Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'
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Lecture 17
Electron Gas in Hartree Fock and Random Phase Approximation

Greetings will continue our discussion on the electron gas in the Hartree Fock approximation. We are interested in discussing the free electron gas in the Hartree Fock approximation and specifically further into the random phase approximation. So, in the last class we recapitulate it a little bit our understanding of the Hartree Fock approximation.

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We dealt with the N electron Hamiltonian we added and subtracted this term capital F uppercase F and this is the notation that we have used the sum over all of these F for each particle. And this is the average interaction which takes into account most of the two electron interactions. So, that the difference between this electron-electron repulsion term and this fourth term is very small very tiny.

So, that is how we built the approximation. Then we stipulated that we have a ground state the N electron determinantal wave function which we represented the ground state as Phi 0 and it consists of N the lowest N occupied states. And our prototype of an excited state was another determinant which we call as Phi q.

We labelled it as Phi q to distinguish it from the ground state in which just one electron is promoted to an excited state. And the electron which is promoted is the one which was in the pth state which is why the ground state Phi 0 was also labelled as Phi p. So, Phi p and Phi 0

both represent the ground states, Phi q is the excited state in which just one orbital is different all the remaining n - 1 orbital's are essentially the same.

And this is the frozen orbital approximation that we are using. Now our variational function would be a mix of this ground state which we believe is the ground state. And if it were not to be the best ground state then it would need to be mixture of this state and some of the excited states. The prototype of which is Phi q the mixing coefficient being epsilon which would be a tiny number.

And subsequently we sought the limit epsilon going to 0 to demonstrate that this is in fact the variational best state, best self consistent field state according to the variational principle. Now Fermi correlations are of course included because we are using a determinant wave function. So, all the statistical correlations are included and all the Coulomb correlations are excluded because that is built into the frozen orbital approximation.

Now we have certainly discussed this in the previous course which is the special topics in atomic physics in unit 4, we discussed some of these details.
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And I will draw your attention to that particular course and in particular I will draw your attention to what we call as the Hartree Fock equation as it appears on slide 104 of the unit 4 of this course okay. So, this is available at this link and this equation is what we obtained in considerable detail in our previous course.

And if you remember this relationship which we call as a Hartree Fock equation was arrived at it emerged as the condition that the expectation value of the Hamiltonian in the N electron

state is a minimum according to the variational principle subject to the constraint that the one electron spin orbitals.

Which go into the Slater determinant are normalized an orthogonal right. So, those were the constraints, so with reference to that constraint how would you get a minimum of the energy functional. The condition that you would get a minimum was expressed in terms of a certain condition that will have to be satisfied. This condition is the Hartree Fock equation which we find over here. And this is in the notation of the previous course.

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So, this is the Hamiltonian that we use which was the sum of the one electron part and the two electron part. The one electron part had the kinetic energy term and also the potential energy in the field of the nucleus and then you had the electron-electron Coulomb repulsion term. Now I am going to change the notation a little bit and rewrite this equation.

And it would not have mattered but I want to bring the notation very close to what we find in the book by Raimes Many Electron Theory because it is a notation of Raimes that we are going to carry forward for the development of the Feynman diagrams okay. And for the discussion on the random phase approximation using the Bohm Pines formalism for example we are going to be using the notation of Raimes.

So I am going to rewrite this equation first in the notation of Raimes and that is a very simple exercise all you do is to change i to p, j to i and u to Psi, r1 to r and r2 to r prime okay. So, it is a very simple you know change of notation. So, we do that and rewrite this equation, so now you see that you have this f1 operator.

And instead of uir1 you have Psi p of r, because i has gone to p and r1 has gone to r okay. So, this is just rewriting the same Hartree Fock equation in the notation of Raimes and then you have the Coulomb and the exchange terms also rewritten. So, we will work with the Hartree Fock equation in the notation of Raimes

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This is what we have got and you have the Coulomb and the exchange terms put together in this bracket I will now separate them. So, the Coulomb term appears in the first bracket and the exchange term appears in the second bracket. Now all of these terms pop up at the click of the mouse. And I think it is not an issue because you do not have to write down these things PDF copy of these slides is available on the internet you can download it.

And you can get all of these relations. So, you do not have to spend time writing these relations as you are well aware. So, do not worry that okay, all of a sudden a whole integral with three Psi functions in the integrand and it takes a certain while to write it down. So do not worry about all that they will keep popping up at the click of a mouse because then we can cover a lot in just one lecture okay.

So, if you have any difficulty you have to raise your hand and stop me okay. So, you have this four dimensional integral essentially there are three integrations over the continuous space variables X, Y, Z or r theta Phi or whatever coordinate system you are using. And then as explicit some or the discrete spin variable is also implied in this four dimensional integral okay.

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So, we consider non ferromagnetic systems that you have got an equal number of spin up and spin down states like a crow shell atom okay. And you have energies which are doubly degenerates. So, you have got one Eigen function for spin up and one for spin down. And the ground state Slater determinant wave function is a set of these one electron orbitals.

You have got these N orbitals. But Psi one up and Psi down are degenerates Psi 2up and Psi 2 down are degenerate and you have Psi N by 2up and N by 2down. So, those are you have a total number of N by 2 energy states each being doubly degenerate.

