Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 30
The Internal Motion for a 2 particle system

So, welcome to lecture number 20 of the Statistical Thermodynamics course. So, we laid the foundation that for a 2particle system what would be the steady state version of the Schrodinger's wave equation. And we also say now we need to separate the internal and the external energy modes.

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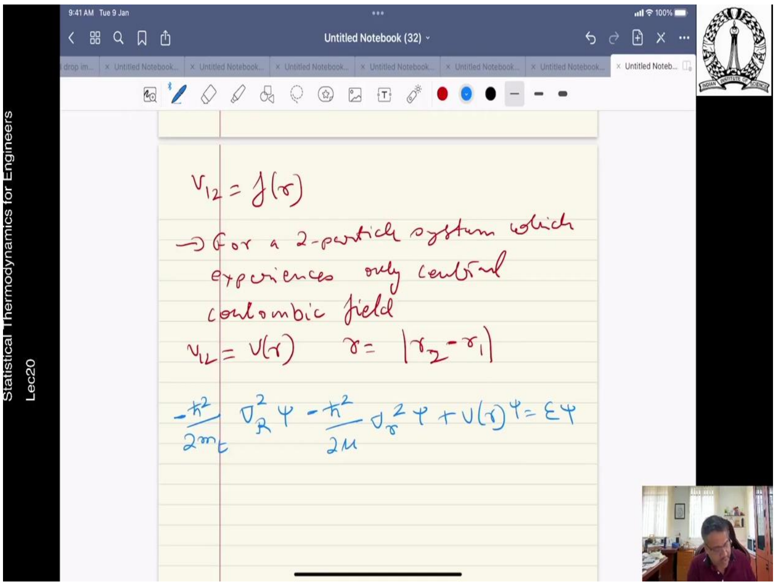

So, for that, if you recall, we wrote that V 12 is a function of r only and for a 2-particle system, 2 particle system(())(00:38) which experiences only central coulombic field, so, V 12 as we said, it can be written as Vr. r is basically r2 minus r1 and the wave function can be written as 2, this is a total mass recall, this is the Laplace operator, this is 2 mew psi epsilon psi. So, this is called, this is a steady state version of Schrondinger's(())(1:40) wave equation and the Hamiltonian operator we already know.

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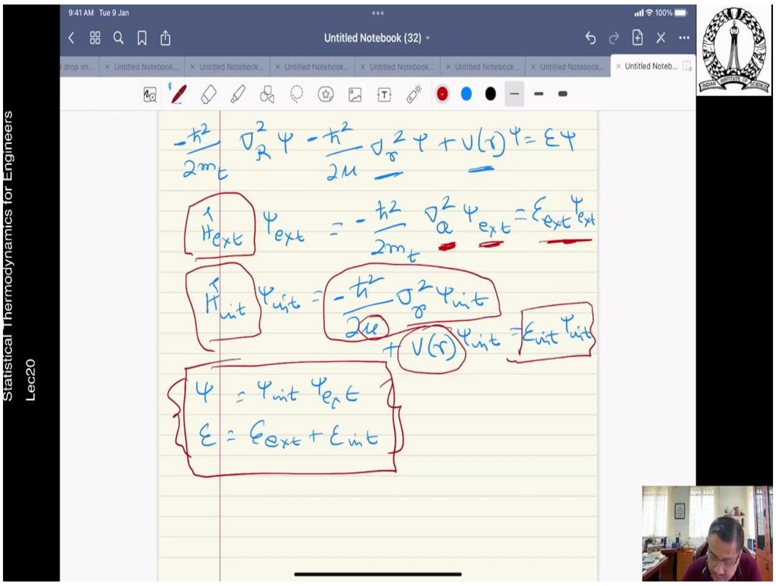

So, H external into Chi external, this is the wave function due to the external energy mode 2 mt r square psi external which is equal to energy external psi external because as we know that this is, these 2 are due to the relative motion extended and internal, h internal psi internal will be equal to the reduced mass mew, this time it will be the r, that is a separation, chi internal, it is equal to plus I have the Vr which is the internal potential, internal energy internal to psi internal.

So, the total psi, the total wave function written as psi internal into psi external energy is equal to E external plus E internal. So, what we did was that we this is the Hamiltonian or the external wave function which is given by remember your r, r is basically the r was this, this is the center of mass. So, it is like the movement of the center of mass so to say.

So, that takes care of external and the total energy like this, whereas, when you go to the internal Hamiltonian, the internal energy modes, it is basically dependent on small r which is the separation distance between the 2 masses and that is given by this, this is the reduced mass if you recall, Vr we say it is always dependent on the relative distance between the 2 particles and it is given therefore by this. So, these are the 2 separated forms and the total wave function is actually multiplicative, the total energy is additive to begin with.

