Statistical Mechanics

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Lecture - 42
Density Matrix in Different Ensembles

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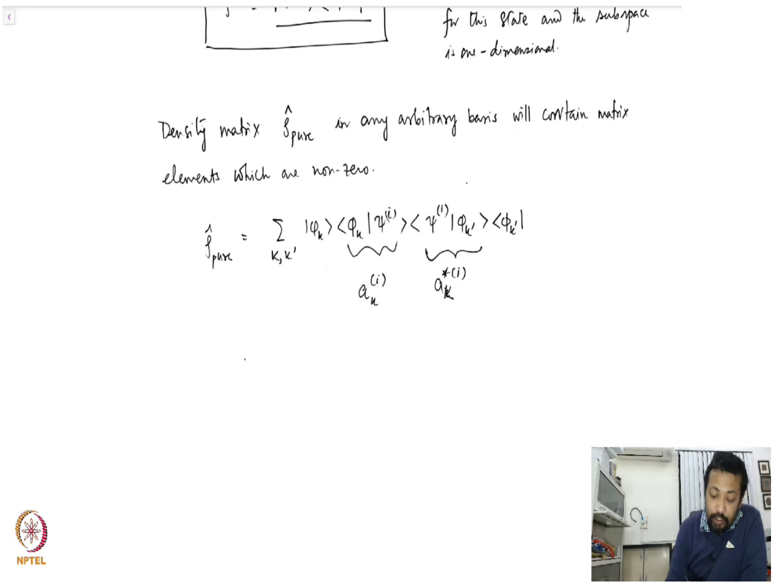

Now, the Density Matrix rho hat pure for a pure state in any arbitrary basis will contain matrix elements; will contain matrix elements which are non-zero. So, I can write down rho hat pure is equal to sum over k comma k prime phi k phi k psi i psi i phi k prime phi of k prime and this quantity we will identify as a of k star i and this quantity we will identify as a of k i.

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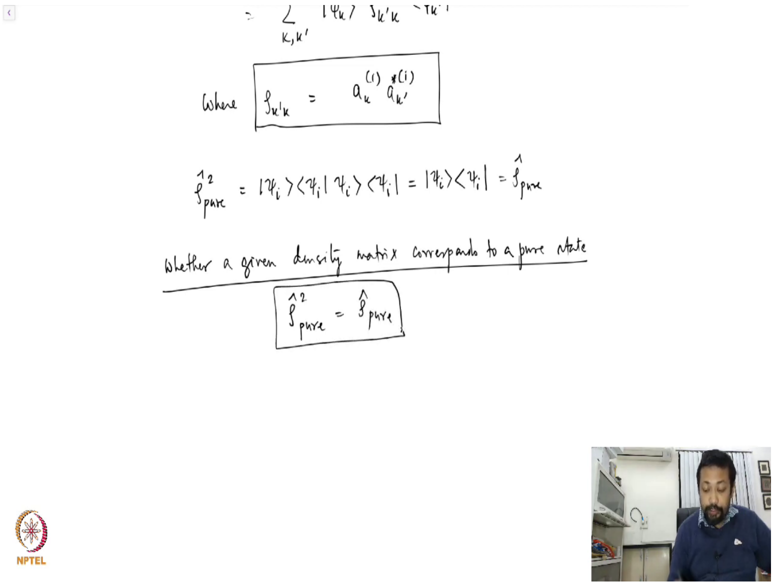

So, this I can recast as k comma k prime phi of k rho kk prime, which is consistent with our definition that we had earlier except that now I have changed the levels and rho kk prime take the form a k i a k prime star of i. So, you see that now you have matrix elements of the density matrix which are non-zero although you started off from pure state.

For a pure state you should also note that rho square pure it is a projection operator, therefore you know that psi i psi i psi i psi i is equal to psi i psi i which is rho hat pure. So, for any pure state if you want to determine whether a given density matrix. If you want to determine whether a given density matrix is a corresponds to a pure state or not, to a pure state you have to check the condition rho hat square pure must be equal to rho hat pure. It is a property of the projection operator for this.

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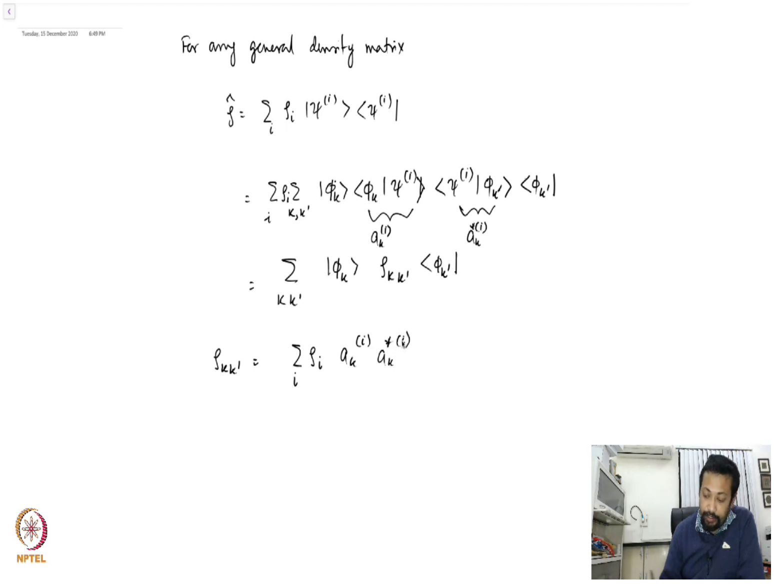

