Statistical Thermodynamics for Engineers

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Lecture 17
Bohr Model for the Spectrum of Atomic Hydrogen

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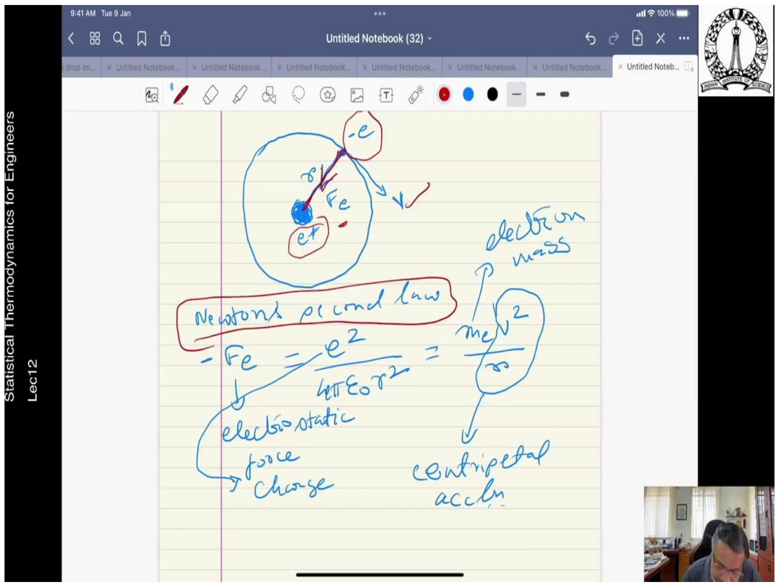

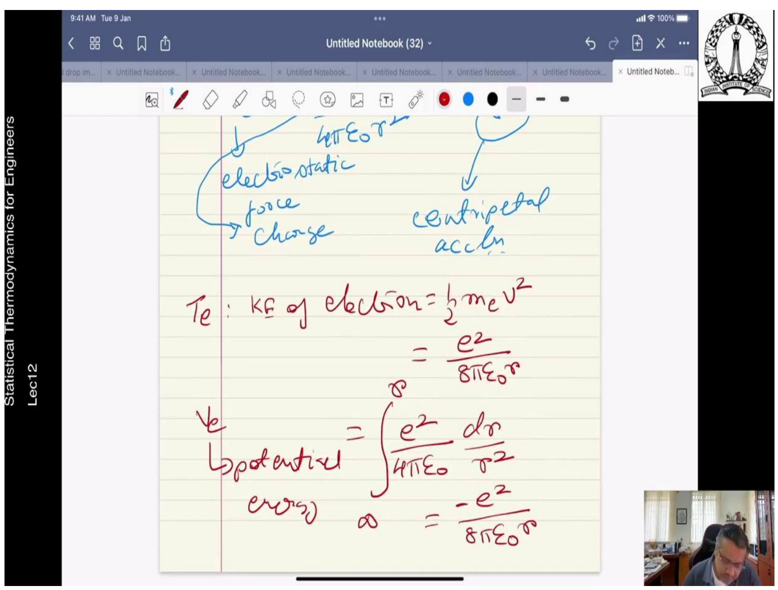

So, welcome to lecture number 12 of Statistical Thermodynamics. So, as we saw that the hydrogen spectra could be explained by the Bohr's model. Let us see how that can be explained by the Bohr’s model. Let us take a very simple system. This is the orbit of electron and this is central nucleus, which has got the positive charge, plus and minus and the radius is r.

Then electron is moving in this particular direction, the velocity we need, let us call that v. And of course, there is an inward force because the electron is moving, let us call that inward force as Fe. So, what we do, this is a very simple system in which there is a nucleus and let us take the hydrogen for example. So, this is the nucleus which is positively charged, the electron is moving around the nucleus. It is like a single electron kind of a system because of hydrogen. It moves with a velocity v.

So, what we do is that we apply Newton's second law here to this particular system. So, let us write the force fe, fe is nothing but an electrostatic force because it is a positive-negative charge, and then that electrostatic force is given as e square by four pi into e naught r square as electrostatic force, e is nothing but a charge and this should be equal to the centripetal at force, which is given as me into v square divided by R.

So, basically this particular part of the term is called a centripetal acceleration. This is the electron mass. So, you have, what we have over here we apply Newton's second law to this particular system which has got an electron which is rotating around the nucleus which is composed of a proton, the velocity of electron is v, so there is an electrostatic attraction which is given by fe and then of course, there is a centripetal acceleration which basically balances this electrostatic force of attraction.

So Te, if I project te as the kinetic energy of the electron that is equal to half me v square. me is basically the mass of electron which is also equal to e square by 8 pi epsilon naught into r as you can see from this particular expression just add a half to it and you can see that this is how it halves because of this valance we can write it like this.

So, therefore, ve which is basically a potential energy, this is different and is not the velocity potential energy that is given by, so this is the kinetic energy of the electron that is a potential energy of electron. It is from infinity to R if you bring an electron in, this e square by 4 pi epsilon naught, dr by r square. This is the force field is the electrostatic force field so this is the potential energy which is equal therefore to the minus e square divided by 8 pi epsilon naught into r.

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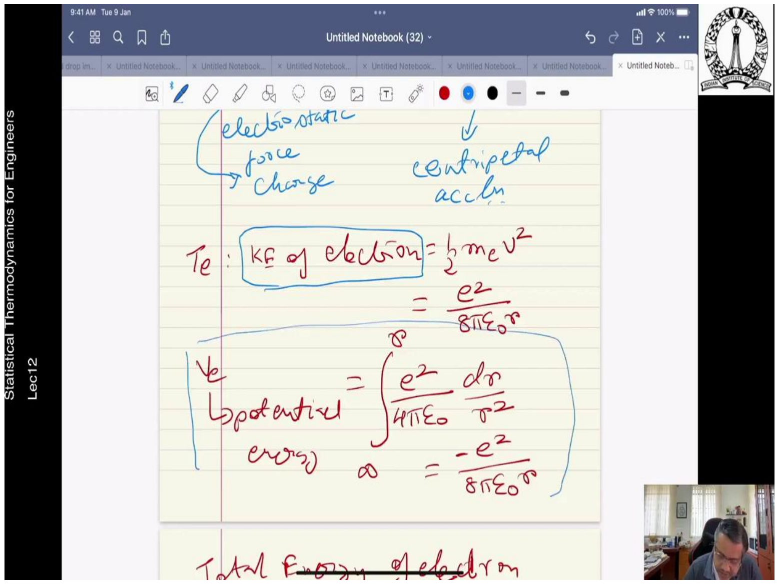

