Quantum Chemistry of Atoms and Molecules

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

Lecture-2
Bohr Model and Beyond…

In this module we are going to go a little further in our discussion of atomic structure. So, far we have studied blackbody radiation and we have seen how Planck distribution explained the blackbody radiation nicely in long wavelength regime as well as a short wavelength regime.

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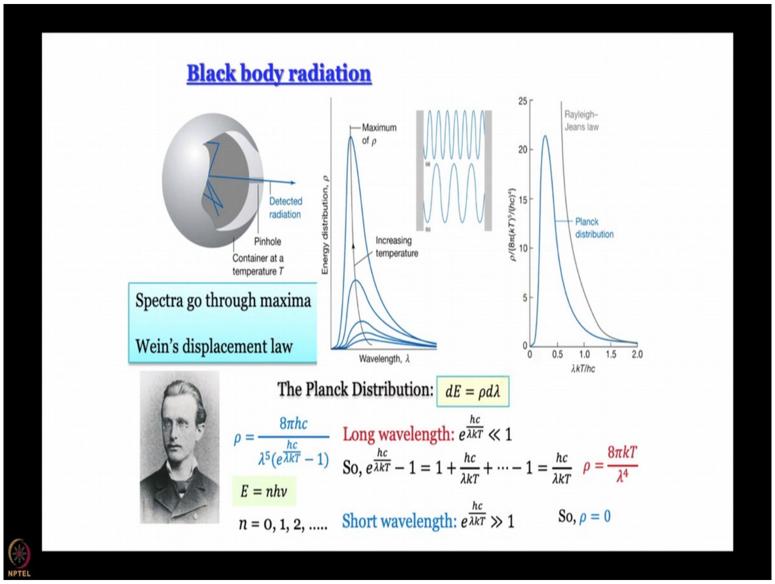

Black body radiation

Spectra go through maxima

Wein's displacement law

The Planck Distribution: $dE = \rho d\lambda$

$$\rho = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{\lambda kT}} - 1\right)}$$

$E = nh\nu$

$n = 0, 1, 2, ...$

Long wavelength: $e^{\frac{hc}{\lambda kT}} \ll 1$

So, $e^{\frac{hc}{\lambda kT}} - 1 = 1 + \frac{hc}{\lambda kT} + \cdots - 1 = \frac{hc}{\lambda kT}$ $\quad \rho = \frac{8\pi kT}{\lambda^4}$

Short wavelength: $e^{\frac{hc}{\lambda kT}} \gg 1$ $\quad$ So, $\rho = 0$

And how it led to this very important understanding that energy has to be quantized this was a revolutionary idea and this is what laid the foundation of quantum mechanics. The name quantum itself comes from here quantum means a packet.

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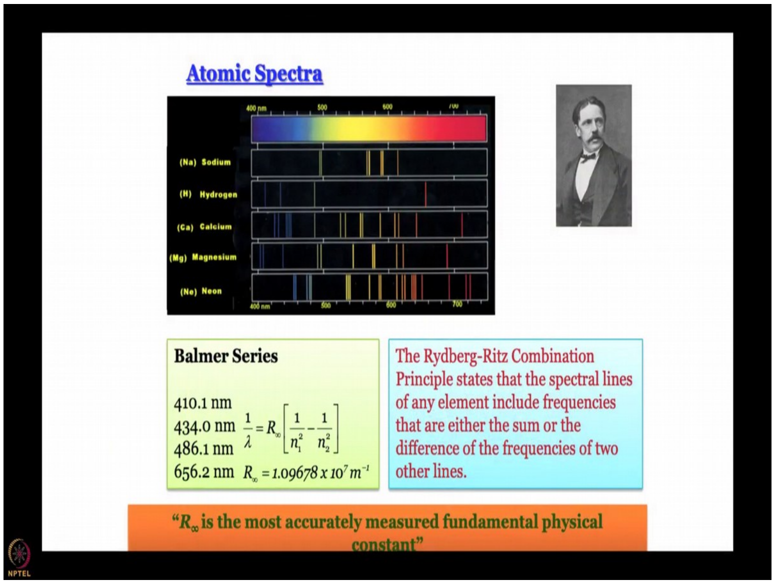

Atomic Spectra

Balmer Series

410.1 nm
434.0 nm $\frac{1}{\lambda} = R_{\infty}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$
486.1 nm
656.2 nm $R_{\infty} = 1.09678 \times 10^7 m^{-1}$

The Rydberg-Ritz Combination Principle states that the spectral lines of any element include frequencies that are either the sum or the difference of the frequencies of two other lines.

