Select/Special Topics in 'Theory of Atomic Collisions and Spectroscopy'
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Lecture 18
Exchange, Statistical, Fermi-Dirac correlations

Greetings let us continue our discussion on the electron gas in the Hartree Fock approximation which we started recapitulating in our previous class. Which was of course a different approach to the Hartree Fock self consistent field then what we did in our previous course on atomic physics.

So, this was a slight variant of that approach and specifically this approach is geared toward introducing the random phase approximation in particular the Bohm Pines formalism of the random phase approximation and that is what I hope to get into in the next couple of classes. So, today our focus will be on the treatment of the kinetic energy part and the exchange energy part which is involved in the electron gas interactions.

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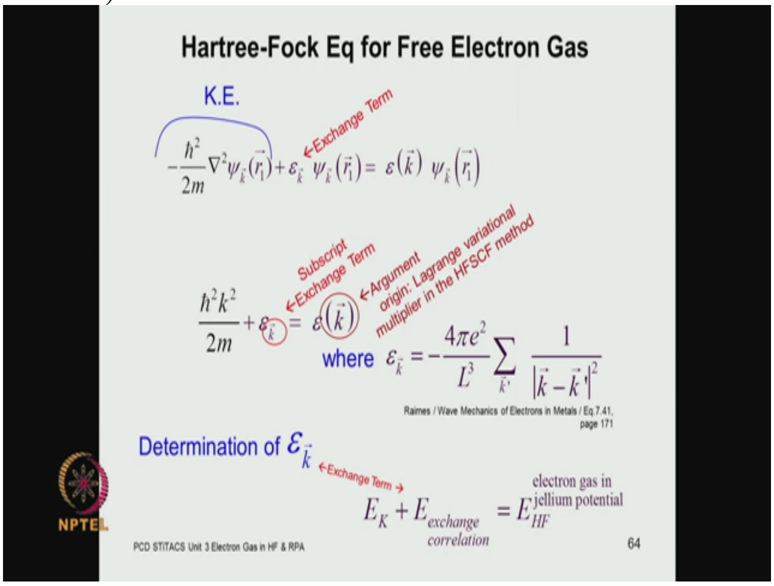

Hartree-Fock Eq for Free Electron Gas

K.E.

←Exchange Term

$$\overbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)}^{\text{K.E.}}+\varepsilon_{\vec{k}}\,\psi_{\vec{k}}(\vec{r}_1)=\varepsilon(\vec{k})\,\psi_{\vec{k}}(\vec{r}_1)$$

Subscript ←Exchange Term

←Argument origin: Lagrange variational multiplier in the HFSCF method

$$\frac{\hbar^2k^2}{2m}+\varepsilon_{\vec{k}}=\varepsilon(\vec{k})$$

where $\varepsilon_{\vec{k}}=-\frac{4\pi e^2}{L^3}\sum_{\vec{k}'}\frac{1}{|\vec{k}-\vec{k}'|^2}$

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.41, page 171

Determination of $\varepsilon_{\vec{k}}$

←Exchange Term→

$$E_K+E_{\substack{exchange\\correlation}}=E_{HF}^{\substack{\text{electron gas in}\\\text{jellium potential}}}$$

So, we wrote the Hartree Fock self consistent field equation which is a condition which must be satisfied, so that you get a self consistent field according to the variation principle. And this relationship we arrived at in our previous class. So, this would be an appropriate time you know point to begin discussion in for today. So, you have got the kinetic energy term and then the exchange term.

Notice that epsilon is used twice in this equation one is in the second term on the right hand side, on the left hand side, second term on the left hand side which is exchanged term. And epsilon is also used on the right hand side but on the left hand side you have got k as a subscript where is on the right hand side you have got k as an argument and these two stand for different things.

So, epsilon subscript k on the left hand side is the exchange term and epsilon argument k is the term that you get from the Lagrange multiplier in the Hartree Fock formalism, so that is something to be kept track of. And we also found in our previous class the complete expression for the exchange term which is -4 pi squared over L cube and you must sum over all the states.

And you have got one over the modular square of the difference between k and k prime when you sum over all the states k prime. Now this is the subscript k corresponding to the exchange term and the argument which comes from the Lagrange multiplier term in the Hartree Fock formalism, so just remember that. So, there is no reason to get confused by the two epsilons which appear in this.

So, essentially you have got the ek plus the kinetic energy plus part plus the exchange part which give you the Hartree Fock energy for the electron gas in the Jellium potential. Of course we have already made some approximation this is an electron gas and the positive nuclear charge which is there in the middle.

Is smeared over the entire region of the metal of the whole area it takes the whole expanse with a uniform charge density. So, that is the Jellium potential which we are making use of. Now we have to determine the kinetic energy part and also the exchange part. So, let us focus on the kinetic energy part for which the k appears as a subscript.

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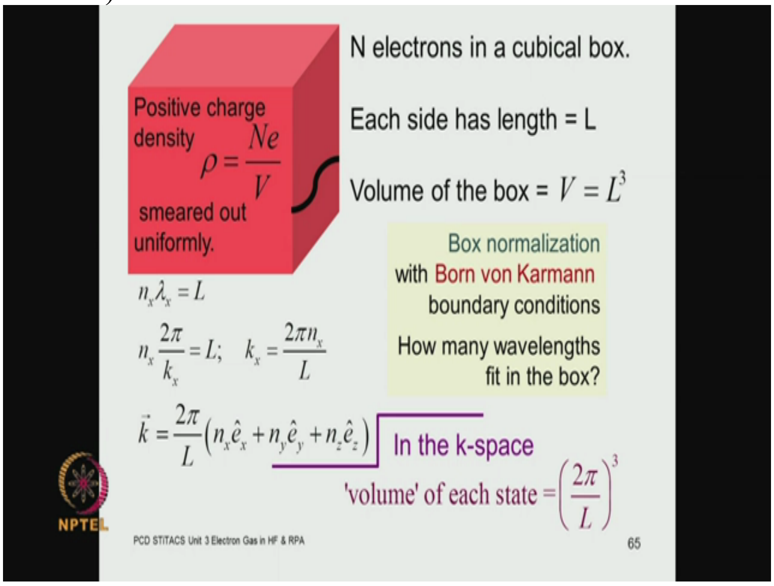

Positive charge density $\rho = \frac{Ne}{V}$ smeared out uniformly.

N electrons in a cubical box.

Each side has length = L

Volume of the box = $V = L^3$

Box normalization with Born von Karmann boundary conditions

How many wavelengths fit in the box?

$$n_x \lambda_x = L$$

$$n_x \frac{2\pi}{k_x} = L; \quad k_x = \frac{2\pi n_x}{L}$$

$$\vec{k} = \frac{2\pi}{L}(n_x \hat{e}_x + n_y \hat{e}_y + n_z \hat{e}_z)$$

In the k-space

'volume' of each state $= \left(\frac{2\pi}{L}\right)^3$

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Now this is the model that we have you got a positive charge. The entire positive charge at all the lattice sites is smeared over the entire region of this metal. And the charge density is uniform it is the number of electrons times the electron charge divided by the total volume so that is the average charge density, the volume of the box let us say is Lq each side being of length L.

What we have done and this is with reference to the discussion in the previous class. We have done a box normalization of the free particle free electron waves. So, that is the kind of normalization we have done. We estimated the number of wavelengths that will fit in a box. And we get a quantization condition so this is the discretization of the continuum in a certain sense and that gives us a condition on the wave vector.

And essentially what you find that you can talk about an average volume for each state. Because you get from one state to the next by changing the integer quantum numbers and the average volume for each state will be the cube of 2 pi over l as you can see quite clearly from this.

