LAB. EXERCISE 2
DETERMINATION OF A 1S GAUSSIAN BASIS SET FOR THE HELIUM ATOM

PART 1: SINGLE-ZETA SCF-LCAO CALCULATION USING A SLATER-TYPE 1S ORBITAL

We consider in this part a SCF scheme in which the 1s orbital is described by a single Slater's function (*single-zeta* calculation):

$$1s(\mathbf{r}) = \frac{\alpha^{3/2}}{\pi^{1/2}} \exp(-\alpha r)$$

1) Plot the curve E = $f(\alpha)$ and find the optimal values of α and of the total energy E. Give a physical interpretation of α related to the Slater's effective model.

2) Compare the results with the double-zeta results obtained in the Lab. Exercise 1, and to the experimental data. Explain the differences.

3) Write down the expression of the radial density D(r) by integrating the total probability density function with respect to the angles θ et φ of the spherical coordinate system.

4) Plot (on the same graph) the D(r) function obtained using $\alpha = Z$ and the optimal value of α, and give an interpretation of the differences between the two curves.

PART 2: SINGLE-ZETA SCF-LCAO CALCULATION USING A GAUSSIAN-TYPE 1S ORBITAL

Using the same approach as in Part 1, we consider now that the trial function of the helium atom is a s-type Gaussian function (GTO):

$$1s(\mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2)$$

5) Write the total energy as a function of the variational parameter α, minimize with respect to α, and deduce the single 1s Gaussian orbital, which, in a variational sense, is the best approximation to the exact 1s STO. Plot in the same graph the 1s STO and its approximation by a single Gaussian (STO-1G). One gives the expression of the nucleus-electron attraction (NEA), the kinetic energy (KE) and electron-electron repulsion (EER) integrals:

$$\mathrm{NEA} = \int 1s(\mathbf{r})\left(\frac{1}{\mathbf{r}}\right)1s(\mathbf{r})d\mathbf{r} = 2\sqrt{\frac{2\alpha}{\pi}}$$

$$\mathrm{KE} = \int 1s(\mathbf{r})\left(-\frac{1}{2}\Delta\right)1s(\mathbf{r})d\mathbf{r} = \frac{3}{2}\alpha$$

$$\mathrm{EER} = \left(1s1s|1s1s\right) = 2\sqrt{\frac{\alpha}{\pi}}$$

PART 3: USE OF CONTRACTED GAUSSIAN FUNCTIONS

Since one GTO does not describe well the radial dependence of a Slater function, it is usual to represent any atomic orbital by a contraction of several primitive Gaussian functions. This has been referred to as the Contracted Gaussian Type Orbitals (CGTO) basis sets. The 1s orbital is thus expressed as:

$$1s(\mathbf{r}) = \sum_{i=1}^{X} a_i \chi_i^G \quad \text{where} \quad \chi_i^G = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp(-\alpha_i r^2)$$

Note that the expansion coefficients (a_i) are not varitational, and are kept constant throughout the SCF cycles.

6) By using the Gaussian program, compute the SCF-LCAO total energy of the ground state of the helium atom using the STO-XG basis sets (with X ranging from 2 to 6). Check the energy values with respect to the number X of Gaussian functions used in the contraction. By using the values of the contraction coefficients a_i and α_i exponents, plot in the same graph the exact 1s STO and its STO-1G, STO-2G and STO-3G approximations.