

Calculation of Ground State Energy of Helium using Hylleraas Trial Function Expansion

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Abstract

Energy calculation of helium ground state has been done using the variational method. In this study the trial wave function of helium has been proposed which has included non linear parameters α and β . This wave function is a modification of the Hylleraas trial function. The trial wave function of helium is used to calculate helium ground state energy by varying the $l > n > m$ series so that the number of terms is 12, 15, 18, 20, 24, 30, 36, 40, 48 terms. By using the Powell method to perform functional minimization of the expectation value equation, the minimum energy obtained is the helium ground state energy which is -2.901501710650829 a.u. The value of variational parameters from the results of optimization is also obtained, which is non linear parameters α and β .

Keywords: Helium, Hylleraas Function, Variational Method.

I. INTRODUCTION

Helium is an atom that has two electrons and two protons, it has more than one particle, helium is called a many body system [1]. In such system there are various very interesting problems to study, one of which is the calculation of helium ground state energy. The calculations of various helium studies have been carried out calculating the helium ground state energy using the perturbation theory [2]. The result obtained from the study was -2.75 a.u. A different method has been carried out by Benerjee *et al.*, (2006) [3], who used the variational method to calculate the helium ground state energy. The result obtained from this study was -2,899 a.u. Montgomery *et al.*, (2010)[4] has examined the helium ground state energy under strong range. Analytically the calculation of helium ground state energy using the variational method has also been done by Griffith, (1992) [4] with the results of the study being -77.5 eV or 2,848 a.u. Furthermore Suleiman [6] has used the Monte Carlo variational method to calculate helium ground state energy and the formation of helium ions in the context of Bohn-Oppenheimer approach.

The results described above have a variety of relatively different values. One of the factors that play an important role in the energy value produced is the form of the wave function used.

From the results of previous research that have been described above, it is known that to get the ground state energy that approaches the experimental value, there should be a more realistic intuition in proposing a trial wave function [4]. The proposed trial wave function can display the presence of electrons in helium [7]. By selecting the trial wave function, the helium ground state energy is obtained and several variational parameter values are obtained. In this paper, we have used the shape of trial wave functions which includes non linear parameters α and β in calculating the helium ground state energy. By including these parameters in the Hylleraas trial function, this can produce minimum energy for Hylleraas trial function used in the expectation value equation.

Hylleraas, (1929) in Hetteema, (2000) [8] has chosen a trial wave function known as the Hylleraas function to calculate the helium ground state energy, but the research only counts up to 5 terms or 5 parameters without including α and β . While research by Thakkar and Koga, (2003) [9] included only α parameters. To study the calculation of helium energy further, this study focused on adding α and β parameters and varying the series $l > n > m$ which is the powers of bases of the modified Hylleraas trial function. This variation is done so that the ground state energy of a helium is obtained which is close to the results of experiments conducted by previous researchers. The value of l, m, n is the base exponent of Hylleraas trial function which consists of positive integers. The minimum energy value obtained by varying series $l > n > m$ can be used to obtain ground state energy results that are closer to the experimental results. In this study a series variation of $l > n > m$ was carried out containing 12, 15, 18, 20, 24, 30, 36, 40, 48 terms which were then solved using the Powell method to perform functional minimization of energy.

II. MATERIAL AND METODOLOGY

The software used in working on the research was the 2017b version of Matlab software for calculating ground state energy of helium and variational parameters. Before using the Matlab software, physics system modeling was done first, in this case the derivation of the helium system expectation value equation, which is the analytic form description, and continued with discrete form description.

1. The derivation of the expectation value equation in analytic form.

The trial function used to calculate the ground state energy of the helium with l, m, n positive integers is:

$$\psi = e^{-\alpha s} e^{-\beta t} \sum_{l,m,n=0}^{\infty} c_{n,l,m} s^n t^l u^m \quad (1)$$

this trial wave function includes α and β in the exponent of s and t . The trial function of equation (1) is a modification of the Hylleraas trial function. This function is used to calculate the helium energy value in this research.