Now, for any general density matrix, where I have rho hat as sum over i rho i psi i psi i. So, this I can write down as sum over k, k prime phi k phi k psi i and then I have psi i phi k prime phi of k prime. So, there is a rho i sitting outside over here. So, this one I rewrite as phi of k rho kk prime phi of k prime with rho of k k prime is sum over i rho i this one is a k i and this one is a k star i. So, you have a k i a k star i.

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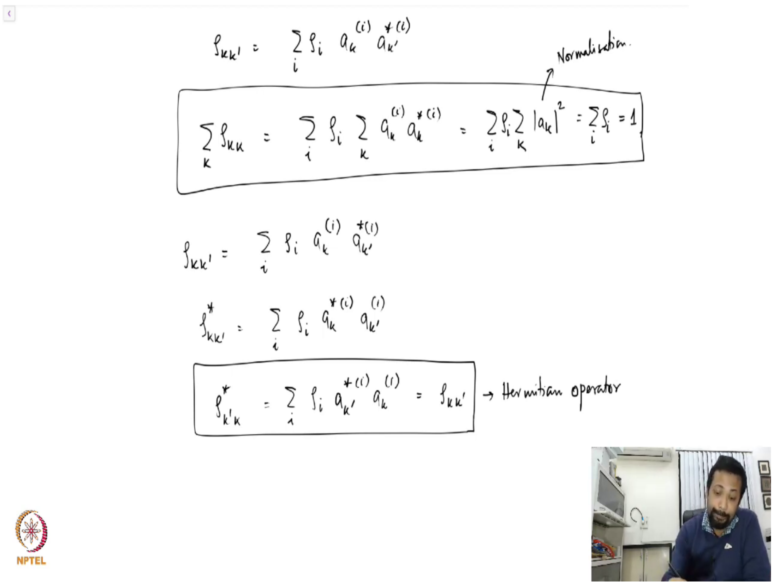

If you now construct take this quantity rho kk the trace the sum over the diagonal elements than you will see that, this is going to be sum over rho i sum of k a k i a k star i which is sum over rho i sum over k mod a k square rho i sitting over here, which is sum over i rho i and this is equal to unity right. Because this follows this is equal to one follows from the normalization of the wave function and sum of total of probabilities over i rho i must be equal to 1.

So, this is the normalization condition that we can have correct. So, further note: that this is a Hermitian operator right. So, I have rho of kk prime as sum over i rho i a k i a k i k prime star let us see this is a k prime this is k prime please I do make such silly mistakes, but you have to be careful with these things right.

So rho of kk prime star then becomes sum over i rho of i a k star i a k prime of i, then this quantity rho k prime k essentially the transpose you are looking at is rho i a k prime star i a of k i which is exactly rho kk prime. So, this essentially tells you that this is a Hermitian operator and therefore since it is a Hermitian operator its eigen-values are real numbers.

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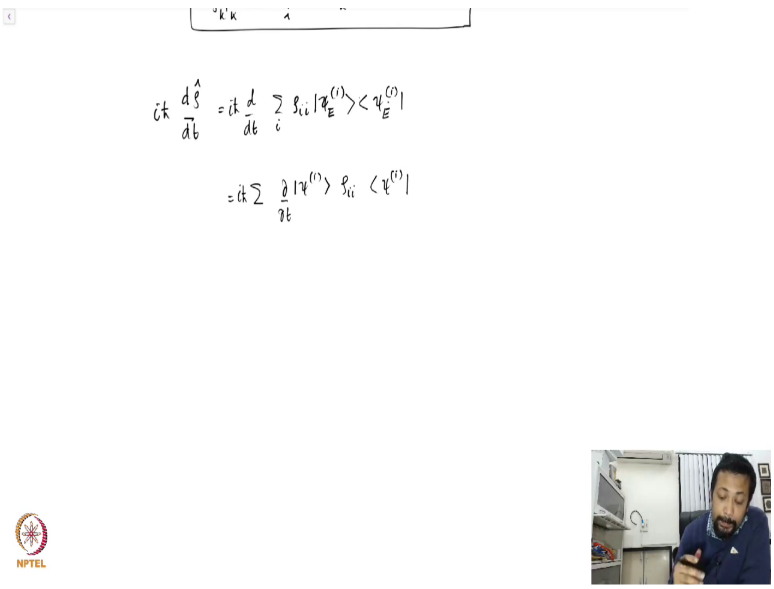

So, now we want to discuss the time evolution of the density operator del and we will start off with this expression right and for this we will write down the density matrix as sum over i rho i in the most simplest of it is form psi i psi i right.

