

Practice Session 1

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Problem 1

To compute the energy of the ground state using the variational method, first the optimal exponent, α , the one that minimizes the variational integral $W(\alpha)$, must be found. To do that, W is computed for a range of α values between 0.01 and 0.5 and the minimum of that representation is found.

In this case the variational integral can be expressed as a function of only the exponent of two GTO:

$$W_{ij} = \frac{T_{ij} + V_{ij}}{S_{ij}} \Rightarrow T_{ij} = \frac{3\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}} \quad V_{ij} = \frac{-2\pi}{\alpha_i + \alpha_j} \quad S_{ij} = \left(\frac{\pi}{\alpha_i + \alpha_j} \right)^{3/2} \quad (1)$$

Where atomic units are employed, and in the case of the same GTO, (1s, in our case), $\alpha_i = \alpha_j$.

The results of the plot of $W(\alpha)$ and the optimized exponent and energy are found in Figure 1 and Table 1.

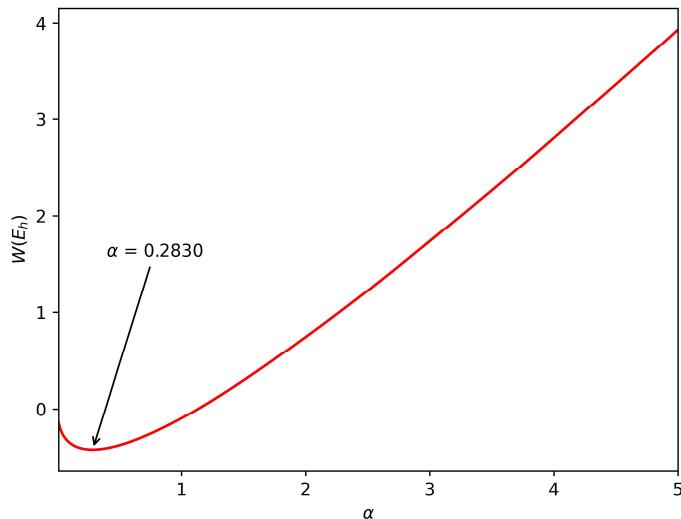


Figure 1. Representation of $W(\alpha)$ as a function of the parameter α . Minimum indicated with the arrow.

Optimal exponent for GTO 1s orbital	0.28298
Energy with optimal exponent (a.u.)	-0.42441
Relative error (respect to -0.5 a.u.)	15.12 %

Table 1. Optimal exponent and energies computed.

- Python Script available at: [GitHub](#) or attached to the task as `p1.py`.

Problem 2

To find the optimal parameter for STO-NG basis one must maximize the overlap integral between a STO function and the correspondent STO-NG. For the case of STO-1G, which consists only of one GTO, the overlap integral reduces to:

$$S = \pi^{-1/2} \left(\frac{2\alpha}{\pi} \right)^{3/4} \int e^{-r} e^{-\alpha r^2} dr^3 = \pi^{-1/2} \left(\frac{2\alpha}{\pi} \right)^{3/4} 4\pi \int_0^\infty r^2 e^{-r} e^{-\alpha r^2} dr \quad (2)$$

Again, S is calculated for a large set of α values, and then the maximum is found. On Figure 2, the representation of S as a function of alpha is shown, while the optimized values are present in Table 2. Very similar values are obtained, although this ones present a slightly higher error than the ones in Problem 1.

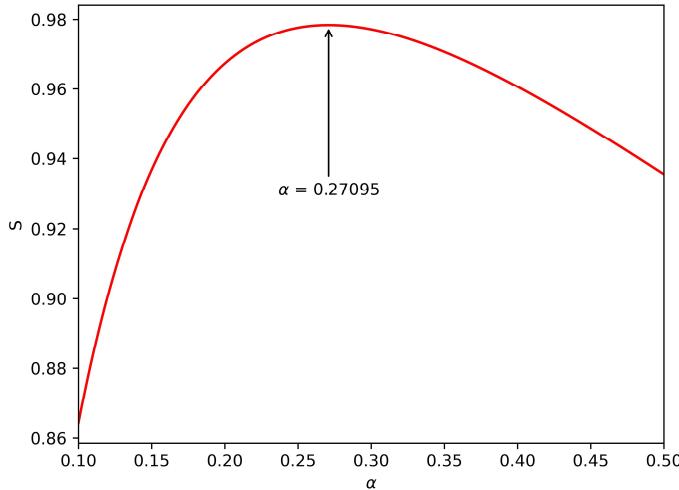


Figure 2. Representation of $S(\alpha)$ as a function of the parameter α . Minimum indicated with the arrow.