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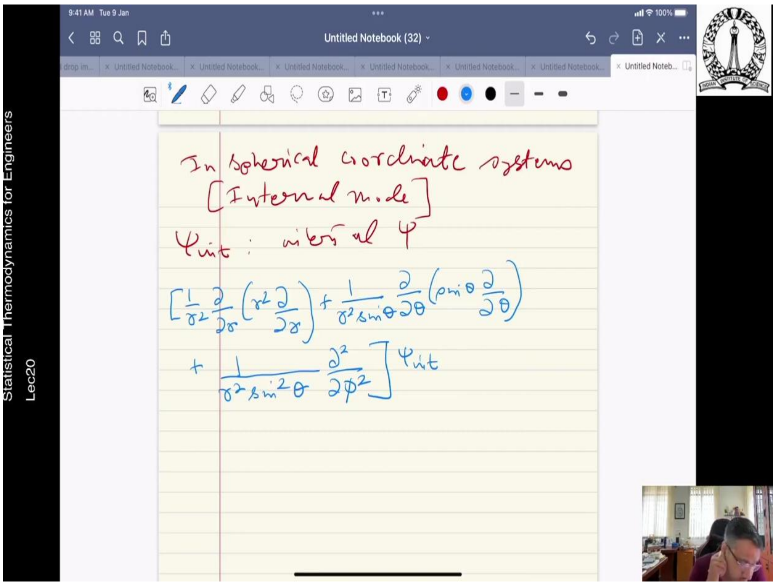

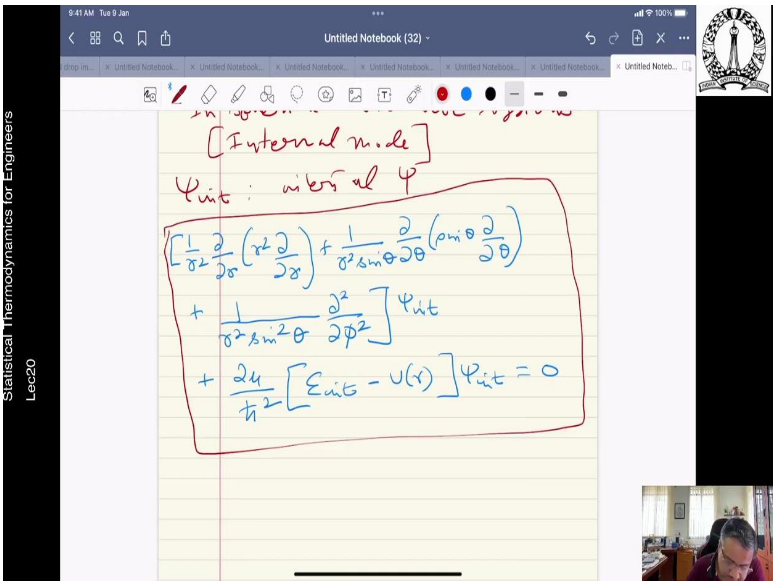

So, in spherical coordinate system and we will have a separate lecture or a tutorial on spherical coordinate system so that there you can be more conversant of what it is. So, this is what internal energy mode. So, this is the internal wave function psi. So, now if you spread out right the total thing in a spherical coordinate system, basically the Laplace operator, you will find it. So, this is basically the Laplace operator. Now, if you try to do that, you will find 1 by r square here is a long equation, so bear with me… (())(02:26) sin theta, delta by delta theta sin theta… then plus 1 by r square sin square theta, delta square by delta phi square… psi internal. So, as you can see that this is how you write the Laplace operator in the spherical coordinate system.

So, this requires a little bit of brushing up your part(())(06:07), this Laplace operator is very common. So, this is basically now internal(())(06:15) minus ur psi internal is equal to 0. So, this is how it is written in the spherical coordinate system, the internal energy part of the wave function and internal and external are independent as we saw earlier.

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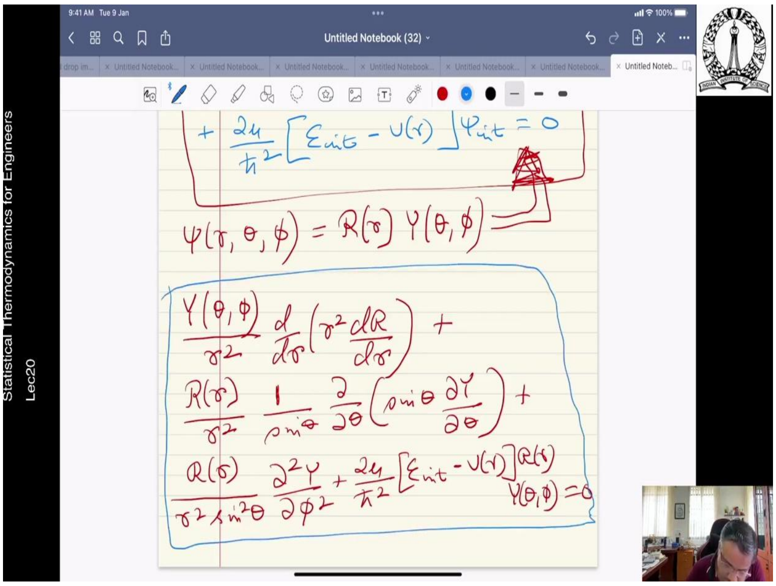

So, psi therefore is r theta phi, these are the 3 coordinates r theta phi for a spherical coordinate system, that is given as R r into Y theta, phi, first level of separation, so, now when you back substitute that this separation into this equation here, substitute it here given as Y theta, phi, r square d by d r plus, this again a long equation, so bear with me…R r by r square 1 by sin theta, delta by delta theta sin theta delta Y by delta theta plus R over small(())(08:07) r square sin theta delta square Y by delta theta square plus 2 mu by h square E internal ur Rr by Y theta, phi is equal to 0, we do now so you can see this is a very complicated equation we have separated out of the two bit.

