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

PART 1: DOUBLE-ZETA SCF-LCAO CALCULATION

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 **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' using the optimal α_1 and α_2 values obtained by Roetti and Clementi [*J. Chem. Phys*. **60**, 4725 (1974)] $\alpha_1 = 1.45363$ and $\alpha_2 = 2.91093$. Note that the 1s orbital is more diffuse than the 1s'.

3) Using $\alpha_1 = 1.45363$ and $\alpha_2 = 2.91093$, and the trial solution:

$$c = 1$$
$$c' = 0$$

use the `helium` program compute the total energy value at each iteration.

4) Compare to the converged value to the experimental value (–2.904 a.u.).

5) 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 the HF result 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.

PART 2: EFFECT OF THE NUMBER OF BASIS FUNCTIONS

6) By using $\alpha_n = 1.6 \times \alpha_{n-1}$ and $\alpha_1 = 1$, compute the occupied orbital energy ε and the total energy E by varying the number of basis functions from 1 to 10.

7) How many basis functions are necessary to reach the HF limit? Compare with the results obtained using the optimal double-zeta basis set and comment on the choice of basis function exponents.