Concepts of Chemistry for Engineering

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Lecture No. 02

Schrodinger's theory

Now that we know that Bohr model is not going to work because it violates uncertainty principle, the field is set for us to discuss a Schrodinger equation. And as you will see, even Schrodinger's equation has its beginning in classical mechanics.

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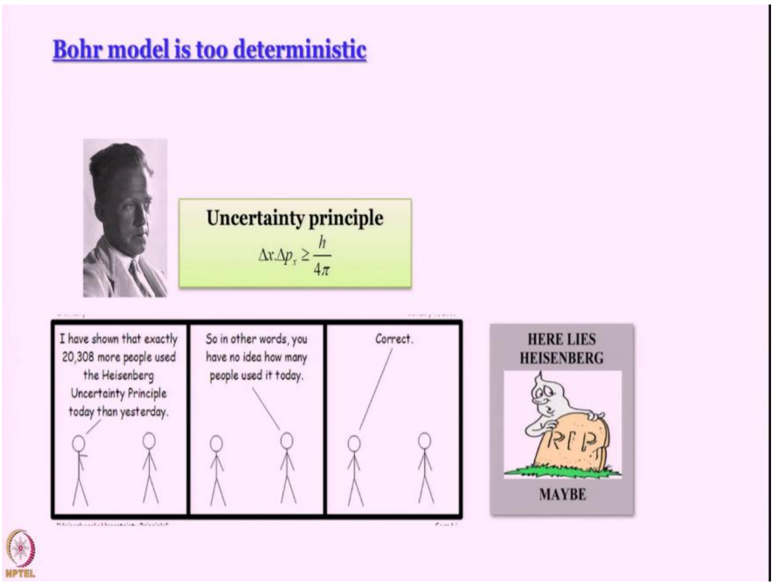

As we said Bohr model is too deterministic.

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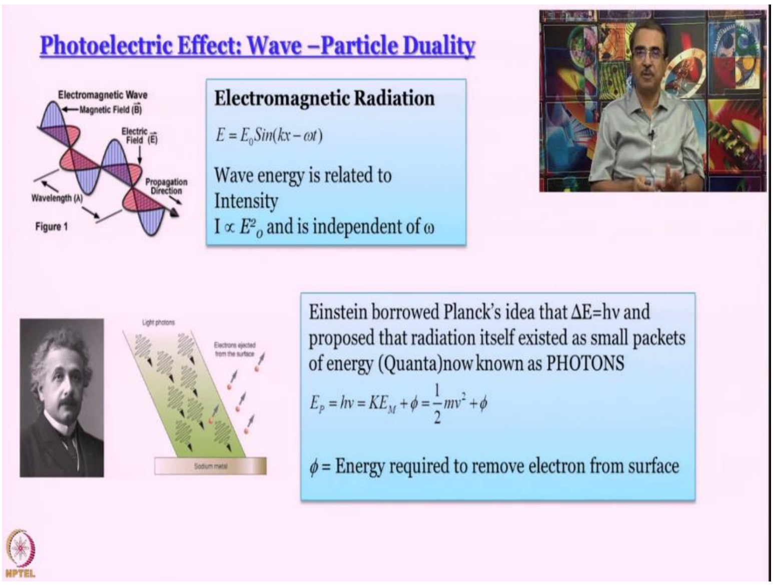

So, now, knowing that it is time to talk about a few more very path breaking kind of discoveries that were made in that point of time. One thing was what got Einstein his Nobel Prize, photoelectric effect. In physical optics, in physics, you have studied Huygens experiment for example, which establishes the wave nature of light. Newton believed that light has corpuscular nature.

In the explanation of photoelectric effect, Einstein established that light has corpuscular nature, particle nature. So, what does it mean? That light can behave like wave, it can behave like particle and whether you see the wave nature or particle nature is determined by what kind of an experiment you do. We will talk about diffraction later on in this course. So, if you do a diffraction kind of experiment, then you get to see the wave nature of light.