"R_{∞} is the most accurately measured fundamental physical constant"

So, with this background and knowing that Rutherford model did not really work because classical mechanics requires it to give out; requires the atom to give out energy continuously electron to give out energy continuously and therefore spiral on to the nucleus and also with another experimental result that is atomic spectra, Bohr formulated this model. What you see here is a collection of emission spectra of several atoms and it is depicted here in the classical way.

What you can think is you have this source, the emitter light that is emitted falls on a grating or a prism which disperses the light and that falls on a photographic plate. So, different regions of the photographic plate have record intensities of different light. So, this is how spectra would look like in that an array in that arrangement. The color has been added to make us understand the color in more reality but actually they are all black-and-white photographs.

Here you can think x-axis is your wavelength and wherever we see a line that is where that is the energy or wavelength corresponding to its emission has taken place. Now see if Rutherford model was correct then what we should see is a continuum something like the top panel. We do not see that depending on which atom you look at you see lines and in fact you see some series of lines. This is something that was known by the time Rutherford proposed his theory.

Now even before a theoretical formulation to explain this was worked out experimentally looking at the energies where the emissions take place for different atoms and empirical formula was already there. And this empirical formula was called the Rydberg formula. It is based on the Rydberg it is combination principle that states that the spectral lines of any element include frequencies that are either the sum or difference of frequencies of two other lines.

And if what it boils down to is that if you take one by lambda wave number that is equal to a constant multiplied by 1 by n1 square - 1 by n2 square where n1 and n2 are two positive integers this constant R is called Rydberg constant and the value of Rydberg constant was found to be 1.09678 into 10 to the power 7 per meter, it might sound ridiculous though so many decimal points are there. Generally when a student reports data like this we always ask that are you sure that your answer is correct to the last place of decimal that you have reported.

Rydberg was sure, experiment it was done many, many times and it was found that we do have accuracy until that many places of decimal. So, Rydberg constant was acclaimed as the most accurately measured fundamental physical constant. So, this is known and different series of lines were observed and mainly will focus on hydrogen emission spectrum. The 5 series of lines that were found where Lyman, Balmer, Bastion, Bracket, front and for each of these this n1 was constant and n2 varied.

Balmer series was the one that was observed first because as you see the values 410 nanometer 434 nanometer, 486 nanometer, 656 nanometers these are all invisible region so they were observed by the eye but then other lines were observed in other portions of the electromagnetic spectrum. So, this is something that was known and as Max Planck put it experimental results are the only truth.

He went on to say everything else is poetry and imagination but of course one should not undermine poetry and imagination that is what sets human beings apart from other animals. So, what clang did is that he said that experimentally since we see this, this has to be correct you cannot challenge it. So, your theory should be such that should match it and this is where Bohr came in.

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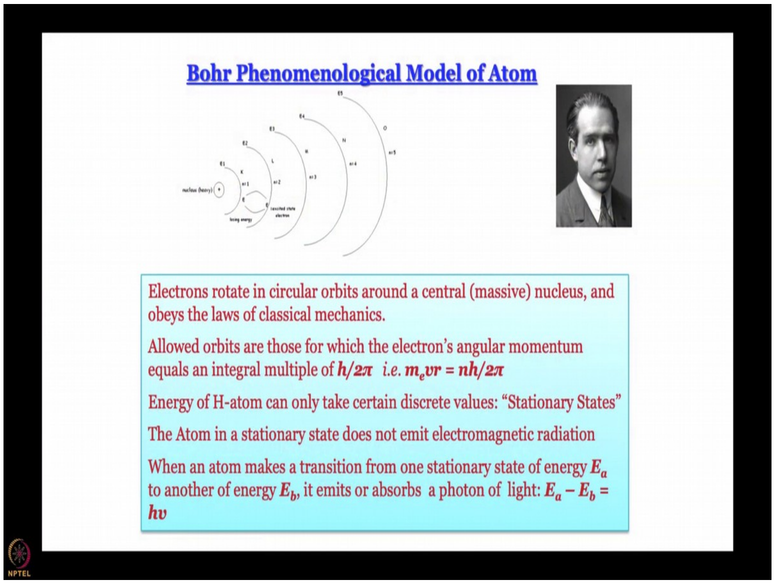

Bohr Phenomenological Model of Atom

Electrons rotate in circular orbits around a central (massive) nucleus, and obeys the laws of classical mechanics.