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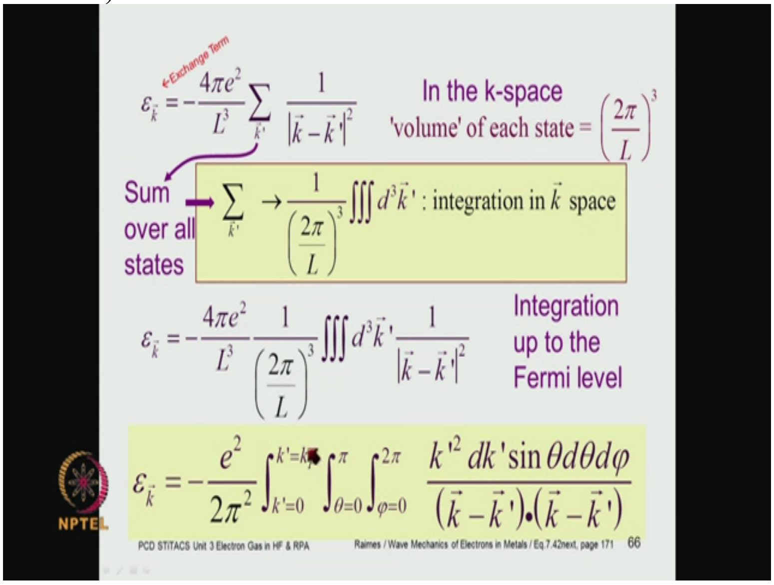

$$\varepsilon_{\vec{k}} = -\frac{4\pi e^2}{L^3}\sum_{\vec{k}'}\frac{1}{|\vec{k}-\vec{k}'|^2}$$

←Exchange Term

In the k-space 'volume' of each state $= \left(\frac{2\pi}{L}\right)^3$

Sum over all states

$$\sum_{\vec{k}'} \to \frac{1}{\left(\frac{2\pi}{L}\right)^3}\iiint d^3\vec{k}' : \text{integration in } \vec{k} \text{ space}$$

$$\varepsilon_{\vec{k}} = -\frac{4\pi e^2}{L^3}\frac{1}{\left(\frac{2\pi}{L}\right)^3}\iiint d^3\vec{k}'\frac{1}{|\vec{k}-\vec{k}'|^2}$$

Integration up to the Fermi level

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{k'=0}^{k'=k_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{k'^2\,dk'\sin\theta\,d\theta\,d\varphi}{(\vec{k}-\vec{k}')\bullet(\vec{k}-\vec{k}')}$$

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Raimes / Wave Mechanics of Electrons in Metals / Eq.7.42next, page 171

66

So, this is the term that we want to work with. We have found that the volume of each state is the cube of 2 pi over l but we are dealing with a sum over all the states. But when we go to a continuum model because you know the electron wave vector if when you take the free particle states which is what we are using e to the ik dot r type of solutions for free particle states.

Then of course you need to carry out integration over all the states rather than summation over the discrete states. So, you have to change over from this discrete summation to integration. So, this will be an integration over all the states and you must integrate over the entire volume and divided by the average volume of each state which is 2pi over L whole cube right.

So, that is what the summation k prime will be replaced by. So, let us go ahead and do this integration now. So, what you have as a summation here effectively becomes you have the same term -4 pi e squared over L cube over here and instead of this discrete sum you now have the corresponding equivalent integration okay. How this is integration in the k space but it is not over all the values of k.

Because in the ground state the uppermost k level which is filled is the one which is at the Fermi level right, so you have to carry out the integration only up to the Fermi level. So, if the Fermi level corresponds to a momentum in units of h cross which is given by kF then integration over the variable k prime will go from 0 through kF.
And then in the spherical polar coordinate system in the momentum space you will have theta going from 0 to pi and Phi going from 0 to 2pi and then of course you have the modular square of this difference vector which is k minus k prime which I have written as a dot product between this vector with itself.
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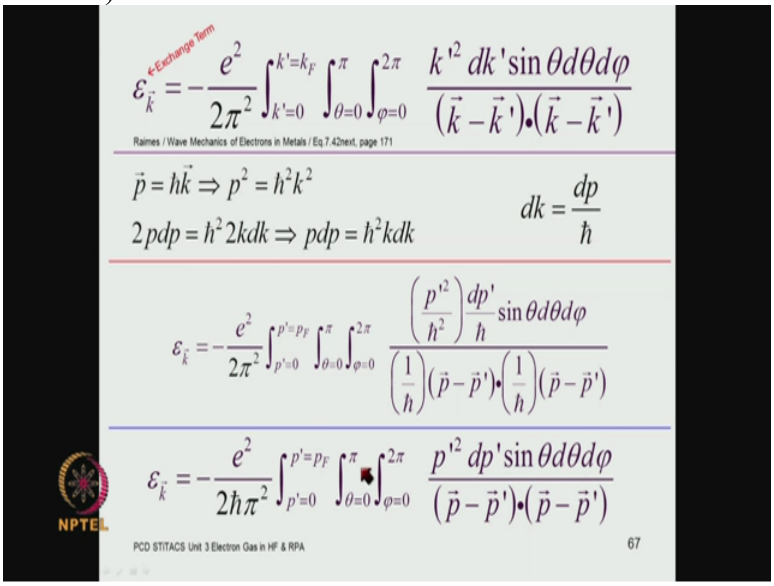

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{k'=0}^{k'=k_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{k'^2\,dk'\sin\theta\,d\theta\,d\varphi}{(\vec{k}-\vec{k}')\bullet(\vec{k}-\vec{k}')}$$

←Exchange Term

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.42next, page 171

$$\vec{p} = \hbar\vec{k} \Rightarrow p^2 = \hbar^2 k^2$$

$$2p\,dp = \hbar^2 2k\,dk \Rightarrow p\,dp = \hbar^2 k\,dk$$

$$dk = \frac{dp}{\hbar}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{\left(\frac{p'^2}{\hbar^2}\right)\frac{dp'}{\hbar}\sin\theta\,d\theta\,d\varphi}{\left(\frac{1}{\hbar}\right)(\vec{p}-\vec{p}')\bullet\left(\frac{1}{\hbar}\right)(\vec{p}-\vec{p}')}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{p'^2\,dp'\sin\theta\,d\theta\,d\varphi}{(\vec{p}-\vec{p}')\bullet(\vec{p}-\vec{p}')}$$

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67

So, this is the integration that we have to carry out which I bring to the top of this slide now and I transfer the variable explicitly from k2p and the difference is only this h cross so that tells us that the differential increment dk is dp over h cross. So, you make corresponding changes over here.

And write this integration over the momentum from zero to the momentum at the at the Fermi level. And then of course the rest of the variables are appropriately adjusted scaled by the factor h cross right. So, let us carry out this integration in the momentum space over the variable p.

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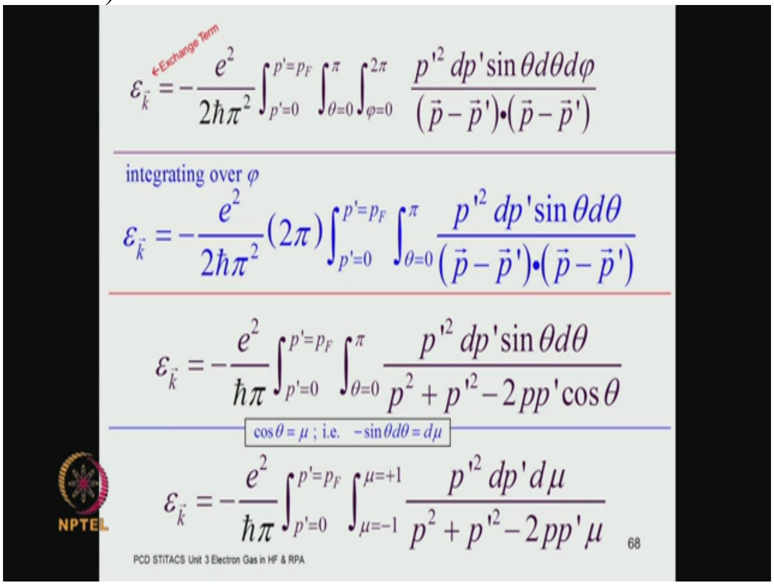

←Exchange Term

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{p'^2\,dp'\sin\theta\, d\theta\, d\varphi}{(\vec{p}-\vec{p}\,')\cdot(\vec{p}-\vec{p}\,')}$$

integrating over φ

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}(2\pi)\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\frac{p'^2\,dp'\sin\theta\, d\theta}{(\vec{p}-\vec{p}\,')\cdot(\vec{p}-\vec{p}\,')}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\frac{p'^2\,dp'\sin\theta\, d\theta}{p^2+p'^2-2pp'\cos\theta}$$

$\cos\theta=\mu$; i.e. $-\sin\theta d\theta = d\mu$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\mu=-1}^{\mu=+1}\frac{p'^2\,dp'\,d\mu}{p^2+p'^2-2pp'\mu}$$

Now here the integration over the Phi variable because there is nothing that will depend on Phi, so this will give you a factor of 2 pi over here then you are left with integration over theta and p. And as you would have done in a large number of exercises it is very easy to carry out this integration.

By changing the variable put mu equal to cos theta and then change the way integration over theta to that over cosine theta which is over mu. And that gives you this integral okay. So now you have integration over mu going from -1 to +1. There is a minus sign here which takes care of the cosine theta correctly.

