Calculation of Energy Expectation Values for He Atom by Using Improved Wave Function 2014

Aliaa'a A. Hassan

Department of Physics, College of Sciences, Thi-Qar University, Nassiriya, Iraq

Abstract: *The energies that evaluated for atomic and molecular systems have a huge important in theatrical and practical calculations and of a big consider in studding the properties of these system. There is clear the effects of correlation weave function in field studding different atomic and molecular structures and given reasons for many behaving of calculation properties of the system sin various physics field such solid state ,materials and atomic ,molecular physics .Through the recent research ,there is calculated the electron correlation in two electrons system by using a new function ,it was found in this study.That represent the correlation function which use configuration interaction principle. Correlation energy is evaluated for two electron (e . I He atom) as a close example .The energy value of research is compared with experimental energy value , with that value was evaluated from famous correlated (like Wiss 1961) and with energy value was calculated from best uncorrelated function that is Hartree – Fock wave function .This results point to wellness behave the new correlated function.*

Keywords: electron correlation, correlation energy, configuration interaction, HF approximation, uncorrelated wave function.

1. Introduction

Spite of the big role that Shrödunger equation did it ,as wave function which scrip a many of microscopic system ,that equation has a limit in treatment the solve of these weave function for miulty electrons systems .In attempts to solve the problem of these systems, many approximation featured, from famous and first and simple of that approximation was Hartree. When Hartree approximation suppose: that every electron moves with average potential result from the others electrons ,so the wave function for groups of electrons will equal to multiplication wave function for single electron [1].

$$\psi(1,2,3,.....,N) = \phi_1(1)\phi_2(2)\phi_3(3).......\phi_N(N) \quad (1)$$

Where $\phi_i(i)$ represents :the function of the coordinates of the location of the electron (i) . N:electronnumber in the atom .The basic decreaesment of this approximation – addition to neglecting of the correlation is neglecting indestigushbility principle ,because the wave function which describes fermions must be not anti symmetric and with represents of exchange for any groups of position and spin ordinates and that unfulfilled [2].

Hartree –Fock approximation is introduced by 1930 to treatment and solve the problems which appears in Hartree approximation .Hartree - -Fock approximation used self consisted filed (scf) ,which means that con approximate description between fermiouns systems in limit or through an effective single – particle model .The last model represents one of the basis in entanglements as measure. Fock used idea of spin movement through approximation for obtain appropriate function for multiple electrons systems, and that was profound impact in treatment the Hartree function 's problems to some extent. The total wave function for N electrons as [3][4]

$$\psi_{HF}(1\ 2\ 3\ldots N) = A\,\Pi(1\ 2\ 3\ldots N) \quad (2)$$

Where A:represerents antisymmetrized operator given as:

$$A = \frac{1}{\sqrt{N!}}\sum_p (-1)^p\ p \quad (3)$$

Operator have influent (-1) takes values from +1 to -1 for positive and negative substitutes, p is any electron's substitutes ,operator $\frac{1}{\sqrt{N!}}$ ensures the normalized of wave function [5] , Π can be defined by the following equation:

$$\Pi(\,1\,2\,3....N) = \left|\phi_1(1)\phi_2(2)\phi_3(3).......\phi_N(N)\right| \quad (4)$$

And as a slater matrix as:

$$\psi(1,2,3,\cdots\cdots N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix} \quad (5)$$

HF function has a part of position correlation between the electrons of parallel spin, that part is called Fermi – Hole ,which represented the difference between the inter particle distribution function for single and triple inter shells [4].

$$\Delta f_F(r_{12}) = f(r_{12})_{KL(^3s)} - f(r_{12})_{KL(^1s)} \quad (6)$$

That correlation make the energy of HF approximation less than that of Hartree approximation. In Quantum mechanics correlation energy is defined as the energy error of HF limit energy of HF w.f , i.e that is the difference between the HF function and the exact solution for nonrelativistic shrödinger equation. There also exists other of electron correlation such as the statically correlation coefficients and shanon entropy as measure of the correlation strength[6] .The old defining of correlation energy that of Löwdin that was the difference between exact eigen value of energy Hamiltonian operator and it is expectation value in HF function for state interest

[2] . Electron correlation has a strong effect on many atoms , molecules and solid characteristics ,so developed many correlation function to calculate energies and properties , where Matson 1960 evaluate configurations interaction by using 37 configuration for Be – atom included the ground of HF [7] .Wiss concluded wavefunction include changed criteria [8] and successful approximations for many multi system. Restoration or calculation correlation energies for many systems is stilling representation one of biggest challenges in quantum mechanics .

