Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'

Prof. P.C. Deshmukh
Department of Physics
Indian Institute of Technology-Madras

Lecture 15
Many-particle Hamiltonian & Schrodinger Equation In 2nd Quantization Formalism

Greetings, we have set up the essential machinery to start working the second quantization techniques and these are very powerful techniques to deal with a many body system whether it is a Bose system or a Fermi system. And today I will introduce how many particle Hamiltonian is set up in the second quantization formulation and how the Schrodinger equation is set up in the second quantization formulation.

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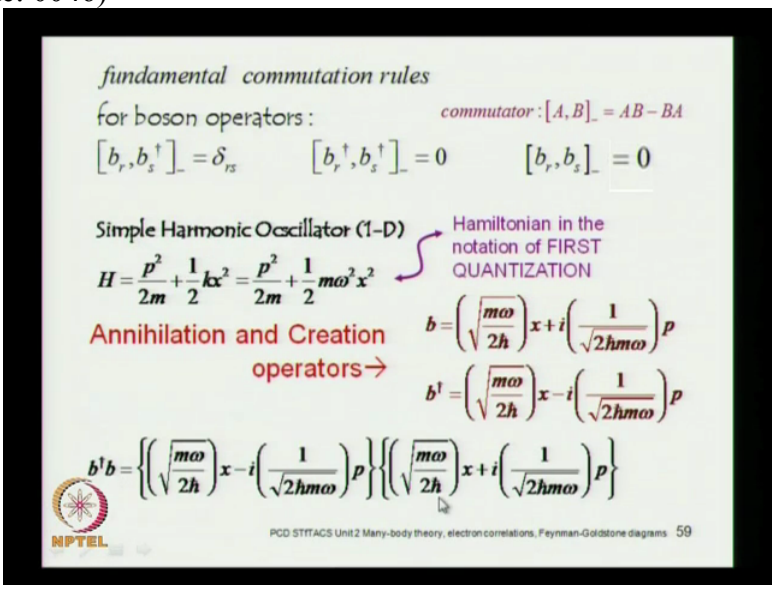

So, essentially we have the fundamental commutation rules for the boson operator's okay. The statistics is now put into the creation and destruction operators and what the commutation properties are. In the first quantization formalism we have the statistics in the symmetry of the wave function. So, as opposed to putting the statistics in the symmetry of the wave function we now put it in the properties of the operators.

And how these operators commute and with regard to the creation operators b dagger and the destruction operators b. You have got these fundamental commutation rules and these contain all information about the statistics of the many-body system. So, these are the fundamental commutation relations for the boson operators.

And let us consider just to illustrate, how it works a simple bosonic system excitations of this simple harmonic oscillator which you would have met even in your earlier quantum

mechanics course. But this will be a very quick recapitulation of the excitations of the simple harmonic oscillator.

So, you have the simple harmonic oscillator Hamiltonian and this has got a quadratic term in the position coordinate, k is the so called spring constant, omega is the natural frequency of the simple harmonic oscillator. And this is your simple harmonic oscillator Hamiltonian in the first quantization notation okay. This is the usual one that we work with. Now what we do is to introduce creation and destruction operators.

Destruction operators are also often referred to as the annihilation operators it is the same thing. And these operators are defined in terms of the operators x and p, so these are linear super positions of x and p. This is the coefficient of x and i times this 1 over root 2 h cross m omega is the coefficient of p. And when you construct this type of a summation, you get the destruction operator b.

If you take it adjoint you get b dagger, so instead of the +i over here you get the –i. So, these are respectively the destruction and creation operators for this system. Now if you now construct the operator b dagger b, so b dagger is this operator it has got these two terms, so these two terms come in the first beautiful bracket. And then b has got these two terms which come in the second beautiful bracket.

So, I have simply written b dagger b in terms of the position and momentum operators. And now you have got two operators over here and two operators over here. So, you can carry out the operator algebra and look at the 4 terms that you will get out of this okay. So, you will get a term in x square from this one and this.

Then you will get a term in xp, this is x and this is p, then you p and x and then finally in p square okay. And the appropriate coefficients have to be properly taken care of right.

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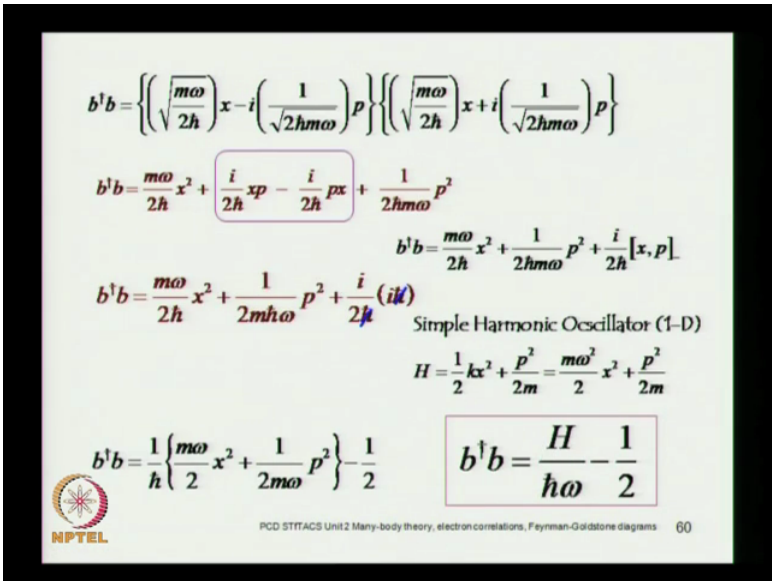

So, all we have done is to write b dagger b and now if you look at this term over here you see that i over 2h cross is common to both of these terms. And essentially you have got the famous commutator between position and momentum okay. You get xp - px and you know what it is from the uncertainty principle.

So, that is the famous x, p commutator which you know is ih cross and you can write ih cross in place of this. You got a term which is quadratic in x and the term which is quadratic in p. And then this ih cross, so this i together with this i will give you -1, this h cross will cancel the h cross in the denominator. And you will get - 1 over 2 from the last term okay.

So, you have got the first quantization Hamiltonian which is quadratic in x and quadratic in p and if you write this Hamiltonian recognize these terms. Then essentially it is the Hamiltonian divided by h cross, this h cross has cancelled. So, you get -1 over 2 and b cross b is nothing but the Hamiltonian divided by the energy h cross omega -1 over 2 okay.

So, you can now place the Hamiltonian on one side and everything else on the other. And that will give you the expression for the Hamiltonian in terms of the destruction and creation operators.

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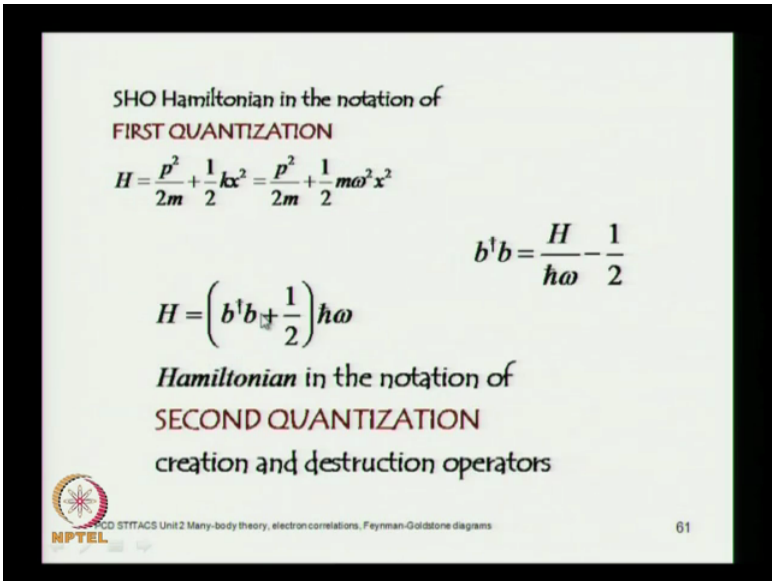

So, let us do that so this is the Hamiltonian in the first quantization notation. You have got b dagger b equal to H over h cross omega - 1 half which is what we just obtained. And if you flip this equation you get H is equal to b dagger b + 1 half h cross omega are you expect this to be you know that this half h cross omega will be the zero point energy right.

Which is a well known result for the simple harmonic oscillator and typically the energy will be n + half h cross omega, so that will identify the operator b dagger b with the number operator okay. So, this is the Hamiltonian for the simple harmonic oscillator in the notation of second quantization destruction and creation operators.

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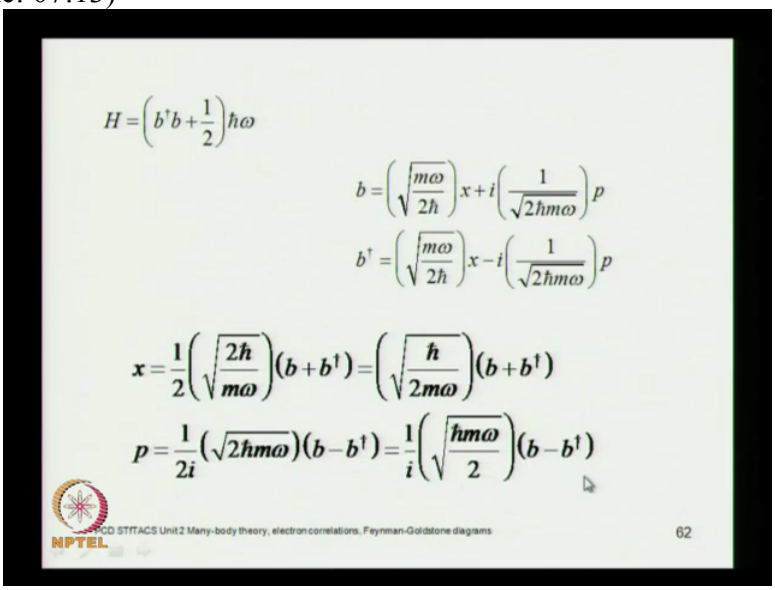

Now these are the main results that we have got this is the Hamiltonian, these are the destruction and creation operators in terms of position and momentum fundamental operator's okay. And you can now add and subtract these results and take care of the coefficients and you can write x and p in terms of b and b dagger okay.

You have got these two linear equations b and b dagger in terms of x and p. So, you can flip them and get x and p in terms of b and b dagger. So, you get x in terms of b + b dagger and p in terms of b - b dagger weighted by appropriate coefficients okay, so that is very easy to see. So, this is now your number operator b dagger b.

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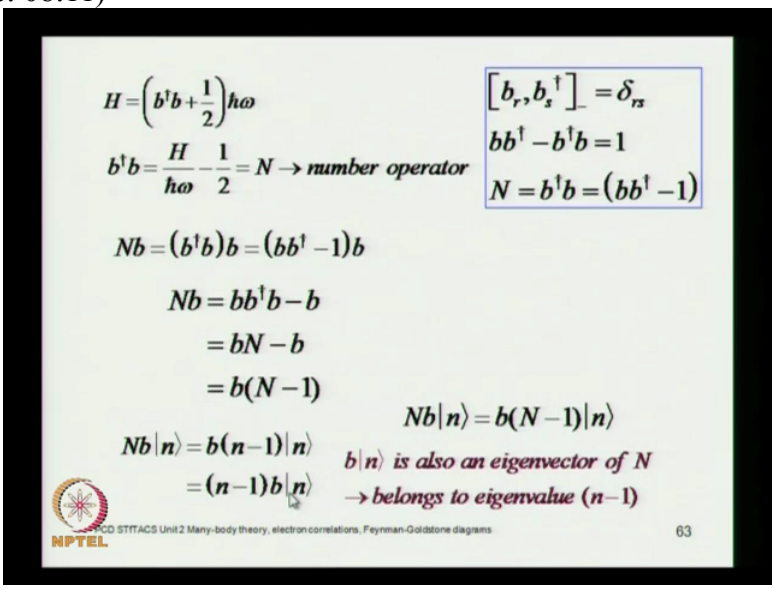

Because this will give you n + half h cross omega right this is your number operator and the fundamental commutation rule if you remind yourself of what it is it is b b dagger - b dagger b = 1 okay, which means that b dagger b is b b dagger – 1. Now we can play with these terms to get some very useful results. So, what we do is find the operator Nb, N is this number operator b dagger b.

