Republic of Iraq
Ministry of Higher Education
And
Scientific Research
AL-Nahrain University
College of Science

Determination the Effect of Coulomb Correlation for He And He-Like Ions Using Different Wave Functions

A Thesis
Submitted To the College Of Science Al-Nahrain University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Physics

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June *2007*

بسم الله الرحمن الرحيم

ويسألونك عن الروح قل الروح من أمر ربي وما أوتيتم من
العلم الا قليلا

صدق الله العلي العظيم

سورة الإسراء
الآية (85)

الى من اهب لة دمي الى و طني العراق ....

الى من رباني و رعاني في طفولتي و شبابي و عانى من اجلي و علمني الشهامة و الاخلاص الى ابي الذي رحل عن هذة الدنيا ....

الى من سهرت الليالي و علمتني الصدق و الوفاء الى و الدتي العزيزة .....

الى من اتوسم بهم المستقبل الزاهر اخوتي و اخواتي .....

الى رفاق الدرب الطويل اصدقائي .....

اهدي رسالتي هذه
حميد

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I certify this thesis ***"Determination the Effect of the Coulomb Correlation for He And He-Like Ions Using Different Wave Functions"*** By ***Hamid Jabber Al-Jibbouri*** was prepared under my supervision at the College of Science, AL-Nahrain University as a partial fulfillment of the requirement for the degree of Master of Science in Physics.

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We certify that this thesis entitled ***"Determination the Effect of the Coulomb Correlation for He and He-Like Ions Using Different Wave Function"***, is submitted by the student ***Mr. Hamid Jabber Al-Jibbouri*** and as Examination Committee, examined the student in its contents and that in our opinion, it meets the standard of thesis for the degree of Master Science in Physics.

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Acknowledgments

I would like to express my thanks and deep appreciation to ‘God‘for all helpful in the production of this work.

I would like to express my thanks and deep appreciation to my supervisor, Dr. Khalil H. AL-Bayati for suggesting the project of research, and for helpful comments and stimulating discussion through the work.

I also wish to express my thanks to the Department of Physics Staff Members and College of Science in AL-Nahrain University.

I also wish to express my thanks to my friends for their help, support, and encouragements during my study.

Hamid, 2007

Abstract

In this research the effect of electron correlation can be described by evaluating the difference in the one-particle radial distribution function. The other effect of the electron correlation can be described by evaluating Coulomb hole. It also can be described by evaluating the change which occurs in the two–particle radial distribution function to study the radial correlation for He atom and compared the result with the series of He-like. Four types of wave functions can be used in this research, the Hartree-Fock HF (uncorrelated wave function), configuration interaction, Eckaret-Hyllears and Simple Configuration-Interaction wave functions.

We conclude that the difference in one-particle increase as Z increase and the location is closed to nucleus. And the radius of Coulomb hole decrease and the area increase as Z increase. Also the radius of Coulomb hole for Configuration-Interaction and Hartree-Fock wave function is larger Simple Configuration-Interaction and Hartree-Fock wave function is larger Eckart-Hyllears and Hartree-Fock wave function for He atom. And the change in the two-particle increase and the location of this change decrease as Z increase. Also we conclude that the electron correlation increase as Z increases.

The properties and parameters studied in this work:-

1. The inter-particle distribution function $f(r_{12})$.
2. Two-particle distribution function $D(r_1, r_2)$.
3. One-particle distribution function $D(r_1)$.
4. The inter-particle expectation value $\langle r_{12}\rangle^{\wedge n}$ where $-2 \leq n \geq 2$.
5. One-particle expectation value $\langle r_1\rangle$ where $-2 \leq n \geq 2$.
6. Coulomb Hole $\Delta f(r_{12})$.
7. Partial Coulomb Hole $g(r_{12}, r_1)$.

8. The change $\Delta D_{CI\text{-}HF}(r_1, r_2)$ which occurs in the two –particle radial distribution function.

All results were obtained numerically using computer program (MathCAD/ 2003).

الخلاصة

في هذا البحث نستطيع وصف تاثير الترابط الكولومي من خلال حساب الفرق في دالة التوزيع القطرية لجسيم واحد . كذلك يمكن حساب الترابط الكولومي بواسطة حساب فجوة كولوم .وكذلك يمكن حساب الترابط الكولومي من خلال حساب الفرق الحاصل في دالة توزيع الكثافة القطرية لجسيمن لذرة الهليوم و المقارنة مع الايونات الشبيهة بذرة الهليوم . اربع دوال موجية تم استعمالها في هذا البحث هارتري-فوك و هي دالة غير مترابطة و (Configuration-Interaction) و هي دالة موجية مترابطة و كذلك تم استعمال (Eckart-Hyllears) و كذلك (Simple Configuration-Interaction).

استنتجنا في هذا البحث أن التغير الحاصل في دالة التوزيع الكثافة القطرية لجسيم واحد يزداد و اقتراب مواقعها من النواة بزيادة العد الذري. وكذلك وجدنا نصف قطر فجوة كولوم يقل و مساحة الفجوة تزداد بزيادة العدد الذري . و كذلك نصف قطر فجوة كولوم لهارتري فوك (HF) و (CI) اكبر من (HF) و (SCI) و اكبر من (EH) لذرة الهيليوم. و وجدنا التغير الحاصل في دالة التوزيع الكثافة القطرية لجسيميين يزداد مع نقصان مواقع دالة التوزيع بزيادة العدد الذري . و لاحظنا ان الترابط الالكتروني يزداد بزيادة العدد الذري.

الخواص التي تم دراستها هي :

1- دالة التوزيع البينية $f(r_{12})$.

2- دالة توزيع الكثافة القطرية لجسيمن $D(r_1,r_2)$.

3- دالة توزيع الكثافة القطرية لجسيم واحد $D(r_1)$.

4- بعض القيم المتوقعة بين الالكترونيين $\langle r_{12}\rangle$ عندما $-2\leq n\geq 2$

5- بعض القيم المتوقعة لجسيم واحد $\langle r_1\rangle$ عندما $-2\leq n\geq 2$

6- فجوة فيرمي $\Delta f(r_{12})$

7- دالة التوزيع الجزيئية $g(r_{12},r_1)$

8- التغير الحاصل لكثافة التوزيع القطرية لجسيمين $\Delta D_{CI\text{-}HF}(r_1,r_2)$

جميع هذه النتائج تم حسابها بواسطة برامج حاسوبية (MathCAD /2003)

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List of Abbreviations

Symbol	**Meaning**
∇^2	*Laplacian operator*
D(r1)	*One-particle radial density distribution function*
D(r1,r2)	*Two-particle radial density distribution function*
f(r12)	*Inter-particle distribution function*
g(r12,r1)	*Partial distribution function*
HF	*Hartree-Fock approximation*
EH	*Eckart-Hyllears Wave function*
CI	*Configuration Interaction*
$n,\text{ª},m$	*Quantum numbers*
$N_{n\text{ª}m}$	*Normalization constant*
$\left\langle r_{12}^{n} \right\rangle$	*Inter-particle distance expectation values*
$\left\langle r_{1}^{n} \right\rangle$	*One-Particle distance expectation values*
$R_{n\text{ª}}(r)$	*Radial factor function*
STO	*Slater-Type Orbitals*
SCF	*Self-Consistent Field*
$Y_{\text{ª}m}(\theta,\phi)$	*Angular function*
Z	*Atomic number*
α,β	*Spin up, spin down*
ζ	*Orbital exponent*

Symbol	***Meaning***
$\Psi(1,2,..N)$	*Total wavefunction*
Ψ^{*}	*Conjugate wavefunction*
$\sigma(s)$	*Spin part function*
$\Gamma_{ij}(x_m, x_n)$	*Two-particle density*
$\Delta r_1, \Delta r_{12}$	*Standard deviation*
$d\tau$	*Volume element*
Π	*Product of all occupied spin orbital*
SCI	*Simple Configuration Interaction*
c	*Expansion coefficients*

Appendices

Chapter One

Introduction

Introduction

1-1 General Introduction:

It is well known that the laws of classical physics are applicable only to motion of macroscopic particles and not applicable to electron motion in atoms and molecules. Consequently the microscopic particle requires a new form of mechanics, termed quantum mechanics (or wave mechanics). Quantum mechanics is based on many hypotheses postulated by Plank, Einstein, Bohr and de Broglie [1].

In (1927), Heisenberg found that impossible to measure the momentum and place of a particle in same time with infinitesimal (uncertainty principle), where he found that as the place is measured accurately will be an account of uncertainty in measurement of momentum. Likewise, if the momentum is measured accurately on account of uncertainty in measurement of place. There are two variables followed the uncertainty, energy E and the time t. While in the principle of classic mechanics the accurate measurement of the momentum and the place in the same time is possible [1].

The quantum mechanics is primarily described by two different methods [1]. The first method is applied by Werner Heisenberg. He used in this description properties of mathematic matrix, called *matrix mechanics*. The second method is applied by Schrödinger. Schrödinger method which is formulated in term of partial differential equation, to describe the behavior of matter waves.

Paul Dirac found that the formula of those two methods are identical and described the system with mathematical function called *ket*, gave it a sign **|*i*⟩**, where ***i*** is the definite case of the function. He described the coupling of this function with mathematical function called bra, has a sign **⟨*j*|**.

The central feature of which partial differential equation knows as [2]:

$$\hat{H}\psi = E\psi \qquad \text{…. 1-1}$$

where Ψ represent the wave function (eigen function) and it determined the behavior of the electron. When Schrödinger equation is written as in equation (1-1), it seen to be an eigen value equation E , so the factor E is called the eigen value of the operator $\hat{H}$.

The German scientist M. Bron in 1926 gave the exact physical interpretation of the square of wave function at any point gives the probability of finding the particle at that point

$$\int_{-\infty}^{+\infty} \Psi^2 dx = 1 \qquad \text{….1-2}$$

Equation (1-2) is the mathematical statement of Borns interpretation is $\Psi^2 dx$ is equal to the probability of finding the particle in region between x and x+dx. A wave function which satisfies (1-2) is said to normalized. We are justified by the physical interpretation of Ψ which will be discussed below, but are best regarded as postulate of the theory; they can be summarized as following:

1-Ψ must be a well-defined function of position particle; it must be single-valued.

2- Ψ cannot be infinite.

3- Ψ must be continuous, and not jump abruptly from one value to another

4- The first differential of Ψ must be continuous, except at a point where the potential is infinite [3].

The important property for the wave functions is antisymmetric property. In case a system has two electrons, although the electrons are indistinguished particles then the permutation process in coordinates impossible change $|\psi(r_1,r_2)|^2$, where the permutation process leave two probabilities to influence on ψ as following[4]:

$\psi(r_1,r_2)=\psi(r_2,r_1)$ (Symmetric wave function)

$\psi(r_1,r_2)=-\psi(r_2,r_1)$ (Anti-symmetric wave function)

For system contains several electrons, the two probabilities can be written as:

$$P\psi(r_1,r_2,r_3,\ldots\ldots,r_N)=(-1)^P\psi(r_1,r_2,r_3\ldots\ldots r_N) \qquad \ldots 1\text{-}3$$

where ***P*** is permutation operator which effects only on the particles coordinates permutation $\psi(r_1, r_2, r_3, \ldots\ldots, r_N)$ and $(-1)^P$ equal to (±1) and this equivalent material or singular numbers of the permutations.

The particles that have spin movement equal to integer number or 0 such as photons and deuterons and helium nucleus that called *bosons* are described by identical wave functions. While the particles that have spin movement accounted to half integer number such as electrons, protons, and neutrons which called fermions are described by contrary identical wave functions [5]:

From equation (1-1) the factor $\hat{H}$ is the Hamiltonian operator which defined for a single atom of charge Z as:

$$\hat{H} = \frac{-\hbar^{2}}{2me}\nabla^{2} - \frac{ze^{2}}{r} \qquad \text{....1-4}$$

where $\hbar$ constant equals to $\frac{h}{2\pi}$, ∇^2 is Laplacin operator and identify by spherical coordinates [3, 6]:

$$\nabla^{2} = \frac{1}{r^{2}}\frac{\partial}{\partial r}(r^{2}\frac{\partial}{\partial r}) + \frac{1}{r^{2}\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^{2}\sin^{2}\theta}(\frac{\partial^{2}}{\partial\phi^{2}}) \qquad \text{....1-5}$$

The Hamiltonian for an atom with k electrons is given by:

$$\hat{H} = -\frac{\hbar^{2}}{2m}\sum_{i=1}^{N}\nabla_{i}^{2} - \sum_{i=1}^{N}\frac{Ze^{2}}{r_{i}} + \sum_{i \langle j}\ \sum_{i=1}^{N}\frac{e^{2}}{r_{ij}} \qquad \text{....1-6}$$

or

$$\hat{H} = \hat{T}_{e} + \hat{V}_{en} + \hat{V}_{ee} \qquad \text{....1-7}$$

where the first term represents the kinetic energy operators for the n-electrons; the second term is the potential energy for the attractions between the electrons and the nucleus of charge Z, and r is the distance between the nucleus and the electron, and the last term is the potential energy of an electron at infinite distance from the nucleus is zero. The potential energy of an electron in an atom is a negative quantity because the energy is lower than that when the nucleus and electron are separated by an infinite distance. The restriction j > i avoids counting the same interelectronic repulsion twice, and avoids terms like e^{2}/r_{ij}.The Schrödinger equation for the atom is not separable because of the interelectronic repulsion terms e^2/r_{ij} [7].

The Schrödinger equation for a multi-electron atom can be solved numerically, although V $_{electron\text{-}electron}$ cannot be included as an explicit term in the Hamiltonian. Rather, its effect on Ψ can be accounted for by a mathematically simpler approach: that each electron interacts with an average of the nucleus + all other electrons (*Self-Consistent Field)* approximation. The techniques were originally introduced by D.R. Hartree (before computer was available) and V. Fock to take into account the Pauli principle correctly. In broad outline, the Haretree-Fock self-consistent field (SCF) [7].

There unit system defined the atomic unit, the unit mass in atomic unit system is electron mass while the unit distance is half Bohr-atom diameter (a_{o}). The unit energy is defined by Hartree and can be expressed as [3]:

$$1\,Hartree = \frac{me^4}{\hbar^2} = \frac{e^2}{a_0} = 27.21\,eV \qquad \text{....1-8}$$

The Hamiltonian operative in Eq. (1-6) can be expressed by using atomic units ($\hbar \equiv m_e \equiv e \equiv 1$) as:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i}^{N}\frac{z}{r_i} + \sum_{i\langle j}\sum_{i=1}^{N}\frac{1}{r_{ij}} \qquad \text{....1-9}$$

Eq. (1-9) contains a boundary that represents the repulsion between electrons, and because of this boundary the Schrödinger equation can not be solved accurately. Therefore, we have to be used an approximation method to solve Schrödinger equation. Simplest methods return to Hartree, where he assumed that every electron moved in an effort range arises from other electrons. i.e. the number of electrons movement (***e***) is independent of each other. Thus, the wave function for sum of electrons will equal to multiply results of singular electron wave functions (orbital) [8]:

$$\psi(1,2,3,.....,N) = \phi_1(1)\phi_2(2)\phi_3(3).......\phi_N(N) \quad \text{.... 1-10}$$
$$= \prod_{i=1}^{N} \phi_i(i)$$

where $\phi_i(i)$ represents the spatial coordinates function of electron ***i***, while ***N*** is number of electrons in the atom.

One of the difficulty and main problems in Eq. (1-10) is represented by neglecting the electrons correlation movement at their moving around the nucleus. A consequence of that the measurement of repulsion energy will be differed from the exact value. This difference called correlation energy and is neglected in Hartree pattern as mentioned above.

As the Hartree approximation mentioned in Eq. (1-10) cannot verify the Pauli principle, and can not verify the indistinguishable property between electrons and unconformity wave function property. In order to verify that the Fock used spin idea in 1930 and this method called *(Hartree-Fock method)*, where treated the weak point in Hartree equation and the wave function defined by Slater determinant [1, 9]:

$$\psi(1,2,3,\cdots\cdots N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(1) & \phi_1(2) & \cdots & \phi_1(N)\\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N)\\ \vdots & \vdots & \vdots & \vdots\\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N)\end{vmatrix} \qquad \ldots.1\text{-}11$$

Where $\frac{1}{\sqrt{N!}}$ is the normalization factor and $\phi_i(i)$ represents the spatial spin function that it’s multiply result of spatial wave function and spin function α orβ. The number between brackets referred to the electrons and the numbers under the function referred to the spin orbital [9].

The Slater determinant can be characterized as following:

1. The determinant sign changed at replacing two rows or two columns in the determinant.
2. The determinant value is 0 if two rows or two columns in the determinant are equalized.

The first characterize referred that at replacement of two electrons in this determinant, the determinant sign is changed without change in its value. Hence, the wave function verifies exception Pauli principle where it’s reverse conformity. While the second characterize mean, if equalized two spin orbital in the determinant, hence the determinant value equal to 0 and this equivalents to exception Pauli principle (in any atom can not be the forth quantum number (***n, l, m_l, m_s***) of two electrons equalized. i.e. the quantum spin number (α orβ) has to be different for two similarity electrons in the spatial wave function (ϕ) [9].

Eq. (1-11) explained that the repulsion of electrons has parallel spin more than electrons has reverse spin, which causes to decrease

Coulombic repulsion energy between parallel spin electrons and this symmetry to Hund’s rule [10].

By opening Eq. (1-11) results ***N!*** Limits, every limit are consisted of multiply results of ***N*** from wave function of singular particles. Thereby those limits (***N!***) is consisted of definite series where the particles, ***N***, in the limits is attributed to the once ***N*** levels. Therefore, those limits (***N!***) will cover almost the possible permutation probabilities of ***N*** particles in between ***N*** levels, and example for once of that limits$\phi_1(3),\phi_2(4),......\phi_N(\boldsymbol{N})$. I.e. the particle (3) is located in level 1, while the particle (4) located in level 2, etc… [11].

In Hartree-Fock approximation is taking coulomb repulsion value between two electrons by integration repulsion, and this gave the range of repulsion effect [12].

Thereby the Central-Field Approximation method is developed through discovering the electron spin by Uhlenbeck and Coudsmit and exception pauli rule in 1925, then completed with using Self Consistent Field (SCF) method by Hartree in 1928 and Hartree-Fock in 1930 [7,8].

The self particle wave function for the multiple electrons system is preferment throughout energy insight; it’s introduced by Hartree-Fock approximation that allowed of some spatial correlation between parallel spin electrons which lead to form Fermi-effect or Fermi-hole [12]. Indeed all electrons repulsion among each other because of Coulomb potential ($\frac{\boldsymbol{e}^2}{\boldsymbol{r}_{12}}$) that present among them. Therefore, each electron is covered by Coulomb-hole [13].

1-2 Historical Review:

A-General Historical Review of Electron Correlation in Atomic Systems:

Roothaan et al. (1960) [14] have developed the generalized SCF formalism in their paper and applied it to atomic configurations and they have presented in there work the results that are obtained for the configurations $1s^2$,$1s^2 2s$ and $1s^2 2s^2$ for atoms and ions up to Z=10.

Roothaan and Weiss (1960) [15] have obtained an accurate wave function for the ground state of Helium-like systems. They have chosen a convenient function with adjustable parameters and determined the best wavefunction within this class by minimizing the expectation value of the energy, computed from that wavefunction with respect to these parameters. They have found one of the most successful models is the Hartree-Fock approximation.

Watson (1960) [16] has done a configuration interaction calculation involving thirty-seven configurations and including the $1s^2 2s^2$ Hartree-Fock function for the ground state of Beryllium atom. The results indicate the effect of the “correlation hole”.

Weiss (1961) [17] has done successful approaches to many-particle quantum mechanics for the ground and excited state of Helium, Lithium and Beryllium atoms using a configuration interaction approximation

Banyard (1968) [18] has analysed and compared five wave functions for H^-, two functions were based on the single determinant independent-particle model and three were correlated wave functions. He has discussed the two-particle density $\rho(r_1,r_2)$ and the radial density $D(r)$.

Banyard and Baker (1969) [19] have studied the electron correlation of an isoelectronic series possessing electrons with antiparallel spins H^-, He, and Li^+

The study was of three wave functions, two introduce correlation: one by configuration interaction and the other by including Hylleraas-type correlation factors. For comparison, the third function is based on the Hartree-Fock approach. The correlation within the wave functions was demonstrated by presenting two-particle density difference maps, $\Delta D(r_1,r_2)$ relative to the uncorrelated approach, and graphs of the radial density $D(r)$. The maxima values of $D(r)$ were decreased with the nuclear charge (atomic number Z) increasing.

Taylor and Banyard (1973) [20] have applied the method of Sinanoğlu in his many-electron theory, which arise from electron-correlation effects, for *He* (^{1}S state), *Li* (^{2}S and ^{2}P states) and *Be* (^{1}S state) like ions, which gave an improved orbital representation as far as the one-particle density is considered.

Brown and Larsson (1977) have calculated one-electron properties such as $\rho(0), < \frac{1}{2}\nabla >, < r^{-2} >, \ldots, < r^2 >$ and $< r_{12}^{-1} >$. Calculations have made on various small atoms and their positive and negative ions.

Cohen and Frishberg (1983) [21] have obtained the probability of the inter-particle distance for the N-body problem where the potential is an attractive delta function. This was done for both the exact wavefunction and the Hartree wave function allowing the calculation of the correlation hole.

Koga et al. (1999) [22] have studied electron-pair intracule (relative motion) and extracule (center-of-mass motion) densities in both position and momentum spaces for the 1p and ^{3}p terms of the group 2 atoms Be (atomic number Z=4), Mg (Z=12), Ca (Z=20), Sr (Z=38), Ba (Z=56) and Ra (Z=88). The extracule density in momentum space shows that the 1P term has a distribution larger in a large center-of-mass momentum region than the 3P term.

B-Historical Review of Coulomb Hole:

Coulson and Neilson (1961) [23] have obtained formulae for the distribution function $f(r_{12})$ of the inter-electronic distance r_{12} in the ground state of Helium, and for the mean value of r_{12}. Five different wave functions were considered, showing varying degrees of electron correlation. They have also evaluated the Coulomb hole.

Curl et al. (1965) [24] have calculated the Coulomb hole $\Delta f_c(r_{12})$ in the ground state of two-electron atoms, where the Coulomb hole was defined by Coulson and Neilson (1961).

Banyard and Seddon (1973) [25] have examined, in depth, several wave functions for the two-electron systems $H^-, He, Li^+, and\ Be^{++}$. Three noncorrelated wave functions and ten explicitly correlated wave functions. For each wave function they have calculated the inter-particle distribution function $f(r_{12})$, by comparing the results for different wave functions some insight were obtained into the roles played by different types of correlation factor.

Seddon and Banyard (1973) [26] have calculated the Coulomb hole and several two-electron expectation values using a series of configuration interaction (CI) wave functions of differing accuracy for helium like ions. The behaviour of these properties was examined. As the basis set was increased a comparison with the values obtained using explicitly correlated (EC) wave functions.

Boyd (1975) [27] has discussed the radius of the Coulomb hole in an atom or molecule in general terms and illustrated in detail for the ground state of the helium isoelectronic sequence. The calculations demonstrate a general tendency for the radius of the Coulomb hole to increase as a function of the distance of the reference electron from the nucleus

Banyard and Mashat (1977) [28] have obtained an expression for the Coulomb hole associated with any pair of occupied HF spin orbitals for a many-electron system. The required partitioning of the known correlated was achieved in their work by using the many–particle theory proposed by Sinanoğlu. Ground state wavefunctions were then analyzed for the *Be*-like ions when $3 \le Z \le 8$ which, besides validating the partitioning technique, provided insight into the radial and angular components of intra-shell correlation effects.

Banyard and Mobbs (1981) [29] have used a partitioning technique to examine correlation trends in individual electronic shell for a series of ions. It has been extended and applied to a detailed comparison of four well-correlated wave functions for *Be* atom. For each correlated description of Be, Coulomb holes have been evaluated.

Banyard and AL-Bayati (1986) [30] have examined electron correlation in detail within the $K_\alpha K_\beta, K_\alpha L_\alpha \text{ and } K_\beta L_\alpha$ shells in position space for a series of *Li*-like systems in their ground state. Using existing wave functions, Coulomb holes, partial Coulomb holes and several one-and two-particle expectation values were evaluated for the intra-and inter-electronic shells. The findings for the *Li*-like intra-and inter-shells were compared both with a previous analysis of *He*-like and Be-like series of ions and with a similar examination of the 2 ^{1}S and 2 ^{3}S excited states of *He*

Youngman and Banyard (1987) [31] have analysed the electron correlation effects in momentum space for excited states of *He*, Coulomb shifts and partial Coulomb shifts had been determined, as well as certain radial and angular distribution functions. Angular and radial correlation had opposing effects on the momentum distribution.

Banyard and Youngman (1987) [32] have examined electron correlation in momentum space for the individual intra-and inter-shell electron pairs in the ground state of *Li* (^{2}S). It was established that the radial and angular components of correlation have opposing influences on the inter-particle momentum distributions $f(p_{12})$ and $g(p_{12},p_1)$. They have also examined the Coulomb shifts $\Delta f(p_{12})$ and partial Coulomb shifts $\Delta g(p_{12},p_1)$.

Banyard (1990) [33] has examined *K*-shell electron correlation effects with $Li^+(\,^1S),Li(\,^2S),Li(\,^2P),Li^-(\,^1S)\ Be^{2+}(\,^1S),Be^+(\,^2S),Be^+(\,^2P)$ and $Be(\,^1S)$. In position and momentum space, Coulomb holes **$f(r_{12})$** and shifts **$f(p_{12})$** and partial coulomb holes $\Delta g(r_{12},r_1)$ and shifts $\Delta g(p_{12},p_1)$ have been studied.

Banyard et al. (1992) [34] have analysed correlation effects for the doubly excited state 2p^2 3P for $1 \le Z \le 4$. Coulomb holes and partial Coulomb holes have been derived from explicitly correlated wave function.

Ellis (1996) [35] has defined a two-electron spin independent operator to represent the spatial correlation of the electrons in a general atom or ion. The spherical-tensor expansion for this operator has provided a systematic method for evaluating the two-electron correlation function implied by a Hartree-Fock N-electron wavefunction with arbitrary configuration mixing. This technique for computing correlation function provides a useful tool of wide applicability in comparing different theoretical approaches to the structure of complex atoms.

