Statistical Thermodynamics for Engineers
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Lecture 14
Historical Survey of Quantum Mechanics

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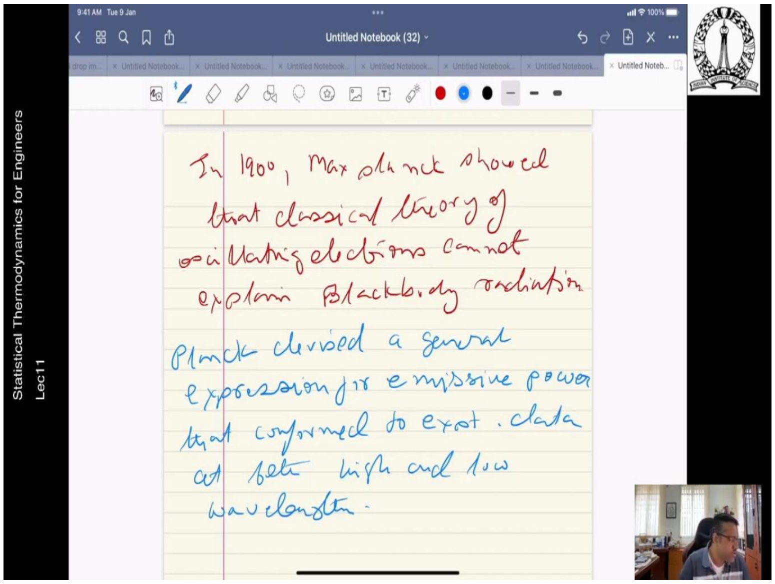

Welcome to lecture number 11 of the Statistical Thermodynamics course. So, this will be our first dabble at quantum mechanics which we say it is needed to find out quantities like energy, energy having Ej‘s and Gj’s, basically, there is a, it is a long path. So, just be a good thing for the time being. So, what happened was this quantum mechanics is a little abstract.

So, we will try to follow a more historical perspective till we get to the historical wave equation. So, what happened was that in 1900, Max Planck showed that the classical theory of oscillating electrons could not explain the behavior of black body radiation. So, he showed that classical theory of electrons are oscillating basically, oscillating electrons cannot explain black body radiation.

So, what he did was that basically they could not explain the black body radiation spectrum. So, Plank, what he did was that he devised or developed a general expression for emissive power the emissive power that is conformed to the experimental data at both wavelength limits, to experimental data at both high and low wavelengths. So, both the limits were basically satisfied.

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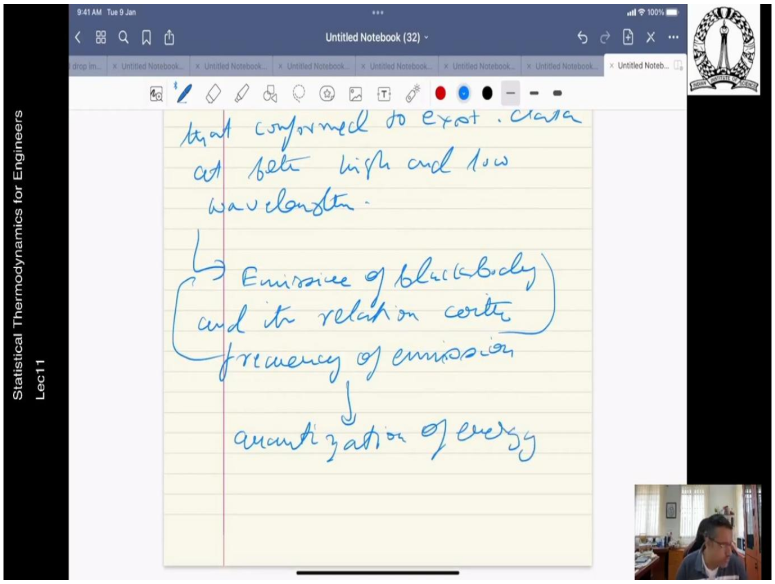

So, he investigated a little further and found and he found this very unique thing that the quantization of energy is needed to derive his empirical relation between the emissive power of black body and the frequency of its emitted radiation. So, the emissive power of black body and its relation with the frequency of the emission is actually given by his empirical relation, but to write that empirical relation he needed quantization of energy. So, he needed quantization of energy which we always say has been the cornerstone of quantum mechanics.

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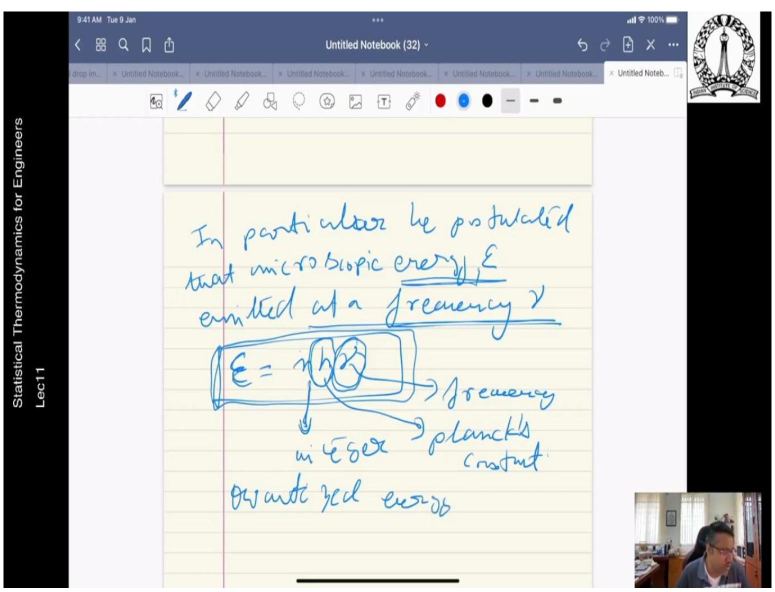