The Hamiltonian for helium atoms can be shown as follows [5, 10] in a.u:

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

in which p_1^2 and p_2^2 is the sum of kinetic energy of electron 1 and electron 2. The next two terms $-(Z/r_1) - (Z/r_2)$ are the potential energy of electron 1 and electron 2, and the last term $\frac{1}{r_{12}}$ is the Coulomb interaction between two electrons. r_1, r_2 is distance electron 1 and electron 2 than nucleus. r_{12} distance between electron 1 and electron 2, Z is nuclear charge. The ground state of helium atom has zero spatial angular momentum, that is the state S , only the coordinates between particles $\{r_1, r_2, r_{12}\}$ can describe the ground state wave function. The Hamiltonian for S symmetry in coordinates $\{r_1, r_2, r_{12}\}$ can be written in the form [11]:

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + 2 \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}} \right) \frac{\partial}{\partial r_1} \frac{\partial}{\partial r_{12}} \right) - \frac{1}{2} \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - 2 \left(\frac{r_1^2 - r_2^2 - r_{12}^2}{2r_2 r_{12}} \right) \frac{\partial}{\partial r_2} \frac{\partial}{\partial r_{12}} \right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (3)$$

By using the Hamiltonian in equation (3), the Schrodinger equation can be written in the form [11, 12]:

$$\left\{ \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{4}{r_2} \frac{\partial}{\partial r_2} + \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \right) \frac{\partial}{\partial r_1} \frac{\partial}{\partial r_{12}} \right) + \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \left(\frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \right) \frac{\partial}{\partial r_2} \frac{\partial}{\partial r_{12}} \right) + 2 \left(E + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right) \right\} \psi = 0 \quad (4)$$

by substituting Hylleraas coordinates $s = r_1 + r_2$; $t = -r_1 + r_2$; $u = r_{12}$ to equation (4), the Schrodinger equation above can rewritten to

$$\left(\frac{\partial^2 \psi}{\partial s^2} + \frac{\partial^2 \psi}{\partial t^2} + \frac{\partial^2 \psi}{\partial u^2} \right) + 2 \frac{s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial^2 \psi}{\partial s \partial u} + 2 \frac{t(s^2 - u^2)}{u(s^2 - t^2)} \frac{\partial^2 \psi}{\partial u \partial t} + \frac{4s}{s^2 - t^2} \frac{\partial \psi}{\partial s} + \frac{2}{u} \frac{\partial \psi}{\partial u} + \frac{4t}{s^2 - t^2} \frac{\partial \psi}{\partial t} + \frac{4sZ\psi}{s^2 - t^2} + \frac{\psi}{u} = 0 \quad (5)$$

The volume element in the integral is $d\tau = 2\pi^2 (s^2 - t^2) u ds dt du$. Integral associated with Laplace operators can be written using theorem Greens, i.e.

$$-\int d\tau \psi \nabla^2 \psi = \int d\tau (\text{grad } \psi)^2 \quad (6)$$

So that the expectation value can be written in the form

$$\int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u(s^2 - t^2) \left[\left(\frac{\partial \psi}{\partial s} \right)^2 + \left(\frac{\partial \psi}{\partial t} \right)^2 + \left(\frac{\partial \psi}{\partial u} \right)^2 \right] + 2s(u^2 - t^2) \frac{\partial \psi}{\partial s} \frac{\partial \psi}{\partial u} + 2t(s^2 - u^2) \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial u} - (4Zsu - s^2 + t^2) \psi^2 \right\} = E \quad (7)$$

with normalization conditions of

$$\int_0^\infty ds \int_0^s du \int_0^u dt u(s^2 - t^2) \psi^2 = 1 \quad (8)$$

with Hylleraas coordinates for two electrons are $s = r_1 + r_2$; $t = -r_1 + r_2$; $u = r_{12}$ [8, 12, 13].

2. Derivation of energy expectation value by changing L, N, M to closed form

The trial function in equation (1) is ground state wave function of a helium, which is then substituted into the following equation:

$$M = \int_0^\infty ds \int_0^s du \int_0^u dt u(s^2 - t^2) \left[\left(\frac{\partial \varphi}{\partial s} \right)^2 + \left(\frac{\partial \varphi}{\partial t} \right)^2 + \left(\frac{\partial \varphi}{\partial u} \right)^2 \right] + 2s(s^2 - t^2) \frac{\partial^2 \varphi}{\partial s \partial u} + 2t(s^2 - t^2) \frac{\partial^2 \varphi}{\partial t \partial u} \quad (9a)$$

$$L = \int_0^\infty ds \int_0^s du \int_0^u dt (2Zsu - s^2 + t^2) \rho^2 \quad (9b)$$

