Lecture 19
Limitations of the Hartree Fock Self-Consistent-Field Formalism

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Greetings, we will continue our discussion on the free electron gas in Jellium background potential. And we already initiated the discussion on this in the previous lectures of unit 3. What we found is that the self-consistent field Hartree Fock energy for the electron gas and Jellium potential gets factored into two pieces one is the kinetic energy part and the other comes from the exchange-correlation.

So, the Coulomb interaction the repulsion electron-electron repulsion due to the Coulomb potential which is coming from the direct Coulomb interaction not the exchange, the direct Coulomb interaction that cancels the attractive Jellium potential right, so you will remember that. And we are now left with these two terms of which the kinetic energy part is given by this integral.

So, this result we obtained in our previous class and I am just summarizing the essence of this result. So, you have this angular integration which gives you a factor of 4 pi and then you have a p squared term here and a p squared term here. So you need to integrate the 4th power of p and that gives you the 5th power of p divided by 5.

So, that is the result that we obtained last time. And this was in terms of momentum you can write it in terms of k which is the 5th power of k. And if you plug in the numbers f is of course the Fermi energy Fermi level label.

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

$$N \times \left(\frac{4}{3} \pi r_s^3 \right) = V = \frac{3\pi^2 N}{k_f^{\ 3}}$$

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

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

$\boxed{r_s : \text{Bohr units}}$

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

r_s : Seitz parameter

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

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

$$= \frac{2.21}{r_s^2} Ryd$$

Raimes / Many Electron Theory / Eq 3.68, page 63

$1\ Ryd = \frac{me^4}{2\hbar^2} = 13.60569...\ eV;$ $1\ Bohr\ unit = \frac{\hbar^2}{me^2} = 0.5292\ \text{Å}$

And what we did was to estimate an average radius which an electron would have compared to and in consideration of that we have the total volume occupied by N of electrons. So, that gives us some estimate of an average radius for an electron. And you find that this rs + kf are inversely related. So, this is our s to the power 3 which is proportional to the inverse third power of kf.

So, rs goes as 1 over kf as a result of which kf of course is mass times velocity in units of you know you have the factor h cross over here. So, when you take care of that and put the value of kf in terms of rs then you get an expression for energy which goes as 1 over rs square. Now other than 1 over rs square everything is a constant if you determine the energy Ek per unit electrons.

So, if you divide both sides of this equation by the number of electrons you get the kinetic energy contribution to the average self-consistent field Hartree Fock energy coming from the kinetic energy term which goes as Ek over N and we find it to be 1 over rs square into 2.21. So, I think few days ago, I think Veda on did some calculations to check that this number actually turns out to be 2.21, so you can do it quite easily.

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Now you look at the second term now which is the exchange-correlation term. The kinetic energy part is what we did in the previous class the exchange-correlation term require us to evaluate this integral. And this term we have discussed earlier we know what it is this exchange term is given by this expression which has got this logarithmic term of the ratio of pf + p and pf – p.

So, this is the term that you get for the exchange-correlation term for the momentum p. Now this is what we now have to determine. Now this factor of half cancels the factor 2 here and you have this integral to be evaluated over p theta and Phi in the reciprocal space in the momentum space.

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And if you look at this expression here again the angular integration gives you a factor of 4pi as before and the integration is over p which you can easily translate to integration over k because p is nothing but h cross k. So, p square dp will become h cross cube k square dk

right. And this substitution gives us this expression for the exchange-correlation. There is a factor of 1 over pi here which I have factored out in common.

The 1 over 2 also comes out, so this is 1 over 2pi but then you get a factor of 2 in the first term over here, so that is what gives us 2kk square when you just arrange the term. So, it is just a little bit of manipulation of these terms it is quite straightforward. So, now this is the integral over k involving this logarithmic term. Now this is what we have to evaluate and again this can be evaluated using similar techniques as we discussed earlier.

There are the standard integrals having logarithmic functions and you can refer to these tables or you can work it out a priority by hand. And you will get the result which is the exchange-correlation term turns out to be this total volume in which you have box normalized all those electrons. And then you have -e square k to the 4 by 4 p cube. So, this is the result of this integration, so we will use this result.
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$$E_{\substack{exchange \\ correlation}} = V\left\{ -\frac{e^2 k_f^4}{4\pi^3} \right\}$$

$$k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3} ; \& N \times \left(\frac{4}{3}\pi r_s^3\right) = V$$
from : slide 85, last class

$$-\frac{e^2 k_f^4}{4\pi^3} = -\frac{e^2}{4\pi^3}\left(\frac{9\pi}{4}\right)^{4/3}\frac{1}{r_s^4}$$

$$E_{\substack{exchange \\ correlation}} = N\left(\frac{4}{3}\pi r_s^3\right) \times \left\{ -\frac{e^2}{4\pi^3}\left(\frac{9\pi}{4}\right)^{4/3}\frac{1}{r_s^4} \right\}$$

$$= N \times \left\{ -\frac{e^2}{3\pi^2}\left(\frac{9\pi}{4}\right)^{4/3}\frac{1}{r_s} \right\}$$

$$\frac{E_{\substack{exchange \\ correlation}}}{N} = \frac{-0.916}{r_s} Ryd$$

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Now this is the k to the 4 term that you get this is again f represents the value of k at the Fermi level which is the highest occupied state in the free electron gas. And we have already seen that kf goes as 1 over rs, so this kf to the 4 goes as 1 over rs to the 4. And there are these other constants which take care of the balance okay.

And you can rewrite this expression this volume is nothing but the number of electrons times the average volume of each electron which is in this bracket 4 third pi r cube with the Wigner radius rs. And the second factor in this beautiful bracket is what appears away here with k to the power 4 or kf to the power 4 replaced by 1 over rs to the power 4 and then there are these other constants which take care of the numerical balance.

Now this is the result that we get the exchange-correlation energy you if you divided by N on both sides you get the exchange-correlation energy per unit electron. And plug in the values of all these constants 9 pi e square and everything. Then essentially turns out to be - 0.916 by rs. So, this is a very simple calculation just the way we did it the previous calculation and got the kinetic energy term as 2.21 by rs square this turns out to be -0.9 16 by rs.
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Now we can add both the terms, so these are the two terms that we are adding up and the result is essentially 2.21 by rs square - 0.916 by rs which is the average Hartree Fock energy per electron for a free electron gas which is described in a potential in which all the nuclear charges are spread out in a Jellium potential.

