# Week 41: Hartree-Fock theory and the Homogeneous Electron gas

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Week 41, October 6-10

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**Thursday:**

1. Stability of Hartree-Fock theory, wrapping up discussions from lecture October 3, see slides from last week
2. The homogeneous electron gas in three dimensions
3. Hartree-Fock solution and ground state energy

**Friday:**

1. Calculating the ground state energy of the electron gas
2. Discussion of first midterm
3. Lecture Material: These slides and handwritten notes
4. First midterm set at
   https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/2025/FirstMidterm2025.pdf.
   Available Friday October 10, deadline October 20, at midnight

# The infinite electron gas

The electron gas is perhaps the only realistic model of a system of many interacting particles that allows for an analytical solution of the Hartree-Fock equations. Furthermore, to first order in the interaction, one can also obtain an analytical expression for the total energy and several other properties of a many-particle systems. The model gives a very good approximation to the properties of valence electrons in metals. The assumptions are

▶ System of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary.

▶ The system as a whole is neutral.

▶ We assume we have $N_e$ electrons in a cubic box of length $L$ and volume $\Omega = L^3$. This volume contains also a uniform distribution of positive charge with density $N_e e / \Omega$.

# Attractive background

The homogeneus electron gas is a system of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary and the system as a whole is neutral. Irrespective of this simplicity, this system, in both two and three-dimensions, has eluded a proper description of correlations in terms of various first principle methods, except perhaps for quantum Monte Carlo methods. In particular, the diffusion Monte Carlo calculations of Ceperley and Ceperley and Tanatar are presently still considered as the best possible benchmarks for the two- and three-dimensional electron gas.

# Two or three dimensions

The electron gas, in two or three dimensions is thus interesting as a test-bed for electron-electron correlations. The three-dimensional electron gas is particularly important as a cornerstone of the local-density approximation in density-functional theory. In the physical world, systems similar to the three-dimensional electron gas can be found in, for example, alkali metals and doped semiconductors. Two-dimensional electron fluids are observed on metal and liquid-helium surfaces, as well as at metal-oxide-semiconductor interfaces. However, the Coulomb interaction has an infinite range, and therefore long-range correlations play an essential role in the electron gas.

# Low densities

At low densities, the electrons become localized and form a lattice. This so-called Wigner crystallization is a direct consequence of the long-ranged repulsive interaction. At higher densities, the electron gas is better described as a liquid. When using, for example, Monte Carlo methods the electron gas must be approximated by a finite system. The long-range Coulomb interaction in the electron gas causes additional finite-size effects that are not present in other infinite systems like nuclear matter or neutron star matter. This poses additional challenges to many-body methods when applied to the electron gas.

# The infinite electron gas as a homogenous system

This is a homogeneous system and the one-particle wave functions are given by plane wave functions normalized to a volume $\Omega$ for a box with length $L$ (the limit $L \to \infty$ is to be taken after we have computed various expectation values)

$$\psi_{k\sigma}(r) = \frac{1}{\sqrt{\Omega}} \exp{(ikr)}\xi_\sigma$$

where k is the wave number and $\xi_\sigma$ is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \xi_{\sigma=-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

# Periodic boundary conditions

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \quad i = x, y, z \quad n_i = 0, \pm 1, \pm 2, \ldots$$

We assume first that the electrons interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |r_1 - r_2|$. The interaction is spin independent.

The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy can be written as

$$\hat{T} = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} a^{\dagger}_{k\sigma} a_{k\sigma}.$$

# Defining the Hamiltonian operator

The Hamiltonian operator is given by

$$\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|r_i - r_j|}}{|r_i - r_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \to 0$ is performed after having calculated the various integrals).

# And the positive background

Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int dr dr' \frac{n(r)n(r')e^{-\mu|r-r'|}}{|r-r'|},$$

which is the energy contribution from the positive background charge with density $n(r) = N/\Omega$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^{N} \int dr \frac{n(r)e^{-\mu|r-x_i|}}{|r-x_i|},$$

is the interaction between the electrons and the positive background.

