Quantum Chemistry of Atoms and Molecules
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Lecture-3
The wave nature of matter

In this module we will try to understand the wave nature of matter and it sounds quite maddening because it is very difficult to believe that matter can have wave nature.

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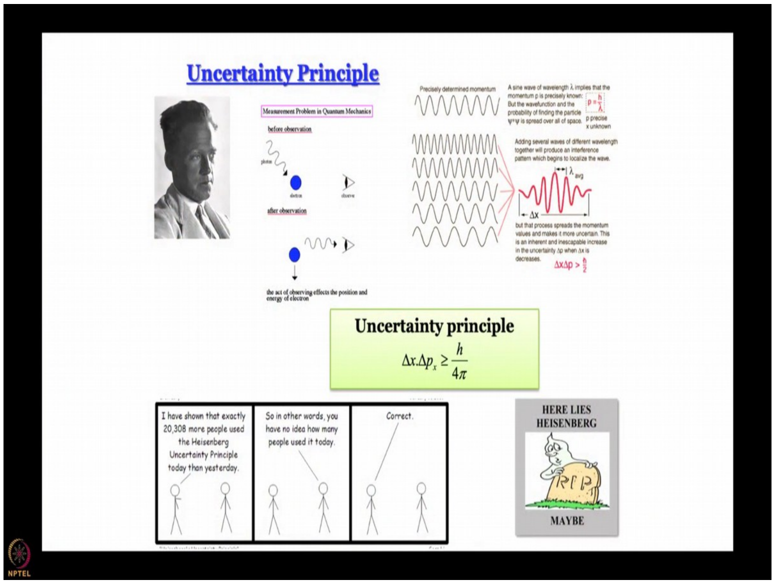

Uncertainty Principle

Measurement Problem in Quantum Mechanics

the act of observing effects the position and energy of electron

A sine wave of wavelength λ implies that the momentum p is precisely known: But the wavefunction and the probability of finding the particle $\psi^*\psi$ is spread over all of space.

$p = \frac{h}{\lambda}$

p precise
x unknown

Adding several waves of different wavelength together will produce an interference pattern which begins to localize the wave.

but that process spreads the momentum values and makes it more uncertain. This is an inherent and inescapable increase in the uncertainty Δp when Δx is decreases.

$\Delta x \Delta p > \frac{\hbar}{2}$

Uncertainty principle

$$\Delta x.\Delta p_x \geq \frac{h}{4\pi}$$

But then; as we have seen that uncertainty principle sort of last nail in the coffin of Bohr theory, so such a deterministic approach of describing atomic structure is clearly not going to work.

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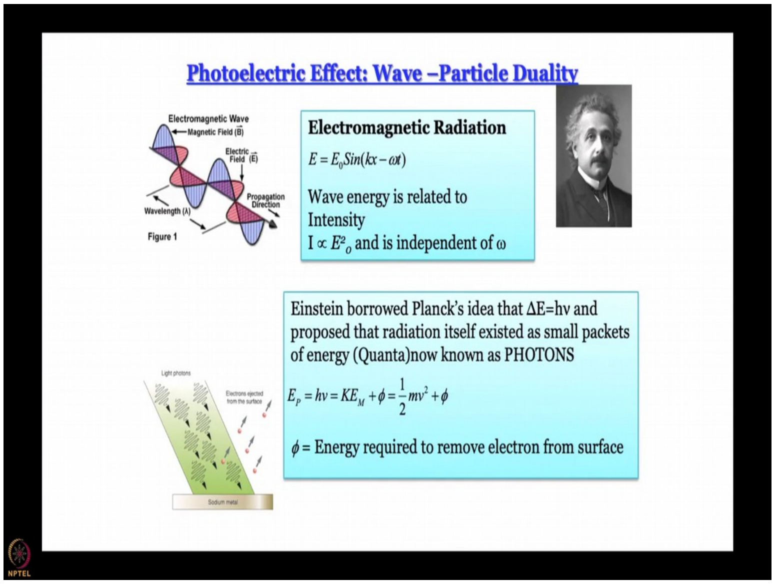

Photoelectric Effect: Wave –Particle Duality

Electromagnetic Radiation

$E = E_0 Sin(kx - \omega t)$

Wave energy is related to Intensity

$I \propto E^2_0$ and is independent of ω

Einstein borrowed Planck's idea that ΔE=hν and proposed that radiation itself existed as small packets of energy (Quanta)now known as PHOTONS

$E_P = h\nu = KE_M + \phi = \frac{1}{2}mv^2 + \phi$

ϕ = Energy required to remove electron from surface

And then in photoelectric effect the wave particle duality of light was already established. So, the question was does such a duality exists for matter as well?

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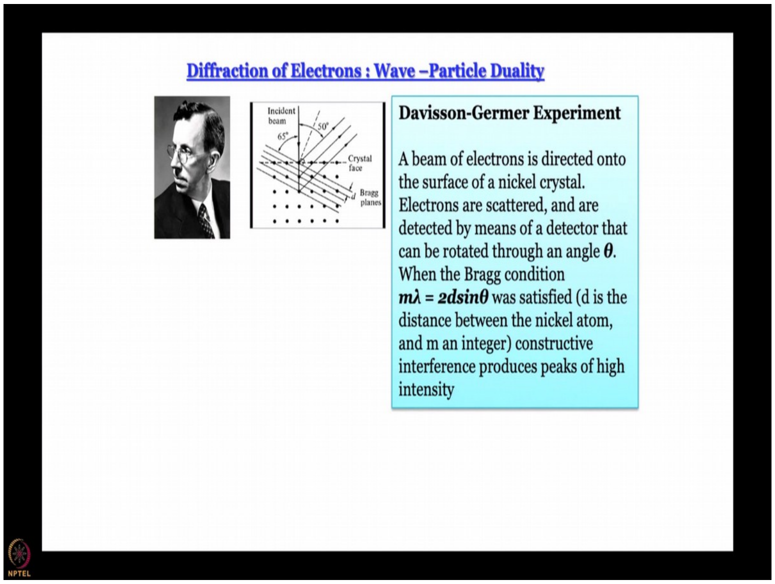

