Quantum Chemistry of Atoms and Molecules

Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-4

Ground Rules: Postulates of Quantum mechanics: Part I

Today we are going to talk about some ground rules of quantum mechanics. What we have discussed so far is how one gets Schrodinger equation and how Schrodinger equation can handle the wave-like nature of matter. So, today we will start with a restatement of what we have said already and then from there we will try and see how we can postulate the fundamental tenets of quantum mechanics.

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Ground rules

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The cartoon we see here is fashioned after the famous statement of Einstein which was made in a letter that he wrote to Max Born which is paraphrased as God does not play dice and as Hawking had said later on that actually he does and does some more. So, far this is what we have got.

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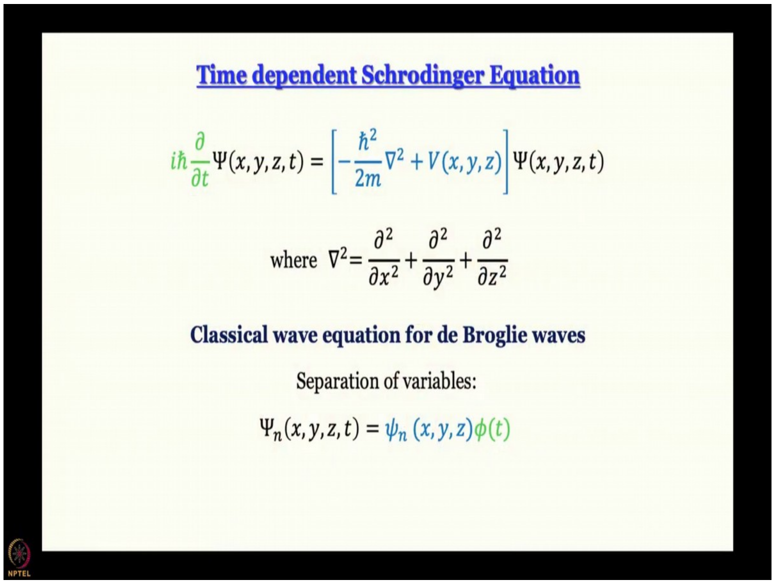

Time dependent Schrodinger Equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]\Psi(x,y,z,t)$$

$$\text{where } \nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Classical wave equation for de Broglie waves

Separation of variables:

$$\Psi_n(x,y,z,t) = \psi_n(x,y,z)\phi(t)$$

We have time dependent Schrodinger equation which is essentially the classical wave equation for de Broglie waves and here on the left hand side we have the operator which is time dependent on the right hand side where the Hamiltonian operator which is time independent space dependent. We have abbreviated del 2 del X 2 plus del 2 del Y 2 plus del 2 del Z 2 by the Laplacian del square. So, the way to handle this classical wave equation for de Broglie waves which is a mixture of spatial and temporal coordinates is to express the wave function as a product of a space dependent part and a time dependent part and hence use the technique of separation of variables which is quite well known in differential equations.

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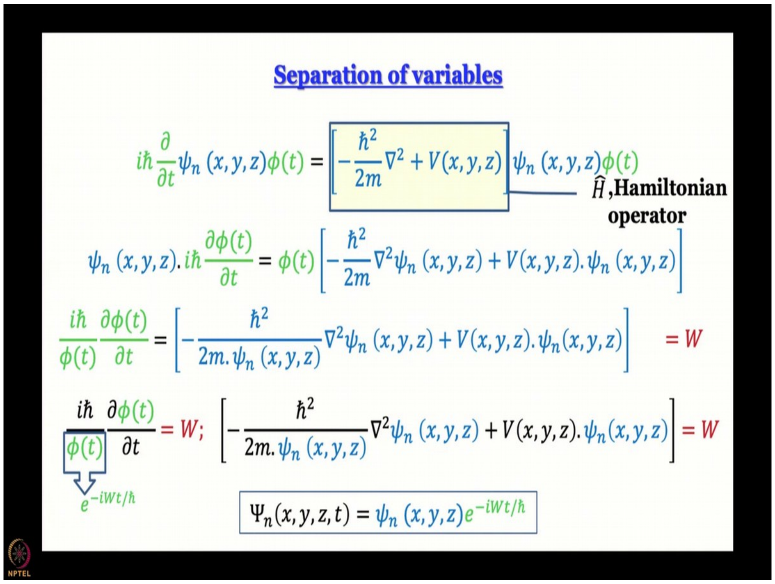

Separation of variables

$$i\hbar\frac{\partial}{\partial t}\psi_n(x,y,z)\phi(t) = \boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]}\psi_n(x,y,z)\phi(t)$$