If you study photoelectric effect, then you get to see the particle nature of light, it is all about what kind of experiment you perform. So, this was already known. So, where are we now, Bohr model, the problem is it is too deterministic, uncertainty principle is violated, that is one side of the story. The other side of the story was that, for light, this wave particle duality had been established already.

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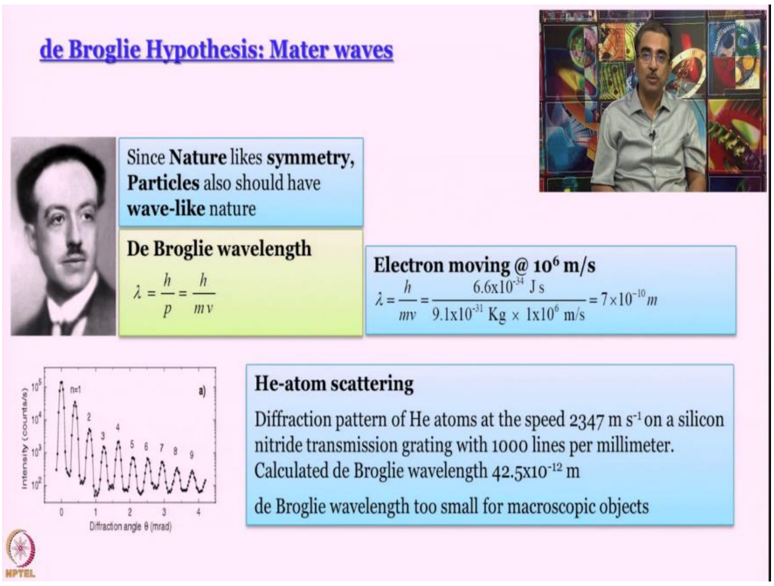

At this point of time in came de Broglie, who was at that time a PhD student, and I am sorry for the mistake in spelling here. It is not mater wave is matter wave. But well matter wave is the mater mother of our current understanding of this quantum world. So, it is a Freudian slip, but perhaps it is not a bad idea to call it mater wave also.

So, de Broglie's thesis is perhaps the shortest in the history of mankind, I encourage you to do a Google search and find out how many pages were there in that thesis. But that small little thesis was a completely disruptive phenomenon in our understanding of what everything is made up of. And it involves very sophisticated mathematics, we will skip all that and we will just share with you the philosophy of de Broglie hypothesis.

Well, the correct pronunciation is apparently de Broy, but then, I am not good at pronouncing European names, I will just say de Broglie. So, de Broglie sort of said is that nature manifests itself in two forms - energy and matter. Energy, light has a dual nature. Sometimes, you can see the wave nature, sometimes you can see particular nature and then de Broglie made this philosophical statement that nature likes symmetry.

So, particles matter should also have wave like nature. What does that mean? Absolutely mind boggling on the face of it, it sounds very esoteric, philosophical and impossible to understand, agree with that. But let us see what de Broglie has to say. What he said was taking lesson from light, he could work out an expression for wavelength associated with this so-called matter waves. That wavelength turns out to be $\frac{h}{mv}$.

And from here, if you take this $\lambda = \frac{h}{mv}$, and plug it back, you will see mvr = nhπ turns out to be an essential condition. The thing is this what is the circumference, 2πr. So, in this 2πr, you should have an integral multiple of half wavelengths n $\frac{\lambda}{2}$ should be there in 2πr. And what is lambda? $\frac{h}{mv}$, you substitute, you are going to get this mvr = $\frac{nh}{2\pi}$, that kind of a relationship.

And one can calculate the de Broglie wavelength. So, this is a calculation on electron moving at 10^6 ms^{-1}. You see, λ turns out to be 7 X 10^{-10} m. And this was experimentally verified as we are going to see very soon. So, mathematically there is no problem, you can have wave nature in the small little particles.

If you calculate the de Broglie wavelength of a cricket ball moving at, say, what is the speed at which Bumrah bowls? 140 kilometer per hour or something. So, you can work out what that frequency, what that wavelength is going to be and you can understand what will be, here in λ what will happen is that v for electron is 10^6 ms^{-1} fine; in the place of 10^6, you are going to have maybe 10^2, 4 orders of magnitude less.

