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CORRELATION EFFECTS IN He-LIKE IONS: AN ANALYSIS OF THE GROUND STATE IN MOMENTUM SPACE

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ABSTRACT

An electron correlation has been examined in detail for the $1s^2$ -state of He and comparisons are made with the ground state of Li^+, Be^{2+} and B^{3+}. An expression has been obtained for the partial Coulomb hole associated with any pair of occupied HF spin orbital for many electron systems. The required partitioning of the correlated second order density matrix was achieved here, up to and including the pair-correlation effects. Partial coulomb holes were determined in momentum space. The concept of partial coulomb holes and their collective presentation as surfaces has been demonstrated to be particularly informative. These surfaces enabled us to interpret correlation effects in momentum space providing a rationalization of the correlation mechanisms in each state.

Key words: Correlation effects, He-like ions, Momentum space.

INTRODUCTION

Two electron atoms or ions present an excellent testing ground for checking new calculation approaches and for studying photoelectron and other atomic processes. However, the Schrodinger equation for atoms/ions with more than one electron cannot be solved analytically. Approximation must be applied order in to solve the problem. A large variety of techniques were developed to obtain the nonrelativistic bound energies and wave functions for mentioned systems[1,2].

The Hartree–Fock self-consistent field approximation, which is based on the idea that we can approximately describe an interacting Fermion system in terms of an effective single-particle model, remains the starting point and the major approach for quantitative electronic structure calculations. The correlation energy is defined as the energy error of the Hartree-Fock wave function, i.e., the difference between the Hartree- Fock limit energy and

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exact solution of nonrelativistic Schrodinger equation[3]. Electron correlation has been examined within electron shells for a series of He-like systems in the ground state. Inter-shell description was obtained using a Haretree-Fock (HF) level (Weiss 1963)[4] by partioning the second order density into its pairwise components. Correlation effects were then analyzed in terms of various partial Coulomb holes.

RESULTS AND DISCUSSION

Electron correlation has a direct influence on distribution function for inter particle separation r_{12}. Following Coulson and Neilson[5], the total Coulomb hole for any two electron m and n within an N-electron system described by uncorrelated wave function (HF) a Coulomb hole can be defined as –

$$\Delta f\,(p_{12}) = f_{corr}\,(p_{12}) - f_{HF}\,(p_{12}) \qquad \ldots(1)$$

Both functions satisfies the normalization conditions[6]:

$$\int_0^\infty f\,(p_{12})\,dp_{12} = 1 \qquad \ldots\,(2)$$

Partial distribution function g (p_{12}; p_1) represents the probability of finding an inter electronic separation r_{12}, when a test electron is located at distance r_1 from the nucleus[7].

The partial Coulomb hole, Δ g (p_{12}, p_1, Θ_1), allows us to analyze a characteristics of the Coulomb hole, when a test electron, say particle 1, is located at specified radial distance r_1 from the nucleus. When the system possesses a unique axis of symmetry, a partial Coulomb hole, Δ g (p_{12}, p_1, θ_1), may be defined. θ being measured relative to the symmetry axis. These functions are related to, Δ f (p_{12}) as follows[8]:

$$\int_0^\infty\int_0^\pi \Delta g\,(p_{12};p_1,\theta_1)\sin\theta_1 d\theta_1 dp_1 = \int_0^\infty \Delta g\,(p_{12};p_1)\,dp_1 = \Delta f\,(p_{12}) \qquad \ldots(3)$$

For (i, j) labels, a pair of occupied spin orbitals φ_i and φ_j in the restricted HF description of the system, then the associated Coulomb hole can be written as[9]:

$$\Delta f_{ij}\,(P_{mn}) = \int_0^\infty \Delta\Gamma_{ij}\,(x_m, x_n)\,\frac{dx_m dx_n}{dr_{mn}} \qquad \ldots(4)$$

Where $\Gamma(x_n, x_m)$ is the second order density matrix, which is already normalized to the number of electron pairs within the system.

$$D_{ij}(p_1, p_2) = \iint \Gamma_{ij}(p_1, p_2)\, p_1^2 p_2^2\, d\Omega 1\, d\Omega 2 \quad \ldots(5)$$

where D_{ij} (p_1, p_2) represent the two particle density distribution function and, $d\Omega_k = \sin\theta_k d\theta_k d\varphi_k$ where k = 1 or 2.

The one particle radial density distribution function is –

$$D_{ij}(p_1) = \int_0^\infty D_{ij}(p_1, p_2)\, dp_2 \quad \ldots(6)$$

Each inter particle separation function $f_{ij}(p_{mn})$ is normalized to unity and integral of $\Delta f_{ij}(p_{mn})$ against p_{mn} is identically zero[10].

Also, if the position of electron 1 is specified as r_1, then we consider a related distribution function such as $g(p_{12}; p_1)$.

$$g(p_{12}; p_1) = 8\pi^2\, p_{12} p_1\, J_1 \quad \ldots(7)$$

where

$$J_1 = \int_0^{p_{12}} p_1 dp_1 \int_{p_{12}-p_1}^{p_{12}+p_1} \Gamma(p_1, p_2)\, p_2 dp_2 \quad \ldots(8)$$

and

$$\Gamma(p_1, p_2) = \phi_{1S}^2(p_1)\, \phi_{1S}{}^2(p_2) \quad \ldots(9)$$

The influence of the correlation in partial distribution function $g(p_{12}; p_1)$ of p_{12} and p_1 for Z = 2, 3, 4 and 5 for K-shell are shown in Table 1. Fig. 1 shows $g(p_{12}; p_1)$ surface for the S-symmetry states for He-like ions. Selected contour diagrams can be seen in Fig. 2. In HF approximation, each electrons move independently of each other, so this hypothesis neglecting the details of the electronic repulsion will reduce the HF results. The HF model indicates that the average angle between the electronic momentum vectors is 90^o, the

location of the most probable distribution of $g(p_{12}, p_1)$ density can be estimated by using "Pythagoras's theorem". The $g(p_{12}, p_1)$ surface show that the maximum density is always located at the diagonal such that $p_{12} > p_1$ because $< \cos \gamma_{12} > = 0$ where (γ_{12} is the angle between p_1 and p_2).