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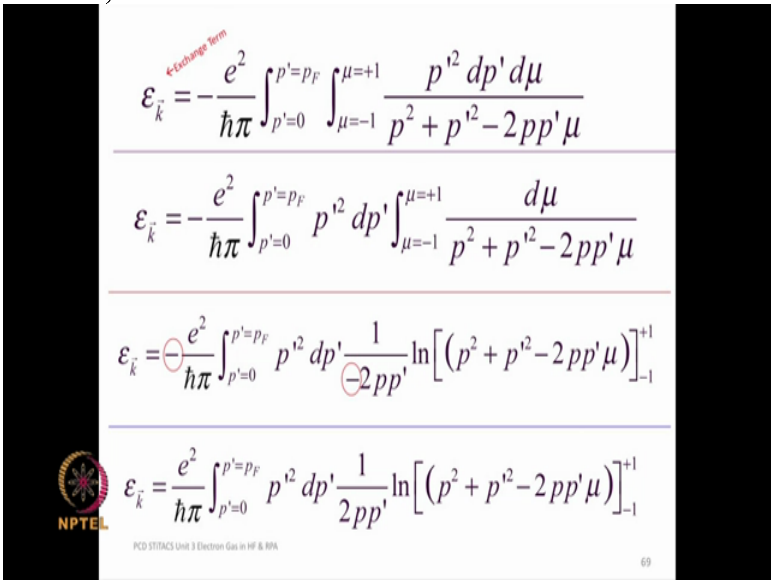

←Exchange Term

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\mu=-1}^{\mu=+1}\frac{p'^2\,dp'\,d\mu}{p^2+p'^2-2pp'\mu}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}p'^2\,dp'\int_{\mu=-1}^{\mu=+1}\frac{d\mu}{p^2+p'^2-2pp'\mu}$$

$$\varepsilon_{\vec{k}} = \boxed{-}\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}p'^2\,dp'\frac{1}{\boxed{-}2pp'}\ln\left[\left(p^2+p'^2-2pp'\mu\right)\right]_{-1}^{+1}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}p'^2\,dp'\frac{1}{2pp'}\ln\left[\left(p^2+p'^2-2pp'\mu\right)\right]_{-1}^{+1}$$

And we will now work with this integral you have to integrate over mu going from -1 to +1 make sure that you have the correct signs and what do you get. So, you have the integration over cosine theta which is to be done first followed by integration over momentum going from 0 to the Fermi momentum to be done next okay.

So, now this is a straight forward integral to be done you get a logarithmic term and then you have to put the limits -1 and +1 right. So, you get the upper term and the lower term which you must subtract for mu = -1 will be the lower term in mu = +1 will be the upper term right. So, this is integration over cos theta which is integration over mu.

So you have a minus sign here in a minus sign here so you can drop both of them and now you have a rather simple expression but you have to put these limits okay. I will, after putting these limits then you have to carry out the integration over the momentum. Now this is fairly straightforward mathematics but I will take you through some of these steps.

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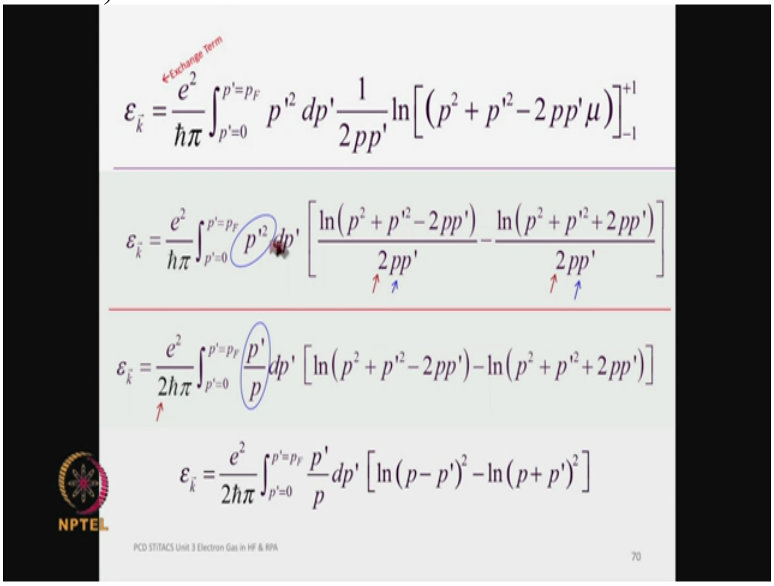

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\,dp' \frac{1}{2pp'} \ln\left[\left(p^2+p'^2-2pp'\mu\right)\right]_{-1}^{+1}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\,dp' \left[\frac{\ln\left(p^2+p'^2-2pp'\right)}{2pp'} - \frac{\ln\left(p^2+p'^2+2pp'\right)}{2pp'}\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}\,dp' \left[\ln\left(p^2+p'^2-2pp'\right) - \ln\left(p^2+p'^2+2pp'\right)\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}\,dp' \left[\ln\left(p-p'\right)^2 - \ln\left(p+p'\right)^2\right]$$

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70

So, this is what we have got in our effort to get an estimate of the exchange term. So, now let us put the limits mu = +1 will give you the logarithm of p square + p prime square -2 into p into p prime with mu = +1, so that is the first term that you get. And from this you subtract the second term corresponding to mu = -1 which multiplies this -1 and gives you a plus sign over here.

So, this is what you get after the integration over mu or cos theta has been completed. Now notice that there is a p prime square here and you have got a p prime in the denominator, so one of these powers can be reduced. And you simplify this expression a little bit, having reduced one of the powers you get p prime over p this p coming from this common p in the denominator in both the term.

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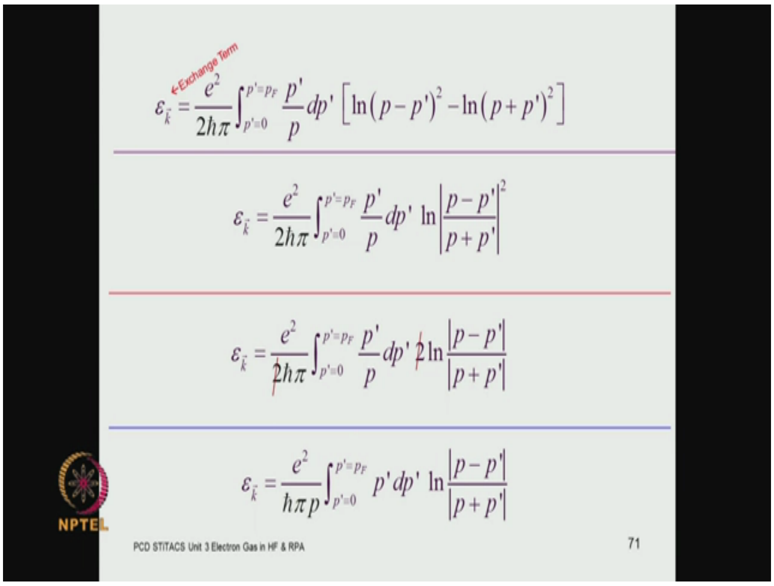

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{2h\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}dp' \left[\ln(p-p')^2 - \ln(p+p')^2\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2h\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}dp' \ln\left|\frac{p-p'}{p+p'}\right|^2$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\cancel{2}h\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}dp' \cancel{2}\ln\frac{|p-p'|}{|p+p'|}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\int_{p'=0}^{p'=p_F} p'dp' \ln\frac{|p-p'|}{|p+p'|}$$

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71

So, we have this integration over p prime going from 0 to the Fermi momentum and then you have got this logarithmic term. And you can play with this log logarithmic term a little bit and write it in this form. These are straight forward substitution you have got logarithm of the modular square, so you get a 2 log over of that ratio. And you can strike out the factor 2 now and then without the two you have the rest of the term.

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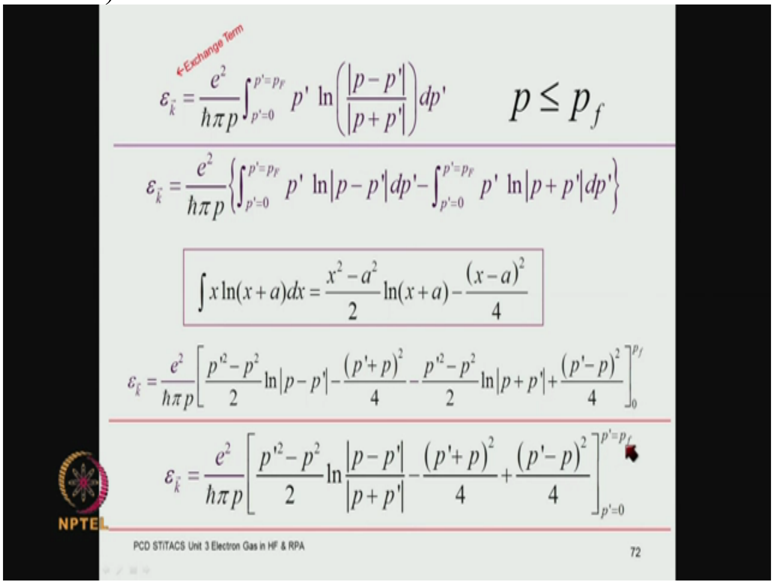

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\int_{p'=0}^{p'=p_F} p' \ln\left(\frac{|p-p'|}{|p+p'|}\right)dp' \qquad p \le p_f$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left\{\int_{p'=0}^{p'=p_F} p' \ln|p-p'|dp' - \int_{p'=0}^{p'=p_F} p' \ln|p+p'|dp'\right\}$$

$$\boxed{\int x\ln(x+a)dx = \frac{x^2-a^2}{2}\ln(x+a) - \frac{(x-a)^2}{4}}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p'^2-p^2}{2}\ln|p-p'| - \frac{(p'+p)^2}{4} - \frac{p'^2-p^2}{2}\ln|p+p'| + \frac{(p'-p)^2}{4}\right]_0^{p_f}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p'^2-p^2}{2}\ln\frac{|p-p'|}{|p+p'|} - \frac{(p'+p)^2}{4} + \frac{(p'-p)^2}{4}\right]_{p'=0}^{p'=p_f}$$

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72

And that is what gives you the expression for the exchange term as this okay. All right we can simplify this further because we want to bring it into a form which is one of the standard forms for integration. So, now we have it as a difference of two integrals and we use this standard form of the integration for x log x + a, which is a well known integral formula. So, we use this in the above expression.

