital T of t to outside and then you will have minus h cross square by 2 m dou square upon dou x square plus v of x operating upon psi of x.

Now, I am going to rewrite this in the in the next step. Before I rewrite what I want to do is, I want to divide throughout by psi of x into capital T of t. Suppose I divided throughout by this, then what is going to be happen is, you will have i h cross divided by psi of x into capital T of t dou capital T by dou t is equal to, well I have made a mistake, there should have been a psi of x here. And on the right hand side, you are going to get capital T of t divided by psi of x into capital T of t, then minus h cross square by 2 m dou square upon dou x square plus v of x operating upon psi of x. And it is obvious, that you can cancel this psi with that psi and that capital T with that capital T.

Well, you know, to make the equation look neater what I will do is, I will rub off these things and same thing here. So, this is the result and if you look at this equation, what do you find? You find that something very interesting. See, this was a partial differential equation, which is dependent upon two variables, t as well as x. These both, t and x, they are independent of each other, they are independent variables of the problem. But when I look at this equation, you want, the left hand side, you have function, which depends only upon time, a function of time alone. So, may be some function of time.

What about the right hand side? This whole thing, you see, that it depends only upon x. It depends only upon possession. So, this equation is actually of the form, function of time equal to f function of x. How that can be satisfied? Well, it is very easy to argue, that in such equation implies, both of them have to be equal to the same constant, ok.

Let me argue, that I mean, in general at most what may happen is, that you see both of them may be equal to some function, which I may denote by lambda, which may depend upon x and t, that is all at the most. What may happen is that they, both of them equal to something, which may depend upon x and t.

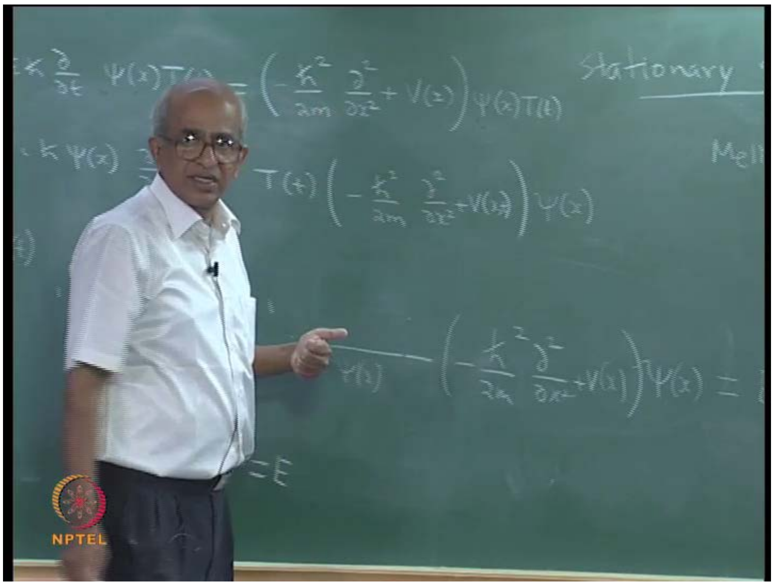
But then this lambda, you see, if you look at this lambda is equal to a function of time alone, therefore it cannot depend upon x, correct. This lambda is equal to, you see, the most what can happen is that the both of them may be equal to some function of x and t because x and t are variables, that you have in your problem, but lambda is equal to f, function of t alone. So, therefore, it cannot depend upon x and lambda is equal to f, function of x alone. So, therefore, it cannot depend upon t and therefore lambda has to a constant; that is the way that you can argue. So, therefore, such an equation is satisfied, f of t must be equal to a constant.

For certain reasons I will call that constant E, where you could have used any symbol, but you will see that eventually it is connected with the energy. It is the energy itself. It is reason that I prefer to use symbol E, right. At the moment it is just a constant and this constant does not depend upon either time or possession, right.

So, what has happened that I have got an equation, which reads, i h cross divided by capital T of t dou capital T by dou t is equal to E. That is one equation that I have obtained, correct. And I have obtained another equation, let me just, as I said, I am somewhat lazy, I do not want to write things again and again, so I will just say, that this is equal to E. So, these are the two equations that I get.

And if you look at these equations you would realize, the first is actually an ordinary differential equation. What about the second? The second also is an ordinary differential equation. The first equation involves only the variable time, the second equation involves only a variable possession, right. So, your original equation, remember, was this. The original equation was a partial differential equation, involved both of the variables. And as I said, the partial differential equations are difficult to solve. But what we have done is, we have divided the function into two parts, psi of x and capital T of t, right, and separated out through ordinary differential equations. So, one is this and other is that and ordinary equation, obviously, are easy to solve than partial differential equations. And now, we can go ahead and try to solve these two equations. And if I solve these two equations and determine the values of psi and capital T, then what I can do is, I can use those values in here and get the total wave function, right.