Now notice that there is a minus sign here okay; this is the minus sign I am referring to which means that in relation to the energy per electron you would get from the kinetic energy term alone. This Hartree Fock self-consistent field energy is actually lowered it is actually reduced and this is.
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To begin with it might appear to be a large slightly strange result because you have got a kind of term coming from the kinetic energy part and then you add an electron gas. Which you obviously know are going to consist of a lot of repulsion between every pair of electrons and you expect the energy to be raised instead you find the energy to be actually lowered. Now that of course should not surprise you.

Because the origin of the reduction comes from the fact that there is a positive Jellium and if you remember how we arrived at the Hartree Fock self-consistent field relation. The attractive Julian potential this term cancelled the electron-electron Coulomb repulsion and the only thing that was left with is the exchange-correlation term which gives you this lowering of the energy. So, that is the origin of this reduction term. So there is nothing very mysterious about it.

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So, this is the result that we get for the Hartree Fock self-consistent field free electron gas. Now it turns out that if we did this using perturbative methods we get actually the same result. And I am going to show it in the next class, so in the meantime I just want to anticipate this result and you know inform you that the first order perturbation treatment will actually give the same result.

But then if you do second-order and higher order Corrections according to a perturbation theory then the perturbation series does not converge what happens is that the electron-electron Coulomb interactions term it gives you a divergence. So, up to first order there is no problem but second order and beyond you start getting diversions.

Now the reason you get divergence is because there is something missing in our model. And that is what we are going to have to address.

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For free electron gas in jellium potential :

$$\left[\frac{E_{HF}}{N}\right] = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right) Ryd$$

COULOMB correlations ignored

Need! Many-body theory – beyond perturbation methods

Bohm & Pines: mid-fiftees

D.Pines (1963) Elementary excitations in solids   (Benjamin, NY)

Random Phase Approximation

$$E_{BP} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \frac{\sqrt{3}}{2r_s^{3/2}}\beta^2 - \frac{0.916}{r_s}\left(\frac{\beta^2}{2} - \frac{\beta^4}{48}\right) \qquad \beta = \frac{k_c}{k_f}$$

k_c : Upper bound to wave number of plasma oscillations

→ Lower bound to wave length; since oscillations get damped by the random thermal motion of the electrons.

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So, what is missing in our model are the Coulomb correlations. And every time we discuss the Hartree Fock we always must remember that there are correlations of two kinds. There are the exchange correlations which come from the Fermi-Dirac statistics because the system wave function of an N electron system must be an anti symmetric function.

So, they all these things go hand in hand the anti symmetry of the wave function the Pauli Exclusion Principle the presence of electron exchange terms okay. So, these are verily called as exchange correlations or Fermi correlations or Fermi Dirac correlations or Pauli correlations because they are associated with the Pauli Exclusion Principle. So, these correlations are included in the Hartree Fock.

Because the Hartree Fock wave function is an anti-symmetrised N electron wave function. So, it takes care of the statistics part the Fermi-Dirac statistics satisfactorily. It of course takes into account to the Coulomb interaction which must be distinguished from the Coulomb correlation in the context of the discussion we have. So we are referring to correlations of two kinds.

The Coulomb correlations which are ignored in the Hartree Fock and the exchange correlations which are actually included in the Hartree Fock, the Coulomb correlations are ignored. And because these correlations are ignored there is something missing in the model and that is part of the reason that you begin to get divergence when you deal with second-order perturbation theory and higher order perturbation theory.

So, perturbative methods actually do not work and we need to find a completely different kind of approach to solve this problem. And that actually requires a many-body theory that is where you use feel theoretical methods, formal many-body techniques and using them you are then able to address the Coulomb correlations not exactly, that we know because no many-body problem has exact solutions.

But you can develop excellent approximations and that is the challenge for theorist that you make an attempt to develop as good an approximation as you possibly can. Because exact solutions are beyond you there are existence theorems we tell you that you cannot get exact solution but at least it offers a challenge that you can develop certain approximation techniques or nothing wrong.

There is no reason to feel embarrassed about using approximations they are necessary intrinsic to the existence of the many-body problem but then the challenge lies in developing good approximations. So, one of the most powerful approximations which people use to address the electron correlations is the random phase approximation this was developed in the mid 50's by Bohm and Pines.

I will not get into the historical development of the RPA because there are different routes to RPA, I will mention some of this after a few classes. But in particular I will like to discuss the approach of Bohm and Pines a little bit because that gives us some understanding of why this approximation is called as the random phase approximation. So, what are the phases that are involved, what is random about these phases?

And what is this phase cancellation that is being referred to in the RPA. So, these are some of the questions that I will discuss in this and in the next few classes. Now this is a technique

which goes beyond the Hartree Fock, it addresses some of the Coulomb correlations it gives you a Bohm Pines energy per electron which has these terms 2.21 by rs square and .916 by rs but then there are certain corrections.

In which, these corrections are parameterised in terms of the ratio of kc over kf, so that is beta is just a ratio of kc over kf, kf is our old friend which is the value of k at the Fermi level and kc is an upper bound to wave number in what turned out to be plasma oscillations and corresponding to that there is of course a lower bound to wavelength.

