

# Evaluated Some Atomic Properties of Helium Atom using Full Configuration-Interaction (CI) Approach

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**Abstract**—Atomic properties of the helium atom are studied using a full configuration –interaction (CI) approach. The radial density distribution function  $D(r_1)$ , single-particle  $\langle r_1^n \rangle$  and pair-particle  $\langle r_1^2 r_2^2 \rangle$  radial expectation values, difference of density  $\Delta D(r_1)$  and the average density at origin  $\rho(0)$  are calculated with trail correlated wave function. The radial density has a peak around the radius  $r_1=0.63$ . The difference  $\Delta D(r_1)$  oscillates up and down at short range until converged to zero at long range, and it has large positive value at point of radius. Near the nucleus, the electron density increases according to positive value of  $n \neq 0$ . The pair- particle expectation value increases with negative value of  $n$ . Finally,  $\rho(0)$  has a large magnitude 3.76.

Calculation show that the current method can produce accurate results. Comparisons are also made with previous works.

**Keywords**—Atomic properties, Configuration –interaction, Helium atom.

## I. INTRODUCTION

The Hartree method is useful introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent field, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate: it is wrong, by construction, since its wave function is not antisymmetric! A better approach, that correctly takes into account the antisymmetric character of the wave functions is the Hartree- Fock approach[1]. The Schrodinger equation for many electrons system:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i < j} \sum_{i=1}^N \frac{1}{r_{ij}} \quad (1)$$

Hartree approach take the form:

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

where  $\phi_i(\mathbf{i})$  is function of spatial coordinate electron  $i$ ,  $N$  is number of electrons. Hartree – Fock theory is fundamental to much electronic structure theory. It is the basis of atomic and molecular orbital ,which posits that each electron's motion can be described by a single- particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. Hartree - Fock theoretical method often provides a good starting point for more elaborate theoretical method which are better approximations to the electronic Schrodinger equation [2]. In this approximation the  $N$ -electron wave

function is written as the antisymmetrised product of  $N$  one-electron functions or orbitals. The introduction of one-electron functions in the description of the  $N$ -electron system is a conceptually and computationally attractive simplification. The total wave function for  $N$ - electron system as:

$$\Psi_{HF}(1\ 2\ 3 \dots N) = A \Pi(1\ 2\ 3 \dots N) \quad (3)$$

$A$ : represents antisymmetrized operator (see [3]). So the  $\Psi$  be as Slater matrix:

$$\psi(1,2,3,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \dots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \dots & \phi_N(N) \end{vmatrix} \quad (4)$$

where  $\frac{1}{\sqrt{N!}}$  is normalization constant , $N$  is number of electrons.

In the calculation of the HF orbitals the instantaneous interaction between the electrons is replaced (approximated) by the interaction of an electron with the average field generated by the other  $N-1$  electrons. The correlation of the electronic movements due to partially the electronic repulsion (Coulomb correlation) is neglected in the HF approximation [4]. Atomic HF equations give physical properties of various atomic systems in the non-relativistic independent particle approximation. But these methods still needs many sophisticated mathematical and programming techniques to evaluate an atomic property. The 1S2 configuration plays an important role in the quantum mechanical calculations for its simplicity and applicability as a system to calculate some of its atomic properties like the evaluation of the [5].

The Hartree-Fock solution is not exact: it would be if the system under study were described by a wave function having the form of a Slater determinant. This is in general not true. The energy difference between the exact and Hartree- Fock solution is known as correlation energy and there are clear correlation effects on atomic properties . The origin of the name comes from the fact that the Hartree-Fock approximation misses part of the "electron correlation": the effects of an electron on all others. This is present in Hartree- Fock via the exchange and electrostatic interactions; more subtle effects are not accounted for, because they require a more general form of the wave function [1]. The CI method is often employed by chemists when studying atom or small molecules, in this

method the energy is minimized by searching through all  $\psi$  which are linear combinations of N -electron determinants . In the method of the configuration interaction, the definition of correlation energy according to Löwdin ,is the difference of energy between the correlated wave function(CI approach) and that calculation of best un correlated wave function that is Hartree-Fock approach[6].the wave function is proposed as a linear combination of many-electron system:

$$\Psi = \sum_i c_i \Phi_i \quad (5)$$

where  $\Phi$  is an anti- symmetrized product of one – electron functions, its bases function Slater Type Orbital (STO's) .The coefficient C is taken to minimize the total energy, output of Self Consisted Field(SCF). It give as [7][8]:

$$\chi_{nlm_\ell}(r, \theta, \phi) = R_{nl}(r)Y_{lm_\ell}(\theta, \phi) \quad (6)$$

where  $R_{nl}(r)$  represented diagonal part and  
represented angular part:

$$R_{nl}(r) = N_{nlm_\ell} S_{nl}(r) \quad (7)$$

where  $N_{nlm_\ell}$  represented normalization constant ,given as :

$$N_{nlm_\ell} = \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} \quad (8)$$

$\zeta$  : orbital exponent ,that who represent the nucleus charge.

