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Optimization of Trial Wave Function in Determining the Ground State Energy of Helium Atom

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ABSTRACT

The atomic ground state properties of helium, especially with regard to the ground state energy, can be studied by using various methods. Such method is the variational method. In this study, the atomic ground state energy for helium was calculated by using the trial wave function with four various parameters. The optimization process was performed by using Nelder-Mead method implied in script-code of Fortran. From calculation results, the symmetry new wave function, which meets both Pauli exclusion principle and Hund's rule, was obtained. This obtained wave function can be written as $\psi = 0.3891\exp(-1.9240\,r_1 - 0.9301\,r_2) + 0.3891\exp(-0.9301\,r_1 - 1.9240\,r_2)$. The atomic ground state energy obtained by this trial wave function is -79.004623 eV (with discrepancy of 0.000671% from the experimental energy), where this result is in good agreement with the experimental energy. It can be inferred that the obtained trial wave function is quite good in explaining the ground state properties of helium atom. In addition, the Nelder-Mead method used in this study has good capability in optimizing the equation with four variation parameters.

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INTRODUCTION

One method that can be used in studying the properties of atoms, especially related to the ground state energy, is the variational method, which is the basic-simple method and well-known in atomic structure. The obtained results by using this method were also quite good in explaining the experimental results of atomic energy (Griffith, 1995; Gasiorowicz, 2000; Irvine, 1999).

In this study, variational method is applied to study helium atom with different trial wave function, i.e. four parameters wave function. Generally, the variational method was applied to study the helium atom by utilizing the hydrogen wave function (Griffith, 1995; Gasiorowicz, 2000).

The basic principle of the variational method is to minimize the wave function in order to obtain the effective value of the used parameters so that the atomic ground state energy can be calculated. The purpose of this study is to calculate the ground state energy of helium atom by using the variational method.

The Hamiltonian operator (non-relativistic) for a many-electron (the n-electron) atom can be approached as (Levine, 1999):

$$\hat{H}_{NR} = \sum_{i=1}^{n}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i=1}^{n-1}\sum_{j>i}^{n}\frac{1}{\vec{r}_{ij}} \tag{1}$$

where Z is the atomic number, r_i represents the distance between the electrons and atomic nucleus, and r_{ij} represents the distance between the two considered electrons. For helium atom, the approximate Hamiltonian operator is written as (Griffith, 1995; Gasiorowicz, 2000; Hu *et al.*, 2006)

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{\vec{r}_{12}} \tag{2}$$

On the right-hand side of eq. (((2), the first two terms represent the kinetic energy of each electron. The next two terms represent the electrons potential energies in the Coulomb field of nucleus. The last term represents the energy associated with the electrostatic repulsion between the electrons. Therefore, the Schrodinger equation for helium atom can be written as:

$$\left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{\vec{r}_{12}}\right]\psi = E\psi \tag{3}$$

In the conventional spectroscopic notation, the electronic configuration in the ground state of helium is $1s^2$, where the quantum numbers, with $n = 1$, $l = 0$, and $m_l = 0$, are the same for the two electrons, so that the singlet is the only possible state. The state is $^1S_0$ since the wave function is spherically symmetric (Powell & Crasemann, 1961). In this case, the used trial wave function with four parameters can be approached as:

$$\psi = C_1\exp(-Z_1 r_1 - Z_2 r_2) + C_2\exp(-Z_2 r_1 - Z_1 r_2) \tag{4}$$

where C_1, C_2, Z_1, and Z_2 are the four variation parameters. The parameter of Z_1 and Z_2 are regarded as describing equaivalently the interaction shield between the electrons where C_1 and C_2 denote the constant. In order to make the helium atom to be at the ground state, the appropriate energy has to be minimized in eq. (((4), so that the four parameters should be set in the optimized value (Hu *et al.*, 2006). The ground state energy of helium atom obtained from experiment is -79.0051538 eV (Kramida *et al.*, 2018).

In this study, Nelder-Mead method was utilized to perform the optimization process because this method does not need the derivation of function. This method is very useful to optimize computational problems by using numerical method or to solve the analytic problems with unknown

gradient (Mathews & Fink, 1999). The ability of this method has been proven successfully in computing the function with two variation parameters (Mathews & Fink, 1999; Yulianto & Su'ud, 2016).

Table 1. The algorithm of *Nelder-Mead* method (Mathews & Fink, 1999).