$\hat{H}$,**Hamiltonian operator**

$$\psi_n(x,y,z).\,i\hbar\frac{\partial\phi(t)}{\partial t} = \phi(t)\left[-\frac{\hbar^2}{2m}\nabla^2\psi_n(x,y,z) + V(x,y,z).\psi_n(x,y,z)\right]$$

$$\frac{i\hbar}{\phi(t)}\frac{\partial\phi(t)}{\partial t} = \left[-\frac{\hbar^2}{2m.\psi_n(x,y,z)}\nabla^2\psi_n(x,y,z) + V(x,y,z).\psi_n(x,y,z)\right] = W$$

$$\frac{i\hbar}{\underset{\Downarrow\; e^{-iWt/\hbar}}{\boxed{\phi(t)}}}\frac{\partial\phi(t)}{\partial t} = W;\quad \left[-\frac{\hbar^2}{2m.\psi_n(x,y,z)}\nabla^2\psi_n(x,y,z) + V(x,y,z).\psi_n(x,y,z)\right] = W$$

$$\boxed{\Psi_n(x,y,z,t) = \psi_n(x,y,z)e^{-iWt/\hbar}}$$

So now when we plug in this value of the wave function into the time dependent wave equation this is what we get for our benefit the space dependent part is written in blue and the time dependent part is written in green. So, not only do the wave functions have space and time dependent part as we said the operators also have one of them is time dependent and one of the space dependent.

And here what we see is that we have a mixture and our job is to separate them out. It is not very difficult to see how one can do that after all ih cross del del t the time dependent operator is going to act only on Phi of t the time dependent wave function and the space dependent wave operator is going to operate it only on the space dependent part. So, from the left hand side we can take Psi n of X Y Z out and on the right hand side we can take Phi of t out here I should say that n does not mean a quantum number it is just an identifier for the particular wave function we are dealing with.

So then when we do a little bit of simplification just divide by the wave function on both sides then now see left hand side is completely green right hand side is completely blue. Left hand side is purely in terms of time space independent and right hand side is purely in time of spatial coordinate's time independent. Now the left hand side is supposed to be dependent on time right hand side is supposed to be dependent on space and they are equated which means that what we have is that we do not have a variation.

Both would better be constants otherwise you cannot equate a space dependent equal part to a time dependent part this constant w is called the separation constant. The left hand the time dependent equation that we have ih cross by Phi of t multiplied by del Phi t del t in fact we might as well write d Phi t dt here because is no longer a partial derivative and the time is independent space dependent part that we have is this.

It is very easy to solve the time-dependent wave equation anybody can do it and when you do it the solution that you get is e to the power minus iwt divided by h cross. Now here one can say why are we not using a linear combination we are not using a linear combination because we have the benefit of hindsight but what we can do at this stage is that we can just plug it back and we have the time and space dependent wave function expressed as Psi n of XYZ the spaceship in their part multiplied by e to the power minus iwt by h cross.

So, what we have been able to find out so far is find the general form of the time dependent part of the wave function we have discussed all this in the previous module we are just going through it once again. One thing that turns out to be very important here is that the operator that we have an operator is something that changes a function the operator that we have in the space dependent part is the Hamiltonian operator which was already known in classical mechanics.

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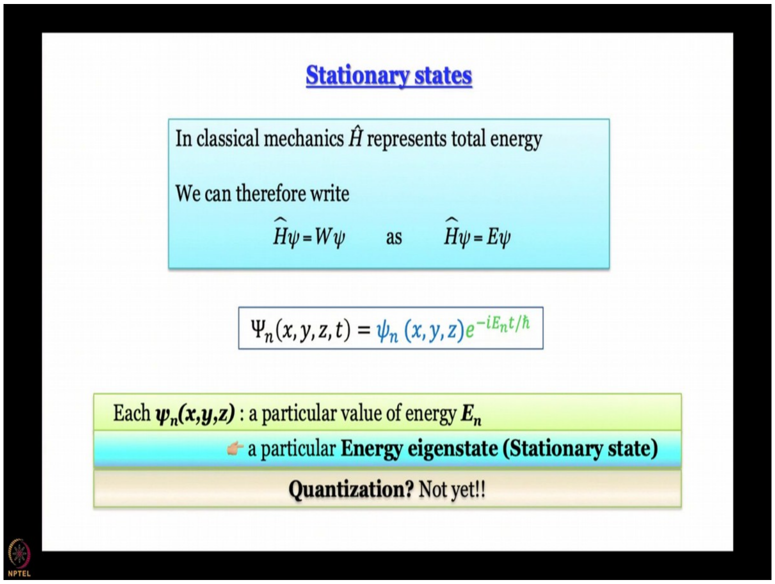

Stationary states

In classical mechanics $\hat{H}$ represents total energy

We can therefore write

$\hat{H}\psi = W\psi$ as $\hat{H}\psi = E\psi$

$\Psi_n(x,y,z,t) = \psi_n(x,y,z)e^{-iE_nt/\hbar}$

Each $\psi_n(x,y,z)$: a particular value of energy E_n

☞ a particular **Energy eigenstate (Stationary state)**

Quantization? Not yet!!