And:

$$S_{nl}(r) = r^{n-1} e^{-\zeta r} \quad (9)$$

The atomic properties give a clear and good seeing about the natural of the system that under working .

Watson at 1960 evaluated configuration –interaction ,that was by used 37 configurations for Be-atom Z=4 and tis included the ground state of Hartree- Fock approach [9]. The Appropriate wave function is concluded by Weiss at 1960 which consisted of changing Standards and he limited the best kind by Reduction of expectation value of energy in that wave function , and find one of best methods of Hartree- Fock approach[10]. Coulson and Neilson have obtained a new form for inter – particle distribution function of ground state of Helium atom and evaluated two particle (paire-particle) expectation value ,they used it to explain diffident degree of correlation of wave function. They calculated coulomb hole, that was at 1961 [11]. Banyard and Baker at 1969, they studied correlation of different (opposite) spin electrons of Li+, He, H- by used three different wave function , first was configuration –interaction, second is included Hylleraas-type correlation factors and the third was foundation from Hartree- Fock approach and from difference of density  $\Delta D(r_1)$ , showed the correlation of wave function rative an correlated approach[12]. Clementi and Rotti 1974, has been found analytical method to calculate Hartree-Fock approach of excitation states for 54 elements [13]. Banyard and AL-Bayati studied spatial correlated for Series of Lithium atom –like systems inside the intra shells ,and they calculated coulomb and partial coulomb – hole and some atomic properties for the shells [14]. Enas Al- Robayi studied electron correlation in spatial and momentum space of closed systems He, Li and Be and atoms like its, that was by studied

coulomb and partial coulomb – hole, at 2006 [15]. Sabah M. Aman Alla ,2007, calculated many function and atomic factors by used two approaches wavefunction :Hartree – Fock and Weiss ,calculated correlation energy for closed shells of some atomic and ionization systems and studied some atomic properties for that system [16].

## II. COMPUTATION DETAILS

Hartree-Fock theory neglects the instantaneous interaction between the electrons, the so-called electron correlation. However, even in a more exact theory: where electron correlation is included, the atomic orbital concept survives - in terms of the natural orbitals. The natural orbital concept has become a powerful tool for analysing complex wavefunctions, and has also been used in developing methods for determining accurate wavefunction . A single configuration description of the electronic structure is not sufficient; the wave function must comprise several electronic configurations in order to be even qualitatively correct. This leads immediately to a multi-configurational self-consistent field (MCSCF) theory as the natural extension of the Hartree-Fock method [17] . Configuration interaction (CI) is one of important formula which used in building correlation function that based on assumed electron configurations. The main idea of correlation interaction CI is based on the expansion theorem. Let  $\psi_i, i=1, \dots, \infty$  be a complete basis of the one-particle Hilbert space [18].

$$\Psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 \dots C_n\psi_n = \sum_{S=1}^n C_S\psi_S \quad (10)$$

In this work ,the wavefunction is created consist to eight terms, which assumed that electronic states or configuration , will be function consists of 13 terms in order to describe correlation function for He –atom. Assumed electronic states is the shape of approximation (configuration interaction) which will use to study and evaluate the atomic properties is[19]:

$$1s^2 + 1s3s + 3s^2 + 1s3s' + 2s3s + 2s3s' + 3s'^2 + 2s'3s' \quad (11)$$

from the form eq.(11),the first configuration represented the ground stat of He-atom, which woke of Hartree- Fock and the second is inter shell 1s and 3s orbitals (that excited state) represented the configuration which some electron have been moved into higher energy orbitals which are un occupied .There is closed and inter assumed shells ,the orbital s' has another direction .

$$\Psi(r_1, r_2) = \frac{1}{2} (\psi_1(r_1, r_2) + \psi_2(r_1, r_2) + \psi_3(r_1, r_2)) \quad (12)$$

the function consisted of three parts because of there is big number of contain on one function and 1/2 represented the normalization . The total density is:

$$\rho(r_1, r_2) = \psi^2(r_1, r_2) \quad (13)$$

we used limited integral ,three orbital exponents, eight constant factories and twelve equation to expression the trail orbitals. We used Mathcad-2007 computer programs ,ver.14 .