Optimal exponent for STO-1G 1s orbital	0.27095
Energy with optimal exponent (a.u.)	-0.42422
Relative error (respect to -0.5 a.u.)	15.12 %

Table 2. Optimal exponent and energies computed

- Python Script available at: [GitHub](#) or attached to the task as p2.py.

Problem 3

To compare the fitting quality of STO-NG to the STO, their functions and radial distributions are plotted with the original STO. On Figure 3 and 4 this representations are displayed for H ($Z = 1$) and He⁺ ($Z = 2$).

First, the STO-NG are constructed with a contraction of primitive GTO, and for the case of 1s orbital:

$$\chi_{1s}^{STO-NG}(r; d, \alpha) = \sum_{p=1}^N d_p \chi_{1s}^{GTO}(r; \alpha_p) \quad \chi_{1s}^{GTO}(r; \alpha) = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2} \quad (3)$$

So, the STO-NG functions will be parametrized by the d and α coefficients of each contracted GTO.

The radial distribution function (RDF), the probability density of finding an electron at a certain r , will be computed with:

$$P(r) = 4\pi r^2 |\chi_{1s}|^2 \quad (4)$$

The calculation of the orbital functions for elements with different effective charge ζ , such as He^+ , can be performed by simply using the relation $\alpha = \alpha(\zeta = 1)\zeta^2$. In the present case, with $1s$ orbitals, ζ takes the value of the nuclear charge Z .

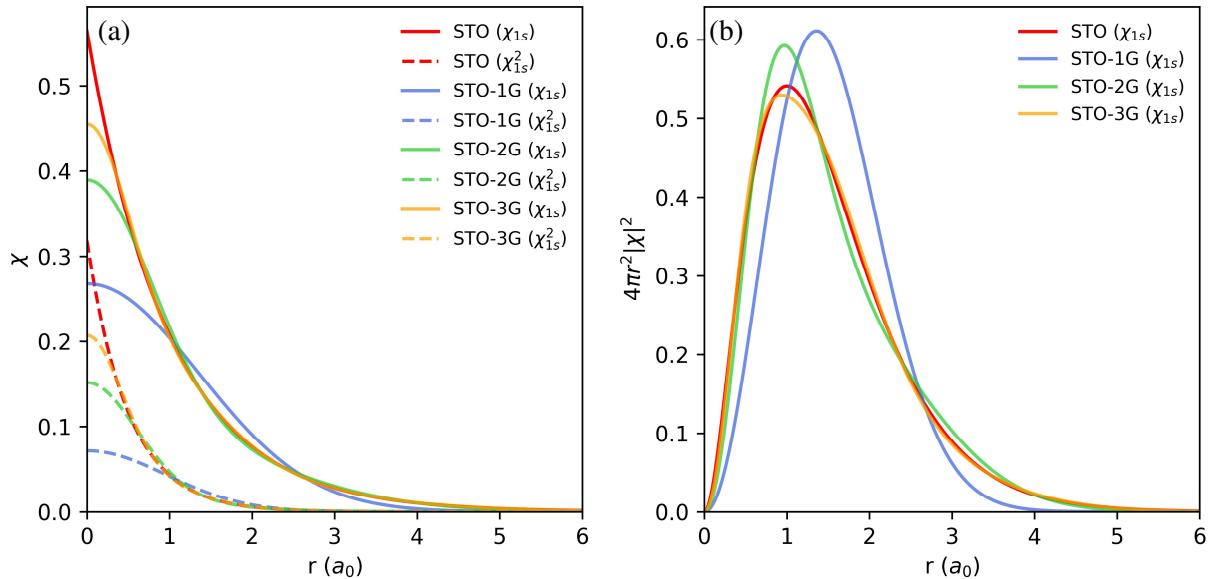


Figure 3. (a) Wave function and its square, and (b) radial distribution function, for the STO and each STO-NG considered for the $1s$ orbital of H. Values in a.u.