Allowed orbits are those for which the electron's angular momentum equals an integral multiple of $h/2\pi$ i.e. $m_e vr = nh/2\pi$

Energy of H-atom can only take certain discrete values: "Stationary States"

The Atom in a stationary state does not emit electromagnetic radiation

When an atom makes a transition from one stationary state of energy E_a to another of energy E_b, it emits or absorbs a photon of light: $E_a - E_b = h\nu$

So, what Bohr said essentially is that I do not know why and I do not care but from the atomic spectra it is quite obvious that electrons reside in specific orbits. The radius of the orbit cannot be just anything it has to be specific. Certain specific orbits are allowed and Bohr sort of said I do not know why and I do not need to why this is the truth that is how it is and also what he worked out was that this allowed orbits where those in which mvr equal to nh by 2 pi angular momentum is an integral multiple of h by 2 pi, h by 2 pi is often written as h cross.

And turns out we the most fundamental entity in quantum mechanics you will see everything that is like angular momentum would be an integral multiple of this will come to several examples later on. Why is it there later on when we get into the wave nature one can sort of find a justification of why m vr has to be an integral multiple of h by 2 pi well that is the only condition that leads to constructive interference of the waves but let that be the story for another day.

So using this so we said that electron cannot reside in any space in between so m vr equal to nh by 2 pi are the only r values that are supported that are allowed and then when an electron jumps from one such allowed orbit to another or allowed orbit energy difference between these two orbits is either emitted or absorbed depending on the relative energies of the orbits and these were given a name by Bohr these were called stationary States and it is important to understand this term because this term is used even now in the most modern approach of quantum mechanics.

When we say stationary States we do not mean that the electron is stationary. According to Bohr model of course it cannot be; it is moving in circles what we mean is that the energy does not change stationary as far as energy is concerned not as far as station as position is concerned, stationary States. So, an electron can only reside in stationary States or allowed orbits where m vr equal to nh by 2 pi when it jumps from one stationary state to the other the difference in energy of the stationary states is either emitted or absorbed as light depending on which energy state is higher and which energy state is lower in energy.

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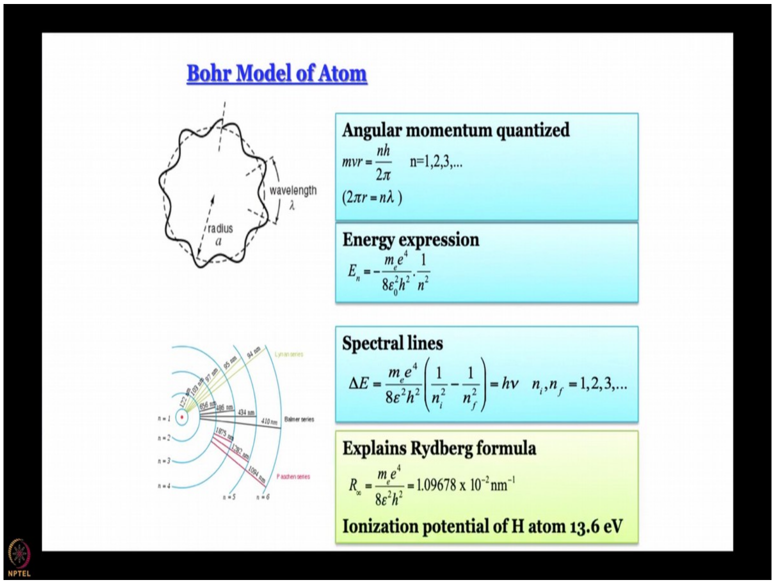

Bohr Model of Atom

Angular momentum quantized

$mvr = \frac{nh}{2\pi}$ n=1,2,3,...