And this bound the lower bound of the wavelength comes because the oscillations get damped by a random thermal motion of the electrons. So, I will tell you what these oscillations are and what is causing them and how to get these parameters.
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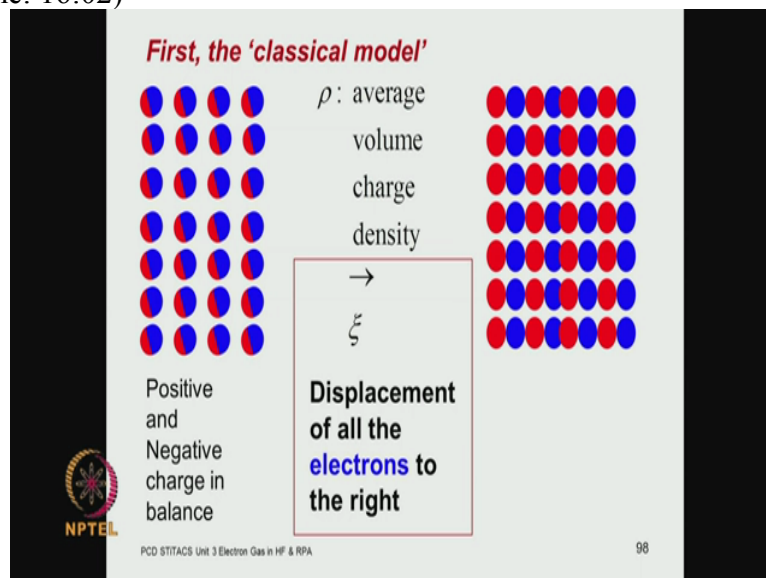
So, we will begin with a very simple classical model. So, let us think of electrically neutral system you have a positive charge and negative charge in balance okay. Both are exactly equal and opposite the red are the positive charges the blue are the negative charges and there is an equal amount of positive and negative charge.

Now we will not be referring to thermal motion for some time at least except for the fact that some thermal motion would have caused a little bit of fluctuation okay. So, you have and on an average a volume charge density which is smeared out. So, the total charge divided by the total volume will give you an average volume charge density.

This is imbalance between the red and blue in their equilibrium positions. But then due to some trigger it could be a thermal source, due to some trigger we would not worry too much

about the origin of this trigger it can be of thermal nature. But beyond that we will not refer to the thermos factor very much at this point of the discussion.

So, let us say that there is a little bit of tiny little displacement of the electron gas to the right. Now once that happens you will have a lot of electron charge on the right face and a lot of positive charge on the left face okay. In the inner size everything will get cancelled. So, you are left with a charge on the two faces.

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Now once you have that this is our classical model you have got a little bit of displacement of the whole electron gas to the right. Now that gives you a surface charge density and negative surface charge density of e Rho times Xi, Xi is the displacement mind you right, on the right. And on the left hand side there is a surface charge density which is plus e Rho Xi. So, these are equal and opposite surface charge densities with opposite signs.

And with that kind of a surface charge density which is written here as sigma which is e Rho times Xi, you can get from simple plain classical electrodynamics that the net field in between will be just the surface change density divided by epsilon zero so that will give you the intensity of the field in between those two regions right.

Yes (Question time: 18:37 –not audible) charge to be it is a Jellium potential; yes, smeared over it, yes now how are we having like it looks like a lattice arrangement I know it is like you have positive and negative then does it you are talking about displacement; yeah actually what you are doing this lattice is shown just to show the displacement.

Necessarily you have got the free electron gas okay. And then you have got the positive charges which are completely smeared out, so nothing is discretized neither the electrons not

the positive charges. And these two generate charge densities which are uniform and that charge density is this Rho.

So these are the uniform charge densities but you have displaced the electronic density to the right. And that leaves the Jellium at the back and that is what generates this electric intensity between them which is 1 over epsilon 0 times the surface charge density.
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Yes (Question time: 19:45 –not audible) how we are making displacement that it is smeared out in whole space you just leave that behind and the whole electron gas most of the right it could be because of some thermal noise okay. So, you have got a background Jullium potential which is positively charged.

And then you have got an electron gas and due to some thermal noise the whole electron gas is displays to the right, the jellium potential remains where it is. That is also heavier because it is high to the nuclei. So, you consider a slight displacement of the electron gas and then you are left with a net effective surface charge density on the right side which is of negative charge and a net positive charge on the left.

So, that gives you an electric field in between. And with that electric field you can set up the equation of motion because mass times acceleration will be the electric intensity times the charge, so that is the equation of motion that you get. And you immediately see that this relationship is nothing but the equation of motion for a simple harmonic oscillator okay.
You have got the displacement and force, the restoring force which are proportional to each other. So, it is nothing but a linear harmonic oscillator, simple harmonic oscillator. So, we immediately know what will be the natural frequency of oscillation for this that will be given by the square root of Rho e square by m epsilon zero.

This is the relation that you get in SI units. In many books you will find that atomic units are used and in CGS units 1 over 4pi epsilon zero is written as 1. So, 1 over epsilon zero goes to 4pi, so the plasma frequency is root of 4 pi Rho e square over m. So, this is just a matter of detail whether you are reading literature which has used CGS units or SI units.

So, you will get the oscillations coming from this particular source. Now we have ignored the thermal motion of the electrons except that we attribute the initial displacement to some thermal noise but other than that we are not concerned very much. At the same time we know that at any finite temperature there will be some thermal noise.

And that is something which you are going to have to take into account. And I will not go into the details of the classical theory of plasma oscillations but only remind you that as a result of this thermal motion you get a dispersion you get a k-dependent omega. And there is this correction you get because of thermal motion. So, this is the relation that we get okay.
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Now just to remind you that this is the Jellium potential, this is the point we were discussing a little while ago. You actually do have these discrete positive charges in a lattice in a metal okay which is what we are trying to solve the problem for and these positive charges can be thought of like these jelly beans. And you smash them into a pudding or into what is called as a Jellium or whatever other desert you like okay.

And smear it out so this is a uniform charge density, so we do not consider discrete charges at discrete locations in the lattice. But charges which are smeared out in uniform charge density the whole system however is electrically neutral. So, this is our picture and in this picture we

are using electron waves which are box normalized. So, you have got this positive charge density in this entire box.

This entire box has got a uniform positive charge density which is simply Ne by V this is the net positive charge the total number of electrons multiplied by the charge of the electron divided by V, this is the net charge density I am referring to the positive charge density the charge of proton and electron is the same okay. So, this is the net positive uniform charge density.

And now we write the total Hamiltonian for the system and what is what is it going to consist of it will have the electron part of the Hamiltonian it will have a part coming from the Jellium background and it will have also an interaction between the electron gas and the background which is written by el – b, b stands for background el are the electronic terms.

So, you have got the electronic Hamiltonian the background Hamiltonian and the interaction term between the electron and the background. So, this is our total Hamiltonian, so let us work with this Hamiltonian now. Let us look at the first term in the Hamiltonian, so you have got the kinetic energy term which is the usual one.

