Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 27
The Pauli Exclusion and the Correspondence Principle

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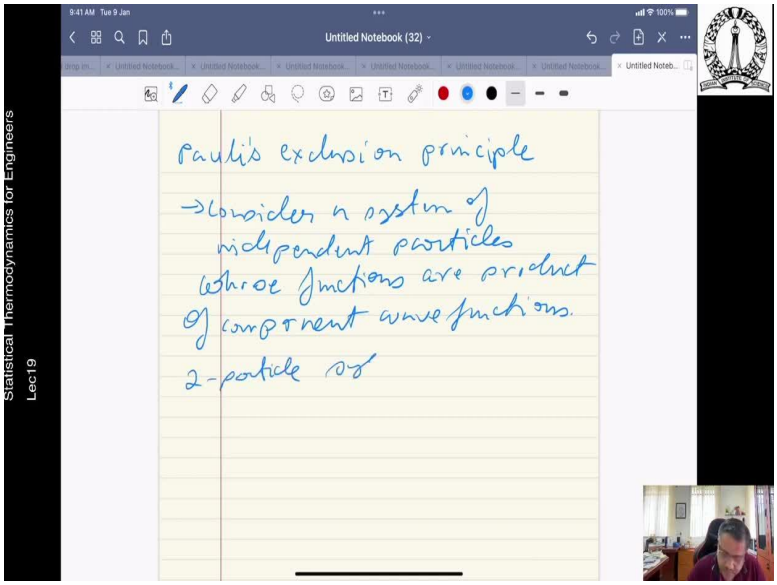

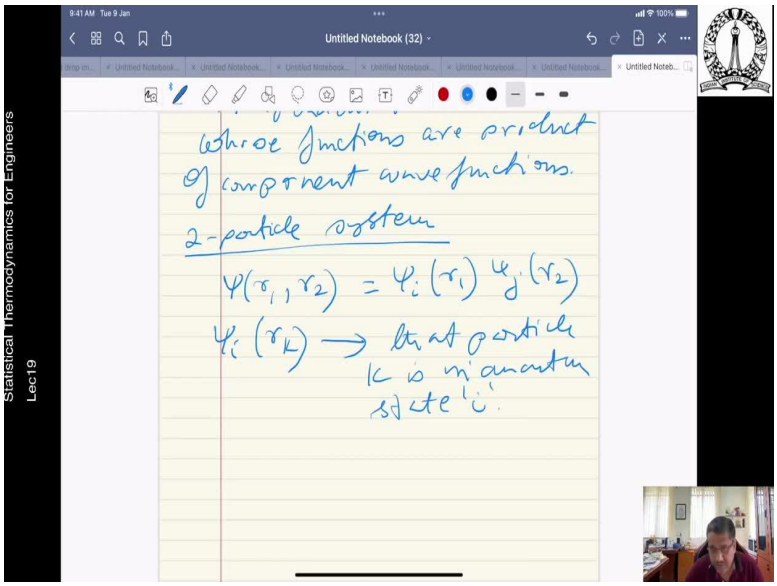

Welcome to lecture number 19 of the statistical thermodynamics course. So, in this particular lecture, we are first going to look at Pauli's Exclusion Principle. So, Pauli's Exclusion Principle as the name suggests was developed by the German physicist Wolfgang Pauli was also known as functions of physics. The principal directive follows from the symmetry requirements of the wave functions that we just covered in the previous lecture. Now, let us consider to rationalize this let us consider a system a system of independent particles whose wave functions can be is like multiplicative is a product of the component wave functions.

So, for us say let us take a 2-particle system here, so in this 2-particle system let us write the total wave function r1, r2, is given as a Psi i r1 into r2. So, product of a two wave functions. So, Psi i rk it is basically designates that particle k is in quantum state i. And fortunately, this particular thing suggest that the wave function is neither symmetric nor anti-symmetric with respect to the exchange of 2 particles. So, if we exchange 2-particles we cannot say whether this wave function is symmetric or anti-symmetric.

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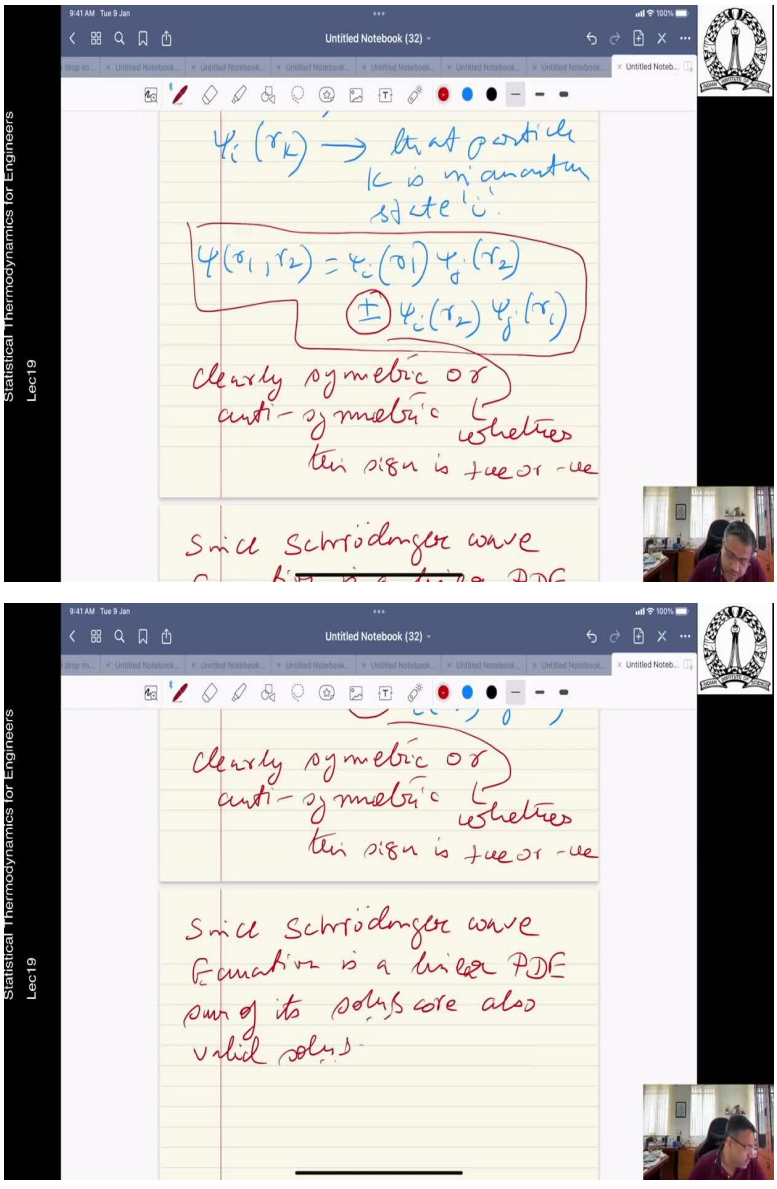