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So here we are we have these integrals inclusive of the summation over the spin variables. So, let us go ahead and carry out the summation over the spin variables explicitly okay. And leave the integration over the space variables is undone at this point. So, when you carry out the discrete sum over the spin variables. You will have twice I going from 1 to N by 2 okay, because there is no spin dependent term in this operator here.

So, notice that the sum over i which went from 1 to N now goes from 1 to N by 2 but you have a factor of 2 over here for the Coulomb term okay. And for the exchange term you will have not this factor of 2 but just the sum over i going from by N1 to N by 2 because whenever you do not have parallel spins this integral would vanish because of the kronecker delta msi, msj that we are well aware of okay.

So, now you have got this factor of 2 over here and with the Coulomb term but the exchange term does not have that factor and you have got to the upper limit of the sum going from i going from 1 to N by 2. Then again the integration variables Xi was a set of 4 coordinates the three space coordinates and one spin coordinate. But now this summation over the spin has been carried out.

So, now you have only the space coordinate namely the position vector r coming over here. And so instead of Psi p Xi, now rights Psi pr okay. And likewise instead of this Psi i Xi, I write Psi ir for exactly the same reason. So, this is our Hartree Fock one electron self consistent field equation that we obtained very extensively in the previous course and now it has been rewritten in the notation of the book by Raimes.

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So, I bring it to the top of this slide now and you have this term e squared over r, is e square over distance. This is the Coulomb term, so this is the Coulomb interaction which I now write as v r, r prime okay. And instead of this e square over the distance I write the term vr r prime here and also here okay. So it is really nice that this entire equation comes at the top at the click of a mouse otherwise it would take that much time to write it on the board.

And we can then do less in an hour then we are what we are able to do now. So, this is the Coulomb in the exchange term and this is in the notation of Raimes, you will find this in the book by Raimes called Many Electron Theory and in the Edition which I have got it is equation number 323 page 53. So, you can follow the book by Raimes as well okay.

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Now let us write this in the second quantized formulation you will remember that when our Hamiltonian was written in the first quantized formulation, in the first quantization rotation it had this form. When this was the Hamiltonian the second quantization form was essentially this okay. We dealt with this term quite extensively in our previous classes. Now our Hamiltonian is not H0 + H prime.

Because what we have done is to add and subtract this capital F okay to this Hamiltonian we have now added this capital F this is the term in blue and we have subtracted the corresponding term in this okay. So, now we can very easily without going through a very detailed and analyses quickly write the corresponding Hamiltonian in the second quantization notation.

So, instead of this term in the first course in the second quantization notation instead of this F you have got the sum of the little f and the uppercase F because these are the one electron operators. The one electron operators are now little f plus the big F the capital F right. So, this is the term that takes place of the first term here.

And instead of the second term which was only this you must subtract the corresponding term which was added extra over here okay. So, that is all there is to it, so now we just exploit the analogy and write this Hamiltonian in the second quantization form in a very neat and very quick manner.

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So, here we are, we have got, you will remember that we made use of the Eigen functions of the single particle operator to have this determinantal Eigen functions. And now we are adding and subtracting this capital F and subtracting the; you are adding it here and subtracting it here. So, now you will also remember that in the previous class we had shown that F was chosen to get self consistent field variational functional minimum.

Such that its matrix element in the state q and p, p is a ground state q is the excited state with just one orbital occupation change what the state's p was occupied in the ground state. Now its occupation number is 0 instead it is occupation number of Psi q which is equal to 1. So, the matrix element of the operator F in these two states is given by this. This is the relationship that we discussed extensively in our previous class.

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And using this we write these this is written in the Dirac's notation I have spelled it out fully as integrals okay. It is the same term but so you have got the sum over i going from 1 through N which is here and then you have these four dimensional integrals inclusive of the summation or the spin variable. And now I am doing a little bit of rearrangement of the term. You will have both the terms are double integrals.

Integrations over as Xi1 and Xi2 okay, so I sandwich the integration over Xi1 in the middle and pack all the terms in Xi1 in this inside term. So, outside this bracket there is nothing with the arguments Xi1, it is all packed inside this Xi1. Likewise all the integration over the Xi2 is packed inside over here and outside this bracket there is nothing which has for its argument is Xi2.

So, it is the same two double integrals which are rewritten slightly differently in a mathematically consistent manner for certain convenience as will become obvious very shortly. And before we get to that convenience we play this trick the Xi1 and Xi2 are dummy variables and you if you interchange them in all the terms then you are okay. Okay you cannot interchange in one and not in the other.

But if you are interchanged them consistently throughout then you have no difficulty at all. So, we interchange Xi1 and Xi2 in the exchange term and rewrite this expression in the box which is what we have got and it comes happily at the click of other mouse okay. And so happy not to be required to write this full expression on the blackboard because that would take really that much time.

And sure enough I would make some typographic errors and write r1 instead of r2 or vice versa and we could lose some more time in that. So, I think this is really very nice that we can carry on and it should not cause any inconvenience to you because all of these expressions are available to you directly okay.
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So, here we are we have got these two terms we have now interchange Xi1 and Xi2 okay. And now we get the summation over i going from 1 through N integration over is Xi2 and all the integration over Xi1 is inside this beautiful bracket which begins over here. There are two terms in this beautiful bracket, the beautiful bracket ends over here, the two term the first one is coming from the Coulomb the second is coming from the exchange okay.