So, this quantity then becomes sorry has to be rho ii and then this becomes del del t. So, there is an ih bar multiplying outside del del t of psi i E rho i rho i psi i of E. So, in the earlier expression we had this as the subscript of the energy eigen state so that is ok.

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$$i\hbar \frac{d\hat{\rho}}{dt} = i\hbar \frac{d}{dt}\sum_i \rho_{ii}|\psi^{(i)}\rangle\langle\psi^{(i)}|$$

$$= i\hbar \sum_i \left[\frac{\partial}{\partial t}|\psi^{(i)}\rangle \rho_{ii}\langle\psi^{(i)}| + |\psi^{(i)}\rangle \frac{d\rho_{ii}}{dt}\langle\psi^{(i)}| + |\psi^{(i)}\rangle\rho_{ii}\frac{\partial\langle\psi^{(i)}|}{\partial t}\right]$$

$$i\hbar \frac{\partial|\psi^{(i)}\rangle}{\partial t} = \hat{H}|\psi^{(i)}\rangle$$

So in fact we understand that the system evolves. So, this is the wave function many particle wave function and involves according to the Hamiltonian right. So, sum over i plus there will be three terms ii dt psi i plus psi i rho i i del psi i del t right. So, ih bar del psi i del t is equal to h bar of psi i. So, this is in fact eigen state of the Hamiltonian.

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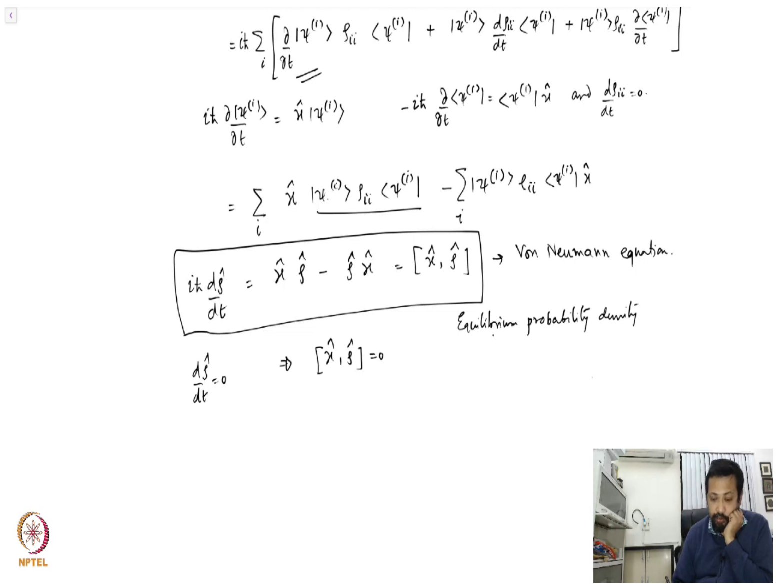

And if such is the keys then we also know that minus ih del del t psi i it is equal to psi i times h bar and this quantity is 0 right. So, if we use this then we can very easily see that the answer is going to be the first term over here is going to be H hat psi i rho ii psi i right minus psi i rho ii psi i H hat.

So, sum over i since the Hamiltonian the sum is over just this I can write down this as rho hat minus rho hat times H so, which is a commutation relation H hat, rho hat. So, ih bar d rho dt is this quantity and this equation is called the Von Neumann equation and this is the counterpart of the classical Von Neumann equation that we had derived.

Now, with this if I set d rho dt is equal to 0 this means that H hat, rho hat the commutation of this is equal to 0. So, the Hamiltonian and the density matrix commute with each other. So therefore, this equilibrium probability densities; the equilibrium probability densities if we you I want to look at the it is equilibrium probability density.

So, if I want to construct that then I can use very well use the energy eigen functions in which case this rho hat is going to be diagonal in that representation right. So now, so we will come back to this, but we want to take a look at the density matrix from a different perspective right.

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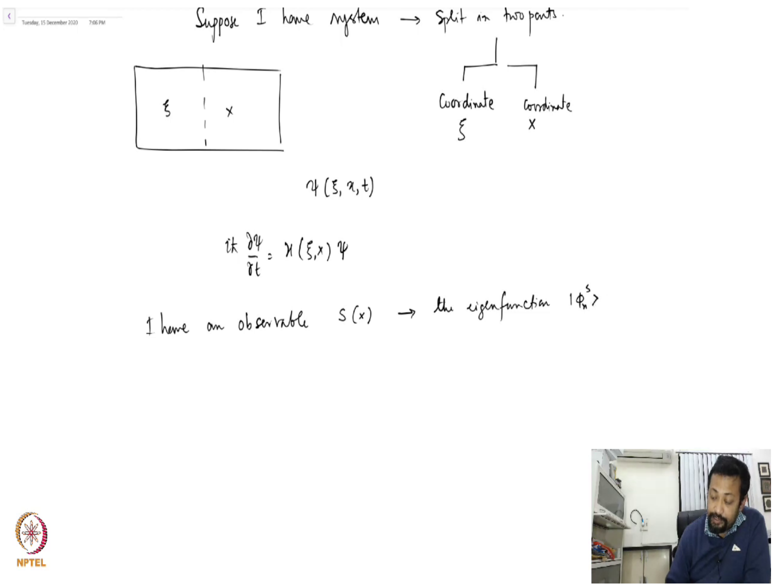