($2\pi r = n\lambda$)

Energy expression

$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \cdot \frac{1}{n^2}$

Spectral lines

$\Delta E = \frac{m_e e^4}{8\varepsilon^2 h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = h\nu \quad n_i, n_f = 1,2,3,\ldots$

Explains Rydberg formula

$R_\infty = \frac{m_e e^4}{8\varepsilon^2 h^2} = 1.09678 \times 10^{-2}\,\text{nm}^{-1}$

Ionization potential of H atom 13.6 eV

Using this and it is a pity that we are not going to go into the detail of this discussion here because well precisely because that we do not really use Bohr model anymore but whoever is interested can look up the classical mechanics books and look up Bohr's papers maybe and books which have discussed both here in detail. Bohr did a fairly simple calculation using the tools of classical mechanics.

This tools of classical mechanics are essentially things like algebra and more importantly calculus. So, using calculus what one can work out from Bohr's theory is the energy. The energy expression that we get is E n, now remember only certain levels are allowed so you cannot talk about a continuous distribution of energies. So, E n is equal to m e multiplied by e to the power of 4 divided by 8 epsilon zero square h square into 1 by n square this is the energy expression.

And this is what takes us directly to the Rydberg constant because the lines that we see in the spectra the lines that are whose energies are given by Rydberg equation essentially come as a result of the electron jumping from one stationary state to the other according to Bohr, so it is going to be this constant multiplied by 1 by n1 square - 1 by n2 square, Rydberg formula. We will come back to it. Also what Bohr could do is that, Bohr could work out a precise expression for the radius that we are not showing here.

So, precision and expression of the precise values of all these things is the hallmark of Bohr theory and as we will come to later on this is both the strength and the weakness of the theory. But now that is let me just say what I actually said without showing you the formula here from the energy expression one can easily work out the energies of these spectral lines and it comes out to be this me to the power 4 by 8 epsilon square h square multiplied by 1 by n1 square - 1 by n2 square that will be equal to h nu, h nu is hc by lambda.

So, 1 by lambda would be this expression multiplied by ch and from there one can obtain a theoretical value of Rydberg constant and the value that we get is 1.09678 into 10 to the -2 per nanometer it is precisely the same value that is obtained experimentally there is a strength of Bohr theory that we have this experimental observe quantity which is so precise Bohr theory can give you that value to the last decimal place.

Also one can work out the ionization potential for hydrogen atom and the experimental value of 13.6, electron volt is reproduced very nicely using Bohr Theory. So, success of Bohr Theory is that it can give you very precise values of physical quantities associated with hydrogen atom. The problem with Bohr theory is that it does not work beyond the hydrogen atom. In fact even in hydrogen atom if one tries to look a little closer it turns out that Bohr Theory has to be extended and this extension was done mainly by Sommerfeld correct.

There is a series of papers published by Sommerfeld where he sort of discusses Bohr's theory and proposes how it can be extended so that it can observe more experimental observation and so that it can explain more experimental observations. So, the first extension was necessitated by the fact that with advent of better spectrometers it was found that what was thought to be one line in but a particular atomic spectra was not one thing sometimes it was two lines. Sometimes it was three lines so it appeared that there are sub levels of energy.

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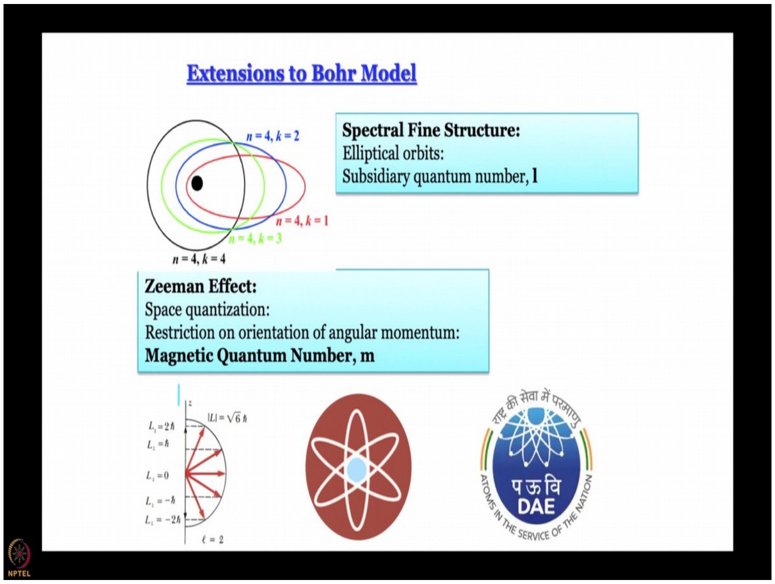