But what about mass? The mass here is 10^{-31} kg. So, if you use a mass of 1 kg that is 10^{31}. So, this denominator will be $10^{31-6,}$ 10^{25} or so. So, that lambda is going to be very, very small and as a preliminary discussion, we can see that the lambda will be so small that you will not be able to see wave nature.

Of course, this is the beginning of the discussion not the end, try to think of yourself what will happen if that cricket bowl is at rest or if it moves very, very slowly. Should we see the wavelength? Should we see wave nature? Actually, we will not see even then, but think about it a little bit I leave it as an open question for you to ponder upon.

But the thing is that it was established that this wave nature can actually be seen for atoms and electrons and so on and so forth. What you see here is real data for helium atom scattering, you take a stream of helium atoms, pass them through a dispersing agent like a grating. And you see this kind of a diffraction pattern. So, manifestation of wave nature of matter is very much there.

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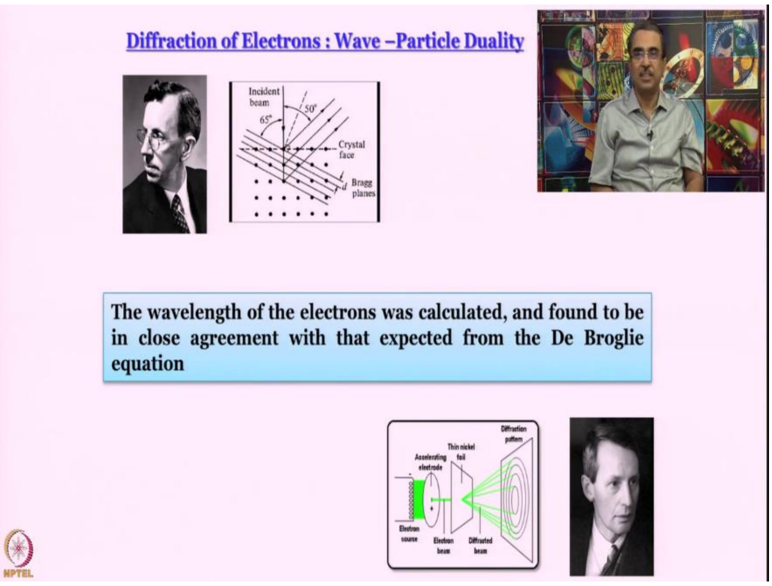

This is, these are two other examples, where this wave particle duality of electrons was manifested. I leave it to you to find out what these two experiments are called, and who these two scientists were. But suffice to say that wavelengths of electrons were found out experimentally to be of close values to those expected from de Broglie equation. So, matter waves. What are matter waves? Still, you can do the math, but it does not seem to make sense what are matter waves, nobody can understand.

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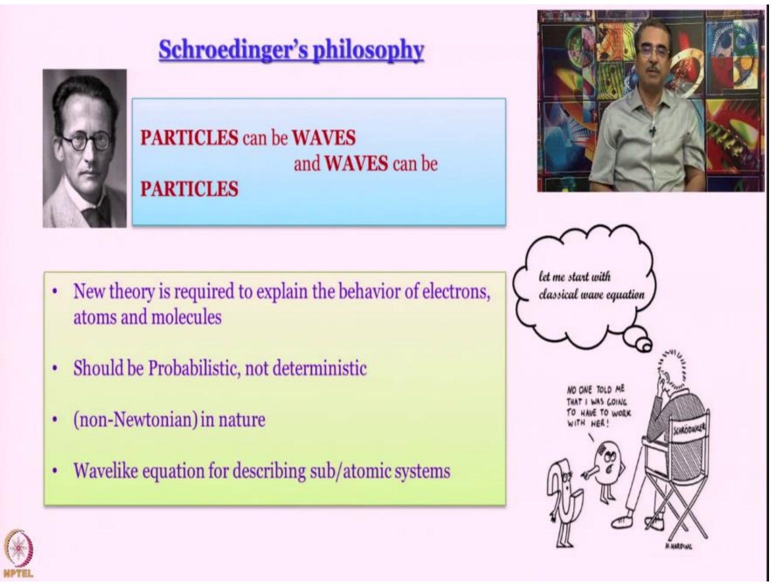

