Statistical Mechanics

Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 47
N - Particle partition function

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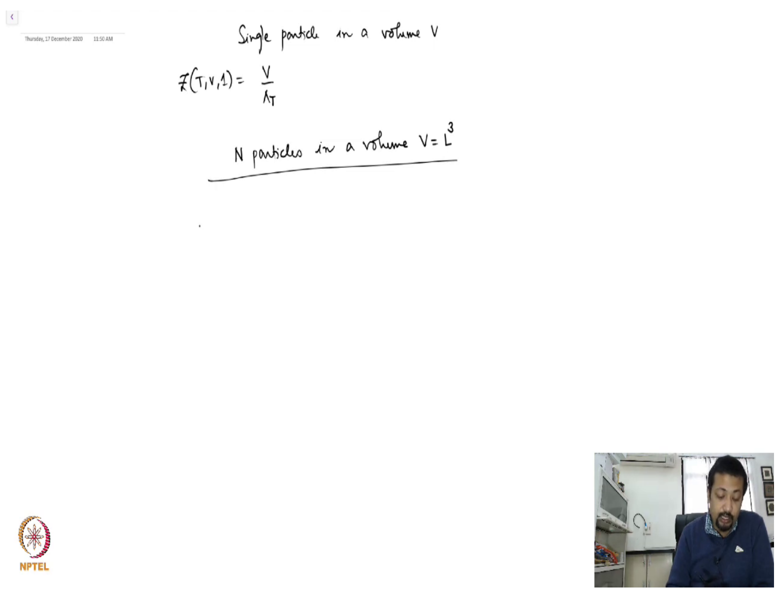

So, we had looked at a single particle in a volume V and we said we determined that the canonical partition function of this single particle is V over lambda T consistent with our classical result.

Now, what we want to do is want to, we want to look at the N particles in a volume V given by l cube and we want to calculate the canonical partition function. So, we start off with the density matrix rho hat, but first before determining that we note that for this N particles in a volume V.

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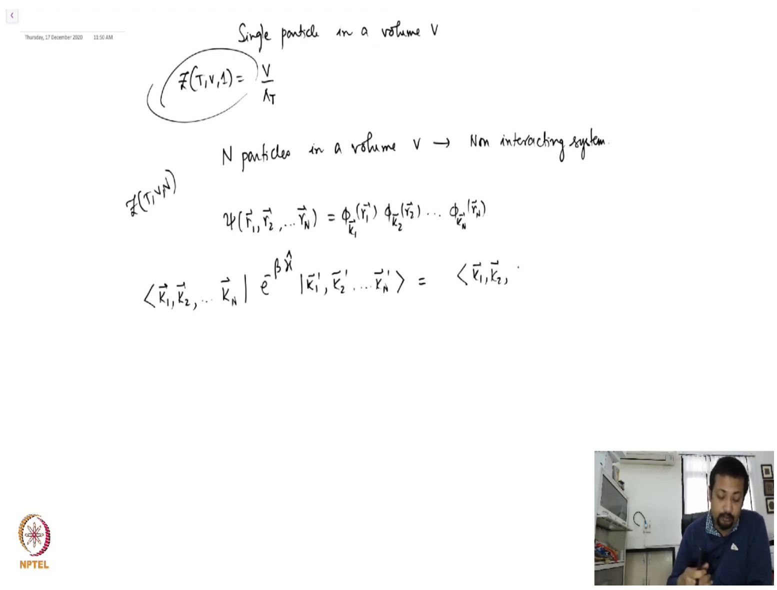

So, now we want to look at N particles in a volume V and this is still a non interacting system. Our idea is to calculate the N particle partition function Z of T V N and see what result that we get. The many particle wave function psi of r 1, r 2, r N can be constructed from the single particle wave function phi K 1 r 1 phi K 2 r 2 all the way phi K N r N.

So that, if I want I want to evaluate the density matrix and we will write down this as K 1, K 2, K N e to the power minus beta H bar K 1 prime K 2 prime K N prime is given by K 1 K 2.

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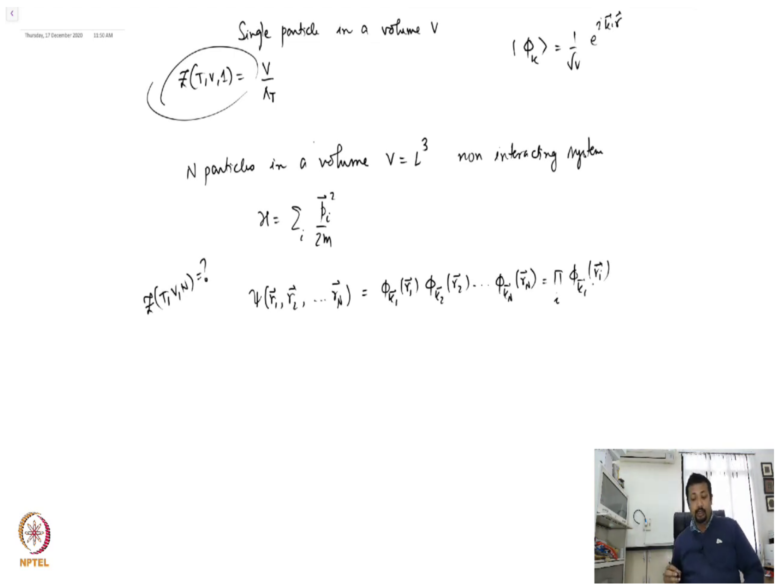

So we now want to look at N particles in a volume V is equal to keep the same setup except that now I have N particles and it is still a non interacting system. So that the Hamiltonian, the N particle Hamiltonian is sum over i P i square over 2 m.

Our goal is to calculate the N particle canonical partition function. So, we start off by constructing the many particle wave function from the single particle wave functions which I know for a single particle I know that this was my wave function right. Which was square root V e to the power i K dot r. So, I can construct the single particle wave function as phi K 1 of r 1 phi K 2 of r 2. So, on all the way up to K N r N which is equal to product over i phi K i r i.