Now, if I on the contrary write it like r1, r2 is equal to Psi i r1 Psi j r2 plus minus Psi i r2 Psi j r1. If I write it like that, this is clearly either symmetric this is clearly either symmetric or anti-symmetric depending on whether this sign is positive or negative. So, clearly so that is the symmetric or the anti-asymmetric wave function. So, because the Schrodinger wave

equation is a linear partial differential equation, since the Schrodinger wave equation is a linear PDE or partial differential equation the sum of its solutions are also valid solutions. So, that means this is therefore clearly a solution, this particular thing that we have written is clearly a solution of the Schrodinger wave equation. So, this equation therefore satisfies a parent wave equation plus any symmetry requirement that you might have.

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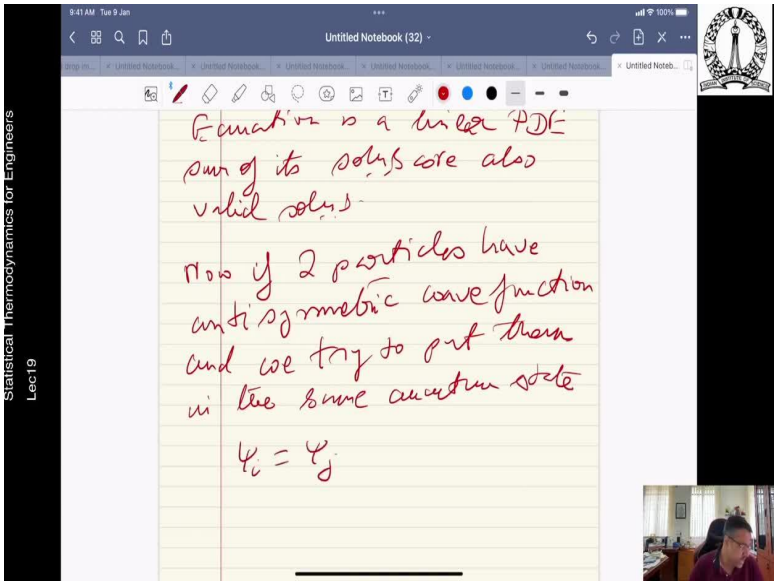

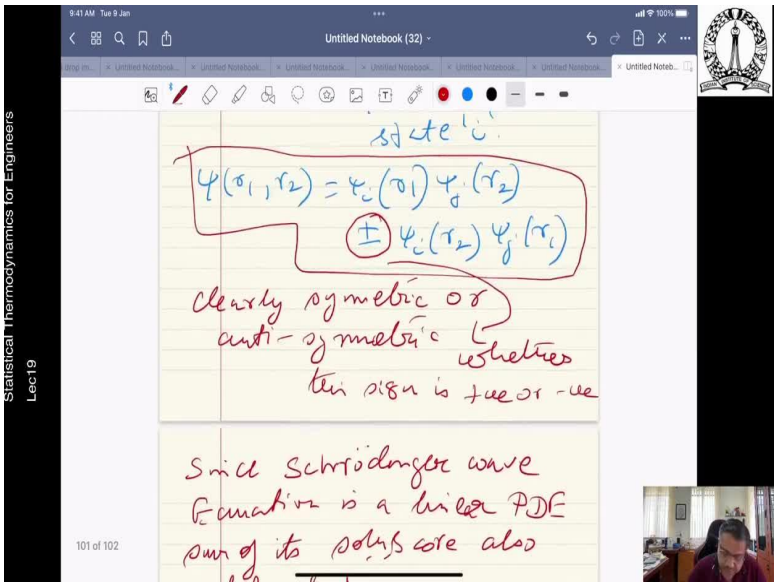

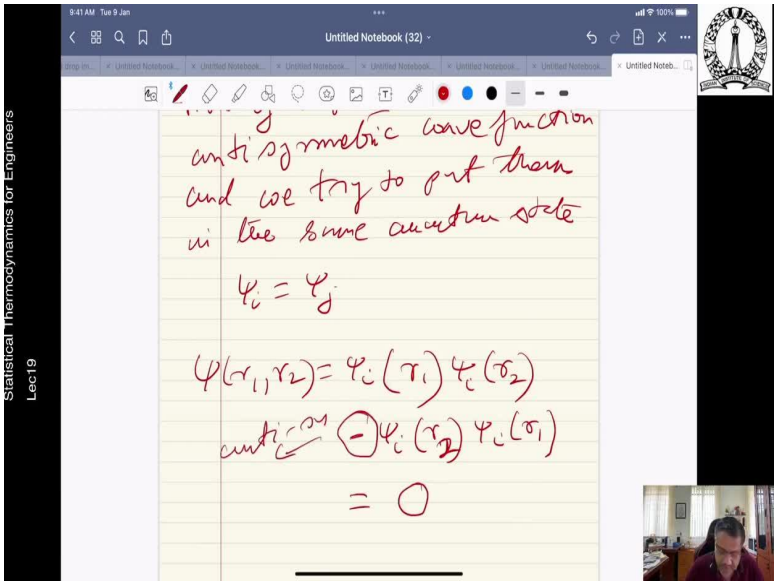

Now, let us assume now if 2 particles have anti-symmetric wave function and we attempt to put them in the same quantum state and we try to put them in the in the same quantum state which essentially means that Psi i will be equal to Psi j. So, therefore, the equation that we wrote previously which is this equation will now become Psi r1, r2 is equal to Psi i r1 into Psi i r2 minus Psi i r1 Psi i r2 Psi r1 that is equal to 0. So, why we have a negative sign because it is anti-symmetric that is the reason.

