International Journal of Sciences: Basic and Applied Research (IJSBAR)

ISSN 2307-4531
(Print & Online)

http://gssrr.org/index.php?journal=JournalOfBasicAndApplied

Ground State Energy of the Helium Using Variational Methods on Trial Wave Functions

Sri Purwaningsih*

Lecturer at department of Mathematic and Natural Science education, Jambi University, Jambi, 36361, Indonesia

Email: sripurwaningsih@unja.ac.id

Abstract

Helium is a quantum system that has two electrons and one proton, the calculation of the ground state energy of helium has been done by variational method, the advantages of variational method is that it can be performed flexible selection of wave function. The objective of this study is to calculate the ground state energy of helium by using variational methods on the new wave function. From the research results obtained the ground state energy of helium equal to -77.333 eV. The result of this calculation is close to the experimental value.

Keywords: Helium; Variational Methods.

1. Introduction

Helium is an atom that has two electrons and one proton [13], since it has more than one particle, helium is called the system of many bodies. In the system many bodies there are various problems that are very interesting to be studied, one of which is the calculation of the ground energy state of helium. These calculations have been performed by previous Researchers, among which [11] have calculated the ground state energy of helium by using the interference theory, the results obtained from the study are -2.75 a.u. Different methods have been performed by [7]. They used a variational method to calculate the ground state energy of helium, the results obtained from this study were -2,899 a.u. [9] has examined the ground state energies of helium under a strong range.

----

* Corresponding author.

Analytically the calculation of the ground state energy of helium by using the variational method has also been done by [5]. The results obtained from the study were -77.5 eV. Furthermore, [1] has used Monte Carlo's variational method in calculating the ground state energy of helium and the paving of helium ions under the Bohn-Oppenheimer annex context. For other systems [2,18] have used the Monte Carlo variational method to calculate the molecular energy of H2. From the results of the previous research described above, it is known that to obtain the ground state energy approaching the value of the experiment must have a more realistic intuition in selecting the wave function [5]. The selected wave function can display the electron behavior in helium [8], by selecting the wave function of helium, ground state energy can be obtained. In this paper the Author has selected a particular waveform function which meets the boundary conditions in calculating the ground state energy of helium. Given the importance of the role of the wave function in assessing the variational method for explicitly calculating the energy of the ground state of helium. In this study formed certain helium wave function that must meet this boundary requirement for enumeration ground state energy of helium using variational method. From the calculation results obtained the ground state energy of helium , where new trial wave function is selected.

2. Material and Methods

2.1. Choosing Trial Wave Function

In choosing a trial wave function, must consider the criterion that must fulfill the ground wave function of helium exact, such as meeting the boundary condition, single value, well behaved. If these criteria are met then the trial wave function is wave function for ground state of helium. The trial wave function of helium was used to calculate of ground state energy selected is

$$\psi_{T1}(\vec{r}_1,\vec{r}_2)=\frac{Z^3}{\pi a_0^3}e^{-(Z/a_0-b)(r_1+r_2)} \tag{1}$$

The selection of the wave function is a constraint for the behavior of the wave function when the distance between the electron and the nucleus or the distance between two electrons is close to zero. Such a constraint is called the cusp condition and is associated with the derivative of a wave function. Furthermore the trial wave function must meet the boundary [7]. Z and b on the wave function are variational parameters, with and representing the distance between each electron with a helium atomic nucleus. The wave function for the helium atoms in the equation (1) has similar features to its exact wave function, since the accuracy of the results obtained by using this variational method is heavily dependent on the function of the used wave [21]

The Hamiltonian for helium atoms can be displayed as follows [5,10]:

$$\hat{H}=\frac{1}{2}\left(p_1^2+p_2^2\right)-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}} \tag{2}$$

which are the kinetic energy of electrons 1 and electron 2, potentials energy of the electron 1 and electron 2 as well as the Coulomb interactions between the two electrons.

