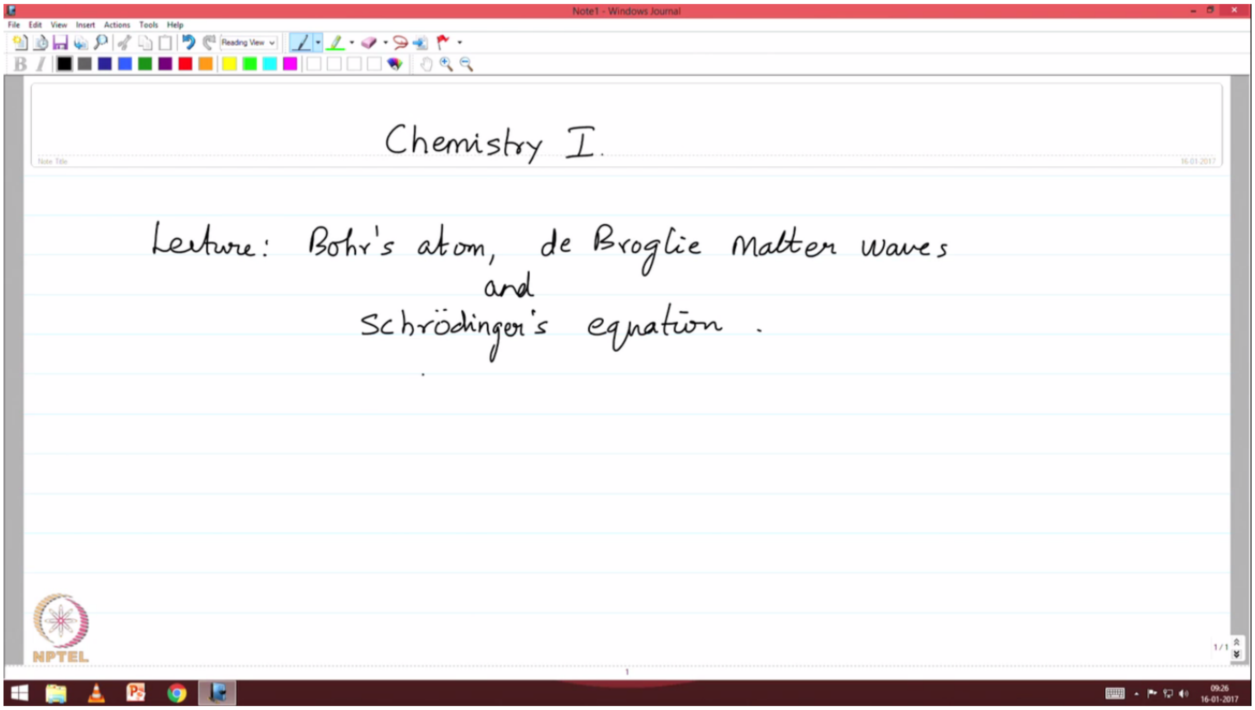
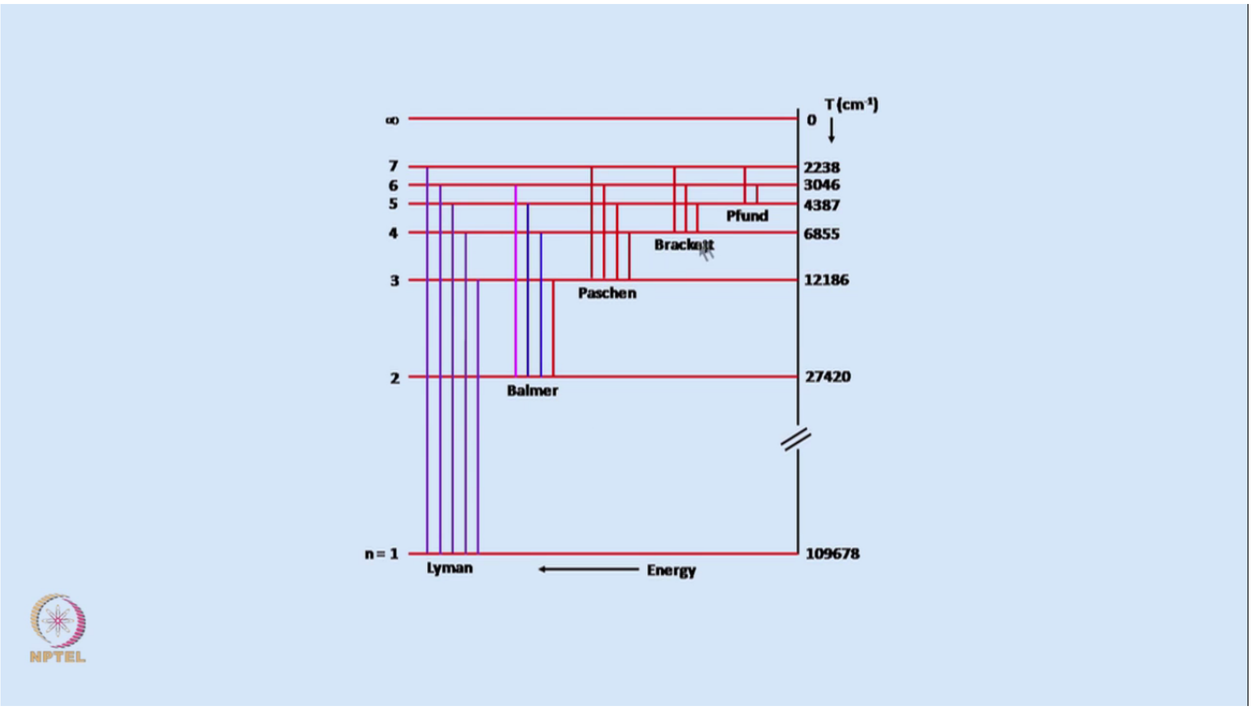