So, in came Schrodinger and even Schrodinger did not really understand at the time, what matter waves were, but what he had in his hand was that, well particles and waves, particles can be waves and waves can be particles. And one thing that was understood at that time is that you need some kind of a new theory and this theory has to be probabilistic and not deterministic.

Since, you cannot really talk about a precise value of position and momentum, you can only talk about things like average value, most probable value, so some kind of statistics would be required. And it would be a deviation from non-Newtonian mechanics from Newtonian mechanics. And since there is wave nature of matter, what Schrodinger thought was well for any kind of wave, wave that you see in the sea or wave that is produced on the surface of tabla when we play it, for all waves, there is something called a classical wave equation.

That essentially describes what is going to be the displacement from mean position amplitude has a function of space as well as time. So, Schrodinger thought sort of was that can we write classical wave equation for de Broglie wave. In many books, you see a so-called derivation of Schrodinger equation, please be advised that Schrodinger equation cannot be derived, it can be arrived at, it is a postulate. But even postulates have some basis, the basis of Schrodinger equation is that it is a classical wave equation for the de Broglie waves to start with.

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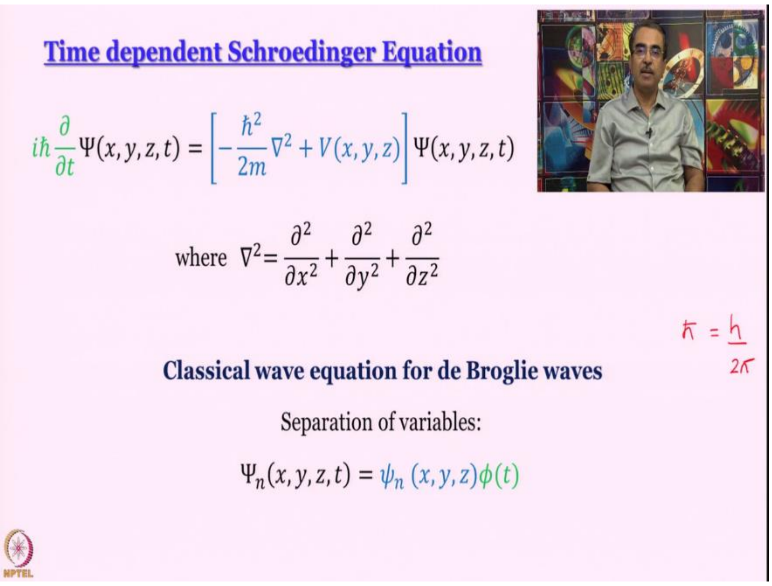

And I will not even show you what the classical wave equation is if it was studied in physics course, but when he wrote it like this classical wave equation for de Broglie waves, Schrodinger got an equation that looked like this, ψ here is amplitude, maximum displacement from mean position. And ψ is dependent not only on spatial coordinates say x, y z, but also on time.

So, Schrodinger equation turned out to be like this $i\hbar$, what is $\hbar$?, $\hbar = \frac{h}{2\pi}$, $\hbar$ is a fundamental quantity in quantum mechanics as you are going to see; $\hbar$ is simply $\frac{h}{2\pi}$. It is a little shorthand notation to write $\frac{h}{2\pi}$, that is all. So, this is what $\hbar$ is. So, $i\hbar\frac{\partial}{\partial t}\Psi$ = - $\frac{\hbar^2}{2m}\nabla^2 + V$, V is potential energy operating on ψ.

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, right now, it looks very intimidating and well, we do not know what you are talking about perhaps, but we will see we will make sense of it. Something that we have done here is that we have written this operator in time and operator in spatial coordinates in different colors. What is an operator? An operator is something that operates on a mathematical function and transforms it in some way or the other, we will have a lot to say about operators in the discussion to come.