From classical mechanics it was known that Hamiltonian operator represents total energy it is a total energy operator. So, when we have an equation like this H Psi equal to W Psi we might as well replace W by E energy and write it as H Psi equal to E Psi. So, we know that this wave function if we take it and if you even neglect the time dependent part just work with the time independent space dependent part Psi n of XYZ this wave function represents a particular value of energy let us call it E n.

We can rephrase it and say that Psi n represents a particular energy eigenstate and it is the time independent energy eigenstate. So, this is essentially the stationary state that Bohr had introduced in a different context Psi n represents a particular energy eigenstate and this is time independent. So, here we have the quantum mechanical representation of the stationary state that was first introduced by Bohr. But do we have quantization; actually we do not because n can take up any value.

Correspondingly E can take up any value so we do not really have quantization all we are saying is that if you know what Psi is you know what energy is but that energy could vary when you go from Psi 1 to Psi 2 to Psi 3 to Psi 4 energy can vary continually. Discreteness is not achieved yet that is what will come a little later. But what we get from here is we get an idea of how to go about framing the ground rules of quantum mechanics and that is what this module is about.

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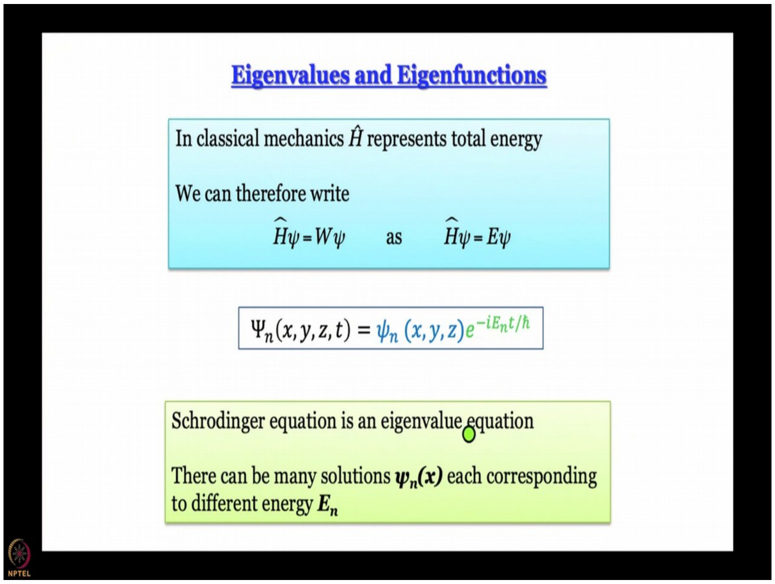

Eigenvalues and Eigenfunctions

In classical mechanics $\hat{H}$ represents total energy

We can therefore write

$\widehat{H}\psi = W\psi$ as $\widehat{H}\psi = E\psi$

$$\Psi_n(x,y,z,t) = \psi_n(x,y,z)e^{-iE_nt/\hbar}$$

Schrodinger equation is an eigenvalue equation

There can be many solutions $\psi_n(x)$ each corresponding to different energy E_n

So you see that we have got Schrodinger equation which is an eigenvalue equation.