Chemistry I.

Lecture: Bohr's atom, de Broglie matter waves
and
Schrödinger's equation.

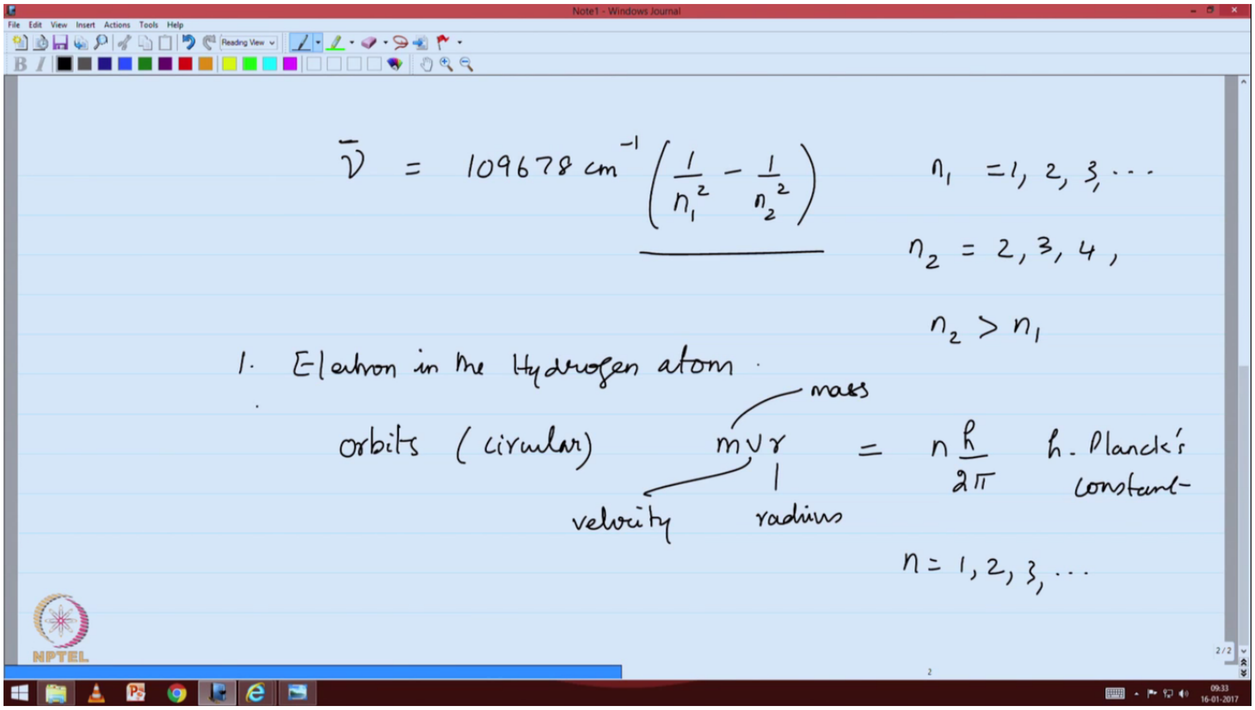
Welcome back to the lectures. The chemistry one is a series of lectures under the massive open online courses program and it's being – and are being given delivered to you through the NPTEL Online courses' program.