The properties under investigation include the following:

### 2-1 One- particle radial distribution function $D(r_1)$

The radial density distribution function  $D(r_1)$  is extreme importance in the study of atoms and ions because it measures the probability of finding an electron in each shell. It is defined as:

$$D(r_1) = \int_0^{\infty} \rho(r_1, r_2) r_1^2 r_2^2 dr_2 \quad (14)$$

where  $r_1, r_2$  are the distance between the two electron and nucleus.

### 2-2 One- particle expectation value $\langle r_1^n \rangle$

It is defined as a probability of electron position in a certain point near the nucleus and electron charge cloud distance for every electronic shells, and it is related to  $D(r_1)$ . The One-particle expectation value is given as:

$$\langle r_1^n \rangle = \int_0^{\infty} D(r_1) r_1^n dr_1 \quad (15)$$

The equation above (eq.(15)) indicate that the one- particle expectation value is taken to different positions of space that from various values of  $n$ . The normalization is done at  $n=0$  so  $\langle r_1^0 \rangle = 1$ .

### 3-2 Inter -particle expectation value $\langle r_{12}^n \rangle$

Before talking about the inter- particle expectation value, it must considering the another important factor, it has a direct relation with inter-particle expectation value, that is inter-particle distribution function  $f(r_{12})$ , where  $f(r_{12})$  is the probability distribution distance between two electrons 1,2.

$$f(r_{12}) = \int \Psi(r_1, r_2) d\tau_1 d\tau_2 \quad (16)$$

The inter - particle expectation value  $\langle r_{12}^n \rangle$  with  $f(r_{12})$  is given as:

$$\langle r_{12}^n \rangle = \int_0^{\infty} f(r_{12}) r_{12}^n dr_{12} \quad (17)$$

which represents expectation value when  $-2 \leq n \leq +2$ . Where:  $n$  is expression position near the nucleus.

### 4-2 The difference between $D(r_1)$ in correlated and uncorrelated wave function $\Delta D(r_1)$ :

It can be determined using the equation :

$$\Delta D(r_1) = D_{CI}(r_1) - D_{HF}(r_1) \quad (18)$$

That shows the part of deference between correlated and uncorrelated function.

### 5-2 Electron density at the nucleus $\rho(0)$

The concept of a spherically averaged electron density  $\rho(0)$  is applicable to both an atom in a molecule and a spherically symmetric atom. The spherically averaged density is then given by [20] The electron density at the nucleus can be evaluated using the following form:

$$\rho(0) = \frac{D(r_1)}{4\pi r^2} \quad (19)$$

## III. RESULT AND DISCUSSION

The above atomic properties which is taken about it, have been results in two way in this work, one by best uncorrelated function that represented Hartree - Fock (that data taken from [21] and result from [3]) approximation another by configuration interaction approximation that is q.(3). The atomic properties take to He - atom which have two electrons in K-shell ( $1s^2$ ) that is original stat of atom, the correlation function has been included addition to this state (7states) (configurations) by made virtual orbital's and that gave the previous function (eq. (11)). The results of the atomic properties mention above by using correlated function and by Hrtree - Fock approximation that were as the following :

### A- One- particle radial distribution function $D(r_1)$

The table (1) and show the results of one - particle radial distribution function by using CI, from eq.(14) data which used in [19] and HF use data from [3] approximations. The table shows that the maximum of  $D(r_1)$  and the radius relative to it. The table shows that there is a difference between the value of CI in this work and of HF approximations, that difference come from the correlated effect. The note is the increasing of Max  $D(r_1)$  when using correlation functions and the same word on the position of that Max  $D(r_1)$ , the little increased appeared in curve of CI work has a few relative perturbation of work approach because the big number of constant factories.

Table 1: Maximum values of  $D(r_1)$  and its position by using CI approach and comparison with another studied and with HF approach. (P.W=present work)

W.F	Result and comparison	$R_1$	Max $D(r_1)$
CI	P.W	0.63	1.1744
	Ref.[3]	0.509	0.7806
	Ref.[22]	0.535	0.9217
HF	Ref.[3]	0.576	0.86646

The [3] used Configuration Interaction approach and [22] used weiss waves approximation.