So, if you now find Nb is b dagger b, so this is Nb, but N we have already found over here is bb dagger - 1 and now you can expand this so that will give you b b dagger b from the first term and -b from the second which essentially gives you b times n - 1 right. So, this is your operator Nb.

Now if you operate by Nb on an occupation number ket okay, n is an occupation number ket, it is a vector in the occupation number space. Then since Nb = b times n – 1, you have effectively b times n - 1 operating on n right. This is of course an Eigen state of the unit operator 1 and the occupation number ket it is also an Eigen ket of the occupation number operator which is capital N.

So, the Eigen value of n -1 operating on n will be little n - 1 right. And this is then further to be operated upon by the operator little b which is the destruction operator. So, you get Nb

operating on n gives you b operating on n - 1 times n but n minus n - 1 is just a number. So, essentially you have got n - 1 times b operating on n.

If you look at this last result you immediately recognize that the vector in the occupation number space you get from the result of the destruction operator b operating on n is also an Eigen value of the number operator okay essentially you have got an Eigen value equation. So, the destruction operator gives you an Eigen value equation and the Eigen value is n - 1 okay.

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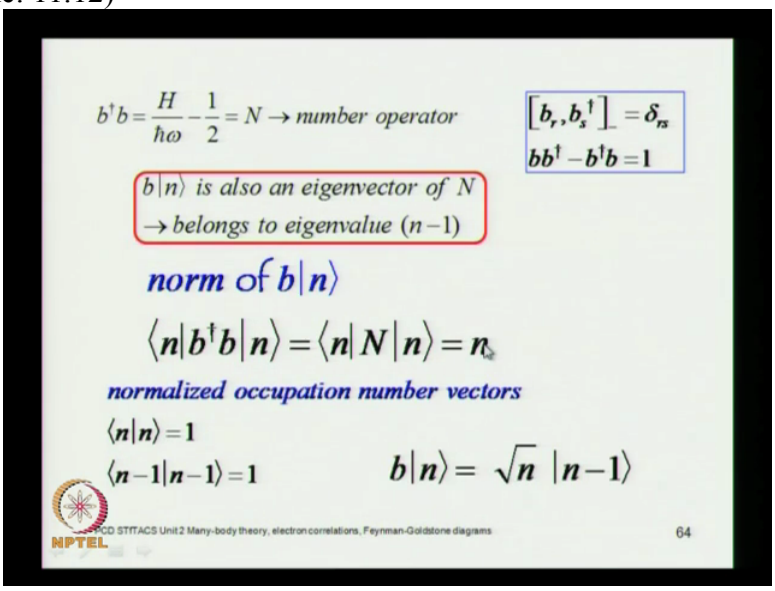

Now let us look at the other possibility say you have got again b dagger b as the number operator. We have already seen that bn is an Eigen vector of the number operator belonging to the Eigen value n – 1. Now let us look at the norm of this vector okay, n is an occupation number vector we presume that all of these are normalized. You have got an orthonormal basis in the occupation number space.

And the norm of b will be bn projected on its adjoint vector which is this right. Now b dagger b is the number operator, so N operating on n will give you the number n times the Eigen vector n whose norm is 1. So, the norm of bn will = n okay. Now if this relation is to be valid also in the context of the fact that these occupation number vectors are themselves normalized which means that the norm of the vector n = 1.

And the norm of the vector with n - 1 excitations is also equal to 1 they are all normalized. So, if both of these are normalized what does it tell you about the result bn, bn must be square root of n times n - 1 right, b operating on n will give you n - 1 but it will scale it by a factor root n because if you now construct the norm of this vector the root n and root n will give you the norm of bn which is equal to n right.

Now I need you to remember this result because we are going to refer back to this in a short while okay. So, make sure that you take note of the fact that when the destruction operator operates on the occupation number ket for a Bose system okay, this is valid we I just use the example of the simple harmonic oscillator. But then this is much more general than that you can take any boson excitation feel and you have got similar results.

And then you get an occupation number vector with the number of excitations reduced by 1. So from n you go to n -1 but then you get a little bit of scaling and the scaling is root of n okay. This is the original number of excitations in the vector on which b operated okay. So, this factor is something that I need you to remember for our discussion which is to follow okay.

Now we had worked with the operator Nb in the previous example now let us work with NB dagger now what is Nb dagger.

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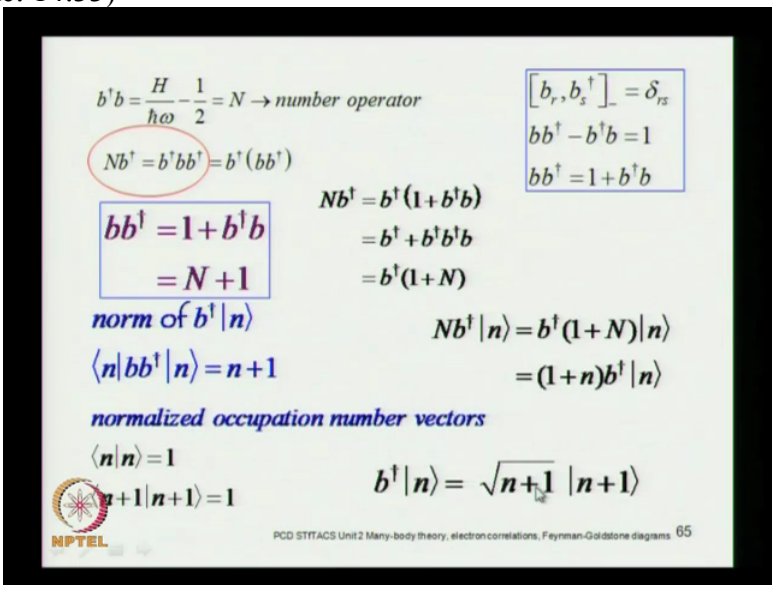

What is Nb dagger? Nb dagger is b dagger b, so Nb dagger b dagger b b dagger which but this operator multiplication is associative. So, I can think of this as bb dagger but bb dagger is 1+ b dagger b or it is equal to n + 1 because b dagger b is the number operator right. So, this operator is N + 1, so this is Nb dagger becomes b dagger times 1 + N or N +1 okay.

Now this being the case let us now use the operator Nb dagger and operate on an occupation number vector n, what do you get? Now b dagger 1 + N is Nb dagger, so this is Nb dagger and this is effectively equal to b dagger N + 1 and this is an Eigen state of N and also of the unit operator belonging to the Eigen value 1 + N.

So, the result is 1 + n times b dagger n right. So, now this is the primary result which we have used and if you now look at the norm of b dagger n okay, if you look at the norm of b dagger n you find that this norm is equal to n + 1, what does it tell you for the result b dagger operating on n? Because again these vectors n and n + 1 are independently normalized, so that means that when b dagger operates on n you get one extra excitation.

So, the occupation number goes from n to n + 1 but then the vector gets scaled by a factor root of n + 1, it is exactly the same kind of analysis as we had in the previous case right. So, you get root of n + 1 and again I need you to take special note of this factor that you not only go from n to n + 1 but in this case you get a scaling through root n + 1. In the previous case you got scaling through root of n when you operated by b.

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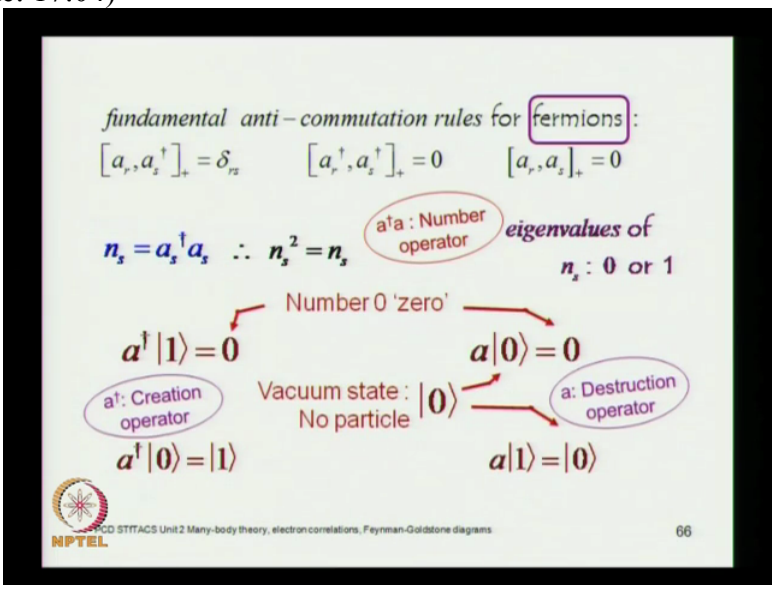

So, do make a note of mental note of these results and we will now consider the fermions. The focal interest in atomic physics is on fermions because you want to study the electronic structure of atoms and how the atom responds to collisions, electromagnetic radiation etcetera. So, a lot of work has to be done with Fermion operators in atomic physics, so the Fermion anti commutation rules.

These are the fundamental for me on anti commutation rules and here you have got ar, as dagger + as dagger ar = delta rs okay. The 2 creation operators always anti commute and the 2 destruction operators for fermions always be 0. And we worked with these operators in our previous class.

Just to get a little handle on these operators and we discovered that why this is the number operator that it's square is always equal to itself. That the Eigen values for fermions will always be either 0 or 1 and we recognize these operators to be destruction and creation

operators and the number operator right. So, we acquainted ourselves with these properties in the previous class.

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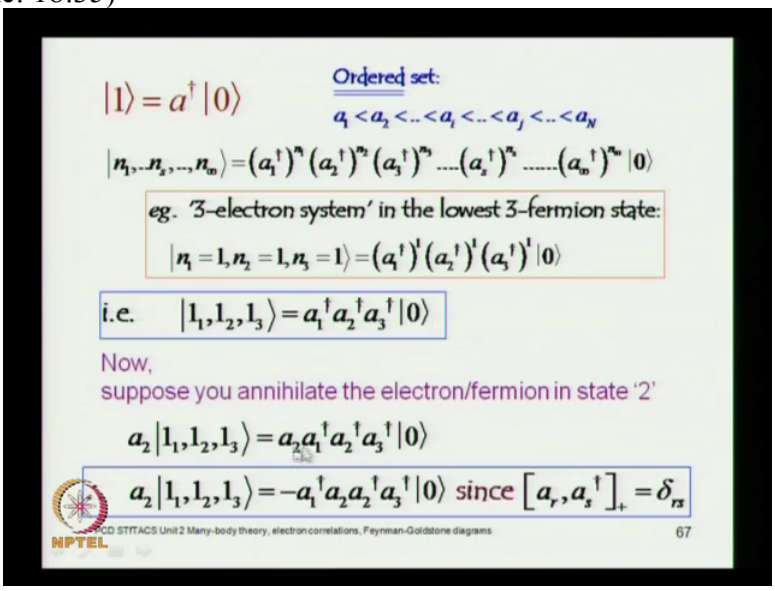

Now let us look at some of these results. So when you have got a creation operator which operates on the vacuum state you get a state with one particle. We will work with an ordered set okay and this I would like to emphasize this does not mean that here you are dealing with numbers which have got this inequality. But here these are quantum labels which are arranged in a particular sequence.

So, that the label a1 comes before a2 and the label a2 comes before label a3 because these labels are not necessarily numbers okay they are just quantum labels. They are in fact a set of four quantum labels. And you order them in a particular manner and having fixed that order. In occupation number state an arbitrary occupation number state in which you have bought n fermions can then be obtained by operating the creation operators.

For all of these states from a1 up to a infinity okay either 0 or 1 time. If you operate it zero times you have got an operator a1 dagger to the power 0 that is a unit operator, so it does not do anything to vacuum it leaves it alone. But if the index here is 1 then of course it will create a particle in that state and that will be the occupation number in this occupation number space representation.