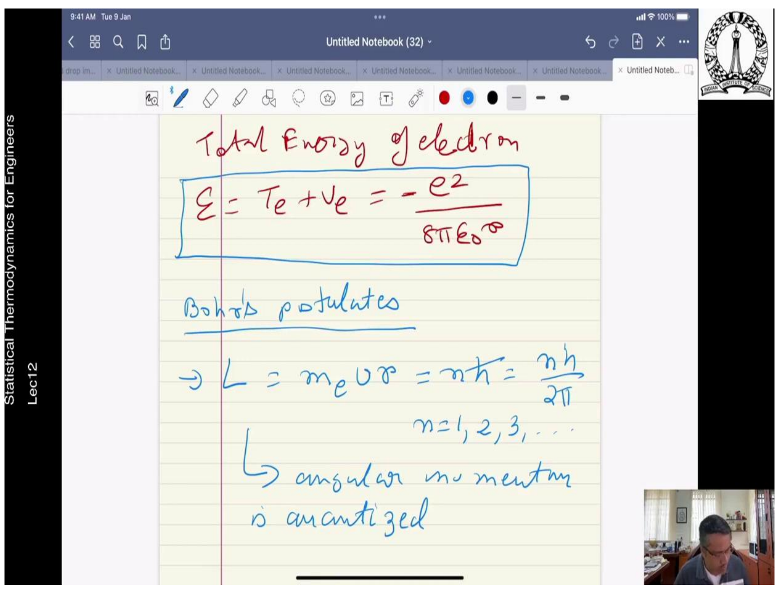

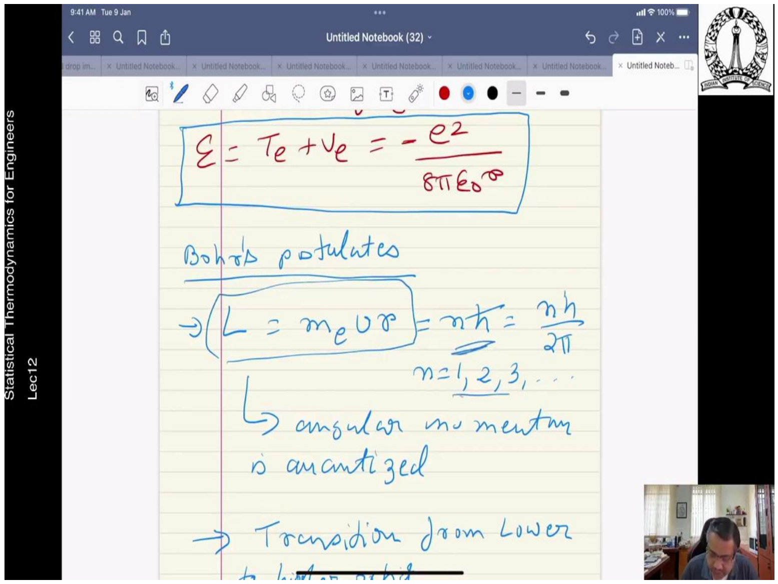

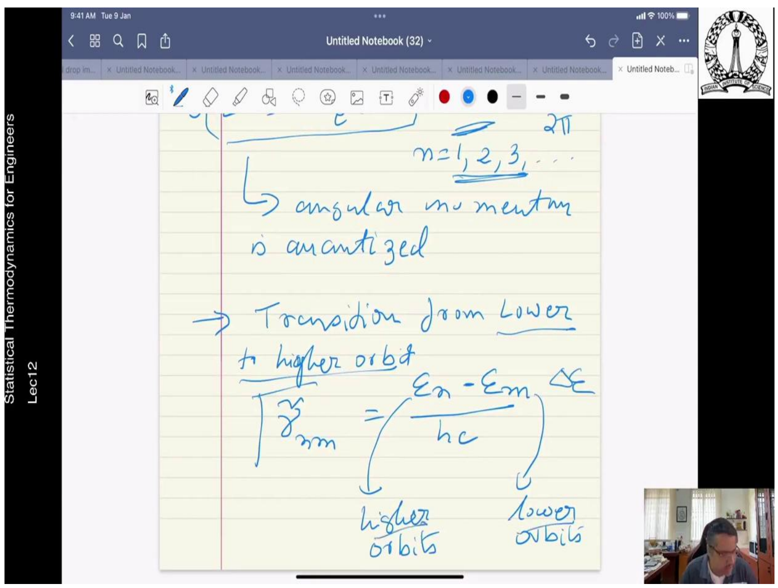

This is the potential energy so the total energy of electron is given as the total energy e, Te plus Ve so it is the kinetic energy plus the potential energy, if you add the 2 it will be e square by 8 pi epsilon naught r. This is the total energy of an electron which is orbiting around at nucleus. So, what did we do? We first balanced the electrostatic force with the centripetal force and then we calculated the kinetic energy of the electrons and we calculated the potential energy of the electron.

This is the energy that is spent to bring the electron from infinity to a radius R. This is the central definition. So, this should be the energy of the electron. Now, Bohr's had the following postulates. So, these are postulates you remember, so he said that the angular momentum, r is quantized, where this is nothing but n h into 2 pi where n is equal to 1,2,3, so n is an integer as we all know that is the integer representation. So, the angular momentum is quantized. It basically says angular momentum is quantized.

This is the first postulate of Bohr's, the second one is that transition from lower to higher orbit is given by we already saw this. This is a wave number is energy en minus energy em divided by hc this is basically delta e.

This is the higher energy and this is lower orbit. so, what did Bohr did apart from this he said that the angular momentum is quantized and it is given by this particular form which is nh by 2 pi, n are integers, so, naturally this is quantized. So, this can have discrete values only and transition from higher to lower orbit is given by this which is nothing but a differential of energy this is delta E basically this is higher orbits and these are the lower orbits. Armed with this, what will be the form for v?