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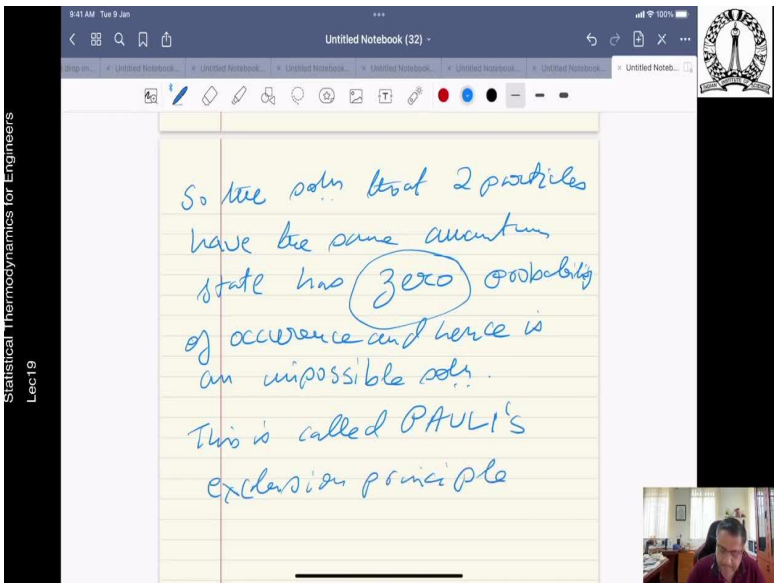

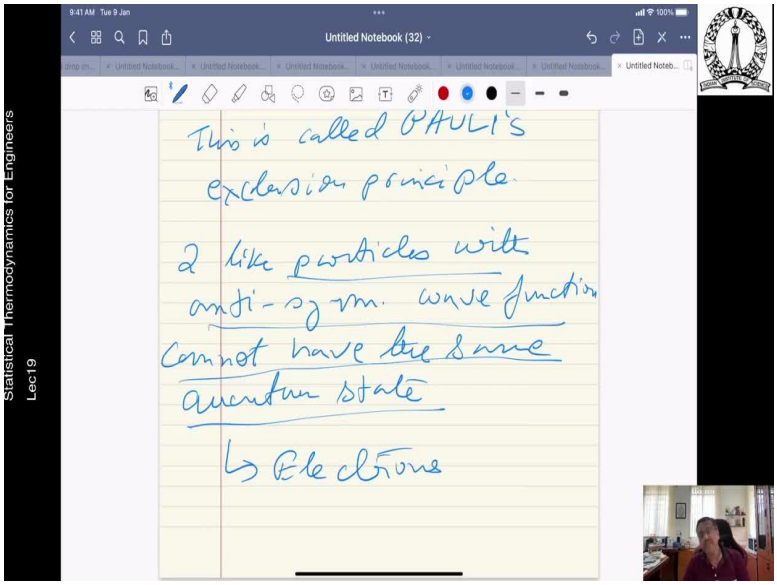

So, this essentially translates to what that means, otherwise the contemplated solution so the solution is that 2 particles have the same quantum state has zero probability as zero probability of occurrence hence is an impossible solution. So, this important result is all the Pauli's Exclusion Principle this is called Exclusion Principle. Or in other words, two light particles with anti-symmetric wave functions cannot have the same quantum state. In other words, 2 particles which has thought the anti-symmetric of 2 light particles with anti-symmetric wave function cannot have the same quantum state.

In the this you write probably your 12 standard and your undergraduate, so this is essentially what it means. So, such particles for example, electrons have such particles, hence because they have anti-symmetric wave function therefore, they cannot have the same quantum state.

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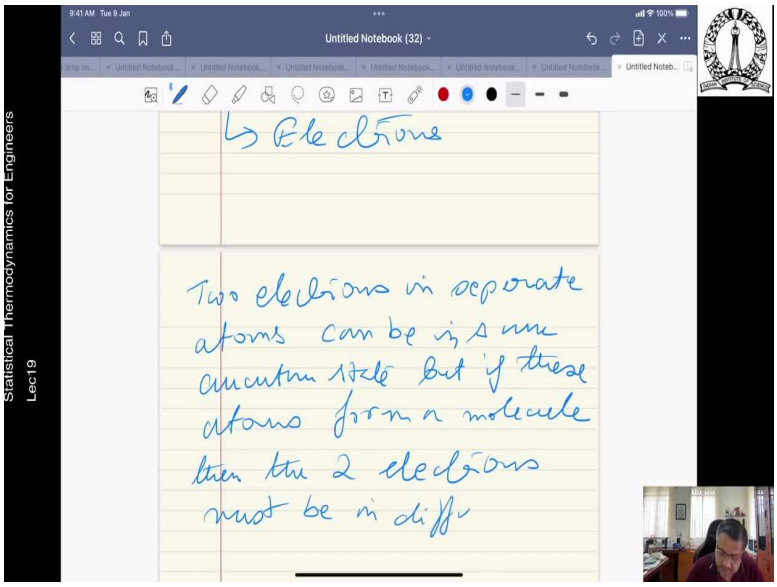

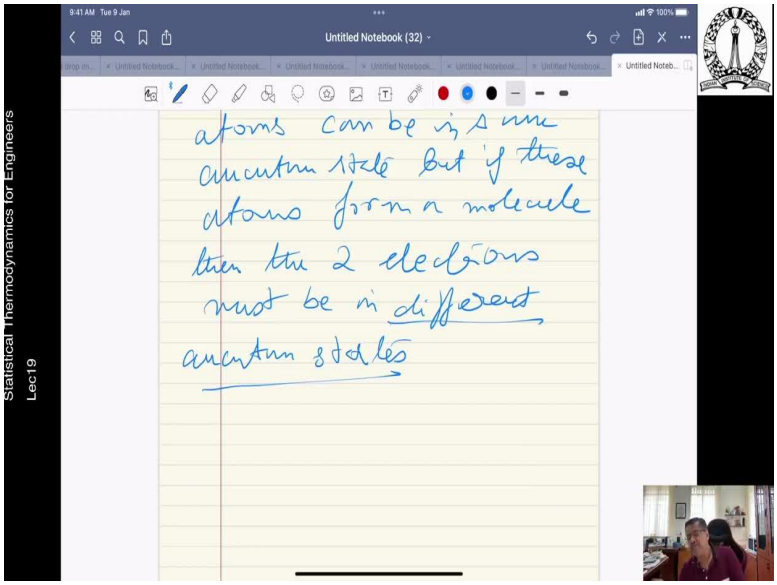

And we will see how the similar other quantum number sounds naturally out of this. So, for example, so 2 particles but they must be belonging to the same multi particle system, that means 2 electrons, just an same example 2 electrons in separate atoms do not classify separate atoms can be in same quantum state but if these 2 atoms form a molecule then then the 2 electrons must feed us to be in different quantum states.