So in this lecture we have a brief summary of Niels Bohr atom, the de Broglie matter waves and also the time-dependent Schrodinger equation. It's a sketchy introduction more details will come later on the Schrodinger equation but the purpose of covering the Bohr's model and the matter waves is to set the stage for the solution of the Schrodinger equation and how that's different and is more general as a quantum mechanical phenomenon.



The lecture is we will start for the summary of the Bohr's atom. There were two assumptions that Niels Bohr made and it's a famous paper in 1913 when he described his theory for the atomic structure or the structure of the hydrogen atom to explain the spectral series or the hydrogen spectral lines. It was one of the most important problems in the atomic domain that needed to be explained. And there are two assumptions that Bohr made. Both these assumptions were to get the picture of the atom with the electron moving around the nucleus in an orbit in the case of hydrogen atoms just being a circular orbit and therefore let to with these assumptions an explanation of the hydrogen spectral series known as the Lyman series, the Balmer series, the Paschen series the Brackett series and Pfund series and so on. Now let's see a small picture of the same.

So here is a picture from one of the IIT Kanpur websites on the ICT Wiki I shall give you the acknowledgement in a separate sheet. The hydrogen atom spectral series are marked here as corresponding to different wave numbers starting with the Lyman series for which the highest wave number is 109678 centimeter inverse and then there are a whole series of lines with wave numbers smaller than that. This is one set of lines seen in the emission spectrum of hydrogen. The other is the Balmer series which is about 1/4 exactly 1/4 of the Lyman series starting line 109678 divided by 4 this is the the beginning of the Balmer series lines and also there is a whole series of spectral lines and likewise Paschen series, Brackett series and Pfund series. [Indiscernible] [00:03:31] earlier recorded these – I mean has had earlier explained these spectra with a simple formula. The mu number 1099678 centimeter inverse this is the wave number as 1 by n1 square minus 1 by n2 square. n1 is 1, 2, 3, etc. and n2 is always greater than n1 starting with 2, 3, 4, etcetera. Therefore, this is the prescription. This is purely and experimentally observed phenomenon and a fit provider and these both theory was to explain this fit of course it explains the fit beautifully as we see it in a very quick summary. What are the two assumptions that Niels Bohr made to understand the spectrum of hydrogen.



$$\bar{\nu} = 109678 \text{ cm}^{-1}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$n_1 = 1, 2, 3, \ldots$

$n_2 = 2, 3, 4,$

$n_2 > n_1$

1. Electron in the Hydrogen atom.

orbits (circular)

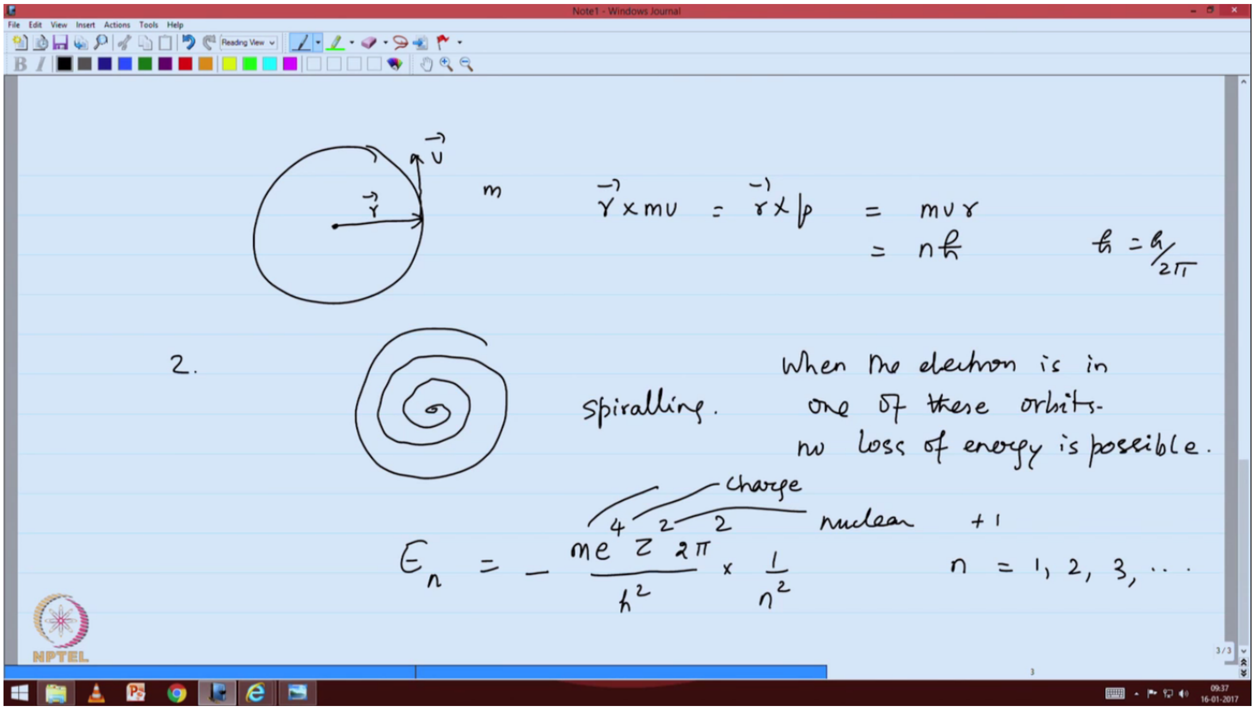
$$\overset{\text{mass}}{m}\underset{\text{velocity}}{v}\underset{\text{radius}}{r} = n\frac{h}{2\pi}$$