You have got the usual e-square over r term in the Hamiltonian but what we have done here is we have introduced a convergence factor instead of 1 over distance, I scaled the 1 over distance by e to the - mu distance and eventually I will take the limit mu going to 0 okay. Now this has got certain advantage and you will begin to see these advantages very soon.

So, this is just a mathematical device which is necessary to avoid certain divergence that we otherwise get. But with this mathematical tool we can handle the divergence very nicely. So, this is the first term in the Hamiltonian the second term is the Hamiltonian corresponding to the Jellium background which has the uniform charge density.

So, you will have the interaction between the uniform charge density at x with uniform charge density at x prime. And you will have the 1 over distance term in the potential. And here again I have introduced the e to the - mu times distance factor which will take care of the divergence. So, this is the second term for the background. So, it is just the Coulomb interaction basically.

But it is Coulomb interaction between uniform positive charge density between different locations of the charges, between each other. What about the third term third term is the electron background interaction. So, you still have the charge density over here. Here again

we have used the e to the - mu distance term okay. In every case eventually we will take the limit mu going to 0, so, this is the third term.
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And let us have a look at the second term now. Now we are going to analyze all of these terms one by one and then put it all together and then try to solve the Schrodinger equation perturbatively okay that is what we are going to do. So, this is the second term which is the Hamiltonian corresponding to the Jellium potential. Now what do you get in this you have Rho at x multiplying Rho at x prime.

And each of these is equal to N over V because you have a uniform charge density. So obviously you will get a term in N over V Square which is what you see now. And then you have the rest of the integration okay. So you will get the square of N over V. Now to handle this integral I will introduce a new variable which is z which is the difference of x prime - x. So, that at a given value of x dx prime will be the same as dz okay.

So, this transformation makes it very easy for us to evaluate this integral. So, now this integral is now written in terms of instead of x and x prime integration is over x and z where z is defined like this okay. Now this is a straightforward integral to evaluate. Because this integral if you evaluate using the usual techniques, integration of product of two functions it comes out very neatly and you will find that this turns out to be 4pi over mu square.

So, that is the result we will plug in. This integral is just the total volume right, this is the integration over the whole space of the volume elements, so you get the total volume over here. And then you have 1 over volume square coming from here and you have got a volume in the numerator, so you are left with N squared over V. You have got a 4pi over meu square and then of course you have the half e square which was here to begin with okay.

So, that is your result for the background Hamiltonian. Notice that this background Hamiltonian it actually diverges in the limit that mu goes to zero. So, we will have to be concerned about it because we promised ourselves that we are going to exploit the fact that we will let mu go to zero which is good to get the Coulomb term out of the screen Coulomb term. But then you also have to worry about what it does to the energy.

And if there is any divergence resulting from that we are going to have to handle it carefully, so we will do that okay. So, this contribution of this term per electron it diverges in the limit mu going to 0, this is referred to as mu square divergence because it is coming from the square of mu in the denominator.

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Reference: Fetter & Walecka - Eq.3.8 in Quantum Theory of Many-Particle Systems; page 22

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Let us look at the third time this was the electron background interaction. So this is the electron background interaction this Rho is nothing but N over V. So, we have this term and we already know how to evaluate this integral, we just did in the previous slide. So, that we know is 4pi over mu square, so this is our result now okay. So, the electron background interaction term this also has got mu square divergence.

So, both the backgrounds Hamiltonian as well as the electron background interaction Hamiltonian both have got 1 over mu square divergence. Both have got the factor e square N square over V and 4pi over mu square. But this is plus half and this 1 is -1, so you have to sum them up okay.

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So, this has got plus half this has got -1, if you combine the two you have a net term which is - half e square N square over V 4pi over mu square. And this term also has mu square divergence okay. We perhaps would have been happy if these two terms had cancelled each other but that has not happened but that is not a worry because there is more to come and that will give us the tools to take care of the mu square divisions okay.

So, what we do is we will take the limits l going to infinity or the volume going to infinity and then take the mu going to 0 because these are artificial parameters at our disposal and we should do it, so that mathematically you do not get any unphysical result. So, that is the advantage of doing it but before we take these limits we should inquire if this mu square divergence does it cancel with any part of the electronic Hamiltonian which is here okay.

We have to look at the form of the electronic Hamiltonian very carefully okay. We have not only packed all the electron-electron interactions in that term okay. But it is made up of so many different pieces, there are the Coulomb interactions, there are the exchange interactions okay. There are so many terms in it.

And we must first examine if there is any cancellation of the mu square divergence with respect to any term or part of the term which is coming from the electronic part of the Hamiltonian which was our first term in the total Hamiltonian. So, that is something that we will examine.

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So, (Question time: 32:35- not audible) yes why should we take the limit l tends to infinity first and mu going to zero sir, if you first take the limit mu going to zero you already hit the infinity. Now that you are going to have to avoid at any cost and these because you should not get any unphysical result you do not want the catastrophic okay.

As there was that as was there in the analysis of blackbody radiation or other things also you want to avoid any catastrophic divergence. If you have the energy blowing to infinity for example okay. So, that is part of the reason and these are just mathematical tools and how we use this mathematics is then at our convenience. So, this is the order in which we take these limits but before we take these limits.

We should also find out if the mu square divergence is cancelling any part of the electronic Hamiltonian. So, let us use the second quantization methods which we have developed earlier. So, in the first quantised notation our electronic Hamiltonian has this usual familiar form the superscript key C stands for the Coulomb interaction between electron at qi and at qj, so that is the Coulomb interaction.

And when this is the form of the first quantised Hamiltonian for the electron N electron system, the corresponding second quantised form we wrote in terms of the electron creation and destruction operators. So, you had the one electron terms and you have the two electron terms. And you had this two center integral consisting of the Coulomb interaction v superscript c.

And this Coulomb term this two center integral, is this integral that you will remember okay.

So, this is the Coulomb interaction term that we have used earlier in second quantized form. Now what we have chosen to do is not use the Coulomb interaction but the screen Coulomb interaction which is scaled by this e to the - mu distance right.

So, instead of this v superscript c, we have v superscript screened Coulomb sc okay. And corresponding to that this is our first quantized Hamiltonian and the second quantized Hamiltonian which we do not have to develop from first principles anymore we have done that in our earlier exercise.

