HOMEWORK 5

LDA of DFT for the Calculation of the Ground State of the Helium Atom

Due: Monday March 2nd, 4:30 p.m.

In this assignment you will need to write a code (by modifying the Hartree-Fock code in HW3) to calculate the ground state of a helium atom using the local density (LDA) approximation to the density functional theory (DFT).

The Kohn-Sham wave-function for He satisfies the equation

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(r) + v_h(r) + v_{xc}(r)\right)\phi(r) = \varepsilon\phi(r)$$

where $v_{ext}(r) = -\frac{2}{r}$ is the external potential due to the nucleus, $v_h(r) = \int \frac{n(r')}{|r-r'|} d^3r'$ is the Hartree potential and $v_{xc}(r)$ is the exchange-correlation potential, which depends on the approximation. In this homework, we will use LDA (see lecture notes) in which the exchange-correlation energy is written as:

$$E_{xc}^{LDA} = \int n(r)\left[\varepsilon_x(n(r)) + \varepsilon_c(n(r))\right] d^3r$$

where the exchange energy density ε_x^{LDA} and the correlation energy density ε_c^{LDA} (Perdew-Zunger parametrization) are given in the introduction to DFT lecture notes on the course web site in terms of the Wigner-Seitz radius r_s. To obtain the potential, notice that $v_{xc} = \frac{\delta E_{xc}^{LDA}}{\delta n} = \frac{\partial(n\varepsilon_{xc})}{\partial n}$.

As with the Hartree-Fock method, we will use here a Gaussian basis:

$$\phi = \sum_i C_i \chi_i(r),\ \chi_i(r) = e^{-\alpha_i r^2}$$

in which the Kohn-Sham equations are written in a matrix form as follows:

$$\sum_j \left(h^{ij} + V_h^{ij} + V_{xc}^{ij}\right) C_j = \varepsilon \sum_j S^{ij} C_j$$

where h^{ij} and S^{ij} are the same as in the Hartree-Fock implementation, and V_h^{ij} and V_{xc}^{ij} are the matrix elements of the Hartree and exchange-correlation potentials, respectively.

Modify the HF codes to implement these calculations and compute the ground state of the He atom. The evaluation of the matrix elements V_h^{ij} can be done using the analytical expression $V_h^{ij} = 2\sum_{kl} C_k C_l Q_{ijkl}$ which should be familiar from your HF program or using numerical integration (quadrature) to approximate $V_h^{ij} = \int \chi_i^*(r) v_h(r) \chi_j(r) d^3 r$, where the Coulomb potential is the solution of the Poisson equation $\nabla^2 v_h(r) = -4\pi n(r)$. Note that the cost of the first approximation is ~O(N^4), whereas the second scales as ~O(N^2), where N is the number of the Gaussian basis functions.

To compute V_{xc}^{ij}, transform the integral of the form $V_{xc}^{ij} = \int_0^\infty 4\pi r^2 F(r) dr$ to a domain where you can do numerical integration, e.g. to $V_{xc}^{ij} = \int_{-1}^{+1} f(x)\sqrt{1-x^2}\, dx$, using $r = \frac{\sqrt{1+x}}{\sqrt{1-x}}$. For this case, you can perform the integration in *x* using the Gauss-Chebyshev quadrature of the 2nd kind (see A First Course in Numerical Analysis, R. Rabinowitz, pp. 111):

$\int_{-1}^{+1} f(x)\sqrt{1-x^2}\, dx = \sum_{j=1}^{n} f(a_j) H_j$, where $H_j = \frac{\pi}{n+1} \sin^2 \frac{j\pi}{n+1}$, and

$a_j = \cos \frac{j\pi}{n+1},\ j = 1, 2, \ldots, n.$