Case (i)	
Determine vertex as B, G, and W	
Compute	
$M = (B + G)/2$, $R = 2M - W$, and $E = 2R - M$	
If $f(R) < f(G)$, then	
Perform case (ii) → either reflect or extend	
Else	
Perform case (iii) → either contract or shrink	
Case (ii)	Case (iii)
Begin	Begin
If $f(B) < f(R)$ then	If $f(B) < f(W)$ then
Replace W with R	Replace W with R
Else	Compute $C = (W + M)/2$
Compute E and $f(E)$	or $C = (R + M)/2$ and $f(C)$
If $f(E) < f(B)$ then	If $f(C) < f(W)$ then
Replace W with E	Replace W with C
Else	Else
Replace W with R	Compute S and $f(S)$
End if	Replace W with S
	Replace G with M
End if	End if
End Case (ii)	End Case (iii)

The step of this method is not so complicated. For example, consider $\boldsymbol{f(x, y)}$ as function. The first step, it is taken three trial coordinates, i.e. $(\boldsymbol{x_1, y_1})$, $(\boldsymbol{x_2, y_2})$, and $(\boldsymbol{x_3, y_3})$. After calculated, those coordinats are noted as follows: $\boldsymbol{B = (x, y)}$ as the best vertex (vertex with minimum value), $\boldsymbol{G = (x, y)}$ as good vertex, and $\boldsymbol{W(x, y)}$ as the worst vertex. Next step, the function is optimized by following the algorithm explained in Table 1. Many examples in optimizing the functions can be found in the following reference (Mathews & Fink, 1999).

METHOD

In this study, calculation process was performed semi-analytically, where the formulas were derivied analytically by using variational method and then the derived formula was optimized numerically by using Nelder-Mead method. All units in this study were set in atomic unit.

Derivation of Energy Formula

For helium atom case, the expected ground state energy showed by eq. ((3), can be determined by the eq. (5)

$$E = \frac{\int \psi^* \hat{H} \psi \, d\vec{r}}{\int \psi^* \psi \, d\vec{r}} = \frac{\int \psi^* \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{\vec{r}_{12}} \right] \psi \, d^3r_1 \, d^3r_2}{\int \psi^* \psi \, d^3r_1 \, d^3r_2} \tag{5}$$

where the integration performed only for radial part because the wave function ψ has only radial part so that the angular part can be neglected. It can be indicated that the helium atom investigated in this study is treated as spherical symmetry. The denominator in eq. (5) should be solved first and the obtained result is eq. (6)

$$\int \psi^* \psi \, d^3r_1 \, d^3r_2 = \frac{C_1^2 + C_2^2}{16 Z_1^3 Z_2^3} + \frac{8 C_1 C_2}{(Z_1 + Z_2)^6} \tag{6}$$

The operator of kinetic energy for radial part of spherical symmetry can be formulated as eq. (7)

$$-\tfrac{1}{2}\nabla_i^2 = -\frac{1}{2}\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{d}{dr_1}\right) \tag{7}$$

and the total of electron kinetic energy can be calculated by using eq. (8)

$$T_{\text{total}} = \int \psi^*\left[-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)\right]\psi\, d^3r_1\, d^3r_2 = \frac{(C_1^2+C_2^2)(Z_1^2+Z_2^2)}{32Z_1^3Z_2^3} + \frac{8C_1C_2Z_1Z_2}{(Z_1+Z_2)^6} \tag{8}$$

After that, the potential energies due to interaction between the electrons and the nucleus are calculated using eq. (9)

$$U_{\text{total}} = \int \psi^*\left[-\frac{2}{r_1}-\frac{2}{r_2}\right]\psi\, d^3r_1\, d^3r_2 = -\frac{(C_1^2+C_2^2)}{8Z_1^2Z_2^3} - \frac{(C_1^2+C_2^2)}{8Z_1^3Z_2^2} - \frac{16C_1C_2}{(Z_1+Z_2)^5} \tag{9}$$

Then, the potential energy due to inter-electron interactions, known as shielding effect, is solved to yield the eq. (10)

$$\begin{aligned} U_{\text{e-e}} = \int \psi^*\left[\frac{1}{\vec{r}_{12}}\right]\psi\, d^3r_1\, d^3r_2 &= \frac{C_1^2}{16Z_1^3Z_2^2} - \frac{C_1^2}{16Z_1^3(Z_1+Z_2)^2} - \frac{C_1^2}{16Z_1^2(Z_1+Z_2)^3} \\ &+ \frac{C_2^2}{16Z_1^2Z_2^3} - \frac{C_2^2}{16Z_2^3(Z_1+Z_2)^2} - \frac{C_2^2}{16Z_2^2(Z_1+Z_2)^3} + \frac{5C_1C_2}{2(Z_1+Z_2)^5} \end{aligned} \tag{10}$$

Finally, the eq. ((5) can be written completely as eq. (11)

$$\begin{aligned} E = \Bigg\{ &\frac{(C_1^2+C_2^2)(Z_1^2+Z_2^2)}{32Z_1^3Z_2^3} + \frac{8C_1C_2Z_1Z_2}{(Z_1+Z_2)^6} - \frac{27C_1C_2}{2(Z_1+Z_2)^5} - \frac{(C_1^2+C_2^2)}{8Z_1^2Z_2^3} - \frac{(C_1^2+C_2^2)}{8Z_1^3Z_2^2} \\ &+ \frac{C_1^2}{16Z_1^3Z_2^2} + \frac{C_2^2}{16Z_1^2Z_2^3} - \frac{C_1^2}{16Z_1^2(Z_1+Z_2)^3} - \frac{C_1^2}{16Z_1^3(Z_1+Z_2)^2} \\ &- \frac{C_2^2}{16Z_2^3(Z_1+Z_2)^2} - \frac{C_2^2}{16Z_2^2(Z_1+Z_2)^3}\Bigg\} \Big/ \left\{\frac{C_1^2+C_2^2}{16Z_1^3Z_2^3} + \frac{8C_1C_2}{(Z_1+Z_2)^6}\right\} \end{aligned} \tag{11}$$

Optimization Process

In this study, optimization process was performed with the help of script-code in Fortran style. The parameters mentioned in eq. ((4) are numerically optimized to obtain an optimal value for the ground state energy as formulated in the eq. (11). The energy tolerance applied in the script-code was set at 10^{-11} eV.