We straight away take this result and just replace this vc by the v screened Coulombs. So, this to Center integral becomes the screen Coulomb interaction here okay. So, it is directly we exploit the result that we have obtained earlier.

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$$H_{el}^{II\,Q} = \sum_i \sum_j c_i^\dagger \langle i \left| \frac{p^2}{2m} \right| j \rangle c_j + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|v^{sc}|kl \rangle c_l c_k$$

$$\langle ij|v^{sc}|kl \rangle = \int dq_1 \int dq_2 \phi_i^*(q_1)\phi_j^*(q_2) \frac{e^{-\mu|\vec{r}_1-\vec{r}_2|}}{|\vec{r}_1-\vec{r}_2|} \phi_k(q_1)\phi_l(q_2)$$

Showing the summation over spin variables explicitly:

$$H_{el}^{II\,Q} = \left[\begin{array}{l} \sum_{k_1} \sum_{\sigma_1} \sum_{k_2} \sum_{\sigma_2} c_{k_1\sigma_1}^\dagger \langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \rangle c_{k_2\sigma_2} \\ + \frac{1}{2} \sum_{k_1} \sum_{\sigma_1} \sum_{k_2} \sum_{\sigma_2} \sum_{k_3} \sum_{\sigma_3} \sum_{k_4} \sum_{\sigma_4} c_{k_1\sigma_1}^\dagger c_{k_2\sigma_2}^\dagger \langle \vec{k}_1\sigma_1 \vec{k}_1\sigma_1 |v^{sc}|\vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle c_{k_4\sigma_4} c_{k_3\sigma_3} \end{array} \right]$$

So, this is what we have got, now let us analyze these terms further. Here these are h, i and j is a set of four quantum numbers that includes summation over spin. And summation over the remaining three quantum numbers which are the wave vectors okay. This is the free electron gas right, so you have got summation over the vector k1 and the vector k2. And then there are summations over two spins Sigma 1 and sigma 2.

So, k2 sigma 2 is the detail that go into summation over j and k1 sigma 1 is the detail that goes corresponding to summation over i. So, I am now writing the summations over the spin variables explicitly okay. Now I do the same with respect to the second term which is the two center Coulomb or screened Coulomb interaction.

This is the screen Coulomb interaction here and now you have summation over for wave vectors k1, k2, k3 and k4. And you have likewise summations over for spin labels which are

sigma 1, sigma 2, sigma 3 and sigma 4 okay. So, these are the four summations which come in corresponding to these four summations i, j, k and l.
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$$H_{el}^{II,Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} c_{\vec{k}_1\sigma_1}^\dagger \left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle c_{\vec{k}_2\sigma_2} \right. \quad \leftarrow \text{First, examine the K.E. term.}$$

$$\left. + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c_{\vec{k}_1\sigma_1}^\dagger c_{\vec{k}_2\sigma_2}^\dagger \left\langle \vec{k}_1\sigma_1\vec{k}_2\sigma_2 | v^{el} | \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right]$$

$$\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \delta_{\sigma_1,\sigma_2} \iiint d^3\vec{x} \left(\frac{1}{\sqrt{V}} e^{-i\vec{k}_1\cdot\vec{x}} \right) \left(\frac{-\hbar^2\vec{\nabla}^2}{2m} \right) \left(\frac{1}{\sqrt{V}} e^{i\vec{k}_2\cdot\vec{x}} \right)$$

$$\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \frac{-\hbar^2 \delta_{\sigma_1,\sigma_2}}{2mV} \iiint d^3\vec{x}\, e^{-i\vec{k}_1\cdot\vec{x}} \vec{\nabla}^2 e^{i\vec{k}_2\cdot\vec{x}}$$

$$= \frac{\hbar^2 k_2^2}{2m} \delta_{\sigma_1,\sigma_2} \boxed{\frac{1}{V} \iiint d^3\vec{x}\, e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{x}}}$$

$$\boxed{\frac{1}{(2\pi)^3} \iiint d^3\vec{x}\, e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{x}} = \delta(\vec{k}_1-\vec{k}_2)} \quad \downarrow \quad \text{Dirac } \delta \text{ function}$$

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Let us examine the first term now which we know is the kinetic energy term okay. Now in the kinetic energy term we certainly know that there will be a Kronecker delta corresponding to parallel spins because the kinetic energy term will not connect spins of opposite which are oppositely oriented. So, this integral is the matrix element of the kinetic energy operator which is -h cross square del square by 2m.

In plane waves these are the plane wave solutions which are box normalized. So, you have got the 1 over square root V in as a box normalization okay. So, what do you get, you get from this 1 over root V and 1 over root V, you get a factor of 1 over V, you guess this Kronecker delta between the two spins sigma 1 and sigma 2 you have - h cross square over 2m and then you get the matrix element of the del square operator.

And essentially you get you have to evaluate this integral now some of you possibly recognize this integral already it is the Dirac delta function okay. So, the only thing you would notice is that normally you define the Dirac delta with 1 over 2 pi cube. We are defined it by 1 over V.
(Refer Slide Time: 38:39)

N electrons in a cubical box. Each side has length = L. Volume of the box = $V = L^3$ $\langle \vec{x} | \vec{k} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{x}}$

Box normalization with Born von Karmann boundary conditions

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

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

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

$$\frac{1}{2\pi}\int dx\, e^{i(K-k)x} = \delta(K-k)$$

$$\frac{1}{(2\pi)^3}\iiint d^3\vec{x}\, e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{x}} = \delta(\vec{k}_1 - \vec{k}_2)$$

$$\frac{1}{L^3}\iiint d^3\vec{x}\, e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{x}} = \delta_{\vec{k}_1,\vec{k}_2}$$

Eq.3.11; page 23; F&W

$$\langle \vec{k}_1 \sigma_1 | \frac{p^2}{2m} | \vec{k}_2 \sigma_2 \rangle = \frac{\hbar^2 k_2^2}{2mV}\delta_{\sigma_1,\sigma_2} \quad \iiint d^3\vec{x}\, e^{i(\vec{k}_2-\vec{k}_1)\cdot\vec{x}} = \frac{\hbar^2 k_2^2}{2mV}\delta_{\sigma_1,\sigma_2} V\delta_{\vec{k}_1,\vec{k}_2}$$

$\rho = \frac{Ne}{V}$

Positive charge density smeared uniformly

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And this again would not surprise you because mind you our wave functions are really not continuum plane waves which expand the entire infinite space which is available to them but these are box normalized pseudo discrete states. So, the continuum is really pseudo discreet because the plane waves are box normalized. So, as a result of that you have got the volume of the box which goes as L cube.