h. Planck's constant

$n = 1, 2, 3, \ldots$

The first one the electron in the hydrogen atom is confined to only those orbits circular for which the angular momentum of the electron mvr where r is the radius of the orbit and v is the velocity of the electron radius velocity of the electron or the speed actually mass of the electron this is mvr n h by 2 pi and n is an integer 1, 2, 3, etcetera. and h is of course Planck's constant. This is a function one and it's easy to see that the angular momentum for a circular orbit is mvr because suppose you do that and you write the radius vector as r and the tangential velocity v of mass m then you see that r cross v, r cross mv which is r cross p in this case is actually mvr because r and pr are are perpendicular to each other. This is a vector cross product and this is equal to nh bar which is h bar is h by 2 pi. This is assumption one. The second assumption that Niels Bohr made which is even more crucial to the whole picture is that electron being a charged particle and moving in an orbit classically if it were to behave classically the electron would lose its energy because any accelerating charge particle loses its energy as it accelerates. Therefore, the electron will not stay in a circular orbit as it loses its energy it will spiral into smaller and smaller and smaller circles and eventually it will fall into the nucleus.

The time taken for the spiraling to happen when you calculate using classical physics is an incredibly small number. Therefore obviously that's not true because the hydrogen atom has been stable for a millions of years at least ever since we started looking at the atom it's a stable atom and therefore what Niels Bohr suggested was that when the electron is in one of these orbits it does not lose any energy. It conserves its energy. No loss of energy is possible. Therefore how do we get a spectrum? The spectrum happens when the electron goes from one of these orbits to another orbit either due to the large amount of energy that the atom has when you heat the atom or in an absorption spectrum when light shines on the hydrogen atom the electron absorbs that energy and goes into another orbit. Therefore to calculate that energy Niels Bohr arrived at the energy of each of these orbitals through a very simple classical formula which I will write and the energy of each of these orbits with the quantum number n he introduced the word quantum number n and in being 1, 2, 3, etc. the expression for the energy through a very simple calculation it's not the purpose of this lecture but through a simple calculation it turns out to be minus m e raise to 4 Z square 2 pi square by h square into 1 by n square. M is the mass of the electron. E is the charge on the electron. The fundamental charge. Z is the nuclear charge which is 1 in this case and the h is the Planck's constant and n is the quantum number given the values 1, 2, 3, etc.



$\vec{r} \times m\vec{v} = \vec{r} \times \vec{p} = mvr$

$= n\hbar \qquad \hbar = h/2\pi$

When the electron is in one of these orbits. no loss of energy is possible.

$$E_n = -\frac{me^4 Z^2 2\pi^2}{h^2} \times \frac{1}{n^2} \qquad n = 1, 2, 3, \ldots$$

Therefore the energy emission happens you can see from this formula that when n is 1 this is the most negative and the electron being in a bound state with hydrogen atom the system has negative energy and the most stable energy is the most negative energy and if you calculate this energy by substituting all these numbers En turns out to be minus 13.6 electron volt 1 by n square and this you can write in the form of hc and the [Indiscernible] [00:09:12] constant into 1 by n square and the [Indiscernible] [00:09:15] constant happens to be 109678 centimeter inverse roughly. There are small differences due to the reduced mass of the electron and so on but it's approximately the same therefore the success story of the Niels Bohr is that he through his assumption he arrived at the quantized orbits with energies e1, e2, e3, etcetera. and therefore you can see that the energy level picture is that e1 is minus 13.6 electron volts n equal to 1 and if you say n equal to 2 then if you put n equal to 2 the orbit has minus 13.6 by 2 square 4 electron volts and for n equal to 3 of course it is minus 13.6 by 9 so if this is the increasing scale of energy you can see that at some point if this is minus 13.6 you can see that the energy reaches 0. This is the 0 and for this n equal to infinity. Therefore the energy levels are such that the lowest energy level is minus 13.6 electron volts and the next one is 1 by 4th of that and the next one is 1 by ninth of that and so on and then Niels Borh could say that the electrons when they jump from one orbit to another if they go up they absorb the energy because the orbits of higher n have higher energies less negative higher values, positive values in that sense.