So, in so this is what it is called this is the rationale so the 2 electrodes must be belong to the same multi particle system. If they belong to 2 different atoms which are not linked with each other then they can have the quantum state but when the from the molecule they can become a part of the same multi particle system as a result of that they have to obey the Pauli's exclusion principle.

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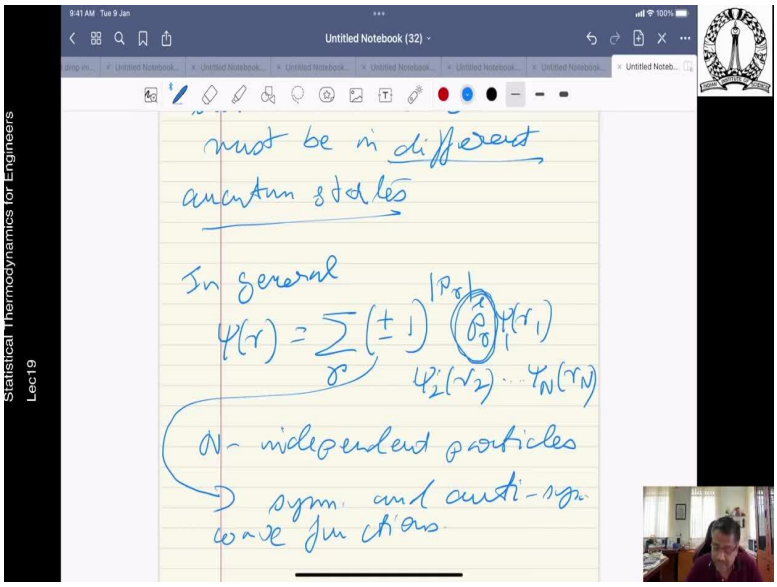

So, in general, we can write it as a wave function is written as r plus minus 1 these are the number of ways in which the particles can be exchanged which we covered in the previous lecture. And this has Psi r1, Psi 2 r2, up to Psi N rN. This is for N-independent particles part of it is, where the positive and the negative signs are invoked respectively for the symmetric and anti-symmetric trade wave functions. So, it is taken over all this is taken over all possible operators by the way. So, hence the overall wave function can vanish only when only if the individual wave functions are anti-symmetric, so that is the reason.

We will be able to use the Pauli's exclusion principle to build up the periodic table for example, I will say chemistry is a lot of quantum mechanics in fact quantum mechanics to be that we talk about. So, just a brief insight that about the correspondence principle right now. So, the correspondence principle was proposed by Niel's Bohr so as we found that the laws of classical physics have been found to work in a macroscopic domain. So, Bohr argued that satisfactory quantum theory must approach his classical counterpart when applied to microscopic behavior.

In essence, the results of quantum and classical mechanics should correspond to each other or larger masses or energy. So, this is the correspondence principle that was proposed by Niel's Bohr. So, more about it later, but you should always take into account that historically quantum mechanics developed from Max Planck and then it is percolated and now, we have this Schrodinger's wave equation and we will see now that what is what we can in the Schrodinger's wave equation, when we start looking at the internal energy moves right now. The translational modes as we saw are miniscule, the energies are miniscule. So, the discretization validation really comes from the internal energy modes.

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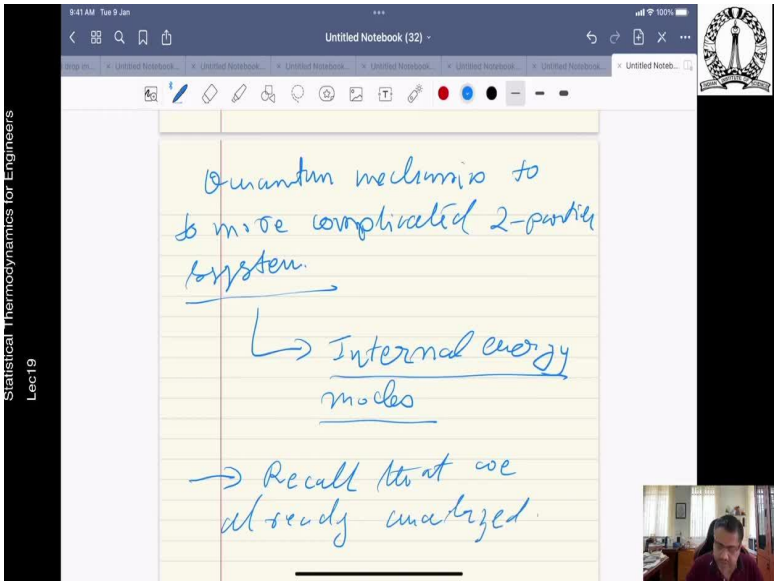

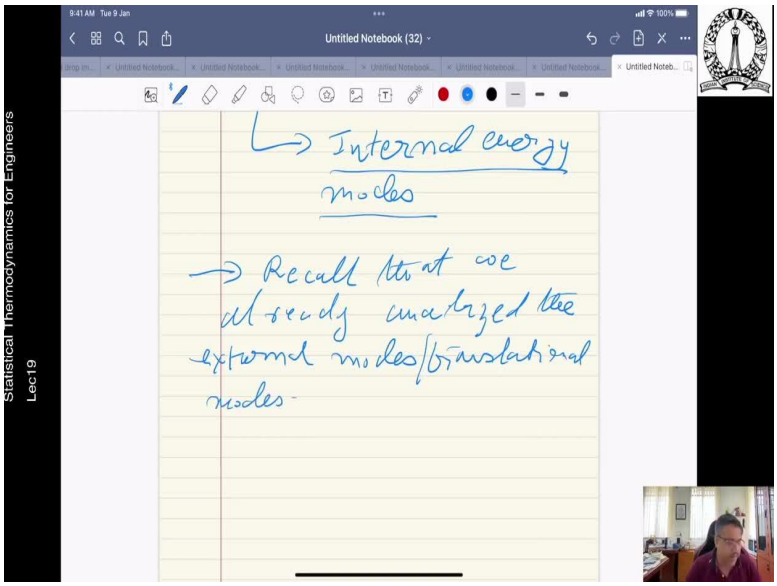

Now to move so we have to apply now the quantum mechanics to in a more complicated system to basically to a more complicated 2 particle system and that sets the stage for the analysis and we will just look at that analysis just a little bit. So, two particle system and we are going to therefore use this to look at the internal energy modes, which we said exists, this is the modes of the atoms the molecules as the vibration, rotation, and stuff like that. So, this is these are the internal energy modes, so we already found the recall that we already analysed the external modes or translational energy modes and that we did it by a single particle system, translational modes.