And that gives us a number of terms over here, so we get similar to this x square -a square by 2 log x + a, we get this term over here. And then for this x - a whole squared over 4 we get p prime + p whole square over 4 from this term. And likewise we get two terms from this okay. Now you do not have to write this down very quickly because you will have access to the PDF file in which all these formulae are available okay.

So, they will be uploaded at the course website but you need to follow how the derivation is being done okay. So, now you have to put the limits because you have an upper limit p prime equal to the Fermi momentum and the lower limit is p prime equal to 0. So, you have to write this expression for the upper limit and subtract from it the corresponding expression for the lower limits.

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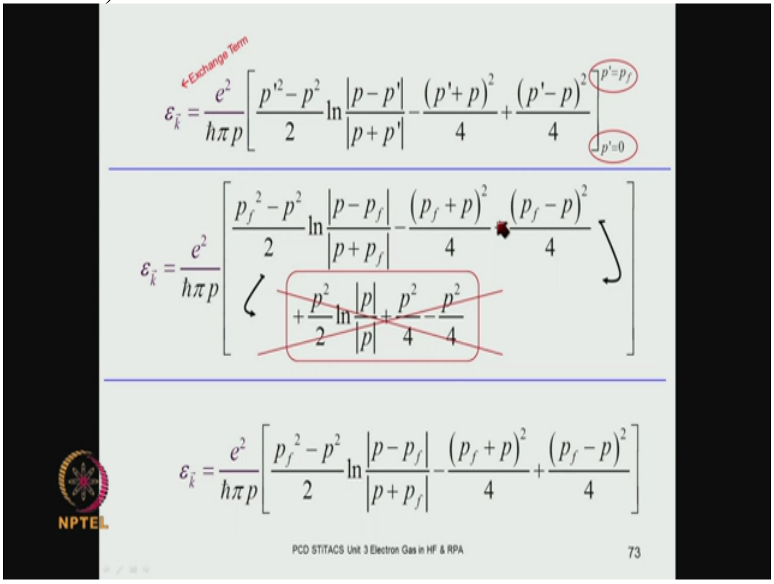

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p'^2-p^2}{2}\ln\frac{|p-p'|}{|p+p'|}-\frac{(p'+p)^2}{4}+\frac{(p'-p)^2}{4}\right]_{p'=0}^{p'=p_f}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\begin{array}{l}\frac{p_f^2-p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|}-\frac{(p_f+p)^2}{4}+\frac{(p_f-p)^2}{4}\\ \boxed{\cancel{+\frac{p^2}{2}\ln\frac{|p|}{|p|}+\frac{p^2}{4}-\frac{p^2}{4}}}\end{array}\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p_f^2-p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|}-\frac{(p_f+p)^2}{4}+\frac{(p_f-p)^2}{4}\right]$$

So, let us do that so we have the upper limits and the lower limits to be respectively the Fermi momentum and 0, so we get this expression with p prime equal to the Fermi momentum, so you instead of p prime square - p square you get pf square - p square and the corresponding terms with pf fermi momentum over here.

And you have the same expression for the p prime = 0, but notice that this term simply vanishes. So, there is nothing that is left of it and now you have only the upper expression which you have to be working with okay.

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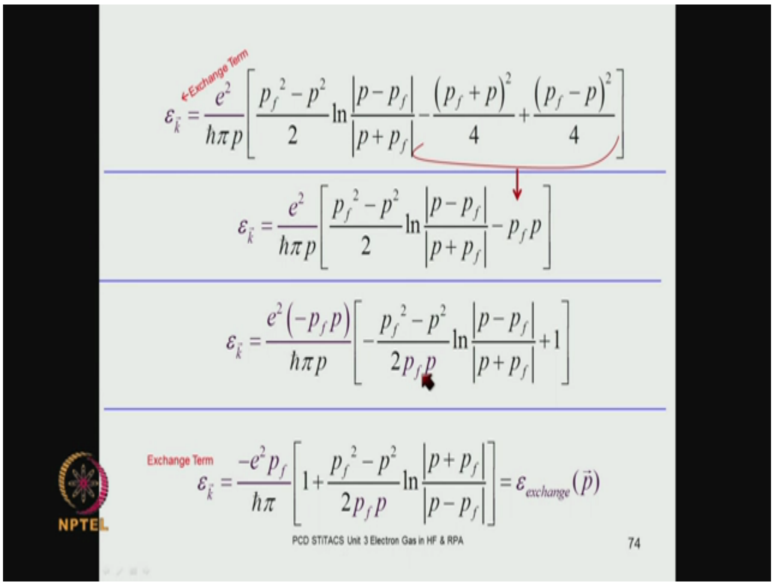

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p_f^{\,2}-p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - \frac{(p_f+p)^2}{4} + \frac{(p_f-p)^2}{4}\right]$$

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{h\pi p}\left[\frac{p_f^{\,2}-p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - p_f p\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2(-p_f p)}{h\pi p}\left[-\frac{p_f^{\,2}-p^2}{2p_f p}\ln\frac{|p-p_f|}{|p+p_f|} + 1\right]$$

Exchange Term

$$\varepsilon_{\vec{k}} = \frac{-e^2 p_f}{h\pi}\left[1+\frac{p_f^{\,2}-p^2}{2p_f p}\ln\left|\frac{p+p_f}{p-p_f}\right|\right] = \varepsilon_{exchange}(\vec{p})$$

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74

So, now you have an expression for the exchange term which is in terms of this Fermi momentum this will depend on the value of the Fermi momentum. This you can simplify because there are common terms over here you get - twice p into pf and from both of these terms. So, you get -4 into p into pf which you divide force you get p into pf and the other terms will cancel each other because there is a minus sign here and a plus sign here.

So, the only thing that is left from these terms the last two terms is this - pf into p okay. So, this is a little bit of further simplification this -p into pf has been factored out as a common between the two terms inside this rectangular bracket. So, you get plus one over here and you have a minus sign sticking out over here and then you have this p into pf in the denominator which takes care of the factorization. And this is the exchange term as we have got okay.

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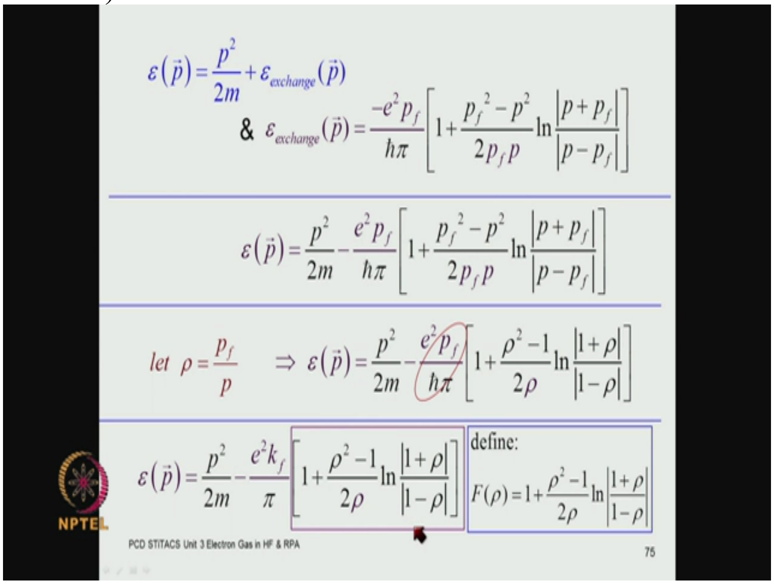

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} + \varepsilon_{exchange}(\vec{p})$$

$$\& \ \varepsilon_{exchange}(\vec{p}) = \frac{-e^2 p_f}{h\pi}\left[1+\frac{p_f^{\,2}-p^2}{2p_f p}\ln\left|\frac{p+p_f}{p-p_f}\right|\right]$$

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 p_f}{h\pi}\left[1+\frac{p_f^{\,2}-p^2}{2p_f p}\ln\left|\frac{p+p_f}{p-p_f}\right|\right]$$

$$\text{let } \rho = \frac{p_f}{p} \quad \Rightarrow \varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 p_f}{h\pi}\left[1+\frac{\rho^2-1}{2\rho}\ln\left|\frac{1+\rho}{1-\rho}\right|\right]$$

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 k_f}{\pi}\boxed{\left[1+\frac{\rho^2-1}{2\rho}\ln\left|\frac{1+\rho}{1-\rho}\right|\right]}$$

define:

$$F(\rho) = 1+\frac{\rho^2-1}{2\rho}\ln\left|\frac{1+\rho}{1-\rho}\right|$$

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75

Now here this is the expression that we got from the Hartree Fock equation, this is the kinetic energy part and this is the exchange part. We found out after substituting this term over here.