So, that is what we have got. In this term in the red box the only difference from the previous expression is a fact that the summation over i going from 1 through N does not affect anything over here because the only i dependent terms are inside this beautiful bracket okay. So, the only terms which have anything to do with i are inside this beautiful bracket.

So, I bring the summation over i this symbol over here just behind this beautiful bracket okay. And now what does it tell us what is this? This is an integral over as Xi2 of Psi q stars Xi2 and then you have got this term which is just the integration notation off the Dirac matrix element Phi q F Phi p that is it right. So, this is just the Dirac notation this is the corresponding you know De Broglie Schrodinger a full integral expressions.

And if you compare this with the Dirac notation on the left side you immediately recognize that the result of the operation by the operator F on Phi p is given by the summation over i going from 1 through N and this term in the beautiful bracket okay. It is just a immediate translation from the Dirac notation to the integration notation clear enough Moorthy got it yeah (Question time: 20:26-not audible) it is just this F Phi p right.

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$$\Rightarrow F\psi_p(\xi_2) = \sum_{i=1}^{N} \left\{ \begin{array}{l} \left[\int d^4\xi_1 |\psi_i(\xi_1)|^2 \, v(\vec{r}_1,\vec{r}_2)\psi_p(\xi_2) \right] \\ -\left[\int d^4\xi_1 \psi_i^*(\xi_1) v(\vec{r}_1,\vec{r}_2)\psi_p(\xi_1)\psi_i(\xi_2) \right] \end{array} \right\}$$

$$\Rightarrow$$

$$F\psi_p(\xi_2) = \sum_{i=1}^{N} \int d^4\xi_1 |\psi_i(\xi_1)|^2 \, v(\vec{r}_1,\vec{r}_2)\psi_p(\xi_2)$$
$$- \sum_{i=1}^{N} \int d^4\xi_1 \psi_i^*(\xi_1) v(\vec{r}_1,\vec{r}_2)\psi_p(\xi_1)\psi_i(\xi_2)$$

carrying out the summation over the discrete spin variable:

$$F\psi_p(\vec{r}_2) = 2\sum_{i=1}^{N/2} \int d^3\vec{r}_1 |\psi_i(\vec{r}_1)|^2 \, v(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_2)$$
$$- \sum_{i=1}^{N/2} \int d^3\vec{r}_1 \psi_i^*(\vec{r}_1) v(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_1)\psi_i(\vec{r}_2)$$

So, that is what we have over here and I have now written it at the top of this slide. There are two terms, so I write them separately one more time okay. It is nice to do this go back and forth because then it gives you some flexibility on rearranging the terms. So, now once again we rewrite them as two separate terms that you will see why. So, now we carry out the summation over the discrete spin variables.

So, this is d4 Xi1 this is d4 Xi1 as well which means that it includes the discrete summation over the spin variable. We carry out this discrete summation explicitly as before this becomes twice summation i going from 1 through N by 2 for the Coulomb term okay. And for the exchange term it goes as summation over i going from 1 through N by 2.

Because all the components which are contributing to the summation with spin up and spin down. Those will go to 0 because of the orthogonality when you carry out the summation right.
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So, now we have a fairly compact expression in which the summation of where the spin variable has been carried out. Now this F Psi p has been spelled out over here and you have these two terms over here. So, you have got the one electron operators Psi p that is just the Hartree Fock equation that we are working with we are rewriting it in equivalent but more convenient forms okay.

So, there is no new physics which is emerging as yet but it soon will. So, we are equipping ourselves with a certain notation which is convenient for us to develop subsequent analysis of the random phase approximation. And if you know do a little further transformation of variable you what you have done is in this term you recognize that instead of r2 you have used r.

And instead of r1 you have used our prime, so there is variable integration not over r1 but integration over V Prime and this is integration also over r1 which is over V Prime. And here the argument r1 is replaced by r prime and r2 by r okay. So, it is just a matter of change of some notation what does it tell us this term is nothing but F operating on Psi p of r2 which is what we have just seen in the previous slide.

And therefore this whole term which is inside this closed loop okay is nothing but F operating on Psi p. So, now we write this Hartree Fock self consistent field equation in terms of what we see at the bottom of this slide. And essentially you have got the sum of the one electron operator this was a little f this is the capital F.