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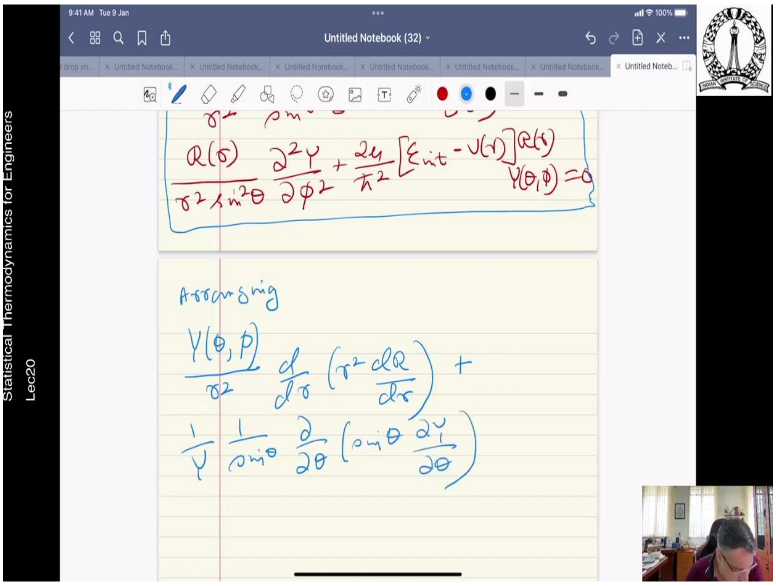

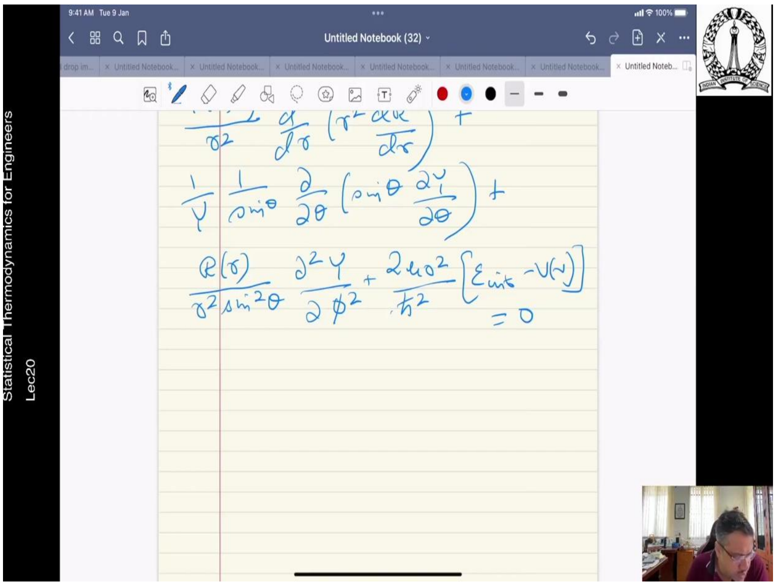

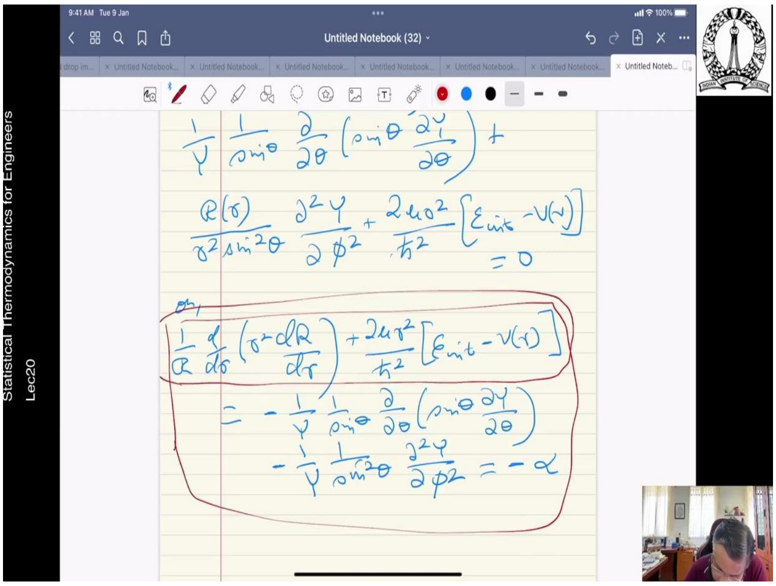

So, arranging, what you do is arranging, this is Y theta, phi divided by r square d by dr square dR upon dr plus Rr by r square plus 1 by Y sin theta delta by delta theta sin theta dY by d theta plus Rr by r square sin square theta delta square Y by delta theta square plus 2 mu by h square E internal ur Rr Y theta, phi is equal to 0 (())(10:32)… 2 mu r square divided by h square E internal minus Vr is equal to 0, so, that is the total expression….

