The Ground State Energy of Helium Using Hartree-Fock Roothaan With Six Expansion Terms of Gaussian Type Orbital (GTO-6G)

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Article Info	ABSTRACT
	An implementation of the Hartree-Fock Roothaan with six expansion terms of Gaussian Type Orbitals (GTO-6G) is described and used to study the Helium atom's ground state accurately. The objective of this research is to calculate the ground state energy of the Helium atom. The analysis was conducted using the numerical method using Matlab 2017b. By using the Hartree-Fock Roothaan method, the complexity of Hartree-Fock in integrating the differential equations of eigenvalues for each electron is repeatedly successfully overcome by expressing Hartree-Fock orbitals in the form of linear combinations, known as STO (Slater Type Orbitals) and GTO (Gaussian Type Orbital). The Hartree-Fock Roothaan approximation procedure begins by assigning an initial guess value to the elements of the density matrices and then constructing the first Fock matrix from these matrices. The calculation is performed using the various iterations in multiples of 50, show that the error value expressed in relative uncertainty is getting smaller at the 150th iteration, which is around 1.84%. Compared with some literature, the relative uncertainty value is still within tolerance (below 5%). The contribution of theoretical implications in this study can be used as input for other researchers to review the Hartree-Fock Roothaan method and improve accuracy.

I. Introduction

One of the important in the study of an atom is the determination of the ground state energy. Many methods can be used to determine the ground state energy of an atom. It can be done by solving the Schrodinger equation. However, this tends to be very difficult in atoms with many electrons because it involves a fairly complex equation [1].

Helium is an atom with two electrons and two protons. It has more than one particle, called a many-body system [2]. In such a system, there are various problems to study. One of those is the calculation of the Helium ground state energy. The Helium ground state energy calculates using the perturbation theory [3].

The variational technique, commonly known as the Rayleigh-Ritz method, is one of the approximation methods suited for handling such problems. The variational method helps determine upper-bound values for the energy eigenvalues of a system whose Hamiltonian is known. In contrast, its eigenvalues and eigenstates are not known. It helps figure out what the ground state is. Determining the energy levels of excited states becomes extremely difficult [4]. Previously, this variational method was used to determine the ground state energy of Berillium atoms with two parameters. The variational method with two parameters is well for explaining the properties of the ground state of an atom [5].

The ground state energy of the atom can be performed analytically and numerically. We can calculate the ground state energy with analytical calculation. However, this calculation has limitations, especially in atomic systems with many electrons. A method is designed to approach the exact value to solve this problem, namely the numerical method. The Hartree-Fock approach, with a Slater determinant as the trial function, is a well-known

classical example. The Hartree-Fock approximation has been the starting point for most electronic structure computations since Hartree publicized the independent particle model and Fock's addition of antisymmetry. Designing a numerical solution for multi electronics atoms was extraordinary due to the absence of computational resources at the time [6]. Hartree-Fock also contributed to developments in approximate density functional theory [7], [8]. However, a theoretical estimate of how far the Hartree-Fock energy deviates from the correct conclusion in this scenario is impossible [9]. In the late 1920s, Hartree presented Self-Consistent Field (SCF) methods to explore the electronic structure of atoms with more than one electron, which Slater, Fock, and others further developed. These Hartree-Fock methods are commonly used to compute the properties of atomic, molecular, and solid.

Some difficulties must be faced in finding a solution of the Hartree-Fock equation numerically because, in the process, the integration of the differential equations of eigenvalues for each electron must be repeatedly integrated. Placing arbitrary constraints on the wave function makes Hartree-Fock theory more difficult to understand than the exact solution in many ways [10]. The complexity of this technique was overcome by Roothaan, who proposed the critical idea of expressing the Hartree-Fock orbital in the form of a linear combination of a complete set of previously known before, for example, the Slater Type Orbital (STO) and Gaussian Type Orbital (GTO) [11], [12].