So, suppose I have a system right, now this system I can spilt in two parts, in one of the parts the coordinates are xi, coordinate xi and in the second one the coordinate is x right. So, the total wave function of the system is xi, x, t and I know that the evolution of this wave function is governed by the Hamiltonian of xi, x, psi right, well. So now let us say I have an observable; I have an observable S which only depends on x and the eigen functions, which form a complete set are given by phi n of S right.

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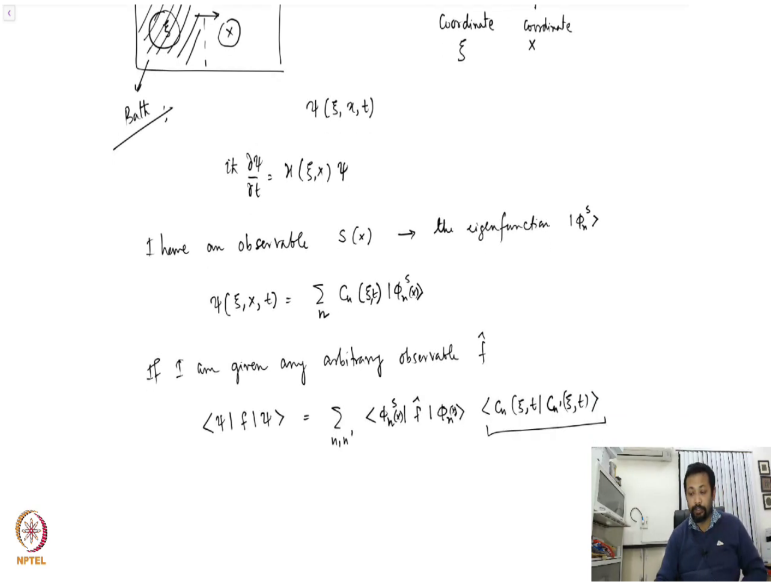

In which case I can write down x comma t is equal to C n of xi comma t, phi n of S with the sum over n good. So, if I am given any arbitrary observable; if I am given any arbitrary observable f.

And I want to calculate the expectation value of f, then you see that I can write down this as sum over this is going to be n comma n prime phi n prime and I am going to have C n of xi comma t times C n prime of xi comma t. So, this phi n of as it depends only on the coordinate x that is something which you must remember, right.

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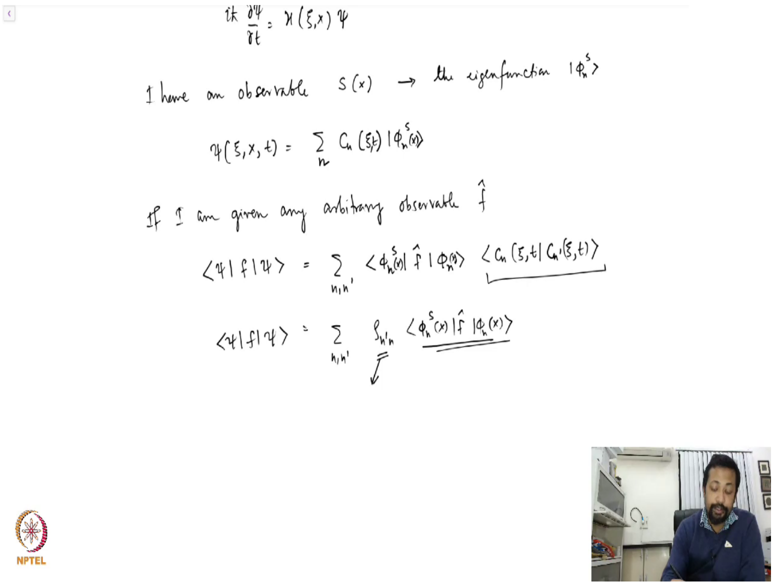

Now, strikingly if you look at this expression then this expression is rho of n prime m I can identify this quantity as phi n as of x f phi n x. So, you see that in this average psi of f psi this average of this observer able f essentially I have the same statistical expression that I had started of that, this is my quantum mechanical average and this is the probability with which I find a wave function.

