ARTIKEL RISET

Numerical Calculation of Energy Eigen-values of the Hydrogen Negative Ion in the $2p^2$ Configuration by Using the Variational Method

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Abstract

Calculation of energy eigen value of hydrogen negative ion (H^-) in $2p^2$ configuration using the method of variation functions has been done. A work on H^- can lead to calculations of electric multipole moments of a hydrogen molecule. The trial function is a linear combination of 8 expansion terms each of which is related to the Chandrasekhar's basis. This work produces a series of 7 energy eigen values which converges to a value of -0.2468 whereas the value of this convergence is expected to be -0.2523. This deviation from the expected value is mainly due to the elimination of interelectronic distance (u) coordinate. The values of the exponent parameters used in this work contribute also to this deviation. This variational method will be applied to the construction of some energy eigen functions of H_2.

Keywords: variational method; energy eigen values; hydrogen negative ion.

1 INTRODUCTION

A variational method for constructing eigen functions is known as the method of linear variation functions [1]. The procedure of this method always starts with determining a trial function which is basically able to be considered as a combination of several terms.One term can be associated with a certain form of a basis function. In the central field approximation, the basis functions are the results of solving the Hartree-Fock equations. The forms of these basis functions constitute those of the radial functions of a hydrogenic atom. This work presents the process of constructing an eigen function for $2p^2$ configuration of hydrogen negative ion (H^-). H^- can be considered as the simplest molecule thus this work can be developed to an investigation of the properties of molecules. Since H^- has the properties of a molecule the central field approximation fails to describe the properties of H^- [2, 3]. This work uses the Chandrasekhar representation as the basis function which does not belong to the central field approximation.

As it is already mentioned the method of linear variation function starts with determining a trial function. This step is followed by calculating the average Hamiltonian where the average is carried out over the trial function. It is noted that each term in the trial function has a coefficient. The condition of the minimum value of the average Hamiltonian is formulated by varying the values of the coefficients. The result of this minimizing is an n^{th} power equation with the energy eigen value as the variable. n is the same with the number of terms in the trial function. This n^{th} power equation is actually a representation of an $n \times n$ determinant of zero value.

Most of the works concerning the method of linear variation functions are based on considering the trial function as an expansion of the analytic solution of the Schrödinger equation. In this work this solution is denoted by Ψ_{exact}. And the energy eigen value associated with Ψ_{exact} is E_{exact}. If the trial function consists of $q (q > 2)$ terms then $(q-1)$ steps have to be performed for verifying that the trial function is an expansion of Ψ_{exact}. The i^{st} step deals with the first $(i+1)$ terms of the trial function which means that $(i+1)$ energy eigen values are produced. If the lowest energy eigen value in each step is assumed to be the right value of the energy eigen value of $\mathrm{H}^- 2p^2$ then

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the result of these $(q-1)$ steps is a series of energy eigen values which is expected to converge to E_{exact}. This work presents a trial function which has 8 terms. The following paragraph presents several works which produces a series of energy eigen values.

Froese Fischer [4] showed a series of energy eigen values where one term in the trial function is associated with a configuration. The expansion of the wave function can be represented as

$$\Psi = \Psi_{1s^2} + \Psi_{2s^2} + \Psi_{3s^2} + ... + \Psi_{5g^2} \qquad (1)$$

The last term in equation (1) is the 11^{th} term. The series produces energies of helium $1s^2$ which converges to -5.806066 Ry. Her work is within the central field approximation framework. Hylleraas reported an energy eigen value calculation of the helium atom in the ground state in a paper edited by Hettema [5]. Bylicki and Bednarz presented their work on $2p^2\,{}^3P$ of H^- [6]. The trial function is the Hylleraas type wave function. A series of energy eigen values is showed by Fontenelle and Gallas in their investigation of the ground state of H^- [7]. The expansion of the wave function can be written in the form

$$\Psi(s,u,t) = cosh(\frac{1}{2}\varepsilon t(1+c_1 s+c_2 u+...+c_{15}s^4) \qquad (2)$$

This trial function is constructed based on the Chandrasekhar representation. In the case of helium $1s^2$, the series shown in (2) gives energies which converges to -5.807402 Ry. Ruiz applied the Hylleraas type wave function in her work on the ground state of B [8] which can be written as

$$\Psi(s,u,t) = Ne^{-s/2}\sum_{l,m,n} C_{l,m,n} s^{l-m}u^{m-n}t^n \qquad (3)$$

The $150^t h$ term of (3) gives energy of ground state of boron which has value of -49.082492 Ry. A series of H_2 ground state energy eigen values is produced by Sims et al [9] with the Hylleraas type functions as the constituents of the trial function. Albert in his thesis [10] presented a series of Li ground state energy eigen values. The trial function is a Hylleraas type function.

The present work is a modification of the work by Fontenelle et al.[7]. Reason to choose the work of Fontenelle et al is that the number of terms in the expanded wave function can be made small. Chandrasekhar representation is used for constructing a trial function which is then applied for evaluating energy eigen value of $2p^2$ configuration of H^-. It is noted that this work will be developed to the calculations of electric multipole moments of H_2. Since H_2 can produce H^- in a chemical reaction [2], results of evaluation of H^- structure may give valuable contributions to these calculations.