This method employs the principle that each electron's movement can be described as a single particle function. In this research, the Hartree-Fock Roothaan method is implemented on the Helium atom to calculate the ground state energy. Helium atoms are composed of an atomic nucleus with two protons and two protons, accompanied by two electrons surrounding the core [13]. In contrast to the Hydrogen atom case, the Hamiltonian of the Helium atom involves the interaction terms between electrons that do not have closed solutions or are expressed in elementary function through analytical calculations. The solution of the case must be done numerically [14]. Tjia and Sutjahja [11] have also carried out this related research, but the calculations use STO type (Slater Type Orbital) expansion terms. The Hartree-Fock Roothaan method is implemented in this research with six expansion terms with the GTO type (Gaussian Type Orbital). The results obtained from this calculation are compared to other numerical and analytical results.

II. Theory

The atomic orbitals in Slater's determinant are described according to Roothaan in equation (1).

$$\varphi_n = \sum_i C_{ni} \chi_i \tag{1}$$

Theoretically, as long as the basis χ_i is complete, the translation in equation (1) can be justified in principle.

Only the accuracy of the choice of basis itself will affect the accuracy of the computation results and the convergence speed of the iteration process. The primary meaning of applying Roothaan's ideas expressed by equation (1) is the result in reducing the integration problem of the differential equations for atomic orbitals to the simultaneous algebraic equation for the linear combination coefficients $\{c_{ni}\}$.

$$\sum_\beta \left(F_{\alpha\beta} - \varepsilon_n \right) c_\beta = 0 \tag{2}$$

The Fock matrix ε_n is the diagonal matrix of the eigenvalues (orbital energies), which can be solved by matrix algebra.

The algorithms used in this study is determining the basic GTO function. We take $\varphi(r)$ an orbital (depending on the spatial orbital only) shared by the two electrons. We bring $\varphi(r)$ as a linear combination of four fixed, real basis functions (both C_i and χ_i are real):

$$\varphi(r) = \sum_{i=1}^{6} C_i \chi_i (r) \tag{3}$$

With,

$$\chi_i (r) = e^{-\alpha_i r^2} \tag{4}$$

Then, determine the six exponential coefficients using equation (5) [15].

$$\begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \alpha_5 \\ \alpha_6 \end{bmatrix} \rightarrow \begin{bmatrix} 0.0366871 \\ 0.2387262 \\ 0.7245867 \\ 1.2425670 \\ 5.2829480 \\ 38.474970 \end{bmatrix} \tag{5}$$

Determination of the matrix elements of the overlap matrix for the orbital basis, S_{pq} ($p,q = 1, 2, …, 6$),

$$S_{pq} = \langle \chi_p | \chi_q \rangle \tag{6}$$

$$S_{pq} = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2} \tag{7}$$

Determination of the Hamiltonian,

$$H_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 - \frac{2}{r} \right| \chi_q \right\rangle \tag{8}$$

$$H_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 - \frac{2}{r} \right| \chi_q \right\rangle + \left\langle \chi_p \left| \frac{2}{r} \right| \chi_q \right\rangle \tag{9}$$

$$H_{pq} = T_{pq} + V_{pq} \tag{10}$$

Determination of the matrix elements of the kinetic energy,

$$T_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 \right| \chi_q \right\rangle = \frac{3\alpha_p \alpha_q \pi^{3/2}}{\left(\alpha_p + \alpha_q\right)^{5/2}} \tag{11}$$

Determination of the matrix elements of the Coulomb energy,

$$V_{pq} = \left\langle \chi_p \left| -\frac{2}{r} \right| \chi_p \right\rangle = \frac{4\pi}{\alpha_p + \alpha_q} \tag{12}$$

After that, iteration of the self-consistency field (SCF). The matrix equation for the unknown prefactor coefficient vector $\mathbf{C} = \{C_1, C_2, C_3, C_4, C_5, C_6\}$. Calculation of the density matrix ρ,

$$\rho_{rs} = 2 \sum_{n}^{occ} c_{nr} c_{ns} \tag{13}$$

Calculation of the matrix G,

$$G_{pq} = \sum_{p,q} \rho_{rs} \left[\langle pq|rs \rangle - \frac{1}{2} \langle pr|qs \rangle \right] \tag{14}$$