We have this general form and it is very often customary to write this in terms of the ratio Rho which is the Fermi momentum.

Over the momentum variable p which simplifies this or enables you to write this term in an equivalent form. So, there is nothing new with this except that it is being written in terms of the ratio rather than p and pf okay. So you get Rho square - Rho over here and here inside you will get 1 + Rho and 1 - Rho.

Now pf over h cross gives you the kf. So, that is all there is to it, rest of the terms being the same. And it is often you will find in some of the literature especially we in the books by Raimes or the articles by Bohm that he writes this factor inside this box as f of Rho because then it becomes simple to write and one can even examine the behaviour of f as a function of Rho.

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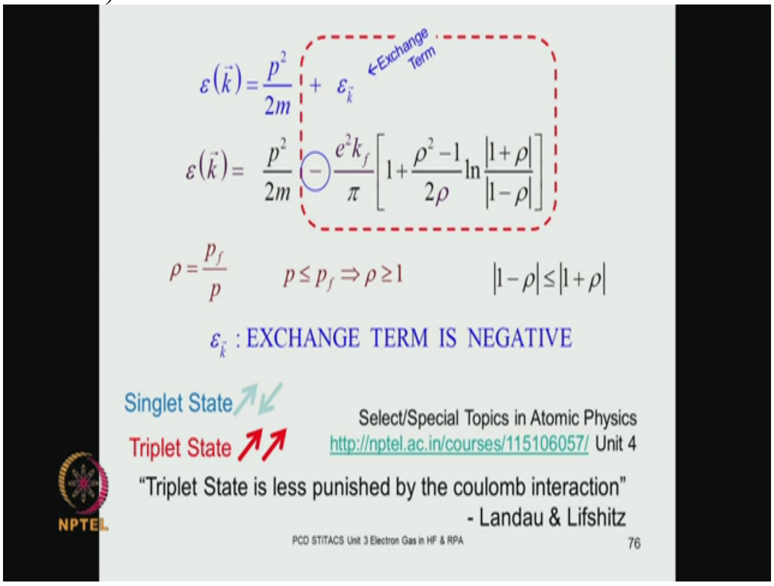

$$\varepsilon(\vec{k}) = \frac{p^2}{2m} + \varepsilon_{\vec{k}} \quad \leftarrow \text{Exchange Term}$$

$$\varepsilon(\vec{k}) = \frac{p^2}{2m} \ominus \frac{e^2 k_f}{\pi}\left[1 + \frac{\rho^2 - 1}{2\rho} \ln \frac{|1+\rho|}{|1-\rho|}\right]$$

$$\rho = \frac{p_f}{p} \qquad p \le p_f \Rightarrow \rho \ge 1 \qquad |1-\rho| \le |1+\rho|$$

$\varepsilon_{\vec{k}}$: EXCHANGE TERM IS NEGATIVE

Singlet State ↗↙

Triplet State ↗↗

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"Triplet State is less punished by the coulomb interaction"
- Landau & Lifshitz

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So, this is the result that we have got keep track of the sign you had a plus sign here and a minus sign here which essentially means that the exchange term has got this minus sign, Rho is pf over p but the variable p is always less than the Fermi momentum because all the electron states are occupied only up to the Fermi level. So, by definition this p is always less than pf which means that Rho is always greater than or equal to 1 okay.

So, Rho being always greater than or equal to 1, Rho square - 1 will always be positive and it is you can see that the exchange term will be essentially negative. So, it reduces the energy with reference to the kinetic energy term okay. It does not add to that energy it actually reduces it.

Now this is a result that we have actually met before because when we did the previous course and atomic physics we discussed the singlet and the triplet states and we quoted from Landau–Lifshitz that the triplet state is less punished by the Coulomb interaction because you have this exchange interaction.

And in the triplets, the triplet state for a two electron geminal wave function always has a lower energy than the singlet state. So, it is the same kind of result and we let me remind you of this result a little bit because the singlet wave function has got an anti symmetric spin part and the orbital part is symmetric okay.

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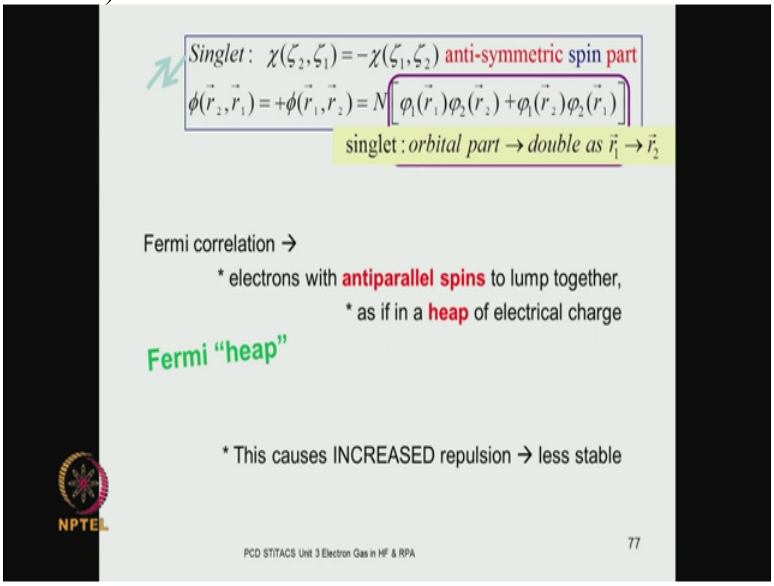

$Singlet:\ \chi(\zeta_2,\zeta_1) = -\chi(\zeta_1,\zeta_2)$ anti-symmetric spin part

$\phi(\vec{r}_2,\vec{r}_1) = +\phi(\vec{r}_1,\vec{r}_2) = N\boxed{\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]}$

singlet : *orbital part* → *double as* $\vec{r}_1 \to \vec{r}_2$

Fermi correlation →

* electrons with **antiparallel spins** to lump together,

* as if in a **heap** of electrical charge

Fermi "heap"

* This causes INCREASED repulsion → less stable

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77

So, this is the singlet state and as you can see from this what happens that as r1 tends to r2 as these two arguments get close to each other. The first term and the second term would add and double each other right. So, it is like you know you will have a doubling of that wave density and you will be stacking the charges together. So, you generate a heap of electrons this is actually called as Fermi heap.

And what it will do is that in this heap the electrons the two electrons will get closer to each other and as a result of that there will be increased repulsion okay. Because the closer they get the force of repulsion goes as you know 1 over r square. So, there will be increased repulsion and that will make this state less stable. So, that is the reason it has got higher energy.

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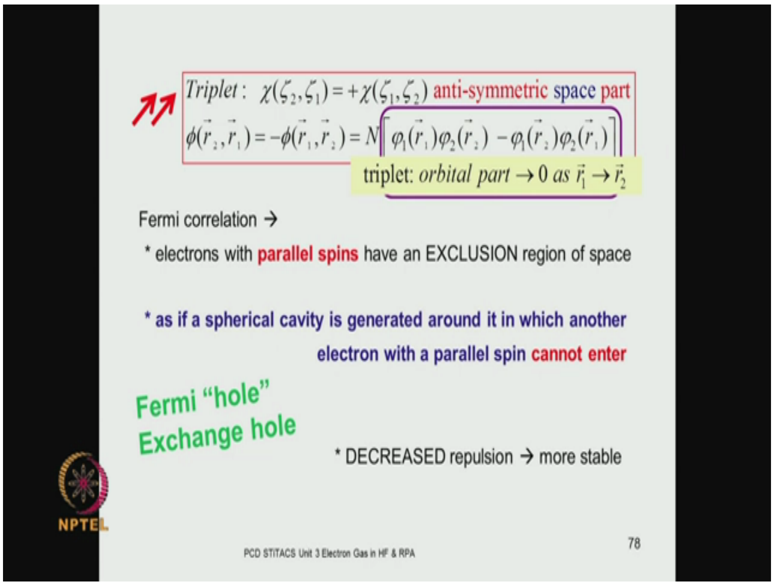

$Triplet: \chi(\zeta_2,\zeta_1)=+\chi(\zeta_1,\zeta_2)$ anti-symmetric space part

$\phi(\vec{r}_2,\vec{r}_1)=-\phi(\vec{r}_1,\vec{r}_2)=N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)-\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$

triplet: *orbital part* → 0 *as* $\vec{r}_1 \rightarrow \vec{r}_2$

Fermi correlation →

* electrons with **parallel spins** have an EXCLUSION region of space

*** as if a spherical cavity is generated around it in which another electron with a parallel spin cannot enter**

Fermi "hole"
Exchange hole

* DECREASED repulsion → more stable

And correspondingly if you look at the triplet state you have got an anti-symmetric space part. So, you have got the argument r1 and r2 in this geminal wave function and what will happen as r2 tends to r1 then you will have the orbital part practically vanish. And that is part of the reason that the triplet state if it has to exist will tend to keep the particles separated and it once they are separated that will reduce the repulsion between them.