$$N = \int_0^\infty ds \int_0^s du \int_0^u dt u (s^2 - t^2) \rho^2$$

$M L N$ can be converted into discrete form and by using the integral below for powers of Hylleraas coordinates, each term can be written in the form

$$[a, b, c] = \int_0^\infty ds \int_0^s du \int_0^u dt e^{-2\alpha s - 2\beta t} s^a t^b u^c$$

$$= \frac{b! (a+c+1)!}{(2\alpha)^{a+c+2} (2\beta)^{b+1} (c+1)} - \sum_{k=0}^b \frac{b! (c+k)!}{k! (2\beta)^{b+c+2}}$$

$$+ \sum_{k=0}^b \frac{b! (c+k)!}{k! (2\beta)^{b+c+2}} \sum_{p=0}^{c+k} \frac{(2\beta)^p}{p!} \frac{(a+p)!}{(2\alpha + 2\beta)^{a+p+1}} \quad (10)$$

Then $N L M$ can be described as follows

$$N_{ij} = \langle \psi_i | \psi_j \rangle = \int_0^\infty ds \int_0^s du \int_0^u dt \varphi_i \varphi_j u (s^2 - t^2)$$

$$= \int_0^\infty ds \int_0^s du \int_0^u dt e^{-2\alpha s} e^{-2\beta t} s^{l_i} t^{m_i} u^{n_i} s^{l_j} t^{m_j} u^{n_j} u (s^2 - t^2) \quad (11)$$

$$= [l_i + l_j + 2, m_i + m_j, n_i + n_j + 1]$$

$$- [l_i + l_j, m_i + m_j + 2, n_i + n_j + 1]$$

and so is L_{ij} can be displayed in discrete form, which is

$$L_{ij} = \int_0^\infty ds \int_0^s du \int_0^u dt (4Zsu - s^2 + t^2) \varphi_i \varphi_j$$

$$= \int_0^\infty ds \int_0^s du \int_0^u dt e^{-2\alpha s} e^{-2\beta t} s^{l_i} t^{m_i} u^{n_i} s^{l_j} t^{m_j} u^{n_j} (4Zsu - s^2 + t^2)$$

$$= 4Z [l_i + l_j + 1, m_i + m_j, n_i + n_j + 1]$$

$$- [l_i + l_j + 2, m_i + m_j, n_i + n_j] + [l_i + l_j, m_i + m_j + 2, n_i + n_j] \quad (12)$$

In the same way, M_{ij} can be described as follows

$$M_{ij} = \int_0^\infty ds \int_0^s du \int_0^u dt \left\{ u (s^2 - t^2) \left[\left(\frac{\partial \varphi}{\partial s} \right)^2 + \left(\frac{\partial \varphi}{\partial t} \right)^2 + \left(\frac{\partial \varphi}{\partial u} \right)^2 \right] \right.$$

$$\left. + 2s(u^2 - t^2) \frac{\partial \varphi}{\partial s} \frac{\partial \varphi}{\partial u} + 2t(s^2 - u^2) \frac{\partial \varphi}{\partial t} \frac{\partial \varphi}{\partial u} \right\}$$

$$= \int_0^\infty ds \int_0^s du \int_0^u dt (\alpha^2 u s^2 - 2\alpha d u s + l^2 u + \beta^2 u s^2 - 2\beta m u s^2 t^{-1} + m u s^2 t^{-2}$$

$$+ n^2 s^2 u^{-1} - \alpha^2 t^2 u + 2\alpha d u t^2 s^{-1} - l^2 u t^2 s^{-2} - \beta^2 u t^2$$

$$+ 2\beta m u t - m^2 u - n^2 t^2 u^{-1}) \varphi_i \varphi_j$$

$$+ \int_0^\infty ds \int_0^s du \int_0^u dt (-2\alpha n s u + 2l n u + 2\alpha n s t^2 u^{-1} - 2l n t^2 u^{-1}) \varphi_i \varphi_j$$

$$+ \int_0^\infty ds \int_0^s du \int_0^u dt (2m n s^2 u^{-1} - 2\beta n s^2 t u^{-1} + 2\beta n t u - 2m n u) \varphi_i \varphi_j \quad (13)$$