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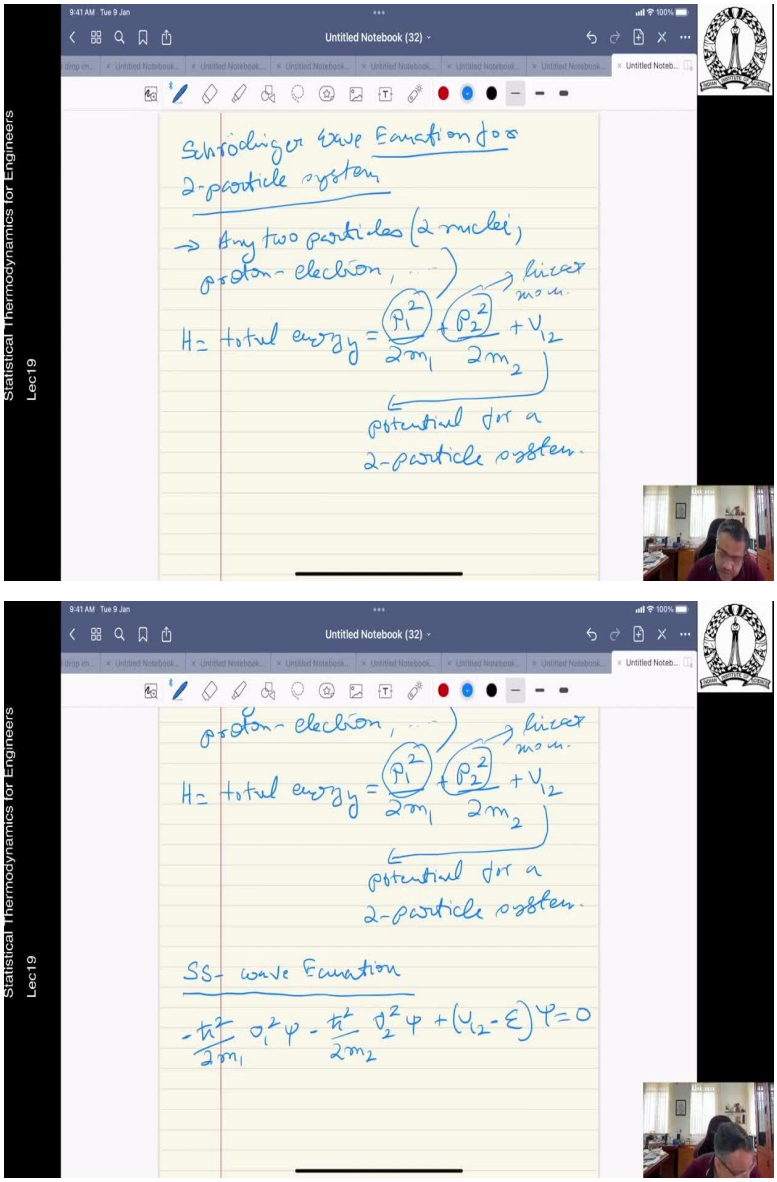

So, let us go to a fresh page and write the Schrodinger's equation, Schrodinger's wave equation for two particle system. So, it can be for example any 2 particles, 2 nuclei, proton-electron, so forth, any 2 particle system. So, let us write first the energy which is H this will be the total energy, for the single particle system remember we said that the potential energy was zero, so in this case of course it is not. P1 square by 2m 1 plus P2 square by 2m 2 plus v 1 2, this is the potential for the 2-particle system. And these are nothing but the linear momentums.

So, what we do next? So, we know the total energy, now we write down what we call the steady state version of the Schrodinger's wave equation, SS-wave equation. So, recall how we did wave equation for multi particle system 2 m 1 into first operator(())(16:50) h square

bar by 2 m 2, m 1 can be equal to m 2 also depending on what particle system you are dealing with plus v 1 2 minus (())(17:02) Psi equal to 0. So, we want to as we said there is a potential for the 2-particle system. So, this is the steady state version of the wave equation.

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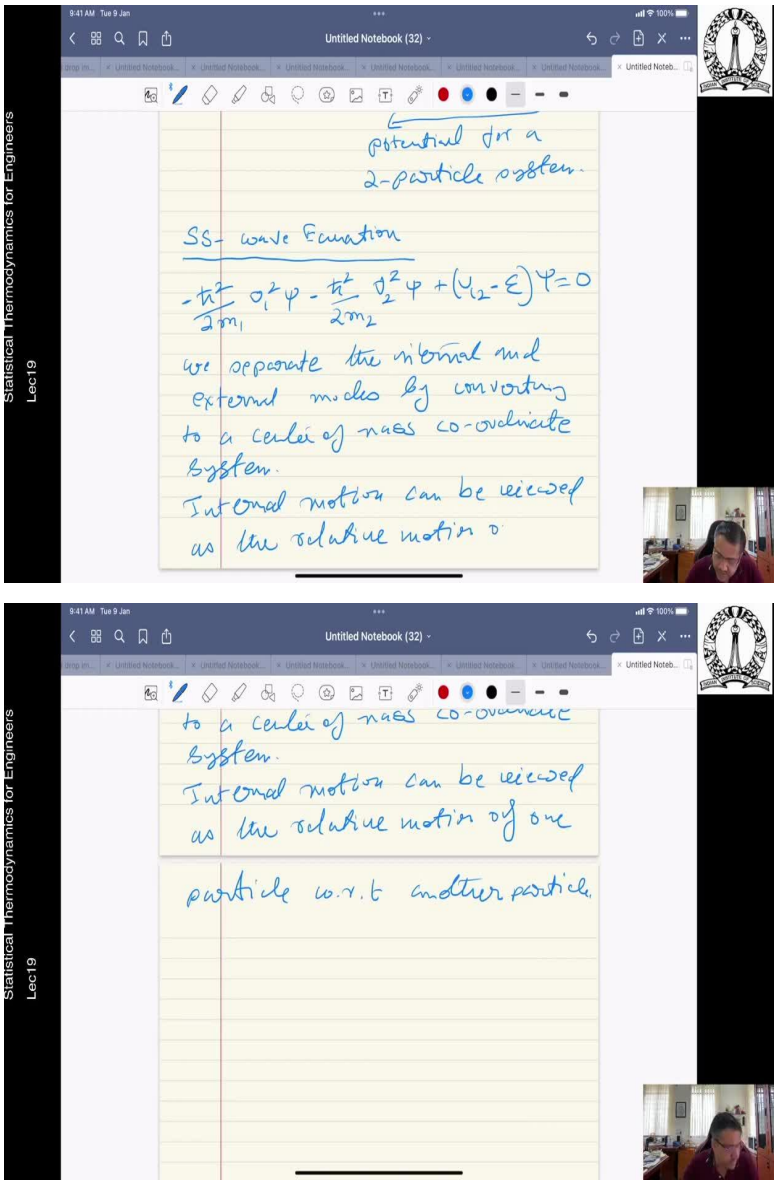