The electron gas model allows closed form solutions for quantities like the single-particle Hartree-Fock energy. The latter quantity is given by the following expression

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{k' \leq k_F} \int dr e^{i(k'-k)r} \int dr' \frac{e^{i(k-k')r'}}{|r - r'|}$$

# First step

We will show first that

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi} \left[ 2 + \frac{k_F^2 - k^2}{kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

# Convergence factor

We introduce the convergence factor $e^{-\mu|\mathbf{r}-\mathbf{r}'|}$ in the potential and use $\sum_k \to \frac{V}{(2\pi)^3} \int dk$

We want to show that, given the Hartree-Fock equation for the electron gas

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{p \leq k_F} \int d\mathbf{r} \exp\left(i(\mathbf{p} - \mathbf{k})\mathbf{r}\right) \int d\mathbf{r}' \frac{\exp\left(i(\mathbf{k} - \mathbf{p})\mathbf{r}'\right)}{|\mathbf{r} - \mathbf{r}'|}$$

the single-particle energy can be written as

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi} \left[ 2 + \frac{k_F^2 - k^2}{k k_F} \ln\left|\frac{k + k_F}{k - k_F}\right| \right].$$

# Rewriting

We introduced the convergence factor $e^{-\mu|r-r'|}$ in the potential and use $\sum_k \to \frac{V}{(2\pi)^3} \int dk$. We can then rewrite the integral as

$$\frac{e^2}{V^2} \sum_{k' \leq k_F} \int dr \exp\left(i(k'-k)r\right) \int dr' \frac{\exp\left(i(k-p)r'\right)}{|r-r'|} = \tag{1}$$

$$\frac{e^2}{V(2\pi)^3} \int dr \int \frac{dr'}{|r-r'|} \exp\left(-ik(r-r')\right) \int dp \exp\left(ip(r-r')\right), \tag{2}$$

and introducing the abovementioned convergence factor we have

$$\lim_{\mu \to 0} \frac{e^2}{V(2\pi)^3} \int dr \int dr' \frac{\exp\left(-\mu|r-r'|\right)}{|r-r'|} \int dp \exp\left(i(p-k)(r-r')\right). \tag{3}$$

# Change of variables

With a change variables to $x = r - r'$ and $y = r'$ we rewrite the last integral as

$$\lim_{\mu \to 0} \frac{e^2}{V(2\pi)^3} \int d\mathsf{p} \int dy \int d\mathsf{x} \exp\left(i(\mathsf{p} - \mathsf{k})\mathsf{x}\right) \frac{\exp\left(-\mu|\mathsf{x}|\right)}{|\mathsf{x}|}.$$

The integration over x can be performed using spherical coordinates, resulting in (with $x = |\mathsf{x}|$)

$$\int d\mathsf{x} \exp\left(i(\mathsf{p} - \mathsf{k})\mathsf{x}\right) \frac{\exp\left(-\mu|\mathsf{x}|\right)}{|\mathsf{x}|} = \int x^2 dx d\phi d\cos\left(\theta\right) \exp\left(i(\mathsf{p} - \mathsf{k})x \cos\left(\right.\right.$$

# Further manipulations

We obtain

$$4\pi \int dx \frac{\sin(|\mathsf{p} - \mathsf{k}|)x}{|\mathsf{p} - \mathsf{k}|} \exp(-\mu x) = \frac{4\pi}{\mu^2 + |\mathsf{p} - \mathsf{k}|^2}. \qquad (4)$$

This results gives us

$$\lim_{\mu \to 0} \frac{e^2}{V(2\pi)^3} \int d\mathsf{p} \int d\mathsf{y} \frac{4\pi}{\mu^2 + |\mathsf{p} - \mathsf{k}|^2} = \lim_{\mu \to 0} \frac{e^2}{2\pi^2} \int d\mathsf{p} \frac{1}{\mu^2 + |\mathsf{p} - \mathsf{k}|^2},$$
$$(5)$$

where we have used that the integrand on the left-hand side does not depend on y and that $\int d\mathsf{y} = V$.

## Spherical coordinates

Introducing spherical coordinates we can rewrite the integral as

$$\lim_{\mu \to 0} \frac{e^2}{2\pi^2} \int d\mathbf{p} \frac{1}{\mu^2 + |\mathbf{p} - \mathbf{k}|^2} = \frac{e^2}{2\pi^2} \int d\mathbf{p} \frac{1}{|\mathbf{p} - \mathbf{k}|^2} = \quad (6)$$

$$\frac{e^2}{\pi} \int_0^{k_F} p^2 dp \int_0^\pi d\theta \cos(\theta) \frac{1}{p^2 + k^2 - 2pk\cos(\theta)}, \quad (7)$$

and with the change of variables $\cos(\theta) = u$ we have

$$\frac{e^2}{\pi} \int_0^{k_F} p^2 dp \int_0^\pi d\theta \cos(\theta) \frac{1}{p^2 + k^2 - 2pk\cos(\theta)} = \frac{e^2}{\pi} \int_0^{k_F} p^2 dp \int_{-1}^1 du \frac{1}{k}$$

which gives

$$\frac{e^2}{k\pi} \int_0^{k_F} pdp \left\{ ln(|p + k|) - ln(|p - k|) \right\}.$$