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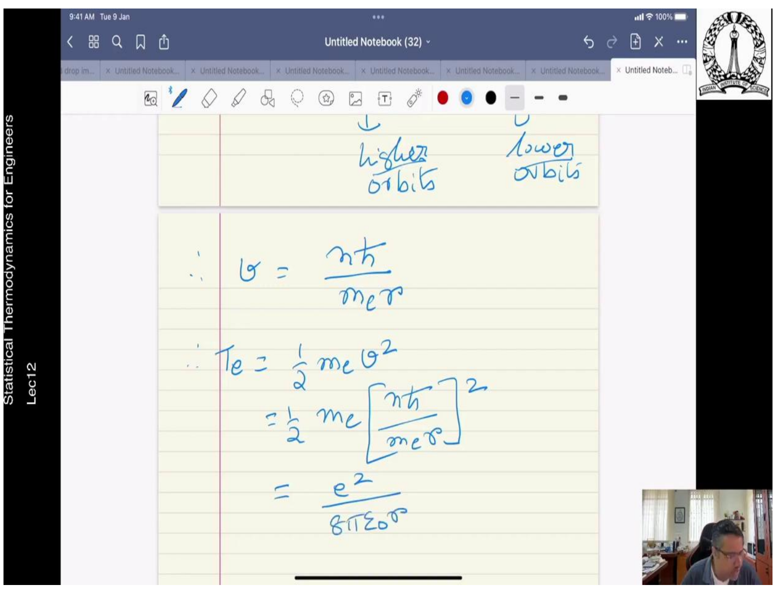

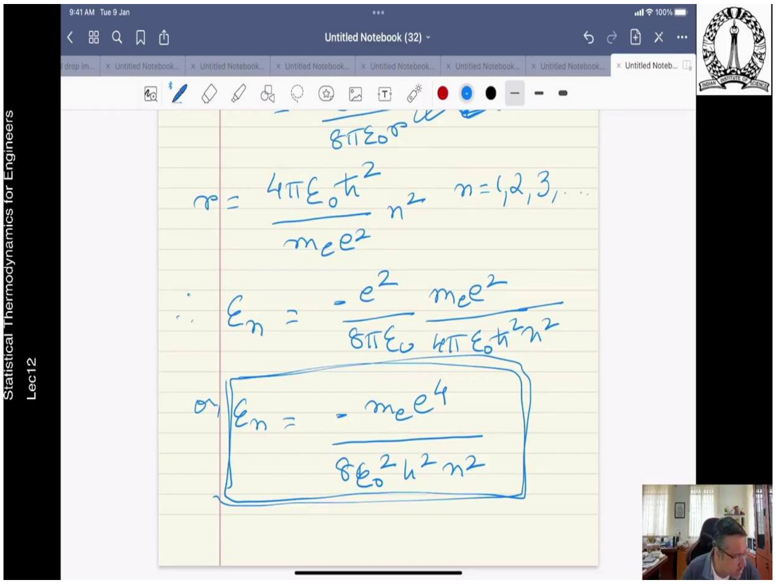

Let us look at v. Therefore, v is equal to n h bar divided by m e r because of the quantization. From the quantization we can say v is equal to n h bar by m e r that is exactly what we have written. So, therefore Te is equal to half me v square, which is further represented as r, m e let us put it as n h bar by m e r square.

Now if you substitute from the previous expressions it will be e square by 8 pi epsilon naught r and r therefore, if you equate the 2 will be given by 4 pi epsilon naught h bar square divided by me e square into n square. Basically we equated the 2 and we have substituted for V which is given by this particular form. So, this additional form, if you could look at it here from here it was it was not quite evident that how the quantization comes into the picture.

Here you can be clear that because the angular momentum was quantized this readily offers that expression to calculate V and V can be now further substituted in the kinetic energy term. And therefore, now equating with the existing expression for kinetic energy, which we already did over here. Taking this and equating these two, we get a definition for r, where n is equal to 1,2,3. So, as you can see r is naturally quantized.

Therefore, En the energy at any particular at nth energy level is therefore, 2 pi naught m e e square divided by 4 pi e naught h bar square n square that comes from the expression that we just now saw here or in other words E n is given as minus m e e to the power of 4 divided by 8 epsilon naught square h square n square. So, this is the energy at any particular energy level and it is given by this particular expression that we have over here.

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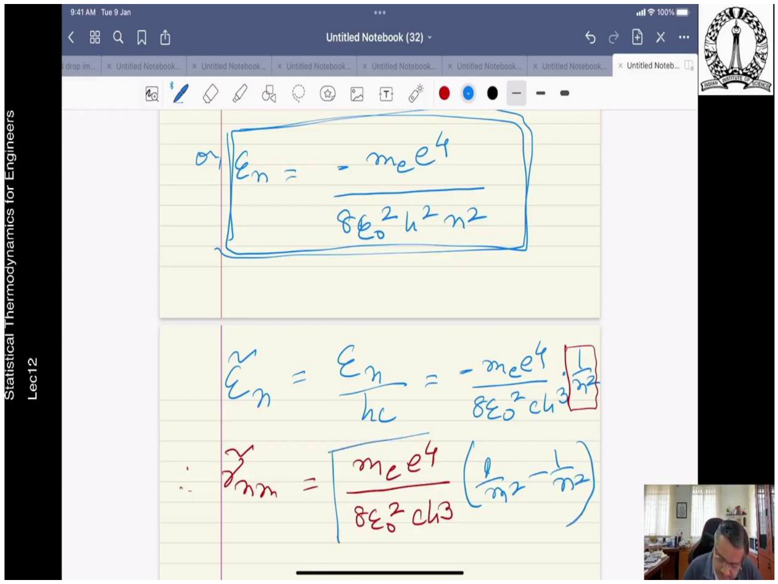