And that will stabilize that particular state, so you have essentially the exclusion principle and the anti symmetry of the wave function which is influencing these dynamics. So, it is as if there is a cavity around each electron which prevents any other electron from the same with the same spin enters that space okay.

So, that cavity is called as a Fermi hole, so as opposed to a Fermi heap of the previous case you now have a Fermi hole. So, these terms are sometimes used and you have, it is called as a Fermi hole, it is also called as an exchange hole and what it does is it reduces the repulsion and it stabilizes this state.

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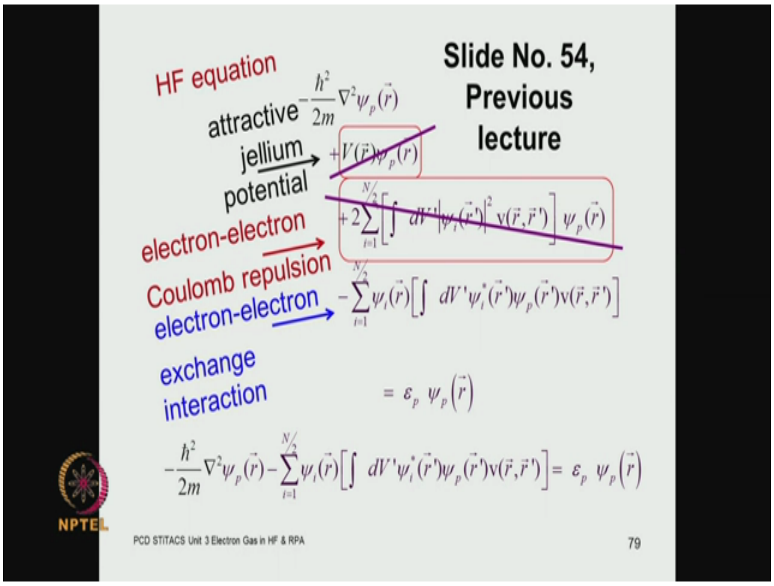

HF equation

Slide No. 54, Previous lecture

attractive jellium potential

electron-electron Coulomb repulsion

electron-electron exchange interaction

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r}) \boxed{\cancel{+V(\vec{r})\psi_p(\vec{r})}} \boxed{\cancel{+2\sum_{i=1}^{N/2}\left[\int dV'|\psi_i(\vec{r}')|^2 v(\vec{r},\vec{r}')\right]\psi_p(\vec{r})}} -\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}')\psi_p(\vec{r}')v(\vec{r},\vec{r}')\right] = \varepsilon_p\,\psi_p(\vec{r})$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}')\psi_p(\vec{r}')v(\vec{r},\vec{r}')\right]= \varepsilon_p\,\psi_p(\vec{r})$$

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79

I will now refer to the Hartree Fock equation which I recapitulate from the previous class which was on slide number 54 of the previous class. This is the Hartree Fock equation for the electron, for the free electron gas. This is very similar to the Hartree Fock equation that you have in atomic physics with the difference that the term over here was the nuclear attraction between an electron and the nuclear attractive potential.

In this case this is the Jellium on potential in the present case this is free electron gas in a Jellium potential. So, this is not an atom we are working with so the relationship is similar but of course there are important differences which we have to keep track of. You have got a Jellium on potential and as we discussed in the previous class the electron-electron Coulomb repulsion which is the direct interaction term.

Now this direct interaction term and then you have got an exchange term. So, these are the two terms which are similar to what we have in the atomic case as well. But in the present case these two terms which is the Jellium attractive potential term and the electron-electron repulsion term they are exactly equal and opposite. This one is attractive, this one is repulsive and they are exactly the same so they will cancel each other okay.

So, the Hartree Fock equation for a free electron gas is now left with only this kinetic energy term and this exchange term okay. These two happily cancel each other, so these are the two terms this is the kinetic energy part and this is the exchange part. So, this is now the Hartree Fock equation as we have.

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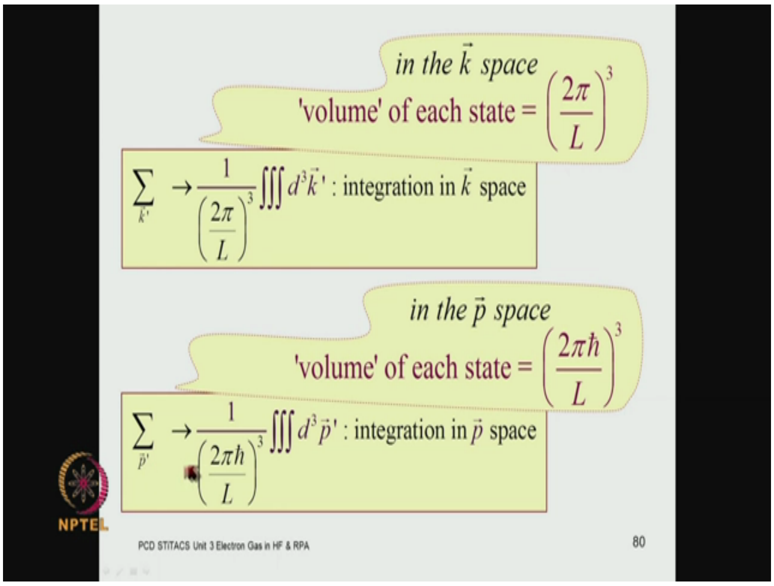

in the $\vec{k}$ space

'volume' of each state = $\left(\frac{2\pi}{L}\right)^3$

$$\sum_{\vec{k}'} \rightarrow \frac{1}{\left(\frac{2\pi}{L}\right)^3} \iiint d^3\vec{k}' \text{ : integration in } \vec{k} \text{ space}$$

in the $\vec{p}$ space

'volume' of each state = $\left(\frac{2\pi\hbar}{L}\right)^3$

$$\sum_{\vec{p}'} \rightarrow \frac{1}{\left(\frac{2\pi\hbar}{L}\right)^3} \iiint d^3\vec{p}' \text{ : integration in } \vec{p} \text{ space}$$

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80

And we have already seen that in the momentum space; now let us try to get some numbers for the exchange term, for the kinetic energy term and exchange term. So, because eventually we will have to do some calculations for these, so we already know that the discrete summation is equivalent to this integration over the momentum space up to the Fermi momentum divided by the average volume of each state.

In the momentum space of course there is an extra factor of h cross right. So, the momentum summation over p prime will give you a corresponding term over here. So, we are now going over to integration over a momentum space rather than integration over the k space. They are linear with a factor of h cross.

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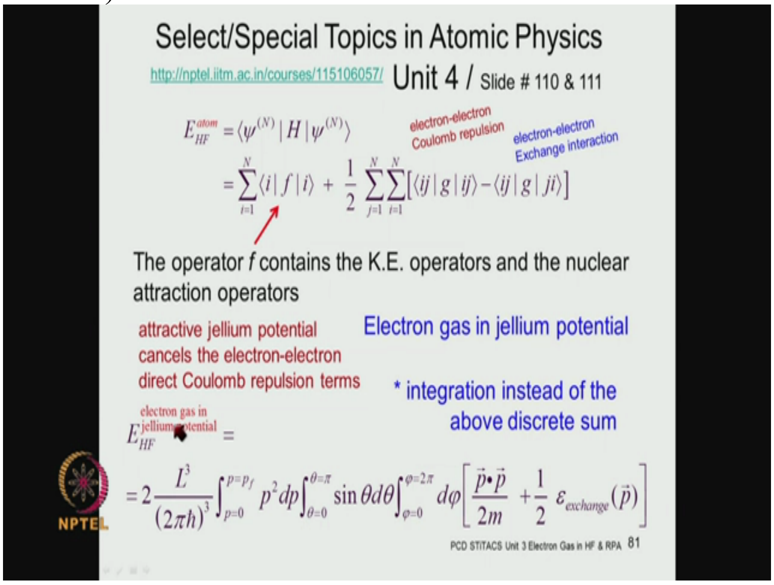

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electron-electron Coulomb repulsion

electron-electron Exchange interaction

$$E_{HF}^{atom} = \langle \psi^{(N)} | H | \psi^{(N)} \rangle = \sum_{i=1}^{N} \langle i | f | i \rangle + \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} [\langle ij | g | ij \rangle - \langle ij | g | ji \rangle]$$

The operator *f* contains the K.E. operators and the nuclear attraction operators

attractive jellium potential cancels the electron-electron direct Coulomb repulsion terms

Electron gas in jellium potential

* integration instead of the above discrete sum

$$E_{HF}^{\text{electron gas in jellium potential}} = 2\frac{L^3}{(2\pi\hbar)^3} \int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p} \bullet \vec{p}}{2m} + \frac{1}{2} \varepsilon_{exchange}(\vec{p}) \right]$$

PCD STiTACS Unit 3 Electron Gas in HF & RPA 81

And we will get expression for the Hartree Fock in the, for the electron free electron gas in the Jellium and potential by simply looking at the comparison between the corresponding expression for the atom which we have done in considerable detail in the unit 4 of our previous course. And these are the references which are available to you. So, this whole lecture is available at this link and the corresponding PDF files are also there.