# And new varibales

Introducing new variables $x = p + k$ and $y = p - k$, we obtain after some straightforward reordering of the integral

$$\frac{e^2}{k\pi} \left[ kk_F + \frac{k_F^2 - k^2}{kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right],$$

which gives the abovementioned expression for the single-particle energy.

# Function of density

We rewrite the above result as a function of the density

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3},$$

where $n = N/V$, $N$ being the number of particles, and $r_s$ is the radius of a sphere which represents the volum per conducting electron.

## Dimensionless quantities

Introducing the dimensionless quantity $x = k/k_F$ and the function

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|,$$

we can rewrite the single-particle Hartree-Fock energy as

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F(k/k_F),$$

and dividing by the non-interacting contribution at the Fermi level,

$$\varepsilon_0^F = \frac{\hbar^2 k_F^2}{2m},$$

we have

$$\frac{\varepsilon_k^{HF}}{\varepsilon_0^F} = x^2 - \frac{e^2 m}{\hbar^2 k_F \pi} F(x) = x^2 - \frac{4}{\pi k_F a_0} F(x),$$

where $a_0 = 0.0529$ nm is the Bohr radius, setting thereby a natural length scale.

# Introducing the radius

By introducing the radius $r_s$ of a sphere whose volume is the volume occupied by each electron, we can rewrite the previous equation in terms of $r_s$ using that the electron density $n = N/V$

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3},$$

we have (with $k_F = 1.92/r_s$,

$$\frac{\varepsilon_k^{HF}}{\varepsilon_0^F} = x^2 - \frac{e^2 m}{\hbar^2 k_F \pi} F(x) = x^2 - \frac{r_s}{a_0} 0.663 F(x),$$

with $r_s \sim 2 - 6$ for most metals.

It can be convenient to use the Bohr radius $a_0 = \hbar^2/e^2 m$. For most metals we have a relation $r_s/a_0 \sim 2 - 6$.

# Plot of the energy

We can now make a plot of the free electron energy and the Hartree-Fock energy and discuss the behavior around the Fermi surface. We can also also the Hartree-Fock band width $\Delta\varepsilon^{HF}$ defined as

$$\Delta\varepsilon^{HF} = \varepsilon^{HF}_{k_F} - \varepsilon^{HF}_0.$$

# Band gap

We can now define the so-called band gap, that is the scatter between the maximal and the minimal value of the electrons in the conductance band of a metal (up to the Fermi level). For $x = 1$ and $r_s/a_0 = 4$ we have

$$\frac{\varepsilon^{HF}_{k=k_F}}{\varepsilon^F_0} = -0.326,$$

and for $x = 0$ we have

$$\frac{\varepsilon^{HF}_{k=0}}{\varepsilon^F_0} = -2.652,$$

which results in a gap at the Fermi level of

$$\Delta\varepsilon^{HF} = \frac{\varepsilon^{HF}_{k=k_F}}{\varepsilon^F_0} - \frac{\varepsilon^{HF}_{k=0}}{\varepsilon^F_0} = 2.326.$$

# What does the band gap measure?

This quantity measures the deviation from the $k = 0$ single-particle energy and the energy at the Fermi level. The general result is

$$\Delta\varepsilon^{HF} = 1 + \frac{r_s}{a_0}0.663.$$

The following python code produces a plot of the electron energy for a free electron (only kinetic energy) and for the Hartree-Fock solution. We have chosen here a ratio $r_s/a_0 = 4$ and the equations are plotted as funtions of $k/f_F$.

```python
import numpy as np
from math import log
from  matplotlib import pyplot as plt
from matplotlib import rc, rcParams
import matplotlib.units as units
import matplotlib.ticker as ticker
rc('text',usetex=True)
rc('font',**{'family':'serif','serif':['Hartree-Fock energy']})
font = {'family' : 'serif',
        'color'  : 'darkred',
        'weight' : 'normal',
        'size'   : 16,
        }

N = 100
x = np.linspace(0.0, 2.0,N)
```