Diffraction of Electrons : Wave –Particle Duality

Davisson-Germer Experiment

A beam of electrons is directed onto the surface of a nickel crystal. Electrons are scattered, and are detected by means of a detector that can be rotated through an angle ***θ***. When the Bragg condition ***mλ = 2dsinθ*** was satisfied (d is the distance between the nickel atom, and m an integer) constructive interference produces peaks of high intensity

And first let us talk about the experiments that led to the realization that indeed matter can have wave-like nature and those experiments are of electron diffraction. As you said in the last module diffraction is sure short sign of waves only when something has wave nature can it exhibit diffraction can they can it give you fringes. So, the experiment that was done well we are talking about to talk about two experiments the first one well very similar experiments actually.

The first one there is Davisson-Germer experiment in this a beam of electrons from an electron gun and when I see electron gun one can think of a cathode ray tube with a hole at an end, so that the cathode rays that are generated would go through the electrode and come out of the other end. So, the beam of electrons collimated beam of electrons was made incident on a nickel crystal and then the dispersed electrons were detected by a detector that could be rotated through an angle theta.

And it was found that a diffraction pattern was obtained. According to this n lambda or were sitting here is m lambda equal to 2d sine theta this is what tells us that even electrons can actually give diffraction and therefore have wave-like nature.

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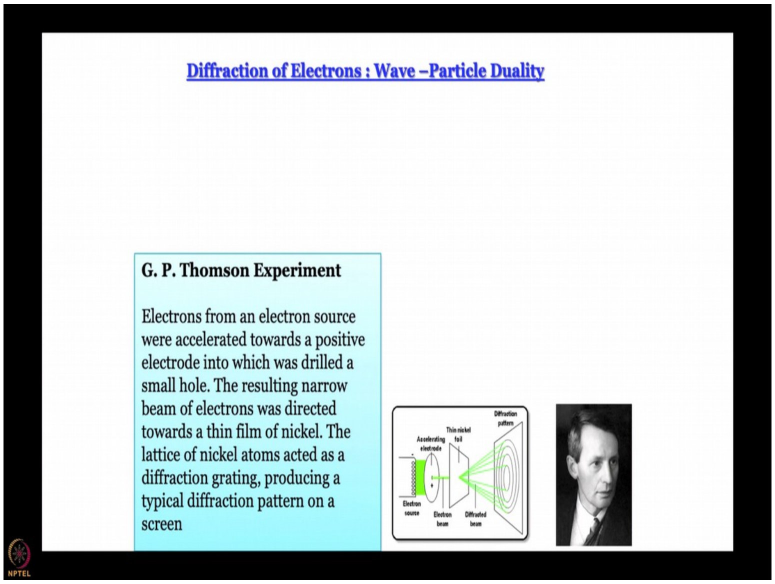

Diffraction of Electrons : Wave –Particle Duality

G. P. Thomson Experiment

Electrons from an electron source were accelerated towards a positive electrode into which was drilled a small hole. The resulting narrow beam of electrons was directed towards a thin film of nickel. The lattice of nickel atoms acted as a diffraction grating, producing a typical diffraction pattern on a screen

The other experiment quite similar was performed by G.P. Thompson in G.P. Thompson experiment electrons from an electron source were accelerated towards the positive electrode in which hole was drilled as I said a little while ago. The resulting narrow beam of electron was directed through a thin film of nickel so the difference between this experiment and that the earlier experiment there was a Davisson-Germer experiment is that in there is a Davisson-Germer experiment it was done in a reflective mode.

Here G.P. Thompson's experiment is performed in a transmission mode since it is done in a transmission mode one takes not a crystal of nickel but a thin film of nickel. So, what happened then is that for the electron beams that went through a screen was placed after the nickel film and a clear diffraction pattern was obtained. So, these two experiments indicate that might have manifested in electrons can have wave-like nature. What does it mean? We do not know yet.

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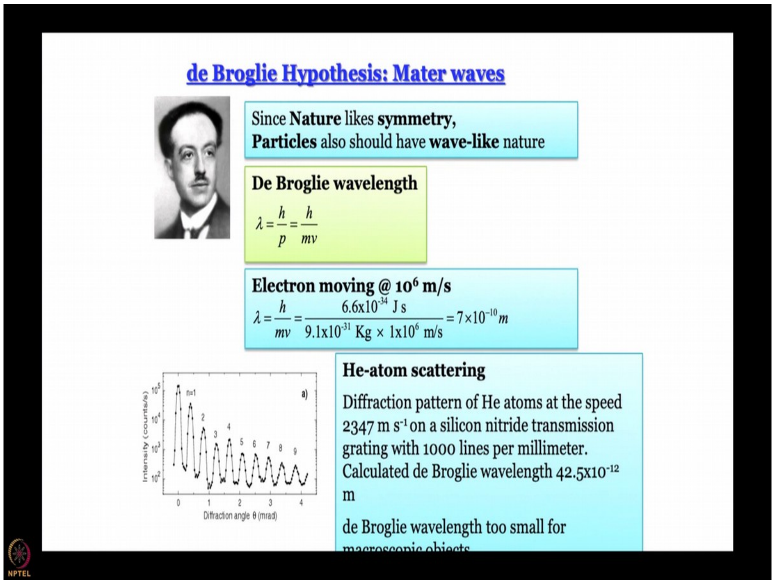

de Broglie Hypothesis: Mater waves

Since **Nature** likes **symmetry**,
Particles also should have **wave-like** nature

De Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Electron moving @ 10^6 m/s

$$\lambda = \frac{h}{mv} = \frac{6.6\text{x}10^{-34}\text{ J s}}{9.1\text{x}10^{-31}\text{ Kg} \times 1\text{x}10^{6}\text{ m/s}} = 7\times10^{-10} m$$

He-atom scattering

Diffraction pattern of He atoms at the speed 2347 m s^{-1} on a silicon nitride transmission grating with 1000 lines per millimeter. Calculated de Broglie wavelength 42.5x10^{-12} m

de Broglie wavelength too small for macroscopic objects

But then at that point of time de Broglie came in and what de Broglie did is that he said that well nature like symmetry and nature manifested its in two forms energy and matter. Since energy has dual nature so it's no surprise that matter also has dual nature well that is only the philosophy of it, rest of it is non-trivial mathematics and after doing that de Broglie arrived at this expression which one can arrive at very easily for photons for example where lambda is given by h by p where p is the momentum.

So for anything de Broglie proposed that wave nature is of course associated with a wavelength that wavelength of anything at anything can be electron, cricket ball, Jupiter or dinosaur. For anything this lambda is equal to h by p which is h by mv in our tutorials we are actually going to work out the de Broglie wavelength of things that are very light like electron and things that are seemingly like; like say a dust particle and maybe that is something that is a little heavier like a cricket ball and when we do that we will see for ourselves what happens to these de Broglie wavelengths.

And that will give us an answer to why is it that we do not see wave nature manifested in you, me, chair, table all these things de Broglie wavelength this lambda equal to h by mv. So, for an electron which moves at 10 to the power 6 meters per second, 10 to the power 6 meter per second is a very high speed. But if we consider the speed of light that is 3 into 10 to the power 8 meters per second so the speed of this electron here is about hundred times almost hundred times less than the speed of light so it is very high but achievable.

So for an electron moving at 10 to the power 6 meters per second lambda one can calculate to be is 7 into 10 to the power -10 meter angstrom and that is why one can see this diffraction patterns using an atomic lattice because for diffraction to occur the D separation between the planes of a lattice have to be comparable with the wavelength. If you take a lattice where the spacing is very small then we do not see diffraction if you take a lattice where the separation is too much compared to the wavelength light just passes through.

So this value of lambda is very appropriate to be seen using a an atomic lattice. So, now thing think of a human being wearing 50 kg moving at 10 meters per second, one can work out what the wavelength will be and if you work out you will see that the wavelength is such that one cannot have any grating physically that can give you diffraction of that human being and show diffraction patterns we will understand it better when we work out the assignment problems.

But well remember what we said we had quoted Max Plack experimental results are the only truth without showing experimental results I cannot claim anything. So, here we show the experimental results of helium atom scattering and here the diffraction pattern is such for helium atoms moving at 2347 meters per second and impinging on a silicon nitride transmission grating which has thousand lines per millimeter.

So, all parameters are very well defined. The calculated de Broglie wavelength is 42.5 into 10 to the power -12 meter. So, even for helium it is for 2.5 and 10 to the power -12 meter rather small. So, for de Broglie wavelength for particles that are bigger you require something that is even smaller.

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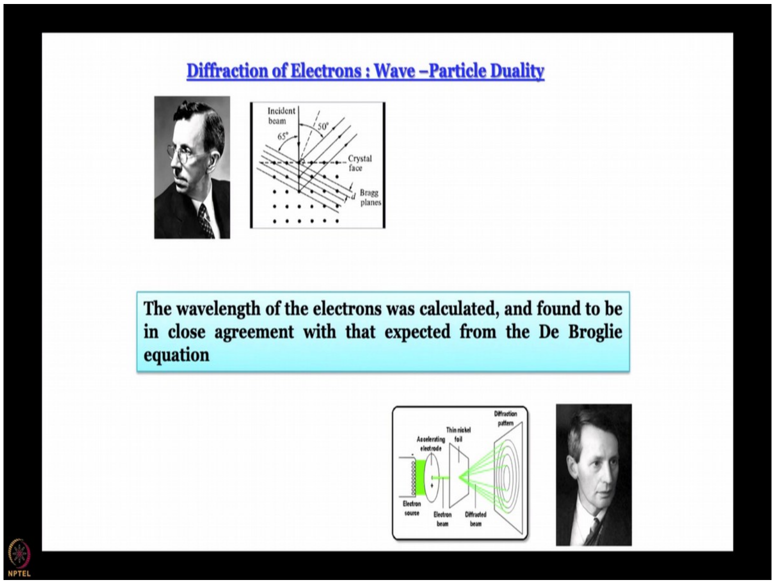

Diffraction of Electrons : Wave –Particle Duality

The wavelength of the electrons was calculated, and found to be in close agreement with that expected from the De Broglie equation

However for electrons in these experiments that we talked about a little while ago in both the experiments the wavelength that was calculated turned out to be in very, very close agreement with that which we expect from de Broglie equation and this is the vindication of the Broglie theory. The experimentally observed result matches very nicely with what de Broglie theory predicts.