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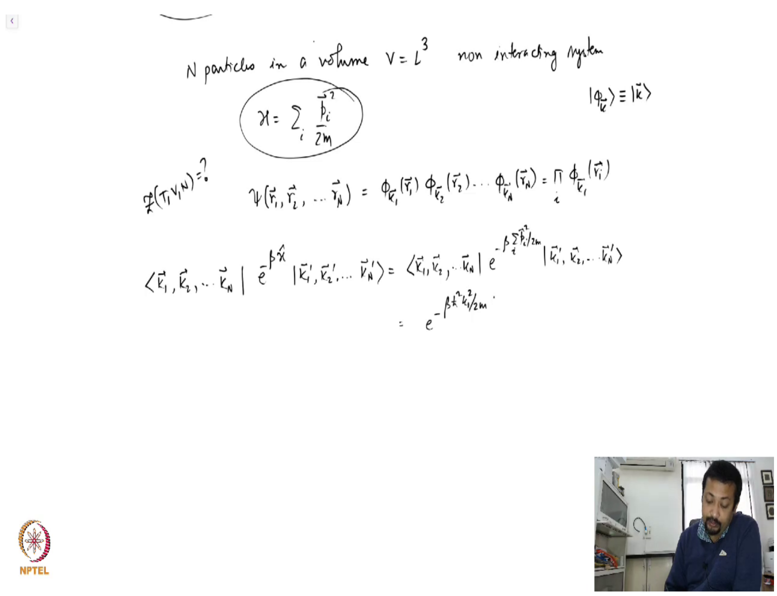

The density matrix, so now we will interchangeably use phi K is identical to this. So, the density matrix K 1, K 2 the density matrix if I want now I want to calculate this K N is e to the power minus beta H K 1 prime K 2 prime K N prime and it is very easy to do that and therefore, you immediately see that this is going to be K 1, K 2, K N, you put in the Hamiltonian from this expression is minus beta sum over i P i square over 2 N K 1 prime K 2 prime K N prime and this becomes e to the power minus beta h bar square K square over 2 m K 1 square.

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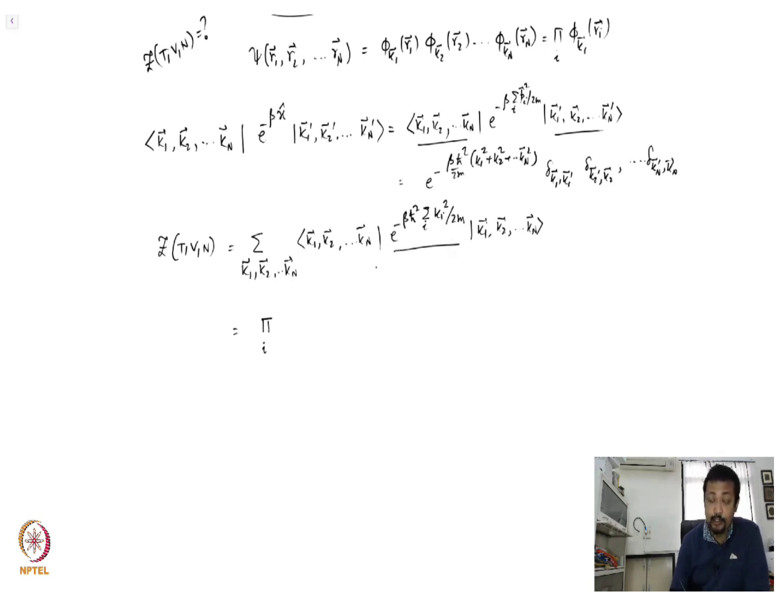

So, let me just write down this first as h bar square over 2 m K 1 square plus K 2 square K N square and the normalization orthonormalization of this essentially since they are orthonormal gives you delta K 1 K 1 prime delta K 2 prime K 2 so on and delta K N prime K N.

Now, the partition function follows from the normalization of the density matrix and this is T V N sum over K 1, K 2, K N, K 1, K 2, K N. We will write we will write down this as sum over i K i square over 2 m K 1, K 2, K N. So, this is product over i. So, you have you can split this because the exponential splits into products and then you have K 1.

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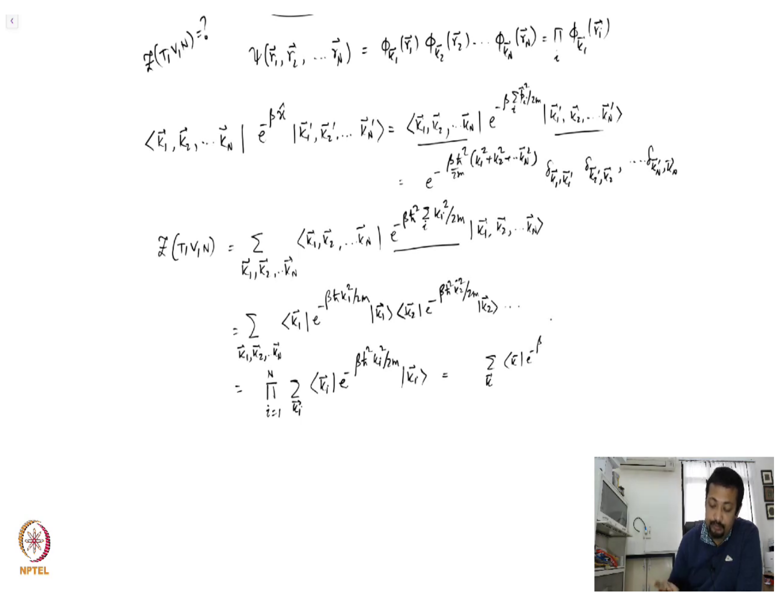

So, let us write down this explicitly first and then you will see this is going to be K 1 minus beta h bar K 1 square over 2 m K 1, K 2 e to the power minus beta h bar square K 2 square over 2 m K 2 so on and so forth.