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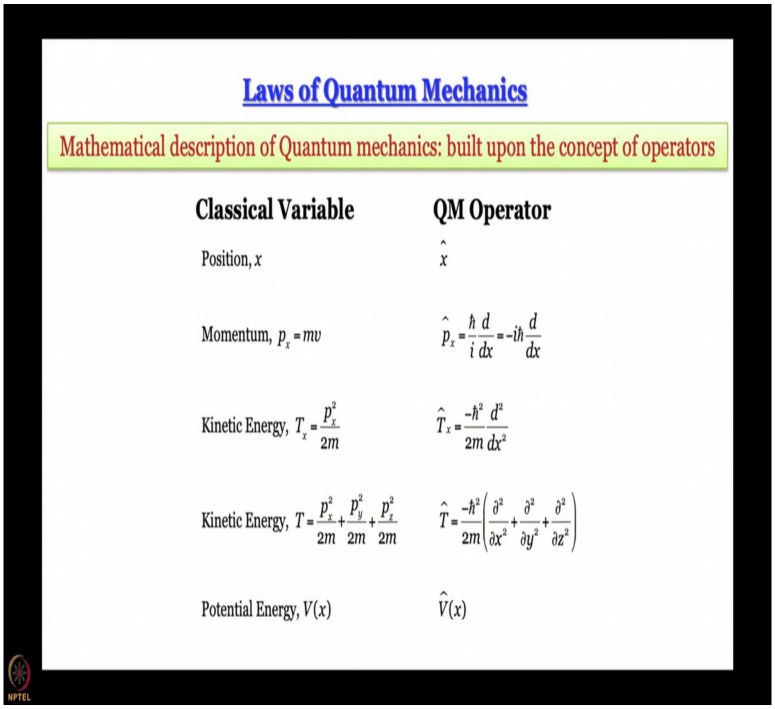

Laws of Quantum Mechanics

Mathematical description of Quantum mechanics: built upon the concept of operators

Classical Variable	QM Operator
Position, x	$\hat{x}$
Momentum, $p_x = mv$	$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} = -i\hbar\frac{d}{dx}$
Kinetic Energy, $T_x = \frac{p_x^2}{2m}$	$\hat{T}_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy, $T = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$	$\hat{T} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Potential Energy, $V(x)$	$\hat{V}(x)$

So from here we go to this postulate that first of all for every quantum mechanical; for every classical variable physical observable there is going to be a quantum mechanical operator. We have already come across the total energy operator Hamiltonian so it is not listed here but if you remember what Hamiltonian is it is the potential energy V of X or V of X Y Z if it is three dimensional problem plus this operator -h cross square by 2 m multiplied by del 2 del X 2 + del 2 del Y 2 + del 2 del Z 2 in case of a three dimensional problem.

And simply minus h cross square by 2 m d 2 dx 2 in case of a uni dimensional problem. So, since we know that already it is not very difficult for us to understand that the kinetic energy operator is -h cross square by 2 m d 2 dx 2 in one dimension and this case 3 dimension. Once we know that we know the relationship between kinetic energy and momentum. Kinetic energy is well it is easier to handle one dimension to start with.

Kinetic energy for motion along one direction let us say X is given by px square by 2 m in classical mechanics. So, if the operator of kinetic energy is -h cross square by 2 m d 2 dx 2 it must have come by operating the px operator twice and dividing it by 2m with that understanding it is not very difficult to figure out that the momentum operator would better be for motion along one direction h cross square by id dx or we can write it minus ih cross d dx.

If we make it operate twice then what do we get minus, let us take the first one the second one will give the same result h cross by id dx operates twice so we get d 2 dx 2 and h cross multiplied by h cross is h square i multiplied by is minus 1 so finally we get -h cross by 2 m d 2 dx 2 so what we have shown just now is the compatibility in the definition of the kinetic energy operator and the momentum operator.

We are going to come back and talk a little more about co-operators and their commutivity at a later stage. For now let us just remember that for every physical quantity that is their quantum mechanics has an operator.

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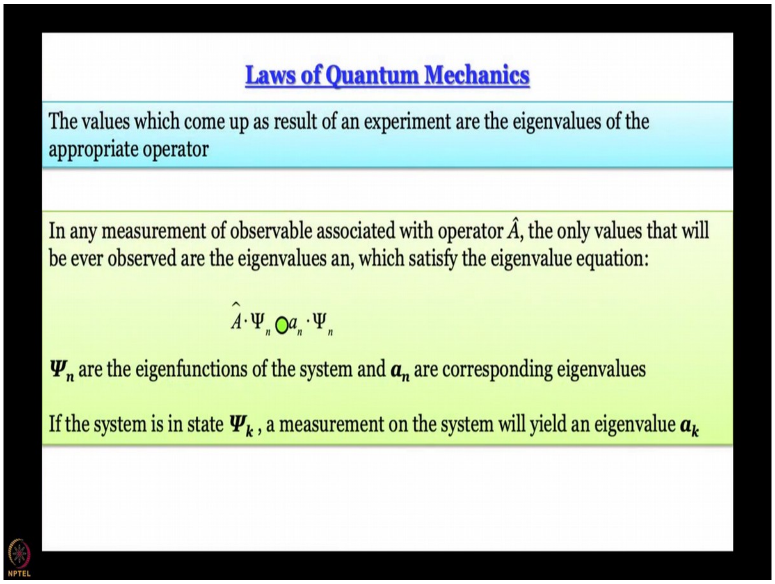