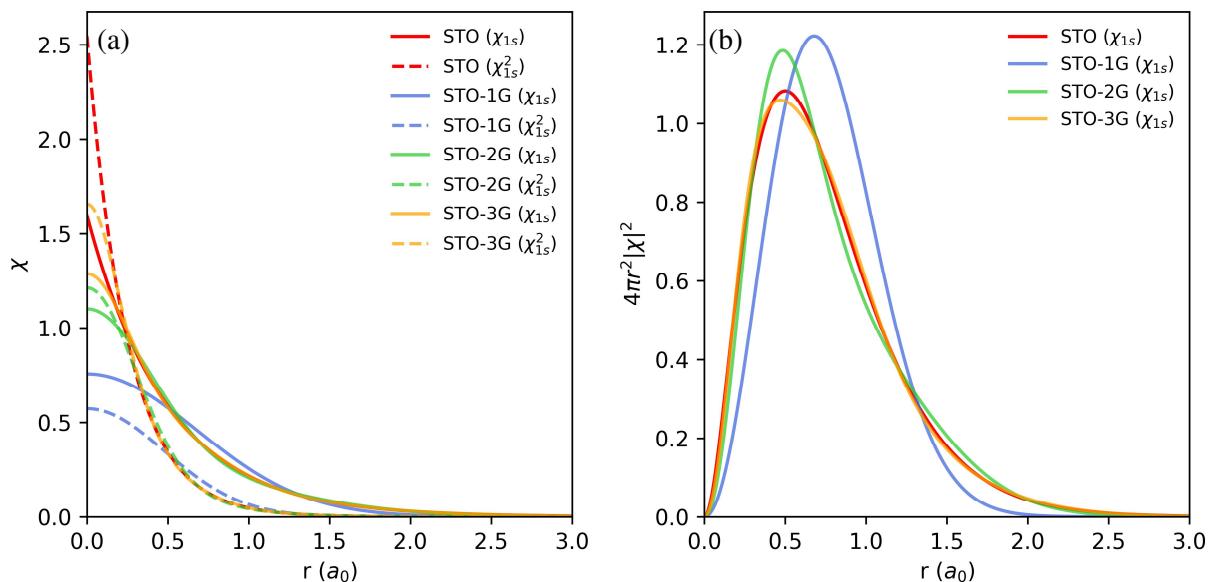


Figure 4. (a) Wave function and its square, and (b) radial distribution function, for the STO and each STO-NG considered for the $1s$ orbital of He^+ . Values in a.u.

In the Figures, it can be seen that as the number of primitives increases, the STO-NG fits better to the STO, as expected. Looking at the RDF, the STO-1G is the one that is further from the STO, adding one more primitive, in the STO-2G, the radius at which the probability density is maximum (r_{max}) aligns better with the STO, but the RDF maximum value still presents some deviation, finally, with the STO-3G, that deviation is corrected and presents a very good fitting to the original STO.

The wave functions and its squares, follow a very similar trend, where the STO-3G is the best fitted. At distances $r > a_0$ the functions and functions squared have almost the same values, but at $r < a_0$ higher deviations are quickly observed. The main difference between the STO-NG functions and original STO, is that, given the gaussian form of the GTOs, the STO-NG will present a maximum at $r = 0$, and this the function slows down closer to that region, while for the STO its not the case, and higher values are observed.

Moreover, to better asses the fitting and behaviour of the STO-NG functions, the most probable electron-nucleus distance (r_{max} , distance that maximizes the RDF), the average electron-nucleus distance, $\langle r \rangle$, and the orbital radius (r_{orb} , the radius of a sphere centered in the nucleus containing the electron with a 99% probability) is computed and presented in Table 3.

The r_{max} is calculated in a similar fashion as in Problems 1 and 2, by calculating the RDF and searching for the value that maximizes it. The average distance, $\langle r \rangle$, is calculated with the expected value on the correspondent basis, see Equation 5. And r_{orb} is computed by calculating the probability of finding the electron in a certain sphere of volume r_o , see Equation 6, and increasing r_o until that probability is 0.99.

$$\langle r \rangle = \langle \chi_{1s} | r \chi_{1s} \rangle = 4\pi \int_0^{\infty} r^3 |\chi_{1s}|^2 dr = \int_0^{\infty} r P(r) dr \quad (5)$$

$$P(r < r_o) = 4\pi \int_0^{r_o} r^2 |\chi_{1s}|^2 dr = \int_0^{\infty} P(r) dr \quad (6)$$

		STO	STO-1G	STO-2G	STO-3G
H	r_{max}	1.0000	1.3584	0.9682	0.9418
	$\langle r \rangle$	1.5000	1.5328	1.5032	1.5004
	r_{orb}	4.2033	3.2357	3.9911	4.2191
He^+	r_{max}	0.5000	0.6792	0.4840	0.4708
	$\langle r \rangle$	0.7500	0.7664	0.7516	0.7502
	r_{orb}	2.1018	1.6180	1.9956	2.1096

Table 3. Most probable distance, r_{max} , average distance, $\langle r \rangle$, and orbital radius ($P = 99\%$), r_{orb} , for the 1s orbitals of H and He^+ using the STO and STO-NG basis ($N = 1, 2, 3$). All distances in atomic units.

Comparing between H and He^+ , the values of Table 2 for He^+ , are lower, almost exactly the half of the ones obtained for H. Also, the RDF and wave functions decay much faster to lower values. This has to do with the atomic charge, the He^+ has 2 protons⁺ at the nucleus which imply a higher attraction force on the electron, resulting in the electron being closer to the nucleus.

- Python Script available at: [GitHub](#) or attached to the task as p3.py.