So, the occupation numbers vectors can then be written as a result of the creation operators for each state operating n number of times on the vacuum okay. Now this is your representation of an arbitrary occupation number state. And because of completeness you require all of these infinite single particle states. Out of which only a certain number of finite number depending on how many electrons you have in the system.

Those many states are occupied all the others are vacant okay. So, only those creation operators corresponding to those occupied states would have operated on vacuum giving you an occupation number state. So, this is your Fermion occupation number state. Now let us take an example, let us take three electron system in the lowest three formion state.

So, n1 is = 1, n1 is the lowest one corresponding to this state a1. Lowest in the sense it is the first one in this sequence I am NOT referring to energies okay. I am not referring to angular momentum; I am just referring to a certain order in which the quantum numbers are written up. You have got infinite number of single particle states.

I have written all of these single particle states which are coming from Eigen values of commuting operators. They are coming from measurements what are compatible measurements okay. Those measurements give you a set of quantum numbers those are four of them stack together in one label, which is a1.

Similar you have another set of four labels in a2 and these are now arranged in a certain sequence. What that sequences is? It does not matter I can write 5p before 1s if I wanted okay. It is just an ordered set of these quantum states. So, I have got n1 = 1, n2 = 1, n3 = 1 and all the other ones are 0.

Which means that you have got these 3 creation operators which operate on the vacuum to give you this state and the creation operators for all the other single particle states are missing okay so their powers in this expression would be 0 which would give you a unit operator okay so this is your 3 electron system.

For the first three lowest in the sense, the first three states are occupied and not any of the other. So, this is your three particle three electron system, so you have got one n1 = 1 in state 1. The number of particles in state 2 is also equal to 1; the number of particles in state 3 is also equal to 1. Now let us destroy an electron in the stake 2 okay suppose you have some mechanism, you can shine light on it okay and extract one of the electrons out of it okay.

You can do various things, so you destroy one electron out of these three which one, the one which was in state number 2. Now this is the one that we have chosen for the purpose of this discussion to be destroyed. So, you have got the anti annihilation operator for the state2, a2 operating on this occupation number state. Now this state itself is the result of a1 dagger, a2 dagger, a3 dagger operating on vacuum. So, now you have got a2 operating on this okay.

Now what happens now when a2 operates on this, if you want to move a2 to the right okay does a2 commute with a1 dagger it anti commutes okay. And because the state's 2 and 1 are different they have to be different. They may have the same energy but there are different states okay. Because we are not referring to an energy sequence or something we are talking about a sequence of quantum numbers okay.

So, this could be the lithium atom for example, so you have got 1s2 2s1 the energy of the 1s up and the 1s down is the same okay. So, the energy ordering is not of significance but clearly 1s up is different from 1s down and one of them is what I have labelled as a1 and the other is a2. So, I know precisely which one is being destroyed.

So, now a2 is certainly different from a1 because the labels 2 and 1 are different. And therefore a2, a1 dagger will be equal to - a1 dagger a2 because this anti commutater is equal to delta rs okay. So, since r is not equal to s in this case this is equal to 0 and if a2 a1 dagger will be equal to – a1 dagger a2 okay.

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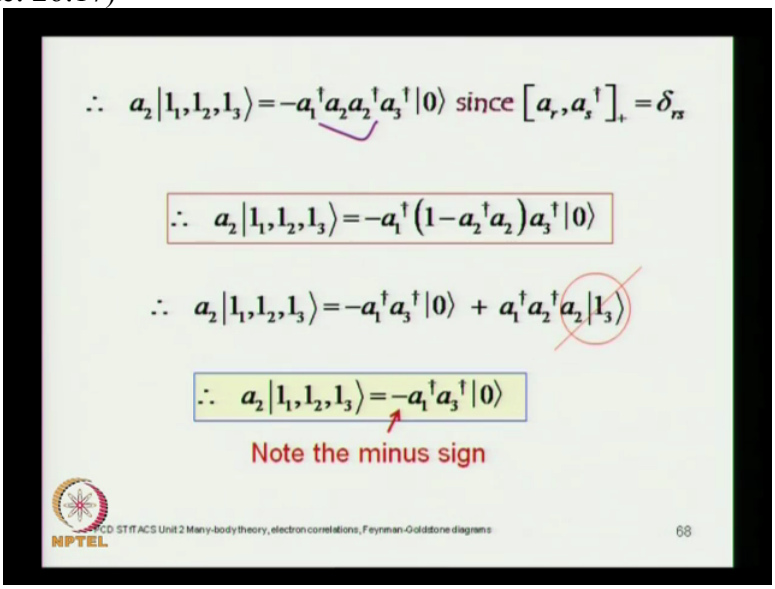

Now let us take this result to the next slide which is here and now you want to move a2 further to the right of a2 dagger. Now when you do that again you have this anti commutation relation but this time a2 a2 dagger will be equal to 1 - a2 dagger a2 because these are the same labels okay. So, this time you will get 1 - a2 dagger a2 and now you will get two terms one which is this - a1 dagger one operating on a3 dagger operating on vacuum.

And the second is - a1 dagger operating on this - sign do not forget. And then you have got a2 dagger a2 operating on a3 dagger operating on the vacuum right. So, you get two terms so these are the two terms first is - a1 dagger a3 dagger operating on vacuum. Second is now it

comes with the + sign because of these two – signs, so you have got a + sign here and you have got a1 dagger a2 dagger a2 operating on a3 dagger which is operated on vacuum.

Which gives you one particle in the state 3 okay, now your state vector look at the second term here in the second vector you have got one particle in the state 3 and this fellow can only destroy a particle if it existed in the state number 2. It cannot destroy a particle in state number three right.

So this term will vanish okay because the operand of a2 has got a particle it has got an electron but not in the state for which the destruction operator is a2 can destroy a particle only in state 2 not in state 3 okay. So, this second term vanishes and you are left with only the first term that when a2 you try to destroy particle number 2, electron number 2 in a 3 electron system.

And you are destroying the one in the second state the result is you are left with a state in which you have got particles electrons in state number 1 and state number 3. But now you have picked up a minus sign okay. So, note that there is a minus sign which has resulted, so far as occupation number phase is concerned. It gets multiplied by -1 okay.

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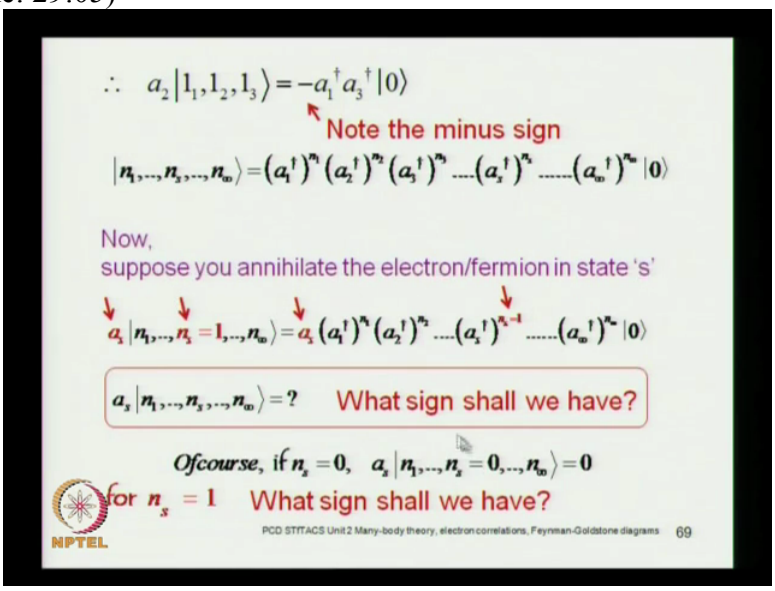

So, there is a minus sign which results in this process. So, now let us look at a general occupation number state. And now we will take not just a three electron system but an n electron system and some of these infinite states are occupied some are not occupied a total number of n are occupied whichever it does not matter that depends on which of these powers of the creation operators are unity.

Those whose powers are 0 will be missing right. So, you may have a very complicated configuration not necessarily in the lowest energy n state but you have got n electrons in n single particle states. But these can be any combination of n from an infinite number of possibilities. Now from these possibilities you know annihilate the electron in the fermion state s in the previous case we destroyed an electron in the state number two okay.

Now we are going to do it we are going to destroy an electron out of these n electrons in a particular state which is state number s which is labelled by s. So, this is your result as can destroy an electron only if the occupation number of the sth state = 1 not otherwise okay. Because that is the only one it can destroy, so ns will have to be equal to 1. And this is now your expression that as now operates on this occupation number state.

And how do you get this occupation number state by operating by a1 dagger n1 times where n when may be either 0 or 1 depends on whether a1 is occupied or not right. And then it will have the creation operator for the sth state operating one time okay. Because only then you will get ns = 1 not otherwise. If this was equal to 0, ns would be unoccupied. So, here ns = 1 and then other one's it does not matter.

Because the only thing is can kill is a state in which the sth single-particle state is occupied. So, keep track of the fact that you are dealing with the destruction operator which can destroy a particle only if the sth state is occupied. So, here is your destruction operator and this occupation number state must have the creation operator raised once and not 0 times okay. Now the question is what sign will we get?

Because when we destroyed the electron in state 2 in the 3 electron system you remember we got a minus sign. (Question time: 32:25 – not audible) yes you have to define what that s is? Yeah we are we are going to count that okay. So, what is the sign that you should get, so let us see how you get the correct sign because you already know that if ns = 0, you will get 0 because you will get the number 0 not the vacuum state right.

And if ns = 1 that is the question that we have now raised as to what is the sign that we will get?

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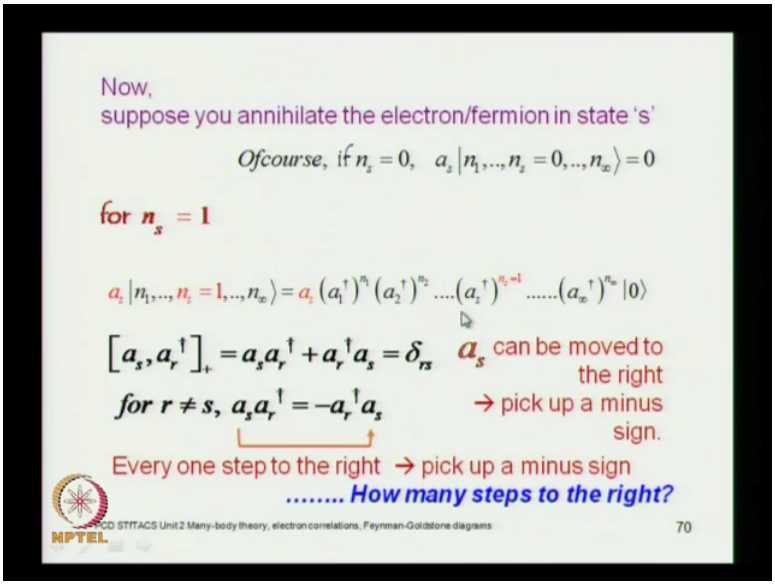

So now what you have to do is to move as to the right. Now again we are going to make use of the anti commutation relations and these are the fundamental anti commutation rules. So, if as to be moved to the right of a creation operator you can certainly do so when r is not equal to s okay. But when you do so you must get a minus sign.

So, this is what happens that every time as is moved to the right of a creation operator you get a minus sign, every time okay. So, how many times we have to move it to the right is the question that is what it boils down to that you have to move this as operator to the right of this all the way up to here. But then again you have to also move it beyond this creation operator mind you. So, let us first move it up to here.