Laws of Quantum Mechanics

The values which come up as result of an experiment are the eigenvalues of the appropriate operator

In any measurement of observable associated with operator $\hat{A}$, the only values that will be ever observed are the eigenvalues an, which satisfy the eigenvalue equation:

$$\hat{A}\cdot\Psi_n \bigcirc a_n\cdot\Psi_n$$

$\boldsymbol{\Psi_n}$ are the eigenfunctions of the system and $\boldsymbol{a_n}$ are corresponding eigenvalues

If the system is in state $\boldsymbol{\Psi_k}$, a measurement on the system will yield an eigenvalue $\boldsymbol{a_k}$

And then the way we get to know the value of the physical quantity is that you make the operator operate on the wave function and then you get an eigen value equation, how do we know this? We do not know we are guessing at this point. We are guessing because you have already got an eigenvalue equation that is Schrodinger equation where the total energy operator Hamiltonian operated on the wave function to give us back the same wave function multiplied by the value of the energy.

So that is a specific form of this general eigenvalue equation where A hat of operates on Psi n the wave function to give us the same Psi n multiplied by a value which is called the eigenvalue. So, the postulate here is that this is how you go about trying to find out the values of physical quantities in quantum mechanics. So, it also says implicitly that the wave function has all the information about the system.

If one can make an appropriate operator operate on the wave function then we can get the value of that variable as the eigenvalue provided it can be determined provided it can be determined might sound a little strange at the moment but once again we will come back to it later on. But this is where we start from. Of course the other postulate is that if it is a physical observable let us say we are talking about momentum, it has to be real.

You cannot have a momentum that is something like e to the power minus ikx that can be the wave function. Wave functions can be imaginary you might remember that some of the operators themselves have iota h cross by i del del x is the operator for px so when this operates on a wave function to give a real value the wave function is going to have an imaginary part that is fine but the eigenvalue this is important to understand.

The eigen function can have an imaginary part and more often than not it has we already said that e to the power -i iet putting W equal to e is what we are going to get from Schrodinger equation. So, similarly we will have other eigen functions which are going to be imaginary. But the eigenvalue can never be imaginary if it is going to be the value of real observable quantities. So, another way of putting this is that quantum mechanical operators must be hermitian. A hermitian operator always has eigenvalues.

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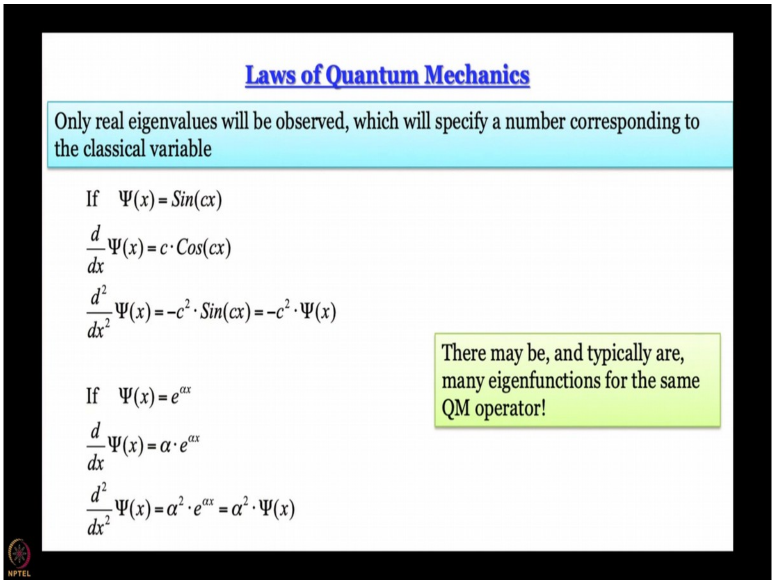

Laws of Quantum Mechanics

Only real eigenvalues will be observed, which will specify a number corresponding to the classical variable

If $\Psi(x) = Sin(cx)$

$$\frac{d}{dx}\Psi(x) = c \cdot Cos(cx)$$

$$\frac{d^2}{dx^2}\Psi(x) = -c^2 \cdot Sin(cx) = -c^2 \cdot \Psi(x)$$

If $\Psi(x) = e^{\alpha x}$

$$\frac{d}{dx}\Psi(x) = \alpha \cdot e^{\alpha x}$$

$$\frac{d^2}{dx^2}\Psi(x) = \alpha^2 \cdot e^{\alpha x} = \alpha^2 \cdot \Psi(x)$$

There may be, and typically are, many eigenfunctions for the same QM operator!