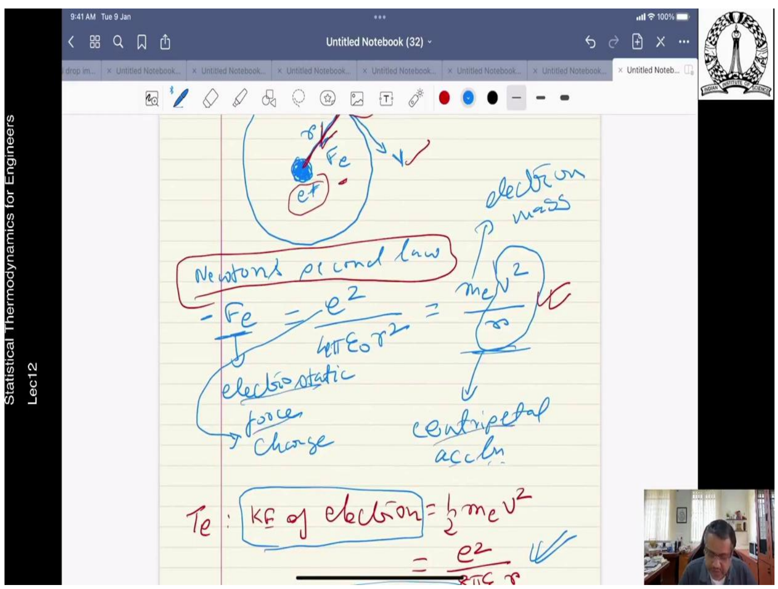

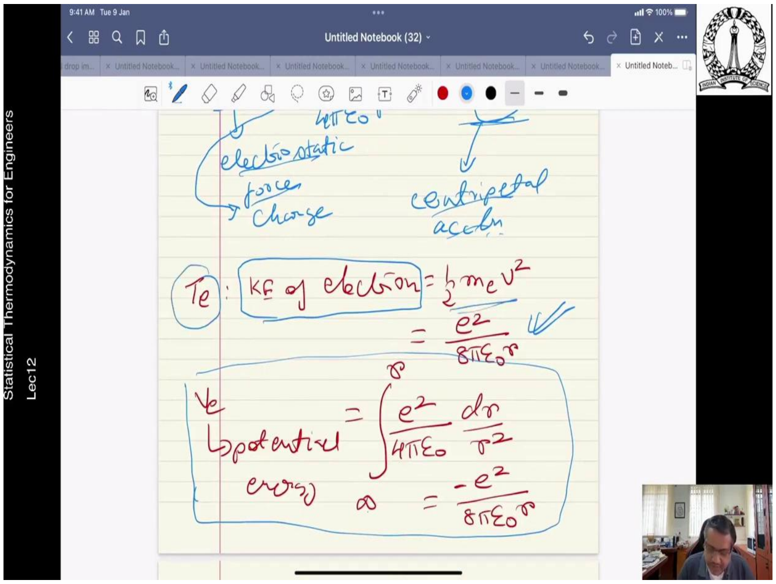
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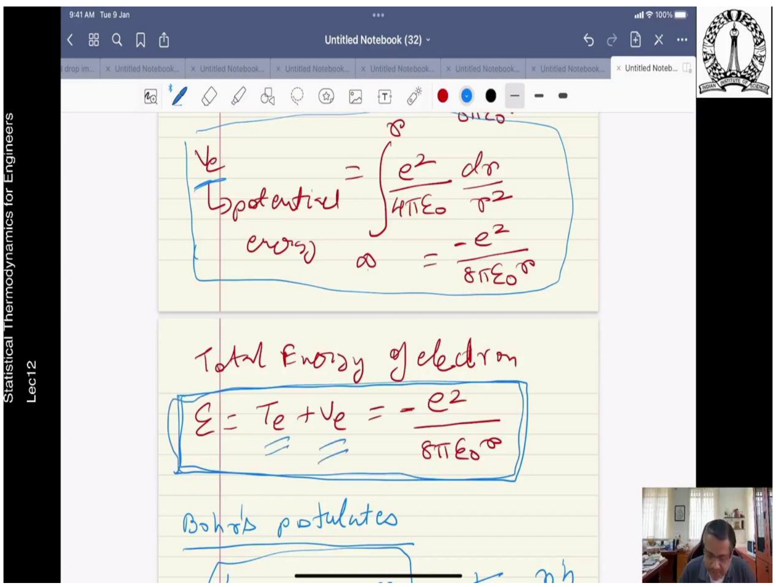
electrostatic force
charge
centripetal accln
T_e : KE of electron $= \frac{1}{2} m_e v^2$
$= \frac{e^2}{8\pi\epsilon_0 r}$
V_e potential energy $= \int_{\infty}^{r} \frac{e^2}{4\pi\epsilon_0} \frac{dr}{r^2}$
$= \frac{-e^2}{8\pi\epsilon_0 r}$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V_e potential energy $= \int_{\infty}^{r} \frac{e^2}{4\pi\epsilon_0} \frac{dr}{r^2}$
$= \frac{-e^2}{8\pi\epsilon_0 r}$
Total Energy of electron
$\mathcal{E} = T_e + V_e = -\frac{e^2}{8\pi\epsilon_0 r}$
Bohr's postulates

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$$\ldots = \ldots \quad 8\pi\varepsilon_0 r$$

Bohr's postulates –

→ $L = m_e v r = n\hbar = \frac{nh}{2\pi}$

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

↳ angular momentum is quantized

→ Transition from lower to higher orbit

$E_n - E_m, \Delta E$

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

↳ angular momentum is quantized

→ Transition from lower to higher orbit

$$\bar{\nu}_{nm} = \frac{E_n - E_m}{hc} \quad \Delta E$$

E_n ↓ higher orbits

E_m ↓ lower orbits

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higher orbits — lower orbits

$$\therefore \; v = \frac{n\hbar}{m_e r}$$

$$\therefore \; KE = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \left[\frac{n\hbar}{m_e r}\right]^2 = \frac{e^2}{8\pi\varepsilon_0 r}$$