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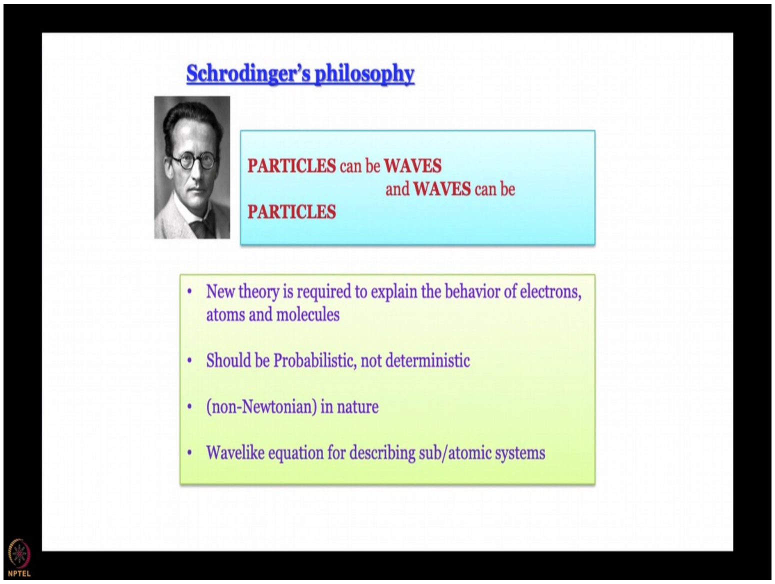

Schrodinger's philosophy

PARTICLES can be WAVES
and WAVES can be
PARTICLES

- New theory is required to explain the behavior of electrons, atoms and molecules
- Should be Probabilistic, not deterministic
- (non-Newtonian) in nature
- Wavelike equation for describing sub/atomic systems

With all this background Schrodinger tried to develop a treatment for atomic structure so what did Schrodinger have in his hand? First of all particles can be waves, waves can be particles and there is duality and when we say it like that nobody understands anything anyway. So, what he realized that you need a new theory if you want to explain the behavior of electrons atoms molecules and so on and so forth.

Also since we are handling things that are waves as well as particles, deterministic theory is not going to work. Deterministic here too much of determinism was the reason for downfall of bohr theory remember. So, what we need really is a probabilistic theory and that is what is going to eventually lead to our understanding of what is the meaning of this wave nature of life of matter. This of course is expected to be non-newtonian in nature but then what Schrodinger really wanted to do is he wanted to write a wave-like equation for describing subatomic or atomic systems.

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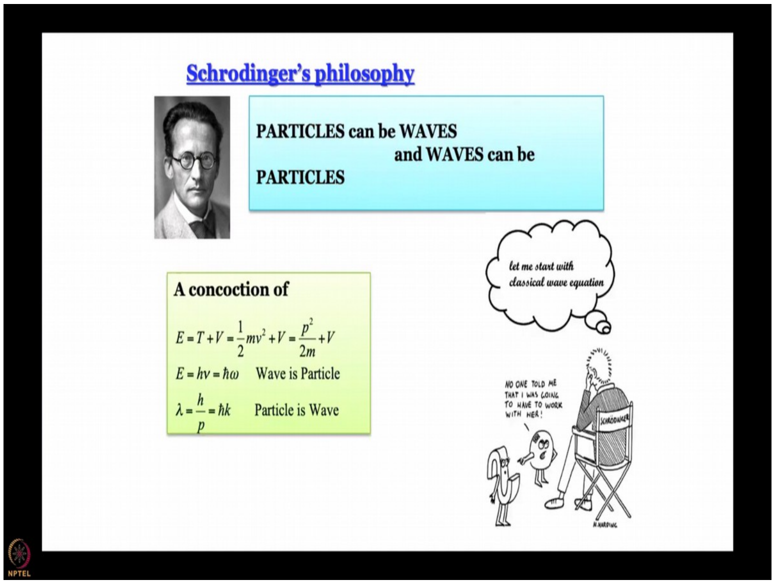

Schrodinger's philosophy

PARTICLES can be WAVES
and WAVES can be
PARTICLES

A concoction of

$E = T + V = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V$

$E = h\nu = \hbar\omega$ Wave is Particle

$\lambda = \frac{h}{p} = \hbar k$ Particle is Wave

Now the tools were all there because we know that total energy of a system like that would be a sum of kinetic energy and potential energy and then we know that E equal to hv and we know de Broglie relation.

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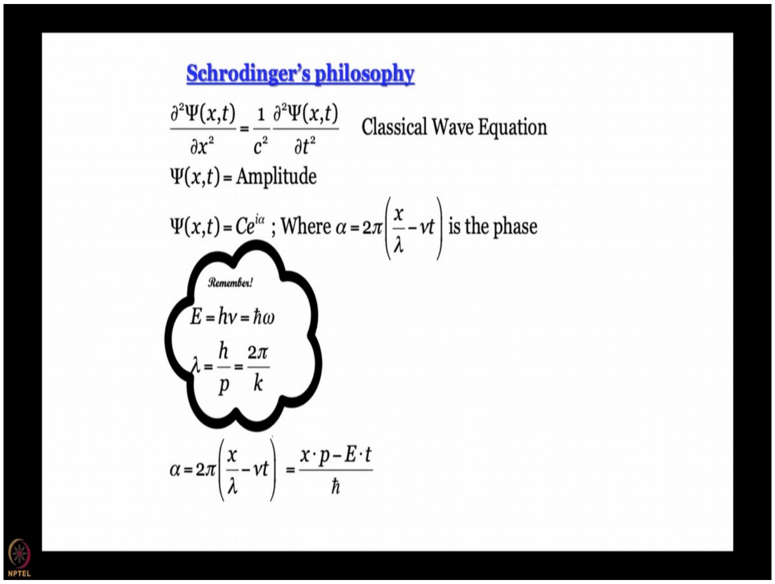

Schrodinger's philosophy

$$\frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2\Psi(x,t)}{\partial t^2}$$ Classical Wave Equation

$\Psi(x,t) =$ Amplitude

$\Psi(x,t) = Ce^{i\alpha}$; Where $\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right)$ is the phase

Remember!