And your plane waves are 1 over root V times the e to the ik dot x that is coming from the Box normalization. And then because of these boundary conditions which are the Born Von Karmann boundary conditions as they are referred to. You have a quantization which is the pseudo discrete quantization as we get for box normalization, so this is the Box normalization condition.

And this immediately tells you that in the k space if you go from one allowed state to another allowed state in that discrete spectrum then the volume of each state will be 2 pi over L whole cube because you go from one to the next simply by changing these nx, ny and nz by one integer value. So, the volume of each state is 2 pi over L whole cube and that is the reason instead of this 1 over 2 pi cube over here.

You have a 1 over L cube over here which is the result that we are using okay. So, now we have this term in our previous result which is the matrix element of the kinetic energy operator we had this term over here. And this is the Dirac delta which is V times k1, k2 okay. So, now this we will cancel this V and you get this result for the matrix element of the kinetic energy part of the operator okay.

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We have got the first term done okay. This is the first term the kinetic energy part; now let us look at the second term which has got this two center interaction. These are not the Coulomb interactions but the screened Coulomb interactions. So, this is the term that we will now work with which is the screened Coulomb term.

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Now here again because the Coulomb interaction or the screened Coulomb interaction does not tamper with the spin, so you will have a delta sigma1 sigma3 delta sigma2 sigma4, the kronecker delta contraction over those to spin variables. And we can carry out that contraction because of we can exploit these kronecker deltas, this is the screen Coulomb interaction. So, you get the e square e to the - mu distance over distance so that is the screen Coulomb interaction.

And you plug in the plane waves which are box normalized as 1 over root V, so you got one over root V coming from 4 plane waves. This is the complex conjugate of one, this is a complex conjugate of another and these are the third and the fourth plane waves. So, you get

1 over root V four times. So that gives you a 1 over V square you have got the e square coming from here and now you have these integrals.

Now that I am going to do a little bit of you know simple mathematical manipulation which is very straight forward but just to make sure that there is no mystery about how we are handling those terms. I will point out to you how this manipulation is done, it is very simple. It is like undergraduate mathematics nothing more than that.
(Refer Slide Time: 42:46)

But it is nice to see that we are not mixing up the terms okay, so we have got 4 plane wave functions 1, 2, 3 and 4 each coming with a factor of 1 over root V. So, you get 1 over V square and then you have got the e square coming from here the two Kronecker delta's designed over here.

And then we are left with these plane waves I have combined k3 - k1, k3 will comes with a positive sign, k1 comes from this complex conjugation. So, it comes with a negative sign which is why you have k3 – k1 here and likewise you will have k4 - k2 because k2 is campaigning from the complex conjugate okay. So those are the terms that we are going to work with okay.
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$$\langle \vec{k}_1\sigma_1 \vec{k}_2\sigma_2 | v^{sc} | \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{e^{-\mu|\vec{r}_1-\vec{r}_2|}}{|\vec{r}_1-\vec{r}_2|}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{r}_1}e^{+i(\vec{k}_4-\vec{k}_2)\cdot\vec{r}_2}$$

$$\vec{r}_2 \to \vec{x}$$
$$\vec{r}_1 - \vec{r}_2 \to \vec{y} \qquad \vec{r}_1 = \vec{y}+\vec{r}_2 = \vec{y}+\vec{x}$$

$$\langle \vec{k}_1\sigma_1 \vec{k}_2\sigma_2 | v^{sc} | \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1)\cdot(\vec{y}+\vec{x})}e^{+i(\vec{k}_4-\vec{k}_2)\cdot\vec{x}}$$

$$\langle \vec{k}_1\sigma_1 \vec{k}_2\sigma_2 | v^{sc} | \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot(\vec{y}+\vec{x})}e^{-i(\vec{k}_4-\vec{k}_2)\cdot\vec{y}}$$

$$e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot(\vec{y}+\vec{x})}e^{-i(\vec{k}_4-\vec{k}_2)\cdot\vec{y}} = e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot\vec{x}}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

$$\langle \vec{k}_1\sigma_1 \vec{k}_2\sigma_2 | v^{sc} | \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot\vec{x}}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

Now we will do a little bit of you know variable change instead of r2 and r1 we will use x and y. So, x will stand for r2 and y will not stand for r2 but why will stand for the difference between r1 and r2 okay. What it does to r1 is it expresses r1 as y + r2 which is y + x okay. So, these are simple transformations of the variables but they make it possible for us to extract the terms that we can handle very easily.

So, eventually we are going to hit the Fourier transform of the screen Coulomb potential as you can possibly anticipate. But to extract that term these transformations are very handy. So, this is what we have got we have now read it in this integral in terms of x and y instead of r1 and r2, you can work out these things in details. So, I will just point out how this is done but then these slides will be uploaded at the course webpage anyway.

So, all the relations will be there, so you do not have to write down anything right now okay. So, these are the transformations that you will be using and in terms of this the other manipulation I do is I just multiply and divide by some terms over you are which is why this k3 - k1, I multiply it by e to the ik4 - k2 and then I divide it by the same term. So, this is e to the minus ik4 - k2.

So, that is all there is to it, so I have just multiplied and divided by this term okay. Now this is, this particular term we can again separate out into those parts which contain x alone and those parts which contain y alone, so you just separate out the factors this makes it very easy to handle these terms. So, I have now separated the terms because the first exponential term has on y + x.