So, what he did was that in particular he postulated that the microscopic energy emitted at a peak energy say that let us call that e and emitted at a frequency, let us call the gamma, they are proportional to each other and such that this energy is given as n h gamma. So, n is basically an integer integer. So, as you can see there is no in 1.5 or 1.125 stuff like that. This is nothing but the frequency. And this is called the Plancks constant. So, the understanding is what did Max Planck did?

He looked at the black body radiation spectrum. He was able to come up with a thermodynamic relation which could explain the black body emissive power at both the high as well as the low wavelengths. Now, the aftermath of that was he found that if his empirical formula has to be explained properly then the emissive power and the emissive frequency or the wavelength, they are basically quantized.

So, based on this, he postulated that the microscopic energy e emitted at a frequency gamma is basically given by this particular form, where n is an integer. So, this in this ensures the packeted nature of the energy and h is the Planck's constant and gamma is the frequency. So, what happened after this? So, this is a quantized. So, the energy is quantized, quantized energy.

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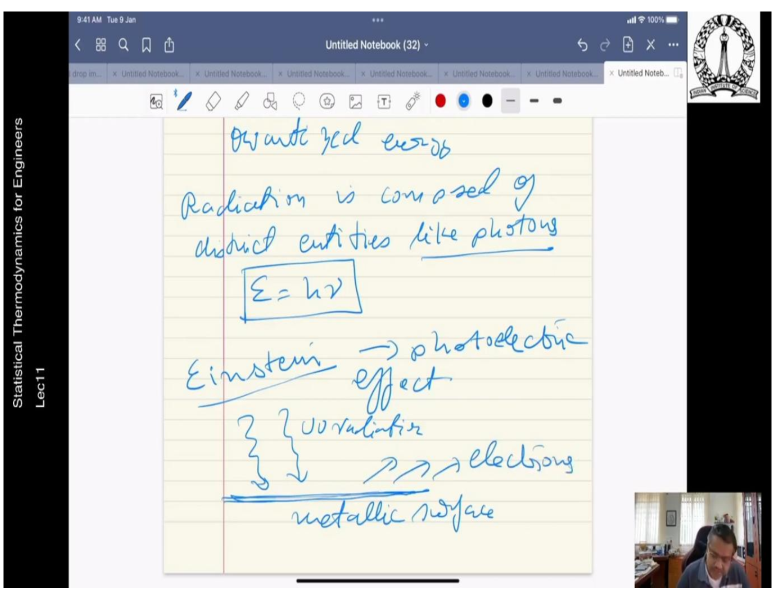

Also, as a corollary of this, you can also say that the radiation is composed of distinct entities like photons, radiation is composed of distinct entities like photons that energy is h nu. Now, Albert Einstein, what he did? So, Einstein, in this photoelectric effect, he try to provide an explanation of the photoelectric effect.

So, what did Albert Einstein do? So, photoelectric effect occurs when electrons are injected from a metallic surface as a result of bombardment with ultraviolet radiation. So, if you have UV radiation bombarded on a metallic surface, this is the metallic surface, it give out electrons. So, what did Einstein do?

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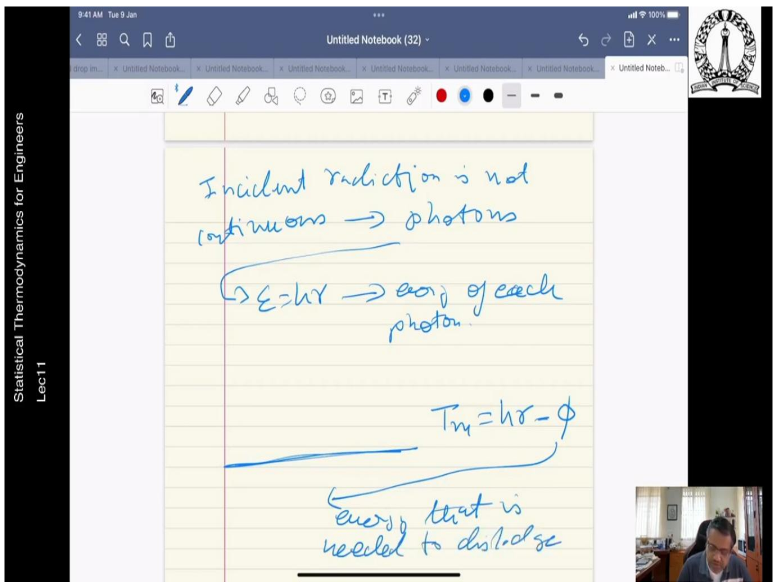