The trial function consists of 8 terms thus a series of 7 energy eigen values is produced. The series converges to a value of -0.2468 while the expected value is -0.2523 [6]. A function constructed from Chandrasekhar's basis normally uses three coordinates : s,t and u. s and t are the elliptic coordinates and u is the inter electronic coordinate. The existence of u makes the volume element in the integrals to be changed. In this paper the trial function does not involve u thus the integral calculations especially related to inter electron distance can be solved using the well known radial integrals. The deviation from the expected value is suspected to be due to the elimination of u.

2 METHODOLOGY

A form of the Hamiltonian for $\mathrm{H}^- 2p^2$ in rydberg unit is $(Z=1)$

$$\widehat{H} = -\frac{\partial^2}{\partial r_1^2} - \frac{\partial^2}{\partial r_2^2} - \frac{2}{r_1}\frac{\partial}{\partial r_1} - \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{2}{r_1^2} + \frac{2}{r_2^2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} \qquad (4)$$

r_1 and r_2 are the radial distances from the nucleus to the electron 1 and electron 2 respectively. r_1 and r_2 are the coordinates of the trial wave function which have to be evaluated from the Schrödinger equation:

$$\widehat{H}\Psi(r_1,r_2) = E\Psi(r_1,r_2) \qquad (5)$$

The trial function consists of 8 terms

$$\begin{aligned}\Psi(r_1,r_2) = N\varphi(r_1,r_2)(c_1+c_2(r_1+r_2)+c_3(r_1+r_2)^2 \\ +c_4(r_1+r_2)^2+c_5(r_1+r_2)(r_1-r_2)^2+c_6(r_1+r_2)^3+ \\ c_7(r_1+r_2)^2(r_1-r_2)^2+c_8(r_1+r_2)^4)\end{aligned} \qquad (6)$$

with

$$\varphi(r_1,r_2) = r_1 r_2(e^{-r_1/2}e^{-r_2/7}e^{-r_1/7}e^{-r_2/2}) \qquad (7)$$

which can be related to the Chandrasekhar representation. N is the normalization factor. The values of the exponent parameters (1/2 and 1/7) are determined based on the exponent parameters in the ground state radial function of H^- [2].

According to (6) there are seven steps which have to be done. Each step contains minimizing the average Hamiltonian

$$\left\langle \Psi \mid \widehat{H} \mid \Psi \right\rangle \qquad (8)$$

Table 1: The results of minimizing

Step	Energy eigen value
1	-0.23982036
2	-0.24345722
3	-0.24503189
4	-0.24632601
5	-0.24682411
6	-0.24632449
7	-0.24681800

Where Ψ in the i^{th} step is the first $(i+1)$ terms of (6). It is noted that the calculation of $\langle 2/r_{12} \rangle$ follows the work of Ruiz [8].

3 RESULTS AND DISCUSSIONS

The results of minimizing are shown in the following array

As it is already mentioned the energy is in the rydberg unit.

From the work of Bylicki and Bednarz [6], it can be noted that the expected value is -0.2523. Normally the Chandrasekhar function uses three coordinates : s,t and u whose relations with r_1 and r_2 are

$$s = r_1 + r_2; t = r_2 - r_1; u = r_{12} \tag{9}$$

Applying this coordinate system makes the Hamiltonian in equation (4) has to be transformed since u is independent of r_1 and r_2. This work remains in the r_1, r_2 coordinate system even though the trial function is a modification of that in the work by Fontenelle and Gallas [7]. The deviations of the results from the expected value can be related to the applied coordinate system.

4 CONCLUSIONS

The Chandrasekhar's basis is suitable for $2p^2$ of H^-. Improvement of the results can be done by optimizing the exponent parameter values. Construction of a trial function for H_2 in an excited state from Chandrasekhar's basis is recommended. Electric dipole moments in H_2 may be able to be related with electric dipole moments in H^- and H.

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References

1. Margenau H, Murphy GM. The mathematics of chemistry and physics. van Nostrand, Princeton, NJ. 1956;p. 438–442.
2. Rau ARP. The negative ion of hydrogen. Journal of Astrophysics and Astronomy. 1996;17(3-4):113–145.
3. Utomo Y. Application of linear variation method ontwo-electron system. Universitas Gadjah Mada; 2015.
4. Fischer CF. Hartree–Fock method for atoms. A numerical approach. 1976;.
5. Hettema H. Quantum chemistry: classic scientific papers. vol. 8. World Scientific; 2000.
6. Bylicki M, Bednarz E. Nonrelativistic energy of the hydrogen negative ion in the 2 p 2 3 P e bound state. Physical Review A. 2003;67(2):22503.
7. Fontenelle MT, Gallas JAC. On the use of Chandrasekhar's basis for helium and its isoelectronic series. The Journal of chemical physics. 1992;97(7):4986–4988.
8. Ruiz MB. Hylleraas method for many-electron atoms. I. The Hamiltonian. International journal of quantum chemistry. 2005;101(3):246–260.
9. Sims JS, Hagstrom SA. High precision variational calculations for the Born-Oppenheimer energies of the ground state of the hydrogen molecule. The Journal of chemical physics. 2006;124(9):94101.
10. Albert VV, Guevara NL, Sabin JR, Harris FE. Few-parameter exponentially correlated wavefunctions for the ground state of lithium. International Journal of Quantum Chemistry. 2009;109(15):3791–3797.