Now, what we do now is basically you separate the two things to the 2 sides like if you do in a typical separation variable, so it will be 1 over R d by dr square plus 2 mu square by h bar square E internal minus Vr which is equal to, so right hand side is O r minus 1 over Y sin theta d by d theta sin theta dy by d theta minus 1 by Y sin square theta d square y phi square is equal to minus lambda… So, that is the expression that you get by separating out. So, this part is the function r, this part is a function of theta and phi and this is basically the constant that you are dealing with.

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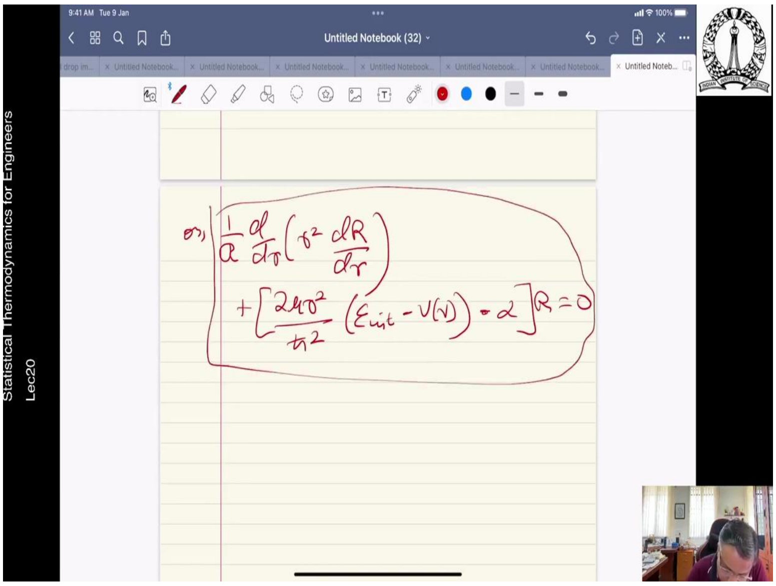

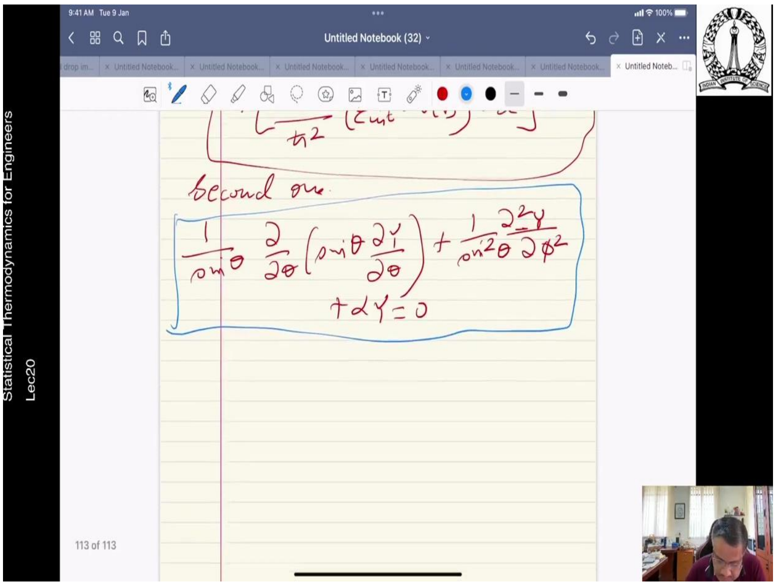

So, if we now separate the 2 things out, it will be 1 over r d by dr square dR by dr plus 2 mu square by h bar square to the internal energy minus Vr minus alpha into capital R is equal to 0, so, that is the first expression and the other one. So, this is one, second one, so let us write it as plus R… Second one is 1 over sin theta d by d theta sin theta into dY by d theta plus 1 over sin square theta square Y sin square plus alpha y is equal to 0.

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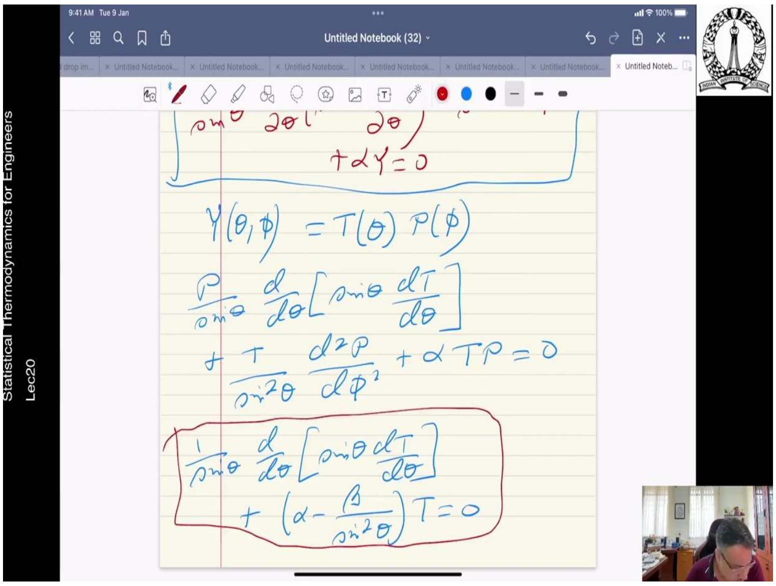

Now, similarly Y, as you know is a function of theta, phi, so this can be written as T theta P phi. So, this can be further then broken up by P sin theta dT by d theta plus T by sin squared theta d square p by d theta square plus alpha TP is equal to 0. Now, 1 over sin theta d by d theta sin theta dT by d theta plus alpha minus beta sin squared theta is equal to 0, alright equal to 0.