So, what we need to do next is that we separate the internal and external modes by converting to a centre of mass coordinate system. So, the internal motion therefore, once you do this the internal motion can be viewed as a relative motion of one particle with respect to another particle. So, you are sitting on the centre of mass right now, and you are watching the motion so as a result of that the internal motion can be viewed as a relative motion with respect to another particle.

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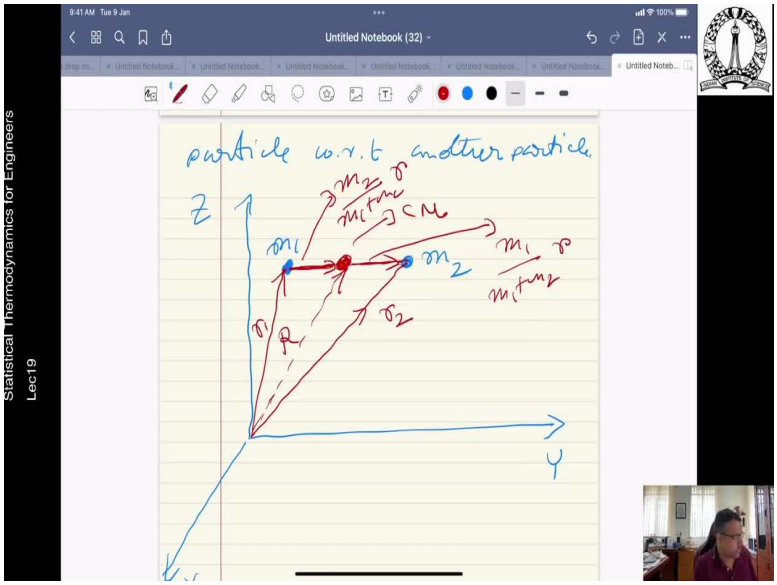

So, if we now draw coordinate axis like this how well I can draw. So, this is x, this is y, and this is z. So, let us say m1, this is say m2 and (())(19:16) let us just put it in a different color now, this is the centre of mass. So, this is your r1, this is your r2, this is your capital R, this mass m1, m2 and. So, this particular so if I joining this particular this is how this centre of mass is located. It is m2 plus m2 into r, r in the total distance, this is this part. This part is therefore written as m1 by m1 plus m2 into r, so (())(20:29) the other part. So, this total distance from r. I think that part is now understood that what this is.

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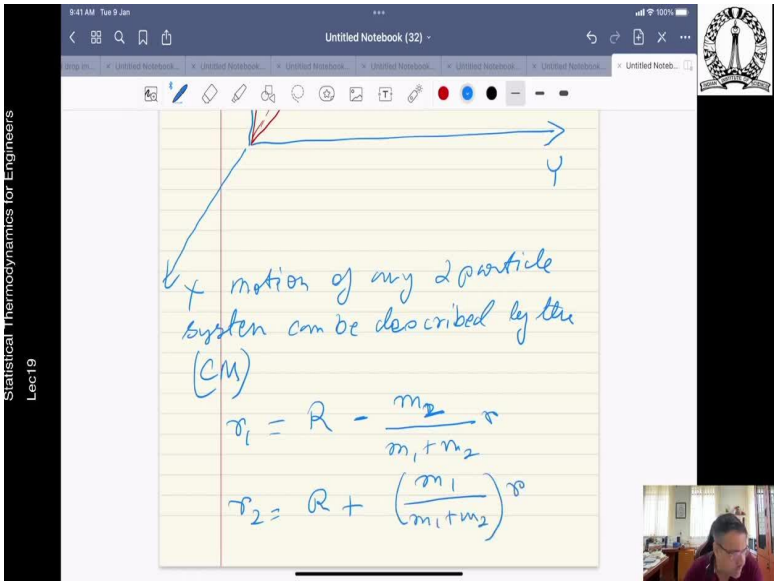