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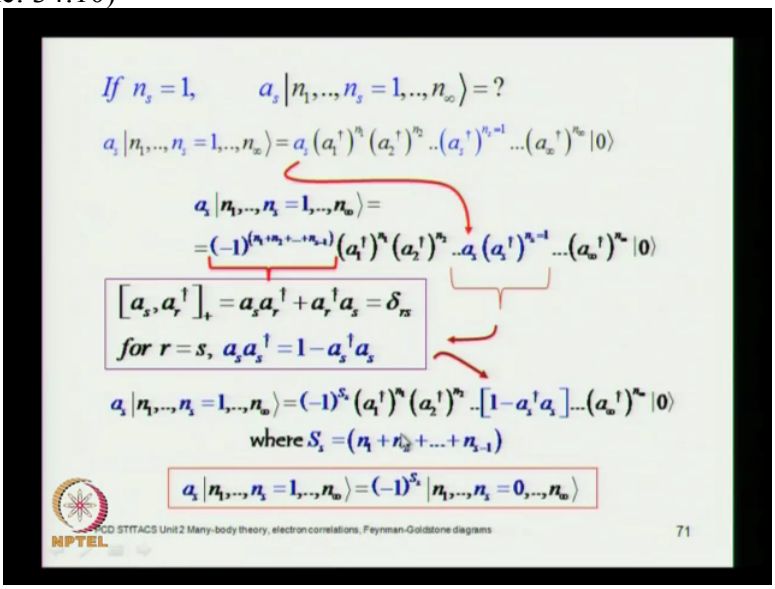

So, when you move it just behind this creation operator you have already; every time you have moved it you will raise -1 to the power a sum of all the occupied states till this okay. All the occupied states if any of those is vacant it will not contribute because that a dagger to the

power 0 is just the unit operator. So, it does not contribute okay. So, you have got -1 to the power n1 + n2 and so on up to ns -1 okay.

And now if you want to move it further to the right you will get 1 - as dagger - as okay because these two labels are now the same, so this label was different from all the previous labels but it is exactly the same as this label, so you get 1 – as dagger as. So now again you get two terms one coming from 1 and the other coming from this - as dagger as right.

So, here -1 has to be raised a certain number of times and this number is given by the total occupancy of all the states till the sth state. So, it is really not s - 1 you have to add the occupation numbers of those states okay. So, you need to add all the occupation number states and these are n1, n2, n3 and so on up to ns - 1 and that is the phase that you pick up. And then you have got as operating on the vector occupation number vector to its right.

But the occupation number to the right occupation space vector to the right of this destruction operator certainly does not have an electron in the sth state. So, that will give you a zero just the way a2 operating on a3 dagger vacuum gave you 0 okay. So, that will give you a 0 null vector and this is now your result. So, it is -1 to the power a certain sum which is not s but it is n1 + n2 + everything up to ns - 1 okay. So, this is the phase that you get. Now here ns must be equal to one.

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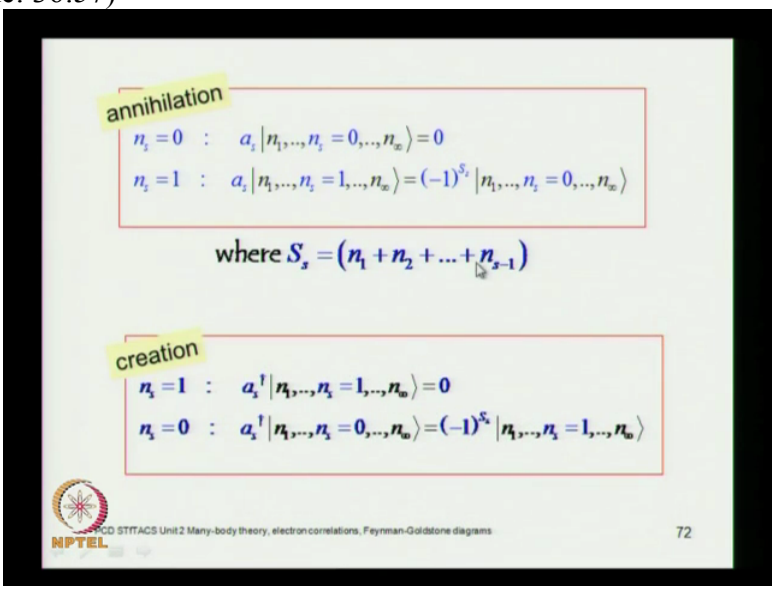

What about annihilation? This is the results that you get that you certainly can annihilate; you can destroy a particle if it is occupied, if it is zero, if it is not occupied, the result is the number zero. If it is occupied you will get a destruction of an electron in that state giving you a new vector occupation number vector in which the occupancy has now dropped by 1, so it becomes zero.

Likewise if you do the same exercise with creation operators you get a similar result, so I leave that as an exercise. It is a very similar kind of analysis and when the creation operator operates it cannot create an electron if the state is originally occupied. So, a dagger operating on a state in which is already occupied the first row will give you the number 0 okay. This we discussed also in the previous class.

This is essentially the Pauli Exclusion Principle and then if the original state is unoccupied, so if ns goes to 0 then certainly the as dagger and thus create an electron in this state giving you a state with increased occupation and then you will get ns = 1. So, you get a phase minus 1 to the power s where s is the sum of all the occupied states till the previous state.

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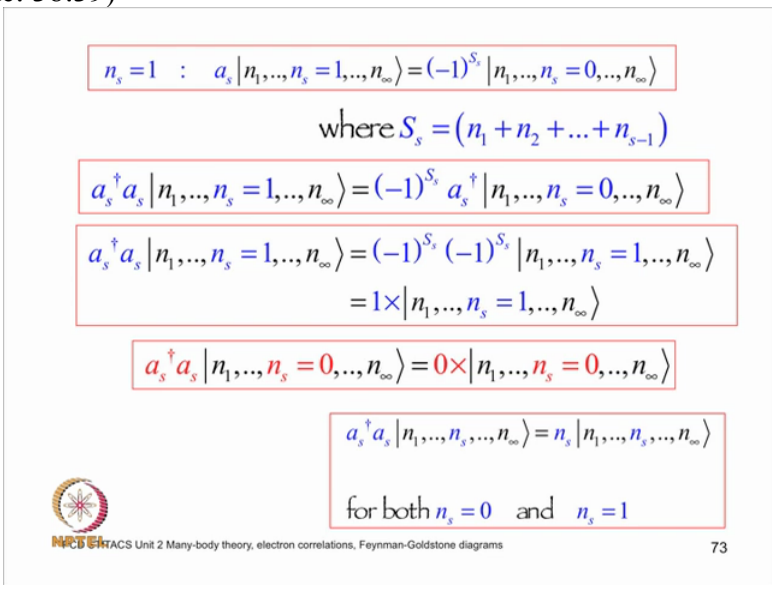

So, this is your result. Now if you, now operate by as dagger on as okay then if ns = 1, this is what you get because first you operate by as, so you have destroyed this particle. So, you get a result in which ns = 0 and on this you will now create as dagger but once you do that again you will get a phase of -1 to the s.

So -1 to the 2s no matter what it is will always be +1. So, this is the number operator which will leave this up vector invariant with ns = 1 right. If it were 0 it would give is 0, so this is the Eigen value of the number operator. It is either 1 or 0, we already know that right. So in this case it is equal to 1 and if it is 0 then you will get ns = 0.

You will get the same state it will not be changed and essentially what you find is that ns the destruction operator would give you a 0 and you will get the Eigen value to be 0, so essentially the as dagger as is a number operator whose Eigen values are either 1 or 0 as we have seen earlier okay.

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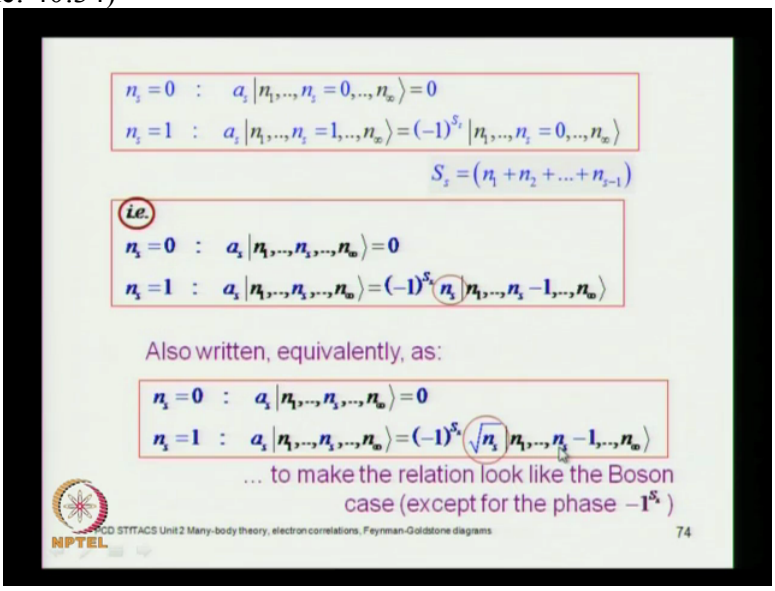

Now I am going to rewrite this result in a slightly different form which is well adapted for the second quantization formulation is the same result but we are going to rewrite it in a slightly different form it is a essentially the same result which we have at the top. But now I have inserted a factor ns over here and this is strictly correct because if ns is 0, you get a 0 that here I can write these expressions okay.

With the occupation number ns over here and this works for both whether it is occupied or unoccupied okay. If it is unoccupied ns is 0 if it is occupied ns = 1 okay. The important thing is that here the occupation number becomes ns - 1 but this is applicable only if ns were originally equal to 1 because there is nothing like a -1 occupancy okay. So, you do not go from 0 to -1 you can only go from 1 to 0.

You can only go from 1 to 0 and not from 0 to -1 when you are operating by the destruction operator. So, this result which is written with ns can be equivalently written with the square root of ns is the same, its numerical value is exactly the same okay. But the advantage here of writing it with the square root ns, so this is the certain convention that you are introduced because this makes it completely equivalent to the Bose case.

Because in the Bose case you remember that you had when the destruction operator operated on an occupation number state you got another state with one boson less but there was a scaling by a factor square root of n. When you created the scaling was square root of n + 1, you remember that is the result which I had asked you to take note off okay. This is where we use it that by writing this as square root of ns.
You can certainly write it as ns times this but by writing it instead as square root of ns you have got a completely equivalent expression with the advantage that you have got a relation

which is identical to what you have got for the Bose case, except for the fact that you now have this phase factor -1 to the power s okay.

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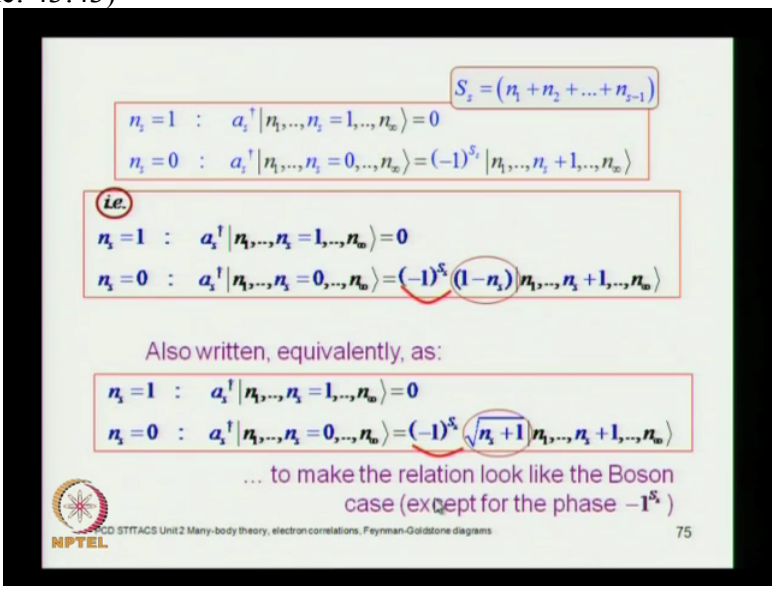

So this is an additional factor that you have to work with. Now likewise you remember that there is this phase factor -1 to the power s. And now if you look at the expressions for the creation operators then you have got; you can write these results as 1 - ns okay because if ns were 0, you get 1 times this and the occupancy goes up by 1 from 0 to 1.