And therefore, there is also a sum over K 1, K 2, K N which also splits, and therefore, you will have product over i equal to 1 to N or more in more compact form. So, let us say sum over K i K i e to the power minus beta h bar square K i square over 2 m K i, and this is simply sum over K e to the power minus beta h bar square.

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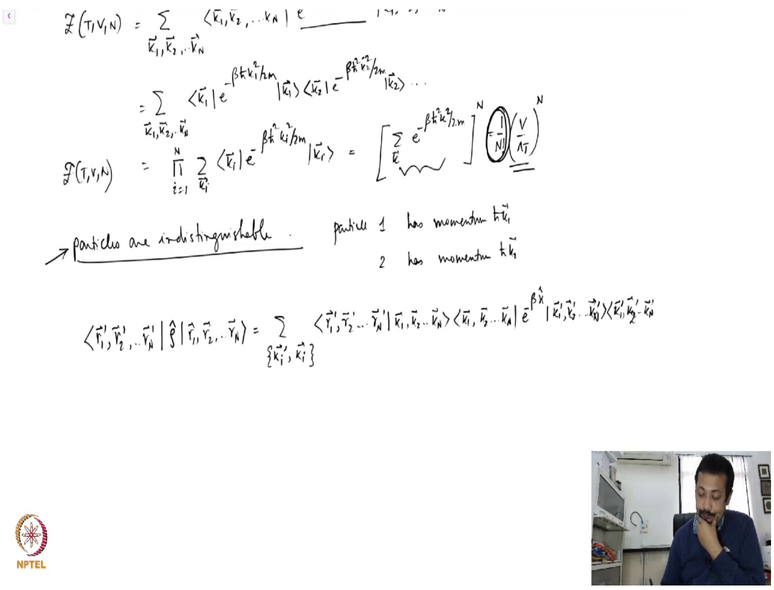

Since it is just a number now, beta h bar square K square over 2 m raised to the power N and this we evaluated for a single particle case, so this is going to be V over lambda T raised to the power N.

So, your Z of T V N is this quantity canonical partition function. Note that this is different from the classical partition function. How is it different? Because, it does not have the 1 by N factorial that we included. So, the 1 by N factorial does not come in and quite naturally within the theory. So, therefore, this still does not resolve the issue that the particles are indistinguishable.

So, in this particular picture we say that particle 1 particle 1 has momentum h bar K 1 2 has momentum h bar K 2 and so on and so forth. But in reality that is not the case, because if I interchange the indices the particle indices nothing changes in the system. But clearly, that somehow has to be incorporated more carefully when we construct this many particle wave function.

So, our starting point was this many particle wave function and clearly we see that this still does not resolve the issue of the indistinguishable. So, the density matrix in the coordinate representation is r 1 prime r 2 prime r N prime rho hat r 1 r 2 r N and then we introduce the completeness of the vector, I am going to compactify the notation. I am going to write this as K 1 prime.

So, K i prime sum over and K i and I have r 1 prime r 2 prime r N prime K 1, K 2, K N K 1, K 2, K N e to the power minus beta H bar K 1 prime K 2 prime K N prime.

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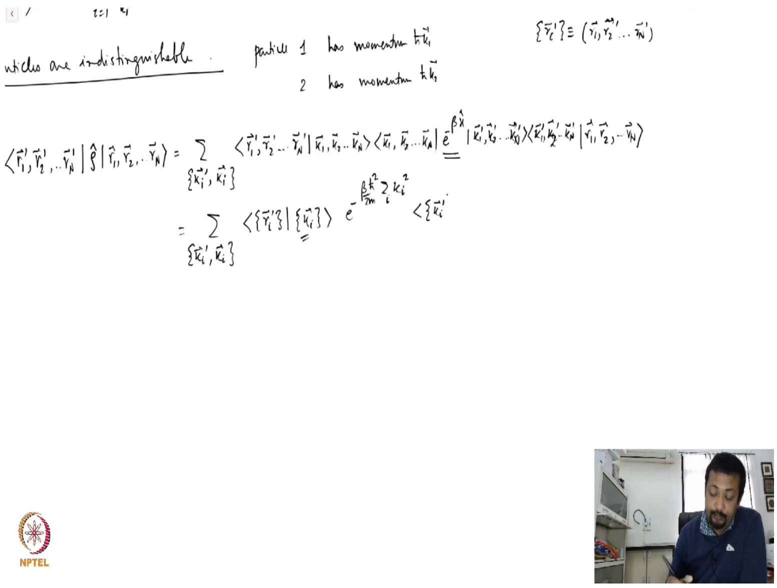

And then I have K 1 prime K 2 prime K N prime r 1, r 2, r N. I know this quantity now. So this is going to be sum of a K i prime K i all the values of K i, further I am going to compactify this notation K i where this set is identical to r 1 prime r 2 prime r N prime and so is the this one with K 1, K 2, K N and this is going to be e to the power minus bet h bar square over 2 m sum over i K i square and this is going to be your K prime i.