So, this is the expression for the Hartree Fock in the atomic case but now we have some differences here because this term which was a single particle operator for in the atomic case which consisted of the kinetic energy operator and the nuclear attraction. Now we do not have that instead of that we have the Jellium potential right. So, we are going to have an electron gas and a Jellium on potential.

So, the one electron part will be somewhat different it has to be modified and we will simply you borrow this result and adapt it to the electron gas in the Jellium potential by making corresponding changes. So, we have first of all the electron gas and a Jellium potential and we also know that this term which is coming from the Coulomb term right.

This would go because this is the one which cancelled the electron-electron direct Coulomb repulsion term this would cancel the attractive Jellium potential as we have seen, as we have discussed right. So, these are the two changes that we shall remember and therefore all we have to do is to replace the summation over these discrete states by integration over continuum states going up to the Fermi momentum.

Now once we make these changes we can straight away adapt to this result of the previous course from unit 4 and write this expression for the energy for the Hartree Fock energy not for the atom but for the electron gas in the Jellium potential. So, now you have this integration over the momentum space. You have got in this the kinetic energy term which is here which is p dot p over 2m right.

You do not have this term anymore because this is the one which has cancelled the Jellium potential. But you do have the exchange term which is here okay. So, this is straight away and a direct adaptation of the Hartree Fock result of the previous course. So, instead of spending extra time and re-deriving this expression I chose to adapt to this relation for the electron gas, for the free electron gas.

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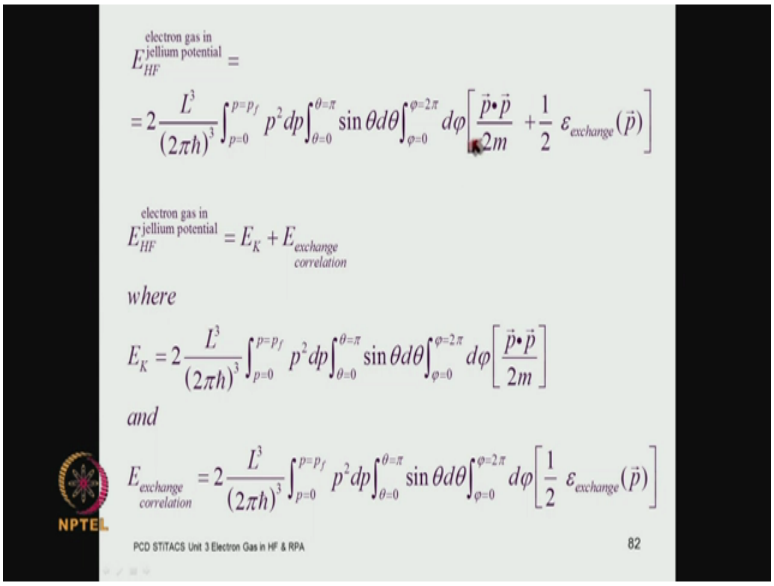

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} =$$

$$= 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m} + \frac{1}{2}\varepsilon_{exchange}(\vec{p})\right]$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

where

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m}\right]$$

and

$$E_{\substack{exchange\\ correlation}} = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{1}{2}\varepsilon_{exchange}(\vec{p})\right]$$

So, here we are this is what we have got this is the Hartree Fock energy for the electron gas in the Jellium potential. And this is now a sum of these two terms the kinetic energy part which is coming from here the p dot p over 2m the p squared over 2m. And then you have got the exchange terms.

So, this is the kinetic energy part which I have now written the two integrals separately Ek the first one which is with a subscript k for kinetic energy part. And the second is the exchange correlation term and these are the two integrals that we have to work with.

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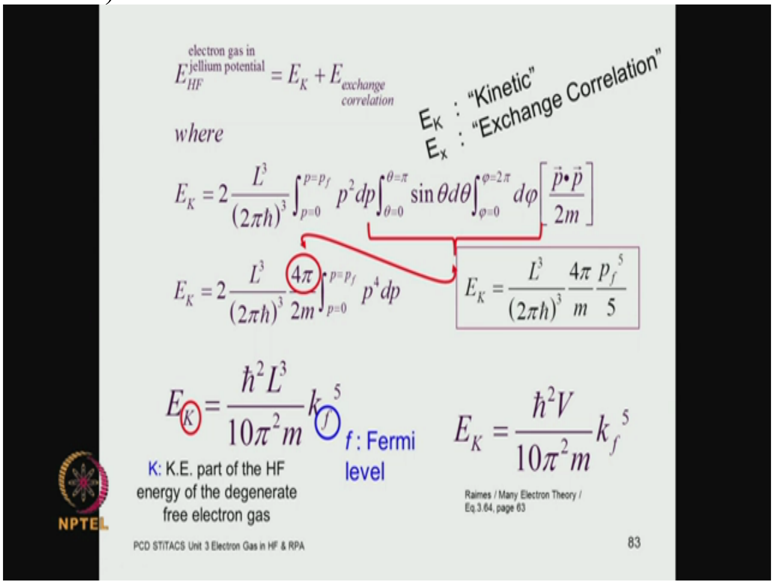

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

where

E_K : "Kinetic"
E_x : "Exchange Correlation"

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \underbrace{\int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m}\right]}$$

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\frac{\boxed{4\pi}}{2m}\int_{p=0}^{p=p_f} p^4 dp$$

$$\boxed{E_K = \frac{L^3}{(2\pi\hbar)^3}\frac{4\pi}{m}\frac{p_f^5}{5}}$$

$$E_{\boxed{K}} = \frac{\hbar^2 L^3}{10\pi^2 m}k_{\boxed{f}}^5$$

f : Fermi level

K: K.E. part of the HF energy of the degenerate free electron gas

$$E_K = \frac{\hbar^2 V}{10\pi^2 m}k_f^5$$

Raimes / Many Electron Theory / Eq.3.64, page 63

So, let us have a look at this here you just have an integration over the solid angle okay which will give you a factor of 4pi. And you have p square and then p square over here, so you will end up integrating a 4th power of p. So, that gives you p to the 5th and the Fermi momentum over Phi and this is the expression for the kinetic energy term you get h cross square after simplification of all the terms.

You have got 2pi h cross to the power 3 and then you had p to the power 5. So, there was an h cross to the power 5 sitting over here. So, that is what leaves you with h crossed to the power 2. So, when you take care of all of these terms this is what you get for the kinetic energy part.

Now the subscript f of course is a Fermi level corresponds to the k value at the Fermi level. And L cube is the volume of the box which is what I have written here, you will this result is straight from the book by Raimes which I strongly recommend for this part of the course okay.

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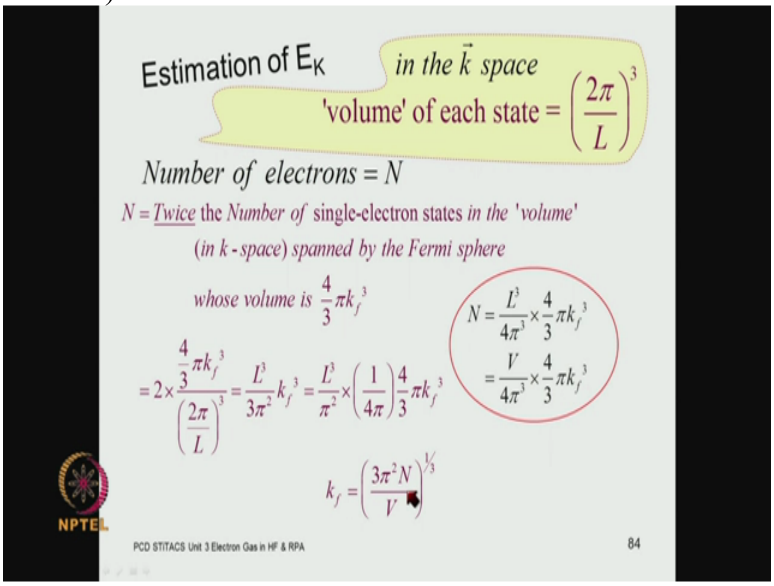

Estimation of E_K

in the $\vec{k}$ space

'volume' of each state = $\left(\frac{2\pi}{L}\right)^3$

Number of electrons = N

N = Twice the Number of single-electron states in the 'volume' (in k-space) spanned by the Fermi sphere

whose volume is $\frac{4}{3}\pi k_f^3$

$$= 2\times\frac{\frac{4}{3}\pi k_f^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{3\pi^2}k_f^3 = \frac{L^3}{\pi^2}\times\left(\frac{1}{4\pi}\right)\frac{4}{3}\pi k_f^3$$

$$\boxed{\begin{aligned} N &= \frac{L^3}{4\pi^3}\times\frac{4}{3}\pi k_f^3 \\ &= \frac{V}{4\pi^3}\times\frac{4}{3}\pi k_f^3 \end{aligned}}$$

$$k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

So, this is let us try to estimate what it will amount to this is in the k space we already know that the volume of each state is the cube of 2pi over L the total number of electrons is N and since there is one electron per state there are those many states that are that we have to work with. So, this will be twice the number of single electron states in the volume spanned by the Fermi sphere and this volume is 4 by 3 pi k cube right.