1-3 Electron Correlation:

The correlation energy is usually defined as the part of the total energy of a system that is not taken into account in the Hartree-Fock description of atoms and molecules. Although there are many definitions for electron correlation found in the literature the one commonly used is the one by Löwdin [36].

“The correlation energy for a certain state with respect to a specific Hamiltonian is the difference between the exact eigen value of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration.”

This does not mean that the Hartree-Fock approximation does not have any electron correlation built in it, but it does not capture the total correlation. The part of the correlation it captures is the so-called Fermi correlation that arises from the antisymmetry of the wave function and basically prevents electrons of the same spin to occupy the same region of space. It is noteworthy to mention that the correlation energy is usually of the same order of magnitude as the dissociation energy of a molecule [36].

Generally there are three factors that affect the electron correlation. The first factor is the Coulomb repulsion that has the $1/r_{ij}$ dependence and thus becomes infinite when electrons are in close and zero when their separation becomes infinite. This generates called Coulomb hole in electronic structure computations. There are molecular systems where this is the only type of correlation present apart from the Fermi correlation. The two classical examples are He and Hydrogen molecular. The second factor of correlation is termed as the Fermi hole. The third factor that has influence on electron correlation is the point group to which the one-electron wave functions are restricted. In this case lower symmetry point groups impose less restriction onto the one-electron wave functions and result in higher correlation effects. [36]

1-4 Electron Correlation Problems:

The many-body problem is not exactly soluble in either classical or quantum mechanics. In quantum mechanics the exact form of the Schrödinger's equation for an atom with more than one electron includes in the potential energy (V) not only the attraction interaction between the electron and nucleus, $-Ze^{2}/4\pi\varepsilon_{-}r_{ij}$, but also the repulsion interaction, $+Ze^{2}/4\pi\varepsilon_{-}r_{ij}$, between each pair electrons, these cross terms (r_{ij}) prevent separation into equations each involving co-ordinates of only one electron, which can be solved exactly. To overcome this problem we must use approximation methods [37].

The simplest approximation is due to Hartree, who assumed that each electron moves only in the average field of all the other electrons of the system. The straight forward products wave function proposed by Hartree dose not satisfies the quantum mechanical requirement that many electron wave functions must be anti-symmetric with respect to the exchange of the coordinates of any two electron [37].

To meet this requirement, Slater and Fock re-derived the equation of Hartree, such that, the wave function written as Slater determinant in eq (1-11).

Although the Hartree-Fock calculation generate a great deal of information about the electronic energy and density of the molecules. It dose have two major shortcomings. The first is that the excited states are difficult to calculate. The second is that the electron correlation is ignored, except in an average sense (electron correlation is the interaction between the motions of the individual electrons in the system). Because Hartree-Fock approximation calculates an electron's motion in the average field produced by the other electrons rather than the exact position of the other electrons, it leaves much of the electron correlation out. Usually, the Hartree-Fock is described as "uncorrelated" wave function [37].

One method of correcting the shortcomings of Hartree-Fock approximation is Configuration-Interaction (CI). CI considers the interaction of excited wave function with ground state wave function, the excited wave function give additional functional freedom to the total CI wave function to find the optimal energy. In addition to CI, there are two types of CI according to electrons arrangement in the orbital basis set, the first, complete CI in which all electrons are arrange in all possible ways (consistent with symmetry requirement) in a complete (infinite) orbital basis set (this is unattainable), the second, full CI in which all electrons are arrange in all possible ways for a finite orbital basis set [37].

1-5 Coulomb Correlation:

In the HF approximation, the motions of an α and β electrons are not correlated; the α-β pair probability is simply the product of the individual (one-electron) probabilities. In reality the electrons try to avoid each other, due to the Coulomb repulsion between them. The resulting correlation of the electronic motions is called (Coulomb Correlation).

Coulomb correlation introduce changes in the pair-probability that two electrons (with respect to the HF pair-probability): the probability that two electrons are at short distance decrease. While the probability that the inter-electronic distance is long increase.

Two electrons of the same spin of course also repel each other. However, two α or two β electrons already try to avoid each other on the

HF level, due to the antisymmetry of the wave function. The changes in α-α and β-β pair probability (and associated changes in energy) when Coulomb Correlation relation is taken into account will therefore be much less important, compared to changes in the α-β pair-probability [38].

1-6 Coulomb Hole:

A *Coulomb hole* is defined as a region surrounding each electron in atom in which the probability of finding another electron is small **[39].**

In Hartree-Fock (SCF) wave function takes into account the interactions between the electrons only in an average way. In reality, all electrons repel each other due to the Coulomb potential e^2/r_{ij} which exist between them, and each electron is therefore surrounded by a *Coulomb hole* with respect to the other electrons this is a region in which the probability of finding another electron is small. The motions of electrons are correlated with each other, and we speak of *electron correlation*.

Within the Hartree-Fock (HF) approximation the probability of finding two electrons with parallel spin ↑↑ at the same point in space is zero. Such appoint may be the centre of a Fermi hole, and is consequence of the antisymmetry of the wave function (one some times refers to a Fermi hole around each electrons in Hartree-Fock (HF) wave function, thereby indicating a region in which the probability of finding another electron with the same spin is small) .Although the Hartree-Fock (HF) method allows electrons with the same spin properties to avoid one another, no allowance is made for any spatial correlation between electrons with opposite spin .The effect of correlation between all electrons can only be examined by means of wave function which are more flexible than the Hartree-Fock(HF) determinant .When described by wave function which go beyond the Hartree-Fock(HF) level of accuracy , each electron lies in a region of space which is largely devoid of other electrons , this is a consequence of a more realistic description of the *Coulomb repulsions*.

Correlation thus refers to the residual error in the Hartree-Fock (HF) model when describing the electron-electron Coulomb interactions.

In a Self Consistent Field (SCF) and Configuration Interaction (CI) calculation are reasonably well-defined as a "hole" around a reference electron centered at any point in space, thereby reflecting a reduction in the simultaneous probability density of finding two unlike-spin electrons there [35].

The *Coulomb hole*, as well as the *Fermi hole* is clearly associated with the notation of a hole is the atomic or molecular charge cloud any chosen electron and therefore, the total amount of electron charge displaced is indicative of the size of the hole interest (*Coulson and Neilson* 1961).Alternatively the size of a hole could be described in terms of its depth and its radius. The two quantities could then be through of as the "dimensions" of the hole whereas the displaced electronic charge provides a measure of the "volume" of hole [27].

The *Pauli principle* keeps electrons of parallel spin apart. And the second kind of the electron correlation is the classical Coulomb repulsion between each pair of electrons leads to the formation of a *"hole"* in the atomic or molecular charge cloud around any chosen electron [40].

The *Coulomb hole* it arises from the classical Coulomb repulsion between each pair of electrons.

Mathematically *Coulomb hole* for the singlet state is defined as a difference between the Correlated and Hartree-Fock wave function approximations [25].

1-7 The Correlation Energy:

The correlation energy is the energy recovered by fully allowing the electrons to avoid each other, and is defined as the difference between the energy in the HF limited and the exact non relativistic energy (E_{-}) of a system [12]:

$$E_{corr} = E_{-} - E_{HF} \qquad \text{....1-13}$$

This energy E_{corr} will always be negative because the HF energy is an upper bound to the exact energy, the exact non relativistic energy can, in principle, be calculated by a full CI in a complete one-electron basis set, where the energy predicted by a correlated wave function takes into account all the instantaneous particle interaction which occurred within a many electron system, therefore, such calculation go well beyond the description provided by independent-particle model.

1-8 The Aim of The Project:

The aim of this research is to study the theoretical properties of He-Like ions, using Hartree-Fock uncorrelated wave function and three different correlated wave functions Configuration Interaction, Eckart-Hyllears and Simple Configuration-Interaction wave functions accounts for only the averaged interaction arising from the classical Coulomb repulsion between each pairs of electrons, this means that the (HF)and exact density distribution are virtually indistinguishable.

Also in this research study the Coulomb correlation (i.e the correlation of the electronic movements due to the electronic repulsion) is neglected in the HF approximation. In this thesis the correlation problem is studied with the purpose to get a better insight into the shortcomings of the HF model and to get a deeper understanding of electron correlation in a physical and visual manner.

Our study aim to analysis the calculations by using of partitioning technique for He-Like ions then compare the results with other workers.

The present work data of Clementi and Rotti [1974] for Hartree-Fock wave function, Wiess [1960] for Configuration-Interaction, Nelsion and Coulsion for Eckart-Hyllaers wave function and Masten and sturat [1964] for the Simple Configuration-Interaction.

Chapter Two

Wave Functions And Some Atomic Properties

2-1 INTRODUCTION:

Any system can be described by wave function $\Psi(r_1,r_2,....r_n)$ where it is a mathematical expression to describe the system properties as position, momentum, energy and etc. The exact calculation of wave functions for many electron atoms becomes difficult because of the much electron-electron repulsion that should be ignored for simplicity. There are four main kinds of the wave function approximation methods,used in the present work, Hartree-Fock (HF), Configuration Interaction approximation methods, Eckart-Hyllears and the Simple Configuration-Interaction wave functions respectively.

2-2 HARTREE-FOCK THEORY (HF)

2-2-1 Wave function and Basis set:

In an independent practical model the total wave function for many electrons system is given by Slater determinant:

$$\Psi_{HF}\left(x_1,x_2,.......,x_n\right)=\left|\Phi_1(x_1)\Phi_2(x_2).....\Phi_N(x_N)\right\rangle \qquad ...2.1$$

where $\Phi_i(x_i)$ is the single electron wave function and x_i denotes spin-orbital components:

$$\Phi(x_i)=\phi_i(r_i)\alpha(\delta) \qquad ....2.2$$

or:

$$\Phi(x_i)=\phi_i(r_i)\beta(\delta) \qquad ....2.3$$

r_i ,denotes a radial and angular co-ordinate , while $\alpha(\delta)$ and $\beta(\delta)$ are the spin wave function of a single electron . an α and β refer to the two components of the spin part , where , α- spin up and β-spin down .

The spin wave functions are orthonormal, where:

$$\int_{\delta} \alpha^*(\delta)\alpha(\delta)d\delta = 1 \qquad \int_{\delta} \beta^*(\delta)\beta(\delta)d\delta = 1 \qquad \text{….2.4}$$

$$\int_{\delta} \alpha^*(\delta)\beta(\delta)d\delta = 0 \qquad \int_{\delta} \beta^*(\delta)\alpha(\delta)d\delta = 0$$

The spatial part $\phi_i(r_i)$ can be written as an expansion in some set of analytic basis function [41]:

$$\phi_{nl}(r) = \sum_i C_n^i X_{nl}^i \qquad \text{….2.5}$$

where C is a coefficient taken to minimize the energy. The basis set of one-electron functions (basis function) chosen here consist of the normalized Slater-type orbital defined by:

$$X_{nlm}(r,\theta,\vartheta) = R_{nl}(r)Y_m^l(\theta,\vartheta) \qquad \text{….2.6}$$

where $R_{nl}(r)$ and $Y_m^l(\theta,\vartheta)$ represent the radial and angular parts respectively.

The radial part is given by:

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n!)}} r^{n-1} e^{-\zeta \cdot r} \qquad \text{….2.7}$$

where n, l and m are quantum numbers and the ζ an exponential parameter.

For the HF ground state calculations of He-like ion we used data for (C, ζ, and n) introduced by [42]

2-2-2 Two–Particle Density:

For any N –electron atomic system, the two particle density can be written as [43]:

$$\Gamma(x_m, x_n) = \begin{bmatrix} N \\ 2 \end{bmatrix} \int \Psi^*(....,x_p....)\Psi(....,x_p,....)dx_p \qquad ....2.8$$

where , dx_p mean that the integration summation takes over all N – electron except m and n and the factor $\begin{bmatrix} N \\ 2 \end{bmatrix}$ is a binomial coefficient and used to ensure that second order density matrix $\Gamma(x_m.x_m)$ is normalized to the number of electron pair , so that :

$$\iint \Gamma_{HF}(x_m.x_m)dx_m dx_n = \begin{bmatrix} N \\ 2 \end{bmatrix} \qquad .... 2.9$$

where:

$$\begin{bmatrix} N \\ 2 \end{bmatrix} = \frac{N!}{2!(N-2)!} \qquad ....2.10$$

For two electron system the wave function can be written as

$$\Psi_{HF}(x_1, x_2) = \frac{1}{\sqrt{2!}}(\Phi_1(x_1)\Phi_2(x_2) - \Phi_2(x_1)\Phi_1(x_2)) \qquad ....2.11$$

then

$$\Psi_{HF}(x_m, x_n) = \frac{1}{\sqrt{2!}} \sum_{(i\langle j)}^{2} B_{ij}^{mn} \Phi_k(x)(-1)^v \qquad ....2.12$$

where

$$B_{ij}^{mn} = \left[\Phi_i(x_m)\Phi_j(x_n) - \Phi_i(x_n)\Phi_j(x_m)\right] \qquad ....2.13$$

The symbol v means the number of interchanges

In a similar way:

$$\Psi^*_{HF}(x_m,x_n)=\frac{1}{\sqrt{2!}}\sum_{(i\langle j)}^{2} B_{ij}^{mn^*}\Phi_k^*(x)(-1)^v \qquad \text{….2.14}$$

The binomial coefficient for He-atom and He-like ions is:

$$\begin{bmatrix}N\\2\end{bmatrix}=\frac{N\,!}{2!(N-2)!}=1 \qquad \text{….2.15}$$

Substituting binomial coefficient and equations (2.12, 2.14) into equation (2.8) and integrating over particle we get [29].

$$\Gamma_{ij}^{HF}(x_m,x_n)=\frac{1}{2}\sum_{i\langle j}^{2} B_{ij}^{mn^*}B_{ij}^{mn} \qquad \text{….2.16}$$

The above equation represent the two-particle density for pair wise component (i, j), where i and j refer to occupied spin-orbital, and m and n are electron labels. For the present work m and n are taken as 1, 2 respectively.

For K_α K_β-shell (i=1, j=2):

$$\Gamma_{12}(x_1,x_2)=\frac{1}{2}\left[\Phi_{1s}(r_1)\alpha(\delta_1)\Phi_{1s}(r_2)\beta(\delta_2)-\Phi_{1s}(r_1)\beta(\delta_1)\Phi_{1s}(r_2)\alpha(\delta_2)\right]^2$$

….2.17

where r_i , contains both radial and angular parts.

$$\Gamma_{12}(x_1,x_2)=\Phi_{1s}(r_1)^2\Phi_{1s}(r_2)^2\left[\frac{\alpha(\delta_1)\beta(\delta_2)-\alpha(\delta_2)\beta(\delta_1)}{\sqrt{2}}\right]^2 \qquad \text{….2.18}$$

For K_α L_α inter-shell (i=1, j=3)

$$\Gamma_{23}(x_1,x_2)=\frac{1}{2}\left[\Phi_{1s}(r_1)\alpha(\delta_1)\Phi_{2s}(r_2)\alpha(\delta_2)-\Phi_{1s}(r_2)\alpha(\delta_2)\Phi_{2s}(r_1)\alpha(\delta_1)\right]^2$$

….2.19

$$\Gamma_{23}(x_1,x_2)=\left[\alpha(\delta_1)\alpha(\delta_2)\right]^2\left[\frac{\Phi_{1s}(r_1)\Phi_{2s}(r_2)-\Phi_{1s}(r_2)\Phi_{2s}(r_1)}{\sqrt{2}}\right]^2$$

….2.20

2-2-3 Two-Particle Radial Density $D(r_1,r_2)$:

In each individual electronic shell of HF-system, the two-particle radial density is given by [18]:

$$D_{ij}(r_1,r_2)=\iint_{\Omega}\Gamma'_{ij}(r_1,r_2)r_1^2r_2^2\,d\Omega_1 d\Omega_2 \qquad ….2.21$$

where $\Gamma'_{ij}(r_1,r_2)$ is a spinless function, r_1 and r_2 are radial co-ordinate. $d\Omega_2=\sin\theta_i d\theta_i d\varphi_i$ (i=1, 2) denote that the integration is taken over all angular co-ordinates of the position vectors r_1 and r_2 such that:

$$\iint D_{ij}(r_1,r_2)dr_1dr_2=1 \qquad ….2.22$$

The two particle radial density function is a measure of the probability of finding the two electrons, simultaneously, in their radial co-ordinate r_1 and r_2 respectively.

2-2-4 One-Particle Radial Density $D(r_1)$:

In each individual electronic shell, this function is defined by **[18]**:

$$D(r_1)=\int_0^\infty D_{ij}(r_1,r_2)dr_2 \qquad ….2.23$$

which is a measure of the probability of finding in its radial co-ordinate r_1. This $D(r_1)$ is very useful to determine the one-particle expectation value, and the coherent X-ray scattering.

2-2-5 One-Particle Expectation Value $\langle r_1{}^n \rangle$:

The moments $\langle r_i^n \rangle$ can be calculated from [19]:

$$\langle r_i^n \rangle = \int_0^\infty D(r_i) \cdot r_i^n dr_i \qquad \text{....2.24}$$

Values for $\langle r_i^n \rangle$ when $-2 \leq n \leq 2$ are evaluated for each electronic shell. For n=0 the expectation value $\langle r_i^n \rangle$ must be equal to one to ensure that $D(r_1)$ is normalized to unity.

The case n=-1 leads to the electron-nuclear potential energy and it is useful to determine nuclear magnetic shielding and when n=2 is used to determine the root-mean-square (standard deviation) [18].

2-2-6 One-Particle Standard Deviation Δr_i:

The measure of the spread or diffuseness of one-particle radial density can be obtained by evaluated Δr_i; the root-mean-square deviation from the mean $\langle r_i \rangle$ is defined as [19]:

$$\Delta r_i = \sqrt{\langle r_i^2 \rangle - \langle r_i \rangle^2} \qquad \text{....2.25}$$

2-2-7 Two-Particle Expectation Value $\langle r_1^n r_2^n \rangle$:

For $-2 \leq n \leq 2$, the expectation value $\langle r_1^n r_2^n \rangle$ is evaluated by using:

$$\langle r_1^n r_2^n \rangle = \int_0^\infty D(r_1, r_2) \cdot r_1^n \cdot r_2^n dr_1 dr_2 \qquad \text{....2.26}$$

At n=0, this leads to normalize $D(r_1, r_2)$ to unity. The two-particle expectation value is important in the determination of the radial correlation coefficient.

2-2-8 Inter Electron-Electron Distribution Function $f_{ij}(r_{12})$:

For the ground state He-atom, the radial electron-electron distribution function $f_{ij}(r_{12})$ for the individual shell is given by [13]:

$$f_{ij}(r_{12}) = 0.5 \cdot r_{12}(I_1 + I_2) \qquad \text{....2.27}$$

where:

$$I_1 = \int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \qquad \text{....2.28}$$

$$I_2 = \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \qquad \text{....2.29}$$

For more detail see appendix (A).

This function is used to determine the inter-particle expectation value $\langle r_{12}^n \rangle$ and the coulomb hole $\Delta f\ (r_{12})$.

2-2-9 Inter-Electronic Expectation Value $\langle r_{12}^n \rangle$:

The mean value of inter-electronic separation can be determined by the formula [13]:

$$\langle r_{12}^n \rangle = \int_0^{\infty} f_{ij}\ (r_{12}) \cdot r_{12}^n dr_{12} \qquad \text{....2.30}$$

where $-2 \le n \le 2$. At n=0 the function $f_{ij}\ (r_{12})$ is normalized to unity, n=1 gives the average distance between electrons and n=-1 leads to electron-electron repulsion energy. **[44]**

2-2-10 Inter-Electronic Standard Deviation Δr_{12} *:*

The measurement of the spread or diffuseness of electron-electron distribution function $f_{ij}(r_{12})$ about its mean value $\langle r_{12}\rangle$ is standard deviation, which is given by:

$$\Delta r_{12}=\sqrt{\langle r_{12}^{2}\rangle-\langle r_{12}\rangle^{2}} \qquad ....2.31$$

2-2-11 The Ground State Energy $\langle E\rangle$ *:*

In term of the expectation value the ground state potential energy is given by **[44, 45]:**

$$\langle V\rangle=-Z\sum_{i}^{N}\langle r_{i}^{-1}\rangle+\sum_{i\rangle j}^{N}\langle r_{ij}^{-1}\rangle \qquad ....2.32$$

but, the total energy of ground state E is given by:

$$\langle E\rangle=\frac{1}{2}\langle V\rangle \qquad ....2.33$$

therefore:

$$\langle E\rangle=\frac{1}{2}\left(-Z\sum_{i}^{N}\langle r_{i}^{-1}\rangle+\sum_{i\rangle j}^{N}\langle r_{ij}^{-1}\rangle\right) \qquad ....2.34$$

where Z is the atomic number and energy is in atomic units (a.u.).

For more detail see appendix (B)

2-3 Configuration-Interaction theory (CI)

2-3-1 Wave function and Basis set:

In this work the CI method is used to study the effect of the electron correlation in term of correlation energy. The correlation description of the ground state of He-atom ions has been taken from Weiss (1960) [17]. Also the partitioning technique is used to describe correlation effects. The use of partitioning technique enables the correlation effects to be examined in depth for various inter-shell electron pair **[17]**.

In this approach, the correlated wave function is expanded as a linear combination of Slater determinants [17]

$$\Psi_{CI} = \sum_i c_i \phi_i \qquad \text{….2.35}$$

where each of ϕ_i s (configurations) is antisymmetrized product of one-electron functions (spin orbital), and the coefficients c_i are taken as those which minimize the total energy. Applying the variation theorem and solving an infinite set of secular equations may in principle, obtain the exact wave function.

The specific form of the configuration used for the two-electron system studied here are the following linear combination of single Slater determinant using fifteen configuration of s symmetry.

$$(\varphi\chi) = \frac{1}{\sqrt{2}} \sum \left| \varphi(1)\alpha\chi(2)\beta \right| \qquad \text{….2.36}$$

The basis set of one-electron function chosen is consisted of the normalized Slater-type orbital defined by eq 2.6 [15, 47, 48].

$$\chi_{nlm} = \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} r^{n-1} \cdot e^{-\zeta \cdot r} Y_{lm_l}(\theta,\varphi) \qquad \text{….2.37}$$

2-3-2 The Two-Particle Density $\Gamma_{corr}(1,2)$ for He-Like ions:

The particle density function $\Gamma_{12}(1,2)$ for He-like ions can be given as [17]:

$$(\varphi\chi) = \frac{1}{\sqrt{2}} \sum \left|\varphi(1)\alpha\chi(2)\beta\right| \qquad \text{….2.38}$$

where:

$$\left|\varphi(1)\alpha\chi(2)\beta\right| = \varphi(1)\alpha\chi(2)\beta - \varphi(2)\alpha\chi(1)\beta \qquad \text{….2.39}$$

where $\phi(i)$ and $\chi(i)$ refers to the one-particle function.

by using eq (2.8) we get

$$\Gamma(r_1, r_2) = \int [\varphi(1)\alpha\chi(2)\beta - \varphi(2)\alpha\chi(1)\beta]^* \cdot [\varphi(1)\alpha\chi(2)\beta - \varphi(2)\alpha\chi(1)\beta] dx_1 dx_2$$

….2-40

$$\text{Let } A = \varphi(1)\alpha\chi(2)\beta \qquad \text{….2.41}$$

$$\text{and } B = \varphi(2)\alpha\chi(1)\beta \qquad \text{….2.42}$$

by integrating over all spins and angular part we can get:

$$\Psi^*\Psi = \frac{1}{2}\left[A^*A + B^*B + A^*B + B^*A\right] \qquad \text{….2.43}$$

$$\begin{aligned} &\int \alpha(1)\beta(1) d\delta = 0 \\ &\int \alpha(1)\alpha(1) d\delta = 1 \\ &\int \beta(1)\alpha(1) d\delta = 0 \\ &\int \beta(1)\beta(1) d\delta = 1 \end{aligned} \qquad \text{….2.44}$$

$$\begin{aligned}\varphi(1)&=R_{\varphi}(1)Y\varphi(1)\\ \varphi(2)&=R_{\varphi}(2)Y\varphi(2)\\ \chi(1)&=R_{\chi}(1)Y\chi(1)\\ \chi(2)&=R_{\chi}(2)Y\chi(2)\end{aligned} \qquad \text{….2.45}$$

$$\Gamma''_{corr}(r_1,r_2)=\frac{1}{2}\left[R_{\phi}^{2}(1)R_{\chi}^{2}(2)+R_{\chi}^{2}(1)R_{\phi}^{2}(2)\right] \qquad \text{….2.46}$$

where $\Gamma''_{corr}(r_1,r_2)$ represents the two-particle density function for He-like ions.

2-3-3 The Change in Two-Particle Density:

For N-electron system, the change in the two-particle density due to the electron correlation which can be written as follows [30]**:**

$$\Delta\Gamma_{ij}(x_m,x_n)=\Gamma_{ij}^{corr}(x_m,x_n)-\Gamma_{ij}^{HF}(x_m,x_n) \qquad \text{….2.47}$$

2-3-4 The Change in Two-Particle Radial Distribution Function:

This change can be given by [19]:

$$\Delta D_{ij}(r_1,r_2)=\iint_{\Omega}\Delta\Gamma_{ij}(r_1,r_2)r_1^2r_2^2\,d\Omega_1d\Omega_2 \qquad \text{….2.48}$$

where:

$$\iint\Delta D_{ij}(r_1,r_2)dr_1dr_2=0 \qquad \text{….2.49}$$

Because the correlated and HF descriptions of $D(r_1,r_2)$ are each normalized to unity.