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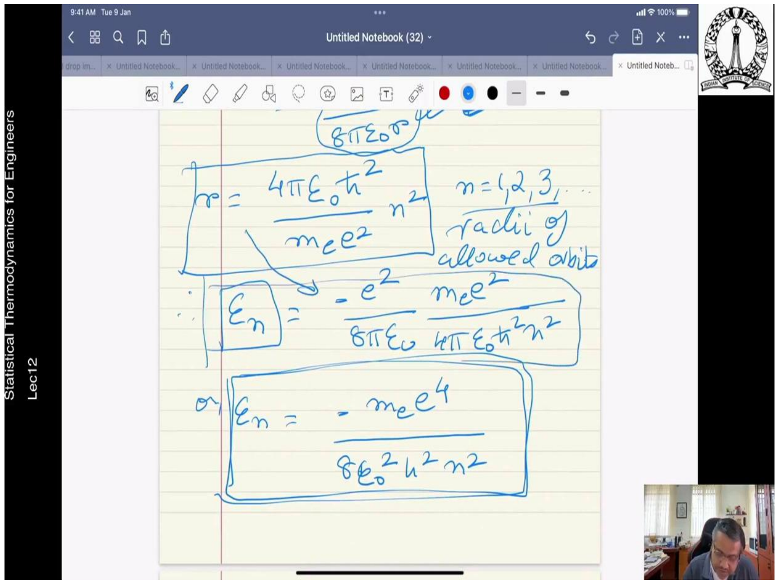
$$= \frac{1}{2} m_e \left[\frac{n\hbar}{m_e r}\right]^2 = \frac{e^2}{8\pi\varepsilon_0 r}$$

$$r = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} n^2 \qquad n = 1, 2, 3, \ldots$$

radii of allowed orbits

$$\therefore \; \varepsilon_n = \frac{-e^2}{8\pi\varepsilon_0} \frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2 n^2}$$

$$\text{or} \quad \varepsilon_n = - m_e e^4 \ldots$$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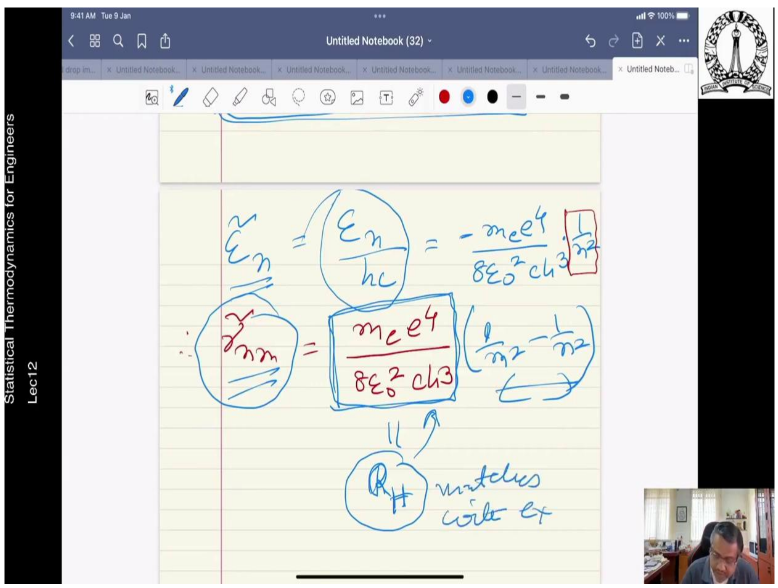
Untitled Notebook (32)
$r = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} n^2$
$n = 1, 2, 3, \ldots$
radii of allowed orbits
$\therefore \varepsilon_n = -\frac{e^2}{8\pi\varepsilon_0} \frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2 n^2}$
or $\varepsilon_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}$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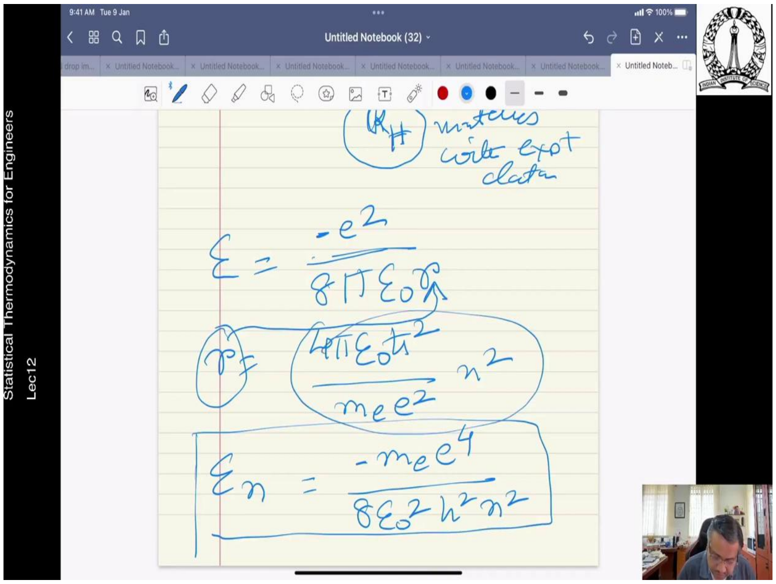
Untitled Notebook (32)
$\tilde{\varepsilon}_n = \frac{\varepsilon_n}{hc} = -\frac{m_e e^4}{8\varepsilon_0^2 c h^3} \cdot \frac{1}{n^2}$
$\therefore \tilde{\nu}_{nm} = \frac{m_e e^4}{8\varepsilon_0^2 c h^3} \left(\frac{1}{m^2} - \frac{1}{n^2}\right)$
R_H
matches with ex



Now, if the energy is written in this form, wave number space form is given as minus me e to the power 4 divided by 8 epsilon naught square c h cube into 1 over n square. This 1 over n square is very important because this is where the quantization comes, therefore, gamma n m is given as m e e to the power 4 divided by 8 epsilon naught square c h cube then let us change the font (())(12:07) 1 over m square minus 1 over n square.

This particular guy that you see over here is supposed to be the Rydberg constant. What did and it indeed turns out to be a very accurate estimate of the right words constant. As we can see. Therefore, in this particular expression that this RH is now represented by this, so, just let us do a very quick recap. What happened was that we first ask this very simple system of an electron rotating around the nucleus we applied Newton's second law in which the electrostatic force was balanced by the centripetal acceleration and then we pass the kinetic energy of the electrons is given by this and the potential energy is given by this form.

This happens because in a conservative system, this is the energy that is you bring the electron from infinity to all the way up to r and that is what gives you the potential energy. That is what gives the potential energy for a conservative system from infinity to r. Now, that gives the total energy. The total energy is nothing but the sum total of the kinetic energy and the potential energy which is given as this.

So, then we move on now that we have got this all sorted out then we went to the Bohr's postulates. In Bohr's postulate what did Bohr's says that the angular momentum is also quantized and it is given in this particular form where n is basically the integer to which the quantization happens and transition from lower to higher orbit is given by this. This is nothing but delta E. Therefore, using this particular expression now, which is the quantization of angular momentum, we found an expression for V which is the velocity.

