Interaction energy between electrons: Hartree-Fock approximation

We discuss here the energy of N interacting electrons within the so-called Hartree-Fock approximation, which is an essential first step beyond the free electron model.

1 Wick's theorem

Consider a set of operators, A, B, C, ... which are all either creation or annihilation operators. We introduce the two following definitions:

- The *contraction* $\langle AB \rangle$ of a pair of such operators is the vacuum (ground state) expectation value,

$$\langle AB \rangle = \langle 0|AB|0 \rangle . \tag{1}$$

- The *normal order* of a product $ABCD...$ consists in rewriting this product such that all creation operators have been moved to the left, and the annihilation operators to the right. It is noted $: ABCD... :$. In the case of fermionic operators, re-ordering goes with multiplying by the sign of the permutation needed to produce the normal order. For example

$$: ba^\dagger : \;\; = \;\; -a^\dagger b \tag{2}$$
$$: a^\dagger b c d^\dagger : \;\; = \;\; a^\dagger d^\dagger bc \tag{3}$$
$$= \;\; -a^\dagger d^\dagger cb \tag{4}$$

Wick's theorem states that any product of creation and annihilation operators is equal to its normal-ordered product, plus the sum of normal-ordered products after taking all single contractions among operator pairs, plus all double contractions, etc., plus all full contractions. Each term of this sum has the sign of the parity of the permutation, which allowed rearranging the terms. We illustrate this complicated statement with a few examples below.

1.1

For only two operators, Wick's theorem states that

$$AB = \, : AB : + \langle AB \rangle. \tag{5}$$

Show that this is true.

1.2

For a string of 4 fermionic operators, Wick's theorem writes

$$
\begin{aligned}
ABCD \;\; = \;\; & : ABCD : \\
& + \;\; : AB : \langle CD \rangle - : AC : \langle BD \rangle + : BC : \langle AD \rangle \\
& + \;\; : AD : \langle BC \rangle - : BD : \langle AC \rangle + : CD : \langle AB \rangle \\
& + \;\; \langle AB \rangle \langle CD \rangle - \langle AC \rangle \langle BD \rangle + \langle AD \rangle \langle BC \rangle.
\end{aligned} \tag{6}
$$

Discuss the conditions for the vacuum expectation value of $ABCD$ to be non zero, and verify that there is no contradiction in the result above.

2 Hartree-Fock approximation

We consider an ensemble of N electrons in a volume L^3, with dispersion relation $\epsilon_{\mathbf{k}} = (\hbar\mathbf{k})^2/2m$. The electrons are subject to a periodic potential provided by the lattice ions, with density n_i and a charge $+e$. Eventually, the electrons repel each other, via Coulomb interaction. Coulomb interaction is given by $V(\mathbf{r}) = e^2/(4\pi\epsilon_0 \mid \mathbf{r} \mid)$, with a sign depending on whether the charges interacting are of opposite or same sign. Recall that in the thermodynamic limit $L^3 \to \infty$ and for $q \neq 0$, one can write $\tilde{V}(\mathbf{q}) = e^2/(\epsilon_0 q^2)$.

2.1

Write the three terms of the second quantized Hamiltonian of the system, $H = T + V_{\text{ext}} + V_{\text{int}}$, in terms of fermionic creation and annihilation operators.

2.2

The *jellium model* consists in taking a uniform ionic density $n_i = \text{const}$. Discuss when this could be a good approximation. If the system is further charge neutral, write a relation between n_i and N. Show that V_{ext} evaluated over the quantum state of N fermions is equal to $-\tilde{V}(\mathbf{q} = \mathbf{0}) N^2/L^3$.

2.3

Show that this energy exactly cancels out (within a factor of 2) with the $\mathbf{q} = \mathbf{0}$ part of V_{int}. Comment.

2.4

The next simplifying assumption, which is the starting point of the Hartree-Fock approximation, is that the ground state of the system is given by the filled Fermi sea of single-particle states

$$|\Psi_0\rangle = \prod_{\substack{\mathbf{k},|\mathbf{k}|<k_F \\ \sigma=\uparrow,\downarrow}} a_{\mathbf{k}\sigma}^\dagger|0\rangle. \tag{7}$$

Assuming a parabolic dispersion relation and using $k_F = (3\pi^2 N)^{1/3}/L$, evaluate the expectation value of the kinetic energy term in $|\Psi_0\rangle$ in the thermodynamic limit, where $\frac{1}{V}\sum_{\mathbf{k}}$ can be replaced by $\int d^3k/(2\pi)^3$.

2.5

Calculate the expectation value of the product of creation and annihilation operators of the interaction term of the Hamiltonian in $|\Psi_0\rangle$.

2.6

Evaluate the interaction term in the thermodynamic limit. We admit that

$$\int_{k<k_F} d^3k \int_{k'<k_F} d^3k' \frac{1}{(\mathbf{k}-\mathbf{k}')^2} = 4\pi^2 k_F^4$$

2.7

One can parametrise the total energy in terms of the dimensionless parameter r_s defined by

$$\frac{L^3}{N} = \frac{4\pi}{3}(r_s a_0)^3, \tag{8}$$

where $a_0 = 4\pi\varepsilon_0\hbar^2/(me^2)$ is the Bohr radius. Introducing the Rydberg $\text{Ry} = e^2/(8\pi\varepsilon_0 a_0)$ as characteristic energy scale, write the total Hartree-Fock energy per particle as a function of Ry and r_s.