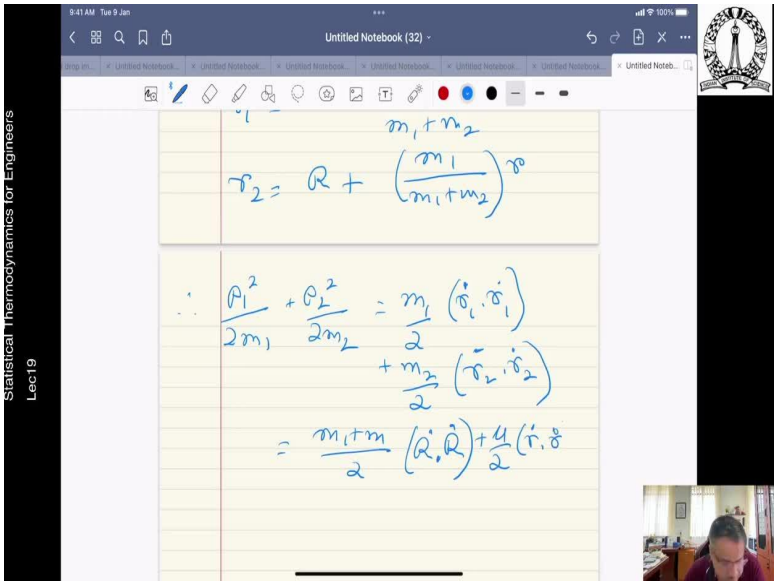

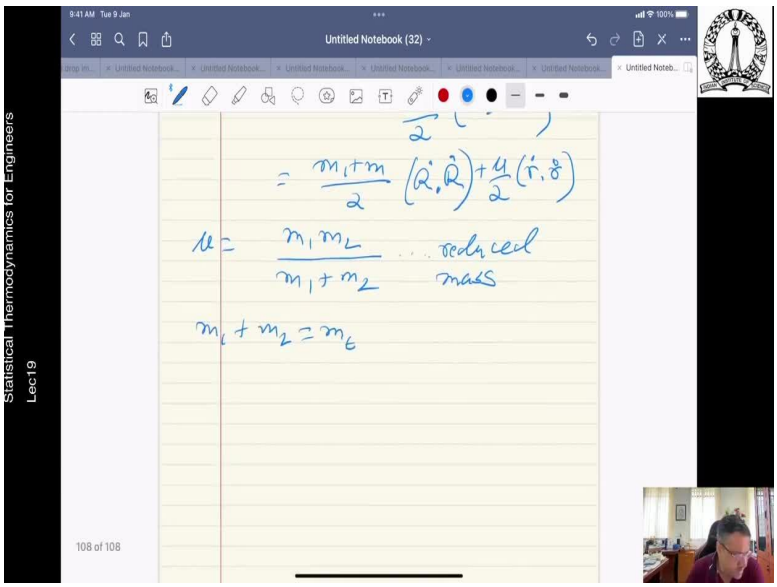

So, motion of any particle any 2-particle system can be described by the CM. So, motion any 2-particle system can be described by the CM nothing but the secular parts. So, r1 is basically equal to R minus m2 by m1 plus m2 into r, r2 R plus m1 divided by m1 plus m2 into r. Therefore, P1 square by 2 m1, P2 square by 2 m2 this give together m1 by 2 into r 1 dot into r1 dot plus m2 by 2 r1 dot into r2 dot is equal to therefore m1 plus m2 by 2 into R dot multiplied by R dot plus mu by 2 equal to small r dot small r dot. Where mu is equal to m1 into m2 divided by m1 plus m2 which is basically nothing but the reduced this is all very classical mechanics as you already know and m1 plus m2 we can write it as a mt.

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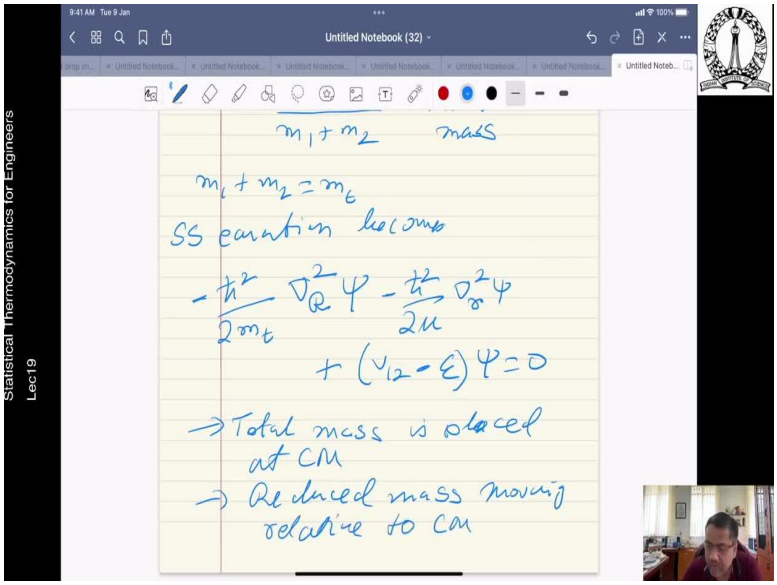

So, the Schrodinger's wave equation therefore, becomes SS equation becomes minus h bar square into 2 mt, into the operator(())(23:32) with respect to R h bar square with respect to the reduced mass this is(())(23:40) square into Psi plus v 12 minus energy into Psi is equal to 0. So, this is an implication is that the total mass is placed at CM, the reduced mass is moving relative to CM.

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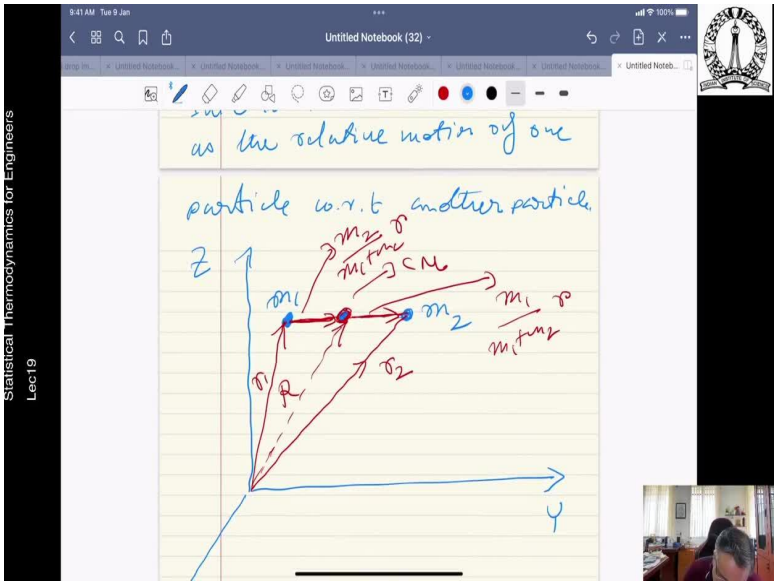