So, another way of saying only real eigenvalues will be observed is that all quantum mechanical operators are actually hermitian operators. Once again if we get the scope we will come back and discuss in a little more detail later on why is it that her hermitian operators have real eigenvalues for us for now let us take it axiomatically.

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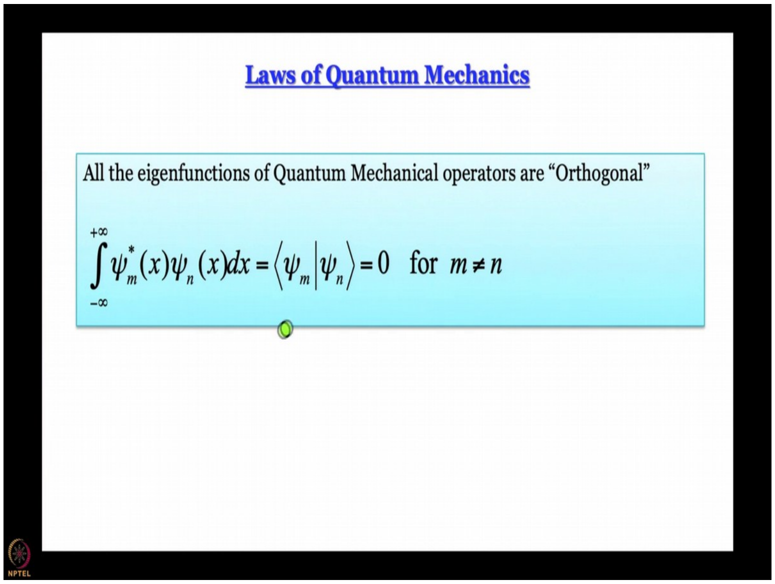

Laws of Quantum Mechanics

All the eigenfunctions of Quantum Mechanical operators are "Orthogonal"

$$\int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x)dx = \langle \psi_m | \psi_n \rangle = 0 \quad \text{for } m \neq n$$

Now we come to the next postulate all eigen functions of quantum mechanical operators are orthogonal. In fact I had like to restate this by saying all eigenfunctions of quantum mechanical operators can be represented as linear combination of functions that are mutually orthogonal. What is the meaning of orthogonality here? Orthogonality means you take two functions take the complex conjugate one complex conjugate of one multiplied by the other function integrate over all space you're going to get zero.

So this integral is often written in Dirac bracket notation in which it is written Psi m in the first angular bracket this bracket the first angular as a first angular vector this is called the bra vector and this is called the ket vector together it is a bracket. So, Psi m Psi n in bracket essentially means integral of Psi m star X Psi n x dx overall space. So, what we are saying is if m is not equal to n then this integral is going to be 0.

Very soon we are going to see an example of functions that are orthogonal to each other. But why is it called orthogonal it is called orthogonal because if you go back and think of say vectors well XYZ they are orthogonal right. What happens if you take their products this is the this is the condition that will be satisfied that is where so the other word that is used for orthogonal is normal here normal means that when you multiply the function by the complex conjugate of the other integrate over all space you can get zero that is the meaning of normal in this context.

And this came from the once again remember these are all postulates you cannot prove them but even a postulate has to have some basis. The basis of this postulate is that if you go back and think what Schrodinger equation is. It is essentially a classical wave equation for de Borglie waves.

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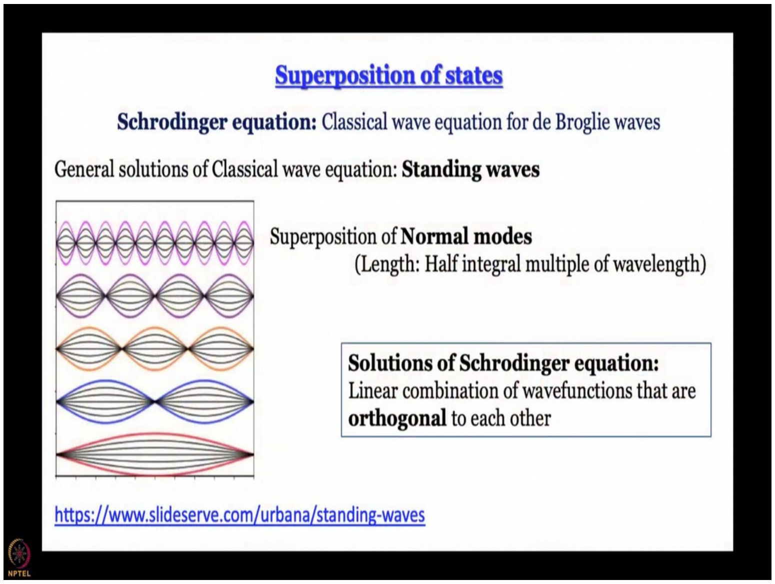