$E = h\nu = \hbar\omega$

$\lambda = \frac{h}{p} = \frac{2\pi}{k}$

$$\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right) = \frac{x \cdot p - E \cdot t}{\hbar}$$

So, with this what Schrodinger did was the classical wave equation that existed at the time and is used even now for any kinds of waves, sound waves for example any kind of wave. When someone plays the tabla, the wave that is generated on the diaphragm even for that wave one can use the classical wave equation del 2 Psi del x2 is equal to 1 by c square del Psi del t 2 well what are we what did we just say, this is what we said. This Psi that we have written here something that keeps on coming back in quantum mechanics is the amplitude.

Displacement from the mean position not the maximum amplitude, amplitude so this displacement from in position for any wave as we know from our knowledge of basic physics is a function of not only space but also time. So, what we are saying that and this is something that is established in classical mechanics. Second derivative of this space and time dependent amplitude which is also called wave function with respect to space is equal to 1 by c square multiplied by second derivative partial derivative of course of the amplitude or wave function which is space and time dependent with respect to time.

And in fact we are going to work this out in any case Psi of xt is equal to c into e to the power i alpha where alpha equal to 2 pi multiplied by x by lambda minus nu t this is the phase, this was known and de Broglie relationship was not referring there. So, what he did is he proposed an equation which is essentially a classical wave equation for de Broglie waves. Let us not forget that Schrodinger's equation is really a postulate it cannot be derived.

Sometimes in some books derivation of Schrodinger equation is given that is not the right terminology. You can arrive at Schrodinger equation you cannot derive it in the same way that you cannot derive any of Newton's postulates there postulates there the starting points and the whole because they are the universal truth. So, Schrodinger equation which is the classical wave equation for the de Broglie waves looks like this;

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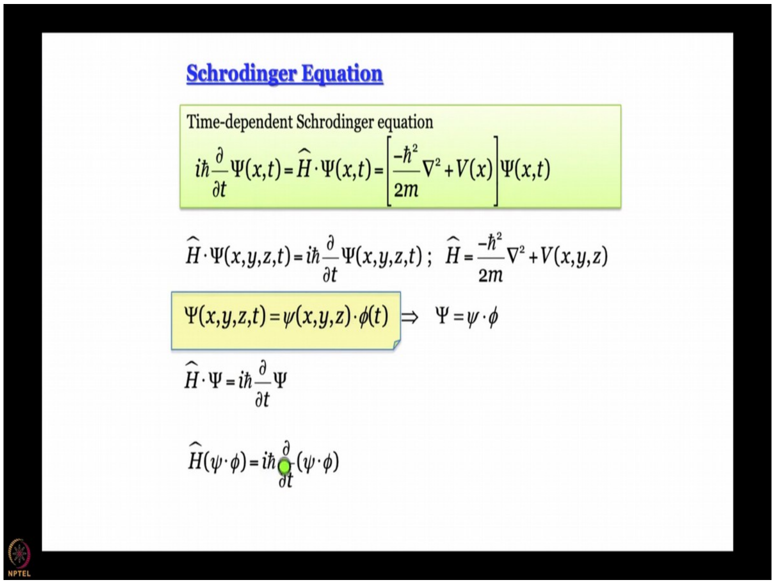

Schrodinger Equation

Time-dependent Schrodinger equation

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

$$\hat{H}\cdot\Psi(x,y,z,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t)\ ;\ \ \hat{H}=\frac{-\hbar^2}{2m}\nabla^2+V(x,y,z)$$

$$\Psi(x,y,z,t)=\psi(x,y,z)\cdot\phi(t) \Rightarrow \Psi=\psi\cdot\phi$$

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

$$\hat{H}(\psi\cdot\phi)=i\hbar\frac{\partial}{\partial t}(\psi\cdot\phi)$$

ih cross multiplied by del del t of space and time dependent wave function is equal to H hat will come back to adage that is my H hat operating on Psi which of course is a function of space and time. What is H hat is important to understand that. H hat is the Hamiltonian operator and it is given by -h cross square by 2 m del square by del square is del 2 del x 2 + del 2 del y 2 + del 2 del z 2 + v of x where v is the potential energy.

Now here for the first time in this course we are introduced to the concept of operators. What is an operator? An operator is something that well it sounds a little silly if I put it that way but it still is the best way of putting it, an operator is something that operates on a function and transforms it in some way. So, the operators that we are going to encounter most of the time are del del x del T del x 2 so on and so forth.

So and it is important to also understand that this concept of operators is not something that came with quantum mechanics. The concept of operators was already there in classical mechanics in fact the Hamiltonian operator was there in classical mechanics and this is the strength of Schrodinger's treatment. The entire problem we have had so far is that it seems that this when you go down to atomic subatomic scales when I talk about quantum mechanics everything is very enigmatic.

And what we have in those length scales is nothing like what we see around us so there seems to be a disconnect. So, the strength of Schrodinger's approach is that Schrodinger took very well-established classical mechanical tool and combined it with de Broglie's expression so the logic of classical mechanics actually is taken forward as far as possible. If you remember in bohr theory the quantum numbers fell from the sky they were invoked just like that whenever there was a requirement.

