Computational Physics - Exercise 4

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Alkali metal clusters by DFT

An interesting system to be studied by mean field techniques is a sphere of uniform positive charge (jellium) containing N electrons. This is a reasonable model for alkali metal clusters that are produced in jets of vaporized metal. The mass spectrum shows clear signs of shell effects, that can be well reproduced by this model. We will consider N_e electrons moving in a spherical distribution of charge with density ρ_B and with radius R_c, such that $\frac{4}{3}\pi R_c^3 \rho_B = N_e$. ρ_B is in turn parametrized by the Wigner-Seitz radius r_s, such that $\frac{4}{3}\pi r_S^3 \rho_B = 1$. The potential generated by the positive charge on a test electron takes the form[1]:

$$V_{ext}(r) = 2\pi\rho_b \times \begin{cases} \frac{1}{3}r^2 - R_c^2 & \text{if } r \leq R_c \\ -\frac{2}{3}\frac{r_c^3}{r} & \text{if } r > R_c \end{cases}$$

We want to use DFT to find the energy of some closed shell jellium spheres for realistic values of the density. As you might remember, for the many Fermion case we the energy density functional employed in a DFT calculation has the form:

$$E[\rho] = \sum_{i_{occ}} \int d\vec{r}\phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\right) \nabla_i^2 \phi(\vec{r}) + \int d\vec{R}\rho(\vec{r}) v_{ext}(\vec{r}) +$$

$$\frac{1}{2}\int d\vec{r}\int d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_{xc}[\rho(\vec{r})]$$

[1] We use throughout the exercise atomic units, defined by $e = m_e = \hbar = 1$. Energies are given in Hartree, and distances in Bohr radii.

where E_{xc} is the exchange-correlation potential. The exchange potential, in the Local Density Approximation (LDA) reads:

$$\int d\vec{r}\rho(\vec{r})\epsilon_{xc}(\vec{r}).$$

The exchange energy density is given by:

$$\epsilon_{xc}(r) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho(r)^{\frac{1}{3}}.$$

As correlation energy you will use the so-called Perdew-Zunger[2] parametrization (here in the form valid only for $r_s \geq 1$):

$$\epsilon_c(r_s) = \frac{\gamma}{1+\beta_1\sqrt{r_s}+\beta_2 r_s}.$$

The parameters, valid for an unpolarized system (i.e. $N^{\uparrow} = N^{\downarrow}$) are taken from the Quantum Monte Carlo calculations of Ortiz and Ballone[3], and read $\gamma = -0.103756$H, $\beta_1 = 0.56371$, $\beta_2 = 0.27358$. Remember that r_s is given in units of a_0.

Questions

1. Consider clusters of Na ($r_s/a_0 = 3.93$) or K ($r_s/a_0 = 4.86$). Consider an *independent electron model* and numerically construct the densities in the external potential V_{eff} for the first four closed shell systems [20 points]

2. Work out explicitly the expression of the direct and exchange Coulomb, and correlation potentials to be inserted in the Kohn-Sham equations [10 points]

3. Write a flowchart for the self consistent code solving the KS equations.[10 points]

4. Reusing the code written for the GP equation, solve the KS equation for the clusters with $N = 8$, $N = 20$ and $N = 40$. Pay attention to the degeneracy of the energy levels when constructing the density! [40 points]

5. Following the paper by N. Van Giai[4] available on Moodle, where you can find some useful data to compare your results to, it is possible to

[2] j.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981)
[3] G. Ortiz and P. Ballone, Phys. Rev. B 30, 1391 (1994)
[4] N. Van Giai, Progress of Theoretical Physics Supplement No. 124, (1996)

estimate the polarizability of a metal cluster from the electron spillout defined as:

$$\delta N = \int_{R_c}^{\infty} \rho(r) d\vec{r}.$$

Produce a table of the clusters polarizability $\alpha(N)$, computing:

$$\alpha(N) = R_c^3 \left(1 + \frac{\delta N}{N}\right)$$

for the various clusters you have worked out. Notice that in the paper a different parametrization of ϵ_c has been used. Discuss the possible differences by comparing the correlation functionals used. [20 points]

computed a) directly from the functional and b) from the eigenvalue μ (remember, μ **is not** the energy!!!).Try to find solutions for $Na = 0.01, 0.1, 1, 10, 100$ and compare the resulting density to the non interacting particle case. Discuss how the convergence speed varies with the coupling parameters (e.g. by looking at value of α necessary to make the procedure converge). [25 points]

4. Solve the GP equation for $Na = -0.01, 0, 1, 1...$ How far can you push Na? what happens if Na becomes too large? Try to give a physical explanation of your result.[10 points]

5. Consider now clusters of Na ($r_s/a_0 = 3.93$) or K ($r_s/a_0 = 4.86$). Derive the Kohn-Sham equations from the energy density functional given above. Consider clusters with N=8 and N=20, and write a flowchart for the code solving the KS equations. [10 points]

6. Reusing the code written for the GP equation, solve the KS equation for the two clusters named above (the first with $N = 8$ containing only 1s and 1p orbitals, the second with $N = 20$ containing 1s,1p,1d, and 2s orbitals). Pay attention to the degenarcy of the energy levels when constructing the density! [40 points]

And remember...

The combined results of several people working together is often much more effective than could be that of an individual scientist working alone.(John Bardeen)