But now, the first thing we should try to do is try to separate these variables, try to simplify the situation because right now it is a mix up of x y z and t. If we can separate them a little bit have smaller equations with fewer number of independent variables, that will nice. So, to separate the variables we use something that is again well known by that time from mathematical treatment of this kind of equations, we use a solution of this equation, where a solution is a product of two parts a space dependent part ψ_n and a time dependent part ϕ, ψ_n which is a function of x y z multiplied by ϕ which is a function of t.

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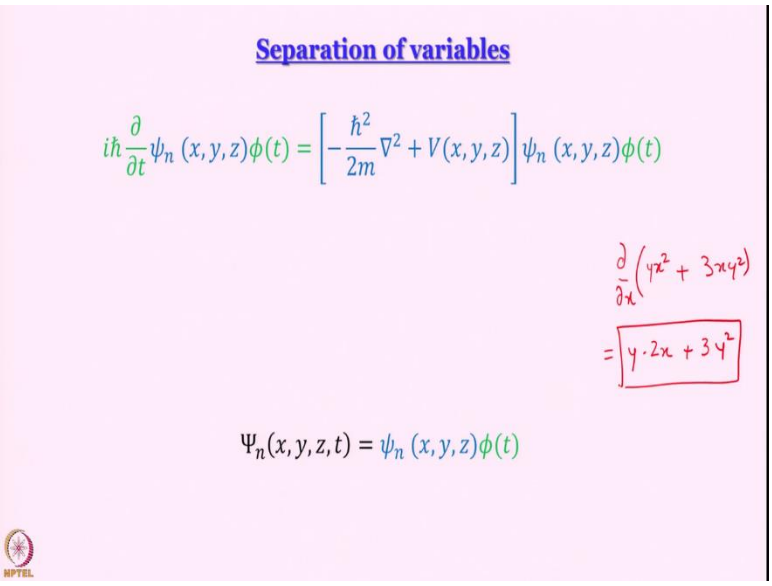

You plug it into the equation. Now, what will happen see on the left-hand side, this $\frac{\partial}{\partial t}$ is the operator, it is going to operate on ϕ(t) fine, but ψ_n is in terms of x y and z. So, as far as $\frac{\partial}{\partial t}$ is concerned, it is going to be a constant. Suppose, I give you xy or maybe x^2y+2xy^2 and ask you to differentiate with respect to x, what will you get? I forgotten what I said just now, so I will just write whatever comes to my mind, yx^2+3xy^2.

How do we find the differentiation? It is like this y will come out because it is not a function of x. So, the $\frac{\partial}{\partial x}$ will operate on x^2 to give you 2x plus, again y^2 will come out as it is a constant then 3, differentiation of x with respect to x gives you 1. So, this is your answer. So, that is the same thing we are doing here, nothing esoteric, nothing very new.

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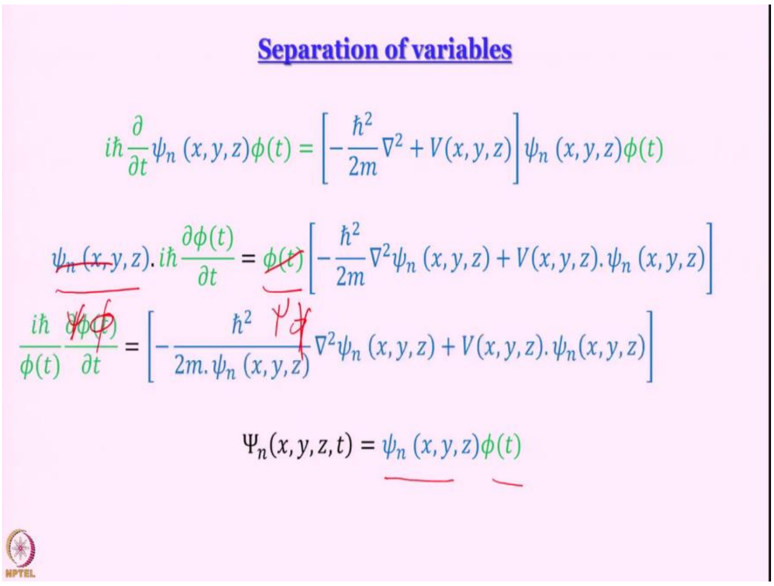