So, it is the sum of f + capital F, the small F + the capital F which is operating on Psi p of r and the right hand side is epsilon p Psi p of r okay. So, this is just the Hartree Fock equation.
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Recall, from Special/Select Topics in Atomic Physics,
STiAP: Unit 4, Lecture 23, Slide 111
Hartree-Fock Self-Consistent Field formalism
Reference→ http://www.nptel.ac.in/downloads/115106057

$$E(N) = \langle \psi^{(N)} | H | \psi^{(N)} \rangle$$

$$= \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} \left[\langle ij | v | ij \rangle - \langle ij | v | ji \rangle \right] \quad \text{Raimes, Eq.3.35}$$

slide 14: $[f(\vec{r}) + F(\vec{r})] \psi_{i\sigma}(\vec{r}) = \varepsilon_i \psi_{i\sigma}(\vec{r})$

i.e. $[f(\vec{r}) + F(\vec{r})]$ is diagonal in $\{\psi_{i\sigma}(\vec{r})\}$

$\Rightarrow \langle i | f + F | i \rangle = \varepsilon_i = \langle i | f | i \rangle + \langle i | F | i \rangle$

$$E(N) = \sum_{i=1}^{N} \left[\langle i | f | i \rangle + \langle i | F | i \rangle \right] - \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} \left[\langle ij | v | ij \rangle - \langle ij | v | ji \rangle \right]$$

Raimes, Eq.3.36

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But now we are going to use this further mind you this epsilon i had come as a Lagrange multiplier in the Hartree Fock theory. This is what looked like the Eigen value of the Hartree Fock equation. We the Hartree Fock equation is not an Eigen value equation it has the resemblance of an Eigen value equation. But all those details we have discussed in the previous course, so I will not go through it.

And it is that epsilon i which had appeared as a Lagrange multiplier in the Hartree Fock formalism for which enforce the constraints that the individual spin orbitals are orthogonal and normalized. So, it is that epsilon i which is appearing over here and this is the energy functional.

But then we also know from the previous class and specifically from slide number 14 that you have this Eigen value equation for the one electron operator f + upper case F right and in terms of this, this epsilon i the this would be the Eigen value because f + F is diagonal in this basis okay, as we have seen earlier. So, since f + F is diagonal in this basis then the energy functional EN becomes this summation over epsilon i.

But epsilon i is the sum of these two terms. So, I have got the sum of these two terms and then you have got the two center terms which is the Coulomb and the exchange and then you must sum over i and j both normally you would exclude it j = i but now you do not have to because for i = j the Coulomb and exchange terms cancel each other okay.
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$$E(N) = \sum_{i=1}^{N} \left[\langle i|f|i\rangle + \langle i|F|i\rangle \right] - \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij|v|ij\rangle - \langle ij|v|ji\rangle \right]$$

$$\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij|v|ij\rangle - \langle ij|v|ji\rangle \right] = -E(N) + \sum_{i=1}^{N}\left[\langle i|f|i\rangle + \langle i|F|i\rangle \right]$$

Also,

$$\langle \Phi^{(N)}|H|\Phi^{(N)}\rangle = E(N) = \sum_{i=1}^{N}\langle i|f|i\rangle + \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij|v|ij\rangle - \langle ij|v|ji\rangle \right]$$

$$\Rightarrow$$

$$E(N) = \sum_{i=1}^{N}\langle i|f|i\rangle - E(N) + \sum_{i=1}^{N}\left[\langle i|f|i\rangle + \langle i|F|i\rangle \right]$$

$$\Rightarrow$$

$$E(N) = \frac{1}{2}\left\{ \sum_{i=1}^{N}\langle i|f|i\rangle + \sum_{i=1}^{N}\left[\langle i|f|i\rangle + \langle i|F|i\rangle \right] \right\} = \frac{1}{2}\left\{ \sum_{i=1}^{N}\langle i|f|i\rangle + \sum_{i=1}^{N}\varepsilon_i \right\}$$

Raimes, Many Electron Theory Eq.3.38 / page 56

PCD STITACS Unit 3 Electron Gas in HF & RPA   47

So, this is the expression for the energy functional okay. These are the two center terms in this red loop. We also know that the energy functional is given by this expression okay. So, we combine these two results by identifying the two center terms okay. So, the energy functional which is equal to this terms which is here plus this term in this red loop. But what is in this red loop is here which is equal to what is in this blue loop here okay.

So, whatever is in the red loop can be replaced by what is in the blue loop because they are completely equivalent. So, I have this energy functional equal to this term which is the matrix element of the one electron operator little f. And then you have got the term corresponding to what is inside this blue loop. And what is what is inside this blue loop is this -EN keep track of the sign here. The minus EN comes here and the other two terms come here okay.

We should be careful that we carry the minus sign behind EN correctly. So, there we are you have got the -EN here, so I can take this -EN to the left hand side that will make it 2EN okay. And if you now write this expression for EN alone then on the left hand side you have got EN = half times this term and this term right.
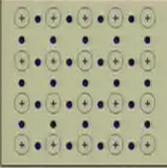
So, that is our expression for the energy functional it is half of i going from 1 through N matrix element of the one electron operator f + i going from 1 through capital N and these are the LaGrange multipliers of the Hartree Fock theory okay.

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Now what we are going to do is to develop the Hartree Fock self consistent field for FEG which is my abbreviation for the free electron gas okay. So, now we are not going to work with the atom anymore. The atom of course has N electrons and these N electrons are not free they are bound to the nucleus by the nuclear potential okay. So, we want to develop the Hartree Fock self consistent field expression for the free electron gas.

And this is the, this is the case for which here you can actually obtain analytical solutions. This is the only many electron system for which you can get analytical solutions for the atomic case you do need the numerical solutions. And our understanding of a free electron gas is that the potential V must be zero okay. A free particle is one which is in no field which can bound, which can bind it.