2-3-5 The Change in One-Particle Radial Density Distribution:

This can give by [49]**:**

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

….2.50

or

$$\Delta D(r_1) = \int_0^\infty \Delta D(r_1, r_2) dr_1$$

….2.51

also:

$$\iint \Delta D(r_1, r_2) dr_1 dr_2 = 0$$

….2.52

2-3-6 The Change in Inter-Particle Distribution Function:

The change is due to the correlation in the inter-particle distribution function $f_{ij}(r_{12})$ defined as coulomb hole and is given by [46]:

$$\Delta f_{ij}(r_{mn}) = \int \Delta\Gamma_{ij}(r_m, r_n) \frac{dr_m dr_n}{dr_{mn}}$$

….2.53

Then as in appendix (A) we get:

$$\Delta f_{ij}(r_{12}) = 0.5 \cdot r_{12}(I_1 + I_2)$$

….2.54

$$I_1 = \int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Delta\Gamma(r_1, r_2) r_2 dr_2$$

….2.55

$$I_2 = \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Delta\Gamma(r_1, r_2) r_2 dr_2$$

….2.56

2-4 Eckart-Hyllears Wave function:

This type of wave function allowed for "in-out" correlation since the two electrons may be supposed to be in distinct orbital. The parameter of the inner orbital has a=1.19, and the outer orbital has b=2.18. [13]. The wave function is:

$$\psi(r_1,r_2)=N\left[e^{-(a\cdot r_1+b\cdot r_2)}+e^{-(b\cdot r_1+a\cdot r_2)}\right] \qquad ....2.57$$

where N is the normalization wave function and equals to:

$$N=\sqrt{\frac{16\cdot(a\cdot b)^{\frac{3}{2}}\cdot(a+b)^{3}}{\pi\cdot\left[(a+b)^{3}+8\cdot(a\cdot b)^{\frac{3}{2}}\right]}}$$

To find the two particle density we used eq (2.8):

$$\Gamma(r_1,r_2)=\int\left[N\left[e^{-(a\cdot r_1+b\cdot r_2)}+e^{-(b\cdot r_1+a\cdot r_2)}\right]\right]^{*}\cdot\left[N\left[e^{-(a\cdot r_1+b\cdot r_2)}+e^{-(b\cdot r_1+a\cdot r_2)}\right]\right]d\tau_1 d\tau_2$$

$$....2.58$$

where τ is equal $r^2\sin\theta d\theta d\phi dr$

So the two particle density for Eckart-hyllears wave function is

$$\Gamma(r_1,r_2)=\psi(r_1,r_2)\psi^{*}(r_1,r_2) \qquad ....2.59$$

2-5 Special Configuration-Interactions for Two-Electron Case:

Consider a simple configuration-interaction normalized wave function [50]:

$$\Psi = \frac{1}{\sqrt{2}}\left[c_1\cdot\left(1s\,1s\right)+c_2\cdot\left(1s\,2s'\right)+c_3\cdot\left(2s'2s'\right)\right] \qquad \text{….2.60}$$

i.e. we have three configurations whose determinates are composed of normalized Slater-type orbital.

For He profile

c_1=1.14803

c_2=-0.01865

c_3=-3.0462

$$\Psi = \frac{1}{\sqrt{2}}\left[c_1\cdot\begin{vmatrix}1\mathrm{s}(1)\alpha(1) & 1\mathrm{s}(1)\beta(1)\\ 1\mathrm{s}(2)\alpha(2) & 1\mathrm{s}(2)\beta(2)\end{vmatrix}+c_2\cdot\begin{vmatrix}1\mathrm{s}(1)\alpha(1) & 2\mathrm{s}'(1)\beta(1)\\ 1\mathrm{s}(2)\alpha(2) & 2\mathrm{s}'(2)\beta(2)\end{vmatrix}+\right.$$

$$\left.c_2\cdot\begin{vmatrix}2\mathrm{s}'(1)\alpha(1) & 1\mathrm{s}(1)\beta(1)\\ 2\mathrm{s}'(2)\alpha(2) & 1\mathrm{s}(2)\beta(2)\end{vmatrix}+c_3\cdot\begin{vmatrix}2\mathrm{s}'(1)\alpha(1) & 1\mathrm{s}(1)\beta(1)\\ 2\mathrm{s}'(2)\alpha(2) & 1\mathrm{s}(2)\beta(2)\end{vmatrix}\right]$$

….2.61

Data for this configuration are taken from Sturat and Matsen [50].

Factoring off the spin yields:

$$\Psi = \left[c_1\cdot 1s(1)1s(2)+c_2\cdot 1s(1)2s'(2)+c_2\cdot 2s'(1)1s(2)+c_3\cdot 2s'(2)2s'(2)\right]$$

$$\cdot\left[\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right]$$

….2.62

$$N = \sqrt{\frac{1}{\begin{gathered}c_1c_2\left[\frac{\pi}{4\left[\zeta_1^{3/2}(\zeta_1+\zeta_2)^2\right]}\right]+c_2c_3\left[\frac{3\pi}{14\zeta_2^{5/2}(\zeta_1+\zeta_2)^2}\right]+c_3^2\left[\frac{\pi}{32\zeta_2^4}\right]+ \\ (c_1c_3+c_2^2)\left[\frac{\pi}{2(\zeta_1+\zeta_2)^4}\right]+c_1^2\left[\frac{\pi}{32\zeta_1^3}\right]+c_2c_3\left(\frac{6\pi}{64}\right)\left[\frac{\zeta_1^{5/2}\zeta_2^{3/2}+\zeta_1^{3/2}\zeta_2^{5/2}}{\zeta_1^4\zeta_2^4}\right]\end{gathered}}} \quad \text{....2.63}$$

where $\zeta_1 = 1.55 \quad \zeta_1 = 2.15$

We have four distinct spin orbital, but since they are made up from doubly-filled spatial orbital, we can now on talk about two natural orbital. We shall ignore the spin function during this analysis.

2-6 Calculation Method of Coulomb Hole:

In this work we have taken into account some of atomic properties such as inter-particle distribution $f_{ij}(r_{12})$ and partial distribution function $g(r_{12},r_1)$ to calculate Coulomb hole $\Delta f_c(r_{12})$ and partial Coulomb hole $\Delta g_c(r_{12},r_1)$.

We have also taken into account the two-particle distribution function $D(r_1,r_2)$ to study the change or the difference in two-particle radial distribution function $\Delta D(r_1,r_2)$.

2-6-1 Coulomb Hole Calculation:

In this section, Coulomb hole $\Delta f_c(r_{12})$, partial Coulomb hole $\Delta g_c(r_{12},r_1)$ and the change in two-particle radial distribution function $\Delta D(r_1,r_2)$ of correlated wave function for He-like ions are calculated.

The correlated wave function for He-like ions shows in eq (2.46).

The HF wave function can be written as follows:

$$\Gamma_{HF}(r_1,r_2)=R^2_{1s}(r_1)R^2_{1s}(r_2) \qquad \ldots.2.64$$

where both two-density functions are normalized to unity.

2-6-2 Calculation Method of Coulomb Hole $\Delta f_c(r_{12})$:

The electron-electron distribution function $f(r_{12})$, which describes the probability of locating two electrons separated by inter-electronic distance r_{12}, was first introduced by Coulson and Nielson [13]. Coulomb hole $\Delta f_c(r_{12})$ was then defined in eq (2.53) **[13, 26, 51, 28].** Where the inter-particle distribution function of K (^{1}S) shell for the correlated wave function show in eq (2.54), (2.55), and (2.56) respectively.

2-6-3 Calculation Method of Partial Coulomb Hole $\Delta g_c(r_{12}, r_1)$:

From the definition, the partial Coulomb hole can be written as follows [51]:

$$\Delta g_c(r_{12}, r_1) = g_{corr}(r_{12}, r_1) - g_{HF}(r_{12}, r_1) \qquad ....2.65$$

The partial Coulomb hole $\Delta g_c(r_{12}, r_1)$ represents the change in behavior of Coulomb hole as the position of the test electron is varied.

The partial distribution function $\Delta g_c(r_{12}, r_1)$ for correlated wave function approximation can be calculated as follows:

$$g_{corr}(r_{12}, r_1) = 0.5 r_1 r_{12} \int_{|r_{12}-r_1|}^{|r_{12}+r_1|} \Gamma''_{corr}(r_1, r_2) r_2 \, dr_2 \qquad ....2.66$$

To calculate $g(r_{12}, r_1)$ for HF wave function approximation we can write:

$$g_{HF}(r_{12}, r_1) = 0.5 r_1 r_{12} \int_{|r_{12}-r_1|}^{|r_{12}+r_1|} \Gamma''_{HF}(r_1, r_2) r_2 \, dr_2 \qquad ....2.67$$

2-6-4 The Change in the Two-Particle Radial Distribution $\Delta D_{CI-HF}(r_1,r_2)$ of the CI and HF Wave function:

The change in the two-particle radial distribution function $\Delta D_{CI-HF}(r_1,r_2)$ is defined as a difference between the two-particle radial distribution function D (r$_1$, r2) for correlated and HF approximation **[52]**

$$\Delta D_{CI-HF}(r_1,r_2)=D_{corr}(r_1,r_2)-D_{HF}(r_1,r_2) \qquad \text{….2.68}$$

where the two-particle radial distribution function of K (^{1}S) for the correlated wave function approximation is given by:

$$D_{corr}(r_1,r_2)=\Gamma''_{corr}(r_1,r_2)r_1^2r_2^2 \qquad \text{….2.69}$$

and the two-particle radial distribution function for HF wave function approximation can be written as follows:

$$D_{HF}(r_1,r_2)=\Gamma_{HF}(r_1,r_2)r_1^2r_2^2 \qquad \text{….2.70}$$

Chapter Three

Results, Discussions and Conclusions

3-Results, Discussion and Conclusions

The analysis of electron position distribution in the He-like ions is performed using 15-trem CI correlated wave function of Wiess [17], Echart-Hyllears wave function [13], Simple configuration-interaction wave function [50], the Hartree-Fock wave function is taken from the work of Clementi and Rotti [42]. In this chapter we will show the result and graphics achieved in this research and its analysis for He-like ions of all properties with conclusion and some future work.(in this chapter the symbols HF refers to Hartree-Fock and CI refer to Configuration-interaction and EH refer to Eckart-Hyllears and SCI refer to simple configuration-interaction).

3-1 One-Particle Expectation Value $\langle r_1^n \rangle$:

Table (3-1) Presents, the one particle expectation value $\langle r_1^n \rangle$ and the standard deviation Δr_1 for n=-2 to 2 for K-shell. These values are displayed graphically in Figures (3-1), (3-2), (3-3). It shows the following statements:

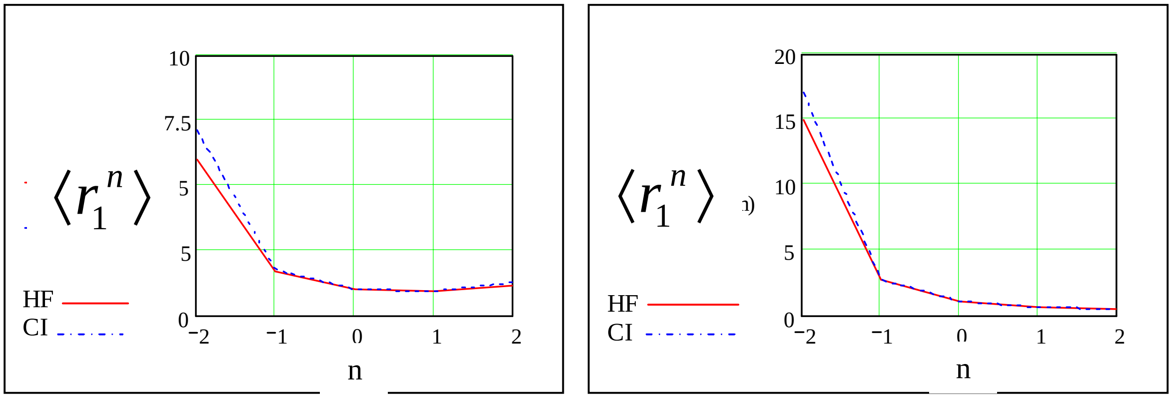
1. In Figure (3-1) for each Z the one particle expectation value $\langle r_1^n \rangle$ for both Hartree-Fock (HF), and Configuration-Interaction (CI) wave function increase when n goes from -1 to -2, and decrease when n goes from 1 to 2, these value mean that expectation values weight different regions of place. For example when we deal with position space, the value of one particle expectation value $\langle r_1^2 \rangle$ indicates how the density distribution is closer to nucleus, so the result of $\langle r_1^2 \rangle$ when n goes from 1 to 2 decrease and the values of $\langle r_1^{-2} \rangle$ indicate how the density distribution is in outer region of the charge clouds.

2. In Figure (3-3) for each wave function Hartree-Fock (HF), Configuration-Interaction(CI), when n = 1 to 2 the one particle expectation value $\langle r_1^n \rangle$ decrease by increasing Z, this is due to the attraction force of nucleus to the charge which leads to decrease the probability of finding the electron near the nucleus.
3. In Figure (3-3) for negative values of n, when n=-1,-2, the expectation values increases by increasing Z due to strongly attraction force between the nucleus and the electron in the outer shell.
4. For n=-1 to -2, the one particle expectation value $\langle r_1^n \rangle$ obtained by Configuration-Interaction (CI)-wave function are larger than those obtained by Hartree-Fock(HF)-wave function. Radial correlation (i.e. the Configuration–Interaction (CI) method takes into account the regulation forces between the electrons) cusses increases in $\langle r_1^n \rangle$ values which is also shown by the change of $\langle r_1^n \rangle$ due to the correlation effect.
5. The one particle expectation value $\langle r_1^n \rangle$ obtained by Configuration-Interaction (CI), wave function smaller than those obtained Hartree-Fock (HF)- wave function when n=1,2 for all Z, because the electron correlation in (CI) approximation is better than that in (HF)-wave function, where the shortcoming of Hartree-Fock (HF) method are due to the neglecting of the electronic repulsions.
6. For n=0 all methods configuration-interaction (CI), Hartree-Fock (HF), Eckart-Hyllears (EH) and Simple configuration-interaction (SCI) wave functions have the same value which equal to unity, because the normalization condition has been applied.

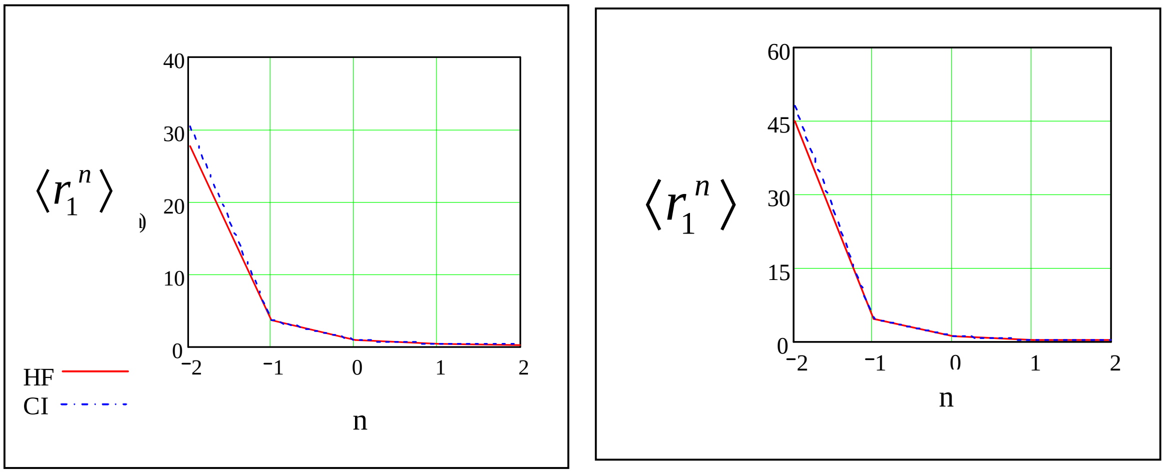
7. Figure (3-1) and Figure (3-3) plot the one particle expectation $\langle r_1^n \rangle$ for He-like ions using both Hartree-Fock (HF), and Configuration-interaction wave function.
8. Figure (3-2) plot the one particle expectation value for K-shell for He atom obtain each Hartree-Fock (HF), and Configuration-interaction (CI), Eckart-Hyllears (EH) and Simple Configuration-Interaction (SimpleCI) wave function.

Table (3-1): The one particle expectation value $\langle r_1{}^n \rangle$ for He –like ions of the Hartree-Fock (HF), and Configuration-Interaction (CI), and Eckart-Hyllraes (EH), and Simple Configuration Interaction wave function.

Atom or ions	shell	$\langle r_1{}^n \rangle$ a.u					Δr1
		n =-2	n =-1	n=0	n =1	n =2	
He	HF	5.981	1.681	1.000	0.919	1.17	0.507
	Ref (51)	5.995	1.687	1.000	0.917	1.18	
	CI	7.148	1.767	1.000	0.94	1.275	0.625
	Ref (49)	6.017	1.688	1.000	0.92	1.193	
	Eckart-Hyllears	5.956	1.685	1.000	0.938	1.237	0.598
	SCI	5.446	1.63	1.000	0.931	1.159	0.540
Li^{+1}	HF	14.912	2.687	1.000	0.572	0.445	0.343
	Ref(51)	14.888	2.685	1.000	0.573	0.446	
	CI	16.947	2.725	1.000	0.61	0.54	0.409
	Ref (49)	14.929	2.687	1.000	0.572	0.446	
Be^{+2}	HF	27.507	3.664	1.000	0.417	0.235	0.247
	Ref(51)	27.753	3.681	1.000	0.414	0.232	
	CI	30.474	3.682	1.000	0.446	0.286	0.295
B^{+3}	HF	44.744	4.687	1.000	0.324	0.142	0.191
	Ref(51)	44.538	4.674	1.000	0.325	0.143	
	CI	48.022	4.66	1.000	0.349	0.173	0.227
	Ref (49)	44.757	4.687	1.000	0.324	0.141	



(A): He (B): Li^{+1}



(C): Be^{+2} (D): B^{+3}

Figure (3-1): The one-particle radial distributions function $\langle r_1^{\,m} \rangle$ for He-Like Ion using Hartree-Fock and Configuration-Interaction wave function.

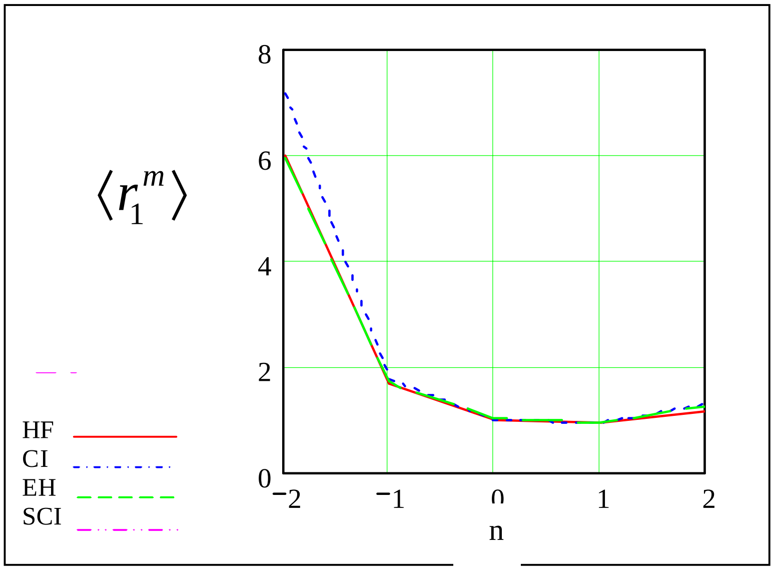
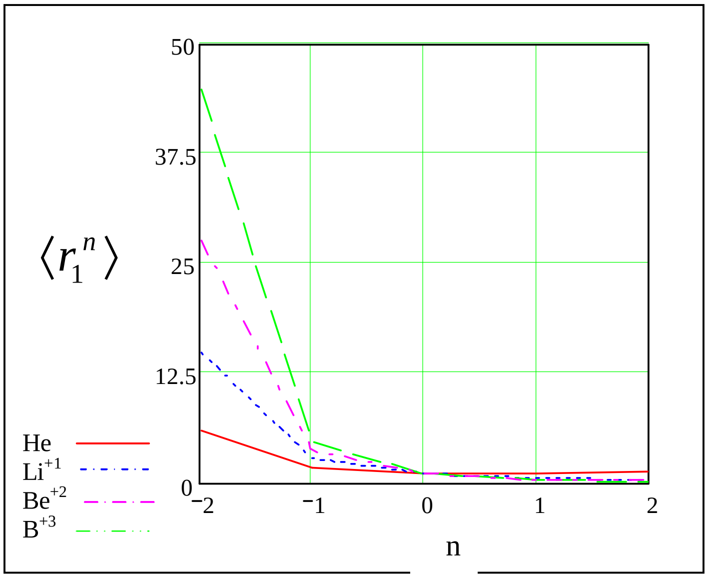
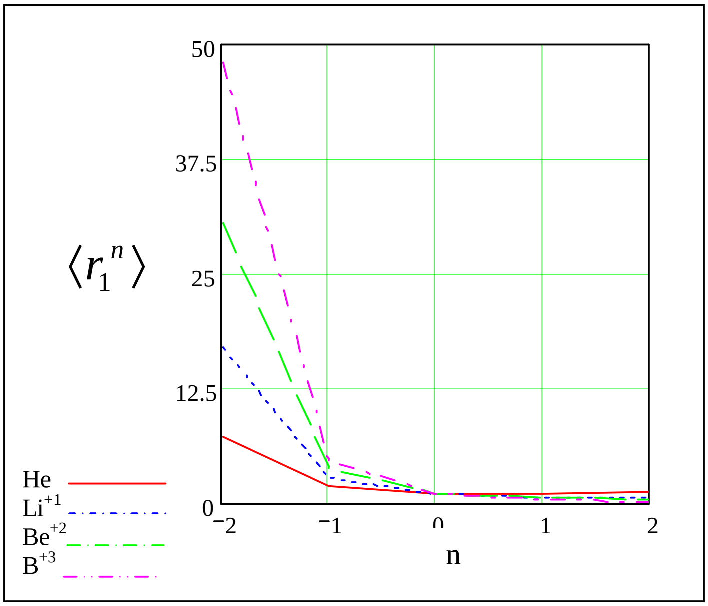


Figure (3-2): The one particle radial distribution function $\langle r_1^n \rangle$ for He atom using Hartree-Fock , Configuration-Interaction, Eckart-Hyllears and Simple Configuration-Interaction wave functions.



(A): Hartree-Fock (HF) wave function.



(B): Configuration-Interaction (CI) wave function.

Figure (3-3): The one particle expectation values $\langle r_1^n \rangle$ for He-like ions when n=-2 to 2.

3-2 The One-Particle Radial Distribution Function $D(r_1)$:

Table (3-2) presents, the location and maximum value for one-particle radial distribution function for He-like ions. These values are displayed graphically in Figures (3-4 to 3-9), These figures showse the following statements:

1- Figures (3-4), (3-5) are shown the one-particle radial distribution function $D(r_1)$ for He-like ions using both Hartree-Fock (HF), and Configuration-interaction wave function.

2- In Figure (3-4) increase the maximum value for one-particle radial distribution function with increasing the atomic number Z, and close the position of maxima value from nucleus with increasing the atomic number Z, this mean that the increase in coulomb attraction for K-shell with nucleus.

3- In Figure (3-4) the maximum value for one-particle radial distribution function by Configuration-Interaction (CI) is smaller from the maximum value for Hartree-Fock (HF) because the electron correlation CI is better than HF.

4- In Figure (3-5) Always r_1(CI) < r_1(HF) for all atom and ions. And in In Figure (3-6) For He atom r_1 (CI) < r_1 (EH) < r_1 (HF) < (SCI).

5- Figures (3-7) shows the one-particle radial distribution function $D(r_1)$ for K-shell for He-like ions using each Hartree-Fock (HF), and Configuration-interaction (CI), Eckart-Hyllears (EH) and Simple Configuration-Interaction (SCI) wave function.

6- The correlation effect on $D(r_1)$ can be seen in Figure (3-8), which represents the difference $\Delta D(r_1)$ between the correlated wave function CI and uncorrelated wave function HF plotted against the distance r_1. The shape difference appears as positive and negative contribution. Where the positive contribution refers to an increase $D(r_1)$ and negative region decrease in $D(r_1)$ this change caused correlation effect, the correlation effect comes from the separation of two electrons of this shell, where we put each one in a virtual state (configuration).

7- Figure (3-9) shows that the difference between Hartree-Fock and Configuration-Interaction the location of maximum value close to nucleus when Z increases because the correlation effect increase as Z increases.

Table (3-2): Maximum and Location of the One-Particle Distribution Function for He-like Ions of the Hartree-Fock HF wave function, and Configuration-interaction CI, Eckart-Hyllears EH wave function and Simple Configuration-Interaction (SCI).