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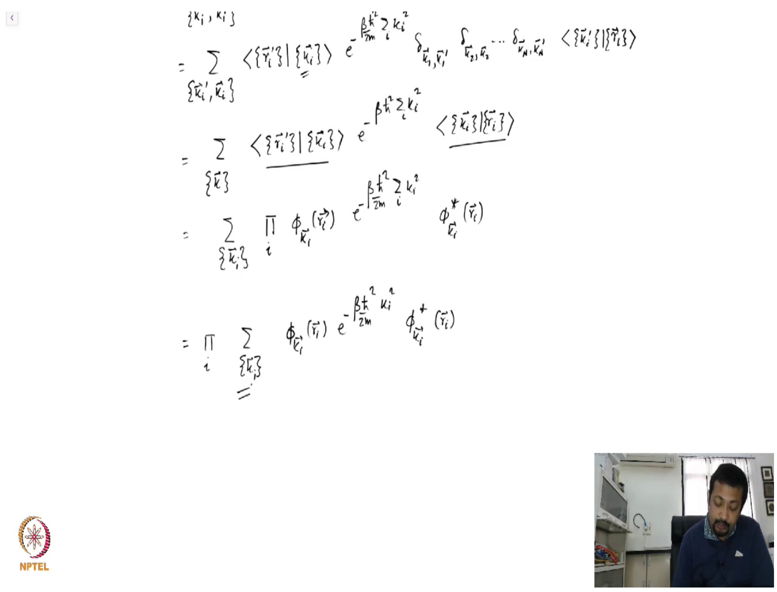

Wait, we have missed one crucial thing, that is the delta functions delta K 1 K 1 prime delta K 2 prime all the way delta K N, K N prime and then we have K i prime and r i. So, one can just do the sum over the delta function then I will be left out with let us say, sum over k. I will have r i prime K i e to the power minus beta h bar square sum over i K i square and then I have K i r i.

So, that this is sum over K this is the wave function many particle wave function in the coordinate representation. So, that I am going to have product over i phi K i r i e to the power minus beta h bar square 2 m sum over i K i square. And this is going to be phi star K i r i. So, the product over i and the sum over K can be converted into an integral and if you do this I will, so let us just first write down the step sum over K i phi K i r i e to the power minus beta h bar squared over 2 m K i square phi K i star r i.

And this sum can now be because, this exponential can be written as a product of exponentials right because I have sum of in the exponential therefore, it splits up into products of these of this term.

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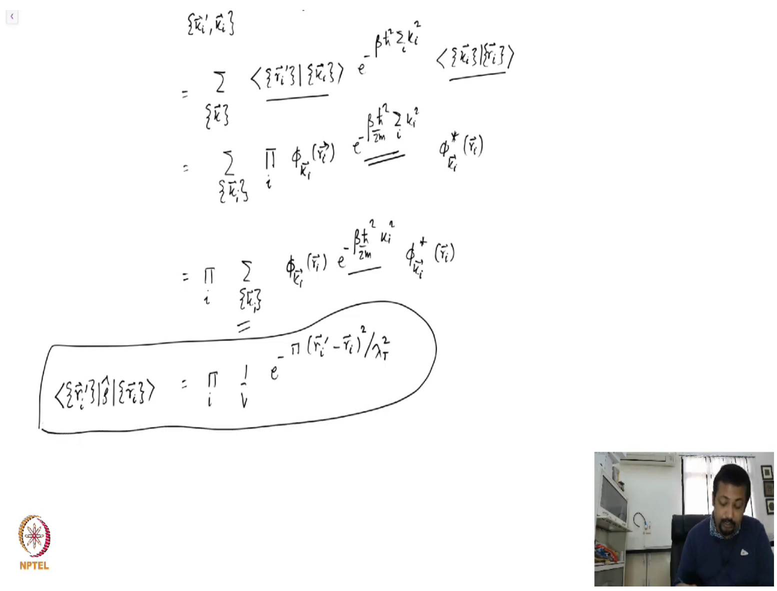

And therefore, if you now evaluate this you are going to get 1 by V e to the power minus pi r prime i minus r i whole square over lambda T square. So, this is your coordinate this is the density matrix in your coordinate representation r i prime rho hat r i. Still, here also the problem is still there is no N factorial. So essentially, our construction of the many particle wave function our construction of the many particle wave function does not resolve the problem with the indistinguishability of the particle.

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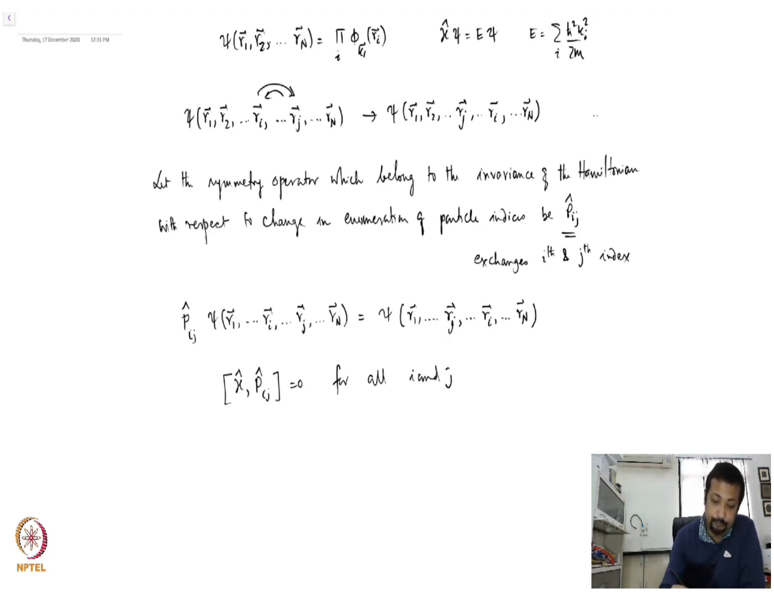

The many particle wave function that we constructed had the form r 1 r 2 all the way up to r N was product over i phi K i r i. This is an Eigen function of the Hamiltonian. So, if you write down this, this is going to be e psi where e is going to be sum of i h bar square K square over 2 m K i square over 2 m.

Even though this is an Eigen function of the Hamiltonian, any wave function that you get by renumbering the particle in distances is also going to be an Eigen function of the Hamiltonian. So, for example, if I have r 1, r 2, r i, r j, r N if I interchange i and j this becomes psi of r 1, r 2, r j, r I, r N this will remain this will be Eigen function of the Hamiltonian, because even though I have interchange i and j nothing in the system has changed your system remains the same, correct.