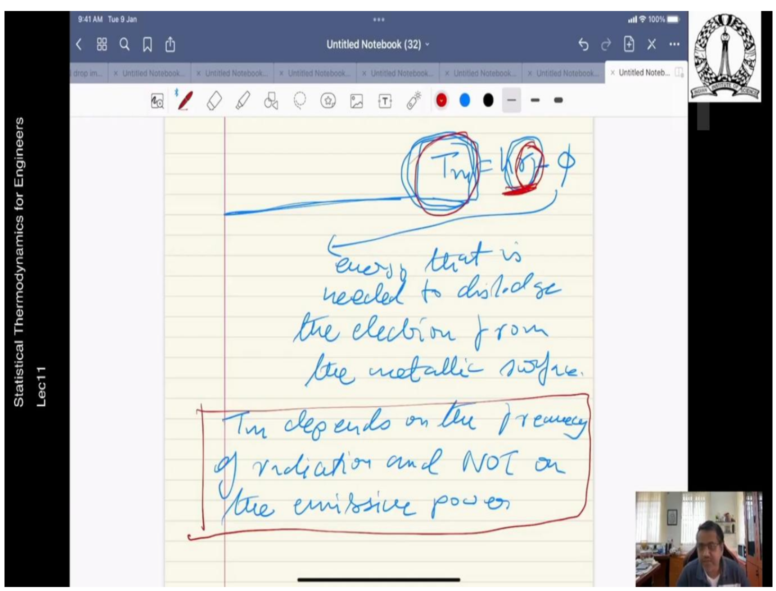

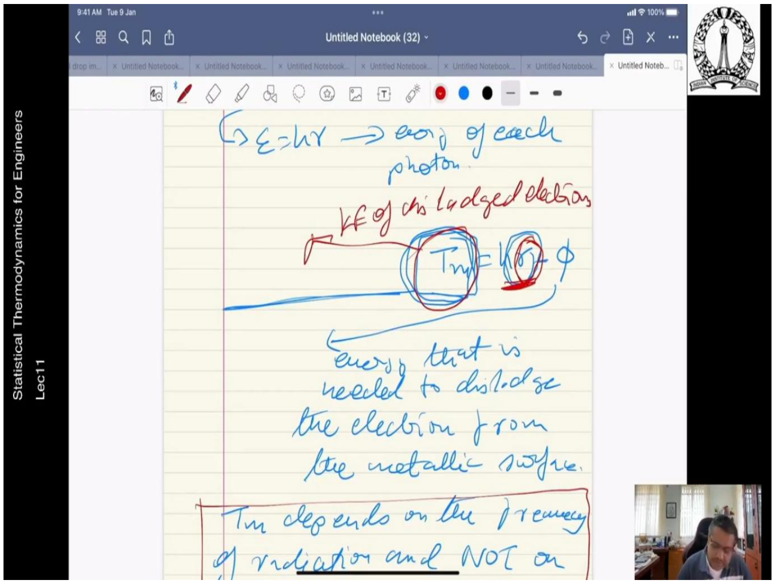

He took this Planck's newly minted expression and suggested that the incident radiation behaves not as a classical electromagnetic wave but as discrete packets or distinct entities of photons. So, he said, so, incident radiation is not continuous by in stretch but it is composed of photons now, which has got energy which you already said of h nu.

So, each photon, this is the energy of each photon, each photon. So, when the ultraviolet radiation strikes a metallic surface, what will happen? If you just take an energy bucket. So, the maximum kinetic energy of the dislodged electron, let us call it T m, would be equal to h nu that is the energy that is carried by each photon minus some phi where phi represents the minimum energy required to remove the electron from a particular surface of a particular material.

So, this is the energy that is needed to dislodge or remove, whatever you call it, dislodge the electron from the metallic surface. So, this is the minimum energy. So, when people actually did the experiments, we found that this maximum kinetic energy expression is quite valid, this agrees with experimental data.

And interestingly, this particular maximum kinetic energy depends on the frequency and not on the emmisive power. That was very interesting. So, this T n depends on the frequency of radiation and not on the emmisive power. And this relationship is leading, it is linearly dependent. More is a frequency, more is kinetic energy of the dislodged electrons.

So, if you think that we put it formally, this is the kinetic energy of dislodged, the maximum kinetic energy of dislodged electrons. So, Einstein was able to provide this beautiful explanation. But this actually revamped the corpuscular theory of light which has been there proposed by Sir Isaac Newton.

But it was abandoned shortly because of the investigation of Young and Fresnel; they showed that the radiation or light actually exhibits both diffraction and interferometry interference that could be explained beautifully if we model light as a traveling wave. And then subsequently James Cloud Maxwell say that light behaved like an electromagnetic wave.

So, hence that viewpoint for corpuscular theory was abandoned for a short period of time before Einstein actually revolutionized it and said that indeed the photon is actually quite revolutionary and it actually is, it does not go by the classical theory of electromagnetism of light in general. So, that is some kind of a historical perspective that how this was done.