So, the kinetic energy is therefore given as this and kinetic energy already found is given in this particular form. So, equating these two we found that what will be the allowed radii, the allowed radius of the orbits. You can write it as radii of allowed orbits. This happens through the quantization of N equals to 1,2, and 3. You cannot have all orbits, this is given in discrete forms. Any energy can be now if you look at this particular expression, the total energy. The total energy is substitute the expression for R.

In that expression that basically you put this here and you get this expression for energy. Now, once you now you can this is just algebraic manipulations and then once you see the differential so when you normalize the energy this is it comes into the wave number space and then you find out what is a wave number for a transition, an allowed transition. So, therefore, this constant that sits in front should be the Rydberg constant and this is exactly what it is, because this matches with experimental data.

You can understand what we did over here if you do not, the energy let us write this expression between so that you get an idea that when we say energy. What does it exactly mean? The energy if you recall was given as minus e square 4 pi epsilon naught, 8 pi epsilon naught into r. And r we found out was given as 4 pi epsilon naught h bar me e square n square.

Now, if you substitute this here, that is how we get the energy of any nth energy level as me e to the power of 4, 8 epsilon square h square n square. This is how you get the final expression. so, you just put this right here. So, that is how you get the energy.

So, what we have got over here we have got an idea of the allowed radius, the allowed orbit, radii of the orbit and we have also got an expression for the energy. Energy of each energy level or the nth energy level has actually got this energy and this is quantized and it is given in terms of electron charge, electron mass, then the E naught permittivity of free space H, the Planck's constant etcetera. That is a very clear idea now that what is going on.

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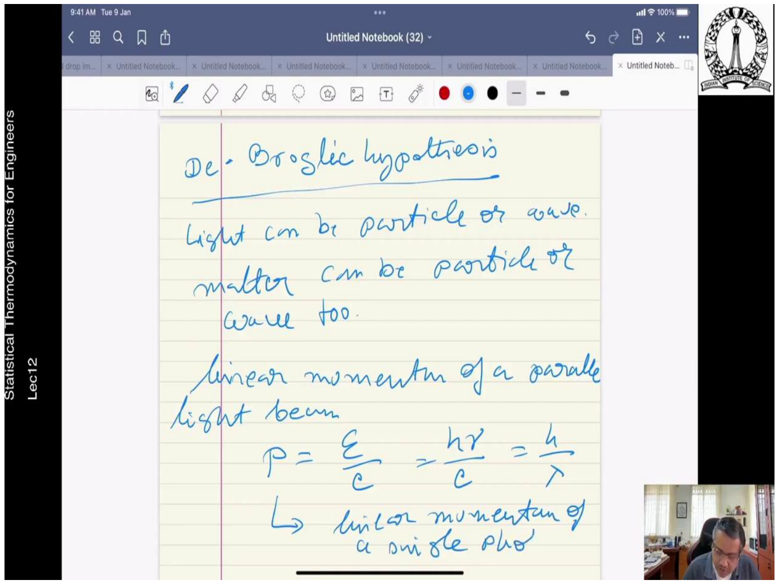

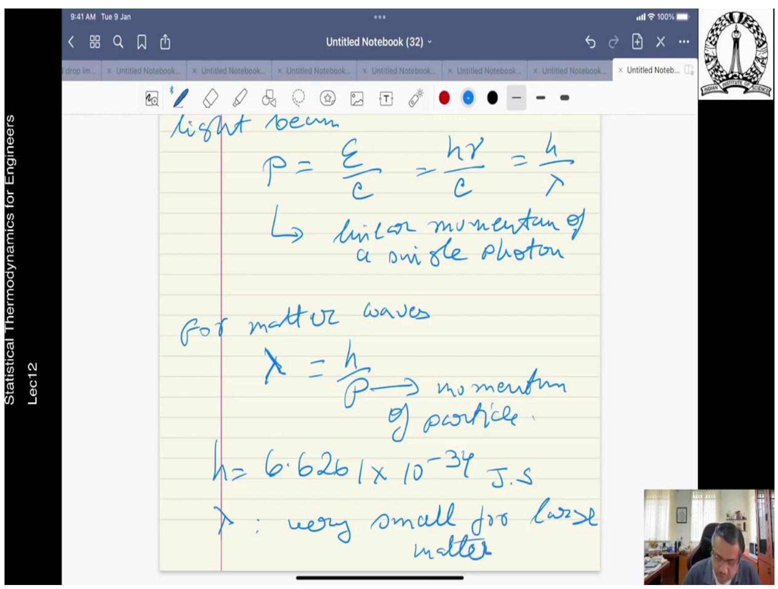

Now, let us quickly take a small you know detour and talk about De- Broglie hypothesis. What did De Broglie actually do? So, as we saw that light can be both particle or a matter. Can be particle, sorry, wave not matter. So, matter can be, matter can be particle or wave too. Electron can also behave like a wave.

The linear momentum of parallel light beam. P is given as epsilon by C, E by C, E as we already know is the energy that is carried this is equal to H by lamda. This is like the linear momentum of a single photon. For matter waves, this lambda should therefore be given as H by P, h is

Planck's constant, p is the momentum of the particle. So, this is like an analogy. So, since the h is about 6.6261 into 10 to the power minus 34, Joule second.

The momentum is of a particle will be kind of small, so, lambda is usually very small for large matter. So, that means when you move to the wave length associated with you is so small that it is almost undetectable. This is definitely not the case with fundamental particles.