# Effective mass

We will now define a quantity called the effective mass. For |k| near $k_F$, we can Taylor expand the Hartree-Fock energy as

$$\varepsilon_k^{HF} = \varepsilon_{k_F}^{HF} + \left( \frac{\partial \varepsilon_k^{HF}}{\partial k} \right)_{k_F} (k - k_F) + \dots$$

If we compare the latter with the corresponding expressiyon for the non-interacting system

$$\varepsilon_k^{(0)} = \frac{\hbar^2 k_F^2}{2m} + \frac{\hbar^2 k_F}{m} (k - k_F) + \dots,$$

we can define the so-called effective Hartree-Fock mass as

$$m_{HF}^* \equiv \hbar^2 k_F \left( \frac{\partial \varepsilon_k^{HF}}{\partial k} \right)_{k_F}^{-1}$$

Compute $m^*_{HF}$ and comment your results. Show that the level density (the number of single-electron states per unit energy) can be written as

$$n(\varepsilon) = \frac{Vk^2}{2\pi^2} \left( \frac{\partial \varepsilon}{\partial k} \right)^{-1}$$

Calculate thereafter $n(\varepsilon_F^{HF})$ and comment the results.

# Hartree-Fock ground state energy for the electron gas in three dimensions

We consider a system of electrons in infinite matter, the so-called electron gas. This is a homogeneous system and the one-particle states are given by plane wave function normalized to a volume $V$ for a box with length $L$ (the limit $L \to \infty$ is to be taken after we have computed various expectation values)

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}\mathbf{r})\xi_\sigma$$

where k is the wave number and $\xi_\sigma$ is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \xi_{\sigma=-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

# Periodic boundary conditions

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \quad i = x, y, z \quad n_i = 0, \pm 1, \pm 2, \ldots$$

We assume first that the particles interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |r_1 - r_2|$. The interaction is spin independent.

# Total Hamiltonian

The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy is given by

$$\hat{T} = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} a_{k\sigma}^{\dagger} a_{k\sigma}.$$

Find the expression for the interaction $\hat{V}$ expressed with creation and annihilation operators.

The expression for the interaction has to be written in $k$ space, even though $V$ depends only on the relative distance. It means that you need to set up the Fourier transform $\langle k_i k_j | V | k_m k_n \rangle$.

A general two-body interaction element is given by (not using anti-symmetrized matrix elements)

$$\hat{V} = \frac{1}{2} \sum_{pqrs} \langle pq \hat{v} | rs \rangle a_p^\dagger a_q^\dagger a_s a_r,$$

where $\hat{v}$ is assumed to depend only on the relative distance between two interacting particles, that is $\hat{v} = v(\vec{r}_1, \vec{r}_2) = v(|\vec{r}_1 - \vec{r}_2|) = v(r)$, with $r = |\vec{r}_1 - \vec{r}_2|$).

# With spin degrees of freedom

In our case we have, writing out explicitly the spin degrees of freedom as well

$$\hat{V} = \frac{1}{2} \sum_{\substack{\sigma_p \sigma_q \\ \sigma_r \sigma_s}} \sum_{\substack{k_p k_q \\ k_r k_s}} \langle k_p \sigma_p, k_q \sigma_2 | v | k_r \sigma_3, k_s \sigma_s \rangle a_{k_p \sigma_p}^\dagger a_{k_q \sigma_q}^\dagger a_{k_s \sigma_s} a_{k_r \sigma_r}. \quad (8)$$

# Plane waves

Inserting plane waves as eigenstates we can rewrite the matrix element as

$$\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle = \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int \int \exp -i(k_p \cdot r_p) \exp -i(k_q \cdot$$

where we have used the orthogonality properties of the spin functions. We change now the variables of integration by defining $r = r_p - r_q$, which gives $r_p = r + r_q$ and $d^3r = d^3r_p$.

The limits are not changed since they are from $-\infty$ to $\infty$ for all integrals. This results in

$$\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle = \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int \exp i (k_s - k_q) \cdot r_q \int v(r) \exp$$

$$= \frac{1}{V^2} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \int v(r) \exp i \left[ (k_r - k_p) \cdot r \right] \int \exp$$

# Recognizing integral

We recognize the integral over $r_q$ as a $\delta$-function, resulting in

$$\langle k_p \sigma_p, k_q \sigma_q | \hat{v} | k_r \sigma_r, k_s \sigma_s \rangle = \frac{1}{V} \delta_{\sigma_p \sigma_r} \delta_{\sigma_q \sigma_s} \delta_{(k_p + k_q),(k_r + k_s)} \int v(r) \exp i \left[ (k_r - \right.$$

For this equation to be different from zero, we must have conservation of momenta, we need to satisfy $k_p + k_q = k_r + k_s$.