If ns were 1 then 1 - 1 would give you 0 which is the fact that you cannot create a particle in an already occupied fermion state okay. So, this expression is completely equivalent to this but again instead of writing this as 1 - ns times this, instead of this coefficient we can use the coefficient root of ns + 1. So, notice that these two are completely equivalent because if ns = 0, then you have got 0 + 1 and you get a square root of 1 right.

If ns is 1 you cannot create any particle any another fermion on that so these two expressions are completely equivalent and this makes it look just like the Bose case except for the phase factor which is -1 to the power s which you must always remember when you are working with fermions.

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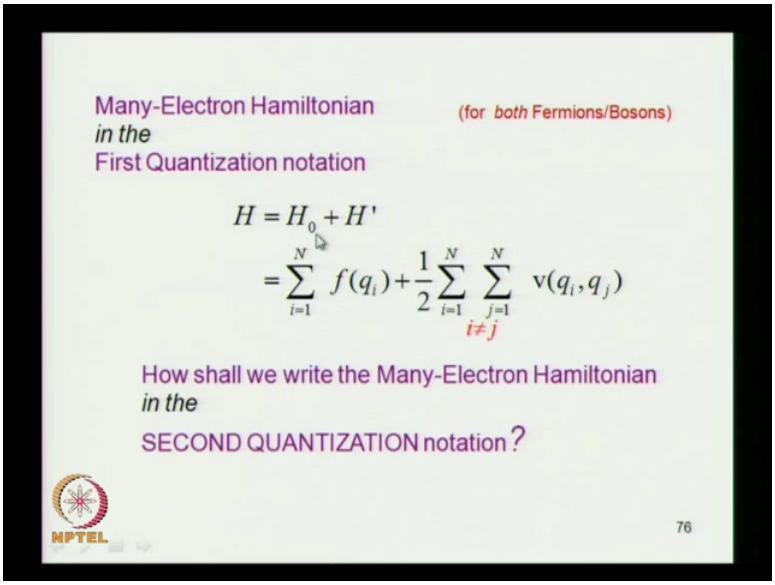

So now let us ask ourselves how to write the many electron Hamiltonian in the second quantization formulation okay. So, we have a many electron Hamiltonian in the first quantization formulation it is a sum of all these single particle operators and the two particle operators.

This we have discussed at great length in the context of the Hartree-Fock formalism in the previous course right. So you have sufficient familiarity with this and I will use that in our discussion now. So, this is your many electron Hamiltonian which is the sum of the single particle and the two electron operators.

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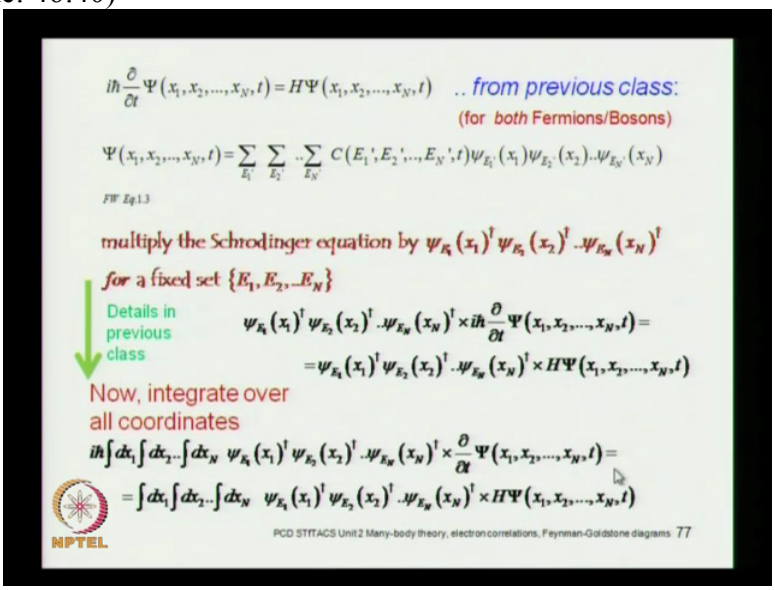

And from the previous class we wrote a general n electron Schrodinger equation, here this is valid for those cases inclusive of correlations not just the uncorrelated system in the single particle approximation. Now you understand what the correlations are, what the single

particle approximation is right. The independent particle approximation is the Hartree Fock Slater determinant.

Then you have multi configurational Hartree Fock when you have a large number of Slater determinants, why large anything more than one okay anything more than one then you have got essentially an interaction between those two configurations which are represented by the two Slater determinant. So if you have a system of that kind then you have a correlated wave function which is again written in terms of product of single particle functions.

So, this is the product of single particle functions okay which is all right because after all these electrons are fundamentally elementary particles. So, which is why you write them as a product of single particle functions but then you must have alternate possibilities because there is no guarantee that the electron at coordinate x1 will be in state E1 prime or the electron at state x2 will be in state E2 Prime.

They could be interchanged the electron at coordinate x1 could be in the nth state and vice versa these are all indistinguishable particles and you must therefore consider all of those possibilities every time you carry out an interchange you pick up a -1 factor because of the anti symmetry of the wave function. But then there is not a single Slater determinant to talk about.

So, E1 prime and up to En prime there is one coefficient corresponding to one Slater determinant right. But then you must sum over all of these possibilities, so each E1 prime can go over the entire infinite set of possibilities. So, E1 prime will have access to infinite single particle states. E2 prime will also have an access to infinite single particle states. And when you sum over all of them you have got the most general many electron wave function.

Now we worked with this in the previous class and we recognize that the symmetry of the wave function is built into the coefficient C and I am just going to remind you of some of the steps that we discussed already in the previous class. But I am not going to spend any time doing it which is why I have got this green arrow which is to tell me and to tell you that we are not going to spend any time on this but you can refer back to the previous class.

And what we did was to take the Schrodinger equation multiply this by a particular set of product of adjoint vectors having done this we integrated over all the coordinates from x1 to xn. We carried out integration over all of these okay, we did it in considerable detail in the previous class.

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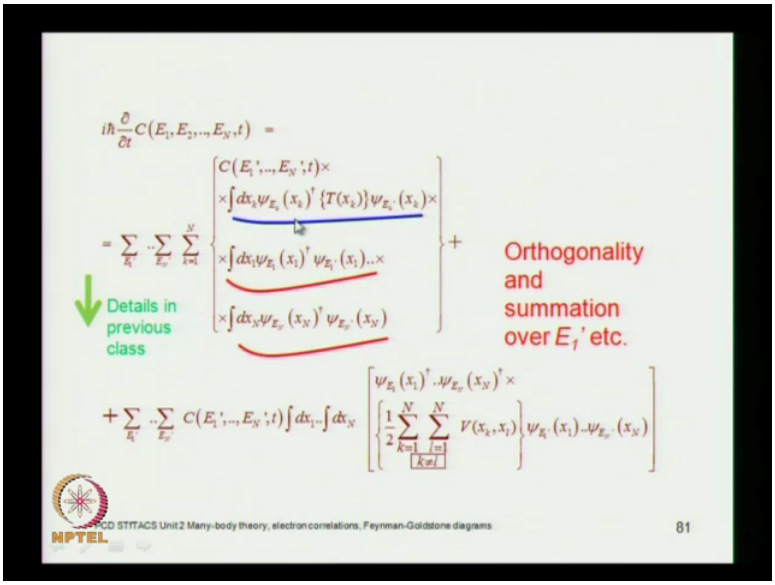

And then what we did was to exploit the orthogonality of these single particle states and that gave us contraction of these over the sums okay. This we did in some detail in the previous class, we exploited this orthogonality and as a result of the exploitation of this orthogonality. Then we plugged in the complete form of the Hamiltonian.

Which is the sum of the kinetic energy terms and the potential energy terms or the single-particle terms at the two-electron terms right. And when we did this we got we separated the kinetic energy term and the potential energy term okay. So, all this we did in some detail in the previous class so I am taking you very quickly through those steps okay.

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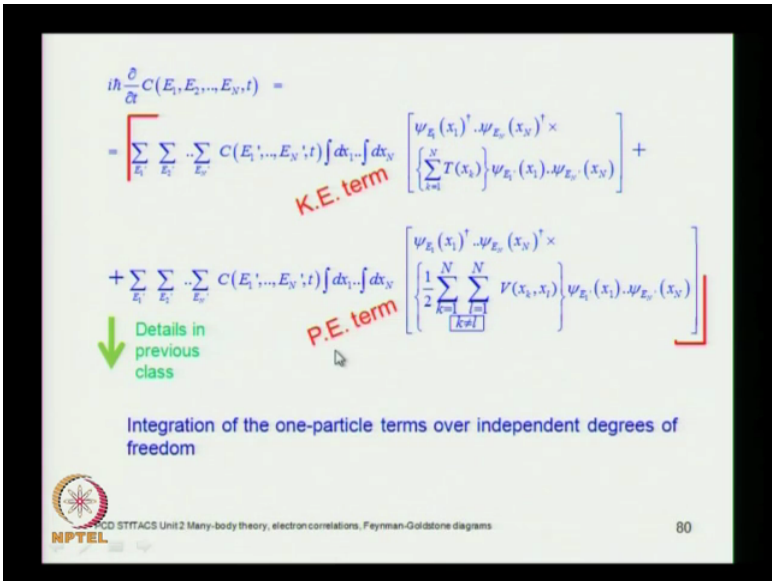

And then we carried out integration over all the independent degrees of freedom separately. So, the only thing which remains to be integrated are those terms such as this like the kinetic energy operator of the single particle operator which is sandwiched between Ek and Ek prime

when the arguments of both of these are xk because the integration over xk is independent of that over any other coordinate.

All of these are independent degrees of freedom so we separated the integrations over various independent degrees of freedom. From the other ones we get orthogonality integrals so they give you either a 0 or a 1 right. And then when you sum over all of these E1 prime, E2 prime and so on. You contract all of those summations so you are left with only 1 sum in the kinetic energy term and with a double sum in the case of the potential energy term.

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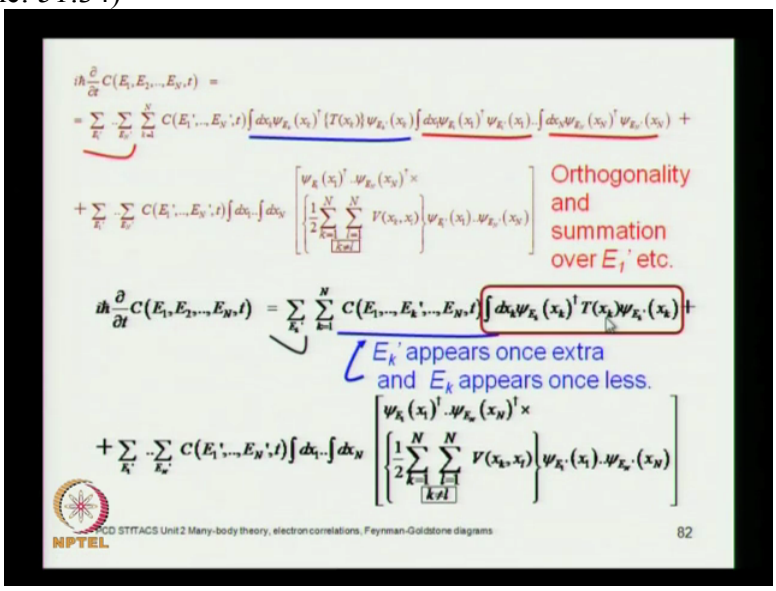

So, this is where you get the contraction. So, you are left with a single summation over Ek prime in the kinetic energy term and what happens in this term is that you have got this integral over xk which has to be carried out. And this is the one which connects Ek prime and Ek and in the corresponding coefficient Ek prime will appear once extra and Ek will appear once less okay.

Now this is the important thing because we are working with this occupation number formalism and counting is important everything is, everything hinges on the number of times the operators operator okay. So counting is important Ek prime appears once extra and Ek appears once less in this term.