Atom or ion	Wave function	r_1 a.u	Max $D(r_1)$
He	HF	0.57	0.86359
	CI	0.52	0.84113
	EH	0.56	0.872
	SCI	0.61	0.85886
Li+1	HF	0.36	1.4076
	CI	0.34	1.3123
Be+2	HF	0.27	1.9353
	CI	0.26	1.8042
B+3	HF	0.21	2.4904
	CI	0.20	2.3169

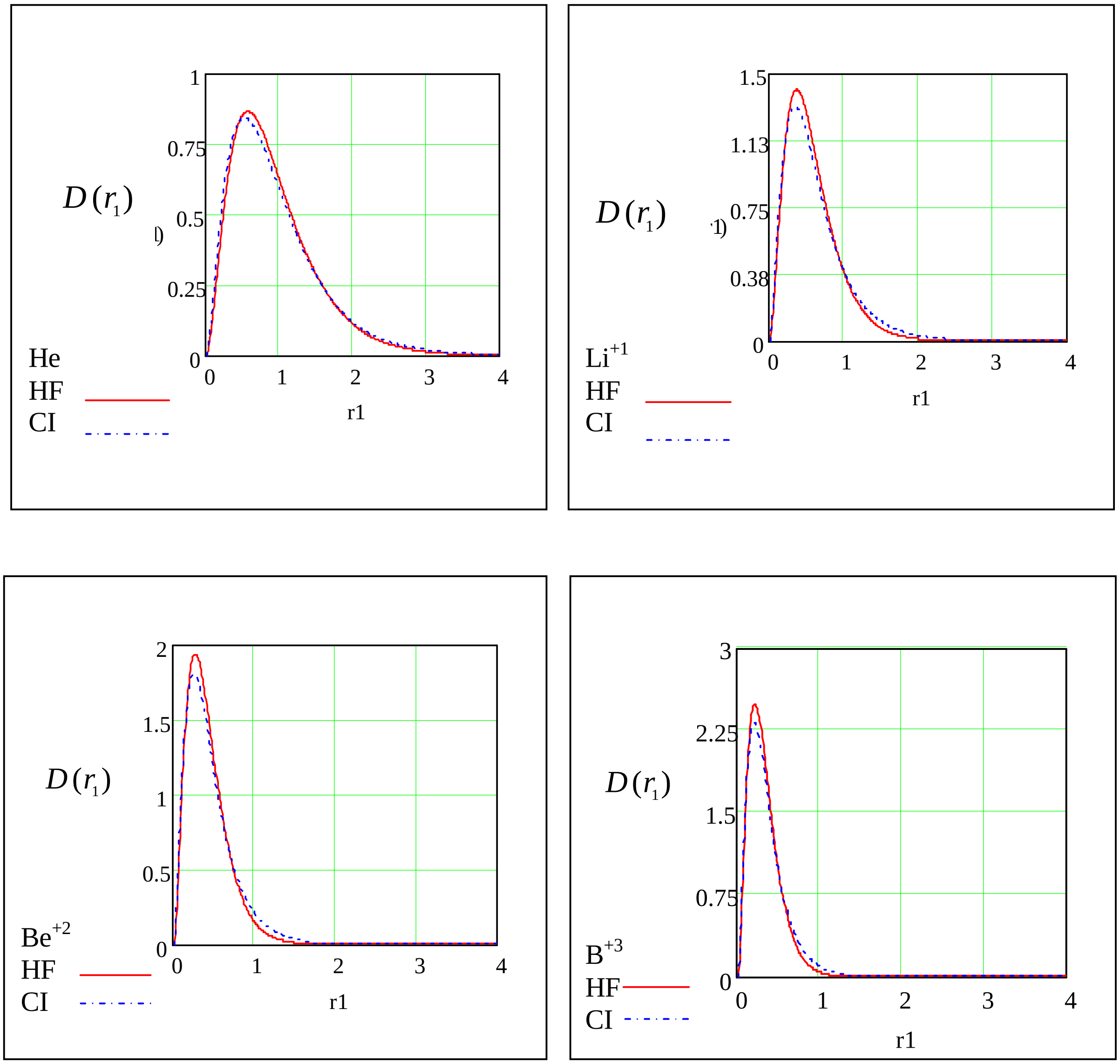
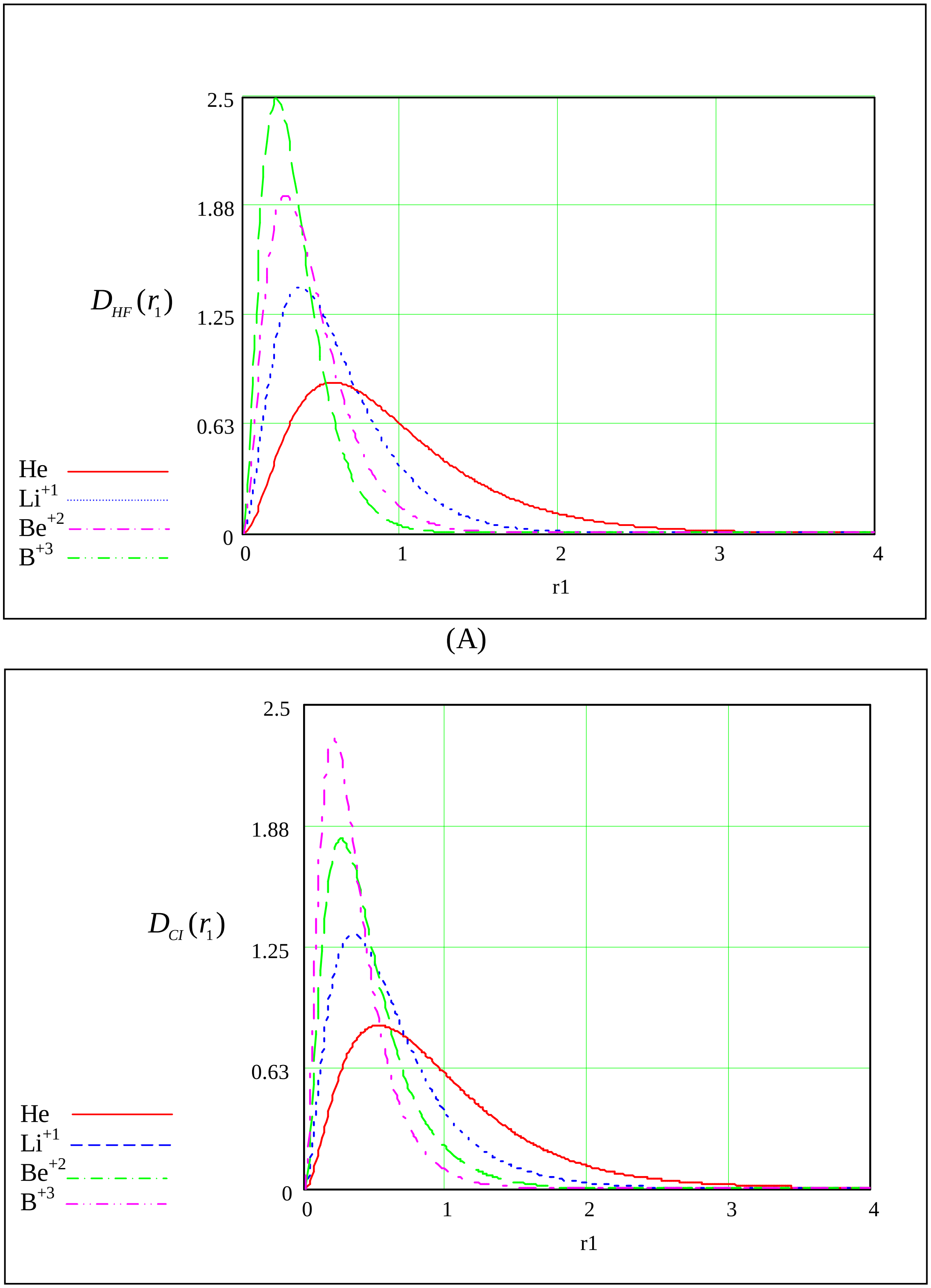


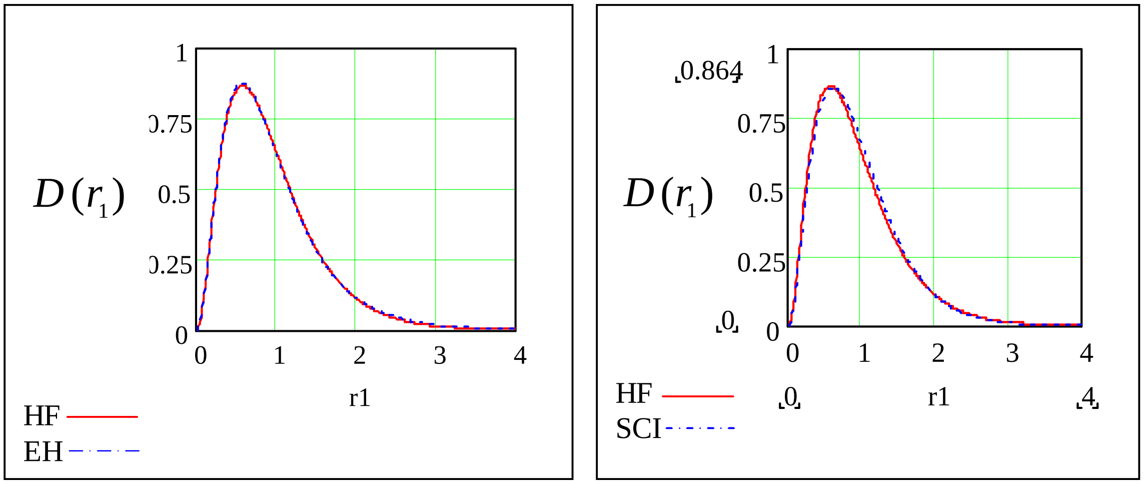
Figure (3-4): The one-particle radial distribution function $D(r_1)$ for He-like ions for Hartree-Fock (HF) and Configuration-Interaction (CI).



(A)

(B)

Figure (3-5): The one-particle radial distribution function $D(r_1)$ for He-like ions using A-Hartree-Fock, B- Configuration-Interaction wave function.



(A) (B)

Figure (3-6): The one particle radial distribution function $D(r_1)$ for He atom using A-Hartree-Fock and Eckart-Hyllears wave function.
B- Hartree-Fock and Simple Configuration-Interaction.

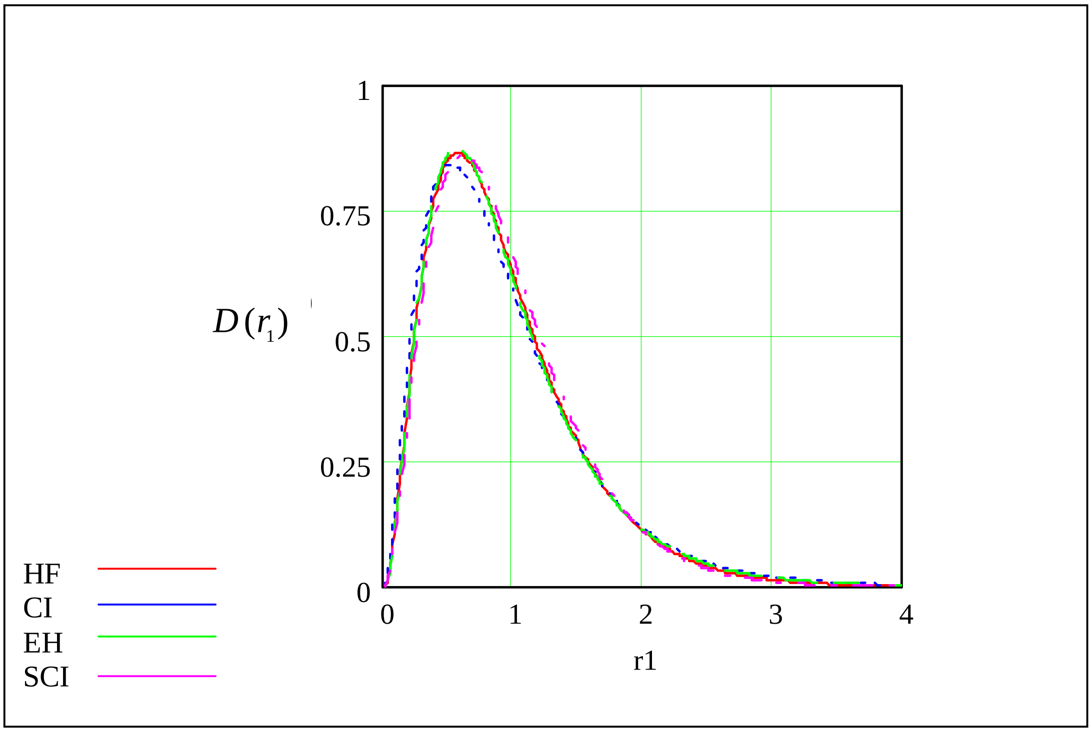
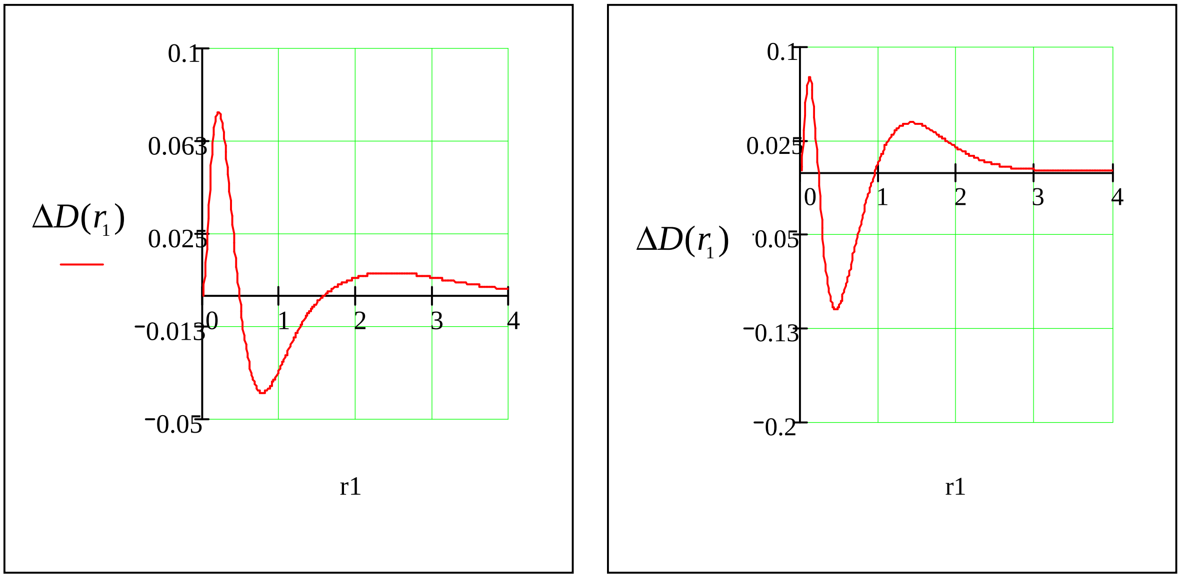
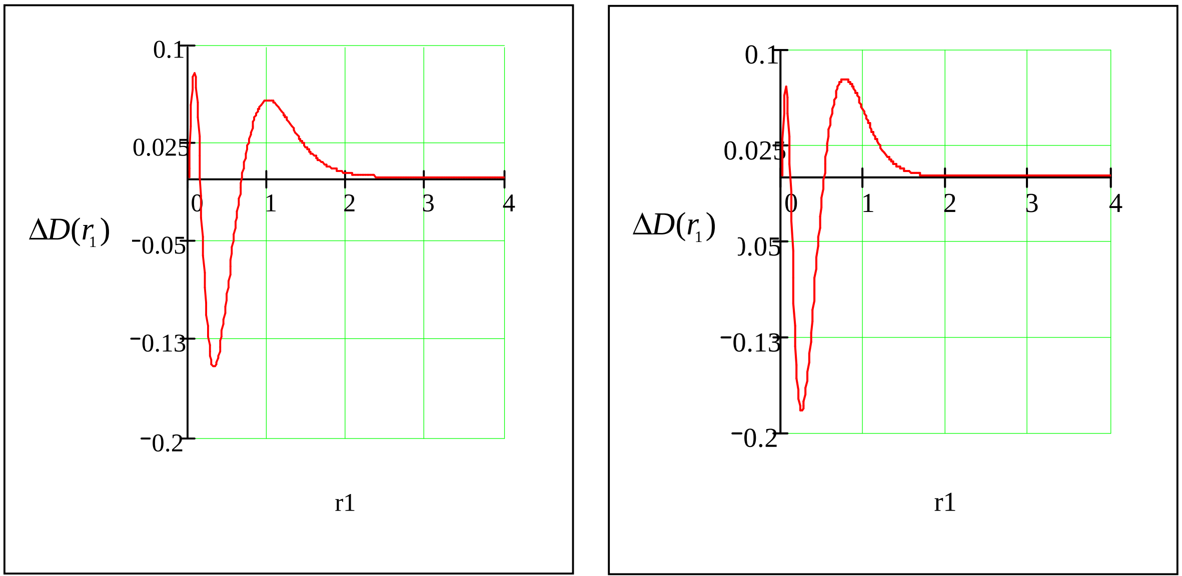


Figure (3-7): The one particle radial distribution functions $D(r_1)$ for He atom using Hartree-Fock, Configuration-Interaction, Eckart-Hyllears, and Simple Configuration-Interaction wave functions.



(A): He (B): Li^{+1}



(C): Be^{+2} (D): B^{+3}

Figure (3-8): The difference of one particle radial distribution functions $\Delta D(r_1)$ between Hartree-Fock and Configuration-Interaction wave function for He-like ions.

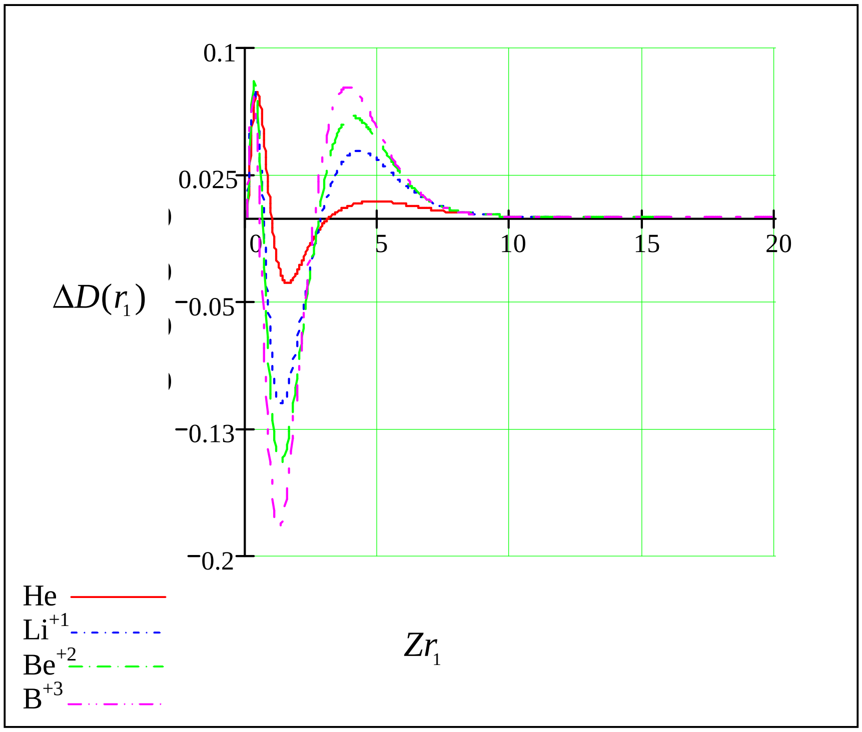


Figure (3-9): The difference of one particle radial distribution function $\Delta D(r_1)$ For He-like ions obtained Hartree-Fock and Configuration-Interaction wave function.

3-3 Coulomb Hole $\Delta f\ (r_{12})$:

The probability of finding the inter-particle distribution function $f(r_{12})$ between electrons with unlike spin in of Hartree-Fock and CI wave function for He iso electronic sequence (He-Like ions) can be observed in the Figures(3-10),(3-11) and (3-12).

1. In Figure (3-16) and Figure (3-17) the maximum value for SCI > EH > HF > CI and the location for each wave function r_{12} SCI > EH > HF > CI.
2. The Coulomb holes plotted as a difference between the $f_{corr}(r_{12})$ figure (3-13-A)and $f_{HF}(r_{12})$figure (3-13-B) are presented in figure(3-14)for each Z.
3. The locations and the maximum values of the density distribution function max$f(r_{12})$ for different types of wave function are tabulated in Table (3-3) for He-Like ions.
4. Figure(3-13) and Table (3-3) show that, as Z increases, the maximum probability of the inter-particle distribution functions $f(r_{12})$ for HF and CI approximations increase and it also observed that the location of these maxima decreases as Z becomes large. Because the electron correlation increases as Z increases.
5. Coulomb holes of the $\Delta f_c(r_{12})$ are presented in figure (3-15) for the He-Like ions. These holes are to possess considerable similarity when plotted against the scaled coordinate Zr_{12}.
6. The balance between the positive and negative contribution for a given $\Delta f_C(r_{12})$ curve is a consequence of the normalization conditions on $f_{corr}(r_{12})$ and $f_{HF}(r_{12})$ whereas the magnitude and ,in particular, the location of each extremum of a Coulomb hole gives valuable insight

into the various effects introduced by correlation. Since the negative region of $\Delta f_C(r_{12})$ indicates a reduction in $f(r_{12})$ relative to the Hartree-Fock curve, the value of r_{12} such that $\Delta f_C(r_{12})=0$ may be interpreted as the radius of Coulomb hole . It was found that radius decreases as Z increases. The radius and the area of the holes for groups of He are tabulated in Table (3-4). From Table (3-4) and figure (3-18) the radius of coulomb hole for HF&CI > HF&SCI > HF&EH. And the area of coulomb hole HF&CI > HF&SCI > HF&EH.

3-3-1 The Inter-Particle Expectation Value $\langle r_{12}^n \rangle$

The inter-particle expectation values $\langle r_{12}^n \rangle$ of HF and CI wave function approximations for the He-Like ions are tabulated in Table (3-5).

1. Figure(3-19) represents the $\langle r_{12}^n \rangle$ for each Z for HF and CI wave functions, The result from this figure (3-19) and Table (3-5) show that $< r_{12}^n >_{HF}$ is greater than $< r_{12}^n >_{CI}$ at n = -1,-2 and at n=1,2 $< r_{12}^n >_{HF}$ is less than $< r_{12}^n >_{CI}$. Comparing between the expectation values for the HF and CI wave functions as Z series are plotted in figure(3-20), that the $< r_{12}^n >_{HF}$ < Li^+ < Be^{2+} < $B^{+3}$for –ve n and for +ve n the $< r_{12}^n >_{HF}$ of He > Li^+ > Be^{2+}> B^{+3} . This influence has caused $f(r_{12})$ to become more contracted towards the origin.
2. Figure (3-21-A) shows that the inter expectation value for Eckart-Hylleras (EH) when n=-1, -2 is less than that for Hartree-Fock, and for n=1, 2 the value of Eckart-Hyllears (EH) is larger than the Hartree-Fock.
3. Figure (3-21-B) shows that the inter expectation value for Simple

Configuration-Interaction (SCI) when n=-1, -2 is less than for Hartree-Fock. And for n=1, 2 the value of Simple Configuration-Interaction (SCI) is larger than the Hartree-Fock.

From Figure (3-21-C) and table (3-5) we found the relation for

n=-2 $\langle r_{12} \rangle_{HF} > \langle r^{n}_{12} \rangle_{CI} > \langle r_{12} \rangle_{EH} > \langle r_{12} \rangle_{SCI}$.

For n=2 $\langle r^{n}_{12} \rangle_{CI} > \langle r_{12} \rangle_{EH} > \langle r_{12} \rangle_{HF} > \langle r_{12} \rangle_{SCI}$.

For n=-1 $\langle r_{12} \rangle_{HF} > \langle r^{n}_{12} \rangle_{CI} > \langle r_{12} \rangle_{EH} > \langle r_{12} \rangle_{SCI}$.

For n=1 $\langle r_{12} \rangle_{EH} > \langle r^{n}_{12} \rangle_{CI} > \langle r_{12} \rangle_{SCI} > \langle r_{12} \rangle_{HF}$.

3-3-2 The partial Coulomb hole

The $g(r_{12},r_1)$ diagrams show the change in behavior of the inter-particle probability functions as the position of the test electron is varied These surfaces are presented in figure(3-22) and figure(3-23) for the HF and CI wave functions for each Z

1. The contour diagrams for the $g(r_{12},r_1)$ surface mentioned above are presented in figure (3-24) and figure (3-25) for HF and CI wave functions respectively.
2. The locations and the maximum values of the partial density distribution function $g(r_{12},r_1)$ of HF and CI for each Z are tabulated in Table (3-6).
3. The surface diagrams show that the maximum of $g(r_{12},r_1)$ increases as

Z increases for He iso electronic sequences and the contour diagrams show that the $g(r_{12},r_1)$ becomes more diffuses and decreases in magnitude as Z increases for He iso electronic sequences.

4. The change in the partial Coulomb holes for He-Like ions is plotted as surface diagrams of the series of Z (He, Li^+, Be^{+2}, B^{+3}) in the figure (3-26). Figure (3-27) show contour diagrams for He-Like ions for the same series.
5. The surface diagrams show that the depth of Coulomb hole increases and the radius decreases as Z increases and the contour diagrams show coulomb hole becomes more diffuses and decreases in magnitude as Z increases.

Table (3-3): Maximum and Location of The Inter-Particle Distribution Function for He-like Ions of the Hartree-Fock (HF) wave function, and Configuration-interaction (CI), Eckart-Hyllears (EH) wave function and Simple Configuration-Interaction (SCI).

Atom or ions	Wave function	r_{12} a.u	$f\ (r_{12})$
He	HF	0.98	0.624
	CI	0.97	0.623
	Eckart-Hyllears	1.04	0.622
	SCI	1.08	0.647
Li+1	HF	0.63	1.029
	CI	0.61	0.945
Be+2	HF	0.49	1.407
	CI	0.42	1.278
B+3	HF	0.35	1.826
	CI	0.33	1.629

Table (3-4): The radius and the area of Coulomb hole $\Delta f_C(r_{12})$ for He-like ions.

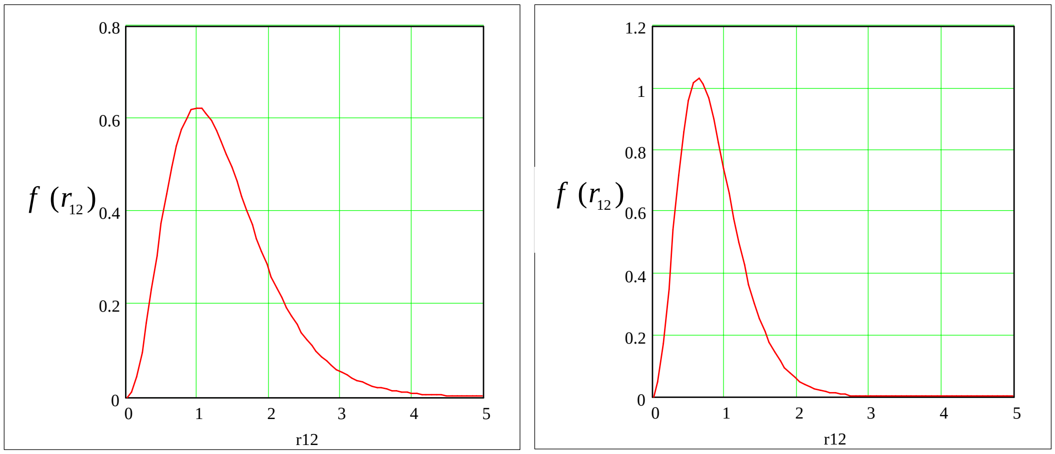
Atoms or ions	Wave Function	Radius of coulomb hole a.u	Area of coulomb hole a.u
He	HF &CI	1.13	0.015
	HF&EH	1.10	0.0176
	HF & SCI	1.11	0.0177
	Ref (13)	1.1	
Li^{+1}	HF &CI	1.05	0.055
Be^{+2}	HF &CI	0.84	0.066
B^{+3}	HF &CI	0.66	0.078

Table (3-5): The Inter-Expectation Value $\langle r_{12}^{n} \rangle$ For He-Like Ions of Hartree-Fock, Configuration-interaction, Eckart-Hyllears and Simple Configuration-Interaction wave functions.