# Conservation of momentum

We can use the conservation of momenta to remove one of the summation variables resulting in

$$\hat{V} = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{k_p k_q k_r} \left[ \int v(r) \exp i\left[(k_r - k_p) \cdot r\right] d^3 r \right] a^\dagger_{k_p \sigma} a^\dagger_{k_q \sigma'} a_{k_p + k_q - k_r, \sigma'} a_{k_r \sigma}$$

which can be rewritten as

$$\hat{V} = \frac{1}{2V} \sum_{\sigma\sigma'} \sum_{kpq} \left[ \int v(r) \exp -i(q \cdot r) dr \right] a^\dagger_{k+q,\sigma} a^\dagger_{p-q,\sigma'} a_{p\sigma'} a_{k\sigma},$$

(9)

# Some definitions

In the last equation we defined the quantities $p = k_p + k_q - k_r$, $k = k_r$ og $q = k_p - k_r$.

# Reference energy

Let us now compute the expectation value of the reference energy using the expressions for the kinetic energy operator and the interaction. We need to compute $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle$, where $|\Phi_0\rangle$ is our reference Slater determinant, constructed from filling all single-particle states up to the Fermi level. Let us start with the kinetic energy first

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \langle \Phi_0 | \left( \sum_{\mathbf{p}\sigma} \frac{\hbar^2 p^2}{2m} a^{\dagger}_{\mathbf{p}\sigma} a_{\mathbf{p}\sigma} \right) | \Phi_0 \rangle = \sum_{\mathbf{p}\sigma} \frac{\hbar^2 p^2}{2m} \langle \Phi_0 | a^{\dagger}_{\mathbf{p}\sigma} a_{\mathbf{p}\sigma} | \Phi_0 \rangle.$$

# Kinetic energy

From the possible contractions using Wick's theorem, it is straightforward to convince oneself that the expression for the kinetic energy becomes

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \sum_{i \leq F} \frac{\hbar^2 k_i^2}{m} = \frac{V}{(2\pi)^3} \frac{\hbar^2}{m} \int_0^{k_F} k^2 dk.$$

The sum of the spin degrees of freedom results in a factor of two only if we deal with identical spin $1/2$ fermions. Changing to spherical coordinates, the integral over the momenta $k$ results in the final expression

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \frac{V}{(2\pi)^3} \left( 4\pi \int_0^{k_F} k^4 dk \right) = \frac{4\pi V}{(2\pi)^3} \frac{1}{5} k_F^5 = \frac{4\pi V}{5(2\pi)^3} k_F^5 = \frac{\hbar^2 V}{10\pi^2 m}$$

# Density of states

The density of states in momentum space is given by $2V/(2\pi)^3$, where we have included the degeneracy due to the spin degrees of freedom. The volume is given by $4\pi k_F^3/3$, and the number of particles becomes

$$N = \frac{2V}{(2\pi)^3}\frac{4}{3}\pi k_F^3 = \frac{V}{3\pi^2}k_F^3 \quad \Rightarrow \quad k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}.$$

This gives us

$$\langle\Phi_0|\hat{T}|\Phi_0\rangle = \frac{\hbar^2 V}{10\pi^2 m}\left(\frac{3\pi^2 N}{V}\right)^{5/3} = \frac{\hbar^2(3\pi^2)^{5/3}N}{10\pi^2 m}\rho^{2/3}, \qquad (10)$$

## Potential energy

We are now ready to calculate the expectation value of the potential energy

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle = \langle\Phi_0|\left(\frac{1}{2V}\sum_{\sigma\sigma'}\sum_{\mathbf{kpq}}\left[\int v(r)\exp-i(\mathbf{q}\cdot\mathbf{r})dr\right]a^\dagger_{\mathbf{k+q},\sigma}a^\dagger_{\mathbf{p-q},\sigma'}a_{\mathbf{p}\sigma}\right.$$

$$= \frac{1}{2V}\sum_{\sigma\sigma'}\sum_{\mathbf{kpq}}\left[\int v(r)\exp-i(\mathbf{q}\cdot\mathbf{r})dr\right]\langle\Phi_0|a^\dagger_{\mathbf{k+q},\sigma}a^\dagger_{\mathbf{p-q},\sigma'}a_{\mathbf{p}\sigma'}a$$