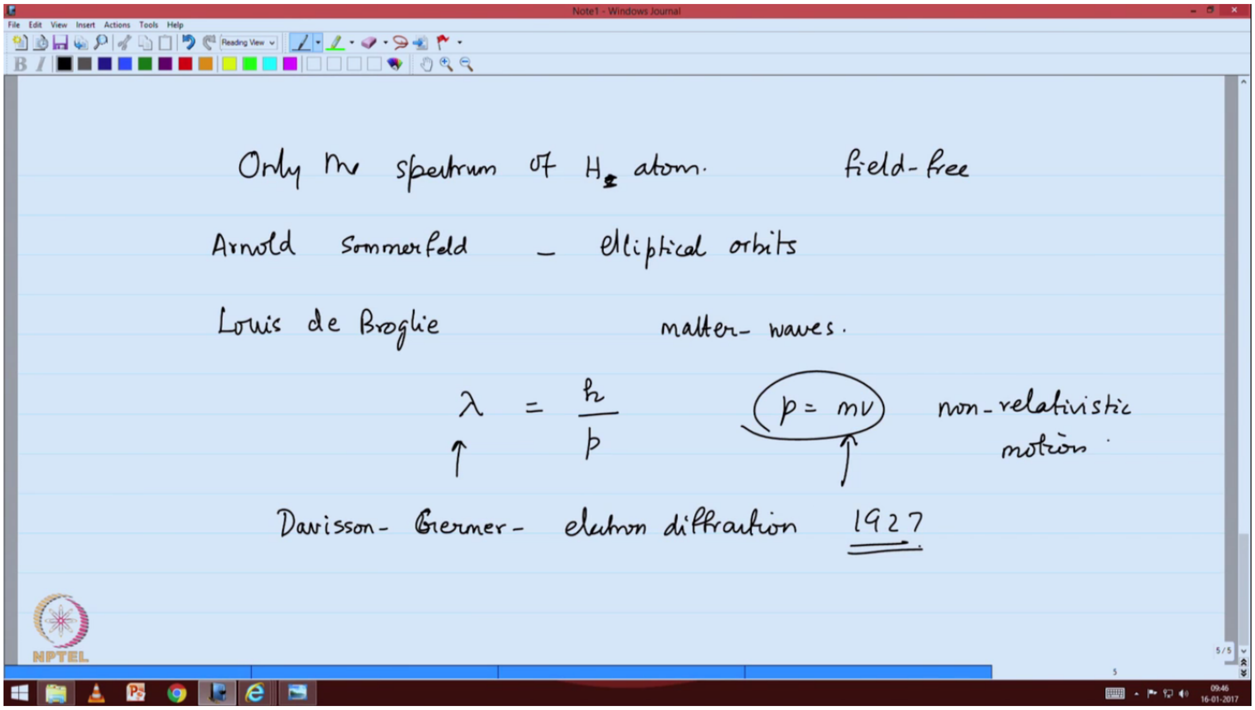
Therefore that's the absorption spectrum and the emission spectrum is when n the the electron from a higher n falls to a lower n and you can see that from any n it can go to any other n and therefore you can see everything that drops into 1 from any of these levels is a line that corresponds to the alignment series line. Everything that drops into 2 n equal to 2 from higher levels forms a Balmer series and then there is the Paschen series line and Brackett series lines and Pfund series lines. The spectra are beautifully seen in some of the pictures here. You can see the Lyman series line. The Lyman series lines are all near the hundred nanometer wavelength what we had was 109678 was a wave number it's a centimeter inverse one by the wavelength but in terms of wavelengths it's hundred nanometers around and then you can see that the Balmer series lines are all here in the visible spectrum and then there are the Paschen series lines which are all here again in the visible spectrum and then there is the Brackett series corresponding to higher values of n1 and n2 and then the Pfund series and so on. So this is actually observed hydrogen atom spectrum that Niels Bohr was able to explain but then what are the difficulties with such a model.