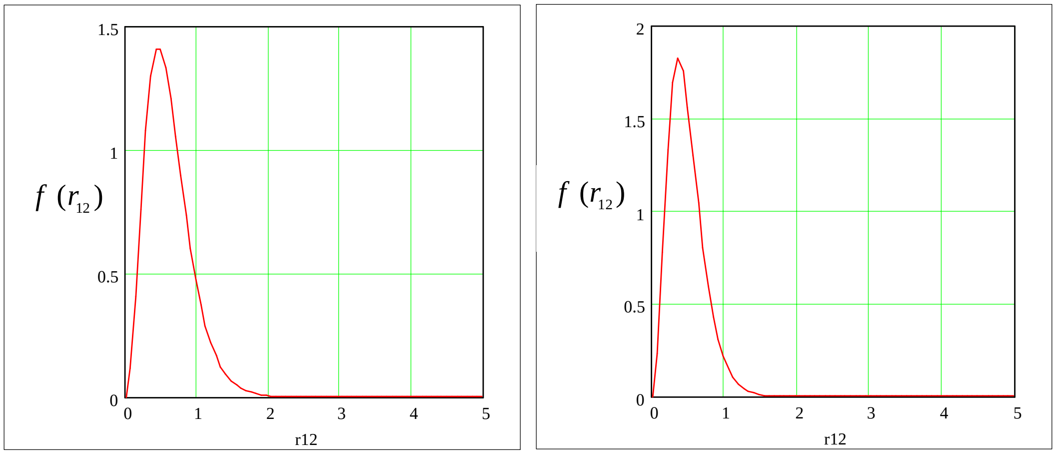
Atom	Wave function	$\langle r_{12}^{n} \rangle$ a.u					Δr_{12}
		-2	-1	0	1	2	
He	HF	1.828	1.017	1.000	1.340	2.313	0.719
	CI	1.815	1.016	1.000	1.389	2.512	0.763
	Eckart-	1.701	0.992	1.000	1.395	2.472	0.725
	SCI	1.612	0.983	1.000	1.368	2.314	0.665
	Ref (26)	1.480	0.946	1.000	1.422	2.513	0.702
Li^{+1}	HF	4.727	1.652	1.000	0.838	0.89	0.433
	CI	4.474	1.583	1.000	0.84	0.91	0.452
	Ref (26)	4.114	1.569	1.000	0.862	0.926	0.427
Be^{+2}	HF	8.827	2.261	1.000	0.609	0.469	0.313
	CI	8.305	2.158	1.000	0.663	0.573	0.365
	Ref (26)	8.078	2.192	1.000	0.618	0.477	0.38
B^{+3}	HF	14.495	2.902	1.000	0.474	0.284	0.243
	CI	13.309	2.721	1.000	0.51	0.342	0.286

Table (3-6): The Maximum and Location of the Partial Coulomb Hole $g(r_1, r_{12})$ for He-Like Ions obtained by Hartree-Fock, Configuration-Interaction Wave function.

Atom or Ions	Wave function	r_1 a.u	r_{12} a.u	$g(r_1, r_{12})$
He	HF	0.57	0.98	0.673
	CI	0.52	0.97	0.622
Li^{+1}	HF	0.36	0.63	1.75
	CI	0.34	0.61	1.64
Be^{+2}	HF	0.27	0.49	3.127
	CI	0.26	0.42	3.025
B^{+3}	HF	0.21	0.35	5.652
	CI	0.2	0.33	5.632

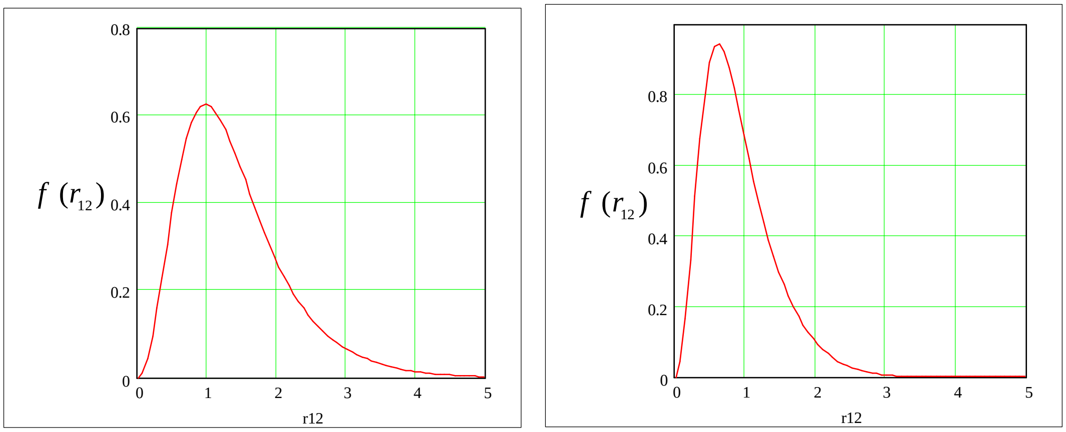


(A): He (B): Li^{+1}



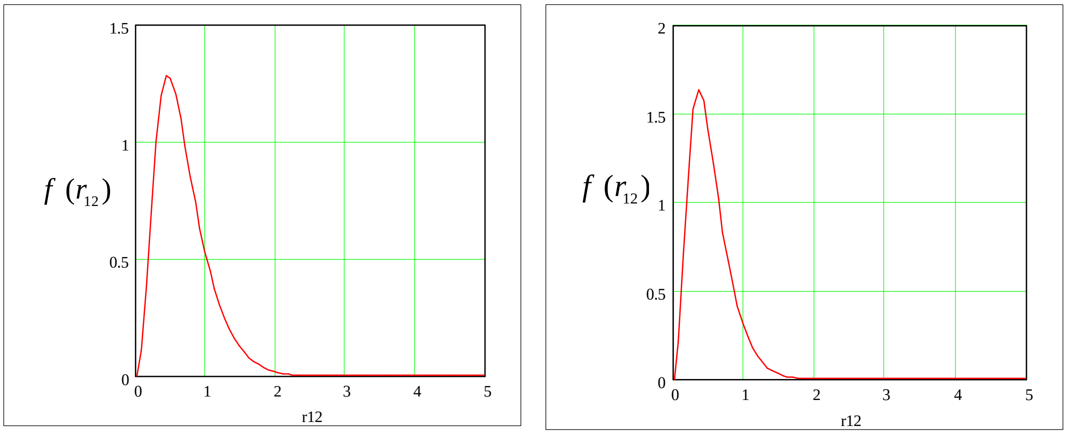
(C): Be^{+2} (D): B^{+3}

Figure (3-10): The Inter-Particle Distribution Function $f(r_{12})$for He-Like ions obtained by Hartree-Fock Wave function.



(A): He

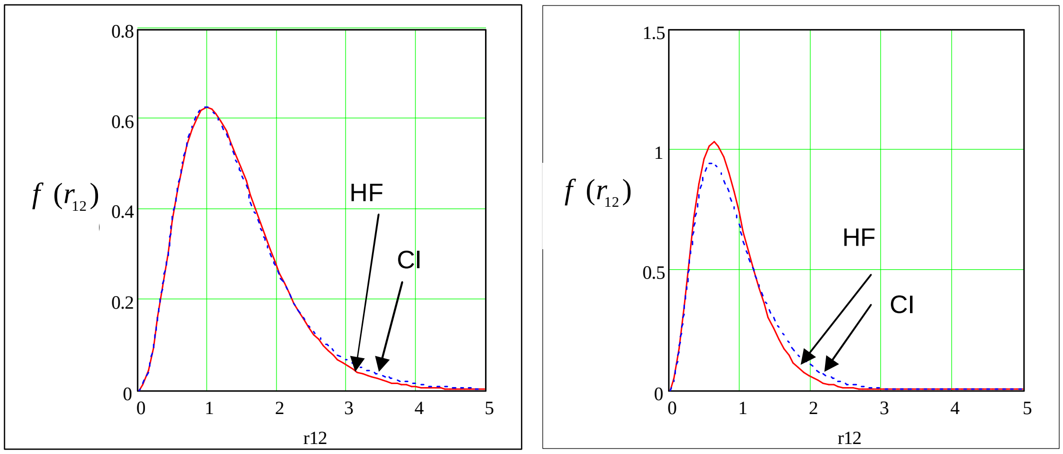
(B): Li^{+1}



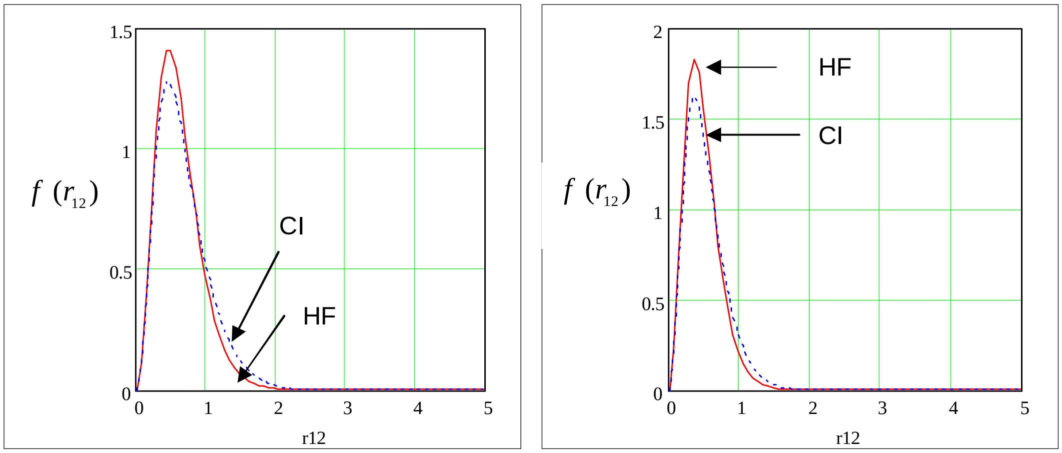
(C): Be^{+2}

(D): B^{+3}

Figure (3-11): The Inter-Particle Distribution Function $f(r_{12})$for He-Like ions obtained by Configuration-Interaction wave function.

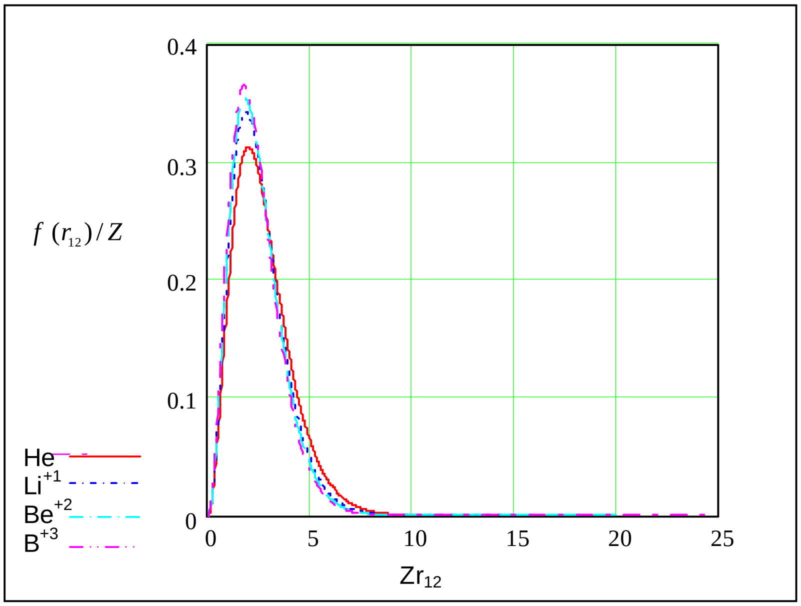


(A): He (B): Li^{+1}

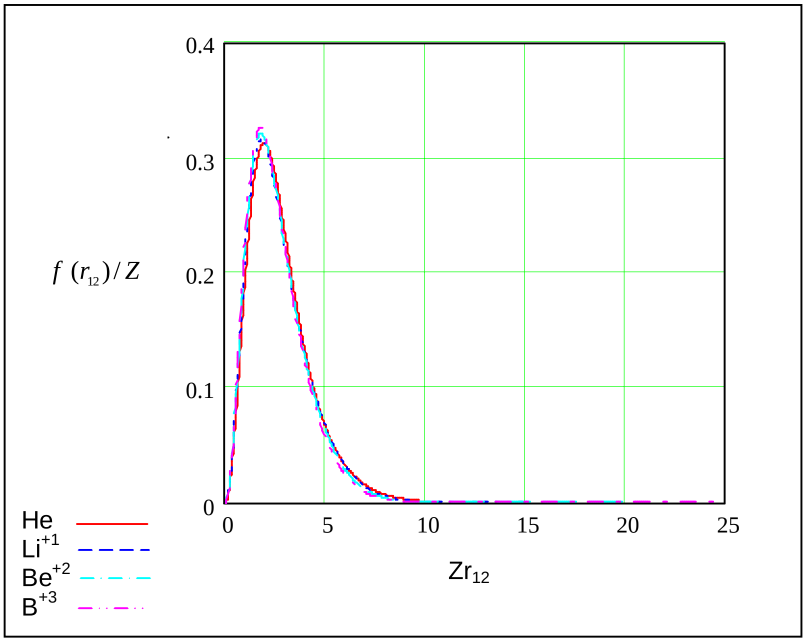


(C): Be^{+2} (D): B^{+3}

Figure (3-12): The Inter-Particle Distribution Function $f(r_{12})$for He-Like ions obtained by Hartree-Fock and Configuration-Interaction wave functions.

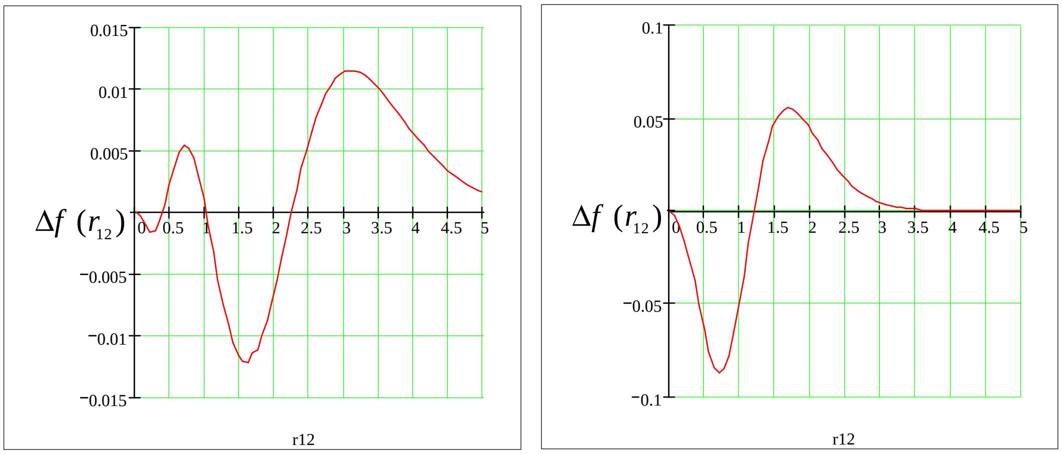


A- Hartree-Fock wave function

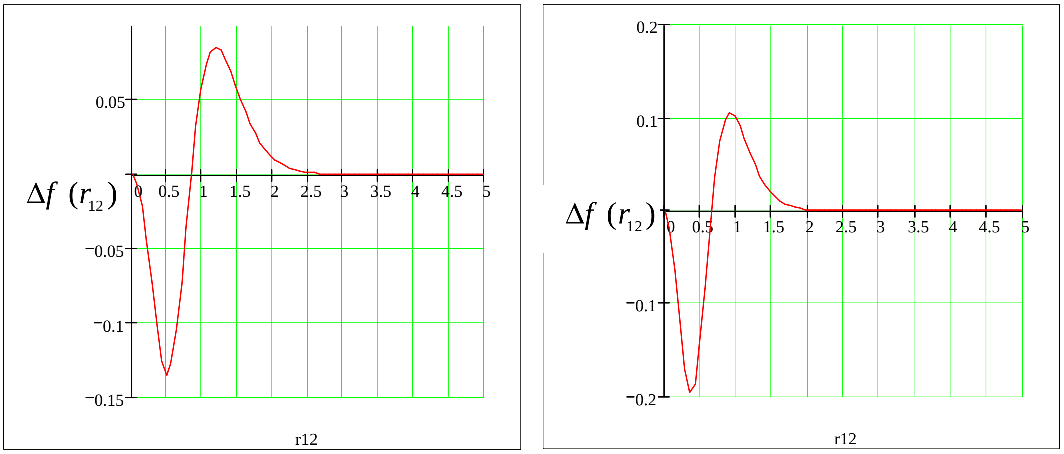


B-Configuration-Interaction wave function

Figure (3-13): The Inter-Particle Distribution Function $f(r_{12})$ for He-Like ions.

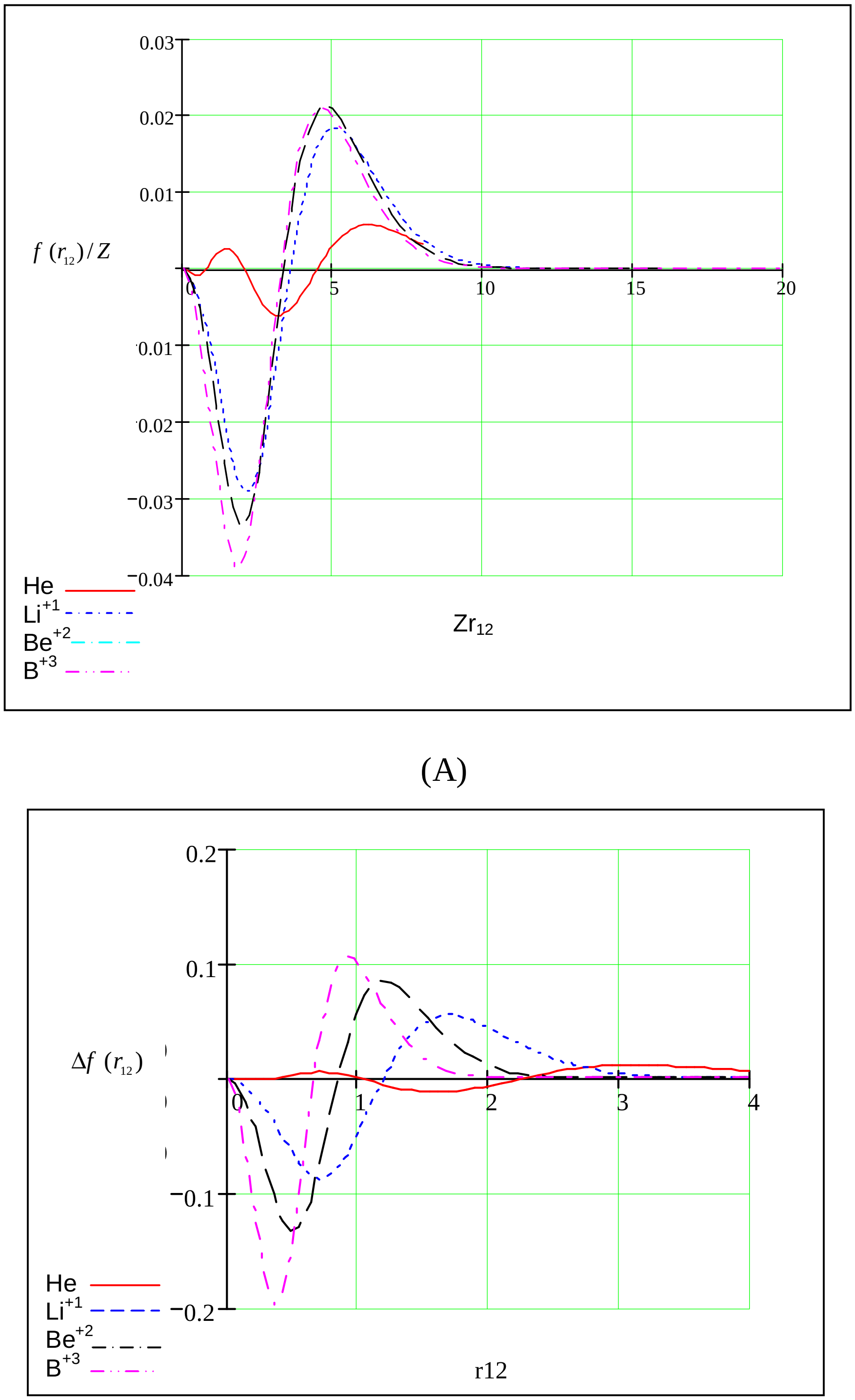


(A): He (B): Li^{+1}



(C): Be^{+2} (D): B^{+3}

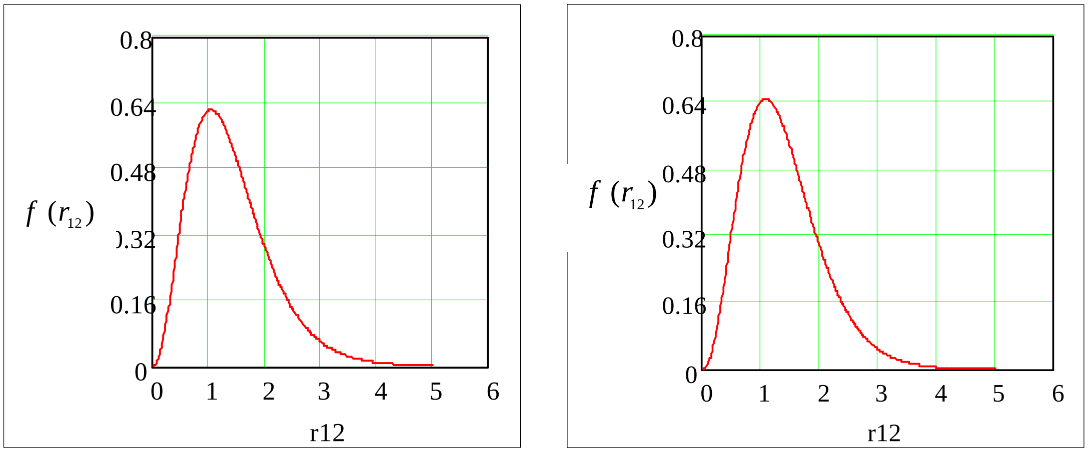
Figure (3-14): The Coulomb hole as a difference between Inter-Particle Distribution Function for He-Like Ions obtained by Hartree-Fock and Configuration-Interaction Wave Functions.



(A)

(B)

Figure (3-15): The Coulomb hole as a difference between Inter-Particle Distribution Function for He-Like Ions obtained by Hartree-Fock and Configuration-Interaction Wave Functions.



(A)

(B)

Figure (3-16): The Inter-Particle Distribution Function *f(*r_{12}*)*for He-Like ions obtained by

A- Eckart-Hylleras Wave Function.
B- Simple Configuration-Interaction Wave Function.

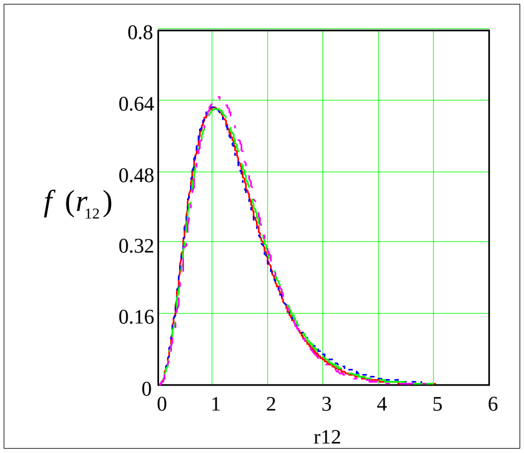
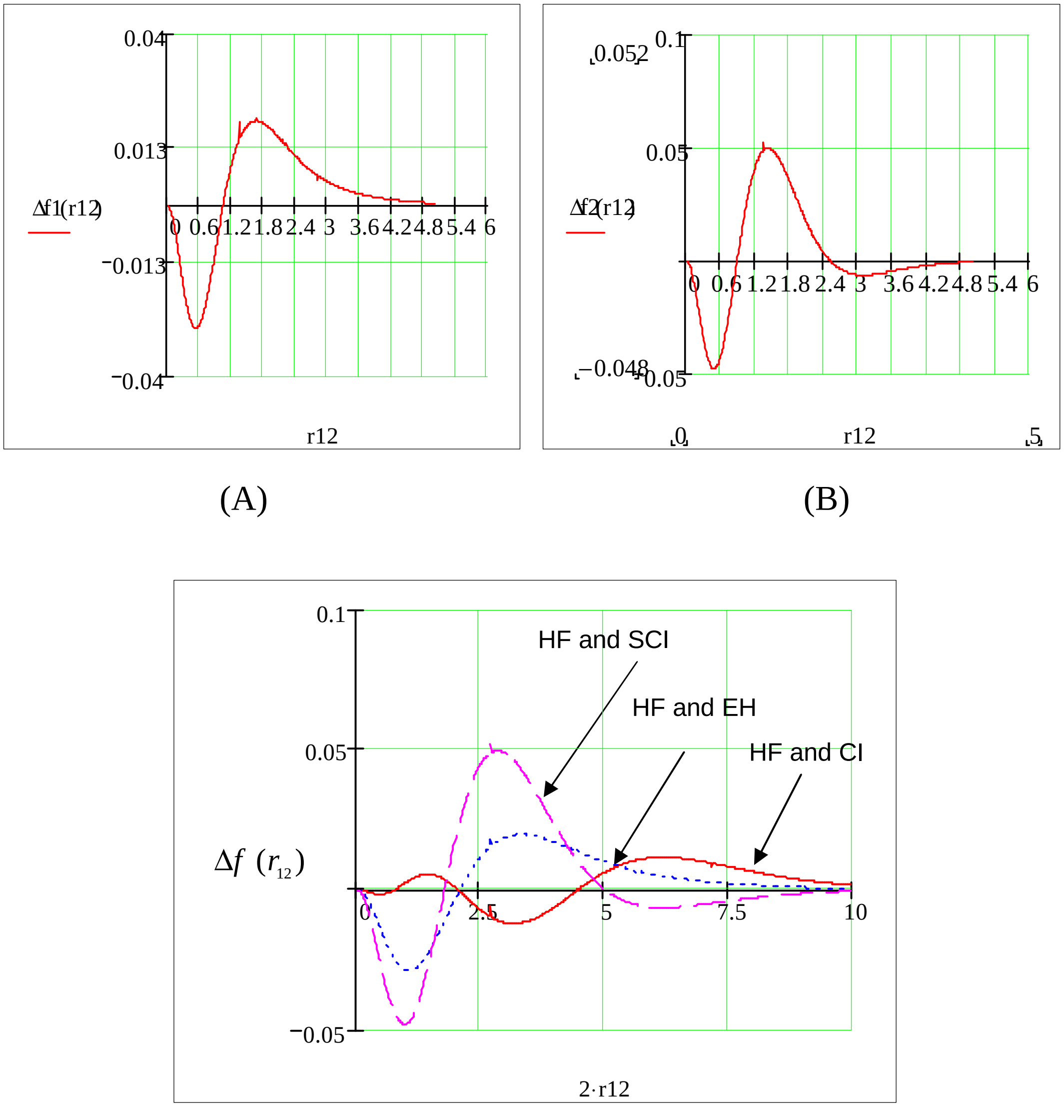


Figure (3-17): The Inter-Particle Distribution Function *f(*r_{12}*)*for He-atom obtained by

A- Hartree-Fock.
B- Configuration-Interaction.
C- Eckart-Hylleras
D- Simple Configuration-Interaction



(A) (B)

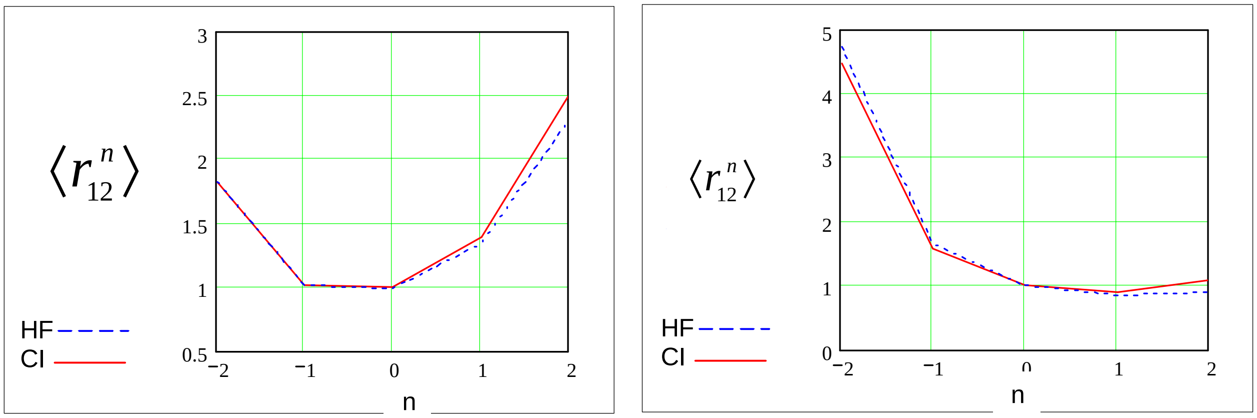
(C)

Figure (3-18): The Coulomb hole as a difference between Inter-Particle Distribution Function for He-atom obtained by and Configuration-Interaction Wave Functions.