### B- The difference between $D(r_1)$ in correlated and uncorrelated wave function

The Figure shows the difference between the results obtained by HF and CI wave functions for one particle radial densities for He. From this figure, we can see that is near the nucleus, the one particle radial density obtained by CI is larger than that obtained by HF because of the effect of electronic interaction which have been neglected in HF wave function and the effect of attraction force of the nucleus. There is a small area in the beginning of carve is represented the effecting of electron correlation that appears as a shifting of a curve

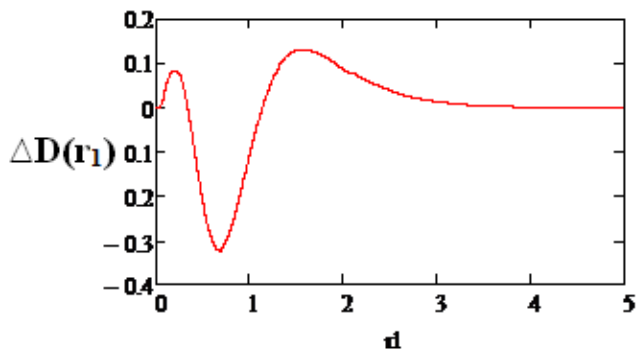


Figure 1: The difference  $\Delta D(r_1)$  between correlated (CI) and uncorrelated wave function (HF).

### C- One particle expectation value $\langle r_1^n \rangle$

Table (2) includes the values of one particle expectation  $\langle r_1^n \rangle$  by applying the eq.(15), and compare our result Eq.(12) uncorrelated wave function that is HF and with Previous studies which used CI approach and weiss functions . In general, the density of electron about the nucleus in the position near the positive charge is increasing  $n = -1$  and  $-2$  ;in the far position of nucleus that is  $n = +1$  and  $+2$  decreasing ,but in He - atom is increasing from  $+1$  to  $+2$  because the shell  $K(1s)$  is distant from the nucleus ,that in both wave function HF and CI and at  $n = 0$  the  $\langle r_1^n \rangle$  is equal to 1, because the normal verifier of the wave functions. The values of  $\langle r_1^n \rangle$  is deferent between HF and present work ,that deferent is because of the electron correlation.

Table 2: the one - particle expectation value  $\langle r_1^n \rangle$  by CI aproch and comparisons with another studied (used CI and Weiss) and with HF approach.

W.F	Result and comparison	n=-2	n=-1	n=0	n=+1	n=+2
CI	P.W	5.6771	1.749	1	0.7719	0.731
	Ref.[23]	6.7622	1.6100	1	1.0273	1.5051
	Ref.[16]	6.5788	1.7706	1	0.9045	1.171
HF	Ref.[3]	5.9941	1.6872	1	0.9273	1.185

### D- Inter particle expectation value $\langle r_{12}^n \rangle$

The results of inter- particle expectation value in table (3) ,that of applied electron correlation in position and compression with another studies and with Hartree - Fock wave function .

Table 3: Inter particle expectation value  $\langle r_{12}^n \rangle$  by CI wave function and comparisons with another studied (used CI and Weiss) and HF.

W.F	Result and comparison	n=-2	N=-1	N=0	N=+1	N=+2
CI	P.W	2.2745	1.1839	1	1.1023	1.4623
	Ref.[16]	1.8247	1.0144	1	2.3696	1.3402
	Ref.[3]	1.54545	0.9183	1	1.5546	3.0986
HF	Ref.[3]	1.8422	1.0258	1	1.3622	2.3705

The one particle expectation values increased from  $n=-1$  to  $n=-2$  (especially for He-atom because of that have one shell (k-shell)) and that values in CI wave approach is more than that of HF approach that cause of correlation effectiveness, the same effectiveness make the value of  $\langle r_{12}^n \rangle$  at  $n=+1$  and  $+2$  less than that of HF. The values of  $\langle r_{12}^n \rangle$  are decreasing from  $+2$  to  $+1$ .The comparison with the another studies shows near the results .

### G- Electron density at the nucleus $\rho(0)$

Table (4) shows the results of the electron density at the nucleus  $\rho(0)$  obtained by Hartree- Fock and correlated wave functions CI for He – atom . It is clear from the results that the result of  $\rho(0)$  obtained by this work, it appears a good close from the previous studies ,and the different between the values by using HF and CI wave function is because of Coulomb attraction forces.

Table 4: Electron density at the nucleus  $\rho(0)$  by CI approach and comparisons with another studied and with HF approach.

W.F	Result and comparison	$\rho(0)$
CI	P.W	3.760
	Ref.[24]	4.001
HF	P.W	3.592
	Ref.[24]	3.596

## IV. CONCLUSION

We conclude that the correlation wave function which obtained by using CI method is a good behavior and that appears from the atomic properties of He atom as present work . Comparison the results with another of HF wave function from one side and with previous studies, all that prove acceptations of the work function. The difference which appear between the result of this work and that of the previous studied it came from the verity of the factories, constant and generally the overall requirements of each method ,may make kind of different between them. One of the future studies is evaluation coulomb hole by using the same correlation wave function and some other atomic properties .

