HomeWork 5 : Hartree-Fock equations for atoms

In this problem we consider atoms (possibly ionized) with N electrons and the nuclear charge number Z. The nucleus is assumed to be fixed.

1 Show that the Hamiltonian describing the system has the following second-quantized form :

$$H = \sum_{i,j} c_i^\dagger \langle i|T|j\rangle c_j + \sum_{i,j} c_i^\dagger \langle i|U|j\rangle c_j + \frac{1}{2} \sum_{i,j,k,m} \langle i,j|V|k,m\rangle c_i^\dagger c_j^\dagger c_m c_k$$

with T, U and V to be specified.

2 We write the state of N electrons as usual

$$|\psi\rangle = c_1^\dagger ... c_N^\dagger |0\rangle.$$

Here $|0\rangle$ is the vacuum state containing no electrons and $c_i^\dagger$ is the creation operator for the state $|i\rangle \equiv |\phi_i, m_{s_i}\rangle$, $m_{s_i} = \pm 1/2$. The $\phi_i(x)$ are single-particle wave functions which are yet to be determined. To achieve this goal, our scheme will be to apply a variational method.

Calculate first the single particle contributions of the energy of the state $|\psi\rangle$ and show that the two-particle contributions are found as :

$$\begin{aligned}
\langle\psi|c_i^\dagger c_j^\dagger c_m c_k|\psi\rangle &= \langle\psi|(\delta_{im}\delta_{jk} c_m^\dagger c_k^\dagger + \delta_{ik}\delta_{jm} c_k^\dagger c_m^\dagger) c_m c_k|\psi\rangle \\
&= (\delta_{ik}\delta_{jm} - \delta_{im}\delta_{jk})\Theta(m,k \in 1,...,N). \qquad (1)
\end{aligned}$$

The first factor implies that the expectation value vanishes whenever the creation and annihilation operators fail to compensate one another. The second implies that both operators c_m and c_k must be present in the set $c_1 \cdots c_N$ occurring in the state $|\psi\rangle$, otherwise their application to the right on the vacuum would give 0.

Therefore, write the total energy as :

$$\begin{aligned}
E = \langle\psi|H|\psi\rangle &= \frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d^3x |\nabla\phi_i|^2 + \sum_{i=1}^{N}\int d^3x U(x)|\phi_i(x)|^2 \\
&+ \frac{1}{2}\sum_{i,j=1}^{N}\int d^3x d^3x' V(x-x')\Big\{|\phi_i(x)|^2|\phi_j(x')|^2 \\
&- \delta_{m_{s_i} m_{s_j}} \phi_i^*(x)\phi_j^*(x')\phi_i(x')\phi_j(x)\Big\} \qquad (2)
\end{aligned}$$

3 The single-particle wave functions are now determined by minimizing the energy (variational principle). Note that we also need to impose a normalization constraint for the ϕ_i, namely $\int |\phi_i|^2 d^3x = 1$. This leads to the minimization of the following functional :

$$L = \langle\psi|H|\psi\rangle - \sum_{i=1}^{N} \epsilon_i \left(\int d^3x |\phi_i(x)|^2 - 1\right)$$

with respect to $\phi_i(x)$ and $\phi_i^*(x)$ (in L, the $\{\epsilon_i\}$ are a set of Lagrange multipliers).

Taking the variational derivative with respect to ϕ_i^*, derive the so-called Hartree-Fock equations :

$$\begin{aligned}(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r})\phi_i(x) \quad &+ \quad \sum_{j=1}^{N}\int d^3x' \frac{e^2}{|x-x'|}|\phi_j(x')|^2\phi_i(x) \\ &- \quad \sum_{j=1}^{N}\delta_{m_{s_i}m_{s_j}}\int d^3x' \frac{e^2}{|x-x'|}\phi_j^*(x')\phi_i(x').\phi_j(x) = \epsilon_i\phi_i(x).\end{aligned}$$

N.B. : use this definition of the functional derivative :

$$\frac{\delta\phi_i(x')}{\delta\phi_j(x)} = \delta_{ij}\delta(x-x')$$

Comment on the physical meaning of the interactions term.

4 Application to the electron gas.
a) Show that the Hartree-Fock equations are solved by plane waves.
b) Replace the nuclei by a uniform positive background charge of the same total charge and show that the Hartree term is cancelled by the Coulomb attraction of the positive background and the electrons.
The electronic energy levels are then given by

$$\epsilon(k) = \frac{(\hbar k)^2}{2m} - \frac{1}{V}\sum_q \frac{4\pi e^2}{|k-q|^2}$$

If you remember Homework 4, this can also be written as

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

with

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