In Schrodinger's equation there is no quantum number. Quantum numbers will arise later on and we will see why they come but it is starting Schrodinger equation per se that is none it is just a classical wave equation written for matter waves that is all that it is. So, this here, is your Schrodinger equation in three dimensions del square is laplacian del 2 del x 2 + del 2 del y 2 + del 2. Now in the next step to simplify the situation a little bit we can write this space dependent and time dependent.

A space as well as time dependent wave function Psi which is a function of xyz special coordinates and t the time coordinate this we can write as a product of two functions small Psi henceforth will just call this Psi small Psi which is a function of spatial coordinates x y and z and the other function is Phi which is a function of t and the use of small Psi and small Phi is quite popular so very often we do not even write these coordinates in brackets we just write capital Psi equal to small Psi multiplied by Phi the thing to remember here is that capital Psi is dependent on spatial coordinates as well as time.

Small Psi depends only on spatial coordinates Phi depends only on time. Why can we write it like this because x y z t, x y z a special coordinate t is temporal coordinate and we can consider them separately. Space has got nothing to do with time if you work in the non relativistic domain that is what we are doing now. There is something called relativistic quantum mechanics but in this course we are not going to get into it.

Here we work in the domain where time and space are completely separable. So, since they are completely separable we can write the wave functions as product of a space dependent part and a time dependent part. So, now we go back to the equation h operates on capital Psi to give you ih cross x del del t of capital Psi so we can write like this Hamiltonian operator H hat operates on the product of small Psi and phi to give you ih cross x del del t of the product of Psi and Phi.

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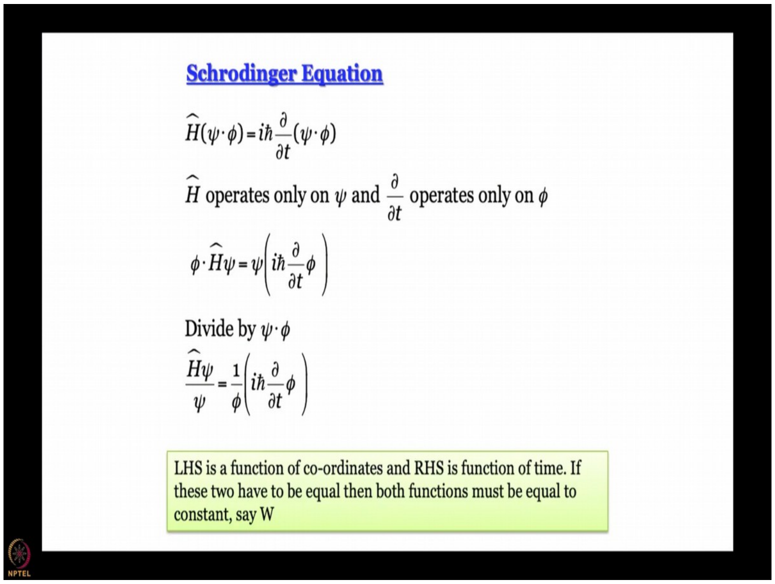

Schrodinger Equation

$$\hat{H}(\psi\cdot\phi) = i\hbar\frac{\partial}{\partial t}(\psi\cdot\phi)$$

$\hat{H}$ operates only on ψ and $\frac{\partial}{\partial t}$ operates only on ϕ

$$\phi\cdot\hat{H}\psi = \psi\left(i\hbar\frac{\partial}{\partial t}\phi\right)$$

Divide by $\psi\cdot\phi$

$$\frac{\hat{H}\psi}{\psi} = \frac{1}{\phi}\left(i\hbar\frac{\partial}{\partial t}\phi\right)$$

LHS is a function of co-ordinates and RHS is function of time. If these two have to be equal then both functions must be equal to constant, say W

Now the thing to understand is the Hamiltonian operator H what is it remember it is some constant multiplied by del 2 del x 2 + del 2 del y 2 + del 2 del z 2 plus potential energy, time independent potential energy. So, the entire operator has no term in time, it is expressed completely in spatial coordinates. So, we can say safely that the Hamiltonian H operates only on Psi and del del t operates only on Phi and this thing is going to hold for stationary states we come back to the stationary states defined by your by Neils Bohr.

H operates only on Psi and del del t operates only on Phi. So, we can write like this we can take on the left hand side we can take Phi out and write Phi H Psi, on the right hand side we can take Psi out and write Psi multiplied by ih cross del Phi del t and then we can divide both sides by the products Psi Phi, this is what we get H Psi divided by Psi on the left hand side on the right hand side we have 1 by Phi multiplied by ih cross multiplied by del Phi del t.

Now see the left hand side is a function of coordinates of space, sorry I have missed off space here LHS is a function of spatial coordinates I should have said and RHS right hand side is a function of time. So, they can be dimensionally consistent only if they are equal to a constant we will write that constant okay so we write it as W.