Extensions to Bohr Model

Spectral Fine Structure:
Elliptical orbits:
Subsidiary quantum number, **l**

Zeeman Effect:
Space quantization:
Restriction on orientation of angular momentum:
Magnetic Quantum Number, m

To account for that to account for this what is called spectral fine structure Sommerfeld invoked the concept of elliptical orbits with so like this what is said is that for every value of n you have a series of elliptical orbits a special case of which is a circular orbit and what is said that now one quantum number is not enough. You have to specify n for the entire set and what was proposed was k now in modern days we say l, l is just k – 1, so this quantum number k was proposed for n equal to 4 it was observed that k can take up values of 1, 2, 3 and 4.

Now we say l can take up values of 0, 1, 2 and 3, so total number of k or l quantum numbers which are called anything secondary quantum number, subsidiary quantum numbers, azimuthal quantum numbers, why azimuthal we will come to that when we talk about wave mechanics. So, these sets of orbits have energies that are close to each other but they are still a little different from each other. And what Sommerfeld proposed was that this difference in energy comes from the eccentricity of the ellipse.

And again looking at experimental results it was also understood that for a given value of n one can have n values of k and these values were designated 1, 2, 3, 4 so on and so forth up to n. Now we all know about S P D and F, S P D and F well the letters came from for historical reasons they came from spectroscopic observations S means sharp D means diffuse and so on and so forth. So, those names were assigned to some of the small k values.

So, this is how the subsidiary or secondary or azimuthal quantum number came. Next came Zeeman effect it was known that upon placing the emitter, emitter atoms in a magnetic field the line split and the number of lines in the spectrum increased, why? So from Zeeman effect and also its split in a particular way. So, from Zeeman effect the idea that came is that for a given elliptical orbit let us say k equal to 2 in k equal to 2 in the diagram that we have shown here.

There can be several sub orbits how many sub orbit not sub orbit sorry actually k equal to 2 is not one elliptical orbit there is more than one for which n is the same k is the same. So, the elliptical the eccentricity is the same what is different than orientation, it was proposed that for every value of well now I will say l not k, l is a little easier for every value of l there are 2l + 1 number of orientations that the orbits can exist in.

So for l equal to 1 you can have this orientation or this or this what that leads to is that if you think of electron going around in a circle roughly then the angular momentum is going to point going to be are normal to the plane of rotation. So, if this is the plane of rotation this is the direction of angular momentum so what it says essentially the main effect is that for say l equal to 1 you can have an orbit pointing in this direction so that the angular momentum points in this direction or in this direction or in this direction this is called space quantization.

Not only energy quantized or angular momentum quantized space is also quantized in the sense that the orbits can be oriented in specific directions or if we want to use a term that survives even beyond Bohr model the angular momentum vector can be oriented only in specific directions this is what it means. So, what is shown here is what happens when l is equal to 2 when l is equal to

2, 2l + 1 equal to 5. So, first of all one thing I forgot to say a little earlier is that the angular momentum itself is given by square root of l into l + 1 multiplied by h cross.

So when l equal to 2 the length of this arrow there is angular momentum is going to be square root of 6 multiplied by h cross square root of 2 into 3 right l into l + 1 and it can take up to l + 1 that is 5 orientations and corresponding to h what what is different is the Z component of the angular momentum. So, actually m stands for Z component of angular momentum even in Bohr model later on what we will see is that we are going to forsake the orbits but we are going to retain the angular momentum vector and it is specific orientations that it can take up.

So that led to a third quantum number magnetic quantum number m and in fact this model of these elliptical orbits oriented in specific directions give rise to one of the most popular widely used motifs that we see in many places to depict atoms and this is that figure what it shows here is a central nucleus and three orbits around it in specific directions. Even now in many places this is sort of used as a cartoon for the atom even though this model is discarded.