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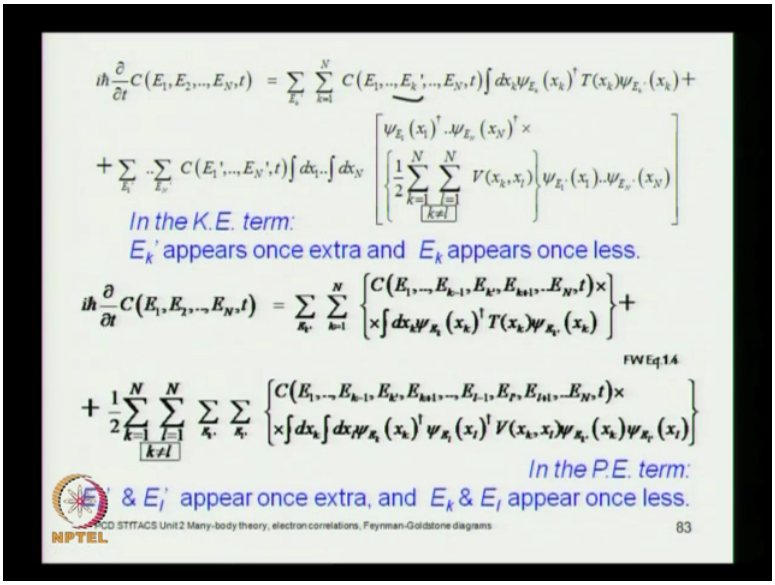

Now this is what happens in the kinetic energy term. In this business in the occupation number formalism it is important to count and you have already seen that in the kinetic energy term Ek prime appears once extra Ek appears once less but then there is a summation over k going from 1 through n.

In the potential energy term Ek prime El prime appear once extra and Ek and El appear once less. But then there is a summation over k and l each going from 1 through n okay. So, we will carry this information into our occupation number formalism.

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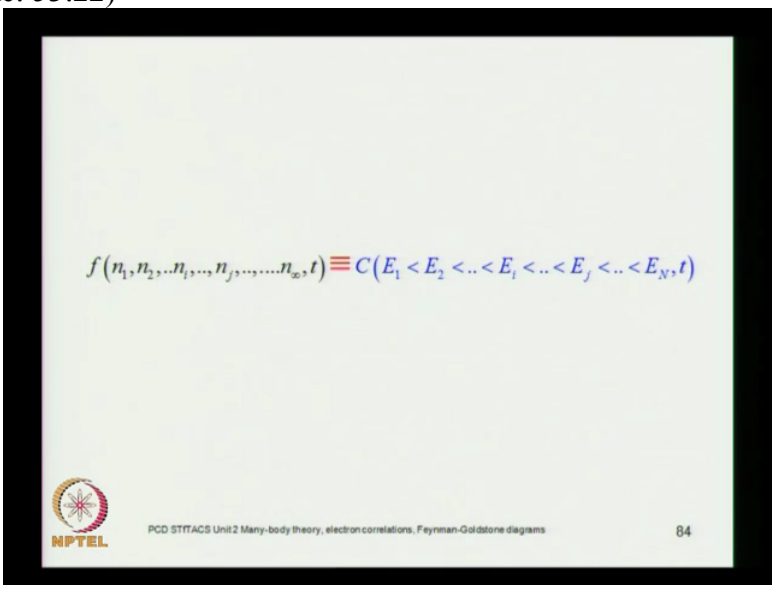

In which we recognize we discussed this point in the previous class. That the coefficients of which the arguments are these single particle states which single particle states those which are occupied okay. Those are the ones which come in those coefficients there is also a time dependence because of our single particle states are completely independent of time all the time dependence is in this coefficient C.

So, there is a time dependence in the function f which is a function of all of these occupation number. And these two coefficients are completely equivalent the one on the left hand side is immediately adaptable to the occupation number formalism. The one on the right hand side is the one that we use in the first quantization formalism okay.

But then when you go over from the first quantization to the second quantization then the information which is contained in which of these coefficients which of these quantum states are occupied that information goes into these occupation numbers because if E2 is occupied then n2 is one, if E2 is not occupied then n2 would be 0 okay. So, there is a one to one correspondence why these two coefficients are completely equivalent okay.

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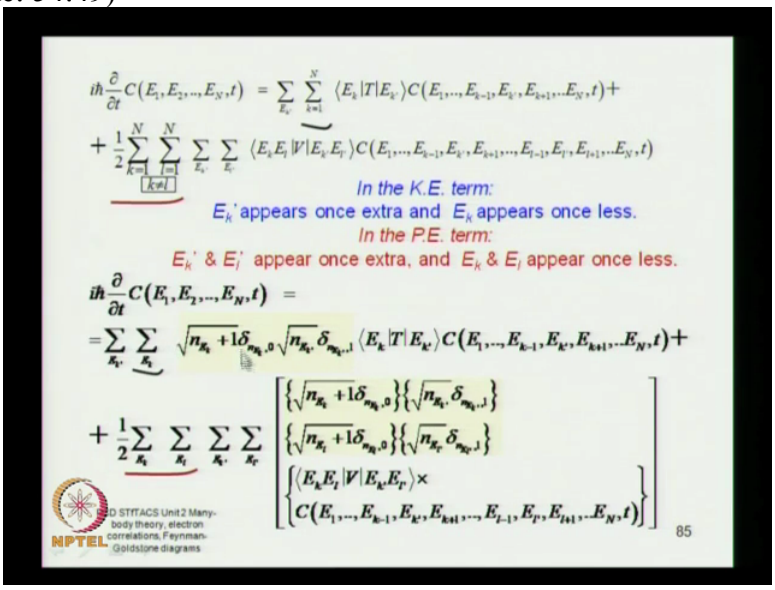

So, this is the information that we are going to carry and let us do that and subject to the consideration that Ek prime appears once extra in the kinetic energy term. And in the potential energy term Ek prime and El prime appear once extra but Ek El appear once less okay. So, with reference to this if you now rewrite the same expression but instead of the coefficient C we will now rewrite this expression for the coefficient F.

Which is completely equivalent okay, so the coefficient F is completely equivalent but you must also carry this information about the occupancies, so let us do that, so to be able to do that I plug in the information about the occupation numbers explicitly over here okay. And here you remember that we had these square root n + 1 + square root n factors because if a term appears once less then you have got a destruction.

If it appears once extra you have got a creation and you have to look at this matrix element of the single particle operator which is the kinetic energy operator over here but it can also

include a single particle potential energy term like what each electron experiences from the nuclear field okay. So, the z over r is also a single particle operator. It is only the E square over rij or r12 which are the two center particles.

So, you have square root of n and this will come into picture only if Ek prime nEk prime this occupation number of the Ek primate state is equal to 1. Because what this kinetic energy integral term is doing is you can think of this as if it is transferring a particle from Ek prime state to the state Ek and that would happen if and only if Ek prime were occupied not otherwise.

If Ek prime were vacant to begin with there is no way this could be done which is why there is this Kronecker delta which takes care of it. Likewise you have got a delta nEk, 0 over here and this is scaled by the square root n + 1 factor. Now in the potential energy term you have got similar terms just like these two but now you have got four of them okay.

It is exactly the same logic and here the potential energy integral is this Ek, El this is the potential energy operator and on the right side you have got Ek prime El prime and now you instead of summing over k from 1 through l. You now will sum over all the Ek states okay, because this was summation over all the occupied states.

Here you will sum over all the single particle states but whether or not they were occupied is taken care of by this square root of n and square root of n + 1 and the Kronecker delta. So, the same information is transferred but we are now equipping ourselves with a reformulation of the many electron problem from first quantization formulation to the second quantization formulation.

So, the occupation information is now contained in these factors but now the summation there is a double summation this summation is over Ek prime and this is a summation over Ek. So, instead of k going from 1 through n you now some over Ek but now the summation is over all the single particle states but all of them will not involve to begin with.

But, so also now because now you have got this delta nEk 0 factor okay and here you have got the Kronecker delta Ek prime, 1 so that takes care of it.

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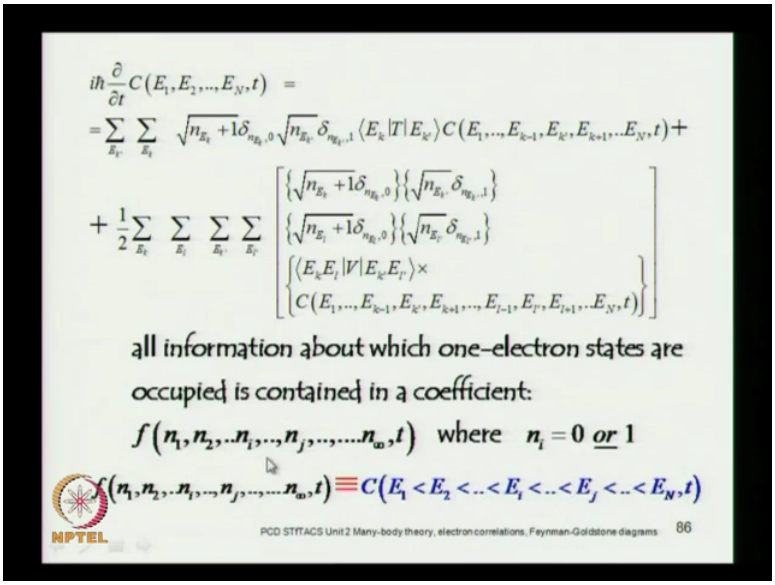

So, now you have plugged in the information about the occupations. And now you have got a double summation over here and the quadrupole summation over here over these four quantum numbers each quantum number is a set of four quantum numbers okay, but here we write it as four labels.

And all the information which is there in the coefficient C is in the coefficient F as you know. So, now instead of these coefficients C with the information we now have about these occupation numbers we can now replace these coefficients C by the coefficients F and go over to the occupation space vector.

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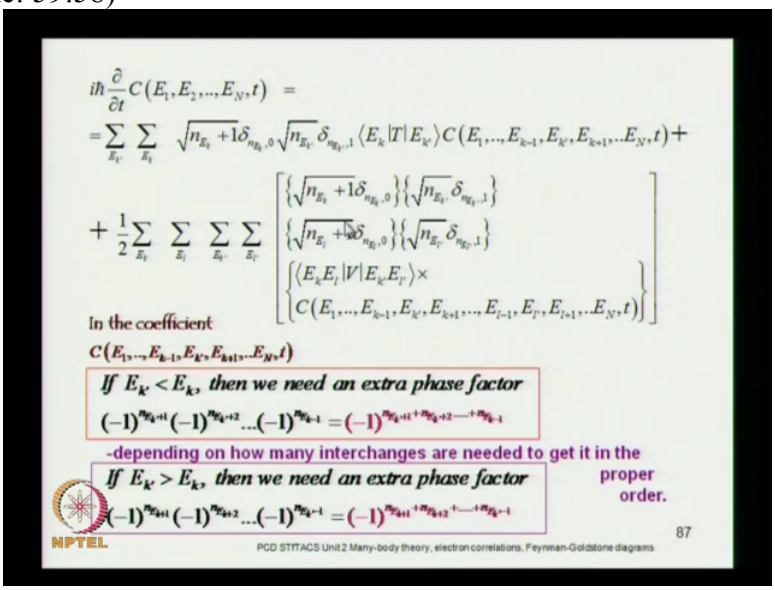

So, let us do that when we do that this Ek prime which had appeared once more if you remember okay, but you are summing over Ek prime and it could this excess Ek prime could be anywhere from the first to the last. But remember that when you go to the occupation

number is space formalism you have to put it in exactly the same order in which you chose to identify your single particle states.

So, we worked with an ordered set a1, a2, a3 up to a infinity right and you have to move this Ek to its appropriate place and when you move it you must pick an appropriate phase which will be -1 to the power a certain number which will depend on how many times you have to move it to get it to its appropriate position okay.

So, when you if Ek prime or less an Ek then you will have to pick up -1 to the power Ek prime +1 because you will have to move it only beyond Ek prime till you get to Ek - 1 to 1 proceeding. So, that is the number of times you will pick -1 factor so you can add all of these powers of -1 and that is the phase you will have to plug in.