2.2 Selected Trial Functions Directly Substituted to Variational Methods

Variational methods are applied in quantum mechanics to calculate the expected value of a quantum system. Variational methods can be used to solve almost the Schrödinger helium equation [14] and [19]. In recent years, the development of modern computers has facilitated the use of various calculation methods based on variational methods. The energy expectation value associated with each wave function can be expressed into the following Hamiltonian operators [3,6,11]:

$$E = \frac{\int \psi \hat{H} \psi \, dr}{\int \psi^* \psi \, dr} \tag{3}$$

The wave form must be selected by applying a boundary condition that depends on one or more independent parameters to minimize. The selection of a try wave function meets the boundary conditions in the two regions, it is zero in value

$$r = 0 \text{ and } r = \infty \quad \psi = 0 = \psi(r = 0) = \psi(r = \infty) \tag{4}$$

With expectant values of pregnancy greater and equal to the energy of the ground state, ie [4]

$$E_0 \le \langle H \rangle \tag{5}$$

The selected trial function can be used to describe the expected value of the energy of a helium atom by substituting equation (2) into the expectation equation (3) and the integral translation is done by examining the distance between each electron and the nucleus and the distance between the electrons , the integral is solved in spherical coordinates. Schrödinger equation for helium system is

$$\hat{H}\psi = \left(\frac{-1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right)\psi \tag{6}$$

and nabla are

$$\nabla_1^2(\psi) = \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} \right)\left(e^{-u(r_1+r_2)}\right) = \left((u)^2 - \frac{2u}{r_1} \right)\left(e^{-u(r_1+r_2)}\right) \tag{7}$$

$$\nabla_2^2(\psi) = \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} \right)\left(e^{-u(r_1+r_2)}\right) = \left((u)^2 - \frac{2u}{r_2} \right)\left(e^{-u(r_1+r_2)}\right) \tag{8}$$

Equations (7) and (8) can be substituted into the value expectation equation. For simpler calculations, let's say $u = Z - b,\ x = Z^3$, so the value expectation equation is

$$\langle H\rangle = \frac{\int \psi\, \hat{H}\, \psi dr}{\int \psi^{*}\, \psi\, dr} = -\frac{x^2}{2\pi}\int e^{-u(r_1+r_2)}\left(\left(u^2-\frac{2}{r_1}\right)+\left(u^2-\frac{2}{r_2}\right)\right)e^{-u(r_1+r_2)}\, d^3r_1\, d^3r_2$$
$$-\frac{x^2}{\pi}\int e^{-u(r_1+r_2)}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)e^{-u(r_1+r_2)}\, d^3r_1\, d^3r_2 - \frac{x^2}{\pi}\int e^{-u(r_1+r_2)}\left(\frac{1}{r_{12}}\right)e^{-u(r_1+r_2)}\, d^3r_1\, d^3r_2 \tag{9}$$

$$\langle H\rangle = -\frac{x^2}{2\pi^2}\int 2ue^{-2u(r_1+r_2)}d^3r_1\, d^3r + \frac{x^2}{\pi^2}\int (u-Z)\frac{1}{r_1}e^{-2u(r_1+r_2)}d^3r_1\, d^3r$$
$$+\frac{x^2}{\pi^2}\int (u-Z)\frac{1}{r_2}e^{-2u(r_1+r_2)}d^3r_1\, d^3r \quad -\frac{x^2}{\pi^2}\int \frac{1}{r_{12}}e^{-2u(r_1+r_2)}d^3r_1\, d^3r \tag{10}$$

then the integral tribes can be done one by one as follows

$$I = -\frac{x^2}{\pi^2}u^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2u(r_1)} r_1^2 dr_1 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2u(r_2)} r_2^2 dr_2 \tag{11}$$

by the using

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{(a)^{n+1}}$$

then this equation (10) can be simplified to be

$$I = -\frac{x^2}{\pi^2}u^2\ 4\pi 4\pi \frac{2!}{(2u)^3}\frac{2!}{(2u)^3} = -\frac{x^2}{u^4} \tag{12}$$

$$II = \frac{x^2}{\pi^2}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} \frac{(u-Z)}{r_1} e^{-2u(r_1)} r_1^2 dr_1 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2u(r_2)} r_2^2 dr_2$$

In the same way then the second and third can be solved as $\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2u(r_2)} r_2^2 dr_2$

$$II = \frac{x^2}{\pi^2}\int_0^{\infty} 4\pi \frac{(u-Z)}{r_1} e^{-2u(r_1)} r_1^2 dr_1 \int_0^{\infty} 4\pi e^{-2u(r_2)} r_2^2 dr_2 = 16x^2(u-Z)\frac{1}{(2u)^2}\frac{2!}{(2u)^3} = \frac{x^2(u-Z)}{u^5} \tag{13}$$