So, V must be zero, so if you have to apply to electron gas and metals for example okay which is what Bohm Pines worked with. If you are going to work with that then you know that in a metal you have got these positive ions positive nuclei in the lattice. And then there are these valence electrons which are not bound to a particular site. But they are free to travel in the rest of the solid okay. So, that is the model that we have got.

But the whole system is electrically neutral. So, we are going to work with electron gas but we are going to work with a neutral system not a charge system. If you just work with N electrons then the total charge of the system would be N times the electronic charge. We are going to work with a neutral system like what you have in a block of a metal okay. So, we do have a neutral system in this block.

But then we also have these positive nuclei which are at the lattice site. So, how are we going to handle them because we want to work with the free electron model? And we know that the

nuclei are there and we need them to be there because it is their presence which will make the whole system electrically neutral.

So, we need them to be there, so what we will do is to we will smear this charge. And ashish are you listening there this is the Jellium model; Ashish you are going to smear these positive charges okay. You are going to smear these positive charges in this entire volume okay in a uniform Jellium type, you know configuration.

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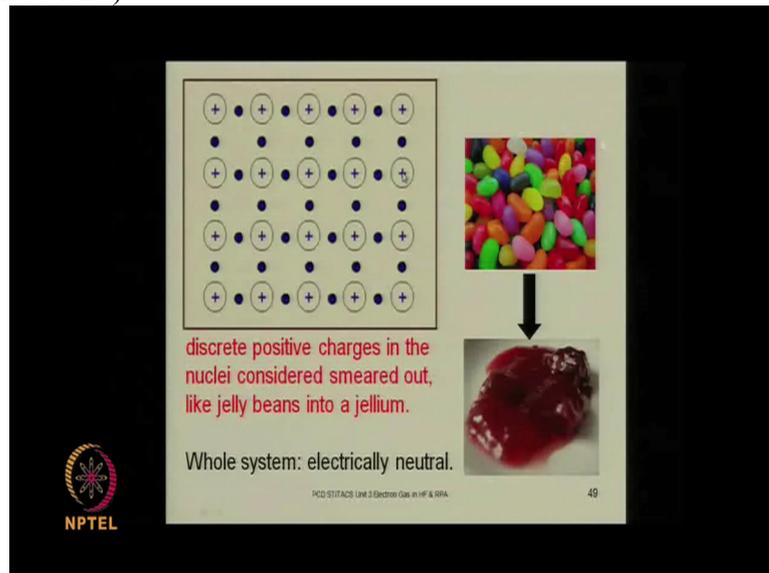
So, how we do that is like this that if you have got these jelly beans okay. You can smash them and make some sort of a Jellium like this right okay. You mean, so do not get tempted by the jelly beans at the nice attractive desert. So, that is not the idea, but this is in fact called as the Jellium potential.

What you do is to you take all of these positive charges and smear them out in the entire configuration space. So, you have an electrically neutral system but the positive charge is not confined to any particular site, it is smeared in the entire region. And you will see very quickly how this allows us to deal with the N electron free electron gas very shortly.

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So, what we are going to do the free electrons will be like plane wave solutions okay. So, this is like a quasi bound state and we will work with box normalization okay. Because the free electron straits will be will have the general form they will be sinusoidal right. They will be like you can write them as e to the ik dot r, these are travelling waves plane wave solutions for a free electrons right.

So, that is the nature of the solution that we are going to work with. But then what we will do is we will normalize them according to box normalization. So these are like quasi continuous spectrum okay. So, that is the model we have so you have got this box a positive charge density in which a total charge N times the electronic charge divided by the volume of the box that is the charge density.

And this charge density is uniform throughout the box okay. That is the model that we have got, that is the Jellium model that we have. Now we will use the Box normalization condition and we know we can easily determine how many wavelengths will fit into the box. Because here I have got a picture of just one wavelength fitting into the box. But you know that a certain integral number of wavelengths can fit into the box.

And this gives you the quantization of the wave vector okay. This condition tells you that k must be 2pi times n over L and this is for the dimension x okay. You will have similar relation for y and z. And the complete expression for the quantization of the k vector will have nx ex + ny ey + nz ez multiplied by 2 pi over L. So, this is the usual box normalization that we use.

And with reference to this you have plane wave solutions e to the ik dot r and the normalization will be 1 over root L cube as we all do in our first course in quantum

mechanics okay. So you have got the orbital part you have got the spin part which is Chi of Zeta. So, this is the spin orbital that we shall be working with.