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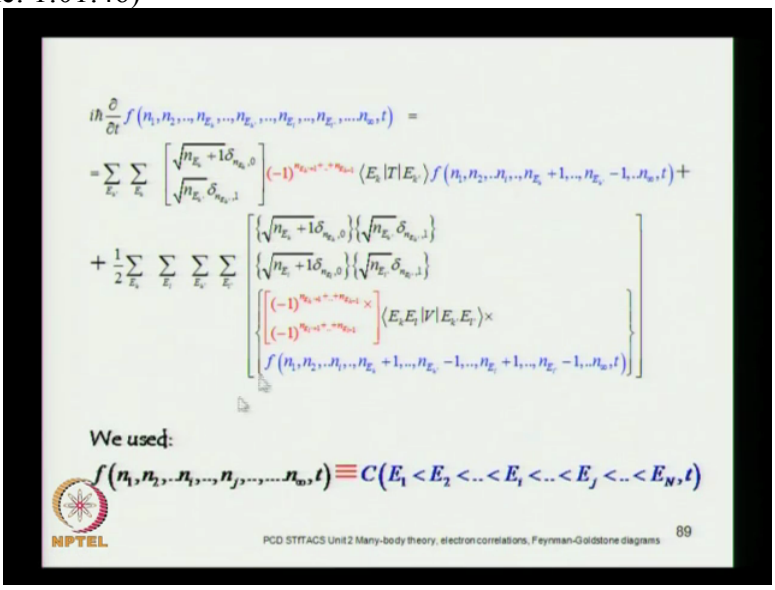

So, now we will put this extra of phase in our factor we have got the number is already now we have to put in this additional information about the phase and now with this additional phase information these numbers and the Kronecker delta's you have got everything that you need to go over to the occupation number vectors. So, now we use this equivalence between the coefficients C and the coefficients F.

And with respect to the equivalence between the coefficient C and the coefficients F, you now have this partial time derivative of the function f which is a function of all these occupation numbers which is equal to h Psi on the right side. But this is also now written in terms of the function f which is a function of all the occupation numbers.

Here notice that the occupation number of Ek prime is one less the occupation number of Ek is one more in the kinetic energy term. In the potential energy term it is occupation number of

Ek which is 1 more Ek prime which is 1 less, El which is 1 more. So, it is nEl + 1 and here El prime it is 1 less.

And then you have got all the phases and all the occupation numbers here. Now you have got everything we have used this equivalence and written the rate equation so this is the time evolution of a state vector. But now we are now able to carry over this discussion into the occupation number space.

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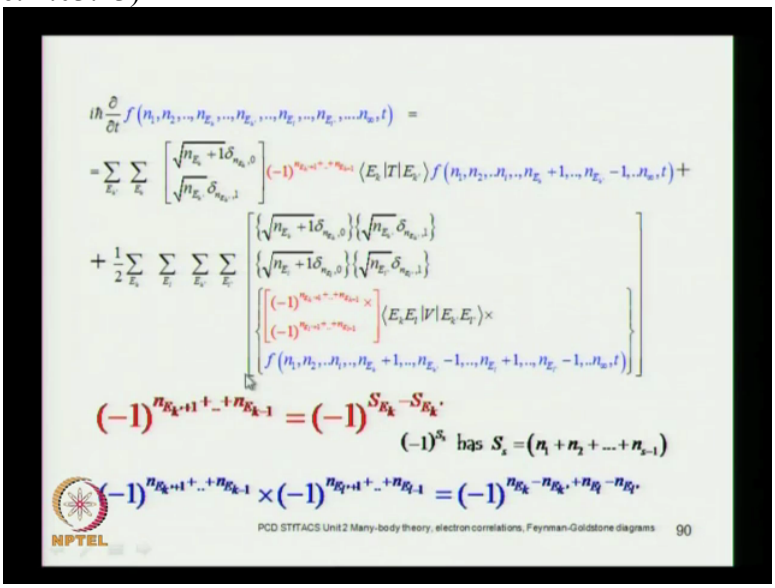

So, we can now do a little bit of simple manipulation of this phase factor because this is very simple because -1 to the power this phase can be written as -1 to the power SEk - SEk prime this is very easy to see I will leave this as an exercise for you to figure out it is very straightforward. And likewise you can work with the phases in the potential energy term also.

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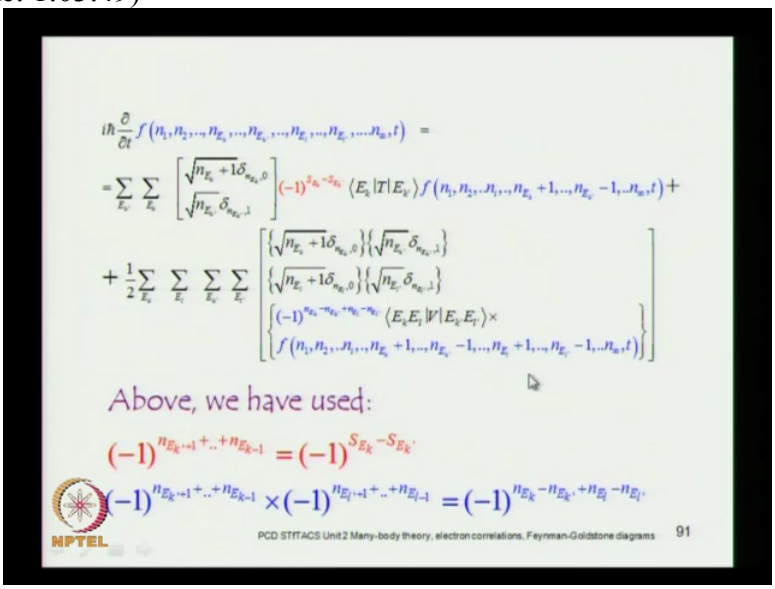

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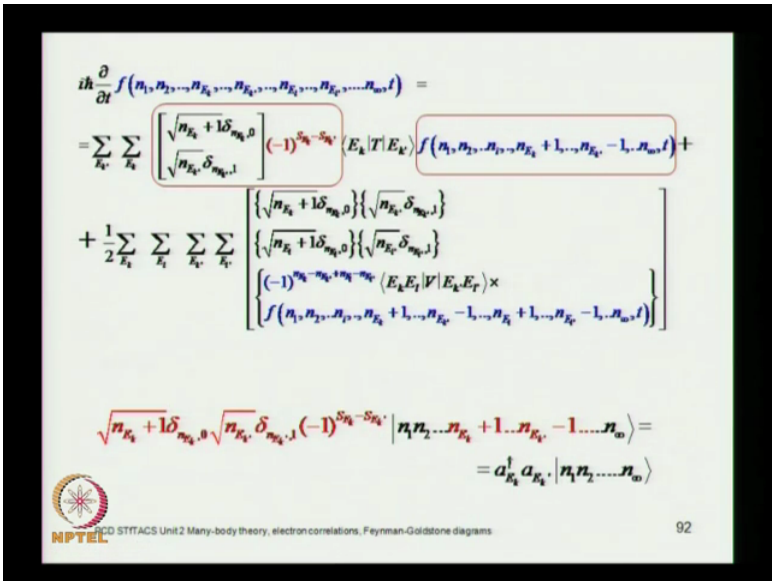

And write all of these phases here in terms of these -1 to the power S and -1 to the power -SEk Prime and using these phase factors you have got this term over here, so I have got the same phases but they have been written in a more compact form.Now what is this now look at this vector here, here what is the information that you have got?

You have got the function f which is a function of all these occupation numbers how can you get this occupation numbers. You can get this if you destroy a particle in the state Ek prime and if you create one in Ek right. And then you also have these phases. Now what you find is that that is exactly what you are doing, that if you have a general occupation number vector n1, n2 all the way up to n infinity okay.

Then only if Ek prime is occupied which is why you have got Ek prime, 1 Kronecker delta. This Kronecker delta would be 0 if Ek prime were not equal to 1 if the occupation number of Ek prime was not equal to 1. So this Kronecker delta would give you a 0, if Ek prime was unoccupied but when it is occupied you can destroy a particle from Ek prime.

And that would give you a new state in which the occupation number of Ek prime would be 1 less which is nEk prime -1. So, this state is completely equivalent to this state on the right hand side okay. And now you can write this result completely in terms of occupation number state vectors.

Because if the kinetic energy term you have got a dagger a, but the destruction is in the state Ek prime and the creation is in the state Ek. This is exactly what gives you the correct phases and the correct square root signs over here.

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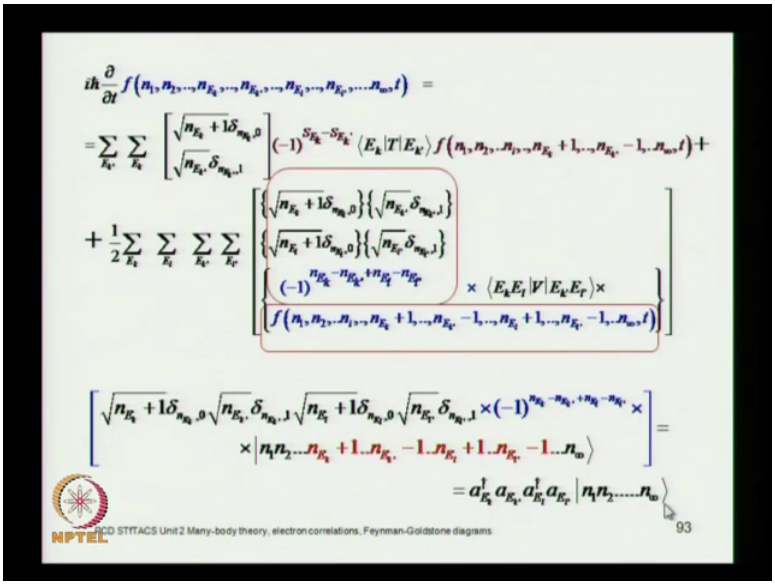

So you have that further kinetic energy term. So, far as a potential energy term is concerned it takes a little more time to see that but it is based on exactly the same logic, there is nothing new in it. It is absolutely no new logic in it that you have got the phases you have got these Kronecker delta's which tells you whether you are going to get a 0 or 1.

And you are going to get a 0 or 1 depending on whether you are trying to if you are trying to destroy a particle destroying an electron from a state which is unoccupied you will get a 0 right because you cannot do that. You can destroy an electron only if that state is occupied. So, that information is sitting in these Kronecker delta's and here you see that the occupation of Ek has gone up by 1, occupation of Ek Prime has gone down by one.

Occupation of El has gone up by 1, occupation of El prime has gone down by one. So, now this result is completely equivalent to the operation of on in general occupation number state by these creation and destruction operators, there are two creation operators for Ek and El and there are two destruction operators Ek prime and El prime.

But mind you they must come in exactly the order in which you see them on the screen okay. Because they must satisfy the anti commutation rule. So, you cannot write them in any arbitrary order you must write them in exactly the in the order in which you see them here. So, what we can do is in place of what you have in these two square boxes you can write the right hand side okay.