And therefore, you see that the effect of this density matrix is nothing but the effect of this system with coordinate xi on the system on which this observable is defined right and this system is what is called the Bath right. So, this is an alternative interpretation of density matrix.

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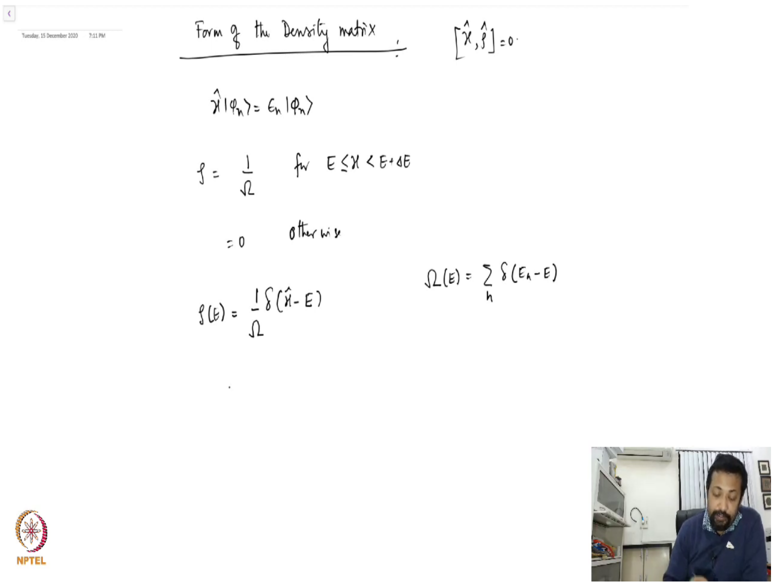

So now, we want to look at Form of the Density matrix and for this I am looking at the equilibrium distribution. Therefore I know that the Hamiltonian and the density matrix commute with each other. And this essentially means that if I work in the eigen function H of phi n in the energy basis.

Then I know that the density matrix is going to be diagonal right. Now, for macro canonical ensemble I know that this density is 1 over omega for energy which lies between E and for the energy, which lies between E and E plus delta E this is for the classical case also perhaps we have seen that right otherwise.

Here for the quantum mechanical case I am going to have delta sorry, this is going to be delta H minus E with a sum over omega. Where omega since I am working in the energy eigen function basis, if the energy is a discreet I have E n minus E right. See if I so now since I am working in the energy eigen basis the density matrix will do diagonal.

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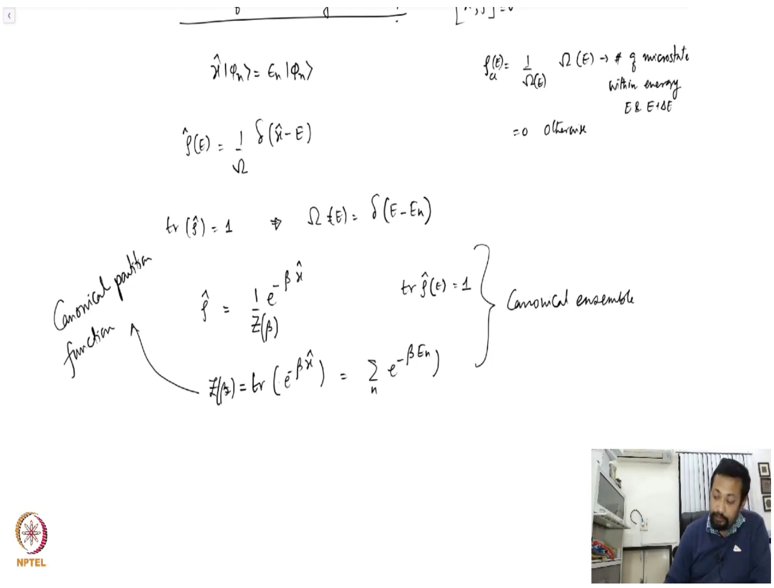

Now, in a micro canonical ensemble in the classical statistical mechanics we have seen that the rho classical for E was 1 over omega, where omega represented the number of micro states within energy E and E plus delta E and is equal to 0 otherwise. So, for a quantum mechanical system we can write down this one as 1 over omega the density matrix rho hat as delta H hat minus E.

And since trace of rho hat is equal to 1, this would imply that omega of E is given by delta of E minus E n right. For a canonical ensemble I have rho hat has e to the power minus beta H hat 1 over Z. So, that again we use the condition trace of rho hat E is equal to 1 and this should mean that I have Z is equal to trace of e to the power minus beta H; which is sum over n.

Because I am working in the energy representation minus beta E n, so, that Z is clearly going to be a function of beta right. So, this is for the canonical partition function sorry, we will write down that canonical ensemble and this is the canonical partition function in the energy representation.