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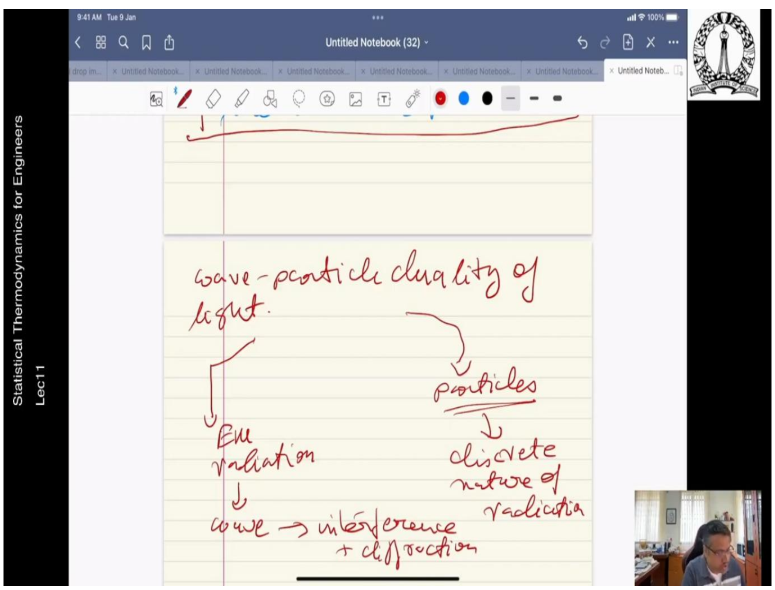

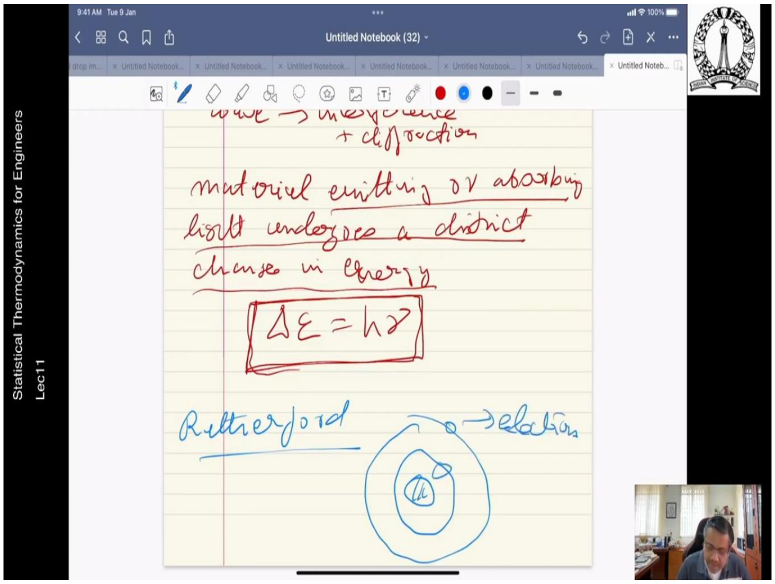

So, however, so, Einstein's seminal work suggested also for the first time that there is something called wave particle duality, duality of light. So, it is like a bit more process sometimes, that sometimes light will behave like E m or the electromagnetic radiation in which the light will behave like a wave and it will show interference diffraction which has been all approved and then sometimes it will act as particles.

Remember, the photons are actually bosons, sometimes as particles and when the particle nature of the light dominates, the radiation is discrete, this leads to the discrete nature of radiation. So, this gives light to the discrete nature of radiation. So, this also subsequently means that the material emitting or absorbing light undergoes distinct change in energy which is given as delta e is given as h nu.

So, the discreetness comes over here that the material that is emitting or absorbing light undergoes a distinct change in energy which is given as this. Now, subsequently what happened was that when all these things were going on Rutherford actually proposed that the atom is composed of a central nucleus and then you have the rotating electrons. So, this is some kind of a of an atom model that was proposed by Rutherford but immediately people jumped into it.

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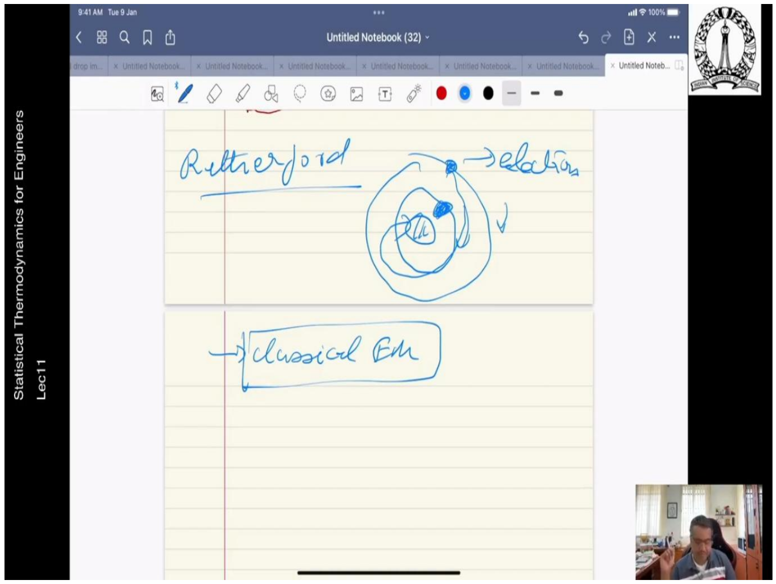

Which is because the electrons are basically charges. So, a charge which is rotating, which is which is moving about to the (())(14:42) elctrons therefore deviate gradually reduce the energy and basically spiral and then it should merge with the neucleas, so, the atom would be very short-lived entity which it is not is very stable as we know. Because you need in a Manhattan project basically to split the atom.