With,

$$\langle pq|rs \rangle = \left\langle \chi_p(1)\chi_r(2) \left| \frac{1}{r_{12}} \right| \chi_q(1)\chi_s(2) \right\rangle \tag{15}$$

$$\langle pq|rs \rangle = \iint \chi_p(1)\chi_r(2) \left| \frac{1}{r_{12}} \right| \chi_q(1)\chi_s(2) d^3r_1 d^3r_2 \tag{16}$$

The Fock matrix elements have the form,

$$F_{pq} = H_{pq} + G_{pq} \tag{17}$$

Found the lowest eigenvalues of the secular equation,

$$\det\left(F - \varepsilon S\right) = 0 \tag{18}$$

Update C from the Roothaan equation,

$$\sum_{q}\left(F_{pq} - \varepsilon_n S_{pq}\right)C_{qn} = 0 \tag{19}$$

Loop up to C is stable (SCF is reached), we calculate the ground state energy as,

$$E = 2\sum_{pq} C_p C_q H_{pq} + \sum_{pqrs} C_p C_q C_r C_s \tag{20}$$

In the end, we compare the energy with a reference value, using the modified Hartree-Fock with Gaussian Type Orbital [16],

$$E_{ref} = -2{,}8616790 \, Hartree \tag{21}$$

III. Method

This research is a numerical method using the Hartree-Fock Roothaan method with six expansion term to get the ground state energy of Helium which closes to the reference value. The Hartree-Fock Roothaan method allows the Schrodinger equations for multiple particle systems to be solved relatively easily. The Hartree-Fock Roothaan method is an iterative calculation so that the solution can be calculated with a computer. The software used in working on the research was the 2017b version of Matlab software. The algorithm used in this study is generally summarized in a flow chart, as shown in Figure 1.
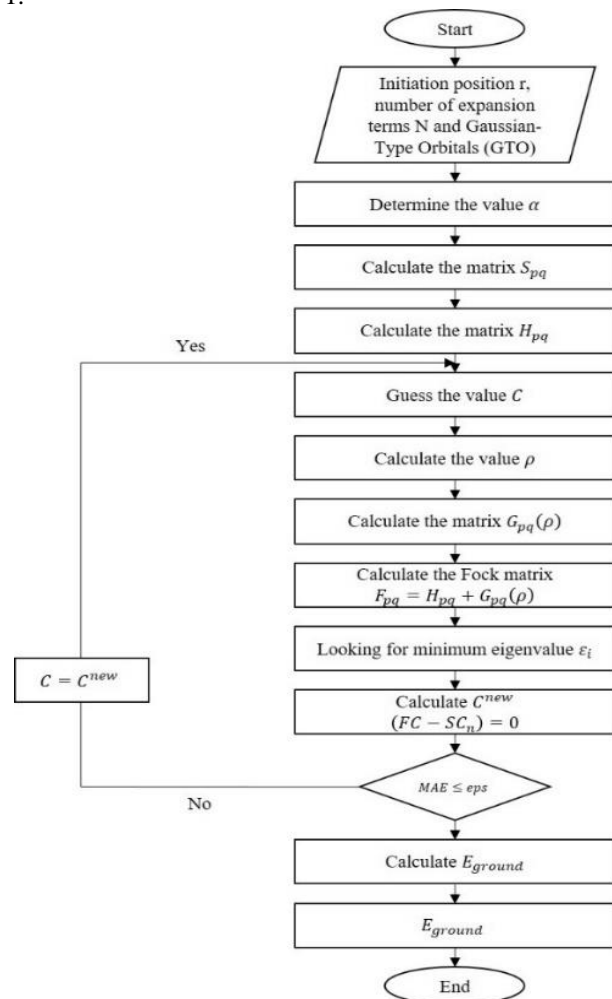

Figure 1. Hartree-Fock Roothaan flow chart

IV. Results and Discussion

One of the most critical problems in quantum chemistry is predicting the ground state energy of many-electron [17]. The Hartree-Fock method is a widely used basic theory of electronic structure and the basis of the

molecular orbital theory, which provides data that the movement of each electron can be explained in terms of a particle function that does not depend on the direct movement of another electron. In 1993, Roothaan applied the SCF (Self Consistency Field) concept to find an eigen solution to the Hartree-Fock method problem. Furthermore, this method is better known as the Hartree-Fock Roothaan method. This concept is necessary to get knowledge in quantum mechanics, electromagnetic theory, and linear algebra.