So also the third term is as follows

$$III = \frac{x^2}{\pi^2} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} e^{-2u(r_1)} r_1^2 dr_1 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} \frac{(u-Z)}{r_2} e^{-2u(r_2)} r_2^2 dr_2$$
$$= \frac{x^2}{\pi^2} \int_0^{\infty} 4\pi e^{-2u(r_1)} r_1^2 dr_1 \int_0^{\infty} 4\pi \frac{(u-Z)}{r_2} e^{-2u(r_2)} r_2^2 dr_2 = 16x^2 (u-Z) \frac{1}{(2u)^2} \frac{2!}{(2u)^3} = \frac{x^2(u-Z)}{u^5} \quad (14)$$

The next fourth term can be calculated as follows

$$IV = -\frac{x^2}{\pi^2} \int \frac{1}{r_{12}} e^{-2u(r_1+r_2)} d^3r_1 \, d^3r_2 = -\frac{x^2}{\pi^2} \int \frac{e^{-2u(r_1)} e^{-2ur_2}}{\sqrt{r_1^2 - 2r_1 r_2 \cos\theta_{12} + r_2^2}} d^3r_1 \, d^3r_2$$

$$I_1 = \int e^{-2u(r_1)} d^3r_1 \int \frac{e^{-2ur_2} d^3r_2}{\sqrt{r_1^2 - 2r_1 r_2 \cos\theta_{12} + r_2^2}} = \int e^{-2u(r_1)} d^3r_1 I_2(r_1)$$
$$I_2(r_1) = \int \frac{e^{-2ur_2} d^3r_2}{\sqrt{r_1^2 - 2r_1 r_2 \cos\theta_{12} + r_2^2}}$$

The above equation is resolved to be

$$\int_{v_1}^{v_2} \frac{dv}{2r_1 r} (v)^{-1/2} = \frac{1}{r_1 r_2} \left(\sqrt{v_2} - \sqrt{v_1} \right) = \frac{1}{r_1 r_2} \left((r_1 + r) - |r_1 - r| \right) = \begin{cases} 2/r_1 \text{ if } \; r < r_1 \\ 2/r \text{ if } \; r > r_1 \end{cases}$$

$$I_2(r_1) = 2\pi \left(\int_0^{\infty} r^2 e^{-2ur} dr (\text{for } r < r_1 \text{ and } r > r_1) \right) = 2\pi \left(\int_0^{r_1} \frac{2r^2 e^{-2ur}}{r_1} dr + \int_{r_1}^{\infty} \frac{2r^2 e^{-2ur}}{r} dr \right)$$
$$= 2\pi(-4u) \left(\frac{1}{r_1} \left(r^2 e^{-2ur} - \int_0^{r_1} e^{-2ur} dr 2r \right) + \left(re^{-2ur} + \frac{e^{-2ur}}{2u} \right)_{r_1}^{\infty} \right)$$

$$I_2(r_1) = -8\pi u \left(\frac{1}{r_1} \left(r^2 e^{-2ur} - 2 \left(re^{-2ur} + \frac{e^{-2ur}}{2u} \right) \right) \right)_0^{r_1} + \left(re^{-2ur} + \frac{e^{-2ur}}{2u} \right)_{r_1}^{\infty}$$
$$= -8\pi u \left(\frac{1}{r_1} \left(r_1^2 e^{-2ur_1} - 2 \left(r_1 e^{-2ur_1} + \frac{e^{-2ur_1}}{2u} \right) \right) - r_1 e^{-2ur_1} - \frac{e^{-2ur_1}}{u} \right)$$
$$= -8\pi u \left(-2e^{-2ur_1} - \frac{e^{-2ur_1}}{ur_1} - \frac{e^{-2ur_1}}{u} \right)$$

Finally $I_2(r_1) = \left(4u + \frac{2}{r_1} + 1 \right) 4\pi e^{-2ur_1}$ y

$$I_1 = \int d^3 r_1 e^{-2ur_1}\left(4u+1+\frac{2}{r_1}\right)4\pi e^{-2ur_1} = 16\pi^2\left[\int_0^\infty (4u+1) r_1{}^2 e^{-4ur_1} dr_1 + \int_0^\infty \frac{2r_1{}^2}{r_1} e^{-4ur_1} dr_1\right]$$

$$= 16\pi^2\left((4u+1)\frac{2}{(4u)^3}+\frac{2}{(4u)^2}\right) = \frac{4\pi^2}{u^2}+\frac{\pi^2}{2u^3}$$

The fourth term can be written as

$$IV = -\frac{x^2}{\pi^2}(I_1) = -x^2\left(\frac{4}{u^2}+\frac{1}{2u^3}\right) \tag{15}$$

By recombining terms I to IV, we expect Hamiltonan's value as

$$\langle H\rangle = \frac{-Z^6}{2(Z-b)^5}\left(2Z+2b+2(Z-b)^3+(Z-b)^2\right) \tag{16}$$

Further calculation is to minimize the functional energy of the ground state of helium equation (16) on the variational parameters, followed by the c part algorithm, so that three-dimensional graphs can be obtained.