Now, the indistinguishability of the particles is closely related to the invariance of the Hamiltonian with respect to this change in enumeration in the particle index. So, clearly this operation of interchange of indices I can define as an operator which does that. And therefore, it is obvious that this operator commutes with the Hamiltonian. So, that one can construct Eigen functions of the Hamiltonian in such a way that it is also an Eigen functions of this operator.

So, let the symmetry operator which commits with the Hamiltonian and essentially which belong to the invariance on the Hamiltonian with respect to change in enumeration of particle indices be P hat i j. So, this operator exchanges i th and j th index. So, that P hat i j psi of r 1, r i, r j, r N is going to be psi of r 1, r j, r i, r N and this commutes with the Hamiltonian for all i and j. We now wish to determine the Eigen values of this operator.

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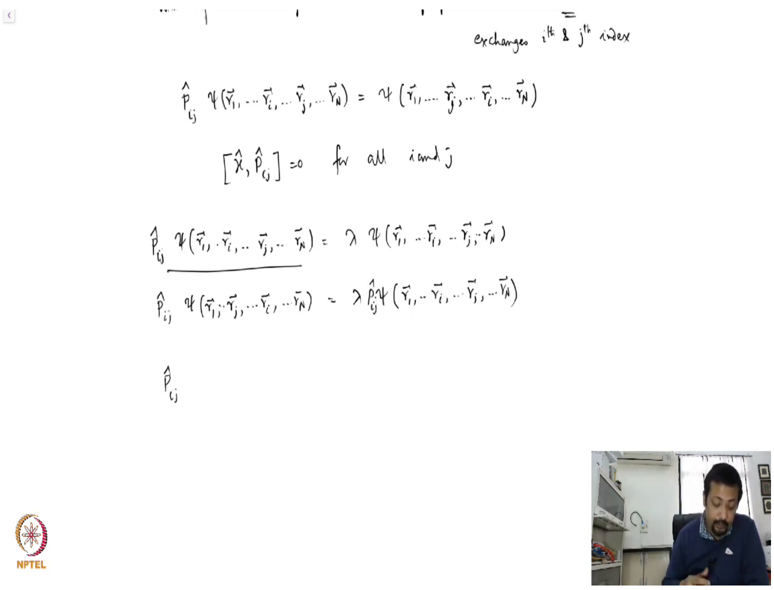

So, P hat i j psi of r 1 , r i, r j, r N is going to be lambda times psi of r 1, r i, r j, r N, but this operation gives me psi of r 1, r j, r i and then I have r N is lambda times psi of r 1, r i, r j, r N. If I operate again P hat i j from the left-hand side to this equation then I have P hat i j P hat i j.

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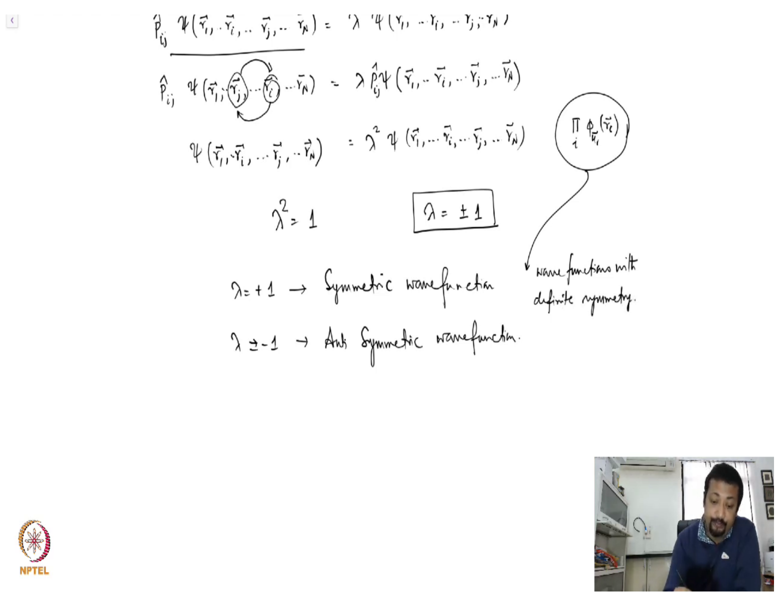

The right-hand side is going to be lambda square of psi r 1, r i, r j, r N, the left hand side is what will it do? It will again interchange this and put it back here and bring it over here. So that you have r 1 r i you get back the original wave function that you started off with. And this essentially tells you that lambda square is equal to 1. So, that lambda is equal to plus minus 1.

So, it can have either a plus 1 Eigenvalue or a minus 1 Eigen value. Lambda is equal to plus 1 corresponds to a symmetric wave function. And lambda corresponding to minus 1 corresponds to an anti symmetric wave function. So, it is now clear what we are trying to do. We started of this naive wave function that we had constructed from the single particle wave functions and we realized that the canonical partition function is definitely not like the classical one that we had derived.

There is a 1 by N factorial which is missing, and we know that this 1 by N factorial essentially comes from the indistinguishability of the particle. And this indistinguishability is very very closely related to the operation of interchange of particle indices. So, there is a symmetric Hamiltonian is invariant under this operation.

So, there is an operator which essentially commutes with the Hamiltonian and therefore, one can construct eigen functions of the Hamiltonian in such a way that these are also eigen functions of the same of the symmetry operator of this exchange operator right. And therefore, one tries to, so what is one trying to do over here is, one is trying from this naive wave function that we see we are trying to construct wave functions with definite symmetry.