by including the function of $\varphi_i \varphi_j = e^{-2\alpha s} e^{-2\beta t} s^{l_i+l_j} t^{m_i+m_j} u^{n_i+n_j}$ into M_{ij} then the term is arranged based on the ground exponent of s, t, u and separated according to the base exponent, so that it can be written into

$$M_0 = (l^2 - m^2 + 2 \ln - 2mn) [l_i + l_j, m_i + m_j, n_i + n_j + 1]$$

$$M_1 = -(2\alpha l + 2\alpha n) [l_i + l_j + 1, m_i + m_j, n_i + n_j + 1]$$

$$M_2 = -(n^2 + 2 \ln) [l_i + l_j, m_i + m_j + 2, n_i + n_j - 1]$$

$$M_3 = (2mn + n^2) [l_i + l_j + 2, m_i + m_j, n_i + n_j - 1]$$

$$M_4 = 2\alpha l [l_i + l_j - 1, m_i + m_j + 2, n_i + n_j + 1]$$

$$M_5 = 2\alpha n [l_i + l_j + 1, m_i + m_j + 2, n_i + n_j - 1]$$

$$M_6 = -l^2 [l_i + l_j - 2, m_i + m_j + 2, n_i + n_j + 1]$$

$$M_7 = m^2 [l_i + l_j + 2, m_i + m_j - 2, n_i + n_j + 1]$$

$$M_8 = (\alpha^2 + \beta^2) [l_i + l_j + 2, m_i + m_j, n_i + n_j + 1]$$

$$M_9 = -(\alpha^2 + \beta^2) [l_i + l_j, m_i + m_j + 2, n_i + n_j + 1]$$

$$M_{10} = -2\beta m [l_i + l_j + 2, m_i + m_j - 1, n_i + n_j + 1] \quad (14)$$

$$M_{11} = 4\beta n [l_i + l_j, m_i + m_j + 1, n_i + n_j + 1]$$

$$M_{12} = -2\beta n [l_i + l_j + 2, m_i + m_j + 1, n_i + n_j - 1]$$

Equation (14) can be summed according to equation (13) above, i.e.

$$M_{ij} = M_0 - M_1 - M_2 + M_3 + M_4 + M_5 - M_6$$

$$+ M_7 + M_8 - M_9 - M_{10} + M_{11} - M_{12} \quad (15)$$

To determine the minimum energy value, this equation can be used:

$$\frac{M_{ij} - L_{ij}}{N_{ij}} = \text{Min} = E \quad (16)$$

with $M_{ij} L_{ij} N_{ij}$ has been described in the equations(15), (11) and (12). Equation (11),(12) and (15) is the closed form of L and M . Equation (16) can be calculated using the Powell method for functional minimization so that the minimum energy is obtained and all the variational parameters of α and β and the series coefficients are obtained from the minimization results.

III. RESULTS AND DISCUSSION

In this section, the results of calculation of helium ground state energy on the Hylleraas trial function that has been modified for various different values (n, l, m) and the values of variational parameters α and β and the series coefficients obtained from the optimization results. Calculations have been made for the trial function containing 12, 15, 18, 20, 24, 30, 36, 40, 48 terms based on the series $l > n > m$. The results of this study can be seen in Table 1 below that the minimum energy obtained from the results of this research is the helium ground state energy for various possible number of terms so that energy values are obtained which are closer to the experimental results. The experimental value the helium

ground state energy is -2.9033 a.u. [14] while the calculation results obtained Thakkar and Koga, (2003) is -2.903724 a.u [9]. From the results of the two previous studies, when compared with the results that have been obtained now, the values obtained in this research are very good and close to the results of previous studies, as shown in Table 1.

In this research variations in the value of series l , m , n are conducted, l is the exponent of s , m is the xponent of t , and n is the exponent of u . In the second column of the Table 1, the series can be formed as $l > n > m$, for the number of 12

terms, it is determined that l starts from zero to 3, m is zero, and n starts from zero to 2, similarly for the other number of terms presented in column 2, Table 1 .Overall, the helium energy obtained of this results is better than helium energy in the results of study Goldman, (1997) [16], while in Goldman, (1997) [16] the result was -2,879 028 767 319 214 au, whereas the result of this research ground state energy of helium was in the range of -2.899926367895268 a.u up to -2.901501710650829 a.u, as can be seen in the Table 1.

Table 1. The results of the helium ground state energy using the Powell method on the trial wave function contain the parameters of α and β obtained from the minimization results.