2. Theory

Electron correlation is a general expression which describes interaction indevisiuall electrons with each others ,in another way and relative electrons' charged ,every electron avoids others electrons ,so any electron moves in multi electron atoms .Other electrons which inside that system will change their location for keeping stability system .There two types of electron correlation ,Fermi hole and Coulomb hole .[9] .Configuration interaction (CI) of important formulas and principles which used in building correlation function that based on assumed electron configurations. In this study ,function is created consist of eight assumed electronic states or configuration ,and that will be function consists of 13 terms in other to describe correlation function for He –atom. Assumed electronic states is:

$$1s^2 + 1s3s + 3s^2 + 1s3s' + 2s3s + 2s3s' + 3s'^2 + 2s'3s' \quad (7)$$

Every one term gives two others ,every terms in above stat are multiplication by C_i constant of self consisted field (scf), where I is numbers are given for sequence's terms . In this study is gotten a normalized for above arrangement and with accurately arrived to nine after decimal ,and obtained have energy for two electrons system by using equation of total density.

Total density for correlation function was:

$$\rho(r_1, r_2) = \psi^2(r_1, r_2) \quad (8)$$

So one – particle radial distribution function was:

$$D(r_1) = \int_0^\infty \rho(r_1, r_2) r_1^2 r_2^2 \, dr_2 \quad (9)$$

And one – expectation value as :

$$\langle r_1^n \rangle = \int_0^\infty D(r_1) \, r_1^n \, dr_1 \quad (10)$$

$$\langle r_{12}^n \rangle_{CI} = \int_0^\infty f(r_{12})_{CI} \, r_{12}^n \, dr_{12} \quad (11)$$

Where $f(r_{12})$ inter – particle distribution function which study the effectiveness of distance's changing between the electrons. The energy has been evaluated as the following :

$$\langle E \rangle = \frac{1}{2} \langle \hat{V} \rangle \quad (12)$$

3. Results and Discussion

Correlation energy is calculation under eq.(12) by using an improved function (2014) as seen before. Experimental energy value for two electrons system such He - atom equal to (-2.90372 Hartree), and energy value which evaluated by used best uncorrelated wavefunction (HF) [10] was (-2.8617 Hartree) .In this study the energy value is calculated from two electrons system and the value equal to (-2.90599 Hartree) . The comparison between the energy value of improved function in this study and experimental energy value, gives that values have a good close from each other. The difference between its apprises (-0.0027 Hartree) , that result point to that the function has a good behavior about electronic correlation.

Table 1: shows the results of calculating the energy values by present work and comparision with other functions for He atom.

Atom	Result and comparison	Wave function	(-) Energy value(Hartree)
He	Experimentalism		2.90372
	P.W(2014)	CI	2.905991
	Ref.[10](2012)	CI	2.92281
	Ref.[10](2012)	CI	2.93572
	Ref.[11](2007)	CI	2.895
	Ref.[12](2007)	CI	2.846
	Ref.[12](2007)	SCI	2.8225

4. Conclusions

Based on the results that appear in the table above from the present work by the improved correlated function, the following can be concluded :the wave function improved in this work has a good behavior about electronic correlation , that appears from the comparisonthe value of energy of He-atom with another values from previous studies,the table shows a little difrent between the P.W and the experimantal value, and that of P.W value is best that of HF (best uncorrelated function) so is neer to the experimental value.

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Author Profile

Aliaa'a A. Hassan got BS physics from science college /Thi-Qar university 2005. Shre received degree of M.SC in theoretical physics from university of Bagdad 2012. She published two papers, one by Journal of Thi-Qar scince 2013, another paper by International Journal of Advance Research 2014. Se was borm in Iraq at Thi-Qar and working as Assistant Lecturer in physics department of science college in university of Thi-Qar.