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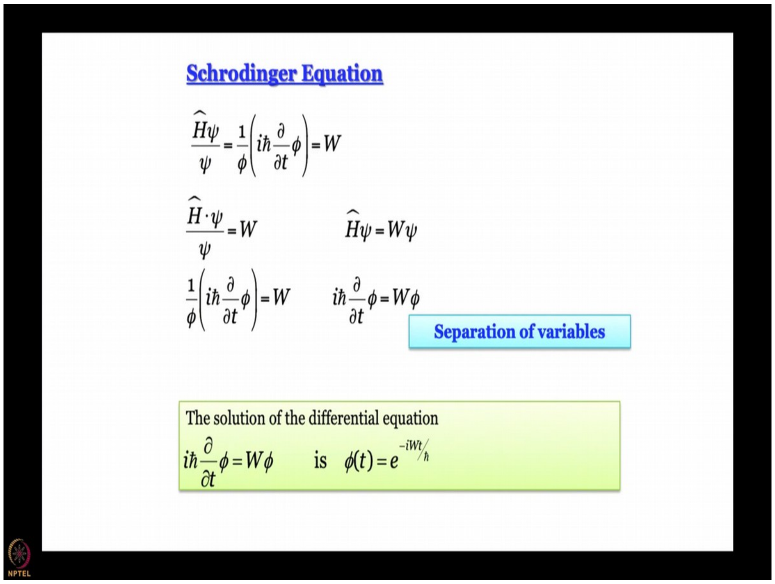

Schrodinger Equation

$$\frac{\widehat{H}\psi}{\psi} = \frac{1}{\phi}\left(i\hbar\frac{\partial}{\partial t}\phi\right) = W$$

$$\frac{\widehat{H}\cdot\psi}{\psi} = W \qquad \widehat{H}\psi = W\psi$$

$$\frac{1}{\phi}\left(i\hbar\frac{\partial}{\partial t}\phi\right) = W \qquad i\hbar\frac{\partial}{\partial t}\phi = W\phi$$

Separation of variables

The solution of the differential equation

$i\hbar\frac{\partial}{\partial t}\phi = W\phi$ is $\phi(t) = e^{-iWt/\hbar}$

And then we can get two equations one is this H Psi equal to W Psi the other is ih cross del Phi del t is equal to W Phi so what we have been able to do so far is that we have been able to break down the time and space and time dependent Schrodinger equation into two equations one of which is completely space dependent the other is completely time dependent. And that is what makes our life a little simple not only because math becomes simpler but also because this space independent as well sorry time independent space dependent Schrodinger equation is the one that we are only going to use for the rest of the course.

Because we are all were working with stationary states. Stationary states are such that Psi Psi star is independent of time such that E is independent of time so there is no need for us to worry about the time dependent part of the wave function anymore in this course. What we should worry about is what is this W? Well we have obtained what is called separation of variables. But just for the records if you just solve the time dependent part of the wave equation that is very simple and that turns out to be e to the power minus iw t by h cross.

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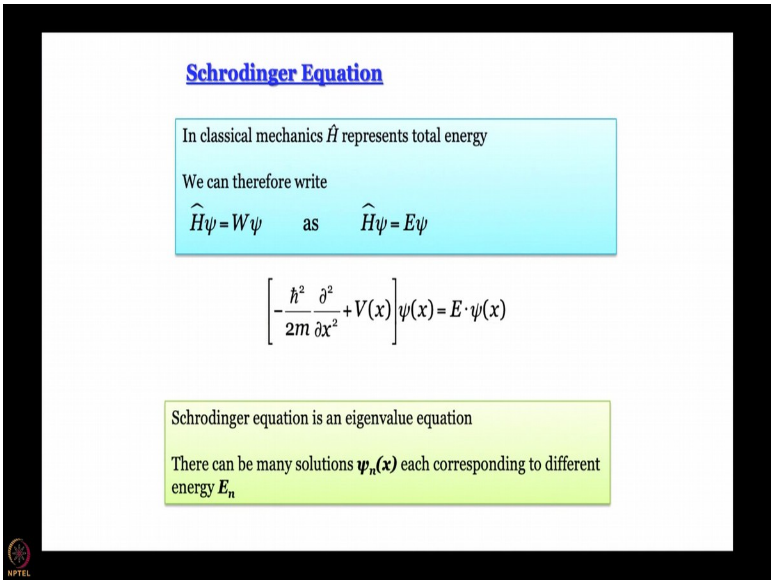

Schrodinger Equation

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

We can therefore write

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

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x)=E\cdot\psi(x)$$

Schrodinger equation is an eigenvalue equation

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

And to answer what is W we take the lesson from classical mechanics. As you said in classical mechanics Hamiltonian represents total energy is the total energy operator, so when Hamiltonian operates on the function and gives you W multiplied by Psi from classical mechanics itself we know that this W has to be equal to E energy. So, H Psi equal to E Psi this is a form of Schrodinger equation that is most popular among chemists because this is what we are going to use for the rest of the time.

So we can expand a little bit and write -h cross square by 2 m del 2 del x 2 + vx operating on Psi x equal to E Psi x. So, this is Schrodinger equation and now we have reached an interesting juncture in our discussion. Because it turns out that Schrodinger equation is a special kind of equation it is called an eigenvalue equation. What is the meaning of eigenvalue equation eigen in German means one you can think unique.

So eigenvalue equation is one is such that an operator operates on a function to give us back the same function multiplied by a constant. In this situation if this is the situation then this function is called an eigenfunction of the operator in question and this multiplier that we get that is called the eigenvalue. So, what we see here is that the total energy operator Hamiltonian operates on the space dependent wave function Psi x Psi of x to give us an eigenvalue equation h Psi equal to E Psi.

So first of all the space dependent time independent wave function is an eigenfunction of the hamiltonian operator. Secondly the energy of the system is obtained as an eigenvalue Psi of x is the eigenfunction of the energy operator and E is the eigenvalue that you get in the eigenvalue equation that we get we obtained when the total energy operator Hamiltonian operates on Psi of x. So, in Schrodinger from this understanding of an equation we see that this eigenvalue equation and eigenvalues, eigen functions they can have rather important implications in quantum chemistry, quantum mechanics. So, Schrodinger equation is an eigenvalue equation from here quantum mechanics really opens up.