The Hartree-Fock Roothaan function has been expanded in the STO term. Studies about Hartree-Fock Roothaan reported significantly improved results using a base set of GTO. The Gaussian Type Orbital (GTO) is also known as the primitive Gaussian function, which can be served in a Cartesian coordinate system or a spherical coordinate system. It should be noted that, unlike the STO function, the GTO function does not present a cusp shape at the location of the atomic nucleus for the radial part of

the two types of atomic orbitals. This means this function provides a less realistic representation of the electron distribution for small r values. However, this GTO function is more widely used in numerical computations because the exponential function, which depends on r^2 allows for more efficient calculations of molecular integrals with its more straightforward formulation. This efficiency factor will reduce the cost of implementing sizeable numerical computation programs.

We offer the findings of our computations in this part and compare them to those already published in the literature. The calculations are performed using the various iterations in multiples of 50. The results are shown in Figure 2. It can be seen that the error value expressed in relative uncertainty is getting smaller at the 150th iterations, which is around 1.842%. The greater iteration is carried out, and the smaller deviation will be generated, which means that the ground state energy produced will be closer to the reference value [16].
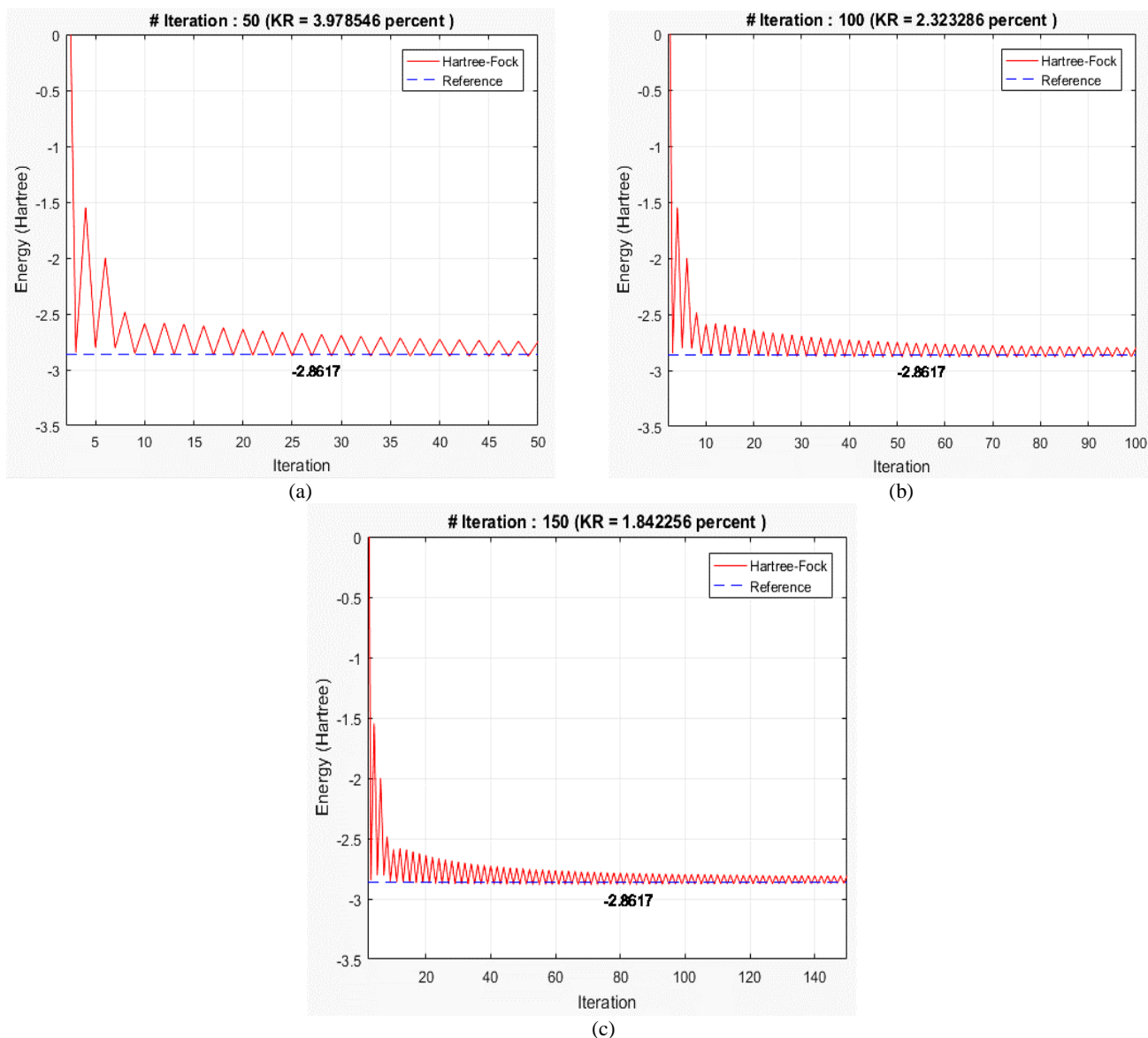