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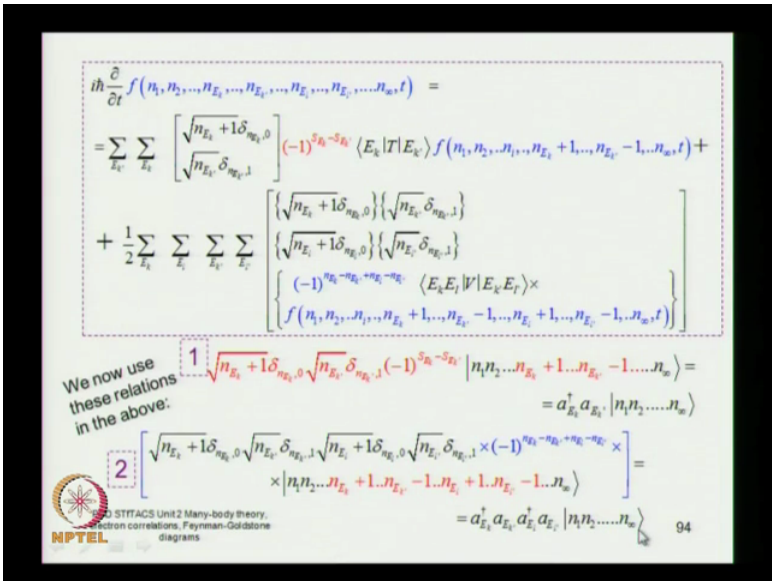

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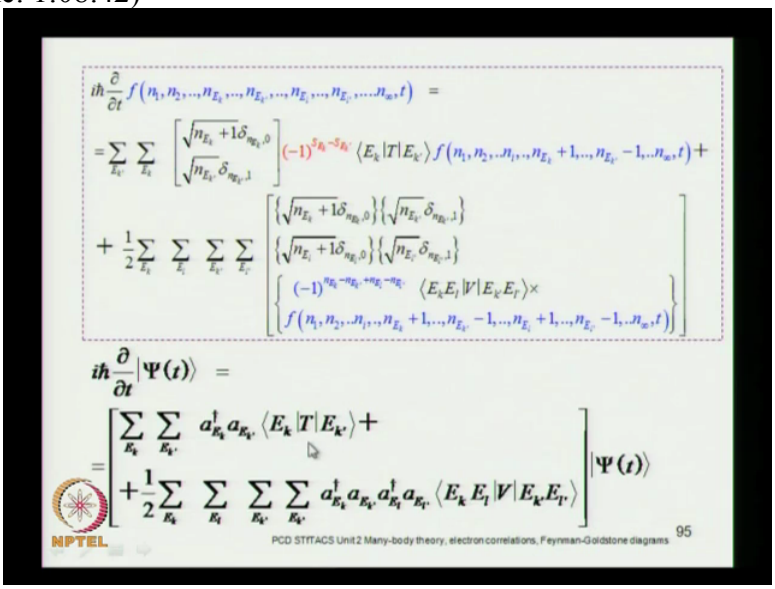

And you have got for the kinetic energy term a right hand side which can replace this and in the potential energy term you have got this information on the right hand side in terms of the occupation numbers state vectors and the creation and destruction operators which can replace the corresponding terms in the first quantized notation or what is some sort of a transition from the first quantization to the second quantization formalism.

So, using these two results you now have the Schrodinger equation okay. The Schrodinger equation which is the time evolution of a state vector in the occupation number space is now given in terms of these are of course integrals these are single-center integrals okay integrals over a certain coordinate. Here you have got two center integral right and then you had a creation and destruction.

But you are must sum over all of these states Ek and Ek prime both going from zero not from 0 to infinity but overall the infinite single particle states okay, all of them must be summed over. So, now we have the final expression for the Schrodinger equation in the second quantization formalism which is this okay.

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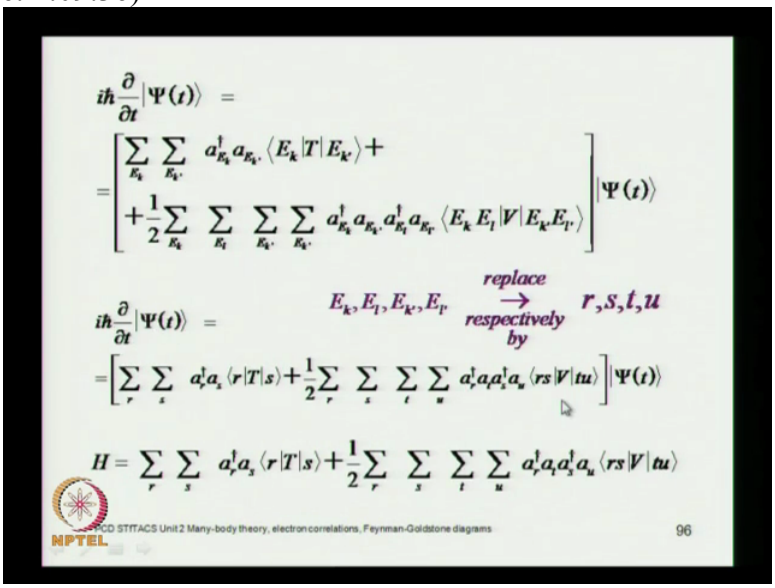

But mind you these operators must be written exactly in this order. So, I have brought that expression to the top of this slide here but now for simplicity I will replace the labels Ek,El, Ek prime and El prime respectively by r,s,t,u and mind you there has to be a one to one mapping do not mix them up because the ordering is very important okay.

So, making the notation a little simple, so that r,s,t,u are effectively single particle quantum states right. And if you just rewrite this expression with Ek,El, Ek prime and El prime written in terms of r,s and t,u. Then you have this expression here okay, I have only renamed this there is no new physics in it it is just a re nomenclature of the expression and this is what the Hamiltonian turns out to be.

So, what is in the square bracket is the Hamiltonian ih cross del by del t of an occupation number state is now equal to h operating on this state in which this is now the Hamiltonian. So, now the Hamiltonian is the second quantization formalism is identified okay, and it is now written in terms of these creation and destruction operators and of course there are these integrals r, t, s and so on okay.

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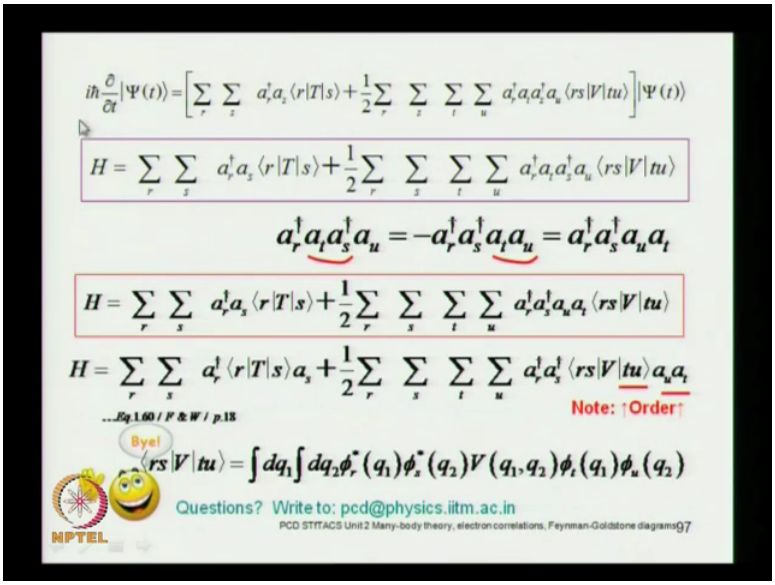

So, this is your Hamiltonian in the second quantization formalism. This is your Schrodinger equation in the second quantization formalism okay. This is for a general n electron state okay. Now we can write these in a slightly different order because you can move at to the right of as dagger but then you pick up a minus sign okay. And you can move at further to the right of u and again it will become a minus sign.

So, it will become plus, so the original ordering ar dagger at as dagger au becomes ar dagger as dagger au at. So, you can rewrite this Hamiltonian in terms of this ar dagger as dagger au at instead of ar dagger at as dagger au okay. This ordering is completely equivalent but please note the fact that you can write it in some equivalent ordering but not in arbitrary ordering okay.

So any equivalent ordering which duly respects the anti commutation rules of the Fermion creation and destruction operators is acceptable but not any arbitrary order. Note that here you have got tu in this two center integral, over here you have got au and at, so this order is different from this and you cannot mess up with that.

Because this to center of integral if you remember this is the, we worked quite extensively with this in the discussion of the Hartree Fock formalism in the previous course okay. This is an explicit in expression for the tools for the integral over q1 and q2 which are dummy variables which get integrated out.

And in this integration you have got on the right hand side fight Phi tq1, Phi uq2 which is telling you that this is the probability amplitude that particle at q1 is in the state t and this is the probability amplitude that the particle at q2 is in the state u. Now you can interchange that

but if you do you must accommodate a minus sign which is what in the Hartree Fock formalism gives you the Coulomb and the exchange integrals okay.

In the boson case it would not matter because au at commute, the fermion case you have to be careful okay. So I will take a break here and we will continue from here in the next class there is any question I will be happy to take. But in a sense you have the Schrodinger equation here.

And this we are now going to use this in our subsequent applications of second quantization to deal with correlations in a main electron system okay. That is the main subject of this unit which is the second unit in this course that we will be working with the Schrodinger equation for a many electron system this is inclusive of all the correlations now okay, all the correlations can be built in.

And now you must keep track of the order in which these operators come because the fermion operators anti commute unlike the boson operators. In the case of boson it does not matter. In the case of boson you also do not have those phase factors which you have in the case of fermions okay. And then with respect to this we will now proceed with our discussion of correlations in the many electron system.

So we now have the Schrodinger equation in the second quantization formulation we have got the Hamiltonian in the second quantization formulation okay. Question (Question time: 1:15:29 –not audible) one general question no Pauli's exclusion principle came much ahead of the second quantization formulation, historically second quantization formulation was developed in the late 40's.

You know Dyson, Feynman you know Wicks there were many contributors to that so there are theorems named after Wicks theorems named after Dyson, Feynman's all of them you know. Pauli's exclusion principle came even before spin because Pauli recognized that if you start filling in electrons in like you begin with the hydrogen atom 1s1, in the helium atom you have 1s2.

And then you go across in the periodic table go to lithium 1s2 2s1 okay. Now if you start doing it over and the entire periodic table you cannot get the correct configurations unless you had some quantum number which had two values this is what Pauli's recognized even before Spin was recognized.

Then subsequently when Spin was recognized which was, which happened through experimental observations these were the interpretations of Alnwick and Gout Smith and they

suggested that to understand Zeeman's spectra not just the Zeeman but the family of Zeeman effect spectra including the Passion back effect and the Anomalous Zeeman effect and everything the entire range of Zeeman's spectroscopy.

To understand that Alnwick and Gout smith proposed that there has to be a half integer quantum number. Then it was recognized in the Dirac equation that there is an intrinsic angular momentum which is half for the electron okay. Then after Hatree's work it was recognized that electrons being identical particles. The symmetry of the function must accommodate the fact that these are half integer particles.

And this is the Spin statistics here which Pauli formulated much later, it came much later because many electron systems were being studied okay Hartree Fock was another 1928 and the Coulomb and the exchange integrals which were completely inspired by the fact that the wave function must change its sign when you interchange two particles.

So, all this preceded this is the formulation of quantum mechanics this is not really new physics. But this is a new formulation which is very elegant which is extremely convenient okay. So, for many electron atomic physics or molecular physics or even condensed matter physics it provides great elegance and great convenience. In relativistic domain it becomes a necessity because you can actually create and destroy particles.

Because energy and matter are convertible but that requires energies which are more than the sum of the energy of a positron and an electron. So, only about 1 1.2 million electron volts will you have to work. With that but the kind of energy is you work with an atomic physics of molecular physics these are of the order of few electron volts, tens of electron volts, hundreds of electron volts even thousands or even tens of thousands.
If you go too deep inner shell x-rays and so on right. We do not go to millions of electrons, so in these processes in atomic physics you are really not considering here you are not working in the energy domain in which an electron positron would annihilate each other and you got energy. And you are not really carrying out creation and destruction in that sense.

But what you are doing is you are considering configuration interaction one Slater determinant is not appropriate to describe n electron system it gives you only one configuration but there may be n number of configurations 2, 3, 4 maybe 100's and to be correct you really need to consider an infinite set.

That is what is being summed over here because each of these states r and s, each r goes over every possible single particle state which is in the Eigen spectrum of the single particle

Hamiltonian. So, you first stack those Eigen states, register them in a certain sequence which you call as a1, a2, a3, a4 and with reference to that ordering the rest of the formalism is developed.

So, now we have got the Schrodinger equation in the second quantization formulation we have got the Hamiltonian in the second quantization formulation. And we are going to find it extremely useful to deal with many electron correlations because the Hartree Fock takes into account only the exchange or the Pauli correlations but not the Coulomb correlations.

Now our interest is in studying these Coulomb correlations and atomic physics okay. That is what this is about. Any other question! Thank you.