In fact you can see this motif in the logo of our Department of atomic energy of India DAE this is what the present logo of DAE looks like here also you can see nucleus and many different orbits so this l value is rather high that is why we have many m values that is what is shown as a motive in the logo of Department of atomic energy of India. So, we got 3 quantum numbers n tells you about the energy l small changes in energy and mostly angular momentum root over l into l + 1 multiplied by h cross is angular momentum and m tells you about the orientation of the orbit or orientation of the angular momentum vector whichever way you want to put it. Eventually we are only going to talk about orientation of angular momentum vector right.

There is a fourth quantum number spin which arises from a completely different experiment and that experiment we will discuss shortly so let us take a rain check on that. So, in all there are 4 quantum numbers that one requires to specify the what we can say address of an electron in an atom. So, all this is great but then Bohr Theory faced severe criticism. First criticism was that it uses classical theory and quantum theory arbitrarily wherever quantum classical theory works calculus can be used it is used extensively.

And then when it does not work it is dumped unceremoniously and resort is taken to the a newly found quantum theory. So, that did not really go down well with the scientific community it was felt that it is a very sort of opportunistic theory. It says whatever is convenient whenever it is convenient but one could perhaps live with that given the accurate values that are predicted by Bohr's theory. The Death knell came in the act in this specialization of Bohr Theory in finding everything accurately.

From Bohr Theory you can find radius which tells you the position and you can also find the momentum.

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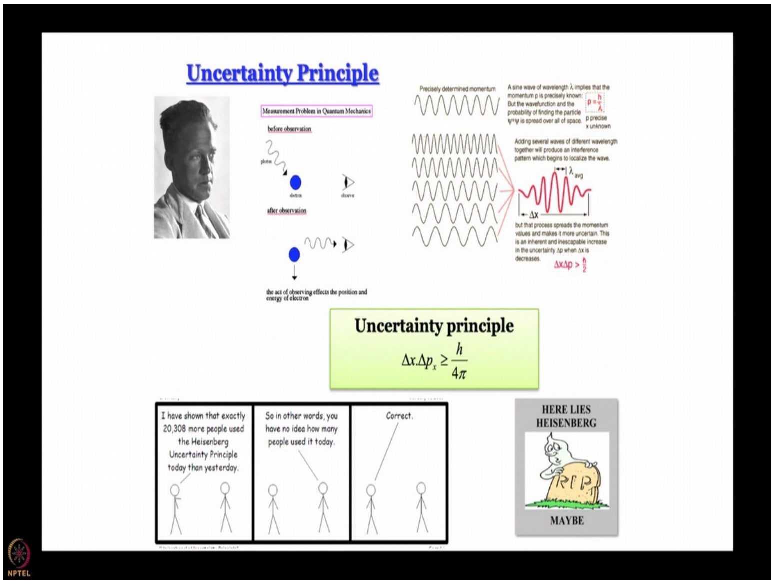

Uncertainty Principle

Measurement Problem in Quantum Mechanics

before observation

after observation

the act of observing effects the position and energy of electron

Precisely determined momentum

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

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

The problem is this uncertainty principle came which said that you cannot determine conjugate properties like position and momentum simultaneously with any great accuracy. Uncertainty principle says Delta x multiplied by Delta px has to be greater than h by 4 pi and this uncertainty principle is important to understand is not something that can be circumvented by making a better instrument. The subsidiary quantum number for example came due to the advent of better spectrometers.

Uncertainty principle has nothing to do with instruments. It is the limit beyond which nature does not let us probe it and will understand it better when we talk about when we discuss a little bit of

Schrodinger equation. But at this time perhaps we can discuss a thought experiment that was proposed by Einstein. The thought experiment is suppose I want to locate an electron I want to know exactly where it is. What will I do I will put it under a microscope and I will shine light so that I can see the electron.

The problem is for electron this energy of the photon light is enough to change its momentum and in fact when momentum exchange position will also change quickly. So, that is why one cannot determine these two simultaneous there is nothing to do with the instrument. And later on we will see that we will talk about wave mechanics a sine wave or a cosine wave is something that is associated with a specific value of momentum.