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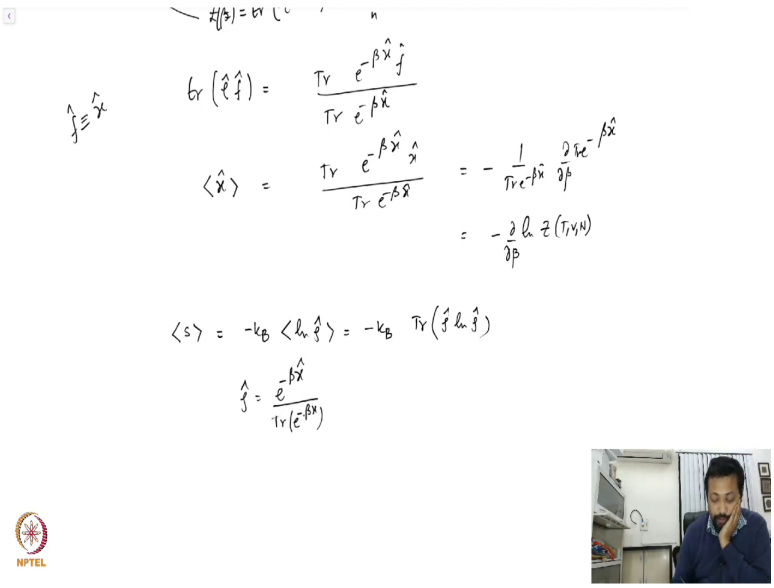

The average of any quantity any physical observable is trace rho hat f hat right, which is going to be trace of e to the power minus beta H hat f hat divided by trace of e to the power minus beta H. And if I want to calculate the average of this Hamiltonian if I substitute f hat as identical to H hat which is equal to the average energy it is going to be trace of E to the power minus beta H hat H hat divided by trace of e to the power minus beta H and which you immediately see a this del del beta of trace of ln.

So, we will write it down as so this is 1 over trace of e to the power minus beta del del beta of e to the power minus beta H trace of this right. So, this becomes minus del del beta of ln Z T, V, N. So, which is the result which we obtained for the classical, canonical, classical statistical mechanics in the canonical ensemble, right.

The average of the entropy is minus k B average of ln rho hat, which is minus k B trace of rho hat ln rho hat right. And now if I want to use rho hat as e to the power minus beta H divided by trace of e to the power minus beta H.

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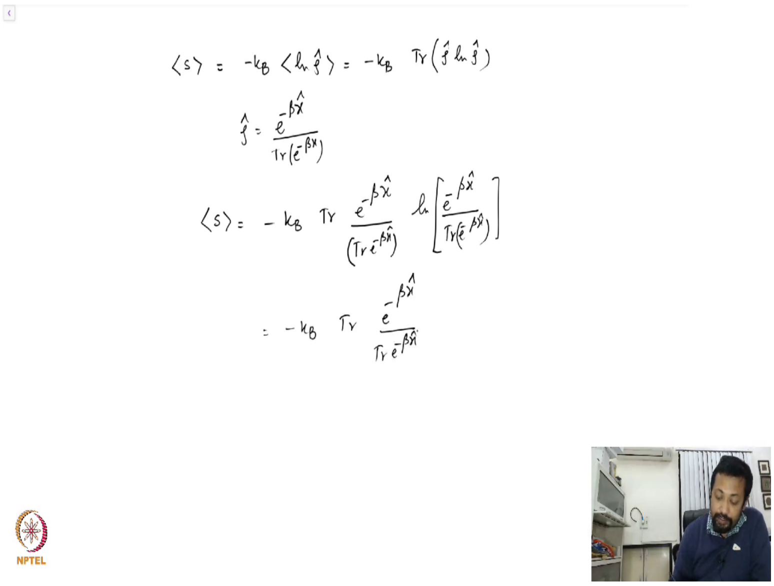

I can substitute this quantity over here this becomes minus k B trace of e to the power minus beta H hat divided by trace of e to the power minus beta H hat times log of e to the power minus beta H hat divided by trace of e to the power minus beta H hat right good. So, this is minus k B trace e to the power minus beta H hat trace e to the power minus beta H hat actually we want to keep this we do not want to write it down explicitly.

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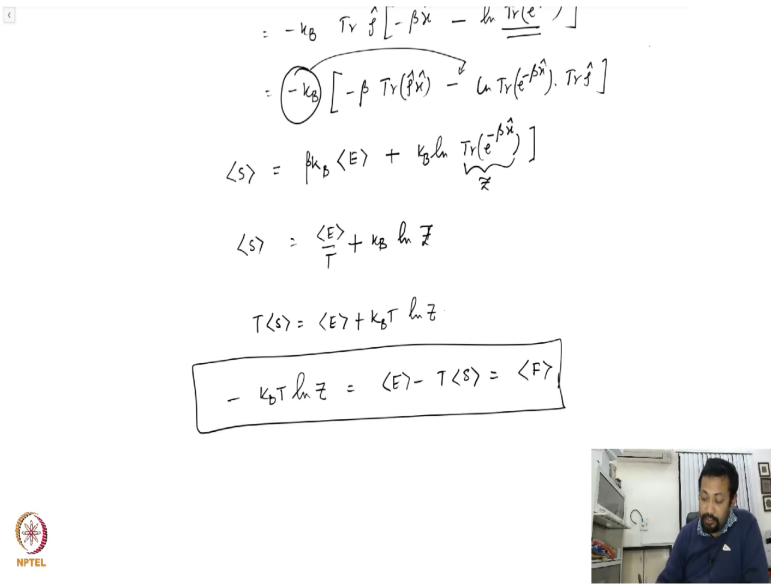