So, this was quickly abandonment as well. This is because it could not be reconciled with classical mechanics at all. A classical electromagnetism which it could not be reconciled because the orbiting electron should actually radiate energy and should actually place with the nuclei. So, here came we Neils Bohr.

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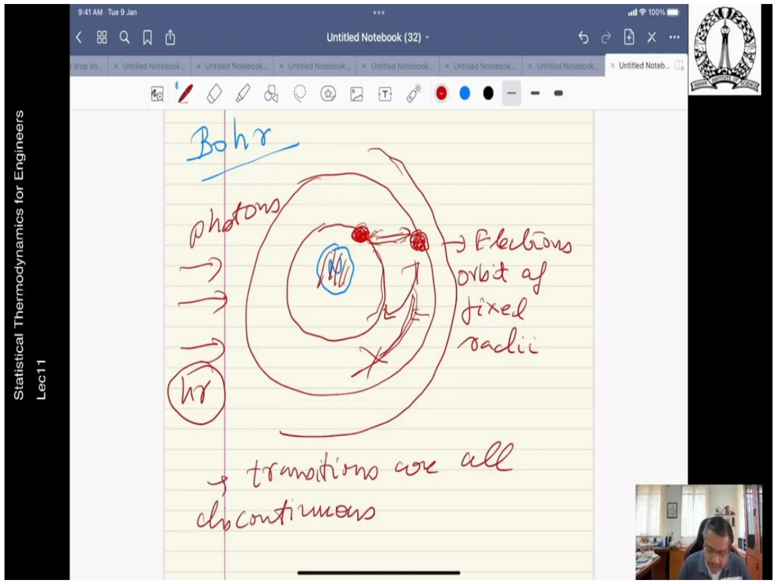

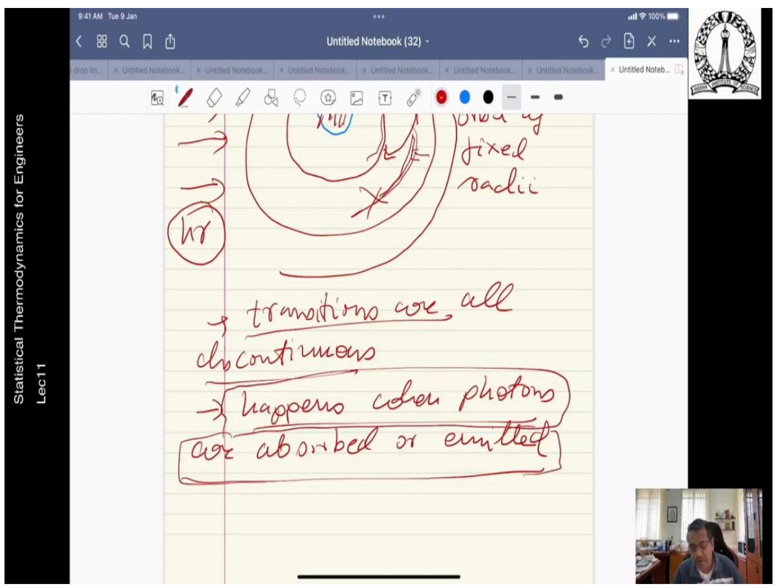

So, what he suggested and gradually became known as a Bohr model. So, he said that there is a nucleus and then there are orbits which is called electrons to rotate between those orbits. So, electrons, orbit at fixed radii. This was the Bohr model. So, what did Bohr suggest? He provided, basically, he refined Rutherford’s model a little bit. He added a little bit of a twist.

He said building on Einstein's work that the electrons actually orbited fixed radius and this continuous transitions between orbits, between orbits occurs when only photons are absorbed or emitted by the atom. So, what will happen is that if you now bombard this atom with photons which is called energy of this, the electrons can actually go from higher or lower radii.

So, they might change their orbit if and only if photons are absorbed or emmited that this can be (())(16:54) and the transitions will be discontinuous. They cannot go to a slightly lower orbited start orbiting, it cannot happen. This is not permissible. They have to absorb a fixed quantity of radiation to go to a higher orbit or they have to lose a fixed quantity of radiation for them to move to a lower orbit.

But these transitions are all discontinuous in nature. Transitions are all discontinuous in nature. Only happens when photons are absorbed or emitted. Only happens when photons are absorbed or emitted. This model offers the first comprehensive explanation of a known spectrum of atomic hydrogen.

We will see how that was actually done. The amazing agreement between the this particular and Bohr‘s model and the spectrum for the first time suggested that how the quantum mechanics can be reconciled with its spectroscopic observations and with that and how it actually deviates from the classical or accepted form of electromagnetism. So, what did?