The difficulties are that only the spectrum of hydrogen could be explained this way. Hydrogen atom and also filled free if the hydrogen atom were to be put in an electric field or a magnetic field the spectral lines become doublets and there are issues. If you have to take this to other atoms like the helium atom and so on you needed not a circular orbit but a slightly more general orbit and it was Professor Arnold Sommerfeld who proposed elliptical orbits. Elliptical orbits have two axes system the major axis and the minor axis and therefore can in principle correspond to two quantum numbers instead of the single quantum number that needs more introduce for the angular momentum nh by 2 pi instead of that you can have two of them but then what's the point of these kind of extensions without any real theoretical basis for that.

So there were questions about the extend ability or the applicability of the Niels Bohr model despite the fact that it was a spectacularly successful model in predicting the hydrogen spectrum and associating a fundamental an atomic formula for the constant known until then as an arbitrary constant the [Indiscernible] [00:13:37] constant.

Therefore given that some generalization of all these things from a more fundamental level was needed and I think soon after that it was Louis de Broglie who came up with a postulate namely that all matter can be wave-like as well that is matter which is localized or which is particulate things move and you can follow the movement as movement of the particles. In motion such matter can also be associated with the wave length and de Broglie called this phenomenon as the phenomenon of matter waves and it is an important extension since until then people believe that matter is either wave-like or particle like with the exception of light because light was shown to be particle like in the sense it's the assumption that light is small packets of energy was used to understand photoelectric effect and later many experiments were done to suggest that light could be particularly like and then of course electromagnetic radiation was known as wave phenomenon ever since the theory of diffraction and interference were known and therefore light was the only thing which had both particle-like behavior and wave like behavior and de Broglie's idea was that it's not just light it's all matter for that matter electron can be a wave like can also have a wave like attributes can also be particle like attributes and so on.

Therefore, de Broglie proposal matter waves and he proposed a wavelength for the matter waves in motion and he called he arrived at this formula where p is mv non-relativistic motion. For our case we will only worry about the non relativistic motion but h is the Planck's constant again and the association of lambda with a concentrator or a localized mass entity during motion was seen as a new phenomenon, as seen as a new type of matter or material and this led to questions whether such matter waves can be actually detected or do they exist and so on.



Only the spectrum of H atom. field-free

Arnold Sommerfeld – elliptical orbits

Louis de Broglie matter-waves.