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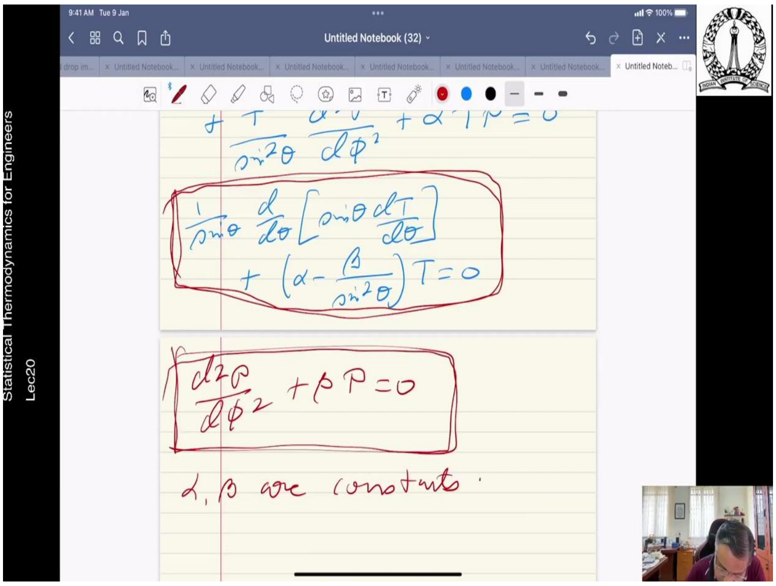

And the other expression is d square P by d phi square plus beta P equals 0. So, as you can see, this is the third one. So, as you can see alpha and beta are constants. So, how many equations did we get? We got this expression which was with a function of r; then we got this expression which was a function of theta and this expression which is a function of pi. Because of r theta pi, 3 expressions and out pops 2 constants, alpha and beta; alpha was to separate r from theta r phi, Beta was to separate between theta and phi.

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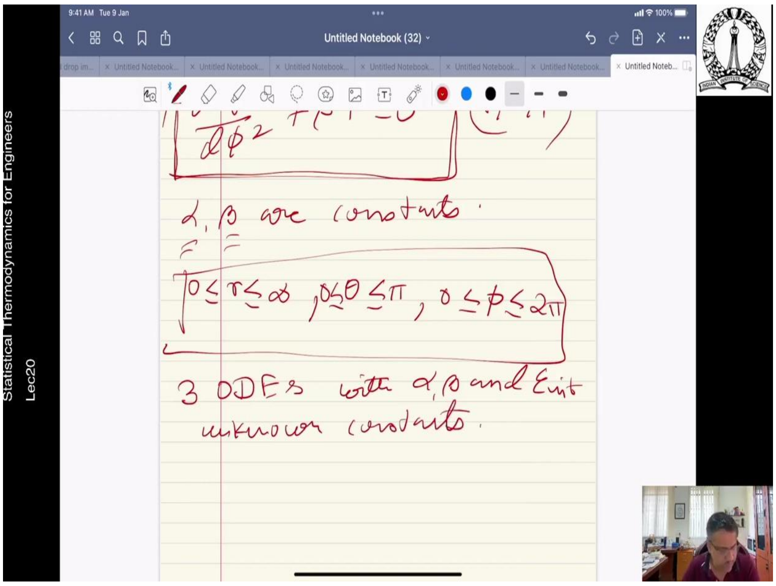

So, the limits are r varies from 0 to infinity, theta of course, varies from 0 to pi and phi is from 0 to 2 pi. So, this is a spherical coordinate system the limits. So, we have basically what 3 ODEs with alpha, beta and E internal unknown constants, correct? Alpha, beta and E internal, unknown constants correct. So, now, let us focus on one by one what we can do with this.