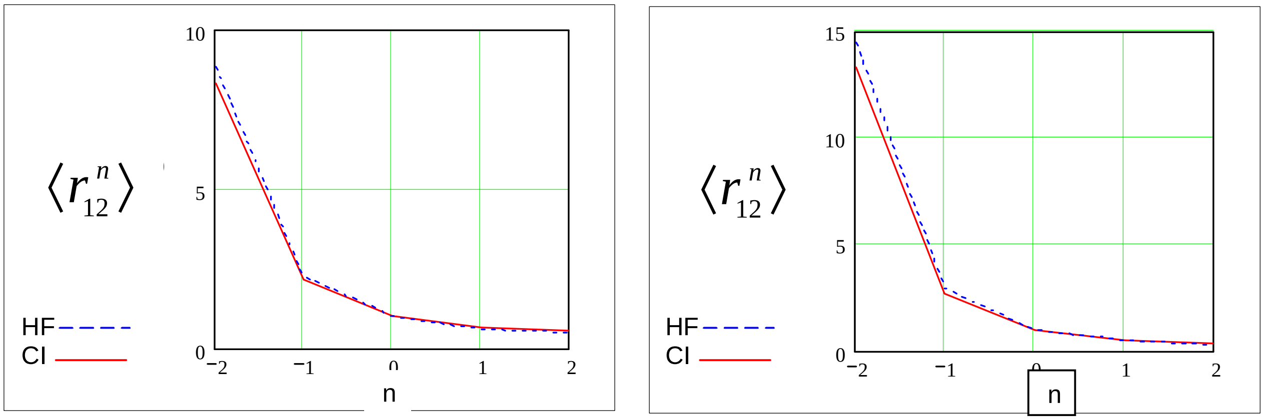
A- Hartree-Fock and Eckart-Hyllears Wave Functions.

B- Hartree-Fock and Simple Configuration-Interaction Wave Functions.

C- Hartree-Fock and Eckart-Hyllears and Simple Configuration-Interaction Wave Functions.

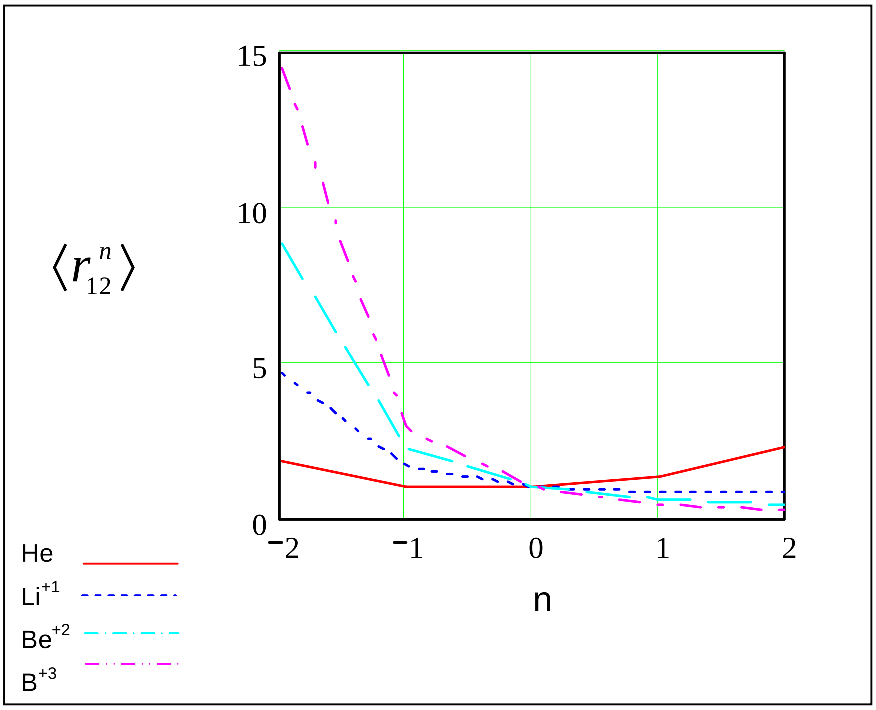


(A): He (B): Li^{+1}

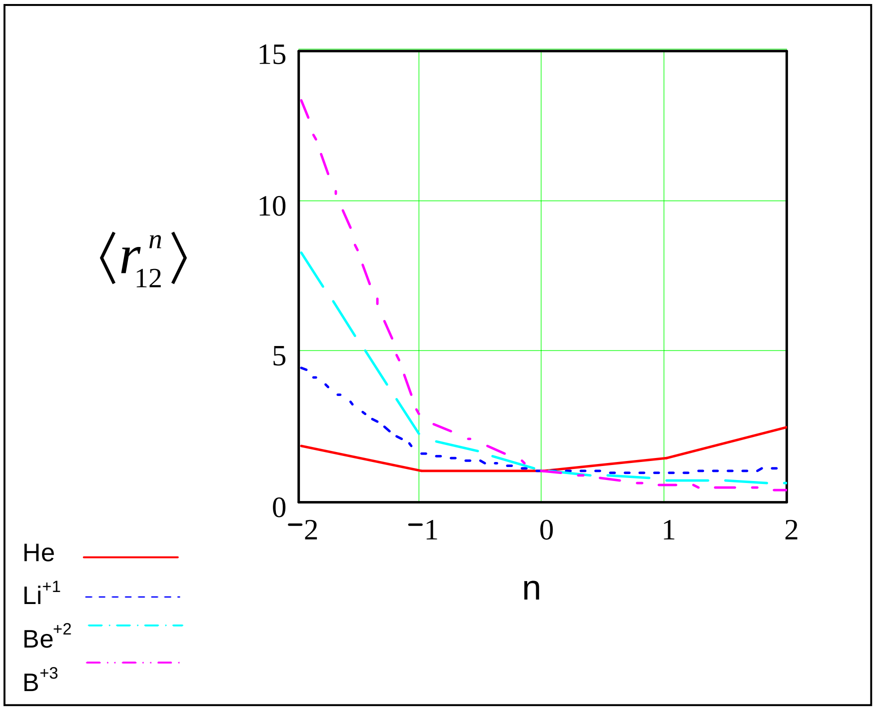


(C): Be^{2} (D): B^{+3}

Figure (3-19): The Inter-Particle Expectation Value $\langle r_{12}^{n} \rangle$ For He-Like Ions using By Hartree-Fock and Configuration-Interaction Wave Functions.

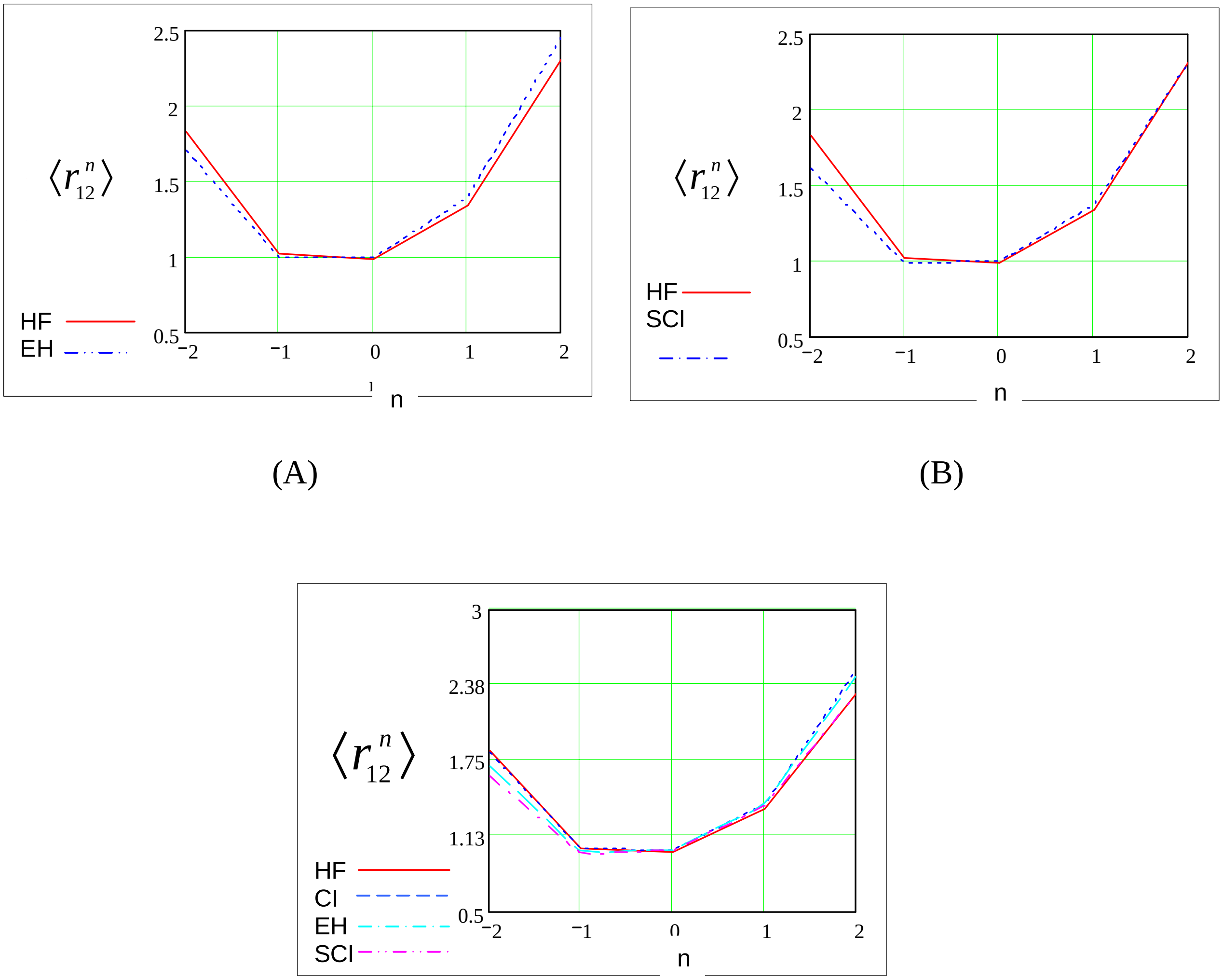


(A): Hartree-Fock



(B): Configuration-Interaction

Figure (3-20): The Inter-Particle Expectation Value $\langle r_{12}^{n} \rangle$ for He-Like Ions

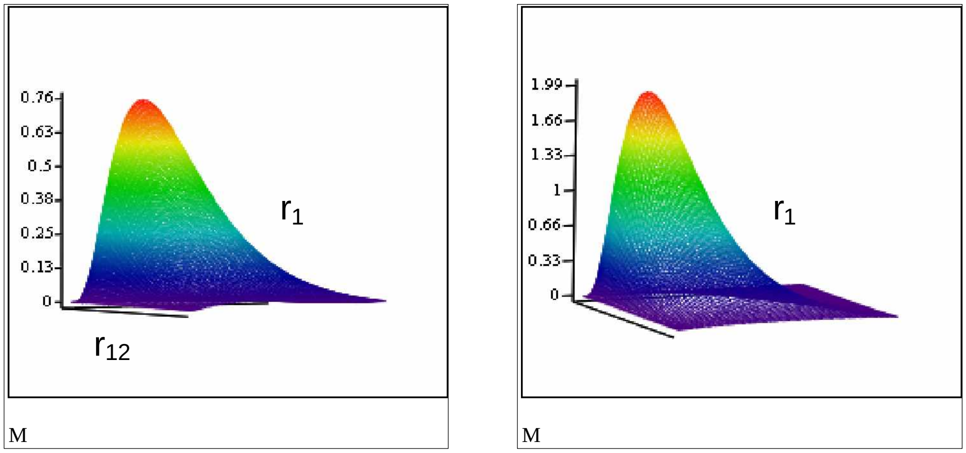


(A) (B)

(C)

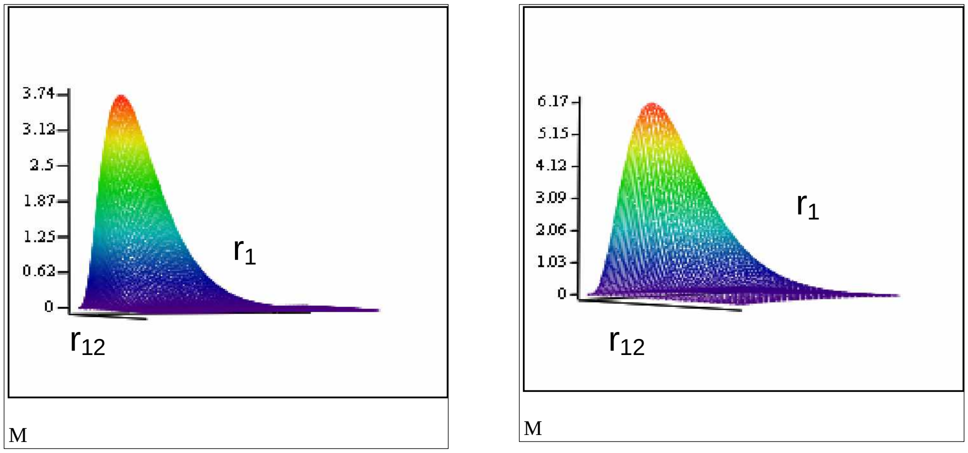
Figure (3-21): The Inter-Particle Expectation Value $\langle r_{12}^{n} \rangle$ for He-Like Ions

A- Hartree-Fock and Eckart-Hyllears.
B- Hartree-Fcok and Configuration-Interaction.
C- Hartree-Fock, Configuration-Interaction, Eckart-Hylleras and Simple Configuration-Interaction.



(A): He

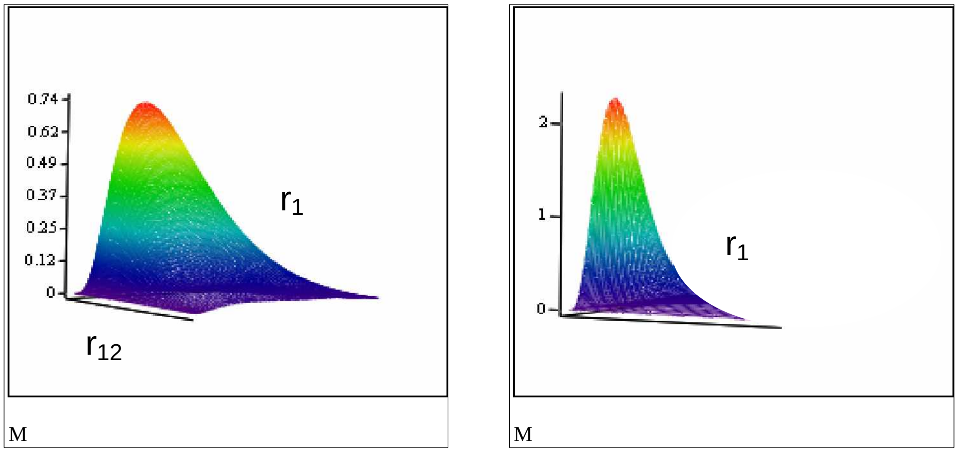
(B): Li^{+1}



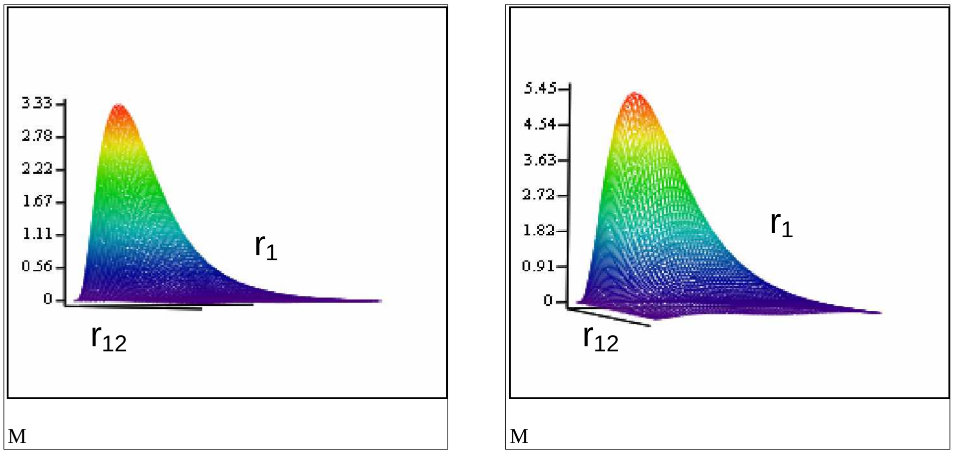
(C): Be^{+2}

(D): B^{+3}

Figure (3-22): The surface partial Coulomb hole *g(r12,r1)* for He-Like Ions obtained by Hartree-Fock.

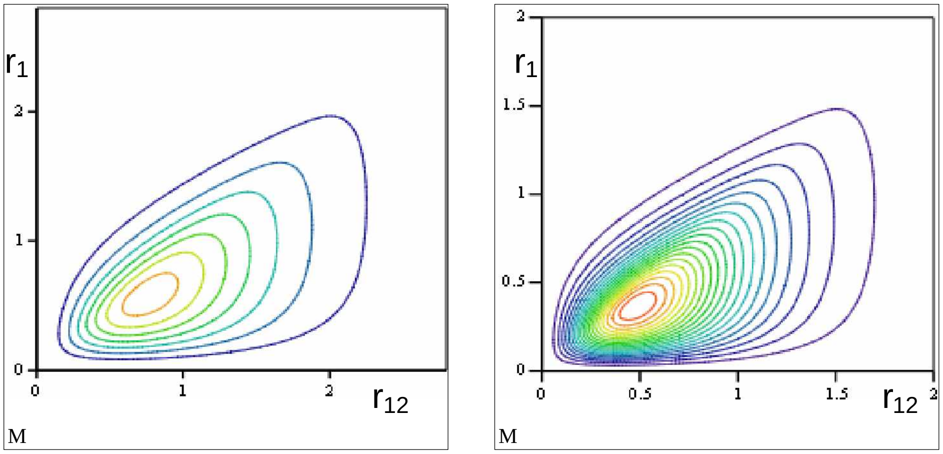


(A): He (B): Li^{+1}



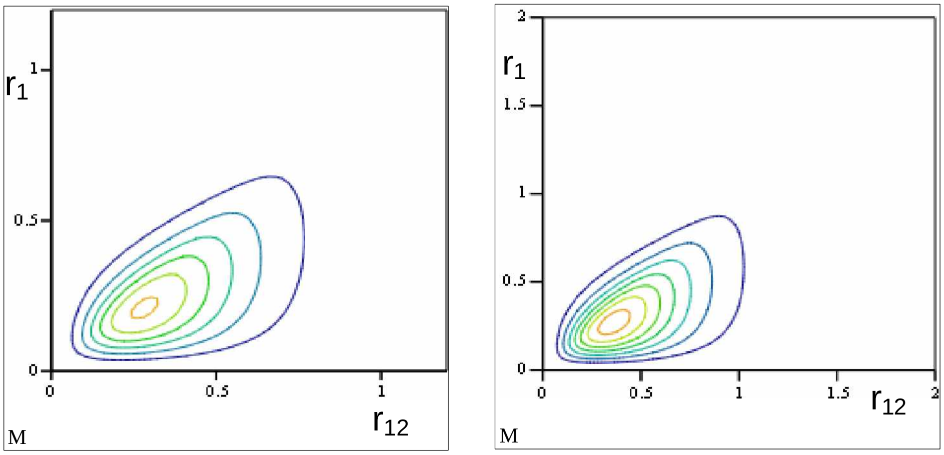
(C): Be^{+2} (D): B^{+3}

Figure (3-23): The surface partial Coulomb hole *g(r12,r1)* for He-Like Ions obtained by Configuration-Interaction.



(A): He

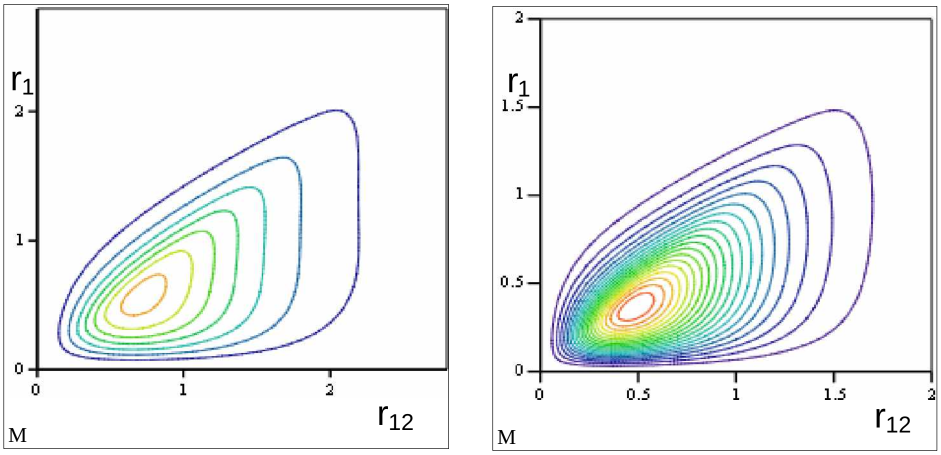
(B): Li^{+1}



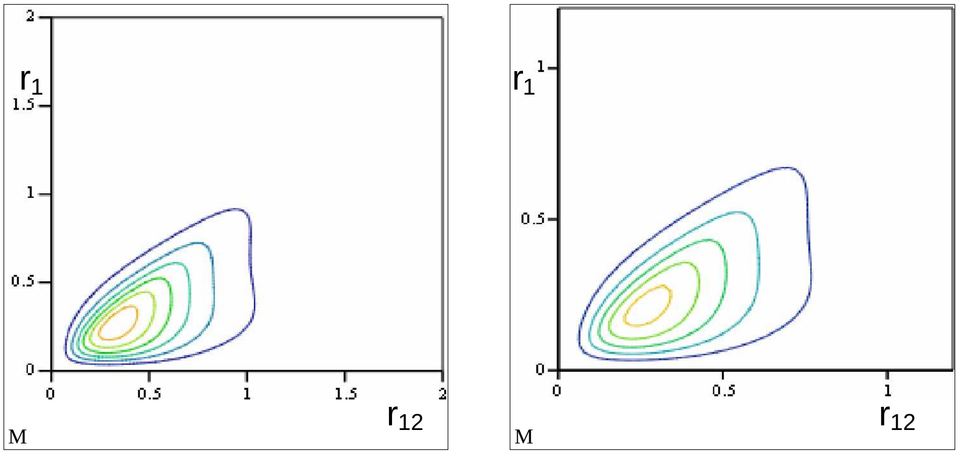
(C): Be^{+2}

(D): B^{+3}

Figure (3-24): The contour partial Coulomb hole *g(r12,r1)* for He-Like ions obtained by Hartree-Fock.