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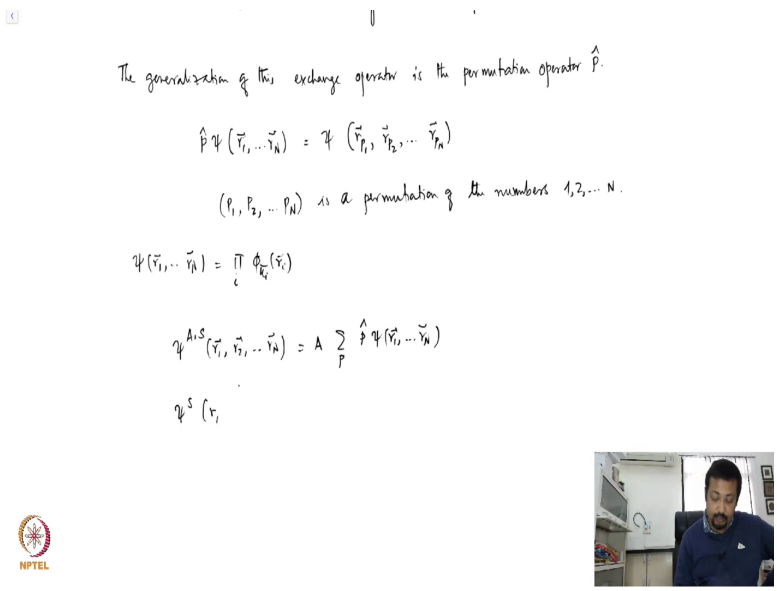

The generalization, the generalization of this exchange operator is the permutation operator. Operator P hat. So, that P hat times psi r 1 r N is going to be psi of r P 1 r P 2 r P N where P

1, P 2. So, this is not the momentum perhaps this is a very poor choice of syntax but let us see P N is a permutation of the numbers and 1 2 N and there are several possible permutations which are there.

So, one if one starts with this wave function psi of r 1 r N which does not have a definite symmetry. I can construct symmetric wave sorry an anti symmetric wave function and a symmetric wave function by using the permutation operator. So, this is going to be A sum of a P P hat psi of r 1, r N, and this is going to be sorry.

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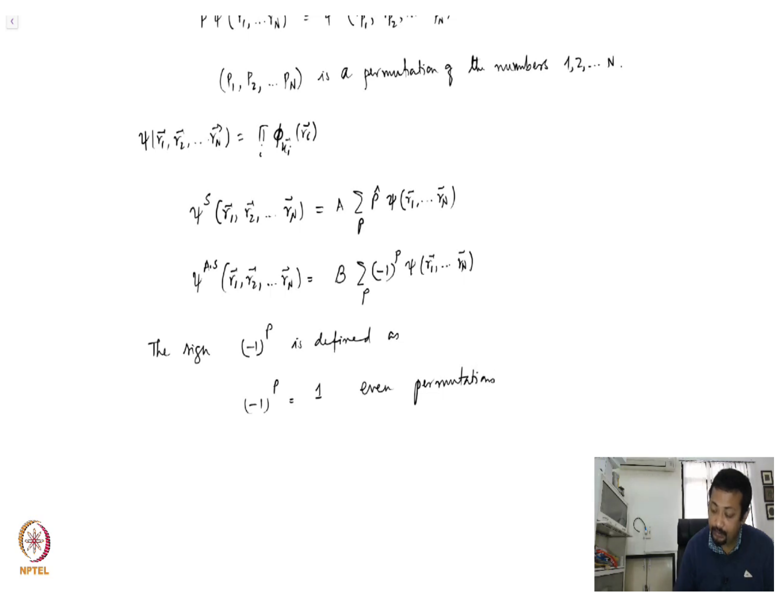

So, starting from the many particle wave function without any definite symmetry which was product over i phi of K i r i, we can construct wave functions, which are symmetric wave functions r N by operating the permutation operator on psi r N and the sum over P, the sum over P essentially means sum over all possible permutations of this numbers 1 to N.

And the anti symmetry operator the symmetric operator has an eigenvalue one therefore, it does not matter over here, but the anti symmetric operator will have an eigenvalue minus 1. So, that this is going to be minus 1 raised to the power P psi of r 1 r N right.

Once again, there is a sum over P which is the sum over all possible permutations. Now, the sign minus 1 raised to the power P is defined as minus 1 raised to the power P is equal to 1 if there are even permutations. And is equal to minus 1 if there are odd permutations.

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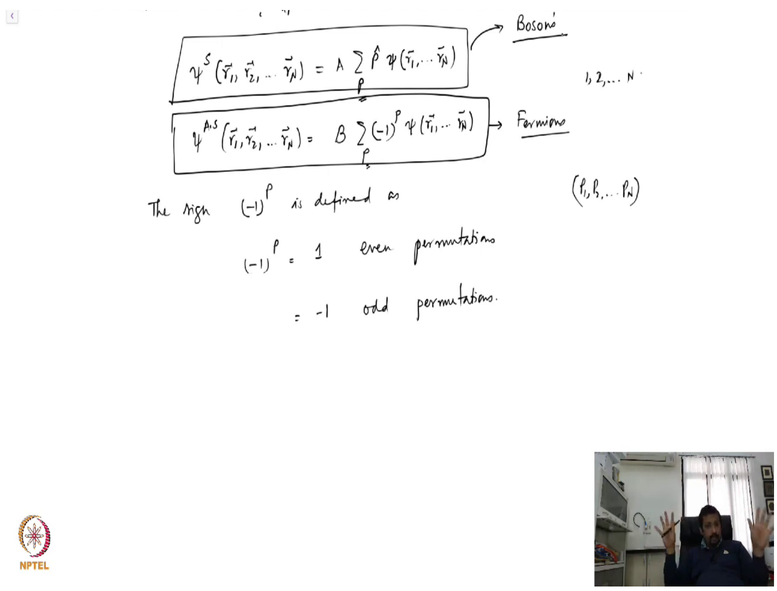

Now, even permutations or odd permutations refer to number of exchanges that you need to do to obtain a certain permutation of the numbers 1 to N right. So, if you need to do 4 permutations to get to the desired set of P 1, P 2, P N, then it is an even permutation. If you need to do 5 exchanges to get to the desired set of P 1, P 2, then its an odd permutations.