$$\lambda = \frac{h}{p} \qquad \boxed{p = mv} \text{ non-relativistic motion.}$$

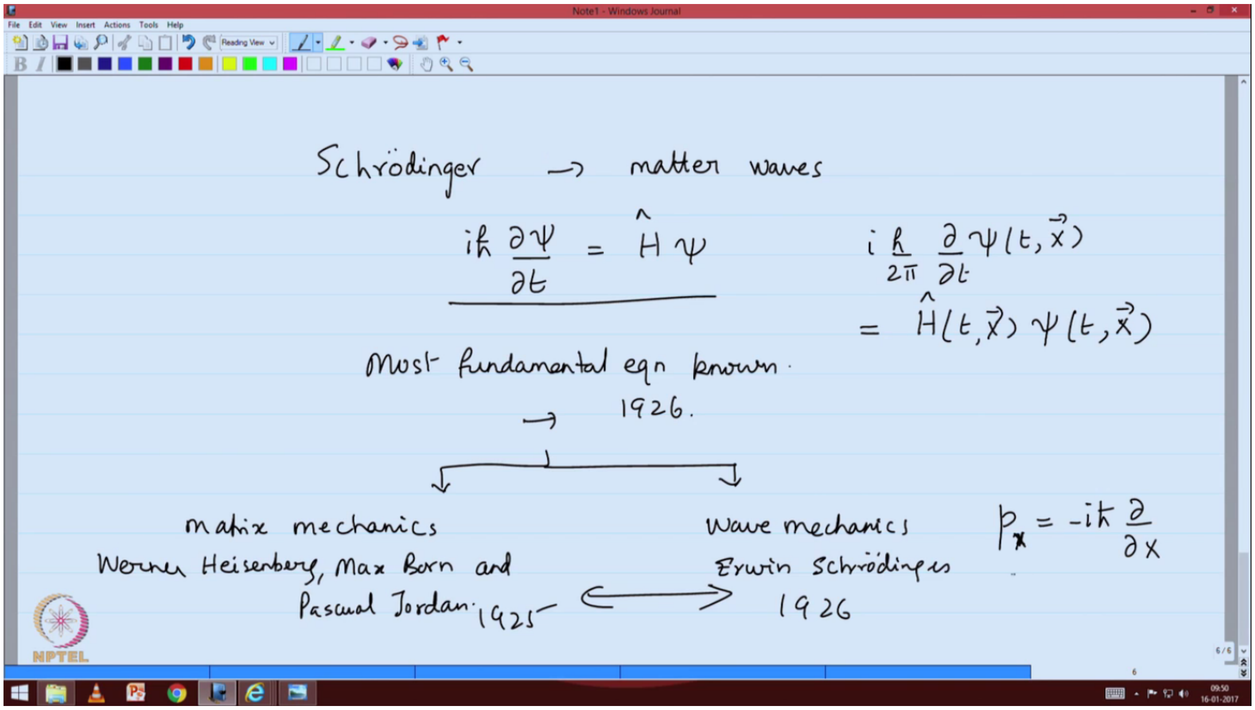
$\uparrow$ $\uparrow$

Davisson-Germer-electron diffraction 1927

We will see later towards the end of the lecture that there was the experiment by Davisson and Germer electron diffraction experiment very famous one around 1927 which showed that electrons could be actually diffracted through passing through a crystal and therefore the electronics exhibited the properties of a wave until then the Millikan oil drop experiments and many others had confirmed that electron was a particle was a localized mass and so on but then electron diffraction experiments showed that electron also had the same property as light. It can be both wave-like and particle-like. Then with this prescription it was Schrodinger who therefore asked the question if substances are like particles and they obey Newton's equations for particle motion and if substances are like wave and they obey the wave equations or the equations of Maxwell what do these matter wave quantities behave due to is there a separate equation which governs them and which in the right limit can go to wave equation or that of a particle equation.

So Schrodinger asked the question whether there was a separate equation for the matter wave and within a few weeks of this question after studying de Broglie's thesis Schrodinger came up with the formula that he said all atomic fundamental particles satisfying this equation in time with a function psi and let me read that out it's ih by 2 pi the time derivative the partial time derivative of a wave function psi which is a function of time and a set of all coordinates of the particle and it's equal to this derivative multiplied by ih bar is equal to the action of the total energy of the system which may depend on time and will of course also depend on the positions because of the potential energy and the kinetic energy and so on and therefore you have its action on the wave function x. So it's ih bar d psi by dt dau psi by dau t is equal to h psi is the most fundamental equation of matter which was proposed in 1926 equation known and 1926 and Schrodinger proposes one year after the another group are from Germany in Göttingen came up with an explanation of the hydrogen atom spectrum and the general framework for the atomic mechanics using matrices.

So there were two groups of quantum mechanical description for that time. The matrix mechanics was proposed matrix mechanics used the idea of matrices for quantum mechanical quantities and it was proposed by Heisenberg, Max Born,Werner Heisenberg, Max Born and Pascal Jordan and this is the wave mechanics proposed by Erwin Schrodinger and it was eventually this was 1925, this was 1926 and it was eventually Schrodinger who connected the matrices with the wave mechanics through his famous formula that the momentum represented by in the matrix mechanics the operator for the momentum provided by Heisenberg and others is the same as the derivative minus ih bar dau by dau x if I have to write this in the x component of the momentum or if in any other coordinate system if the momentum is given in that coordinate system it's the derivative minus ih bar dau by dau of that coordinate.



Schrödinger → matter waves

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

$$i\frac{h}{2\pi}\frac{\partial}{\partial t}\psi(t,\vec{x}) = \hat{H}(t,\vec{x})\,\psi(t,\vec{x})$$

Most fundamental eqn known.

→ 1926.