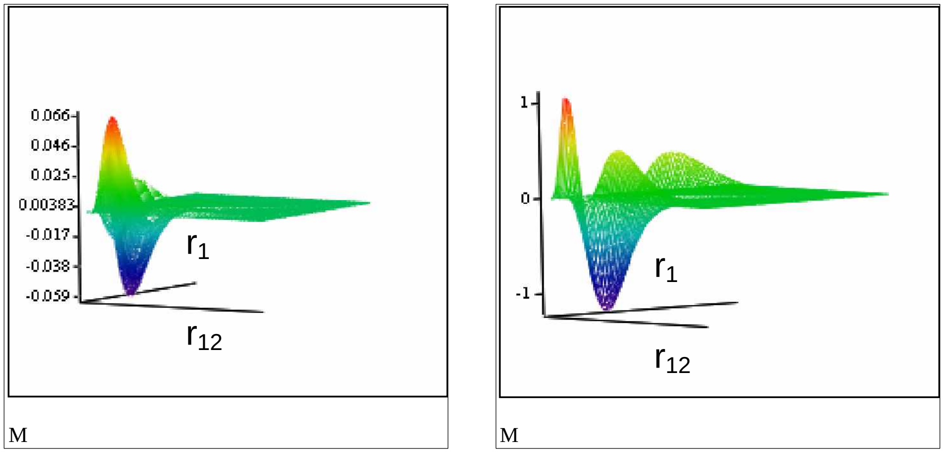


(A): He (B): Li^{+1}

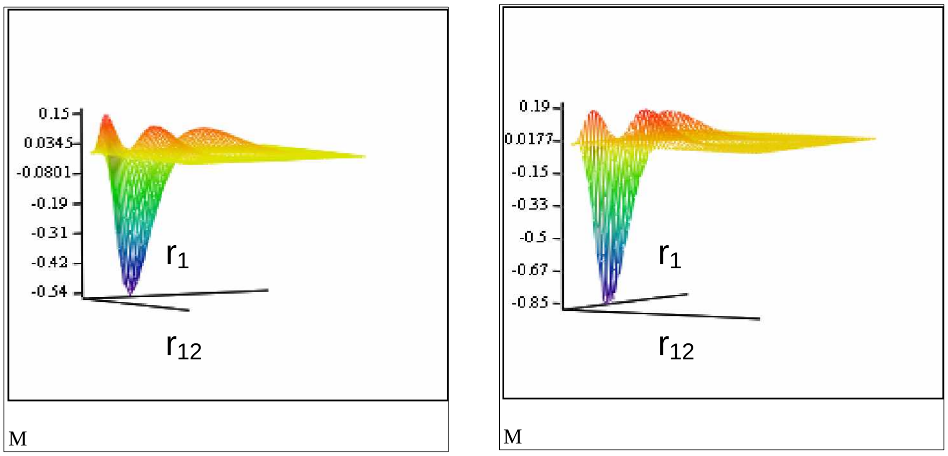


(C): Be^{+2} (D): B^{+3}

Figure (3-25): The contour partial Coulomb hole *g(r12,r1)* for He-Like ions obtained by Configuration-Interaction.

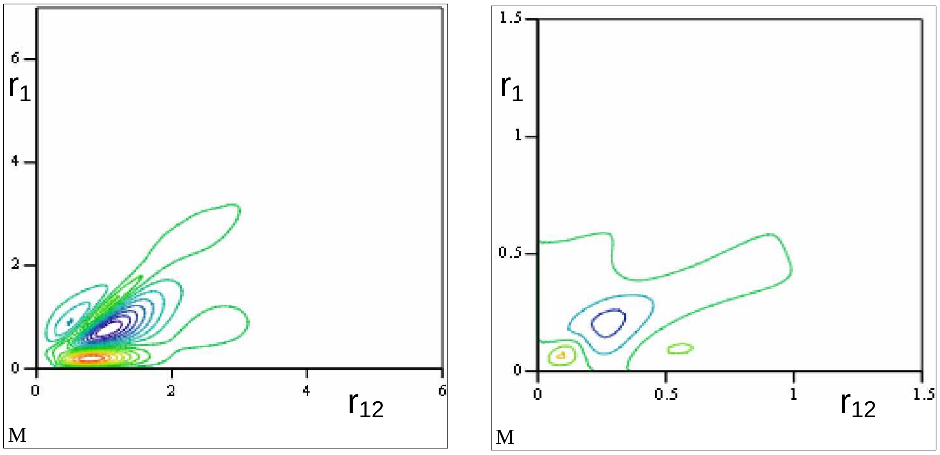


(A): He (B): Li^{+1}

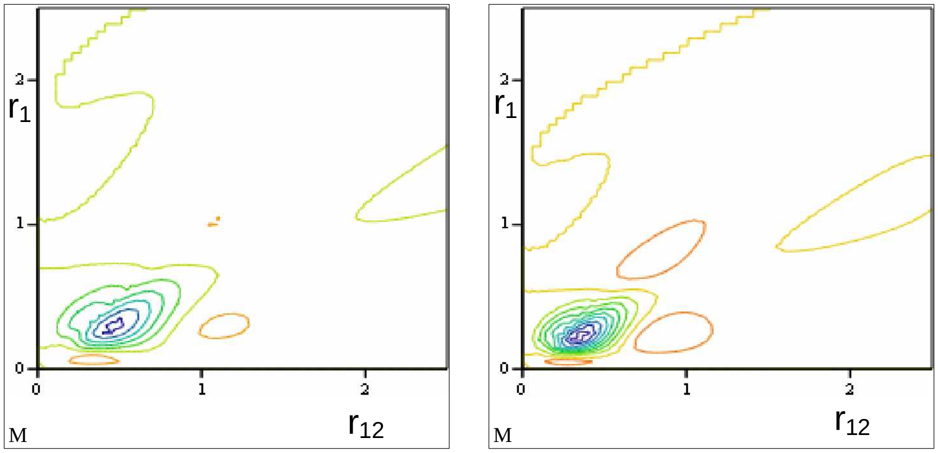


(C): Be^{+2} (D): B^{+3}

Figure (3-26): The surface delta partial Coulomb hole *Δg(r12,r1)* for He-Like Ions obtained by Hartree-Fock and Configuration-Interaction.



(A): He (B): Li^{+1}



(C): Be^{+2} (D): B^{+3}

Figure (3-27): The contour delta partial Coulomb hole *$\Delta g(r12,r1)$* for He-like ions obtained by Hartree-Fock and Configuration-Interaction.

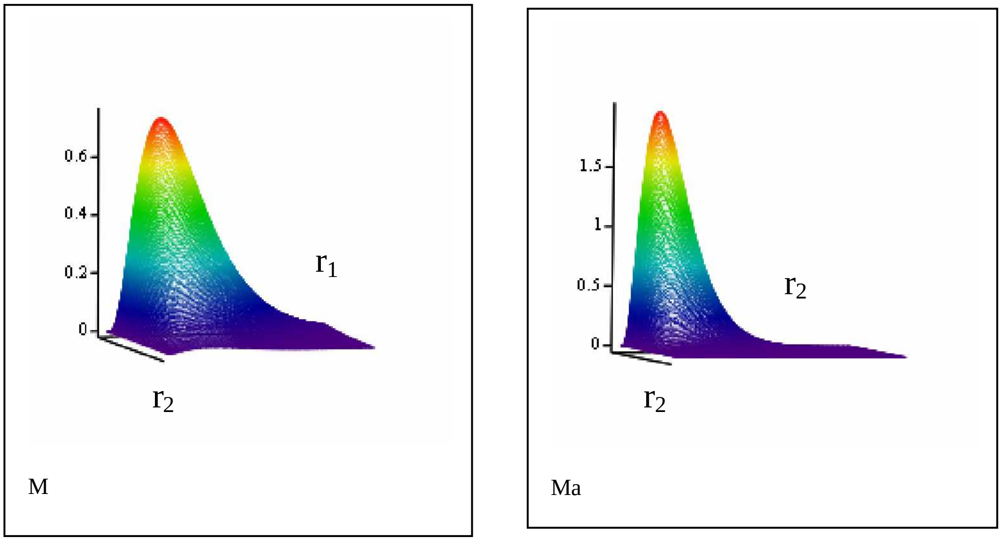
3-4 The Change in the Two-Particle Radial Distribution Function $\Delta D_{CI-HF}(r_1,r_2)$ of CI and HF Wave Functions:

Table (3-7): Presents the maximum value for the two particle radial distribution function $D(r1, r2)$ and the location of r1, r2. These values are displayed graphically

1. The maximum value $D(r1, r2)$ of HF is larger than the maximum value for CI for each Z. The maximum $D(r1, r2)$ increases when Z increases for each HF and CI wave function.
2. The surface diagrams shows in figure (3-28) and figure (3-30) are shows the maximum of $D(r_1,r_2)$ increases as Z increases for both HF and CI wave functions for He iso electronic sequences and the contour diagrams show that the $D(r_1,r_2)$ in figure (3-29), figure (3-31) that becomes more diffuses and decreases in magnitude as Z increases for both HF and CI wave functions for He iso electronic sequences.
3. In Table (3-7) the Max $D(r1, r2)_{\mathrm{HF}} > D(r1, r2)_{\mathrm{CI}}$ and max $D(r1, r2)$ He<Li^{+1} <Be^{+2} <B^{+3} and the location of max $D(r1, r2)$ for He> Li^{+1}>Be^{+2}>B^{+3}.
4. The change ΔD_{CI-HF} $(r_1, r1)$ which occurs in the two-particle radial distribution function $D(r_1,r_2)$ for CI and HF wave functions is plotted as surface diagrams in the figure (3-32). and it is plotted as contour diagrams in figure (3-33) He-Like ions. The surface diagrams show that the depth of the change increases and the radius decreases as Z increases and the contour diagrams show that the change becomes more diffuses and decreases in magnitude as Z increasing, because the nuclear charge increases.

Table (3-7): Maximum and Location of two-particle distribution function $D(r_1,r_2)$for He-like ions of the Hartree-Fock wave function, and Configuration-interaction wave function.

Atom or ions	Wave function	r_1 a.u	r_2 a.u	$D(r_1,r_2)$
He	HF	0.57	0.57	0.746
		0.57	0.57	0.746
	CI	0.52	0.53	0.705
		0.52	0.52	0.705
Li+1	HF	0.36	0.36	1.981
		0.36	0.36	1.981
	CI	0.37	0.38	1.657
		0.38	0.37	1.657
Be+2	HF	0.27	0.27	3.745
		0.27	0.27	3.745
	CI	0.26	0.27	3.138
		0.27	0.26	3.138
B+3	HF	0.21	0.21	6.202
		0.21	0.21	6.202
	CI	0.2	0.19	5.209
		0.19	0.2	5.209



(A): He (B): Li^{+1}

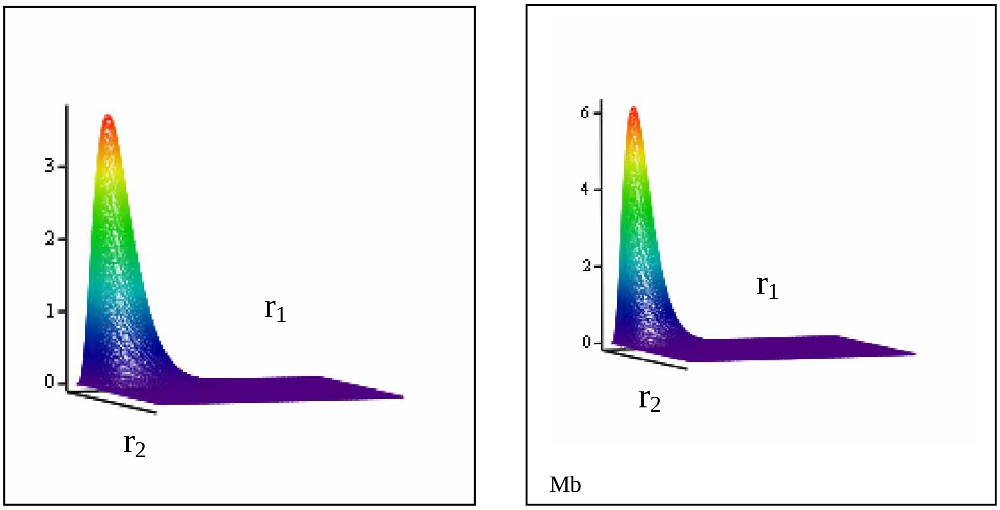


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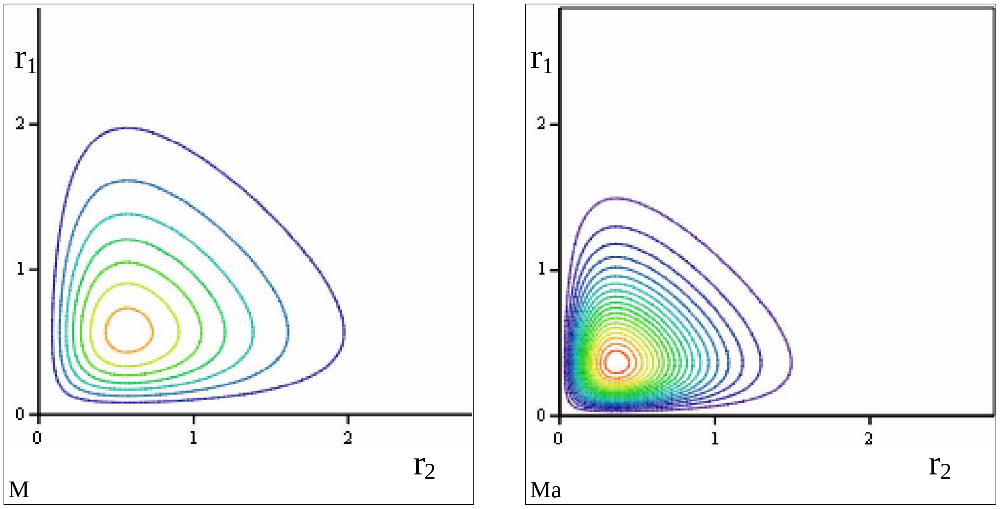
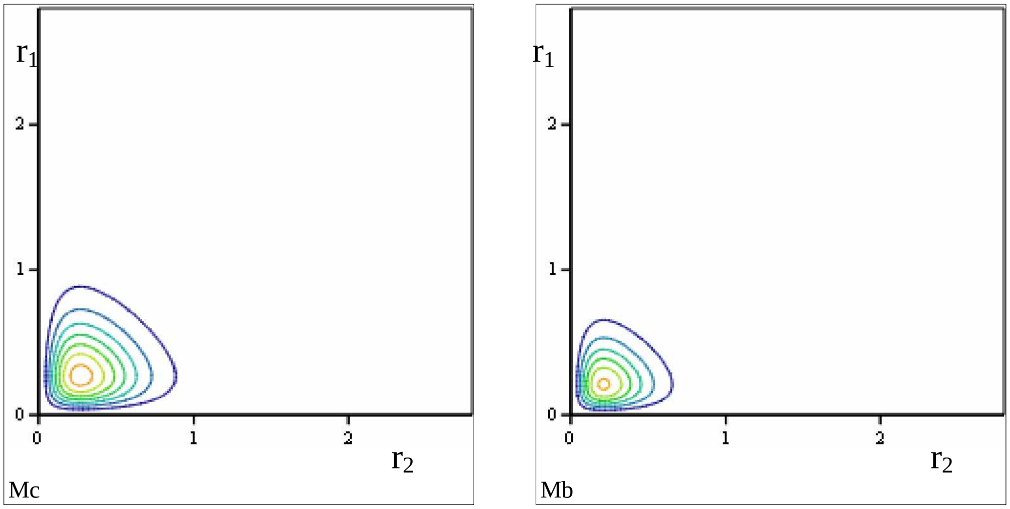
Figure (3-28): Surface Diagram for the two-particle radial distribution function $D(r_1,r_2)$ for HF wave function.

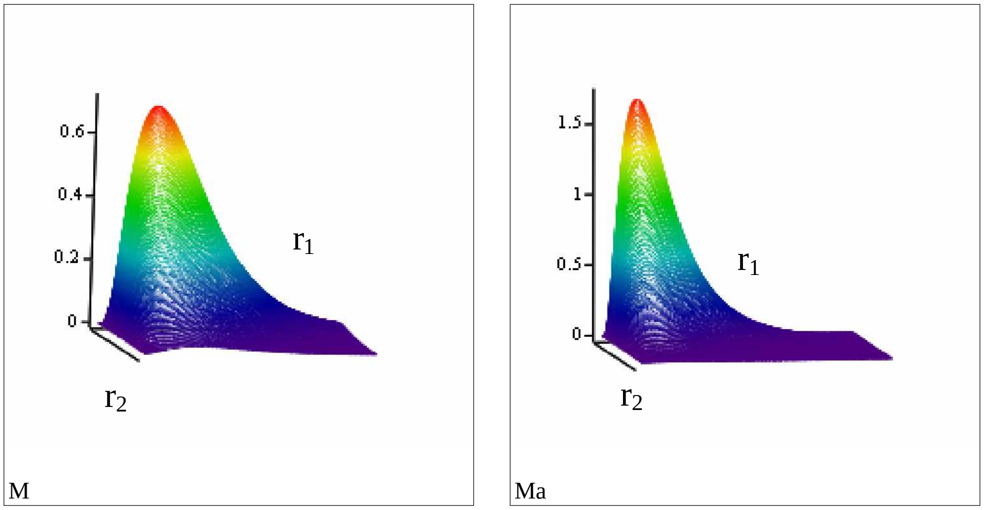


(A): He (B): Li^{1}



(C): Be^{+2} (D): B^{+3}

Figure: (3-29) Counter Diagram for the two-particle radial distribution function $D(r_1,r_2)$ for HF wave function.



(A): He (B): Li^{+1}

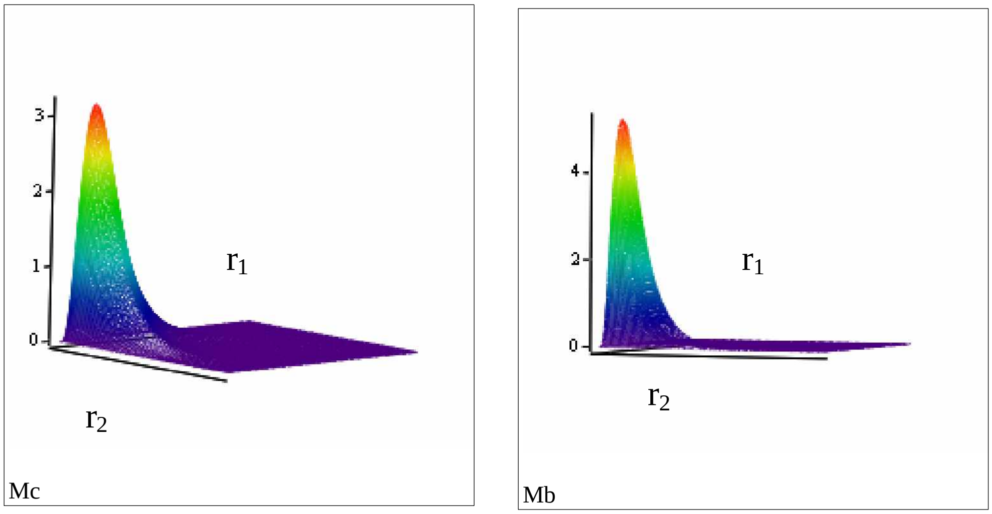
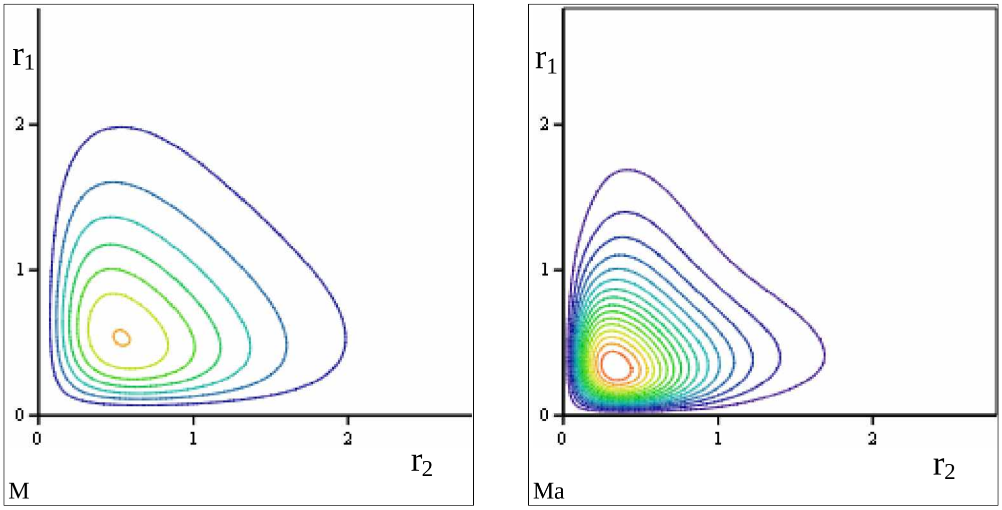
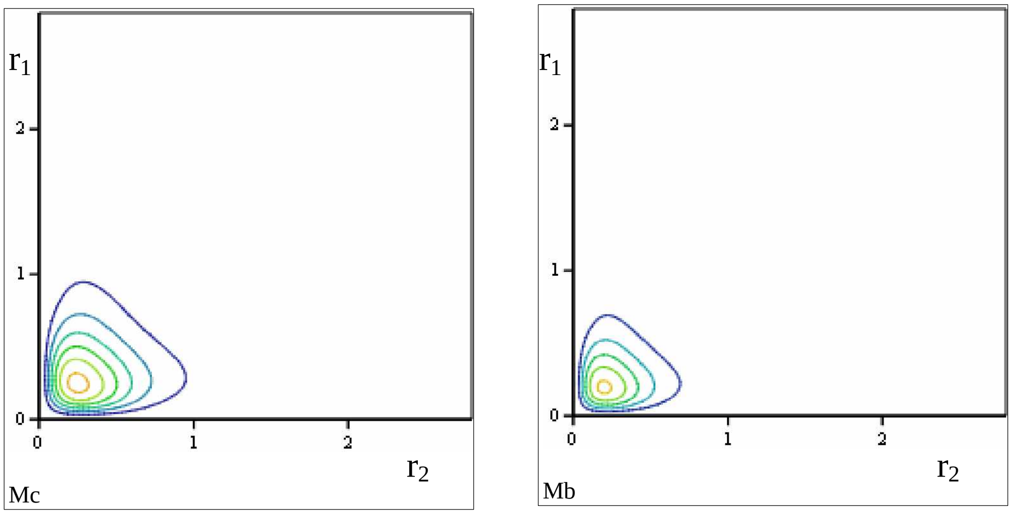


Figure (3-28): Surface Diagram for the two-particle radial distribution function $D(r_1,r_2)$ for CI wave function.



(A): He

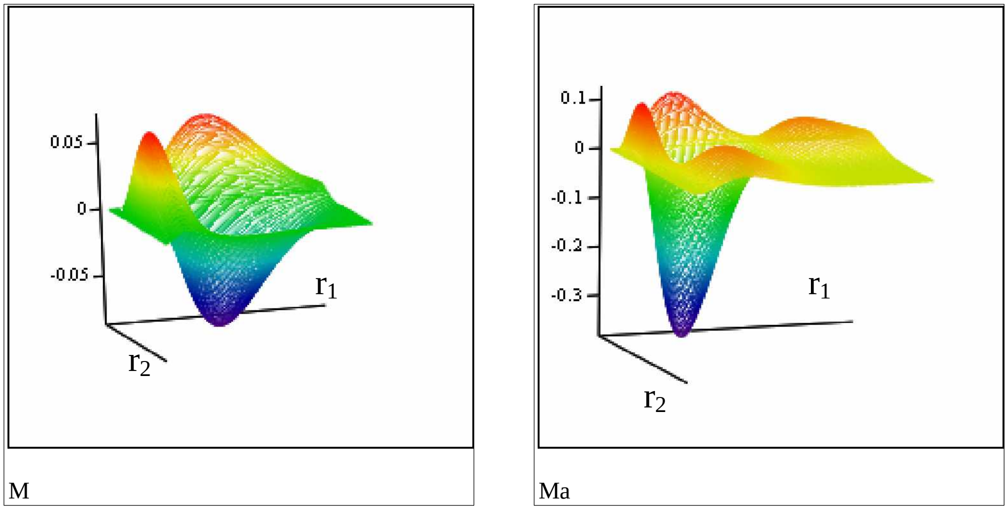
(B): Li^{+1}



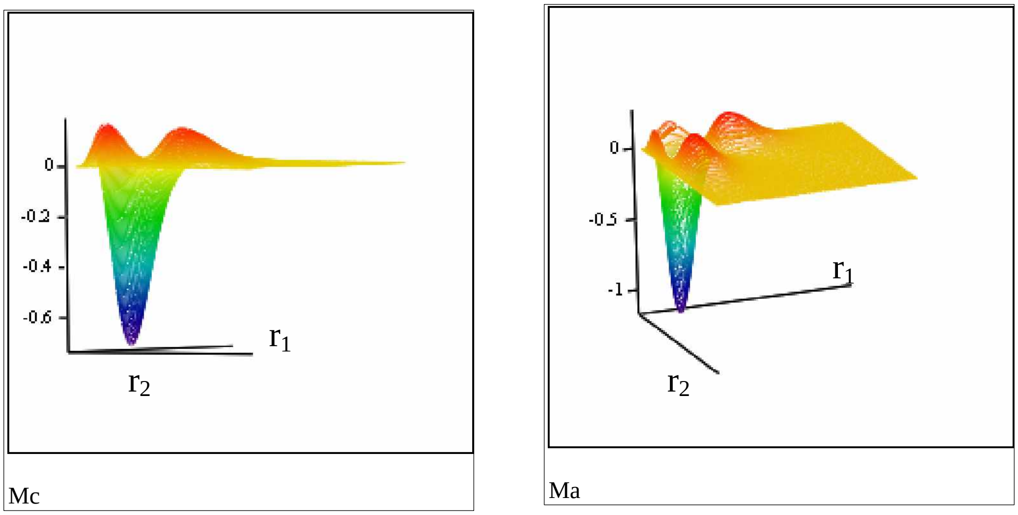
(C): Be^{+2}

(D): B^{+3}

Figure (3-31) Counter Diagram for the two-particle radial distribution function $D(r_1,r_2)$ for CI wave function.