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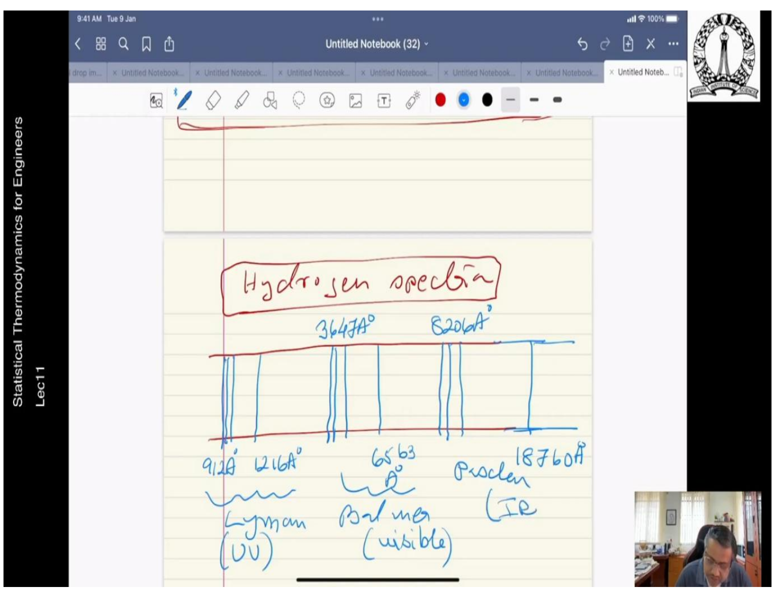

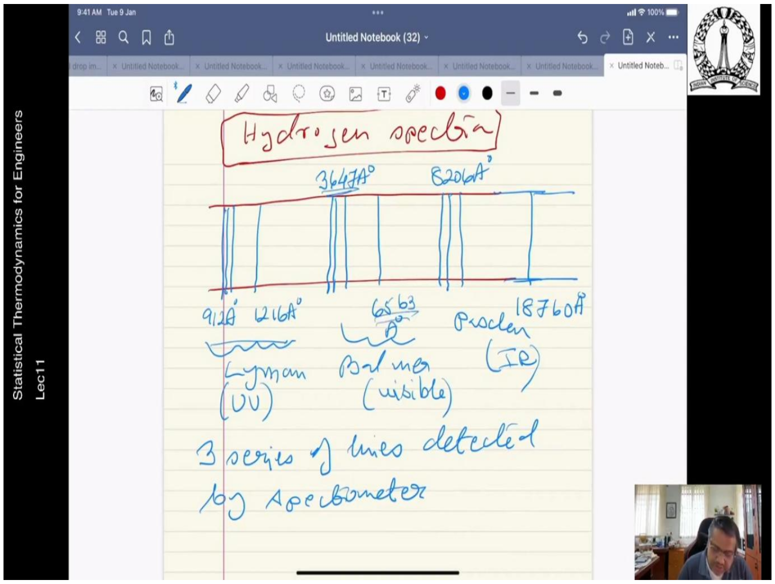

So, that was the Bohr's model. Now, let us look at a hydrogen spectrum. The hydrogen spectrum is obtained in those days by a hydrogen lamp and passed through a prism and then on to a photographic plate. So, if you look at the spectrum. So, that is like the spectrograph. So, as you can find out.

So, let us draw it properly. So, you can see that there are a few lines like this. So, this is all line will represent angstrom. This is about 1216 angstrom. We will draw a little further. So, this is actually 3 6 4 7 angstrom. This one which is 6 5 6 3 angstrom. (())(19.28) which is 8 2 0 6 angstrom. (())(19.38) which is 1 8 7 6 0 angstrom. So, this is called, what we call the Lyman series.

This is UV. This is called the Balme series. This is visible. You see the distinct lines like that. This is called Paschen series which are the infra red. So, these are the lines that were three series of lines, three series of lines detected by the spectrometer. So, these are the three sets of lines that were detected.

And if you look at these particular lines, they are very closely spaced, they are very closely spaced. And then there are these large separations as well. So, there is that there is a dense form of the line and then there is this (())(20:49) reduction in line spacing. So, the upper and the lower limits of each spectral family is between this to this. Then of course, Paschen is about is from more than Balmer is 3 6 4 7 to 6 5 6 3 and so on and so forth.

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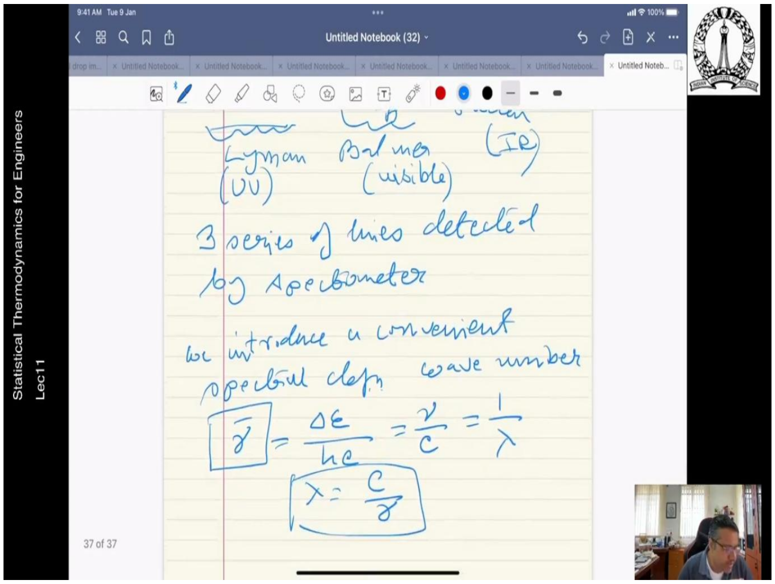