We will write down rho hat and let us expand the law then this becomes minus of beta H hat minus ln of trace e to the power minus beta H hat. Note: that this is just a number. So therefore, you have minus of k B and just look at the first term this is minus beta trace of rho hat H hat and you have minus ln trace of e to the power minus beta H hat times what do you have? You have trace of rho hat.

But trace of rho hat is 1. So essentially you have k B beta k B trace of average of rho hat H hat is the average energy E right and this one is ln trace of e to the power minus beta H hat. But this quantity is the canonical partition function. So, we will write down this as average of S is equal to this.

So, you clearly see that T of average of S is average of E minus ln of Z right. So, that average E minus there has to be a k B T here, because you are multiplying throughout by k B T. So, there is a k B here because k B multiplies throughout and this is nothing but average of T minus k B ln of Z, which is average of S and therefore one has T of average of S as E minus k B T ln Z.

So, that k B T wait a minute this has to be a plus sign over here because minus k B is being multiplied is being taken inside. So, minus k B is being taken inside over here and therefore this becomes a plus, so I have plus, plus. So, a minus of average k B minus of k B T ln Z is average of E minus T of S and which we identify is the free energy. So, nice correspondence with classical, statistical mechanics.

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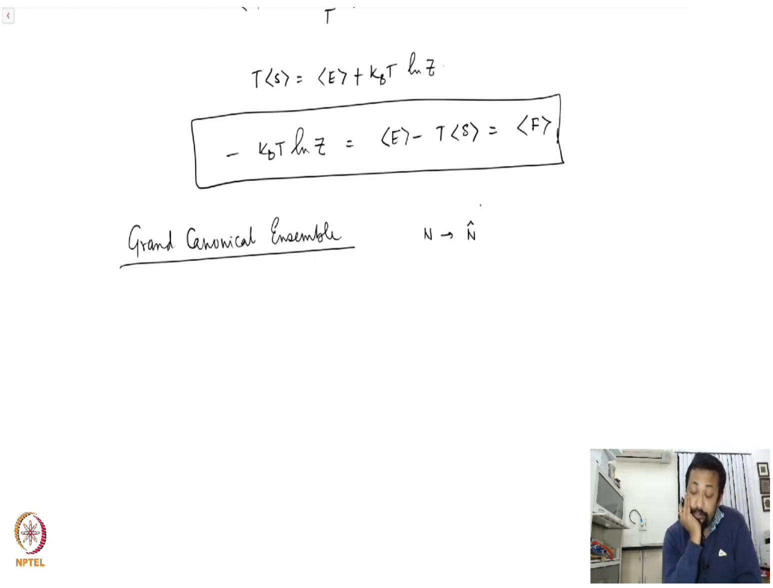

So, then we will look at the; look at the Grand Canonical Ensemble and here the number of particles are not fixed. So, we replace N by the operator N hat but this operator is difficult.

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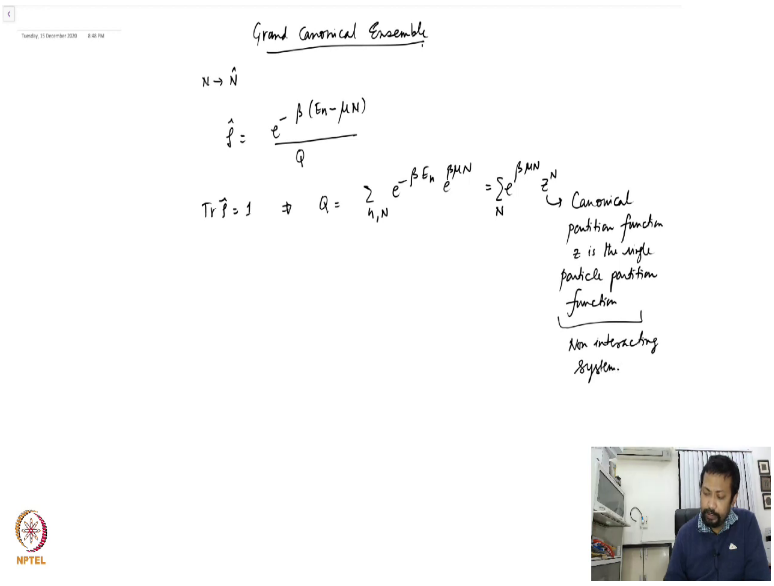

So, now that we have look to the canonical ensemble we look at the grand canonical ensemble right. Now, here of course the particle number is not fixed and N is replaced by the operator N cap. So, for a fixed system we have this operator N cap and the corresponding density is given by e to the power minus beta E n mu N divined by capital Q.