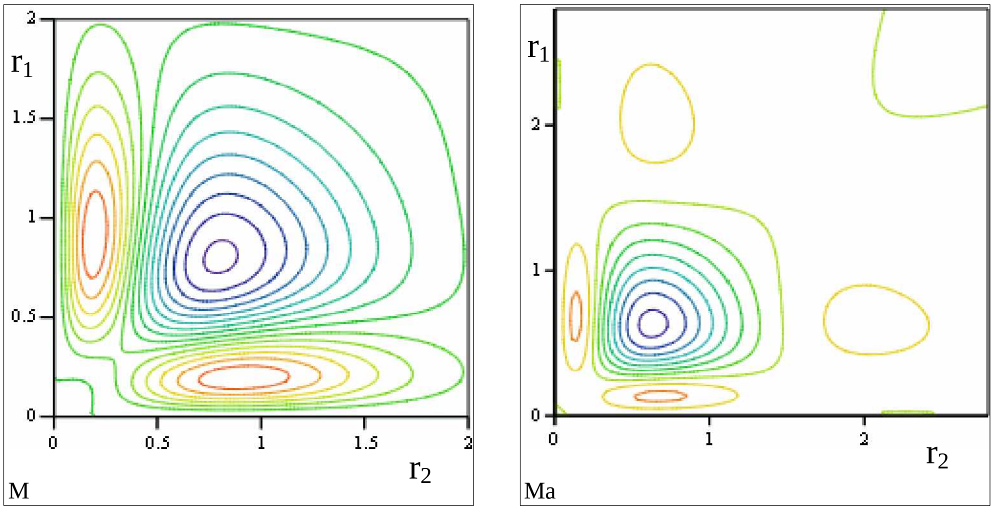


(A): He (B): Li^{+1}

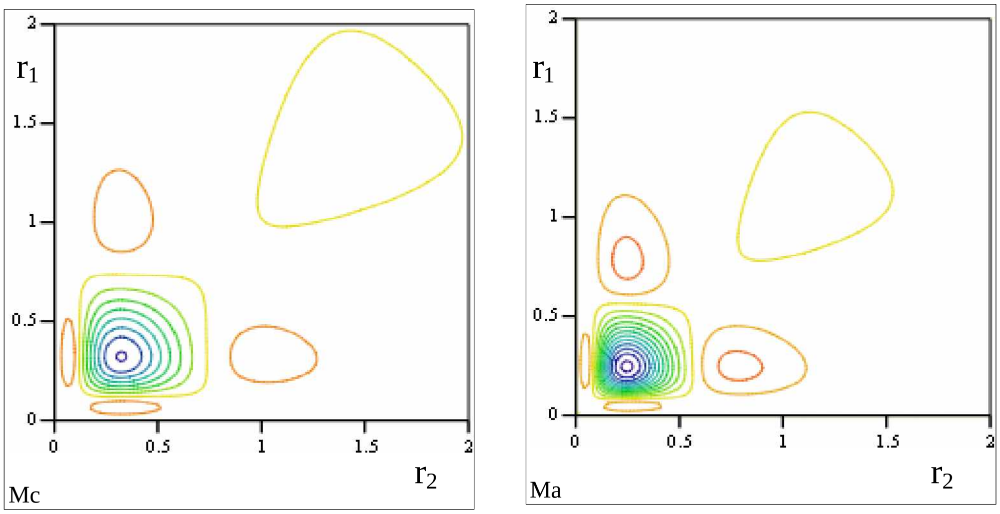


(C): Be^{+2} (D): B^{+3}

Figure (3-32) Surface Diagram for the difference of the two-particle radial distribution function $D(r_1,r_2)$ for each HF, CI wave function.



(A): He (B): Li^{+1}



(C): Be^{+2} (D): B^{+3}

Figure (3-33) Counter Diagram for the difference of the two-particle radial distribution function $D(r_1,r_2)$ for each HF, CI wave function.

3-5 Calculation of Energy:

3-5-1 Repulsion Energy Expectation Values $\langle V_{ee} \rangle$

The values of $< r_{12}^{-1} >$ is used to evaluate the repulsion energy expectation values $<V_{ee}>$ for He-like ions. Examination of the repulsion energy expectation values $<V_{ee}>$ of He-like are presented in Table (3-8) and from this table we report the following statements:

1- If the atomic number (Z) increases the repulsion energy between the electrons increase. This behavior arises from the fact that the each shell shrinkage toward the nucleus because the attraction force between the electrons and the nucleus increase too, while the distances between the electrons decrease so the repulsion energy increase the repulsion energy between two charge proportion with the values of the two charge, and inversely with the squared distance between them).

2- For each (Z) the repulsion energy expectation value $<V_{ee}>$ for correlated wave function is less than that for uncorrelated wave function because the correlation between the electrons was taken in account.

Table (3-8): Repulsion energy expectation value $\langle V_{ee} \rangle$ for He-like ions of Hartree-Focck (HF), Configuration-Interaction (CI), Eckart-Hyllears (EH), and Simple Configuration-Interaction Wave Function.

Atom or Ion	Wave Function	$\langle V_{ee} \rangle = \langle r_{12}^{-1} \rangle$ a.u
He	HF	1.017
	CI	1.016
	EH	0.992
	SCI	0.983
Li^{+1}	HF	1.652
	CI	1.583
Be^{+2}	HF	2.261
	CI	2.158
B^{+3}	HF	2.902
	CI	2.721

3-5-2 Attractive Energy Expectation Value $\langle V_{en} \rangle$

Table (3-9) illustrates the attractive energy expectation values $<V_{en}>$ for He-like ions and it shows:

1- 1-The attractive energy expectation values $<V_{en}>$ increases as atomic number (Z) increases and this behavior from the fact that the K-shell shrinkage toward the nucleus because of the attraction force between the electrons and the nucleus decrease.

2- The attractive energy expectation values $<V_{en}>$ is larger than the repulsion energy expectation value $<V_{ee}>$ by comparison between Table (3-8), and Table(3-9) for atom or ions and this is caused to reduce the distance between the electrons and the nucleus smaller than the distance between the electrons and this difference decreases as the atomic number Z increase.

Table (3-9): Attractive energy expectation value $\langle V_{ee} \rangle$ for He-like ions of Hartree-Fock (HF), Configuration-Interaction (CI), Eckart-Hyllears (EH), and Simple Configuration-Interaction Wave Functions.

Atom or Ion	Wave function	$\langle V_{en} \rangle = -Z\left[N^{*} \cdot \langle r_1^{-1} \rangle\right]$ a.u	
		$\langle r_1^{-1} \rangle$	$-\langle V_{en} \rangle$
He	HF	1.681	6.724
	CI	1.767	7.068
	Eckart-Hyllears	1.685	6.74
	SCI	1.63	6.52
Li^{+1}	HF	2.687	16.122
	CI	2.725	16.35
Be^{+2}	HF	3.664	29.312
	CI	3.682	29.456
B^{+3}	HF	4.687	46.665
	CI	4.66	46.786

3-5-3 Total Energy Expectation Values $\langle E\rangle$

Table (3-10) shows the values of the attractive energy expectation values$<V_{en}>$, repulsive energy expectation values$<V_{ee}>$, and total energy expectation values $<E>$ and we noted that:

1- The total energy expectation value $<E>$ for He-atom of Hartree-Fock (HF) approximation is larger than those for the correlation wave function and that behavior is not found in ions because the electron correlation has been taken in account in the correlated wave function and the electron correlation increase as the atomic number (Z) increases.

2- As atomic number (Z) increases the attractive potential energy (which results from the attractive potential energy between the electrons and the nucleus), and the repulsion energy (which results from the repulsion potential energy between the electrons) increase.

Table (3-10): Total energy expectation value $\langle V_{ee}\rangle$ for He-like ions of Hartree-Fock (HF), Configuration-Interaction (CI), Eckart-Hyllears (EH), and Simple Configuration-Interaction Wave Function.

Atom or Ion	Wave function	$\langle V\rangle$			$-\langle E\rangle=-\frac{1}{2}\langle V\rangle$	E_{corr}	
		$-\langle V_{en}\rangle$	$\langle V_{ee}\rangle$	$-\langle V\rangle$			
He	HF	6.724	1.016	5.388	2.854	HF&CI	0.008
	CI	7.068	1.017	5.692	2.846		
	Eckart-Hyllears	6.74	0.992	5.668	2.874	HF&EH	0.02
	SCI	6.52	0.983	5.645	2.8225	HF&SCI	0.031
Li^{+1}	HF	16.122	1.652	14.47	7.235	0.14	
	CI	16.35	1.583	14.75	7.375		
Be^{+2}	HF	29.312	2.261	27.051	13.526	0.247	
	CI	29.456	2.158	27.298	13.649		
B^{+3}	HF	46.87	2.902	43.968	21.964	0.020	
	CI	46.6	2.721	43.93	21.985		

3-6 Conclusions:

1. As Z increases, the one-particle expectation value $\langle r_1^n \rangle$ for each Hartree-Fock and Configuration-Interaction increase when we study the charge density distribution near to nuclear and decrease when we study the charge density distribution far too nuclear.
2. As Z increases, the one-particle radial distribution functions for each Hartree-Fock and Configuration-Interaction increases $D(r_1)$.
3. As Z increase, the difference one-particle radial distribution function $\Delta D(r_1)$ increase and the location closed to nucleus.
4. As Z increases, the inter-particle expectation value $\langle r_{12}^n \rangle$ for each Hartree-Fock and Configuration-Interaction increase when n=-1, -2 and decrease when n= 1, 2.
5. As Z increases, the maximum probabilities of the inter-particle distribution function $f(r_{12})$ of HF and CI wave functions increases and also the locations of these maxima decrease as Z goes from 2 to 5.
6. The magnitude density of $g(r_{12},r_1)$ of the HF and CI wave functions increases as Z increases.
7. The maximum of $D(r_1,r_2)$ increases as Z increases of HF and CI wave function for K-shell.
8. The radius of Coulomb hole decreases with increasing the atomic number Z, and the area of Coulomb hole increase with increase of the atomic number Z.

9. As Z increases the depth of the change $\Delta D_{CI\text{-}HF}(r_1,r_2)$ which occurs in two-particle radial distribution function $D(r_1,r_2)$ increases, and the location of the two-particle decreases.

3-7Future work and suggestions:

Study the Fermi Hole and Coulomb Hole for some atomic system using new correlated wave function.

References

Appendix A

Determination of Electron-Electron Distribution Function

For any N-electron atomic system, the distribution function $f\ (r_{12})$ of the interelectronic separation r_{ij} is defined as [37]:

$$f\ (r_{ij}) = \int \Gamma^{(2)}(r_i, r_j \,|\, r_i', r_j') \frac{dr_i\, dr_j}{dr_{ij}} \qquad \text{.... (A-1)}$$

$\Gamma^{(2)}$ is the spin-free-2 matrix defined by:

$$\Gamma^{(2)}(r_i, r_j \,|\, r_i', r_j') = \begin{bmatrix} N \\ 2 \end{bmatrix} \iiint \Psi(x_1, x_2, ..., x_i, ...x_j, ...x_n)\Psi^*(x_1', x_2', ..., x_i', ...x_j', ...x_n')\, dx_i\, dx_j\, dx_k$$

.... (A-2)

Where dx_k , indicate an integration- summation over all the combined space and spin co-ordinate x_k except k =i and j. the binomial coefficient $\begin{bmatrix} N \\ 2 \end{bmatrix}$ ensure that the spin-free-2 matrix is normalized to the number of the electron pair with the system.

After setting $r_i' = r_i$, $r_j' = r_j$ the integration is achieved over all co-ordinates except r_{ij} [28] therefore:

$$f\ (r_{ij})dr_{ij} = \iint \Gamma(r_i, r_j)dr_i\, dr_j \qquad \text{.... (A-3)}$$

Such that $\displaystyle\int_0^\infty f\ (r_{ij})dr_{ij} = 1$ .... (A-4)

The integration in equation (A-3) is taken over all positions of the two electrons such that the inter-electronic distance lies between r_{12} and $r_{12} + dr_{12}$ [13].

In order to obtain the final form of the radial electron-electron distribution function, we will transform the volume element [28] see figure (A-1).

$d\mathbf{r}_2 = r_2^2 dr_2 \sin\theta_2 d\theta_2 d\phi_2$ …. (A-5)

At the same way:

$d\mathbf{r}_1 = r_1^2 dr_1 \sin\theta_1 d\theta_1 d\phi_1$ …. (A-6)

Now in a appropriate manner, choosing the r_1- direction as the new polar axis see figure (A-2).

$d\mathbf{r}_2 = r_2^2 dr_2 \sin\omega d\omega d\gamma$ …. (A-7)

Where γ shows an angle of rotation of the plane 012 around 01.

Now from the law of cosine:

$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\omega$ …. (A-8)

Then by dervitation with kept r_1, r_2

$r_{12} dr_{12} = r_1 r_2 \sin\omega d\omega$ …. (A-9)

Therefore, the combined volume element becomes:

$d\mathbf{r}_1 d\mathbf{r}_2 = r_1 r_2 r_{12} \sin\theta_1 \sin\omega dr_1 dr_2 d\theta_1 d\phi_1 d\omega d\gamma$ …. (A-10)

It is convenient to set i=1, j=2, then the equation (A-3) becomes:

$f(r_{12}) = \int \Gamma(r_1, r_2) r_1 r_2 r_{12} \sin\theta_1 \sin\omega dr_1 dr_2 d\theta_1 d\phi_1 d\omega d\gamma$ …. (A-11)

By integration over all the angles gets:

$f(r_{12}) = 8\pi^2 r_{12} \iint \Gamma(r_1, r_2) r_1 r_2 dr_1 dr_2$ …. (A-12)

For a given r_{12}, the allowed values of r_1 and r_2 are defined by the rotations:

$r_{12} - r_1 \le r_2 \le r_{12} + r_1$ at $(r_1 \langle r_{12})$ ….(A_13)

$r_1 - r_{12} \le r_2 \le r_1 + r_{12}$ at $(r_1 \rangle r_{12})$

Generally:

$$f\ (r_{12}) = 8\pi^2 r_{12}\left(\int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 + \int_0^{\infty} r_1 dr_2 \int_{r_1-r_{12}}^{r_1+r_{12}} \Gamma(r_1, r_1) r_2 dr_2\right) \quad \text{…. (A-14)}$$

The vector r in $\Gamma(r_1, r_2)$ means that the density contains both radial and angular part, where the angular part of each orbital is $\left(\frac{1}{\sqrt{4\pi}}\right)$. Therefore, the inter-particle radial distribution function of the individual shells can be written as:

$$f_{ij}(r_{12}) = 0.5 \cdot r_{12}(I_1 + I_2) \quad \text{…. (A-15)}$$

Where

$$I_1 = \int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \quad \text{…. (A-16)}$$

$$I_2 = \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2) r_2 dr_2 \quad \text{…. (A-17)}$$

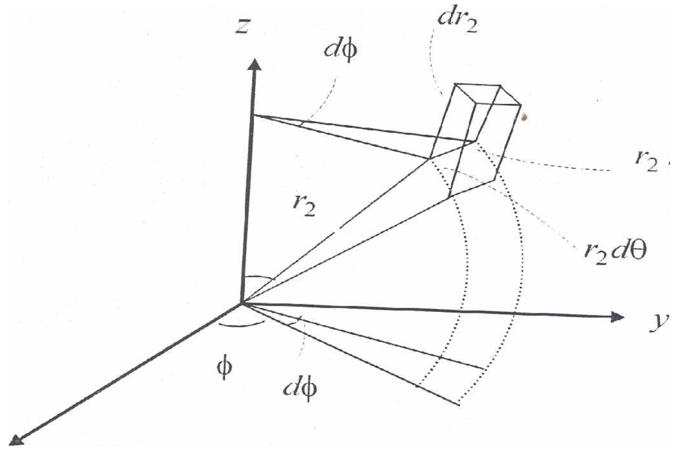


Figure (A-1): Volume element in spherical co-ordinate.

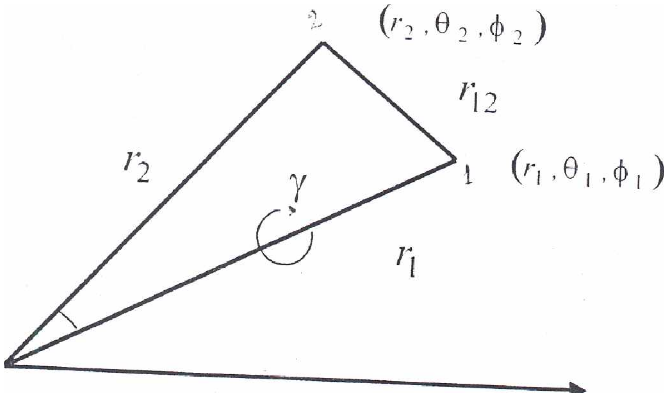


Figure (A-2): Co-ordinate systems of the distribution function determination Numerals l and 2 show the electrons, 0 is the nucleus.

Appendix B

Determination of the Total Energy in Terms of Expectation Values

The total energy of our trail wave function is given by [45]:

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad \text{…. (B-1)}$$

Since the wave function is normalized the denominator becomes one, therefore:

$$E = \langle \Psi | \hat{H} | \Psi \rangle \qquad \text{…. (B-2)}$$

Where:

$$\hat{H} = \sum_i \left[-\frac{1}{2}\nabla_i^2 - \left(\frac{Z}{r_i} \right) \right] + \sum_{i \langle j} \left(\frac{1}{r_{ij}} \right), \qquad \text{…. (B-3)}$$

$-\frac{1}{2}\hat{\nabla}_i^2$, represent the Kinetic energy (T).

The potential energy is represented by:

$$\hat{V} = \sum_i \frac{Z}{r_i} + \sum_{i \langle j} \left(\frac{1}{r_{ij}} \right) \qquad \text{…. (B-4)}$$

Substituting equation (B-3) into equation (B-1) we get:

$$E = \langle \Psi | T + V | \Psi \rangle \qquad \text{…. (B-5)}$$

Now, from the viral theorem [45] $\langle T \rangle = -\frac{1}{2} \langle V \rangle$

$$E = \left\langle \Psi \middle| \frac{1}{2} V \middle| \Psi \right\rangle = \frac{1}{2} \langle V \rangle \qquad \text{…. (B-6)}$$

Then:

$$E = \frac{1}{2} \left[\left\langle \frac{-Z}{r_i} \right\rangle + \left\langle \frac{1}{r_{ij}} \right\rangle \right] \qquad \text{…. (B-7)}$$

Appendix C

Data of Hartree-Fock for He-Isoelectric series [1974]

<table>
<tr><th colspan="4">Data of Hartree-Fock He atom</th></tr>
<tr><td>n</td><td>l</td><td>ζ</td><td>C</td></tr>
<tr><td>1</td><td>0</td><td>1.45286</td><td>0.91795</td></tr>
<tr><td>1</td><td>0</td><td>2.77954</td><td>0.18334</td></tr>
<tr><td>1</td><td>0</td><td>4.34600</td><td>0.00824</td></tr>
<tr><td colspan="4">Data of Hartree-Fock Li^{+1} ions</td></tr>
<tr><td>n</td><td>l</td><td>ζ</td><td>C</td></tr>
<tr><td>1</td><td>0</td><td>2.45055</td><td>0.89066</td></tr>
<tr><td>1</td><td>0</td><td>4.57259</td><td>0.12328</td></tr>
<tr><td>1</td><td>0</td><td>6.67032</td><td>0.00088</td></tr>
<tr><td colspan="4">Data of Hartree-Fock Be^{+2} ions</td></tr>
<tr><td>n</td><td>l</td><td>ζ</td><td>C</td></tr>
<tr><td>1</td><td>0</td><td>3.43071</td><td>0.89855</td></tr>
<tr><td>1</td><td>0</td><td>5.63150</td><td>0.09068</td></tr>
<tr><td>1</td><td>0</td><td>7.35143</td><td>0.02158</td></tr>
<tr><td colspan="4">Data of Hartree-Fock B^{+3} ions</td></tr>
<tr><td>n</td><td>l</td><td>ζ</td><td>C</td></tr>
<tr><td>1</td><td>0</td><td>4.44422</td><td>0.93036</td></tr>
<tr><td>1</td><td>0</td><td>7.90274</td><td>0.07786</td></tr>
<tr><td>1</td><td>0</td><td>11.31380</td><td>0.00013</td></tr>
</table>

Appendix D

Data of configuration-interaction for He-Isoelectric series Wiess [1960]

Data of configuration-interaction He atom

CI	n	n1	ζ	ζ_1	C
1s 1s	1	1	1.48	1.48	0.30709
1s 2s	1	2	1.48	1.48	-0.8623
2s 2s	2	2	1.48	1.48	0.14117
1s 1s'	1	1	1.48	3.7	-0.59306
2s 1s'	2	1	1.48	3.7	0.12052
1s' 1s'	1	1	3.7	3.7	0.07324
1s 2s'	1	2	1.48	3.7	-0.29466
2s 2s'	2	2	1.48	3.7	0.05457
1s' 2s'	1	2	3.7	3.7	0.05529
2s' 2s'	2	2	3.7	3.7	0.07434
1s 3s'	1	3	1.48	3.7	-0.55471
2s 3s'	2	3	1.48	3.7	0.16365
1s' 3s'	1	3	3.7	3.7	0.14812
2s' 3s'	2	3	3.7	3.7	-0.00026
3s 3s'	3	3	3.7	3.7	0.14627

Data of configuration-interaction Li^{+1} ions

CI	n	n1	ζ	ζ_1	C
1s 1s	1	1	2.52	2.52	0.51545
1s 2s	1	2	2.52	2.52	-0.76338
2s 2s	2	2	2.52	2.52	0.15375
1s 1s'	1	1	2.52	5.75	-0.74523
2s 1s'	2	1	2.52	5.75	0.19361
1s' 1s'	1	1	5.75	5.75	0.10743
1s 2s'	1	2	2.52	5.75	-0.39384
2s 2s'	2	2	2.52	5.75	0.10211
1s' 2s'	1	2	5.75	5.75	0.10123
2s' 2s'	2	2	5.75	5.75	0.07174
1s 3s'	1	3	2.52	5.75	-0.64785
2s 3s'	2	3	2.52	5.75	0.19433
1s' 3s'	1	3	5.75	5.75	0.19574
2s' 3s'	2	3	5.75	5.75	0.04921
3s 3s'	3	3	5.75	5.75	0.14061

Data of configuration-interaction Be^{+2} ions					
CI	n	n1	ζ	ζ_1	C
1s 1s	1	1	3.55	3.55	0.52909
1s 2s	1	2	3.55	3.55	-0.77925
2s 2s	2	2	3.55	3.55	0.14548
1s 1s'	1	1	3.55	7.8	-0.77651
2s 1s'	2	1	3.55	7.8	0.21295
1s' 1s'	1	1	7.8	7.8	0.11900
1s 2s'	1	2	3.55	7.8	-0.41769
2s 2s'	2	2	3.55	7.8	0.11532
1s' 2s'	1	2	7.8	7.8	0.11853
2s' 2s'	2	2	7.8	7.8	0.06726
1s 3s'	1	3	3.55	7.8	-0.63526
2s 3s'	2	3	3.55	7.8	0.18946
1s' 3s'	1	3	7.8	7.8	0.20199
2s' 3s'	2	3	7.8	7.8	0.06600
3s 3s'	3	3	7.8	7.8	0.12579

Data of configuration-interaction B^{+3} ions					
CI	n	n1	ζ	ζ_1	C
1s 1s	1	1	4.65	4.65	0.46506
1s 2s	1	2	4.65	4.65	-0.74102
2s 2s	2	2	4.65	4.65	0.13445
1s 1s'	1	1	4.65	9.85	-0.75189
2s 1s'	2	1	4.65	9.85	0.21196
1s' 1s'	1	1	4.65	9.85	0.11866
1s 2s'	1	2	4.65	9.85	-0.40700
2s 2s'	2	2	4.65	9.85	0.11571
1s' 2s'	1	2	9.85	9.85	0.12075
2s' 2s'	2	2	9.85	9.85	0.06176
1s 3s'	1	3	4.65	9.85	-0.59439
2s 3s'	2	3	4.65	9.85	0.17777
1s' 3s'	1	3	9.85	9.85	0.19356
2s' 3s'	2	3	9.85	9.85	0.06968
3s 3s'	3	3	9.85	9.85	0.11181

Appendix E

Compare the result of the repulsion energy with the reference 12

Atom or Ion	Wave Function	$\langle V_{ee}\rangle = \langle r_{12}^{-1}\rangle$
He	Ref 12	1.025
Li^{+1}	Ref 12	1.651
Be^{+2}	Ref 12	2.277

Compare the result of the attraction energy with the reference 12

Atom or Ion	Wave function	$\langle V_{en}\rangle = -Z\left[N^{*}\cdot\langle r_1^{-1}\rangle\right]$	
		$\langle r_1^{-1}\rangle$	$-\langle V_{en}\rangle$
He	Ref 12	1.687	6.749
Li^{+1}	Ref 12	2.687	16.124
Be^{+2}	Ref 12	3.687	29.499

Compare the result of the total energy with the references

Atom Or ions	Wave function	Exact energy
He	Ref 52	2.8616
	Ref 17	2.878 For S symmetry
	Ref 13	2.875
		2.9037
Li^{+1}	Ref 52	7.236
	Ref 17	7.252 For S
		7.279
Be^{+2}	Ref 42	13.611
	Ref 17	13.655
B^{+3}	Ref 42	21.986
	Ref 17	22.030

Compare the result of the one-Particle Radial Distribution Function with result 12

Atom or ion	Wave function	r_1	Max $D(r1)$
He	Ref 12	0.56	0.866
Li^{+1}	Ref 12	0.36	1.4074
Be^{+2}	Ref 12	0.26	1.948

Compare the result of the Inter-Particle Radial Distribution Function with result 13

Atom or ions	Wave function	r_{12}	$f\ (r_{12})$
He	Eckart-Hyllears	1.04	0.622
	Ref 13	1.00	0.625

Compare the result of the Radius and Area of coulomb Hole with reference.

Atoms or ions	Wave Function	Radius of coulomb hole	Area of coulomb hole
He	Ref 39	1.11	0.044
Li^{+1}	Ref 39	0.66	0.042
Be^{+2}	Ref 39	0.05	0.42

Appendices

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وهي جزء من متطلبات نيل درجة الماجستير في علوم الفيزياء

من قبل
حميد جبار حزيران الجبوري
بكالوريوس 2005

باشراف الاستاذ الدكتور
خليل هادي البياتي

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