So, I separate it out into this term you know which has got x alone and then this term which has got y alone. So, you are left with only k3 - k1 dot y when you take the balanced correctly

okay. So, that is what we have got. So, this whole two Center integral for the screen Coulomb potential now has this term. But now all this screen Coulomb interaction takes a rather simple form this goes as e to the - mu y over y okay, in terms of the variable y okay.
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$$\langle \vec{k}_1\sigma_1\vec{k}_2\sigma_2|v^{sc}|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\frac{e^{-\mu y}}{y}e^{+i((\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot\vec{x})}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

$$\langle \vec{k}_1\sigma_1\vec{k}_2\sigma_2|v^{sc}|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\underbrace{\int d^3\vec{x}e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\cdot\vec{x}}}\int d^3\vec{y}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

Conservation of linear momentum in homogeneous space

$$\langle \vec{k}_1\sigma_1\vec{k}_2\sigma_2|v^{sc}|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}V\delta(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4)\int d^3\vec{y}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

$$\langle \vec{k}_1\sigma_1\vec{k}_2\sigma_2|v^{sc}|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V}\delta(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4)\int d^3\vec{y}\frac{e^{-\mu y}}{y}e^{+i(\vec{k}_3-\vec{k}_1)\cdot\vec{y}}$$

Fourier transform of the Screened Coulomb Potential

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So, this is now the integral to be evaluated and the variables x and y we separate we first carry out the integration over y and then integration over x. So, let us evaluate this integral this we already know is the Dirac delta it is coming from conservation of momentum relationship okay.

So, we know it is V times the Dirac delta as we have defined. What about this term so this is the delta this V over V square gives us only 1 over V, so that is the only thing we have done in this step okay. This V over V square giving us 1 over V, this V is coming from the Dirac delta definition because of box normalization.

And here you see that you have to determine nothing but the Fourier transform of the screen Coulomb potential and that is something which you would have probably done in your mathematical physics course okay. So, this is just the Fourier transform of the screened Coulomb potential.
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Small digression: Fourier transform of the Coulomb Potential

Fourier transform $g(\vec{k})$ of $f(\vec{r})$:

$$g(\vec{k}) = \iiint e^{-i\vec{k}\cdot\vec{r}} f(\vec{r}) d^3r$$

When the integral does not converge:

$$g(\vec{k}) = \lim_{\mu\to 0^+} \iiint e^{-i\vec{k}\cdot\vec{r}} \boxed{e^{-\mu r}} f(\vec{r}) d^3r$$

And I would not do it in any detail because I assume that you are familiar with this. But I will just show the path of how it is done very quickly without getting into too many details. So, I will have a very tiny digression without getting into too many details because you have the general definition for Fourier transforms.

And the problem is that when this particular integral does not converge you can do it by introducing and mathematical convergence factor. So, when this integral does not converge as it does not in the case of the Coulomb interaction. You can evaluate this in terms of a mathematical device, introduce this e to the - mu r and then take the limit mu going to zero. So, the Fourier transforms work quite all right using this technique.

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Given $g(\vec{k})$, how do we recover $f(\vec{r})$?

$$f(\vec{r}) = \left(\frac{1}{2\pi}\right)^3 \iiint e^{+i\vec{k}\cdot\vec{r}} g(\vec{k}) d^3k$$

When the integral does not converge:

$$f(\vec{r}) = \lim_{\mu\to 0^+} \iiint e^{+i\vec{k}\cdot\vec{r}} e^{-\mu k} g(\vec{k}) d^3k$$

rotational symmetry:

When $f(\vec{r}) = f(|\vec{r}|)$, then $g(\vec{k}) = g(|\vec{k}|)$; & vice versa

In the case of *rotational symmetry*, $f(\vec{r}) = f(|\vec{r}|) = f(r)$:

$$g(\vec{k}) = g(|\vec{k}|) = g(k) = \frac{4\pi}{k} \int_0^\infty dr\, r\, f(r) \sin(kr)$$

FT of Coulomb potential, $V(\vec{r}) = V(|\vec{r}|) = V(r) = \frac{1}{r}$

$$g(\vec{k}) = g(|\vec{k}|) = g(k) = \frac{4\pi}{k} \int_0^\infty dr\, r\, \frac{1}{r} \sin(kr) = \frac{4\pi}{k} \int_0^\infty dr\, \sin(kr)$$

So, the other thing that is, that we exploit in this case that when this function f of r whose Fourier transform you are interested in, if this has a rotational symmetry then the Fourier transform has got a rotational symmetry in the momentum space or in the k space. So, that is

again a theorem which you can work out and I will not discuss that in any detail. But I will use these results.

And the entire derivation of the Fourier transform of the screen Coulomb potential is based only on these two very simple Conservation's one is to use the mathematical device of mu taking the limit mu going to zero and second is to exploit the rotational symmetry of the Coulomb potential.

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FT of Coulomb potential, $V(\vec{r}) = V(|\vec{r}|) = V(r) = \dfrac{1}{r}$

$g(\vec{k}) = g(|\vec{k}|) = g(k) = \dfrac{4\pi}{k} \int_0^\infty dr\, r\, \dfrac{1}{r}\sin(kr) = \dfrac{4\pi}{k}\int_0^\infty dr\, \sin(kr)$

The above integral does not converge

FT of Screened Coulomb potential, $V^{SC}(\vec{r}) = V^{SC}(|\vec{r}|) = V^{SC}(r) = \lim_{\mu \to 0^+}\dfrac{e^{-\mu r}}{r}$

$g(\vec{k}) = g(|\vec{k}|) = g(k) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\int_0^\infty dr\, r\, \dfrac{e^{-\mu r}}{r}\sin(kr) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\int_0^\infty dr\, e^{-\mu r}\sin(kr)$

$g(\vec{k}) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\int_0^\infty dr\, e^{-\mu r}\sin(kr) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\int_0^\infty dr\, e^{-\mu r}\,\mathrm{Im}(e^{ikr})$

$g(\vec{k}) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\mathrm{Im}\int_0^\infty dr\,(e^{ikr-\mu r}) = \lim_{\mu \to 0^+}\dfrac{4\pi}{k}\mathrm{Im}\left[\dfrac{e^{ikr-\mu r}}{ik-\mu}\right]_0^\infty$

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So, using this result you can get the Fourier transform of the screened Coulomb potential because the Fourier transform of the Coulomb potential this goes as integral 0 to infinity of this sinusoidal wave. So, this sinusoidal wave will just keep oscillating no matter how far you go and the integral does not converge.

