LAB. EXERCISE 1
DOUBLE-ZETA SCF-LCAO CALCULATION OF THE GROUND STATE OF THE HELIUM ATOM

Adapted from: *A Simple Illustration of the SCF-LCAO-MO Method*, by R. L. Snow and J. L. Bills, Journal of Chemical Education, 52, 506 (1975).

1) Write down the single determinant singlet ground-state wavefunction (including spin) of the helium atom based on a doubly occupied orbital $\phi(\mathbf{r})$. Note that $\mathbf{r}$ (written in bold) is the vector position of the electron in the spherical coordinate system, of components $\{r, \theta, \varphi\}$.

2) Using the SCF-LCAO method, expand the atomic orbital $\phi(\mathbf{r})$ in two basis functions (*i.e.* a *double-zeta* basis set) 1s and 1s' having the analytical forms:

$$1s(\mathbf{r}) = \frac{\alpha_1^{3/2}}{\pi^{1/2}}\exp(-\alpha_1 r) \text{ and } 1s(\mathbf{r}) = \frac{\alpha_2^{3/2}}{\pi^{1/2}}\exp(-\alpha_2 r)$$

Plot the radial functions 1s and 1s' with $\alpha_1 = 1.45$ and $\alpha_2 = 2.90$. Note that the 1s orbital is more diffuse than the 1s'.

3) Show that the basis functions 1s and 1s' are normalized. Note the difference between dr and the volume element $d\mathbf{r} = r^2 \sin\theta dr d\theta d\varphi$. In the case of spherical orbitals, $d\mathbf{r}$ can be replaced by $4\pi r^2 dr$.

Useful expression:

$$\int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}}$$

4) Show that the solution of the HF equation in the basis of the two functions 1s and 1s' is equivalent to the solution of the following equations:

$$c\left(F_{ss} - \varepsilon\right) + c'\left(F_{ss'} - \varepsilon S\right) = 0 \qquad (1)$$

$$c\left(F_{ss'} - \varepsilon S\right) + c'\left(F_{s's'} - \varepsilon\right) = 0 \qquad (2)$$

where F_{ss}, $F_{s's'}$ and $F_{ss'}$ are the elements of the Fock matrix,

$$F_{ss} = \int 1s(\mathbf{r})\hat{F}1s(\mathbf{r})d\mathbf{r}$$

$$F_{s's'} = \int 1s'(\mathbf{r})\hat{F}1s'(\mathbf{r})d\mathbf{r}$$

$$F_{ss'} = \int 1s(\mathbf{r})\hat{F}1s'(\mathbf{r})d\mathbf{r}$$

and S the overlap integral:

$$S = \int 1s(\mathbf{r})1s'(\mathbf{r})d\mathbf{r}$$

5) Write the above system of equations in a matrix from.

6) Write down the explicit form of the Fock operator for the ground state of the helium atom as a sum of kinetic, nucleus-electron and repulsion contributions. Write the LCAO expansion of the repulsion operator.

7) Write the LCAO expansion of the Fock matrix elements developed in terms of the kinetic, nucleus-electron and repulsion contributions.

8) Prove that:

$$S = \int 1s(\mathbf{r})1s'(\mathbf{r})d\mathbf{r} = \left(1-\tau^2\right)^{3/2}$$

$$\int 1s(\mathbf{r})\left|\frac{1}{r}\right|1s(\mathbf{r})d\mathbf{r} = \alpha_1$$

$$\int 1s(\mathbf{r})\left|\frac{1}{r}\right|1s'(\mathbf{r})d\mathbf{r} = \frac{1}{2}\left(\alpha_1+\alpha_2\right)\left(1-\tau^2\right)^{3/2}$$

where $\tau = \dfrac{\alpha_1-\alpha_2}{\alpha_1+\alpha_2}$

Useful expression:

$$ab = \frac{1}{4}\left[(a+b)^2-(a-b)^2\right]$$

9) The analytical forms of the full set of one- and two-electron integrals are given in the article of Snow and Bills. Using $\alpha_1 = 1.45$ and $\alpha_2 = 2.90$, compute the numerical values of the overlap integrals and one- and two-electron integrals using 5 digits.

10) Start the iterative process of solving the SCF equation by putting the trial solution:

c = 1
c' = 0

a) Compute the Fock matrix elements F_{ss}, $F_{s's'}$ and $F_{ss'}$.

b) Solve the secular system of equations. Find the two eigenvalues ε of the secular system and select the more stable (the more negative).

c) Find the relative value of c and c', and compute their absolute value by combining their relative values with the normalization condition.

d) Repeat the steps a, b and c with the new set of coefficients c and c'.

e) Iterate the previous steps until the set of coefficients do not vary from one iteration to another (requested threshold = 10^{-5}).

11) Write the expression of the total energy E as a function of the previously defined kinetic, nucleus-electron and repulsion integrals. Compute the total energy value at each iteration.

12) Write an alternative expression of the total energy as a function of the energy of the occupied orbital. Check the consistency of the total energy with the value computed in 11), and compare to the experimental value (–2.904 a.u.).

13) From the values of the ground-state energy of the helium atom and of the positive ion He^+, compute the first ionization energy of He. Compare your results to the experimental value and to that obtained using the Koopman's theorem (opposite of the doubly occupied orbital energy). Give an interpretation to the fact that the latter is larger than that obtained from the energies difference.

14) A more precise energy minimum can be obtained by varying the α_1 and α_2 exponents. Compute the total energy E for different (α_1, α_2) sets and compare your optimal α_1 and α_2 values to those obtained by Roetti and Clementi [*J. Chem. Phys.* **60**, 4725 (1974)].

15) The density matrix **D** for the ground state of the helium atom is defined as follows:

$$\mathbf{D} = 2\mathbf{R} = 2\begin{pmatrix} R_{ss} & R_{ss'} \\ R_{ss'} & R_{s's'} \end{pmatrix} = 2\begin{pmatrix} c^2 & cc' \\ cc' & c'^2 \end{pmatrix}$$

Compute the **R** matrix and verify that the total number of electrons N is equal to:

$N = \sum_p \sum_q D_{pq} S_{pq}$, where S_{pq} are the elements of the overlap matrix.

16) Show that the density matrix **R** is idempotent. For non-orthogonal basis sets, the idempotency property is expressed as: **RSR** = **R**.

17) Show that at convergence, the density and Fock matrices commute. For non-orthogonal basis sets, the commutation relation is expressed as: **FRS** = **SRF**. Conclude about this new stationarity condition.