1	2	3	4
(N)	α	β	Energy (a.u)
12	1.731174090866450	-0.100824878029310	-2.899926367895268
15	1.723909993718208	-0.100832997386271	-2.899918010851687
18	1.716155584772583	-0.101224133547412	-2.899935192479800
20	1.723375068716193	-0.101367746997837	-2.899960976521080
24	1.753668997161519	-0.112850896820017	-2.900381719942969
30	1.759242309657156	-0.110906961903098	-2.900411150330968
36	1.752835178288679	-0.101993834675440	-2.900420928472252
40	1.731688913092266	-0.129621749529181	-2.900558763189716
48	1.687178104707943	-0.133236441747926	-2.901501710650829

But if every number of terms is observed, the more terms are given, the less energy is produced. From the results of the study, it can be revealed that to get more minimum energy, the choice of exponent u must be smaller than the exponent s , and the choice of exponent t must be smaller than exponent u . In this case the series $l > n > m$ is very influential for the minimum energy value produced. In addition to minimum energy, there are also parameters obtained from the optimization results, such as parameters of α and β . These parameters can be observed in column 2 and 3 in Table 1. α value is always greater than value β , in this case α and β are non linear parameters. Furthermore, the other parameters are series coefficients. The number of series coefficients corresponds to the number of terms desired.

In Table 1, it can be explained that N is the number of terms in Hylleraas function, by varying the series $l m n$ as in the Table 1, the number of series of functions depends on the

number of $l m n$ desired. In Table 1, it can be seen that the energy obtained from the results of this study is almost close to helium energy obtained from the experimental results [14] as well as the calculations performed by Thakkar and Koga, (2003) [15].

The results of the study Thakkar and Koga, (2003) [15] included one parameter at the exponential function, while this study included two parameters in their exponential functions, namely α and β . This results show that α is 1.7 and β is -0,1 which are called non linear parameters variational. Either α or β obtained from the results tends to be the same regardless of the number of terms given. In addition, overall, regardless of the number of terms given, the α value is always greater than β value. By using the Powell method to perform functional minimization of the expectation value equation, the helium ground state energy, parameter α and parameter β of trial function are obtained. More details can be

seen in Figure 1 which denotes the energy obtained for each number of terms given.

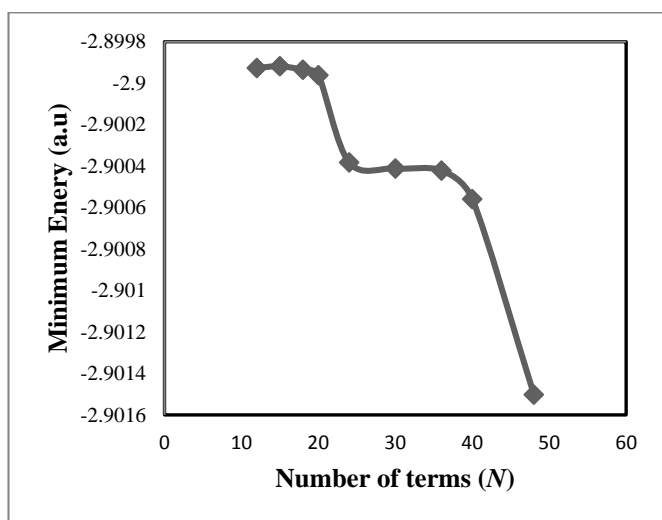


Figure 1: Graph of helium ground state energy vs. Number of terms

The graph in Figure 1 shows that with the increase in the number of terms given, the energy produced is increasingly minimum, the number of terms given starts from 12 terms to 48 terms.

IV. CONCLUSION

From the results of the research it can be concluded that the calculation of helium ground state energy has been carried out using the variational method. The helium ground state energy produced in this study is close to the results of previous research. The calculation of helium ground state energy has used the Hylleraas trial function which includes non linear as variational parameters in addition to the coefficients series of Hylleraas trial function which are other variational parameters. By varying the series of $l > n > m$ which is the exponent of Hylleraas coordinates, the Hylleraas trial function contains various numbers of terms which are 12, 15, 18, 20, 24, 30, 36, 40 and 48. The various numbers of terms have been used to calculate the helium ground state energy. The more number of terms given, the lower is the energy obtained, but variational parameter values are obtained either for α value or β value which tends to be constant for each number of term of function series given.

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