# Non-zero term

The only contractions which result in non-zero results are those that involve states below the Fermi level, that is $k \leq k_F$, $p \leq k_F$, $|p - q| < k_F$ and $|k + q| \leq k_F$. Due to momentum conservation we must also have $k + q = p$, $p - q = k$ and $\sigma = \sigma'$ or $k + q = k$ and $p - q = p$. Summarizing, we must have

$$k + q = p \quad \text{and} \quad \sigma = \sigma', \qquad \text{or} \qquad q = 0.$$

# Direct and exchange terms

We obtain then

$$\langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \frac{1}{2V} \left( \sum_{\sigma\sigma'} \sum_{qp \leq F} \left[ \int v(r) dr \right] - \sum_{\sigma} \sum_{qp \leq F} \left[ \int v(r) \exp{-i(q \cdot r)} \right. \right.$$

The first term is the so-called direct term while the second term is the exchange term.

# Potential energy

We can rewrite this equation as (and this applies to any potential which depends only on the relative distance between particles)

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle = \frac{1}{2V}\left(N^2\left[\int v(r)dr\right] - N\sum_q\left[\int v(r)\exp-i(q\cdot r)dr\right]\right),$$

(11)

where we have used the fact that a sum like $\sum_\sigma\sum_k$ equals the number of particles. Using the fact that the density is given by $\rho = N/V$, with $V$ being our volume, we can rewrite the last equation as

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle = \frac{1}{2}\left(\rho N\left[\int v(r)dr\right] - \rho\sum_q\left[\int v(r)\exp-i(q\cdot r)dr\right]\right).$$

# Interaction part

For the electron gas the interaction part of the Hamiltonian operator is given by

$$\hat{H}_I = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \to 0$ is performed after having calculated the various integrals).

# Positive background

Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int dr dr' \frac{n(r)n(r')e^{-\mu|r-r'|}}{|r-r'|},$$

which is the energy contribution from the positive background charge with density $n(r) = N/V$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^{N} \int dr \frac{n(r)e^{-\mu|r-x_i|}}{|r-x_i|},$$

is the interaction between the electrons and the positive background.

# Positive charge contribution

We can show that

$$\hat{H}_b = \frac{e^2}{2} \frac{N^2}{V} \frac{4\pi}{\mu^2},$$

and

$$\hat{H}_{el-b} = -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}.$$

## Thermodynamic limit

For the electron gas and a Coulomb interaction, these two terms are cancelled (in the thermodynamic limit) by the contribution from the direct term arising from the repulsive electron-electron interaction. What remains then when computing the reference energy is only the kinetic energy contribution and the contribution from the exchange term. For other interactions, like nuclear forces with a short range part and no infinite range, we need to compute both the direct term and the exchange term.

We can show that the final Hamiltonian can be written as

$$H = H_0 + H_I,$$

with

$$H_0 = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} a_{k\sigma}^\dagger a_{k\sigma},$$

and

$$H_I = \frac{e^2}{2V} \sum_{\sigma_1\sigma_2 q\neq 0,k,p} \frac{4\pi}{q^2} a_{k+q,\sigma_1}^\dagger a_{p-q,\sigma_2}^\dagger a_{p\sigma_2} a_{k\sigma_1}.$$

Calculate $E_0/N = \langle \Phi_0 | H | \Phi_0 \rangle / N$ for for this system to first order in

Plot your results. Why is this system stable? Calculate thermodynamical quantities like the pressure, given by

$$P = - \left( \frac{\partial E}{\partial V} \right)_N,$$

and the bulk modulus

$$B = -V \left( \frac{\partial P}{\partial V} \right)_N,$$

and comment your results.

# Density functional theory

Hohenberg and Kohn proved that the total energy of a system including that of the many-body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. In Hartree-Fock theory one works with large basis sets. This poses a problem for large systems. An alternative to the HF methods is DFT. DFT takes into account electron correlations but is less demanding computationally than full scale diagonalization or Monte Carlo methods.

The electronic energy $E$ is said to be a functional of the electronic density, $E[\rho]$, in the sense that for a given function $\rho(r)$, there is a single corresponding energy. The Hohenberg-Kohn theorem confirms that such a functional exists, but does not tell us the form of the functional. As shown by Kohn and Sham, the exact ground-state energy $E$ of an $N$-electron system can be written as

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