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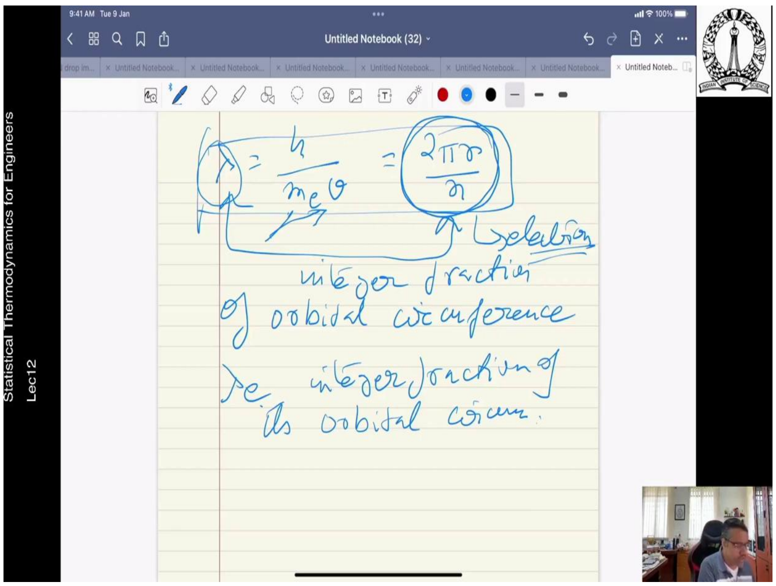

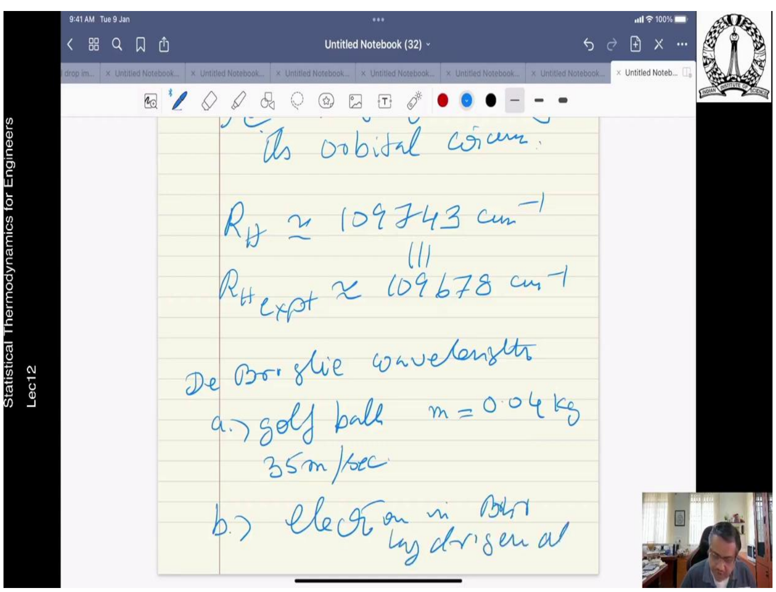

For example, in an electron, Lambda is nothing but h divided by m e v, which is given as 2 pi r into by n. so, it is an integer. This lambda now becomes an integer fraction of its orbitals. This is rather interesting. So, this is for an electron. So, large matter wave forget about that let us talk about electrons. So, electrons if we do then if you substitute all the quantities over here, you get this something like this.

And then as you can see that lambda of an electron is basically an integer fraction of its orbitals circumference. This is quite good. So, this is what we mean by when we actually have this kind of a situation. So, what happened was and also people calculated the Rydberg constant from the Bohr's model, it turned out to be about 109743 centimeter inverse, compare it to the experimental calculation of the Rydberg constant is 109678 centimeter inverse.

So, these are kind of very close to each other. That is what it is. So, we could cast we could explain more or less the hydrogen spectrum with the Bohr's model by using the Bohr's postulate and stuff like that. So, also the, you know, the discrete energies can be always can be well represented pictorially also using the Bohr's model, but in general, despite its rather ad hoc linkage between classical and quantum concepts, the Bohr's model was very successful, it provided for the first time, a robust explanation of the existence of stable electronic orbits in an atom, and its predictions actually matched with experimental spectra of atomic hydrogen.

It could also predict the Rydberg constant. So, all these things were the good part of the Bohr's model, though, it feels a little ad-hoc because of the postulates because of the way that it is stitched together, but he could explain the discrete energies, he could explain the transitions, he could explain a fundamental constant, he could also explain that why this electronic orbits are going to be very stable. So, this was more or less consistent, I should say, a consistent theory which uses classical mechanics and tries to explain from the quantum mechanical concepts that we have over here.

And we also saw the de-Broglie hypothesis, that you know, by what is what is matter wave and how matter wave is associated for large matter, the matter wave is very small not so, when you are actually doing with an electronic orbit of an atomic hydrogen for example. We could actually get these 2 things.

Now, let us do a very quick problem say the de-Broglie wavelength rather destroyed by an example, say A a golf ball with the mass is about 0.04 kg. It starts at a velocity of 35 meter per second. Then of course, the electron. The electron in Bohr hydrogen atom. This is just a quick calculation just to show.

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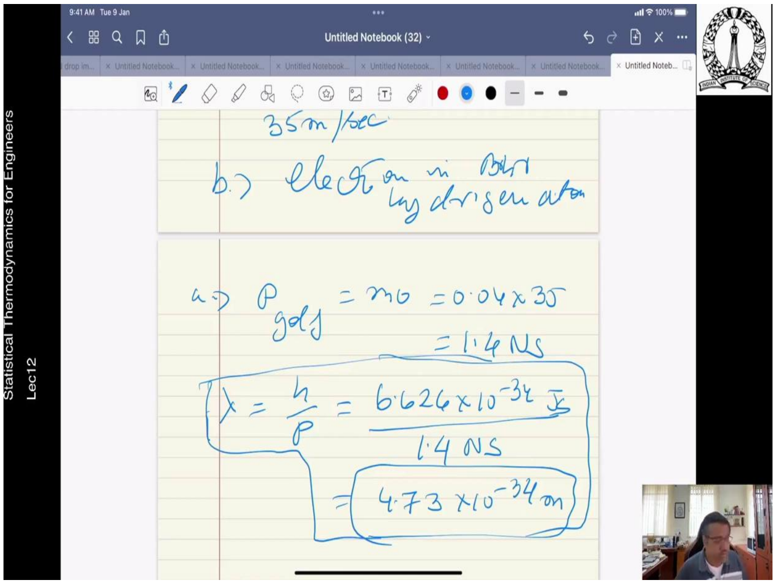