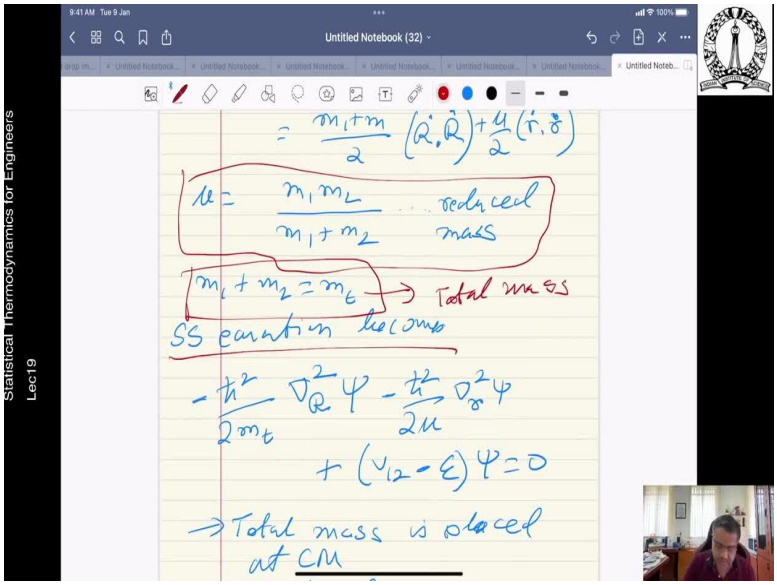

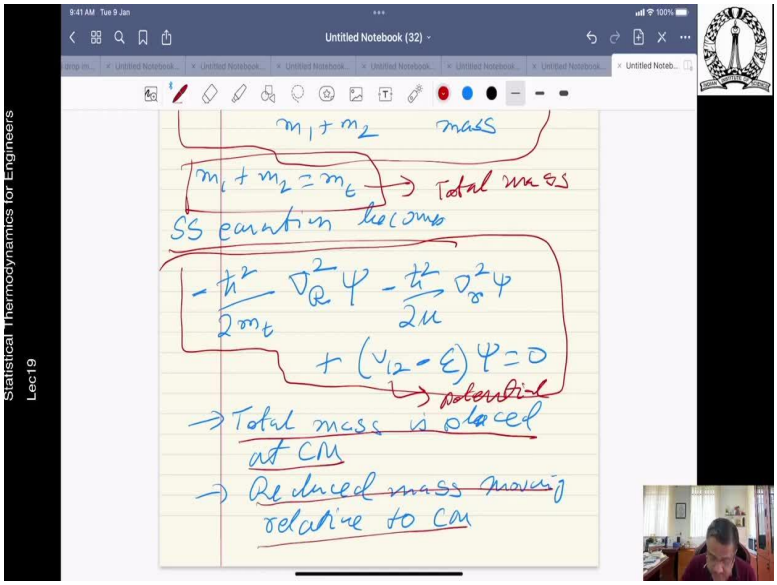

So, this is the total this is how separation happens, if you look at it this is how this was done, two masses replace the centre of mass concept over here and then just working out to play then simple math that we have already done numerous time, these are all dots that we have done. This is the key concept each mass which we already know and this is the total bus that is why it is written as m c m t total mass.

So, the steady state version of the wave equation becomes this, remember v 12 is once again the potential. And so the total mass is placed at the centre of mass and reduced mass is moving with relative C M these are the 2 natural outcomes that you have of this particular analysis.

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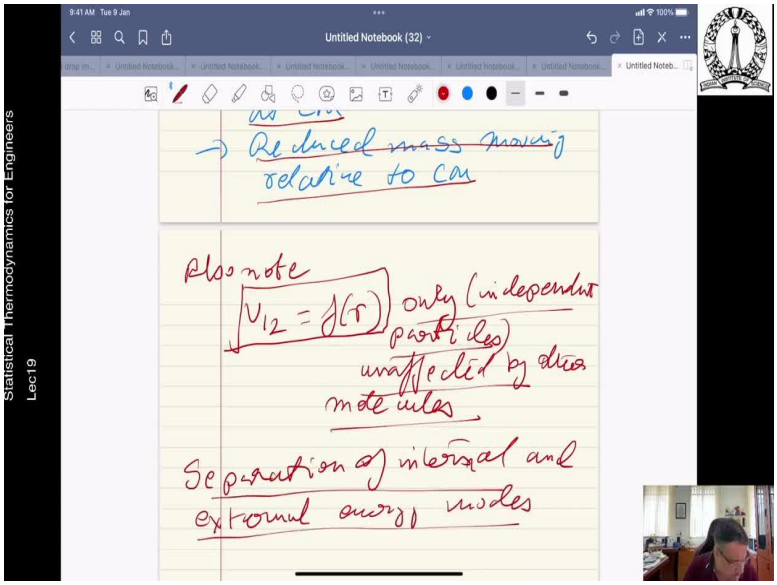

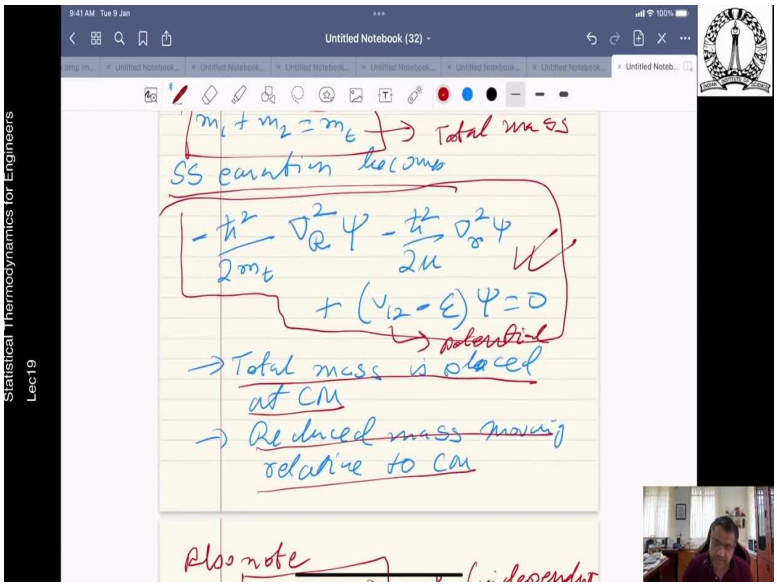

Also please note that also note v 1 2 is a function of f r only it will just independent particles unaffected by other molecules. So, this is basically the potential energy. So, now, what we need to do is we need to separate the external and the internal mode, separation of internal and external internal energy modes, which we are going to do in the next class that all the separation can happen because this is what is going to lead us to a complete analysis of how the internal modes actually evolve. So, that is why we did all this groundwork and we also defined that v 12 is only a function of r for independent particles is unaffected by the other molecules system.

So, in the next class, what we are going to see that how the separation can happen using this tools, using this form that we developed right here, right here using this form that we

developed right here, how the separation of the internal and external energy modes will happen. So, that we will going to cover in the next class, which will be your lecture number 20.