2.3. Algorithm of the Program Calculates the Helium Basic Energy State

1. Enter the parameter value at interval [1,2].
2. Perform the iteration in the specified step.
3. Calculate the energy so that the minimum value.
4. Plot the graph that corresponds to three physical quantities, namely variational parameters Z and b and energy E results iterations.

3. The Results and Discussion

The wave function has been used to calculate the ground state energy of helium

$$\psi_{T1}(\vec{r}_1,\vec{r}_2) = \frac{8}{\pi a_0^3} e^{-(Z/a_0 - b)(r_1+r_2)}$$

the selected waveform function must meet the boundary condition, it is zero $\psi_{T1}(\vec{r}_1,\vec{r}_2)=0$, at the point $r_1, r_2 = 0,\infty$

That point is the integral boundary of the expectation value equation. From the calculation results, obtained energy value close to the experimental value of -77.333 eV, the value of the results of this calculation is not much different from the results of calculations by previous researchers. Graphically can be shown in Figure 1 below.

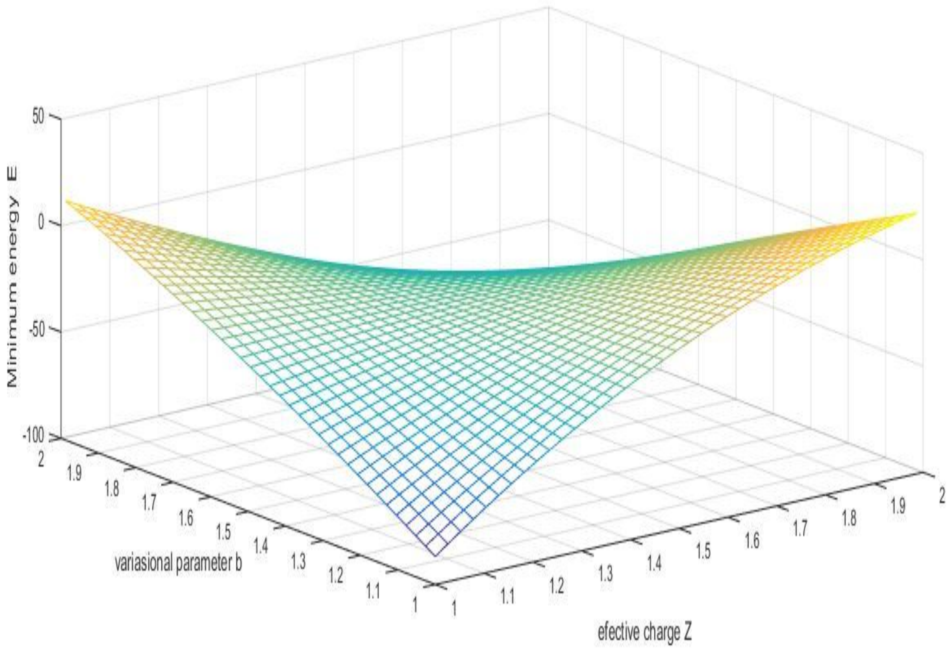

Figure 1: Chart of Z core charge relation, parameter variance b and minimum energy *E*.

From this graph we can show the relationship between minimum energy *E*, *Z* core load and variational parameters *b*. The minimum energy of the calculation is -77.333 eV. The results obtained are still in the energy value scale of the ground state energy of helium. When compared between the results of this study with the results of previous research, as in Table 1 below, then the value obtained in this study is not much different from the results of previous research.

Table 1: Wave functions, methods and results of research already under taken by previous Researchers and Researchers now.

Wave functions	Methods	Referensi, Result
$\psi_T = \exp\left(Z(r_1 + r_2)/a_0\right)$	Variasional secara analitik	[5], -77.5 eV
$\psi_T = e^{\left(Z(r_1+r_2)/a_0\right)} e^{(\alpha r_{12})}$ $\psi_{ion} = \exp(\alpha r)$	Variasional Monte Carlo Born-Oppenheimer	[1] , -78.9 eV
$\psi_T = \dfrac{8}{\pi a_0^3} e^{\left(-(Z/a_0 - b)(r_1+r_2)\right)}$	Variasional	This work, -77.333 eV.