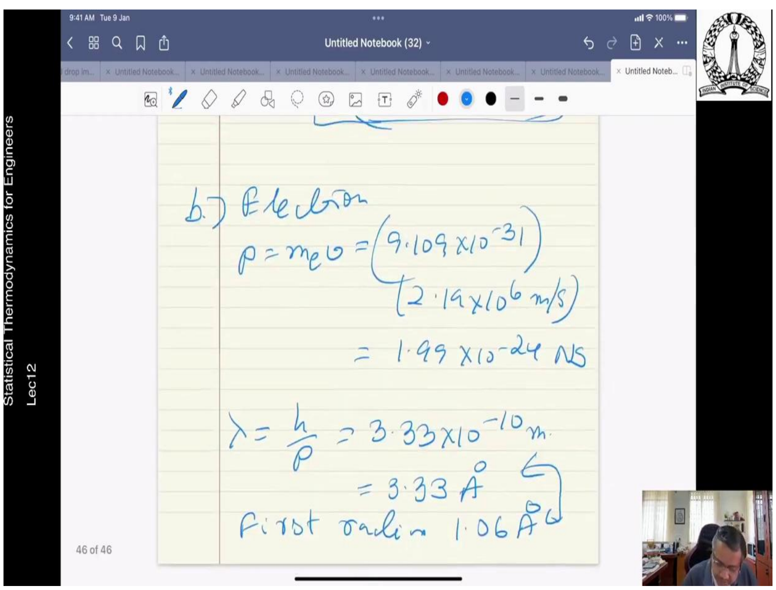

So first what we do the linear momentum of the golf ball is basically mv which is equal to 0.04 into 35, which is about 1.4 Newton second. So the de-Broglie wavelength, the lambda becomes h by p, which is 6.626 into 10 to the power minus 34 joule second divided by 1.4 Newton second which gives you 4.73 into 10 to the power of minus 34 meters.

You can see how small this wavelength is, very small indeed, and more massive objects will have even lower wave length. So, minus 34, this is much smaller than the size consequently, that matters waves do not have any influence on the dynamics, that is why you could hit a golf ball and you could predict where it is going to go, well, the fluid mechanics part of it can be complicated, but technically it is still deterministic. So, you can say where the ball will go.

On the other hand, if we look at the electron, electron p MeV is 9.109 10 to the power minus 31 this is the electrons mass into 2.19 into 10 to the power meter per second that is velocity. So, this gives you 1.99 into 10 to the power of minus 24 Newton's second.

The lambda for the electron will be H by p. So, that is about 3.33 into 10 to the power of minus 10 meter. So, it is about 3.33 angstrom which is comparable. So, Bohr's first radius is about 1.06 angstroms. So, these 2 are kind of comparable, they are in the same ballpark, therefore, we must expect quantum effects for atomic hydrogen which we saw in its initial spectrum.

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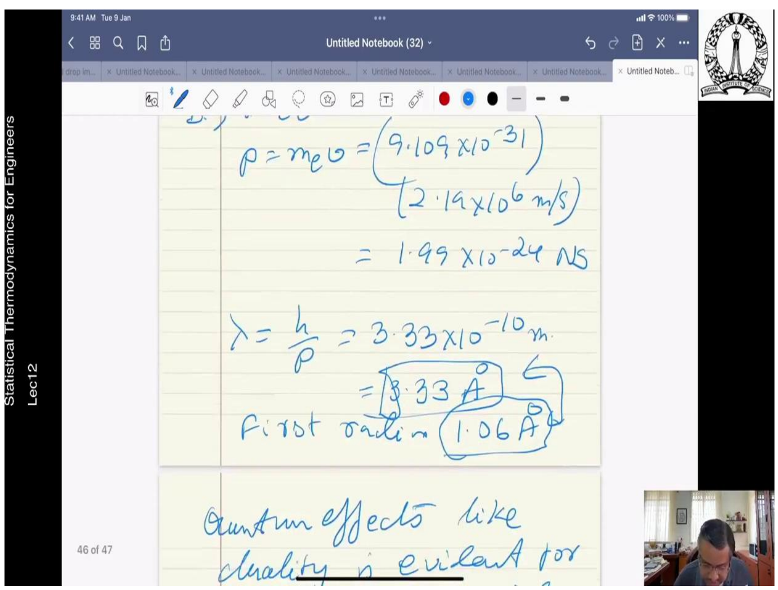

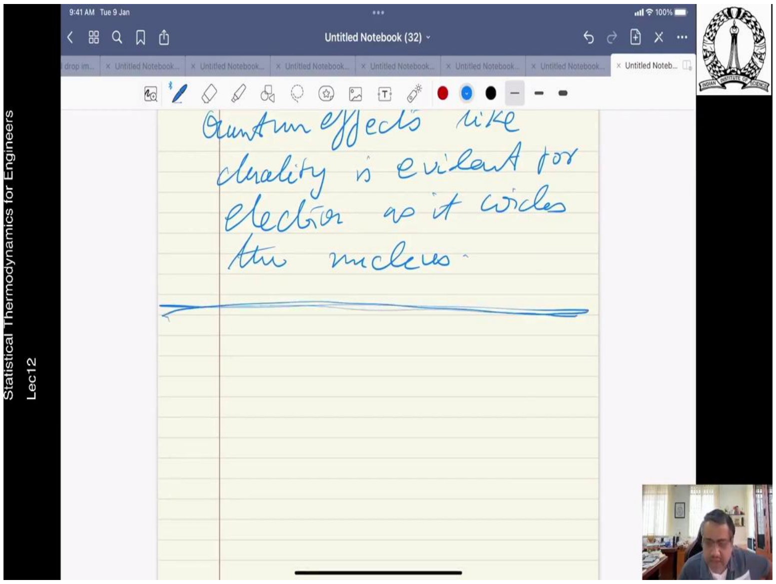

Quantum effects like this duality is evident for electron as it circles the nucleus. So, you cannot avoid it because these 2 are the similar order. Almost close, one is one third of the other, so, this is just to show that why the matter waves are like that and we have provided a more or less good understanding that how the Bohr's model though ad-hoc is actually successfully explaining many of the things in the hydrogen spectrum.

But, however, we can still see that there is a lot of lacunae, there is no clear cut theoretical perspective or theoretical framework as such, as such which we need to go to Schrodinger's wave equation and that we will do in a heuristic fashion, not in a kind of rigorous fashion and we will see how the Schrodinger's wave equation can be used as a first stepping stone to explain the entire Quantum mechanics. See you in the next class. Thank you.