Superposition of states

Schrodinger equation: Classical wave equation for de Broglie waves

General solutions of Classical wave equation: **Standing waves**

Superposition of **Normal modes**
(Length: Half integral multiple of wavelength)

Solutions of Schrodinger equation:
Linear combination of wavefunctions that are **orthogonal** to each other

https://www.slideserve.com/urbana/standing-waves

And it is known for classical equation that the general solutions are standing waves standing waves means waves in which the positions of the nodes do not change. So, if you think of a string if you hold a string on two sides and try to oscillate it. It can oscillate in several ways first in which there is no node the; we hold it at two ends at the middle the string goes up and down any displacement from the mean position and a particular value is Psi at x.

Another way of doing it is at double the frequency where there will be a node in the middle the node will always be in the middle. From the middle to this side what will happen is it will go up and go down. So, in all other places except the node and the terminal points the amplitude is going to change with time. So, these are standing waves and standing waves are obtained by superposing normal modes this is something that is known from classical mechanics.

It is not normal modes are not something that arrows in quantum mechanics there are there already a normal remember it means orthogonal. Normal modes are those in which well if you go back to the analogy of the string normal modes are those in which the total length of the string is a multiple integral multiple of well half integral multiple of the wavelength. So, let us see, let us think of this one.

Here we have a half, half wavelength here we see a full wave just think of the wave and the earth which is on the outside here we have three half waves here we have four half waves that is two waves and it goes on. So, and what we should have shown here is these standing waves that arise out of them. Now if we take the lowest one the so-called first harmonic or the fundamental and the second harmonic it is not very difficult to see that if we take this function and this one multiply them together point by point which means the this function at this point will be multiplied it by this point this function at this point.

Multiplied the two functions point by point and add them what will you get on the left-hand side from the boundary to the middle the products will all be positive when I am talking about this phase. On the right hand side the products will all be negative so when we add all the products we are going to get zero. This is the meaning of normal modes this is the meaning of that integral of Psi m star Psi m integrated over all space being zero.

It is not very difficult to understand the meaning if you think of this picture. So, this is something that is known already that the general solution of classical equation gives you classically gives you standing waves which are superposition of normal modes. So, what do we expect for Schrodinger equation the solutions should also be linear combination of wave functions that are orthogonal to each other that is what leads to the postulate that we have discussed just now that not only Schrodinger equation for any eigen value equation pertaining to quantum mechanics the general solutions are linear combinations of function that are orthogonal to each other.

And this gives us a very useful tool whenever we talk about any system we try to describe it by using and using a set of orthogonal functions. I started a little bit because I was going to use another qualifier orthonormal and something else will come to that. And the advantage of that is that when you have orthogonal functions then; when we have complete set of orthogonal functions then using them one can build a complete description of the functions space that they constitute.

It is very easy to understand in terms of say displacement. Let us say I have displacement a now some direction I can always break it down as a vector sum of displacement along x + y + z. So, once I know these three I can talk about the displacement of the particle completely. So, define any system you need the coordinates. When I talk about position coordinates are x y z when I talk about a particle in motion a xyz also changes with time if it you can also talk about px py pz.

Similarly when we talk about wave functions we should be able to define them completely if we consider an appropriate complete set of wave functions that are orthogonal to each other normal modes that is what the earlier postulate that we discussed is all about. That brings us to an interesting question that has plagued the minds of people working in quantum mechanics and has actually transcended the barrier and created ripples in pop culture as well.

The question is that we are saying that there is a superposition of states. So, when you make a measurement which state do we see? Let us say we make a measurement of some property and we find that the value of the property is something P.

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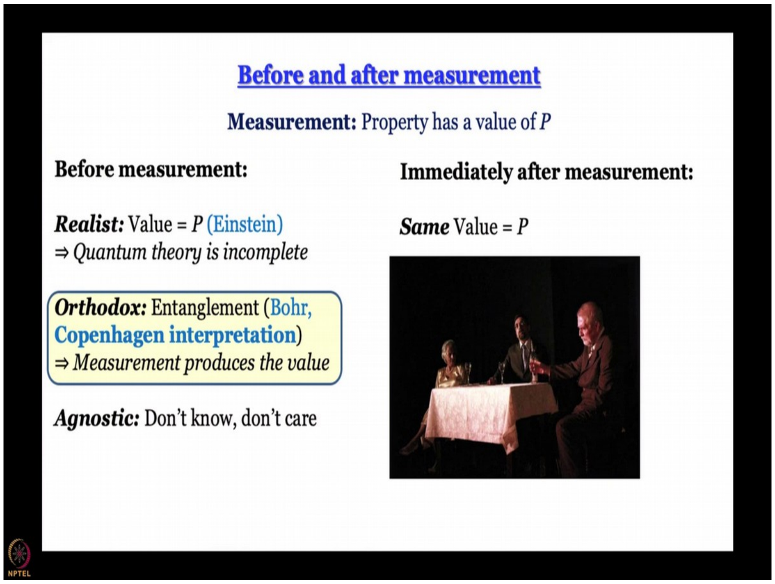