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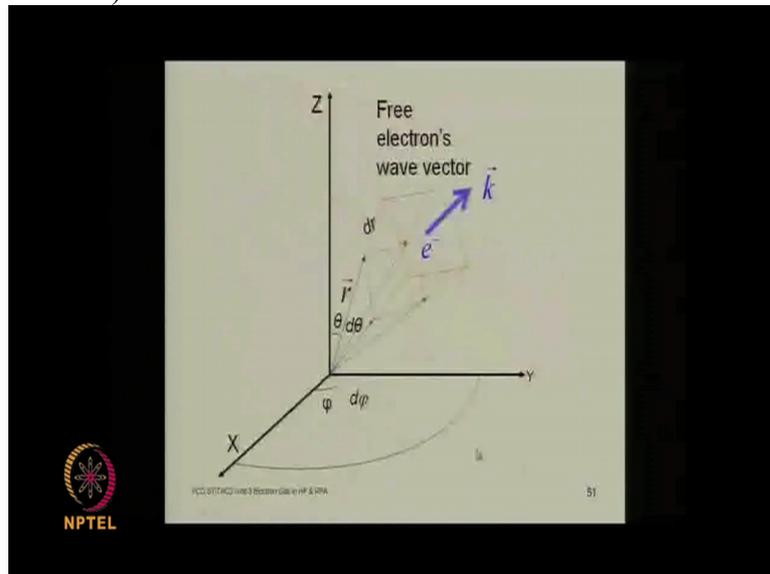
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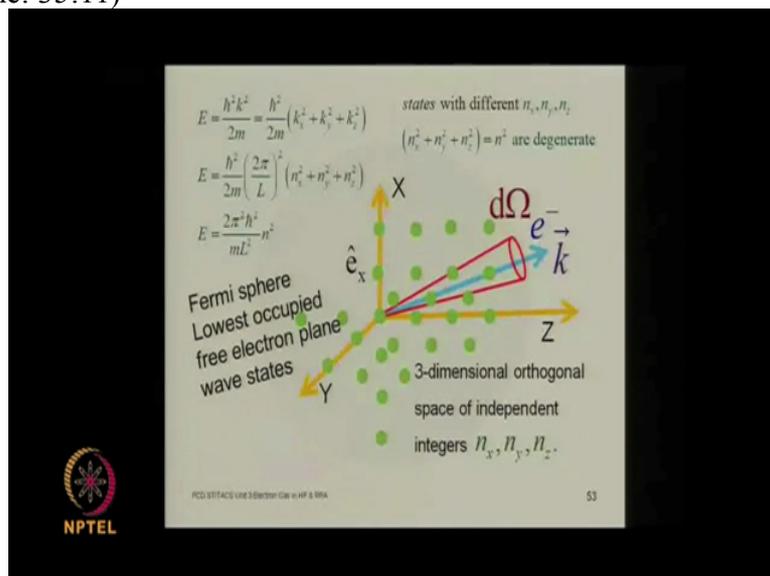
And if you now have a free electron wave vector in the direction k then what we can do is count the number of states. The easiest way to do it is to construct a grid of points labelled by integers. So, you have got the 0 over here okay and then you put another one on coordinate axis 1, 2, 3 and so on right. So, these are just numbers but they give you a counting capability of the number of states in the Fermi sphere.

So, you have got a grid of points which are pinned down by integers along x y and z axis. And then you put them at the intermediate locations also like at coordinates 111, 112, 121 etcetera and fill up the whole space by these dots right. And the number of occupied states are

all those which satisfy this relationship right. And what you do is to all the occupied states lie within a Fermi sphere.

In which you have got the lowest states occupied in the ground state okay. So, that is the Fermi sphere. So, this is our picture of the lowest occupied free electron plane wave states. So, all of these are e to the ik dot r type solutions. There is of course a spin part and there is the normalization one over root L cube.

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Let us look at the Hartree Fock equation now this is the kinetic energy term this is the potential energy term. For the atomic case what was this. this was - z e over r because it was attractive it why I had the minus sign and then you summed over all the N electrons okay. So, that was the situation in the atomic case. In our free electron gas you do not have the -ze over r interaction.

Because the charge is not localized at a nuclear site in the lattice it is smeared over the entire space okay. And that is what is represented by the potential V of r. So, it is an attractive potential because it is generated by the positively charged nuclear lattice. But it is not located at the nuclear sites and the lattice sites smeared over the entire space. And then the other thing we know about it is that it is uniform.

So, this is the attractive Jellium potential this Vr Psi pr okay. This is the attractive Jellium potential. This term over here is the electron-electron Coulomb repulsion; this is the exchange term the last one okay. And now what would you think that this is the Coulomb repulsion term is it is the electron-electron repulsion term.

And there are total of N electrons and as much as there are N electrons there are N positive charges which make the whole system electrically neutral. So, there is as much of repulsive interaction of the Coulomb type as there is the attraction between the Jellium potential and the N electrons. Essentially what we are observing is that these two terms in this little box Vr this is the Jellium potential attraction term.

And this is the electron-electron Coulomb repulsion term this is the Coulomb repulsion term right vr, r prime. So, these two terms are exactly equal and opposite. They are exactly equal and opposite because this is smeared out of our entire space this is integration over whole space dV prime okay.

And this has no reason to be anything other than uniform density and therefore these two terms will happily cancel each other, exactly cancel each other. There is no approximation here, so the Jellium and positive potential cancels the electron-electron repulsion but only the Coulomb part of it. The exchange term which was over here has to be carried forward.

And now our relationship that we have to work with is this kinetic energy term which is here. And then we have this exchange term with some over i going from 1 through N by 2 okay. And then you have this exchange term over here the right hand side remains just as it is, the Coulomb term has cancelled the Jellium attraction.