Because all these wave functions there is a sum over P; all possible permutations that you can imagine with of the numbers 1 to N. A wave function, which is a symmetric wave function is what are called bosons. And, the anti symmetric wave functions are the ones for particles which are called fermions.

So, starting from a system where particles were simply identified by the indices, even though they were indistinguishable, we see that if we construct particles of definite symmetry, we are looking at two different kinds of particles. Particles which have even wave functions are called bosons and particles which have odd wave functions or anti symmetric sorry not odd wave functions, but anti symmetric wave functions are called fermions.

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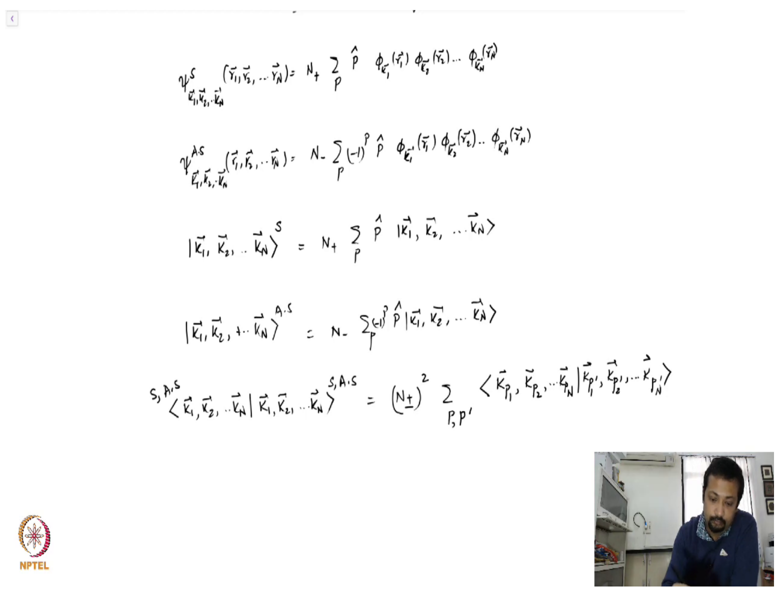

So, we have psi of symmetric K 1, K 2, K N, r 1, r 2, r N is equal to. So, we will just rename the normalization a plus a and b as sum over as n. So, rename a as N plus sum over P all possible permutations, the permutations operator operating on phi K 1 r 1 phi K 2 r 2 phi K N r N.

And similarly, the anti symmetric wave function of K 1, K N we have r 1 r 2 r N is going to be N minus sum over P minus 1 raised to the power P P hat operating on phi K 1 r 1 phi K 2 r 2 phi K N r N. So, for our benefit we are going to write down this in a direct notation which would mean that K 1, K 2, K N the symmetric wave function is N plus sum over P P hat K 1, K 2, K N and the anti symmetric one is going to give me N minus sum over P P hat minus 1 raised to the power P P hat K 1, K 2, K N.

So we have to determine the normalization constants N plus and N minus right. So, let us try to do it one go. Symmetric as well as anti symmetric as well as anti symmetric is N plus minus whole square I will have over P P prime. So, two possible permutations and then I am going to have K of P 1 K of P 2 K P N K P 1 prime K P 2 prime K P N prime.

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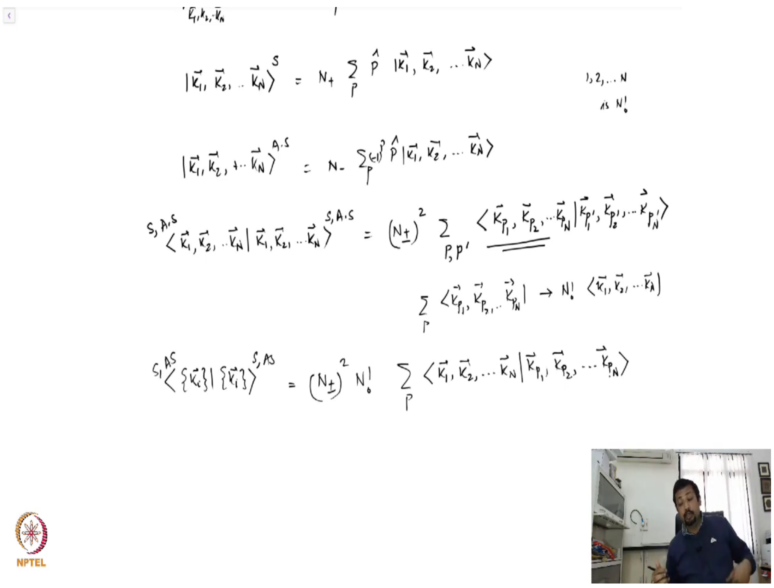

Note that all the total possible permutations of this number 1 to N is N factorial. So, what one can do here, because this is an inner product. So, one can take this and simply replace the sum K P 1, K P 2, K P N we can replace this sum by N factorial times K 1, K 2, K N and this we can do because this is an inner product.

So, that our normalization essentially this means that I have K i I have K i I have symmetric and anti symmetric wave function symmetric and anti symmetric wave function this becomes N plus minus whole square in factorial i will be just left out with one sum, sum over K 1, K 2, K N, K P 1, K P 2, K P N. So now, we bring in the concept of the occupation number.