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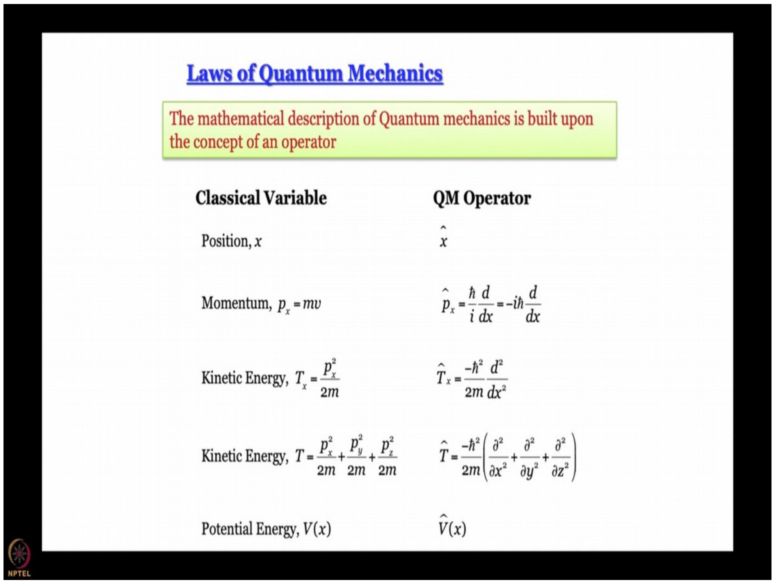

Laws of Quantum Mechanics

The mathematical description of Quantum mechanics is built upon the concept of an operator

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, $V(x)$	$\hat{V}(x)$

Because what one can do knowing this is that one can now propose the laws of quantum mechanics or as they are commonly called postulates of quantum mechanics. So, let us not forget once again that postulates cannot be derived, postulates our beginning points. How do we propose these postulates by looking around and seeing what how nature manifests itself what we have obtained so far is Schrodinger equation which is an eigenvalue equation total energy operator operates on the wave function to give us an eigenvalue equation in which energy turns out to be an eigenvalue.

From this equation it is extended further and these postulates are proposed. The first one is that for every classical variable say position momentum kinetic energy, potential energy there is a corresponding operator one can use in quantum mechanics. For example for position the quantum mechanics quantum mechanical operator will be just x that is multiplied. For momentum it turns out to be -ih cross d dx kinetic energy if we look at the Hamiltonian operator we know already what kinetic energy operator is -h cross square by 2 m d 2 dx 2 in one dimension.

In three dimensions it is -h cross square by 2 m del 2 del x 2 + del 2 l by 2 + del 2 del z 2 potential energy operator actually is the potential energy depending on what kind of system it is the expression is going to change. So, first law of quantum mechanics first postulate of quantum mechanics that there is always an operator for every classical variable every classical property of the system that we might want to know.

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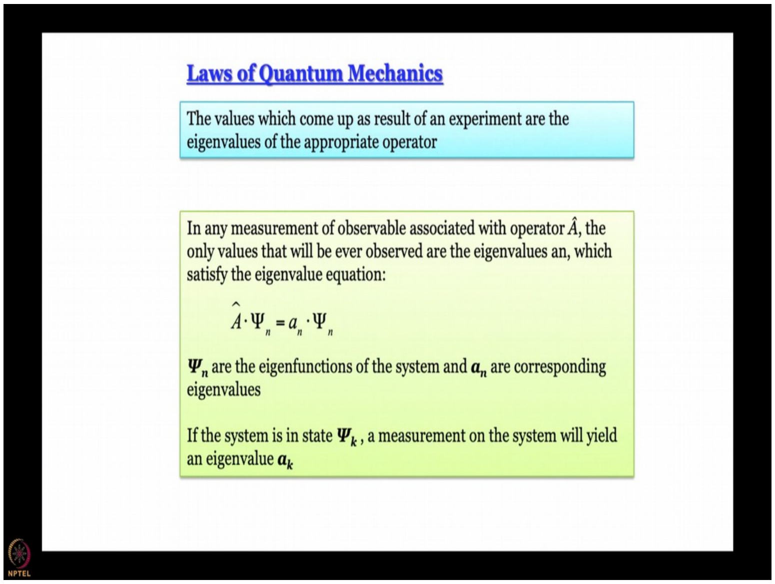

Laws of Quantum Mechanics

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:

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

$\boldsymbol{\Psi_n}$ 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 $\boldsymbol{a_k}$

How do we know we know the value by making the corresponding operator of that physical property operate on the wave function we will get an eigenvalue equation like we did for Schrodinger equation and the eigenvalue is going to be the value of that property. So, operators and eigenvalue equations have a very central role to play in quantum mechanics. So, if you look at this expression we can think like this that the wave function contains all the information of the system.

If you ask it is going to give you the information. How do you ask a question to a wave function by making the appropriate operator operate on the wave function and how does it give you the answer in the form of eigenvalue that we get. So, we can only know the value we can only have a specific value of the property if one can write an eigenvalue equation with the corresponding operator for the wave function that is characteristic of the system.

So in the next module we will start from here, we will have a further discussion of what kind of operators what are the properties of operators that are acceptable in quantum mechanics and what are the other postulates of quantum mechanics. And after that we will try to make sense of this entire wave business of matter because until now we have been we have an equation that describes the wave we have sort of obtained postulates that can work in quantum mechanics.

What we do not have so far is, what is the meaning, what is the real meaning of this wave? What is the real meaning of this wave function that is what we are going to get at the next maybe a couple of modules.