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So, now we are no more working with atoms we are working with a free electron gas like what you have in a metal okay. And this is the kind of system for which Bohm Pines developed their approximation to deal with the Coulomb correlations okay. So, here we are, so this is our Hatree Fock equation in which the Jellium potential and the Coulomb terms have cancelled each other.

You will also remember from our previous course that we had introduced the exchange operator. The exchange operator and I will not spend any time discussing this but I will refer you to lecture 23 of unit 4 of the previous course which is the special topics in atomic physics. And in this we had introduced the exchange operator and this exchange operator has got this result that when it operates on this you get this particular term.

And if you know sum over i you have got the left hand side which has got the index i for particular state so you sum over all the N electrons you carry out the corresponding some on the right hand side. And in the right hand side you have got this integration over q prime, integration over q prime again it includes integration over three space variables and discrete summation over the spin variable.

So, when you carry out the summation or the spin variable you will have these Kronecker deltas okay msi msp and that will reduce this summation from i going from 1 through N to 1 to N by 2 because of this kronecker delta, for spin up and spin down. And you have this result that the exchange operator, operating on the orbital Psi p of q is given by this sum. So, I will now use this result.
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This is the result that I now want to use notice that this term over here the right hand side of this is nothing but the exchange term over here okay. It is exactly the same; it is absolutely exactly the same. So, you can rewrite the Hartree Fock equation along with the exchange operator.

So, you have got the kinetic energy term and instead of this you now write it in terms of the exchange operator you have got the minus sign over here. So, it comes with the -V exchange operator here. The right hand side is epsilon p what is this epsilon p? This is the term which

can which can be traced to the Lagrange variational multipliers of the Hartree Fock theory right in the diagonal form. So, you have got the -V exchange term over here.

And instead of this -V exchange we use the notation F instead of -V that is a small notational compromise we make to bring our expressions in line with what we find in the book by Raimes okay. So, you have this kinetic energy operator plus the F exchange operator because the Raimes exchange operator is defined as the negative of the exchange operator that we had used in the previous course.

So, that is the only reason why we had to go through this exercise. So, you have got this kinetic energy operator + F exchange operating on Psi p and this is nothing other than the Hartree Fock equation itself. So, we are just playing with the Hartree Fock equation but rewriting it in different forms which are convenient to us. And in particular we have now specialized it.

We have moved away from the atomic case and we have specialized it for the Jellium potential for free electron gas in metal okay.

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So, this is what we have got and this energy of course depends on momentum. So, instead of momentum I write it in terms of the momentum vector k in units of h cross okay. Instead of the momentum p I am using k as the quantum label. So, this relation has been written or rewritten in terms of the quantum labels k rather than p it is essentially the same expression but written in terms of k.

And each of these there is a Psi here, there is a Psi here, there is a Coulomb interaction here and there is a Psi here and each of these are plane wave solutions which are box normalized.

These are ie to the ik dot r okay; they are not atomic orbitals anymore. These are plane waves which are box normalized.

So, each spin orbital is a plane wave which is box normalized it has got an orbital part and a spin part and these are the orbital parts of these equations. So, now let us write this exchange term, what is in this red loop and I include the minus sign in the red loop. So, I first place that minus sign over here.

And there are these three wave functions wave orbital's one is here which comes with a complex conjugation. Then there is a Psi k and there is a Psi k prime over here. So Psi k prime let me write as it is which is one over root of L cube e to the ik prime dot r1 right, so that is Psi k prime. Now these two this one is without the complex conjugation and this is with the complex conjugation.

So, this comes with e to the ik - k prime dot what is argument here it r2 in both the cases okay. So, it is e to the power e, e to the power ik - k prime dot r2. So, these are the two wave functions. You have got the 1 over r12 over here or e squared over r12 which is V. So, the e square is here and the one over r12 is here in the denominator okay. So, it is the same term but this is what I will refer to as the exchange term coming from slide number 57.

And I will be referring to this in subsequent classes also so I am identifying this whole term in this red loop as the exchange term from slide 57 okay. So, keep track of this and we will be using this expression in our subsequent discussion again. Mind you that this sign has been appropriately carried over here okay because if we lose the sign it is very easy to get into a mess.

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So, here we are we have got this red loop inclusive of this minus sign, you have got this exchange term. And this exchange term now all I have done to go from this blue box to the last term at the bottom is to multiply and divide it by this wave function which is 1 over root L cube e to the ik dot r1. So, that is also a spin orbital as you can see and all I have done is to multiply and divide by this.

So, I am still all right okay now having done that I can combine these two terms this term in the numerator and this term in the denominator because both have got in the exponent a dot product of two different wave vectors with r1. This is k prime dot r1; this is k dot r1, so essentially this will be k prime – k dot r1, if you bring this to the numerator right.
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So, this will be k prime - k dot r1 or - k - k prime dot r1, so that is what we have got okay, are we all together it is simple. But not keeping track of the sign can make it very messy.
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So, we have got the exchange term of slide 57 which we have now written as this okay, are we all together good. So, you have got k - k prime r2 - r1 here okay. And now this integration is over r2, do we pull out the terms in r1 outside the integration which is e to the power ik - k prime dot r1 okay. Now notice that what is in the square bracket contains integration over r2 of course it contains r1 over here.

