LAB. EXERCISE
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, θ, φ}.

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\left[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right]$$

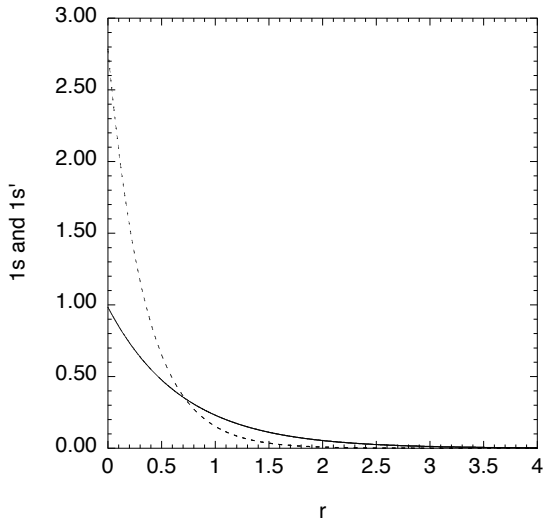
The $\left[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right]$ spin function characterizes a singlet state.

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'.

$$\phi(\mathbf{r}) = c1s(\mathbf{r}) + c'1s'(\mathbf{r})$$



The 1s (plain line) and 1s' (dotted line) functions.

At long distance, 1s is larger than 1s', *i.e.* 1s is spatially more delocalized than 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. Also note the evolution of the coefficients c and c' and of the orbital energies with iterations.

```
Evolution of E with successive iterations
  Total  energy E =   -2.79296107310000
  Total  energy E =   -2.85913598083194
  Total  energy E =   -2.86157585139785
  Total  energy E =   -2.86166892173885
  Total  energy E =   -2.86167245796035
  Total  energy E =   -2.86167259243591
  Total  energy E =   -2.86167259754891
  Total  energy E =   -2.86167259774332
```

Note that in virtue of the variational principle, the convergence behavior of E is monotonic.

```
Evolution of c and c' with successive iterations
iter  0 C =    1.000000    0.000000
iter  1 C =    0.812979    0.215033
iter  2 C =    0.849771    0.173967
iter  3 C =    0.842617    0.181997
iter  4 C =    0.844012    0.180432
iter  5 C =    0.843740    0.180737
iter  6 C =    0.843793    0.180677
iter  7 C =    0.843783    0.180689

Evolution of orbital energies with iterations
iter  0 Epsilon   -0.982989    1.970176
iter  1 Epsilon   -0.905618    2.074162
iter  2 Epsilon   -0.920350    2.053492
iter  3 Epsilon   -0.917465    2.057506
iter  4 Epsilon   -0.918027    2.056723
iter  5 Epsilon   -0.917917    2.056876
iter  6 Epsilon   -0.917939    2.056846
iter  7 Epsilon   -0.917935    2.056852
```

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

The computed value is larger than the experimental value.

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.

The energy of the He^+ ion can be obtained from the energy expression for hydrogenoids:

$$E\left(He^+\right) = -\frac{1}{2}\frac{Z^2}{n^2} = -2 \text{ a.u.}$$

Using the experimental value for the energy of the neutral state, the first ionization energy is:
EI = –2.00 + 2.904 = 0.904 a.u. = 24.60 eV

Using the energy of the neutral state calculated at the HF/double-zeta level:
EI = –2.00 + 2.86167 = 0.86167 a.u. = 24.45 eV

Using the Koopmans' approximation:

EI = 0.917935 a.u. = 24.98 eV

The EI obtained using the Koopmans' approximation is overestimated compared to the EI obtained from the energies difference. This overestimation originates from the fact that the Koopmans' approximation does not take into account the relaxation of the electronic cloud after the removing of an electron.

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.

```
ndim = 1      E =   -2.3750000000000000
ndim = 2      E =   -2.8418673266294521
ndim = 3      E =   -2.8608040478807824
ndim = 4      E =   -2.8615856536206898
ndim = 5      E =   -2.8616447176931703
ndim = 6      E =   -2.8616549035190850
ndim = 7      E =   -2.8616595547099108
ndim = 8      E =   -2.8616618851277433
ndim = 9      E =   -2.8616631383996989
ndim = 10     E =   -2.8616638411357607

ndim = 1      epsilon =   -0.87500000000000000
ndim = 2      epsilon =   -0.90756381682269027
ndim = 3      epsilon =   -0.91677972183723755
ndim = 4      epsilon =   -0.91773361904969608
ndim = 5      epsilon =   -0.91784959824285006
ndim = 6      epsilon =   -0.91787787931314080
ndim = 7      epsilon =   -0.91789125637644564
ndim = 8      epsilon =   -0.91789810352310530
ndim = 9      epsilon =   -0.91790182951653243
ndim = 10     epsilon =   -0.91790393273812898
```

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.

Gain in energy when increasing the basis set size:

```
Ndim = 2      -0.466867327
Ndim = 3      -0.018936721
Ndim = 4      -0.000781606
Ndim = 5      -5.90641E-05
Ndim = 6      -1.01858E-05
Ndim = 7      -4.65119E-06
Ndim = 8      -2.33042E-06
Ndim = 9      -1.25327E-06
Ndim = 10     -7.02736E-07
```

Considering a threshold of 10^{-6} a.u. on the total energy, the HF limit is reached for ndim = 10. The total energy value at the HF limit, E = -2.861664 a.u. is larger than the best double-zeta result obtained using the optimal α exponents (E = –2.861673 a.u.). This result shows the crucial importance of the choice of the adequate basis set.