So, that is the reason you have to use this device, so the Fourier transform of the Coulomb potential will not converge but that for the screen Coulomb potential it does converge. And you can evaluate it using the technique that I just showed you.

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And we will use the result which is 4pi over mu square +k square. So, these are some of the straight forward intermediate steps which you can work out or look at the details on the PDF file which will be uploaded and the course website. So, this is the Fourier transform of the screen Coulomb potential when you take the limit mu going to 0 you get the 4pi over k square for the Coulomb potential itself.

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So, this is the result that we are going to use because we needed the Fourier transform of the Coulomb potential to analyze this term okay. This is the Fourier transform of the screen Coulomb potential. So, we have got everything evaluated now this to Center integral has been evaluated, here you have got the Kronecker Delta is coming from the spin, here you have got Dirac delta coming from the Box normalization right.

And here you have got the Fourier transform of the screen Coulomb potential that we have just evaluated, so we have got everything now. So, just put in all the values, so here you get 4pi over here, the factor is k3 - k1, so you have got the modulus of k1 - k3 whole square right

+ mu square, so this is your two center term. And now we have the expression in second quantized form for the electronic Hamiltonian okay.

Now this is the second quantized form of the electronic part of the Hamiltonian you have these summations. And then you do have these summations over various momenta k1, k2, k3, k4 and so on right. Now when you deal with these there will be certain momentum transfer and you may be able to separate out certain terms. How much momentum is transferred, what are the terms corresponding to zero momentum transfer.

What are the terms corresponding to non zero momentum transfer and when you analyze these terms carefully you will find that some of these terms actually cancel the 1 over mu square divergence, we were getting from the background Hamiltonian and from the electron background Hamiltonian okay. So, that is something that we are going to see after rearrangement of these terms.

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So this is the mu square divergence that we were worried about. This is the second quantized form of the electron Hamiltonian that we have now got. We have got the Fourier transform of the screen Coulomb interaction; we have got the remaining you know the whole Hamiltonian is written in second quantized form in terms of the creation and destruction operators.

And the Kronecker delta over here tells us that k1 + k2 must be equal to k3 + k4 which is a statement of momentum transfer that k4 - k2 must be exactly equal to k1 - k3. And these two momenta differences must be exactly equal. So, what we will do in the next class is to rearrange these terms. We will analyze the terms for different values of q which is the momentum transfer okay.

And what are the terms corresponding to zero momentum transfer, what are the terms corresponding to non zero momentum transfer because obviously when $k_4 = k_2$, $k_1 = k_3$ and the momentum transferred is 0. So, we will look at these terms carefully and we will find happily that the zero momentum transfer terms actually cancel the mu square divergence. But that is something we will do in our next class.

So, we will, when we do this analysis we will proceed to get the perturbative expression for the energy of this system. There is any question I will be happy to take otherwise goodbye for now until the next class. (Question time: 54:40- not audible) Jobin and yes, here we are dealing with free electron gas function corresponding to the RPA .

Yes when it comes to that atomic system is there any distinction or a there any difference; not really the model is the same because ultimately what we are going to use in the atomic case is how the electron terms are handled. And how the electron terms are handled, there are two parts to it one is how the exchange correlations are handled and how the Coulomb correlations are handled.

Now as we develop this technique further in the next few classes it will take us another four classes before we get to the end of this Bohm Pines method which is the random phase approximation, which is also why it is called as a random phase approximation. What this technique is going to tell us is that how are these electron correlations to be handled and there is a certain prescription which a certain recipe which comes out of this.

Now that recipe is something that we are going to use in the atomic case. Now it is not guaranteed that it will be always successful in the atomic case nor is it guaranteed that it is always successful for a metal. In both cases it is conceded that electron correlations cannot be dealt with exactly.
So, to the extent to which RPA correlations will account for the correlations we go ahead and use this model whether it is in the solid state case or in the atomic case. But then we find that when you are applied to real systems you do run across situations in which the correlations are not adequately accounted for by the RPA.

What you do in that case you have to develop a different many-body theory. You have to develop a different approach to deal with correlations and these different approaches to correlations they are sometimes based on configuration interaction methods in the atomic case we use a multi configurational Hartree Fock or the relativistic multi configuration of Dirac Fock and so on.

That is because the usual techniques that we use for it, in using the RPA if they are not adequate you need to go beyond the RPA. So, you are quite right that it is not at all guaranteed that this will be applicable in the atomic case, in every single atomic case. It is applicable in a large number of cases though it is one of the most successful many-body theories.

So, that is where lies its strength but at the same time there are limitations. So, the approximation certainly means there are approximations at so many steps. The Jellium potential itself is an approximation that is not the real potential okay. Then the whole procedure of using the screened Coulomb potential and so on to develop this approximation and then as we proceed further, we will deal with certain terms.

And some of the terms you are simply going to throw okay. Theorists are very good at that that when they cannot handle a term they just throw it okay. And the experimentalists love to find a flaw in that but the point is that with all these approximation steps which go into developing a model. I think the smartness of the theorists and that is something which Bohm and Pines did so beautifully.

But Bohm Pines did was to identify what term should be thrown and having thrown those terms they found some justification for it which is the cancellation of certain terms which are not in phase with each other that is a point that we will discuss in the next few classes. But they threw those terms and arrived at a result which has turned out to be extremely powerful and successful in going beyond the Hartree Fock.

Having conceded that the Hartree Fock does not account for the correlations you have to go beyond the correlations. Then the RPA gives you a very powerful many-body theory to go beyond the Hartree Fock. Now that is its strength but that does not mean that it does not have limitations, of course it has limitations. Every many-body theory has limitation that is a point we often quote Brown Fock.

That if you are looking for exact solutions having no body at all already too many. So, there will not be any exact solution. The best that you can do which is good because that is where the challenge lies that you develop good approximation techniques. That is what we all struggle to do, so we use RPA productively successfully where it works at very does not work we need to go beyond the Hartree Fock beyond the RPA.

You know we do the RPA to go beyond the Hartree Fock but then you want to go beyond the RPA and address some non RPA correlations which is what you know we and some of our

colleagues Boya and others have developed this multi configuration time Dankoff and so on. So, these are various techniques to go beyond the RPA right, goodbye.