Because the denominator is the difference between the position vector r1 and r2 right, so once you integrate it out this term in the square bracket will not depend on r2 at all because it r2 variable is integrated out, what will it depend on it will depend on r1. So, what is inside this bracket the square bracket is now a function of r1 alone. And that function is what I call as Phi of r1 whatever it is okay.

It has nothing to do with r2 because r2 has got integrated out. And now this exchange term is written as - e square over L cube sum over k prime e to the power - ik - k prime dot r1 then there is some function which is essentially this which is a function of r1 alone not a function of r2. And then you have got the orbital Psi k of r1 okay.

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$$ET, S57 = -\frac{e^2}{L^3}\sum_{\vec{k}'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1} \boxed{\phi(\vec{r}_1)} \psi_{\vec{k}}(\vec{r}_1)$$

Exchange Term

$$\phi(\vec{r}_1) = \int d^3\vec{r}_2 \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}}{r_{12}} = \boxed{\frac{4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_1}}{\left|\vec{k}-\vec{k}'\right|^2}}$$

The Wave Mechanics of Electrons in
Metals - by Stanley Raimes, page
170, Eq 7.40

$$ET, S57 =$$
$$= -\frac{e^2}{L^3}\sum_{\vec{k}'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1} \boxed{\frac{4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_1}}{\left|\vec{k}-\vec{k}'\right|^2}} \psi_{\vec{k}}(\vec{r}_1)$$

$$= -\frac{4\pi e^2}{L^3}\sum_{\vec{k}'} \frac{1}{\left|\vec{k}-\vec{k}'\right|^2} \psi_{\vec{k}}(\vec{r}_1)$$

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So, this is the result that we have got and we have essentially written the exchange terms in this. The exchange integral is packed, it is sitting inside this Phi as you can see and if you now look at this function Phi it is this integration over this okay. And what is this integral this integral can be worked out it is nothing but e to the power i k - k dot r1 divided by k - k prime modular square.

So, this integration can be carried out and then leave it as an exercise. And this integration is carried out you get this result. And you can feed in that result over here that the exchange

term now becomes -e square over L cube which is over here, summation over k prime which is over here, e to the power - ik -k prime dot r1 which is over here.

Then you have got this Phi of r1 which is nothing but this 4pi e to the power i, this term over here divided by this square of the difference momentum vector, difference between the momentum vectors. And then you have got the Psi k of r1 here okay. So, you have got e to the power +ik - k prime dot r1 here and e to the power - ik – k prime dot r1 here. So, they multiply each other to give you unity.

And then you have a very simple compact relation. Now you see the advantage of doing what we did okay that you have the exchange term as -4 pi e square L cube summation over k prime 1 over k - k prime modulo square times this orbital okay. Now this term in the blue box inclusive of the minus sign is what I write as epsilon k. Now this is written with the subscript k.

The previous epsilon which came from the Lagrange multiplier was written as epsilon with an argument k okay. So, absolutely the argument k is different from epsilon with the subscript k this is the subscript k okay. So, this is not the argument this is the subscript keep track of that.

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And the argument k is here this subscript k is here this is coming for the exchange term. So, this is the Hartree Fock equation for the free electron gas. And now you have got both the epsilons over here this epsilon has got the argument k, this epsilon has got the subscript k, this is the exchange term, this is the Lagrange multiplier of the Hartree Fock theory okay. So, notice that you have the minus sign here in the plus sign here.

It is because we have carried the signs very consistently and these are the appropriate signs as we should have. You have the kinetic energy operator in the first term. So, that will obviously give you h cross square k square by 2m, what else can it give right. So, you have got the h cross square k square by 2m + this epsilon k both are operating on Psi k of r1.

On the right hand side you have got epsilon argument k multiplying the same orbital. So, you have got this relationship that h cross square k square by 2m the kinetic energy + the exchange term is equal to this Lagrange multiplier term where the epsilon subscript k is this relation okay.

So, now the next question is how to calculate epsilon subscript k okay. That is what we will do in the next class alright. So, thank you very much for today, if there is any question I will be happy to take, question from anybody anywhere. Yeah (Question time: 55:28) I just have a comment yes Jobin, so we could solve this system analytically just because we had a notion about the wave function am I right.

Yeah because what is happening in the Jellium potential case is that the Coulomb term is completely cancelling the attraction term due to the Jellium and potential and the manner in which we introduce the operator uppercase F okay. Our one electron operators were written as small f + the capital F but we chose the capital F rather smartly that is what we did in the previous class.

We did it in a manner such that we got a particular expression for the matrix element of the operator F in the ground state and an any other state which had at least one orbital occupancy different okay. Now as a result of that we were able to get, we were able to show that the variational function which was what was it Phi p + epsilon times Phi q or was its Psi p + epsilon times Psi q, I forget, I thinks Psi p + epsilon times Psi q right.

And we found that in the limit epsilon going to 0 okay, you get a variational minimum. Now it is because of this choice that we are able to get an analytical solution over here. So, that was a very good choice which has come in handy. And now in terms of the box normalized function we dealt with the free electron gas, free electron wave functions.

And now our task is to determine; what is this epsilon subscript k? Which corresponds to the exchange term; so that is what we will discuss in the next class?