So, at this juncture, we introduce a convenient spectral definition, we introduce the convenient spectral definition which is called the wave number. It is got a unit of centimeter inverse. So, the wave number is written like this which is basically equal to this by C which is equal to 1 over lambda.

So, we will recognize that the wavelength is basically this. Wavelength is equal to C by the frequency. So, the wave number is basically just the inverse of the wavelength. The utility of the wave number indicates the number of macro wavelengths in one centimeter that (())(22:11) energy changes are directly related to the inverse of the measured spectral wavelength.

So, that is why this is a very convenient definition that we are going to use here. So, employing this definition, employing this particular definition that discrete wavelengths of all spectral lines that we have seen over here, all spectral lines in figure this can be empirically correlated via the Rydberg formula.

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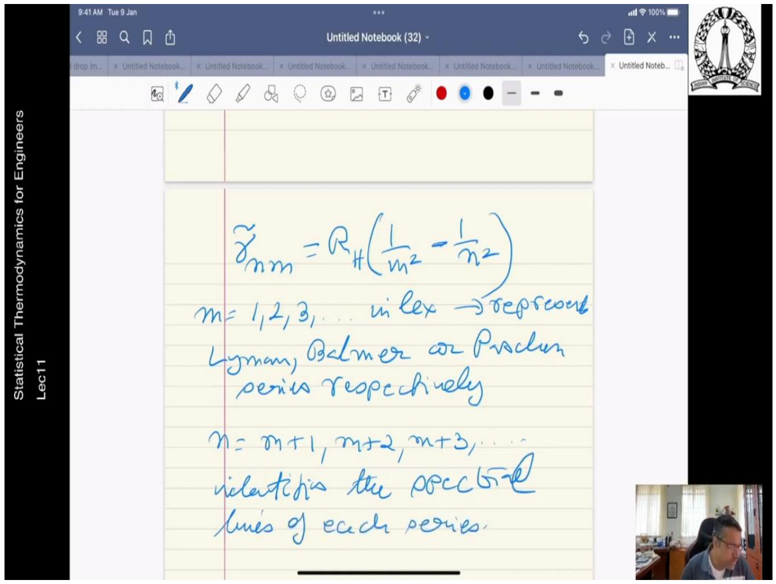

So, if you look at the (())(22:43) in any two transition it is like given by the Rydberg formula, 1 over n square minus 1 over n square. n is equal to 1 2 3, this is an index which represents Lyman Balmer or (())(23:13) series respectively. And on the other hand is basically n plus 1, n plus 2, n plus 3 so on and so forth. This identifies the spectral lines of each series.

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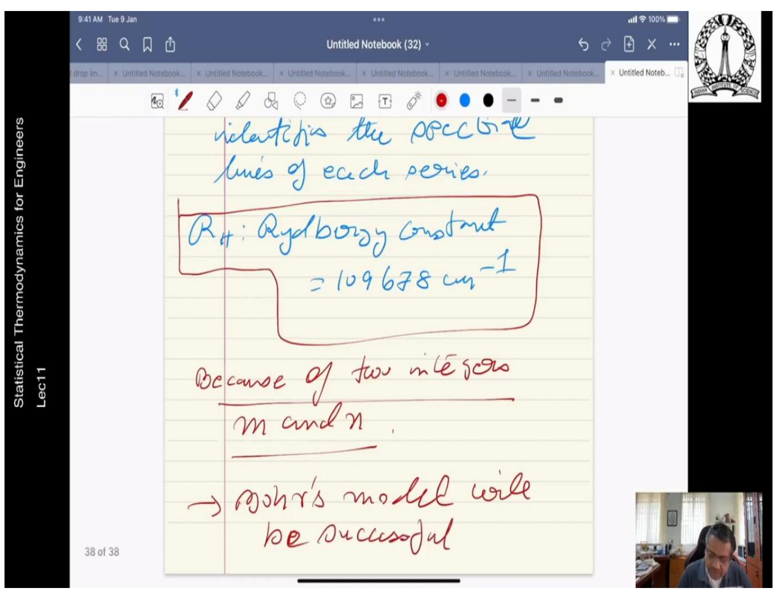