(a)

(b)

(c)

Figure 2. The results of energy calculations use (a) 50 iterations, (b) 100 iterations, and (c) 150 iterations

The primary limitation to the generalization of these results is we obtained the smallest of ground state energy compared to other studies using the other method like references [18–22] because our calculation was restricted to the 150th iteration, we just wanted to find out if this method was efficient enough at determining the ground state energy of the Helium atom. Table 1 shows the result of energy calculation using the various iterations.

Compared with some literature, the relative uncertainty value is still within tolerance (below 5%), which means implementing the Hartree-Fock Roothaan with six expansion terms of Gaussian Type Orbitals (GTO-6G) is entirely accurate in determining the ground state energy of Helium atom. Overall, comparisons against the literature are shown in Table 2.

Table 1. The calculation result of the ground state energy using the various iterations

Iteration	E_{ground} (Hartree)	Relative uncertainty (%)
50	-2.74482	3.939
100	-2.79519	2.323
150	-2.80896	1.842

Table 2. The calculation result of the ground state energy of the Helium atom

Author	Year	Method	Energy (Hartree)
Ludeña [18]	1978	Hartree-Fock	-2.86164
Buendia *et al.* [16]	1997	Modified HF-GTO	-2.86170
Tsubono [19]	2009	Bohr's Theory	-2.90320
Ekong *et al.* [20]	2015	Quantum Monte Carlo CASINO-Code	-2.90369
Purwaningsih *et al.* [21]	2019	Hylleraas Trial Function Expansion	-2.90150
Tjia and Sutjahja [11]	2012	Slater Type Orbital (STO-2G)	-2.86200
Doma *et.al.* [22]	2014	Variational Monte Carlo	-2.90377
This study	2021	Gaussian Type Orbital (GTO-6G)	-2.80896

V.   Conclusion

In this study, an implementation of the Hartree-Fock Roothaan with six expansion terms of Gaussian Type Orbitals (GTO-6G) is described and used to study the Helium atom's ground state accurately. Setting an initial estimate value for the density matrix elements is the first step in the Hartree-Fock Roothaan approximation procedure; with these matrices constructed the initial Fock matrix. The calculation is performed using various iterations. It shows that the relative uncertainty is getting smaller at the 150th iteration, around 1.84%. The Helium ground state energy produced in this study is close to the results of previous research. In the end, we presented a detailed comparison of our energy results to those of other methods showing that the relative uncertainty value is still within tolerance. This proves that the Hartree-Fock Roothaan with six expansion terms of Gaussian Type Orbitals (GTO-6G) is very suitable in explaining the properties of the ground state energy of an atom, like Helium atom.

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