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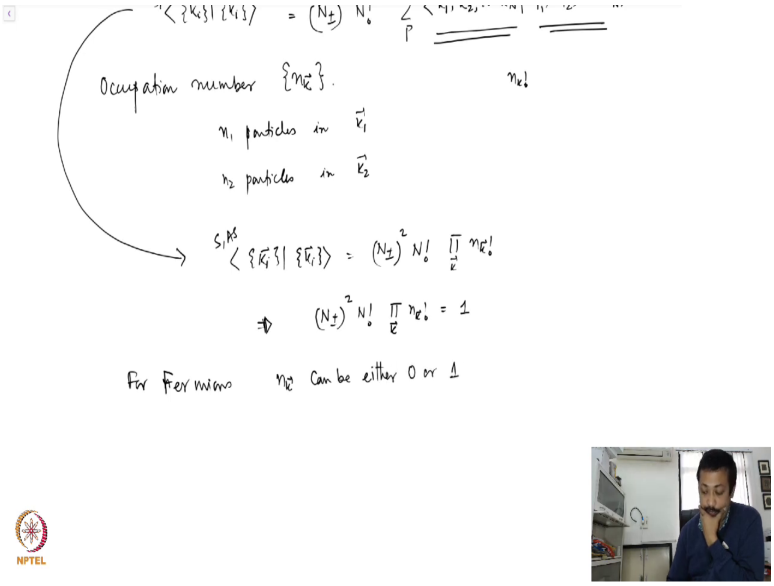

So, we have the occupation number n of k. So, which means; that means, that there are n 1 particles in K 1 n 2 particles in K 2, so on and so forth. Now here, you note that this inner product is 0 unless it corresponds to the original unpermutated order and that only happens N K factorial times, number of particles which are there in the (Refer Time: 34:08) level.

So, your this quantity K i K i take this simple form of N plus minus 1 whole square N factorial product n K factorial over K this implies that your N plus minus square N factorial product over K in K factorial is equal to 1. For fermions n K can be either 0 or 1.

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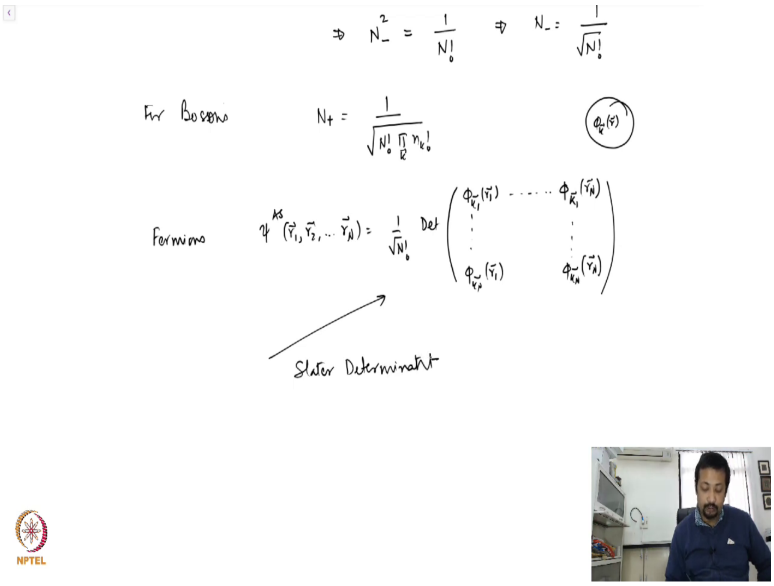

Because of the symmetry of the wave function. So, this implies that N minus is going to be square is 1 over N factorial which implies N minus is one over square root N factorial. For bosons there is which have the symmetric wave functions there is no restriction of, but N K to be either 0 or 1, it can be anything. So, therefore, N plus becomes 1 over square root of N factorial product over K n K factorial.

Therefore, for fermions in terms of the single particle wave functions, the many particles anti-symmetric wave function takes the form 1 over square root of N factorial determinant of the matrix phi K 1, r 1 phi K N r 1 phi K 1, r N phi K N r N and this determinant is what is called a slater determinant.

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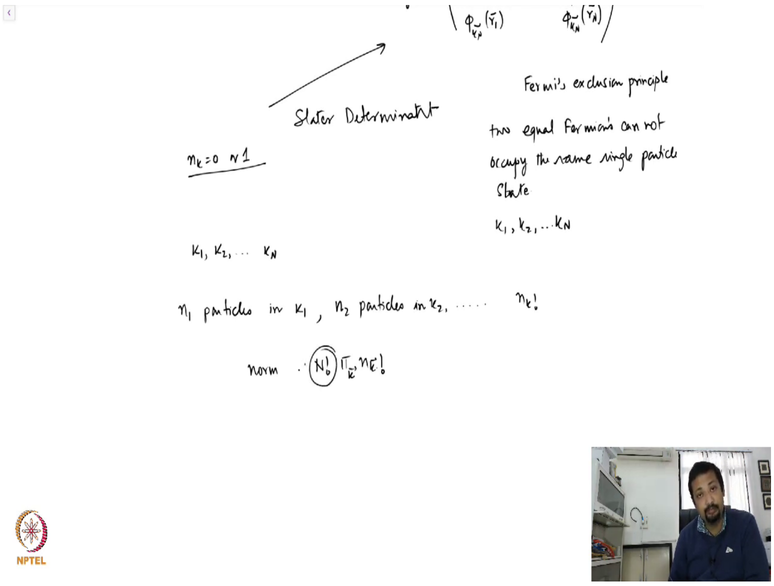

From this form of the wave function, it is clear that the Fermions obey Fermi's exclusion principle, which states that two fermions, two equal fermions cannot occupy the same single particle state. For if that was the case, then you see that two of the quantum numbers in the set K 1 to K N would be equal in which case two of the rhos in the determinant are going to be equal and the wave function identically vanishes.

For bosons, it is slightly more complicated because they do not have the restriction n K is equal to 0 or 1. Many particles can occupy the single particle state and therefore, that makes a normalization a little more complicated that we have seen and essentially one has to see of this quantum numbers K 1, K 2, K N how many of them are equal.

So, if there are N 1 particles if there are N 1 particles in K 1 and N 2 particles N 2 particles in K 2 so on and so forth, then you see this inner product contributes to the sum only n K factorial times. And therefore, the normalization becomes the normalization becomes N factorial product over K n K factorial, where N factorial is the total possible number of permutations you can have.