Where since trace of rho is equal to 1 is equal to 1 this implies that Q is sum over n comma N e to the power minus beta E n e to the power beta mu N, which is again e to power beta mu N z to the power N sum over N, where this is a canonical partition function.

And Z is the single particle partition function and for a non interacting system right. The same way we have done in classical statistical mechanics, of course we identified small z is equal to small q there is no nothing special about the symbol you can as well use small q.

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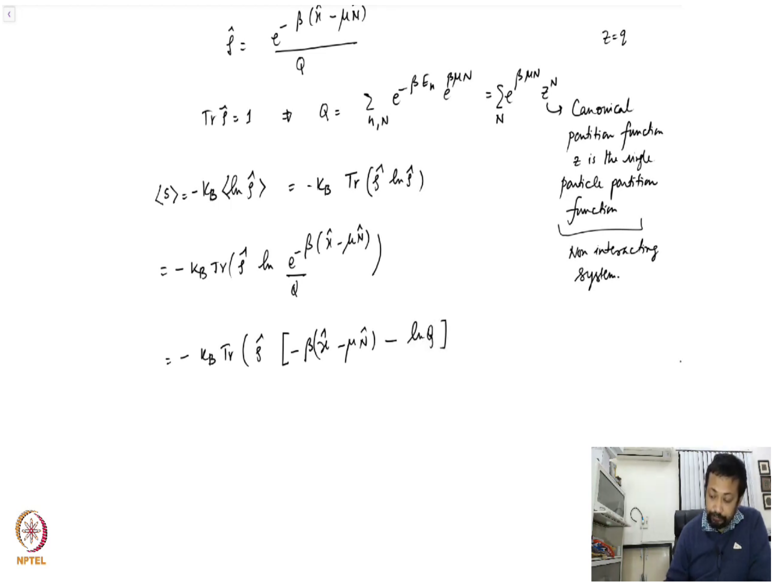

Now, so, the average of the entropy is trace of rho sorry is k B ln of rho hat right. So, the same way that we had used it minus k B ln rho hat, which is minus k B trace of rho hat ln rho hat right. So, minus k B trace will keep the rho hat and we will write down ln rho hat as minus beta E n minus mu N over Q right.

I am sorry if this is the Hamiltonian then this has to be this is the density operator. So, one has to be careful over here, anyway one under can we can use that interchangeably because otherwise this will mean the if you write E n it means that the matrix element in a certain in the energy basis right. So, we have H hat N hat right. So, then this is minus k B trace rho hat minus beta H hat mu N hat minus ln of Q.

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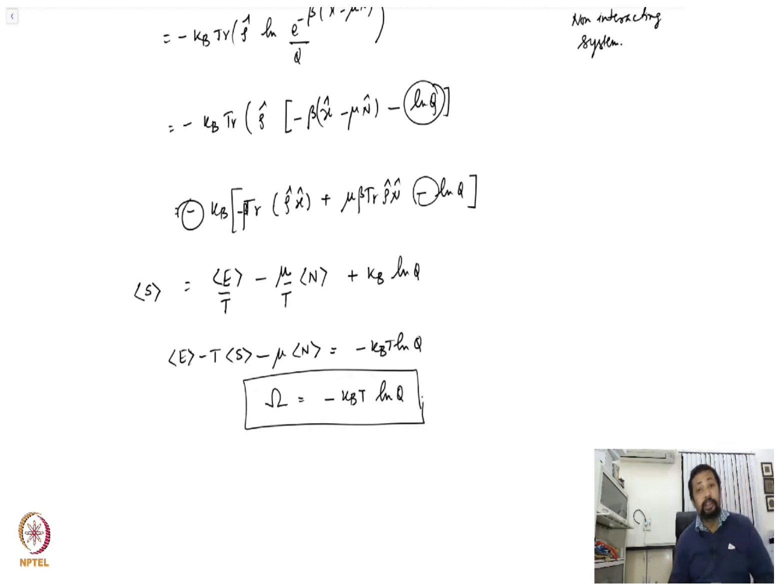

So, the first term is k B trace of we will write down this as minus rho hat H hat and then we will write down plus mu trace of rho hat N hat minus this quantity is just a number. So, this becomes lnQ. If I now put everything together there is a beta here I am sorry there has to be a beta here and there is a mu beta here.

So, this becomes average energy by T plus this is minus if I now multiply throughout by minus this becomes mu by T average of N minus plus k B so this minus and this minus makes a plus k B lnQ. So, I have average E minus T of average S minus mu of average N is going to be minus k B T lnQ and this quantity in the left hand side is the grand potential. So, we have the grand potential as we got it in classical statistical mechanics.