Before and after measurement

Measurement: Property has a value of P

Before measurement:

Realist: Value = P (Einstein)
⇒ *Quantum theory is incomplete*

Orthodox: Entanglement (Bohr, **Copenhagen interpretation**)
⇒ *Measurement produces the value*

Agnostic: Don't know, don't care

Immediately after measurement:

Same Value = P

The question is what happens before the measurement what was the property before the measurement and what is the property immediately after the measurement. So, there are three views or there were three views about what was the property? What is the value before the measurement? The first view is called the realist view and this is what Einstein had and the view was the venue was P immediately before you measure otherwise how did you get P?

But there is a problem with this view and the problem is if this view is correct then Quantum Theory turns out to be incomplete because if the value was P already before the measurement why is it that we could not know it, we are working with Psi and working with Psi we can get the value only at the time of measurement. If we do not know the value before measurement that means Psi is not enough there must be some other coordinate which people called hidden coordinate.

What is that if it is there then clearly our description is not enough. So, realist view does not really turn out to be compatible with the principle of quantum mechanics but Einstein was a die-hard believer of this view and that is why he had written to Born saying God does not create eyes. The second view was by Bohr and his co-workers this is famously known as Copenhagen interpretation. It is also called the Orthodox view. And this view says that before measurement the system exists in an entangled state.

You cannot measure because I mean you cannot know the value because before the measurement it is a superposition of states, entanglement of states and then when you measure that is when you see the value that you see you get one of those values, we will come to what it is called in a moment. And the third view well before going to the third view and this is what we are saying that measurement produces the value.

The third view is that of an agnostic which says we do not know what it was and we do not care but that is not such a great view after all. It is sort of an opportunistic view here. So, over the time due to some experiments performed by Bell in 1964 it is turned out that it is the Orthodox view that seems to be correct and that is the state of understanding at the moment that the system exists in an entangled State.

This is something that is not very easy to visualize and that is why it has given rise to a lot of interest as I said beyond the boundary of scientists. What you see here is a photograph of a play called Copenhagen this was quite popular all across the world and this was a few years ago a Tom Walter who is no more unfortunately had brought this play to IIT and a lot of us went and enjoyed it. This is all about a dialogue between Bohr and Schrodinger that the play depicts and it brings out the conflicts in the minds of these founding fathers of quantum mechanics.

And the outcome is Copenhagen interpretation that the system exists before measurement in an entangled state and it is a measurement that produces the value. All right, so what happens after the measurement? Everybody agrees that after the measurement we have the same value P immediately after the measurement because I mean if it is not P then how is it that in the previous measurement you had it.

Once you make the first measurement if you keep on making measurements in short succession you are going to get P. So, this is called wave function collapse which means that there many wave functions and their entangled before the measurement once you do the measurement if the system collapses into one particular wave function and continues to be defined by that if you keep on making measurement. So, this also gives rise to something that is quite popular it says that in quantum mechanics the property of the observer observable depends on the observer.

How you make the observation which operator you use that is going to tell you which wave function you will have access to and which value you will see. There is a point by Tagore which roughly translates to English as Safire turned green in the color of my consciousness, Ruby turned red. I looked at the Rose and said you are beautiful and it acquired beauty. This sounds very, very quantum mechanical I do not know whether Tagore had come in close contact with scientists of his time.

I do not know if this was influenced by them but this definitely reminds one about the Orthodox view and wave function collapse. But the question that we have not answered after all this discussion we have said that we have a wave function we have a wave equation all that is great. We have even said that using the wave function we can find a property if you use the appropriate operator but the question that continues to bother us even now is what is this wave function?

Once again this question has given rise to a lot of intrigue in the minds of people beyond the realm of scientists.

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But what is this wavefunction?

Google Doodle, December 11, 2017

And what you see here is a Google Doodle that came out in December 11 2017 to commemorate the birthday of Max Born. Whose work went a long way to give us some idea about what wave function actually is what is the meaning of it? That is what we will discuss in the next module.