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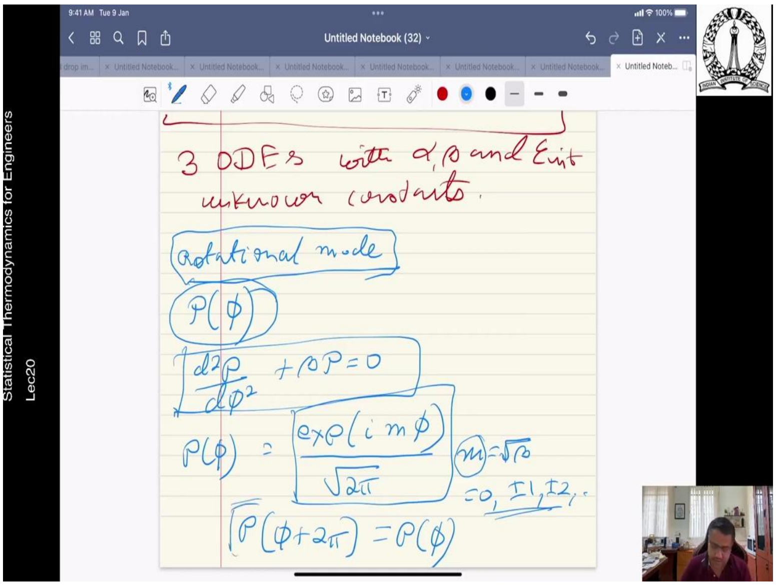

So, first let us take a look at the rotational mode, so rotational mode by P of phi. So, the solution to this actually lies dP by square plus theta p is equal to 0. So, solution to this and P phi is equal to exponential i m phi divided by lambda, where n is equal to root over beta is equal to 0 plus minus 1 plus minus 2 and this also obeys pi plus 2 pi equal to... So, let us take a second pause and let us look at it.

So, this is the rotational mode which is given by E pi and this is the expression and then if we solve this P phi, it is given in this particular form where this is m, m is nothing but root over beta and is given by 0 plus minus 1 plus minus 2 and with argument that P is a periodic function. So, phi plus 2 phi is equal to the d phi once again. So, this gives you the first expression.

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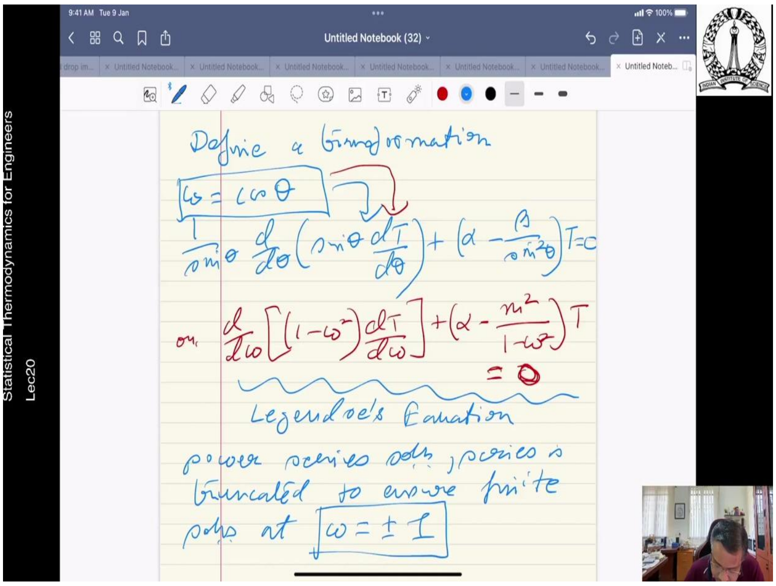

So, now define transformation. What is the transformation? Say, defined omega is equal to cos theta. So, therefore, 1 over sin theta d by d theta sin theta dT by d theta plus alpha minus theta sin squared theta T is equal to 0, this you remember, this is for the theta. If you replace omega equal to cos theta in this particular expression, so, what you get? d by d omega 1 minus omega square dT by d omega plus alpha minus m square T is equal to 0.

So, sin theta is 1 minus sin squared. So, this expression if you look at it closely, this particular expression over here if you look at it closely this is as, this is called the Legendre's equation, comes from spherical harmonics actually, spherical symmetry anything that goes through single symmetry, Legendre's equation.

So, this obviously usually has a power series solution and the series is truncated to ensure finite solutions and omega equal to plus minus 1. So, this is Legendre's equation and this is how this has got a power series solution and the series is truncated to ensure finite solutions and omega equal to plus minus 1.

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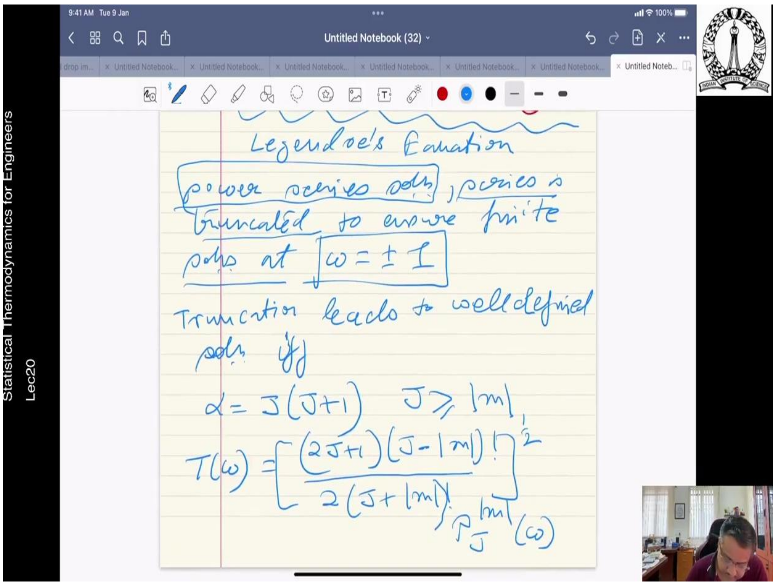

So, truncation leads to well defined solution. Remember, that the wave function has to be well defined and all those things, well defined solution if and only if alpha is equal to J into J plus 1 where J must be greater than or equal to delta m modulus m and the solution of T omega because we have substituted theta with omega is given as 2 J plus 1 into J minus mod m in factorial divided by 2 J plus m factorial and this entire thing is raised to be power of half multiplied by PJ omega.