So, this is twice this number so you have twice 4 by 3 pi k cube which is this Fermi sphere divided it, divided by the volume of each state which is 2 pi over L whole cube. And then you can rearrange these terms do a little bit of simplification okay. Which is quite straightforward and you find that this N turns out to be given by the cube of this k. And k turns out to be the third, one third power of N over V which is the density okay.

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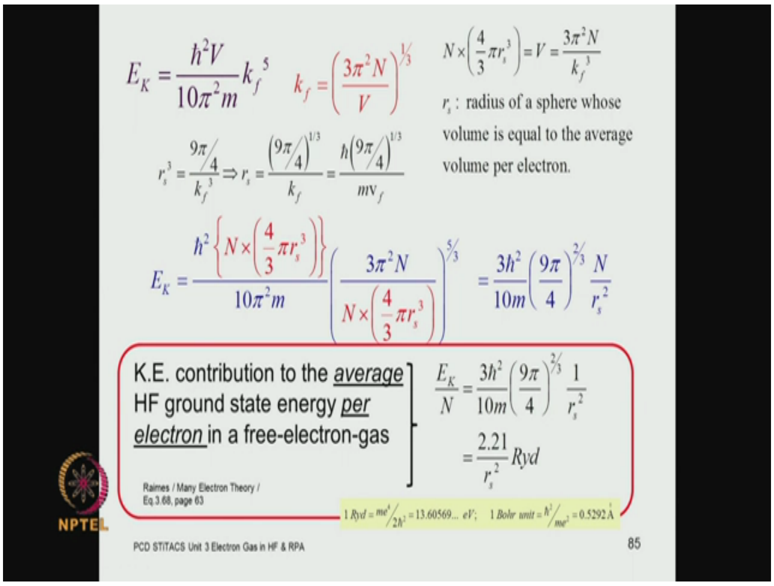

$$E_K = \frac{\hbar^2 V}{10\pi^2 m} k_f^{\,5} \qquad k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \qquad N \times \left(\frac{4}{3}\pi r_s^3\right) = V = \frac{3\pi^2 N}{k_f^3}$$

r_s : radius of a sphere whose volume is equal to the average volume per electron.

$$r_s^3 = \frac{9\pi/4}{k_f^3} \Rightarrow r_s = \frac{\left(9\pi/4\right)^{1/3}}{k_f} = \frac{\hbar\left(9\pi/4\right)^{1/3}}{m v_f}$$

$$E_K = \frac{\hbar^2\left\{N \times \left(\frac{4}{3}\pi r_s^3\right)\right\}}{10\pi^2 m}\left(\frac{3\pi^2 N}{N \times \left(\frac{4}{3}\pi r_s^3\right)}\right)^{5/3} = \frac{3\hbar^2}{10m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{N}{r_s^2}$$

K.E. contribution to the *average* HF ground state energy *per electron* in a free-electron-gas

$$\frac{E_K}{N} = \frac{3\hbar^2}{10m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^2} = \frac{2.21}{r_s^2} Ryd$$

Raimes / Many Electron Theory / Eq.3.68, page 63

$1\ Ryd = me^4/2\hbar^2 = 13.60569...\ eV; \quad 1\ Bohr\ unit = \hbar^2/me^2 = 0.5292\ \mathring{A}$

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85

So, this is what we have got, these are the two forms that we get. We have; if you now consider rs, r subscript s to be the radius of a sphere whose volume is equal to the average volume per electron just have some variable for that which is the average volume that you have per electron. So, this average volume multiplied by the total number of electrons will give you the total volume and this we have found out to be what it is.

Now that gives you rs this radius of a sphere whose volume is equal to the average volume per electron to be given by this relation. And that tells you that this rs you find a mechanism to find what this value of rs is. What it gives us is the expression for this term Ek in terms of rs. But this is Ek in terms of the total number of electrons, so it is best that we normalize it for the number of for the average Ek per electron.

So, you divide Ek by n that gives you an estimate for the kinetic energy contribution to the average Hatree Fock ground state energy per electron because you have divided it by the total number of electrons and that turns out to be this particular value. And all of these are universal constants. So, you can find out the corresponding values in appropriate units okay.

And in terms of energy units it turns out to be 2.21 over rs square Rydberg okay. And the RS itself will be in the bore units. Now this gives you a good estimate of the average energy per electron. Now is this really correct, now we already know that we have to make a correction for the exchange because this is just a contribution coming from the kinetic energy part okay.

So, when you make a correction for the exchange you get a better estimate but then even that is not enough.So, that is what many-body theory is about that is what the random phase approximation is about.

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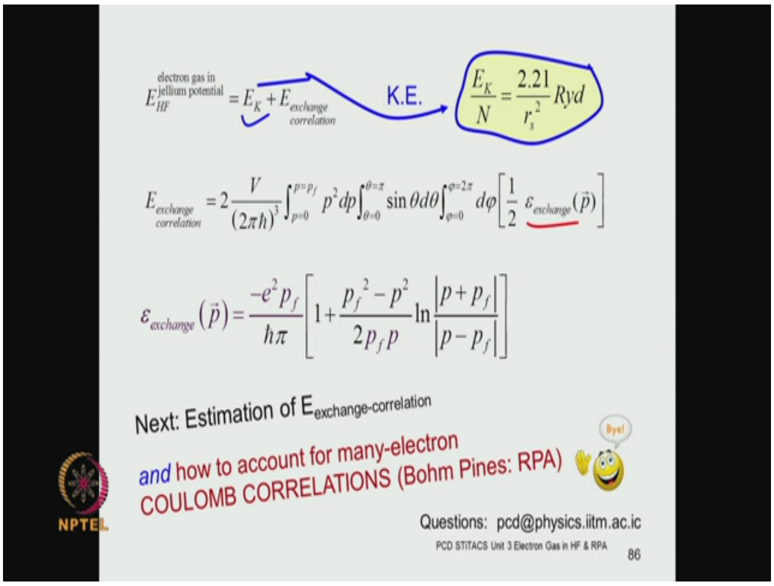

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}} \xrightarrow{\text{K.E.}} \boxed{\frac{E_K}{N} = \frac{2.21}{r_s^2} Ryd}$$

$$E_{\substack{exchange\\ correlation}} = 2\frac{V}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{1}{2}\underline{\varepsilon_{exchange}(\vec{p})}\right]$$

$$\varepsilon_{exchange}(\vec{p}) = \frac{-e^2 p_f}{\hbar\pi}\left[1 + \frac{p_f^{\,2} - p^2}{2p_f p}\ln\frac{|p+p_f|}{|p-p_f|}\right]$$

Next: Estimation of $E_{\text{exchange-correlation}}$

and how to account for many-electron COULOMB CORRELATIONS (Bohm Pines: RPA)

NPTEL

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86

So, first of all we have to make correction for the exchange-correlation term on. This exchange-correlation so we already knew that the Hartree Fock energy is the sum of the kinetic energy part in the exchange-correlation part. And we know that the exchange-correlation is given by this term.

We have this result from our previous analysis. Exchange term we got an explicit expression for this okay. And we will use this to get an estimate of the exchange part, so that will be our subject for discussion in the next class. And what we will find is that when you make an estimate of the exchange term you do get a better estimate of the average energy per electron. You improve upon it but even that is not enough.

Because what we have done in the Hartree Fock is we have taken care of the kinetic energy part we have taken care of the exchange interaction, in other words we have taken care of the Fermi-Dirac statistics. But we have still left out something which is the Coulomb correlations that is where you will need a many-body theory. You will need, you know where you know some new and powerful techniques.

You can try if it can be done with perturbation theory it will turn out that perturbation theory is not adequate for that. But we will get an estimate of the correction, we get by taking into account this exchange term in our next class and subsequently we shall proceed to account for the Coulomb correlations which are left out of the Hartree Fock.

By following the method of Bohm and Pines technique which is known the random phase approximation, so that is what we will discuss in the next class. So thank you very much for today.