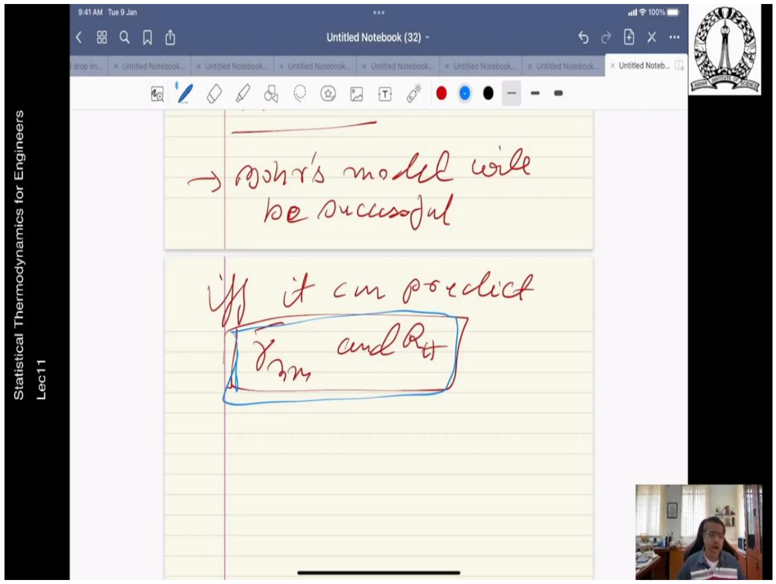

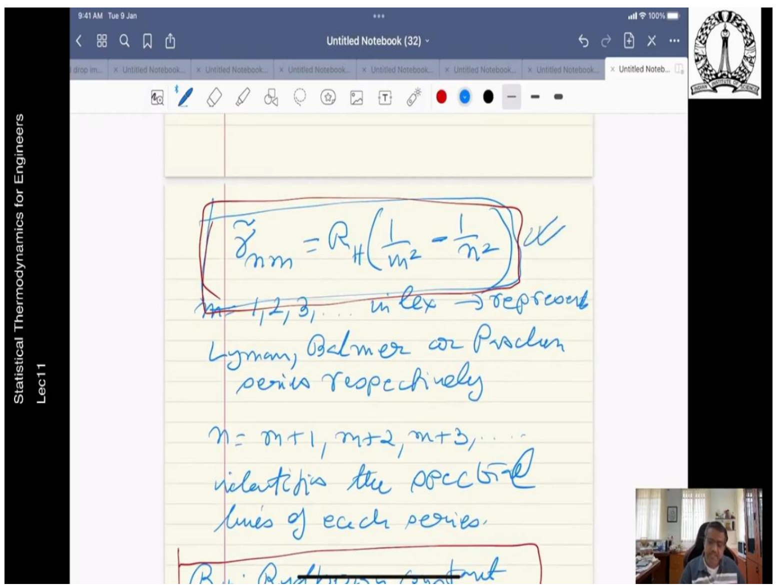

And the Rydberg constant which is Rh, so the Rydberg a constant, this is one of the most accurate constant in physics, the Rydberg constant is written as 109678 centimeter inverse. So, ideally whatever form that you, whatever theory that you propose, it has to replicate this particular equation. It has to conform to this particular equation. It also has to predict this particular constant. Because these are comes from very precise measurements that we can see.

So, as you can see. So, any any formula, any formula that you propose it or whatever ways you want to propose, it has to kind of obtain that particular phase thing expected reproduction of R H is actually needed for the success of the Bohr model which ultimately invoked energy quantization because of the two integers. So, this is energy quantization is inbuilt because of the two integers, two integers m and n.

So, because of these two integers m and n, this is already inbuilt quantization. So, the success of the Bohr's model would mean those models will be successful if and only if it can predict is gamma n m and R H. If it can do that then we on the prima facie (())(25:49) basis we will call it a success. So, Bohr's model was nothing but Rutherford model with a twist where he said that the electrons actually rotate in fixed radius, they cannot give out energy continuously, they can only go from one orbit to the other which would be like a discontinuous transition or a discrete transition while only there is an interaction with photons of fixed energy which is H multiplied by the frequency.

We also introduce the concept of wave number. So, the wave number actually is the inverse of the wavelength, is the number of back home wavelengths per centimeter. So, essentially, the wave number is an important concept because it allows us because as we saw in this particular thing that the energy transitions, the energy transitions you know from is directly discrete energy changes are actually related to the inverse of the measure of spectral wavelength.

So, that is the beauty of the theme. So, and all these things, in this energy packeted concept that energy is equal to n h into the frequency came from Planck, who actually model the entire black body radiation spectrum and found that he cannot reconcile it with classical physics anymore. So, you have to take resort to basically what he did was, he came up with an empirical thermodynamic relation and that led to the fact that if that relation is correct then energy has to be discrepanced and we could match it at both the higher and the lower the wavelengths.

Those two things were independently matched by Rayleigh and Jeans but nobody could match the whole spectrum in that particular case. And Einstein was able to use this and he postulated that okay, this ultraviolet radiation that hits the metal surface is composed of photons, this photon comes and bombards the surface and gives out electrons, and even the kinetic energy of those electrons could be accurately linked using the theory that was proposed by Albert Einstein.

So, this revitalized the particle nature of light as well. And so, it was inferred that light actually shows wave particle to all the pieces, sometimes it creates microwave, sometimes it feels like a particle. So, in the next class what we are going to see is that we look at the Bohr's model and try to understand that how the Bohr's model can explain, how the Bohr's model can actually explain this particular formula that was that we just wrote here, can we explain the spectrum of atomic hydrogen. So, see you in the next class.