RESULT AND DISCUSSION

The results of the calculations in this study were also compared with the results of experiments and the calculations of other researchers. The calculation results obtained by this study and by Hu *et al.* are shown in

Table 2, where it can be seen that the calculation result is in good agreement with the experimental result, where the obtained deviation is less than 0.001% from the experimental result..

Table 2. The obtained parameters.

Parameter	Obtained results	
	This study	Hu *et al.* (Hu *et al.*, 2006)
C_1	0.3891	0.3825
C_2	0.3891	0.3825

Z_1	1.9240	2.1832
Z_2	0.9301	1.1886
Energy	-2.9034 a.u. -79.004623 eV	-2.8757 a.u. -78.251811 eV
Deviation	0.000671%	0.953536%

From the optimization results of these parameters, the eq. ((4) can be written completely as eq. (12)

$$\psi = 0.3891 \exp(-1.9240\, r_1 - 0.9301\, r_2) + 0.3891 \exp(-0.9301\, r_1 - 1.9240\, r_2) \quad (12)$$

This obtained trial wave function is symmetrical and can meet the rules required in the Pauli exclusion principle and Hund's rules. It can be indicated that the obtained trial wave function is quite good in explaining the ground state properties of helium atom. The obtained results of this study and other researchers can be seen in Table 3. Based on those results, it can be seen that the results obtained in this study are quite good as obtained by previous researchers.

Table 3. The ground state energy of helium atom.

Researchers	Energy (eV)	Deviation (%)
Kramida *et al.* (experiment) (Kramida *et al.*, 2018)	-79.005154	–
Hu *et al.* (Hu *et al.*, 2006)	-78.251811	0.953536
Fitzpatrick (Fitzpatrick, 2010)	-78.980000	0.031838
This study	-79.004623	0.000671

The results obtained in this study also imply that the used Nelder-Mead method has a good capability in performing the optimization process. This method is very good in optimizing the formulas without derivation function of those formulas. This is particularly useful when faced with the optimization process of equations whose derivative functions are complex enough to be determined analytically. In addition, this method can also be used to optimize equations with N variation parameters, especially with some modifications.

CONCLUSION

In this study, it has been calculated the ground state energy of helium atom by using the variational method with four variation parameters. The calculation process was performed by using script-code written in Fortran. From the calculation results, the obtained energy of helium atom is -79.004623 eV, where the deviation is 0.000671 % from the experimental results). From these results, it can be seen that the ground state energy obtained by using the variational method is in good agreement with the experimental energy. Thus, the variational method is very potential to be used in studying the atomic ground state properties, especially related to the ground state energy. In addition, the Nelder-Mead method used in this study has good capability in optimizing the equations to obtain a good enough parameter value in explaining the ground state energy of helium atom.

REFERENCES

Bransden, B.H. & Joachain, C.J. (1983). *Physics of Atoms and Molecules*. New York: John Wiley and Sons

Eisberg, R. (1985). *Quantum Mechanics of Atoms, Molecules, Solids, Nuclei, and Particles. Second Edition*. New York: John Wiley and Sons

Fitzpatrick, R., (2010). *Helium Atom*. Downloaded from *http://farside.ph.utexas.edu/teaching/qmech/lectures/node128.html* on Mei 25, 2018

Gasiorowicz, S. (2000). *Quantum Physics - Second Edition*. Singapore: John Wiley and Sons (Asia)

Griffith, D. (1995). *Introduction to Quantum Mechanics*. New Jersey: Prentice Hall

Hu, X.-Q., Xu, *J.,* Ma, Y., Zheng, R.-L. (2006). Four-Parameter Scheme for Ground Level of Helium Atom. *Commun. Theor. Phys.* 45(5): 906-910

Kramida, A., Ralchenko, Yu., Reader, J., NIST ASD Team. (2018). NIST Atomic Spectra Database (ver. 5.5.6). National Institute of Standards and Technology, Gaithersburg, MD. Downloaded from https://physics.nist.gov/cgi-bin/ASD/ie.pl on May 28, 2018

Levine, I.N. (1999). *Quantum Chemistry - Fifth Edition.* New Jersey: Prentice Hall

Mathews, J., Fink, K. (1999). *Numerical Methods Using Matlab - Third Edition*. New Jersey: Prentice Hall

Powell, J.L., Crasemann, B. (1961). *Quantum Mechanics.* London: Addison Wesley Publishing Company

Yulianto Y., & Su'ud, S. (2016). Investigation of nuclear ground state properties of fuel materials of ^{232}Th and ^{238}U using Skyrme-Extended-Thomas-Fermi approach method. *Journal of Physics: Conference Series*. 739: 012142.