matrix mechanics
Werner Heisenberg, Max Born and
Pascal Jordan. 1925

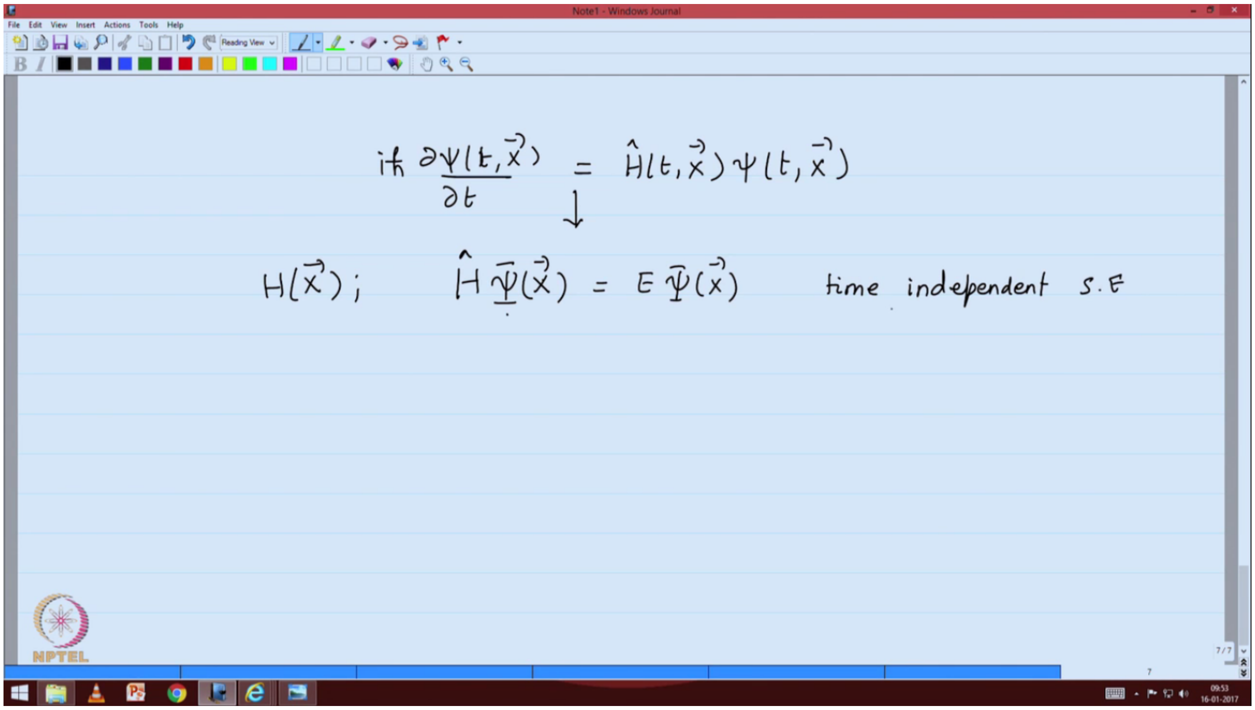
⟷

Wave mechanics
Erwin Schrödinger
1926

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

This formula was also established by Schrodinger establishing the connection between the two different approaches and solving not only the hydrogen atom problem but proposing this equation as the most fundamental equation of matter for the study of atomic systems and systems for which the classical methods the classical mechanical, statistical mechanical and the classical electromagnetic theory were not giving satisfactory answers.

This was proposed as the most fundamental equation and the Schrodinger's equation has stood the test of the time for the last 1995 years. There are no questions about its applicability until now except that one has to discover more and more phenomena newer and newer ways of solving the differential equation please remember this is a differential equation and the matrix mechanics proposed the matrix eigenvalue problem solution as the possible method for solving quantum mechanical problems and these two methods where the ultimately the most important ones which have been proposed in the last century at the turn of the last century and let me complete this lecture with the following statement that it's not this equation that I would solve in the rest of the course I would love to but it's a little bit difficult and it requires other technical details of how to solve differential equations with the Hamiltonian dependent on time. So let me write this equation. When the Hamiltonian is independent of time and is only dependent on the position coordinates this can be written down into two component equation one for a time variable and one for the position variable and the position variable equation gives a function psi of x please remember this is different from this function.



$$i\hbar \frac{\partial \psi(t,\vec{x})}{\partial t} = \hat{H}(t,\vec{x})\,\psi(t,\vec{x})$$

$$\downarrow$$

$H(\vec{x})$; $\quad \hat{H}\,\Psi(\vec{x}) = E\,\Psi(\vec{x})$ time independent S.E

This function is dependent on time and the position coordinate this is a wave function which depends only on the position coordinates and this is equal to E psi of x. This is time independent Schrodinger equation but this time independence relates to the fact that the Hamiltonian is time independent. What is meant by Hamiltonian being time dependent? For example if you shine light on the system and you are studying while light is or the electromagnetic radiation falls on the system the energy of the system is not a constant because the radiation itself is an oscillating electric and magnetic wave in time and therefore the radiation has time dependent energy contribution while it's present in the system.

Therefore the Hamiltonian for such a system is time dependent. The other example is that we may introduce a force, the time dependent force for a brief period of time and then follow the evolution. So what happens during that process? So the Hamiltonian can depend on time in principle but we will study only in this course in a very elementary fashion we will study only those Hamiltonian which are time independent and for time independent Hamiltonian this equation reduces to what is known as their time independent Schrodinger equation and this is what we need to look at.

The rest of the course we'll study partly some introductory spectroscopy where time is important and model problems such as particle in the box Schrodinger, Harmonic oscillator and hydrogen atom examples not in a complete mathematically soluble form but we will try to understand the principles behind the solutions rather than the solutions themselves. It's an elementary course therefore we will try and concentrate on the solution of the time-independent Schrodinger equation for a few simple systems. The next couple of lectures we shall introduce what is the spectra - what is spectroscopy and what we study in spectroscopy and then the week following that we will start looking at the solutions of the Schrodinger equation. Until then thank you very much.