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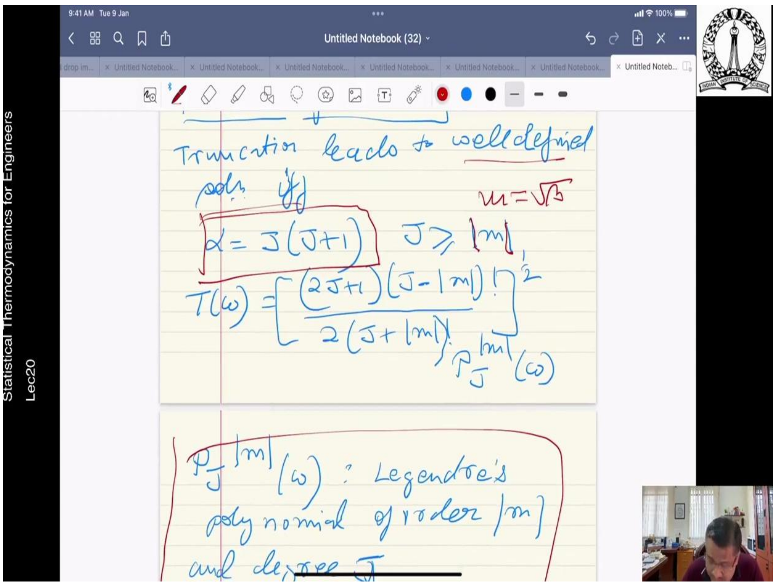

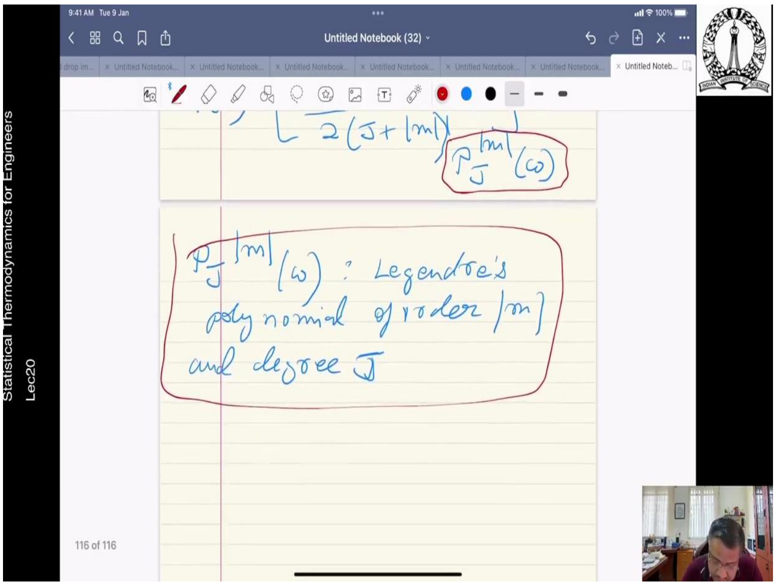

So, out of that this PJ modulus of this m is basically called the Legendre's polynomial of order m and degree J, if you know, so, this is a mathematical manipulation. So, truncation leads to well defined solution if and only if alpha is J to J plus 1 and J must be greater than equal to m where m we know is root over of beta and it has got that 0 plus minus 1, etc and the total solution that becomes T which is the theta part of the solution is given by this, multiplied by this polynomial which is PJ, this is called the Legendre's polynomial of order m and degree j. So, this is the total solution.

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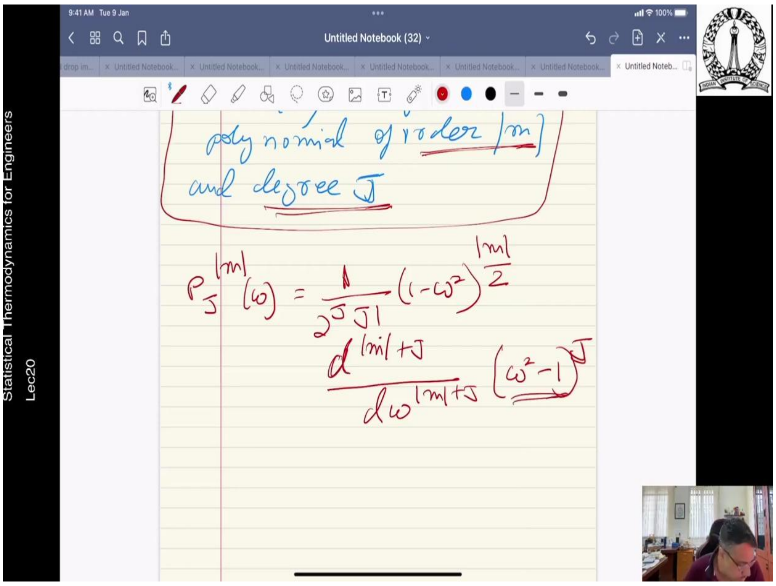

So, the total solution, so, what if I open up the Legendre's polynomial, let us write that also J over m omega is given as again complicated J factorial 1 minus omega square w whatever you call it 2, then write it like this, this is the differential plus J omega by d, this is the lower part of the differential omega square minus 1, this is the order of the differentiation. So, this is the order differentiation with respect to omega and this is done on omega squared minus 1 raised to the power of J. So, this is the Legendre polynomial.