But if you look at sine wave where is in this sine wave stands for a particle where is a particle it can be anywhere from plus and minus infinity to plus infinity. So, the issue is that your if you mix sine waves then what happens? If we mix a large number of waves what will happen is at some point there will be a strong constructive interference and then as you go to the two sides there will be destructive interference. So, the wave will die off if you mix a high number of wave this is called a wave packet.

If your wave packet consists of a large number of waves then there will be a situation where there will be a high degree of location but then you have obtained it by mixing many waves right so there is no way you can tell what the momentum actually is but we will come back to this issue a little later for now let us just take it may be axiomatically that uncertainty principle is something that one cannot violate.

And Bohr Theory tries to do precisely that it tries to determine position and momentum together, cannot do it. Of course uncertainty principle is something that sounds very strange because we do not really have that much of uncertainty in the real world and so it gave rise to a lot of well lot of discussion in fields beyond science when uncertainty principle was proposed in literature, in art, in cartoons. A lot of people had a lot of fun by making cartoons pointing out what seemed to be the ridiculousness of uncertainty principle.

But no matter how much of humor factor it might have provided to the contemporary society the fact remains that until date the understanding is that uncertainty principle is a natural phenomenon a natural limit that one cannot violate. So, even though Bohr theory is great at giving us many values of physical constants and all there is no option but to forsake it and move on. And to move on once again we have to take a step back.

Many of us would perhaps know I mean maybe all of us know that Einstein got his Nobel Prize not for the theory of relativity but for photoelectric effect.

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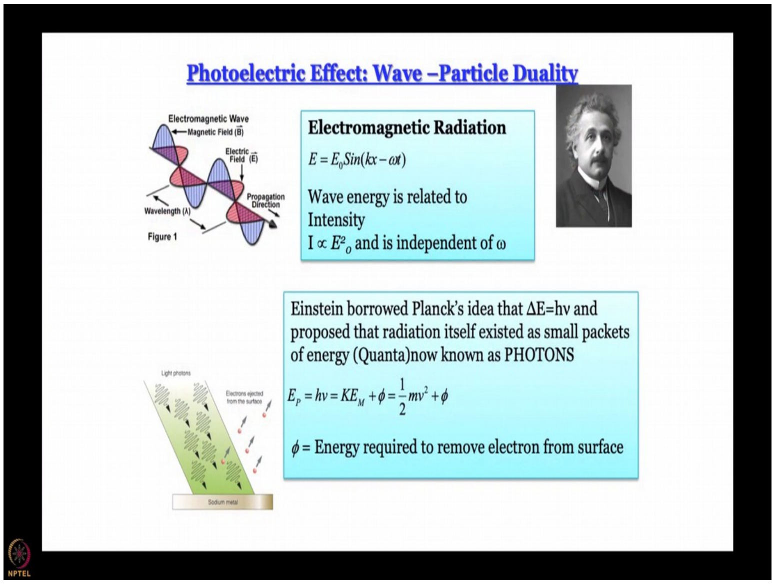

Photoelectric Effect: Wave –Particle Duality

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

So, what is shown in photoelectric effect we are not going to go into the detail of it is that this light behaves like particles but then throughout 19th century Huygens and other scientists had performed a large number of experiments which showed the wave nature of light diffraction, refraction is sure short proof of wave nature, interference. All of us have studied the solid physical optics which is all about wave nature of light.

So, is light a wave or is like a particle Newton said it is particle seeing the results of photoelectric effect Einstein said it is particle what the wave nature is also manifested. So, it turns out that light has a dual nature it can be a wave well when can behave as a wave can behave as a particle. So, this duality of light is established in many different ways one people think of photons as a packet of waves and so on and so forth.

With this background there was some thought that can there be a wave nature of matter as well and the reason for the thought was that actual experiments were performed in which wave nature of matter was established? And those experiments were essentially electron diffraction. Electron diffraction tells us that electrons can have wave nature but then we already know that electrons have particle nature. So, from the experiments it was suggested that wave particle duality might exist.

And then we should call it de Broglie law now it has been called a hypothesis for too long a time. De Broglie actually proposed that; de Broglie worked out the relationship between the wave like properties and particle like properties of these this wave particle of the things that can manifest with particle duality and that was the beginning of the wave mechanical treatment of what everything is made up of we will take it up in the next module.