So, we are trying to separate the variables. While doing that we use this wave function which is a product of a space dependent and time dependent part, when we plug it back, this is what we get ψ_n (x,y,z) multiplied by $i\hbar \frac{\partial \phi(t)}{\partial t}$, well here I might as well write $\frac{d\phi}{dt}$= ϕ(t)[- $\frac{\hbar}{2m}\nabla^2$ + ψ_n (x,y,z) + V(x,y,z). ψ_n (x,y,z)] but operating only on ψ_n.

Now, the way to proceed is to try to get everything in time on one side of the equation and everything in x y z to another side of equation. If we can do that, then things will be a little easier to handle. How do I do it? One easy way of doing it would be to divide the equation both sides by Ψ_n, because, as you know Ψ_n is equal to a product of a space dependent part- and a-time dependent part. So, what happens if I divide this whole thing by ψ and ϕ, ψ ϕ.

On the right-hand side what happens if I divide by ψ and ϕ? Well, ϕ and ϕ cancel, on the left-hand side and ψ and ψ cancel. So, what do you have on the left-hand side then? $i\hbar \frac{\partial\phi(t)}{\phi\partial t}$. So, left hand side is only in terms of ϕ, right hand side is only in terms of ψ. Since it is looking ugly let me delete what I had written here.

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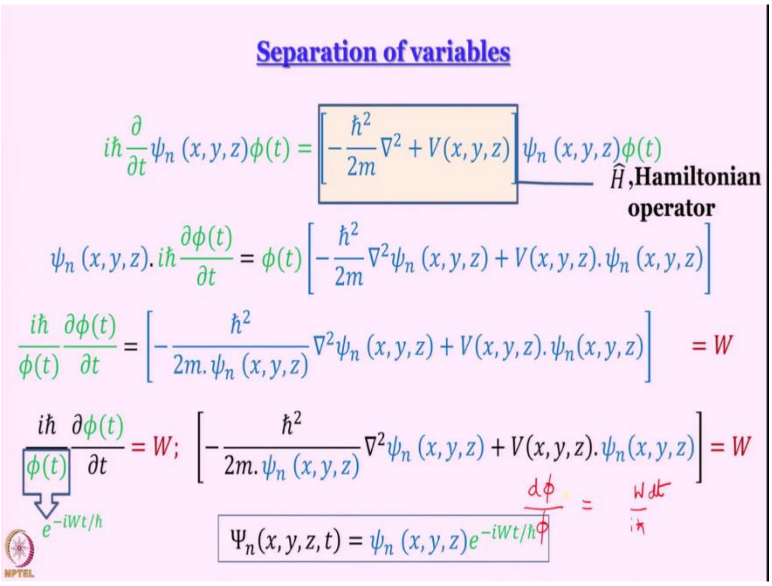

In this case, this is what I get. Left hand side is only in terms of time, right hand side is only in terms of spatial coordinates. So, since one is in time, one in spatial coordinates, both have to be equal to a constant, otherwise it does not make sense. How will you equate something that is in time and something that is in spatial coordinates? So, this constant is called a separation constant.

When you plug that in, the first equation becomes very, very simple, it becomes $\frac{\partial\phi(t)}{\partial t} = \frac{W\phi(t)}{i\hbar}$ or you can write $\frac{\partial\phi(t)}{\phi(t)} = \frac{W\,\partial t}{i\hbar}$. And then when you integrate this is what you get, this is the first equation, this the second equation. When you integrate the left, when you try to solve the left equation, ϕ(t) turns out to be $e^{-\frac{iWt}{\hbar}}$. It is not difficult to understand, I hope.