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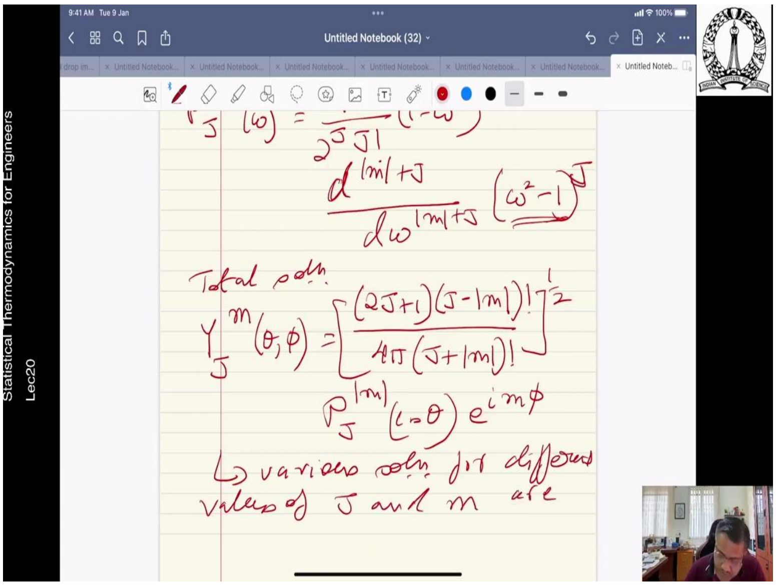

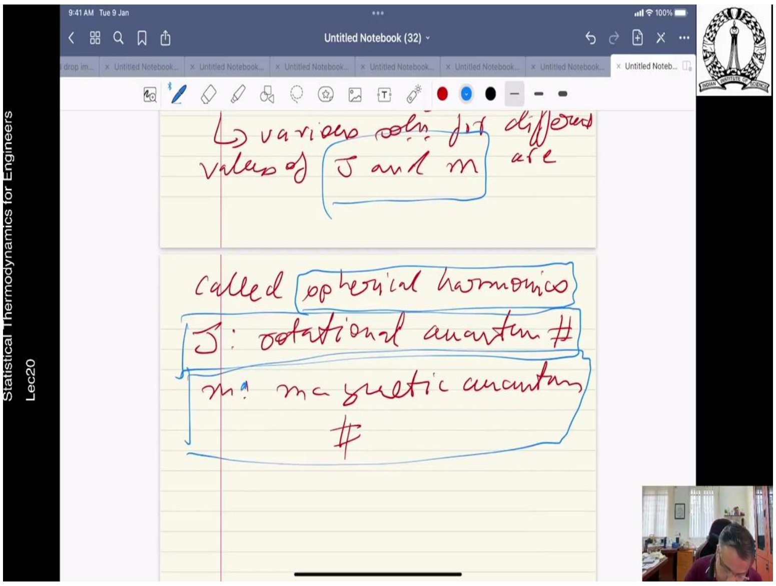

So, the total solution becomes, total solution it is given as Y J m theta, phi is given as 2 J plus 1 into J minus modulus of m factorial divided by 4 pi J plus modulus of m factorial entire thing is raised to the power of PJ modulus m cos theta e i m phi. So, various solutions for different values of J and N are called spherical harmonics. So, J is therefore, the rotational quantum number and m is called the magnetic quantum number.

So, various solutions for different values of J and M are possible, these are basically called as spherical harmonics and J has not the official name of this for the rotational quantum number and M is called the magnetic quantum number. So, from this total(())(26:38) solution y which concerns the theta and pi, this is the solution that we get. So, quick recap what did we do?

We found out the rotational mode. For the rotation we first did d phi, then we defined the transformation, we then cast it in this particular form which is basically nothing but the Legendre's equation well known, it is a power series solution, the series gets truncated to ensure finite solutions and truncation leads to well defined solution if and only if it alpha is like that, and then we wrote that this is cast in terms of a Legendre's polynomial and Legendre's polynomial is of the order m and degree j to the modulus of m because m can be plus minus.

And then of course, the Legendre's polynomial is written in this particular fashion, then the total solution becomes this and this has got various solutions for different values of J and m and these are called spherical harmonics and J is therefore called the rotational quantum number and m is called the magnetic quantum number. So, rotational and the magnetic quantum number. And therefore, this marks the end of theta and phi solutions. In the next class, we will see what happens to the r part of the solution, that we are going to cover in the next class. Thank you.