In view of (3) above, the energy value obtained from the results of this study has satisfied equation (4s), meaning that the ground state energy of helium obtained by using a variational method is greater than the energy of its original ground state. Accordingly, the value of this energy can be approximated by calculating the energy value by using perturbation method [11], interaction configuration [15] and by analytical calculation by [17].

4. Conclusion

From the result of the research, it can be concluded that the selected ground state wave function of helium, its can be used to calculate the basic state energy of helium. The calculation of the ground state energy of helium by using the variational method has obtained an appropriate result done by the previous research . The choosing trial wave function must meet the boundary conditions, by choosing trial wave function that meets the boundary conditions obtained by the ground state energy of the helium in accordance with existing theories and literatures.

References

[1]. A. B. Suleiman , A. Usman , Ionization energy of Screened Helium by Variational quantum Monte carlo Method, International Journal Of Science and Nature, Vol. 4(2) , p. 311-315, 2013.

[2]. Sulaiman, I.O.B. Ewa, Variational quantum monte carlo of the ground state energy of hydrogen molecul, BAJOPAS. 3.1, p. 112-117, 2010.

[3]. R. Shankar, Principles of Quantum Mechanics, Second Editions, Yale University, New Haven Connecticut Springer, 1994.

[4]. D. Part, Introduction to Quantum Theory, third Edition, McGraw-Hill, Inc 1992.

[5]. D.J. Griffith, Introduction to Quantum Mechanic, Secon Edition, Person Prentice Hall, 1992.

[6]. Esposito, Naddeo, Majorana Solutions to the Two Electron Problem, Found Phys, Springer, Vol.42, pp.1586-1608, 2012.

[7]. A. Banerjee, C. Kamal, A. Chowdhury, Calculation of Ground and Excited State Energies of Confined Helium Atom, Physics Latters A 350 , pp. 121-125, 2006.

[8]. J.J. Sakurai, Modern Quantum Mechanics Revised Edition, Addison Wesley Publishing Company, New York, England, Amsterdam, Sydney, Singapore, 1994.

[9]. H. E.Montgomery, N. Aquino, A.F. Riveros, The Ground State energy of a Helium Atom Under Strong Confinement, Physics Latters A 374 , pp.2044-2047, 2010.

[10]. A. S. Davydov, Quantum Mechanics, Second Edition, Pergamon Press, Oxford New York, Toronto, 1973.

[11]. A. F. Riveros, N. Aquino, H. E. Montgomery, Spherically Compressed Helium Atom Described by Perturbative and Variational Methods, Physics Letters A ELSEVIER, 374, pp. 1246-1252, 2010.

[12]. S. B.Doma, F.N. El Gamma, Application of the Variational Monte Carlo Method to the Two-Electron Atom, Journal Applied Mathematics and Information Science, An International Journal, 5(1), pp. 20-33, 2010.

[13]. P.Atkins, R. Friedman, Molecular Quantum Mechanics, Fourth Edition, Oxford University Press, 2005.

[14]. G.W.F. Drake, Z. C. Yan, Variational Eigenvalues for the S State of Helium, Chemical Physics Letters 229, p. 486-490, August 1994.

[15]. J. S.Sims, S. A. Hagstrom, High Precision Hy-CI Variational Calculations for the Ground State of Neutral Helium and Helium-Like Ions, International Journal Quantum Chemistry, Vol 90, p.1600-1609, April 2002.

[16]. C. Amovilli , N.H. March, L.A.Howand, A. Nagy, Exact Hamiltonian for an Analytic Correlated

Ground State Wave Function for He-Like Ions, Physics Letters A, ELSEVIER, 372, pp. 4053-4056, Maret 2008.

[17]. S .Bhattacharyya, A. Bhattacharyya, B. Taludar and N.C Deb, Analytical Approach to the Helium Atom Ground State using Correlated Wave Functions, J. Phys.B: At. Mol. Opt. Phys. 29, pp. L147-L150. 1996.

[18]. S.E.Koonin, D.C.Meredith, Computational Physics Fortran Version, Addison Wesley Publishing Company, 1985.

[19]. C. Schwartz, Ground State of the Helium Atom, Physical Review, Vol. 128, No.3, Nov 1962.

[20]. E. Buendia, F.J. Galvez, P.Maldonado, A.Sarsa, Explicitly Correlated Wave Functions for Atoms and Single Charged Ions from Li through Sr: Variational and Diffusion Monte Carlo Results, Chemical Physics Letters, 615, p. 21-25, October 2014.