(Refer Slide Time: 45:34)



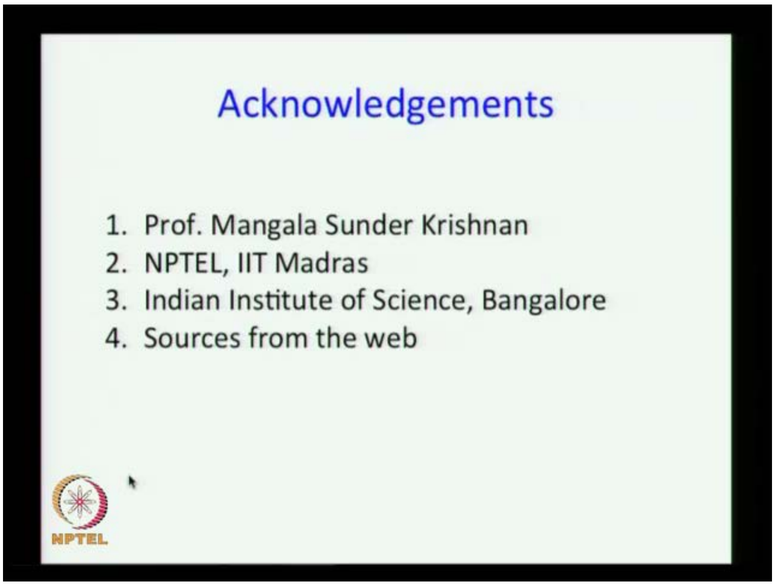
This method is known as the method of separation of variables. So, what do I mean by that? The meaning is I had a function, which depends upon two variables and that I separated into two separate functions, each one is dependent upon only one variable, right. And then I was able to arrive at two separate ordinary differential equations. So, one is this and other one is that. So, my problem has been simplified by this method of separation of variables.

Now, a crucial things to notice is would it have been possible if v depended upon x and time. See, if v depended upon x and time, suppose you had t here what will happen is that you will have t sitting here in this equation, correct. You will have t sitting there and the argument of this method of separation of variables will not hold good. You will not be able to separate the variables and therefore, you see, if your potential energy depended upon time, you will not able to find the solution, a simple solution of this form and the method of separation of variables will ((Refer time: 47:14)), ok.

So, this argument can be carried out only in those cases where the potential energy does not change with time. But then you may ask are there problems where the potential energy is changing with time? The answer is yes. If you are interested in spectroscopy of variables, imagine I have molecule here and I shine light, may be a tubelight acts on the molecule, right. The electric field from the tubelight can act on the molecule. As you know, the electric field in light will be oscillating, it will be changing as a function of time, I mean, the electric field is actually changing.

So, effectively, if you had a molecule and if you subject it to the light, it is an electric field who change time dependent electric field, oscillating electric field acting on the molecule and the molecule is made up of a charger electron, sand, nuclei and so this electric field will affect these chargers. So, the moment you say there is an interaction of the molecule with electromagnetic radiation, your potential energy will become a function of time, right. So, if you are doing spectroscopy, this method will not be, I mean, the procedures that we have adopted will not be valid, you will have to modify it.

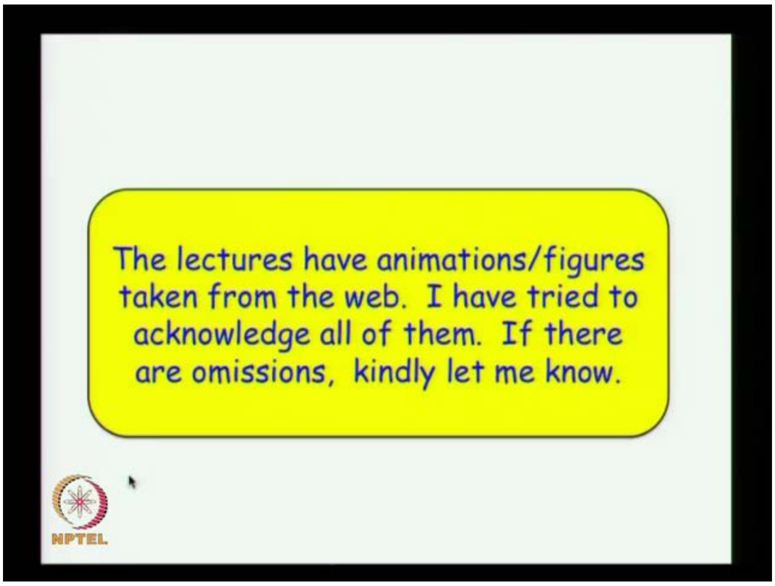
(Refer Slide Time: 48:48)



Acknowledgements

1. Prof. Mangala Sunder Krishnan
2. NPTEL, IIT Madras
3. Indian Institute of Science, Bangalore
4. Sources from the web

(Refer Slide Time: 48:51)



The lectures have animations/figures taken from the web. I have tried to acknowledge all of them. If there are omissions, kindly let me know.

Well, we will continue in the next lecture.