So, I know something already I know what the temporal part of the wave function is, time part $e^{\frac{iWt}{\hbar}}$. What I do not know is what is W. What is W, the answer comes from an inspection of this operator in spatial coordinates. This - $\frac{\hbar}{2m}\nabla^2$+ V, is known from classical mechanics to be the Hamiltonian operator.

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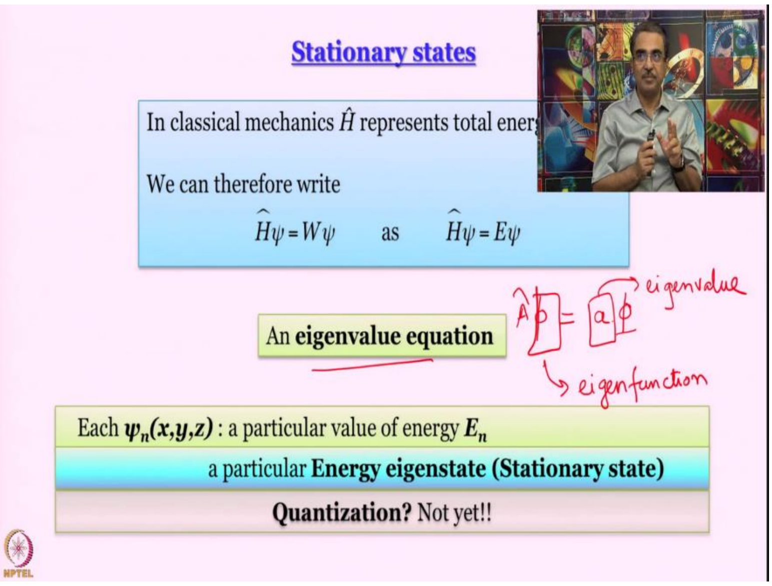

And Hamiltonian operator in classical mechanics represents total energy. So, when the Hamiltonian operator operates on Ψ, it is known that it gives us EΨ. So, W is actually E, the total energy of the system. That is point number 1. Point number 2 is that what you have got here is an eigenvalue equation. What is an eigenvalue equation? It is something like this you have an operator Â, an operator remember is something that something like $\frac{d}{dt}$ that operates on a function, so I will write here.

Â it operates on ϕ, ϕ is a wave function to give me same wave function ϕ multiplied by a constant 'a', this is called an eigenvalue equation. In this equation, the function, wave function is called an Eigen function. Please forgive my bad handwriting. First of all, it is bad. Secondly, I am writing on this smooth screen, which does not really help things. So, I hope you are able to read what I am writing.

So, when operator operates on this function, if it is an Eigen function then you get back the same thing multiplied by a constant which is called an eigenvalue. So, for energy of a quantum mechanical system what we get from Schrodinger's equation is that you can write an eigenvalue equation where the operator is Hamiltonian and the eigenvalue is energy. Extrapolating from here one can work out what is called the or one can formulate the postulates of quantum mechanics.

But before that, let us just realize something what it says is that each wave function until now, we were saying wave function is just a displacement from mean position. But now, wave function gets a little more significance, each wave function is associated with a particular value of energy En. So, it is called a particular energy eigenstate and this eigenstate is a stationary, state stationary state is defined as a state in which, state whose energy does not change with time and even this term stationary state actually came from a Bohr model, remember Bohr had said stationary state.

So, we have not really thrown out everything. Have we achieved quantization? We have not. All we have achieved is that we have learned that you can write an eigenvalue equation for energy. And we have learned that wave function contains the information about the energy which is brought out by making the Hamiltonian the total energy operator, operate on the wave function. This is what we know. We have not obtained quantization yet. How does quantization come? In, we will learn that in module after next day, I think.

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But with this background, we can now talk about postulates of quantum mechanics, which are sort of the ground rules. Again, cannot be derived, that is the beginning. It comes from a well common sense and observations and intelligent assumptions. The ground rules of quantum mechanics are something that we can start talking about once we know Schrodinger equation.