## REFERENCES

- [1] Slater J. C (1963). The electronic structure of Atoms- the Hartree-Fock Method and Correlation. review of modern physics, 35 (3).
- [2] Barone V.( 1994). Inclusion of Hartree-Fock exchange in the density functional approach, Benchmark computation for diatomic molecules containing H, B, C, N, O and F atoms. Elsevier Science B. V, chemical physics letters (226), 392-398.
- [3] Hassan A. A. (2012) ,M.cs. thesis .Calculation of Electronic Correlation of He , Li and Be Atoms by Using Improved Wave functions. College of Science for Women , Baghdad University, Baghdad, Iraq,.
- [4] Buijse M. A. (1991) . Electron correlation Fermi and Coulomb holes dynamical and nondynamical correlation. Centrale Huisdrukkerij Vrije University, Electronic Theses and Dissertation (ETD), Amsterdam.
- [5] Ameen W. A. (2012) . A linear relation to calculate one particle expectation value for  $1S^2$  configuration  $\langle r^{-1} \rangle$  for  $2 < Z < 100$ . J. of university of anbar for pure Science, 6(1).
- [6] Löwdin P. O.( 1959). Correlation problem in many quantum mechanics. Physical Review ,(2), 207-322.
- [7] John p. and Kirk A. (2005). Quantum Chemistry .3rd edition ,Elsevier Chapter .5 Academic Press USA147.
- [8] Blinder S. M. (1965). Am. J. Phys., 33(6), 431.
- [9] Watson R. E. (1960). Unrestricted Hartree-Fock method: electron densities and magnatic form factors for spin polarized  $Ni^{++}$ . Phys. Rev. , 19 (1) , P.170.
- [10] Roothaan C. C. J. and Weiss A. W. (1960) , Rev. Mod. Phys. , 32( 2) , P. 194.



- [11] Coulson C. A. and Neilson A. H. (1961). Electron correlation in ground state of Helium. Proc. Phys. Soc. , 78 ,P.831.
- [12] Banyard K. E. and Baker C. C. (1969). Molecular formation and electron correlation in HeH<sup>+</sup>. J. Chem. Phys. , 51(6) ,p. 2680 .
- [13] Boyd R. J. and Yee M. C. (1982) .Angular aspects of electron correlation and the coulomb hole. J. Chem. Phys. , 77(7),3578-3582.
- [14] Banyard K. E. and Al-Bayati K. H. (1987). Intera-and inter-shell correlation effects in Li-like ions: an analysis of the first excited state. J. Phys . B: Atom. Molec. Phys.,20, 405-473.
- [15] Al- Robyi E.( 2006) , Ph .D Thesis. A study of coulomb hole for the ground study in momentum space for He-like and Li-like ions. Baghdad University (Ibn-Al Haitham), Baghdad, Iraq.
- [16] Aman Alla S.M.( 2007), Ph.D Thesis. Electron Correlation for Many Atomic and Ionic Systems. Baghdad University (Ibn-Al Haitham), Baghdad, Iraq.
- [17] Roos B. O. and Taylor P. R. (Chemical Center), Siegbahn E. M. (institute of theoretical physics). (1980). A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approaches. Chanical Physics (48), 157-173.
- [18] Staemmler V.( 2006). Introduction to Hartree-Fock and CI Methods. Chair of Theoretical Chemistry Ruhr-University at Bochum Universit`atsstr. Bochum, Germany (31), 1-18.
- [19] Hassan A. A. (2014) . Calculation of Energy Expectation Values for He Atom by Using Improved Wave Function 2014. International Journal of Science and Research (IJSR), 3(10), 377-379.
- [20] Mastalerz R., Widmark P., Roos B. O., Lindh R., and Reiher M.( 2010) Basis set representation of the electron density at an atomic nucleus. J. of chemical physics 133, 144111 .
- [21] Sara A., Gálvez F.J. and Buendia E. (2004). Atomic Data and Nuclear. 88(1), 163-202.
- [22] Naji M.N (2004). Ph.D Thesis. Evaluation of X-ray Scattering factor for closed shell atoms using Hartree Fock and correlated wavefunction. College of Education (Ibn-AL-Haitham) Baghdad University, Baghdad, Iraq.
- [23] Hassan A. A. and Al-Bayati K. H.(2014). Calculation of One-particle radial distribution function and One-particle expectation value for K(1S) shell of He and Li atoms by Using Correlated function. J. of Thi \_Qar science, 4(4), 24-27.
- [24] AL-Bayati K. H. , Taki A. K. and Murshed M. N (2007). A study of some tomic properties for He-like selected ions. Um-Salama Science Journal, 4(2), 301-304.