Table 1: Momentum partial radial distribution function of He-like ion

Atomic number Z	shell	gHF(p_{12},p_1)	gCI(p_{12},p_1)
2	KαKβ	0.144647	0.145591
3	KαKβ	0.123550	0.125593
4	KαKβ	0.018233	0.019683
5	KαKβ	0.015388	0.159330

The partial coulomb shift $\Delta g(p_{12}, p_1)$ against (p_{12}; p_1) to study the correlation effects when the test electron be particle 1, with fixed magnitude p_1; and the integral of partial coulomb shift against p_1 is equal to Δf_{ij} (p_{12}). Due to the s-symmetry of inter-shells, K_α L_B $K_B L_\alpha$, the integration procedure in equation (3) and each f_{ij} (p_{12}) is normalized to unity, and Δf_{ij} (p_{12}) against p_{12} is equal to zero. The shapes of the partial coulomb shifts in Fig. 3 and 4 reflect the behaviors corresponding to $g(p_{12}, p_1)$ surfaces, and contour diagrams. For K_α K_B, the HF distribution straddles the ($p_{12} = p_1$) axis with a single peak located at $p_1 \approx p_1$ and $p^{12} \approx (2p^2_k)^{0.5}$, where p_k being the most probable value of p_1, is deduced from the maximum of the radial density distribution function $D(p_1, p_2)$ (see equation 5). This relationship between (p_{12}, p_1) value at g_{HF} peak and mode of $D(p_1)$ follows that found in position space by Banyard and Al-Bayati. The $\Delta g(p_{12}, p_1)$ surface showed strong similarities with that for L_i^+-ion there is reduction in the depth $p_1 < 0.4$, and an increase in height of approximately (10%) when $p_1 >$ 0.4 (and for all Z). For inter-shells, it was found that, as in the K-shift radial correlation alone increases p_{12} whereas angular correlation decreases p_{12}.

These opposing effects produce respective expansions and contraction in the normalized p_{12} distribution. $\Delta g(p_{12}, p_1)$ arises, when the test electron is located in the L-shell. Therefore, the p_{12} variation should reflect the influence of correlation acting on K-shell electron. When $p_1 > 1$, the test electron is located in K-shell, and hence, the diagonal fluence in $\Delta g(p_{12}, p_1)$ represent. For closed –shell system, it was found that both positive regions were equally obvious for each inter-shell; it was also shown that the results for kα Lα were in excess of K_B Lα

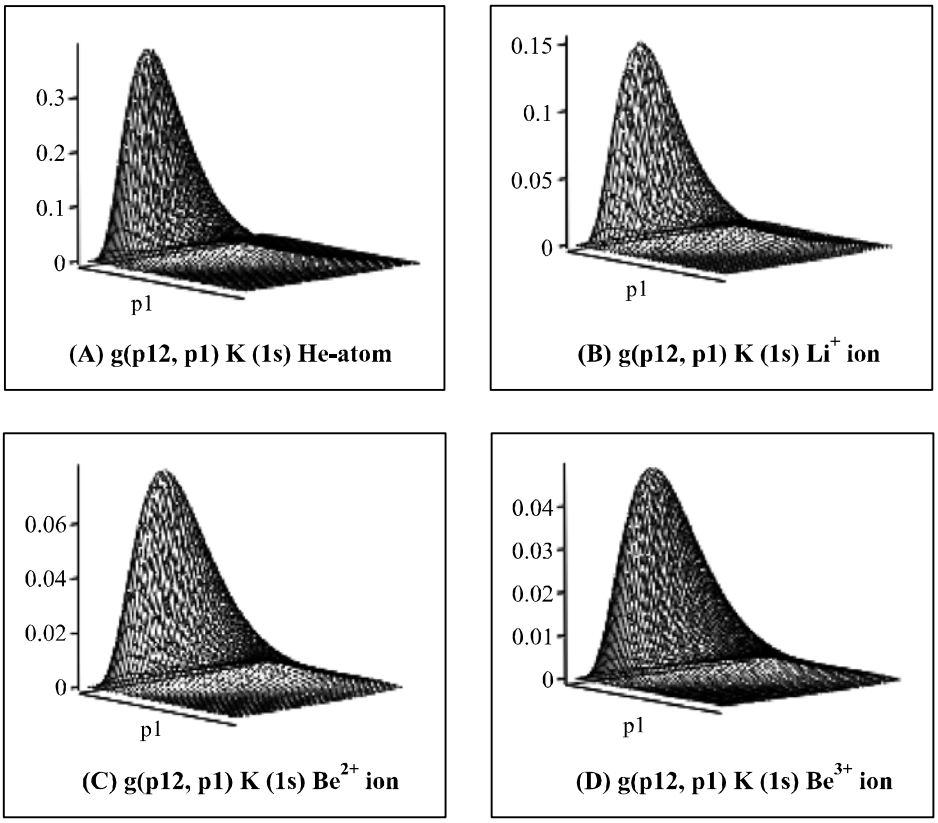
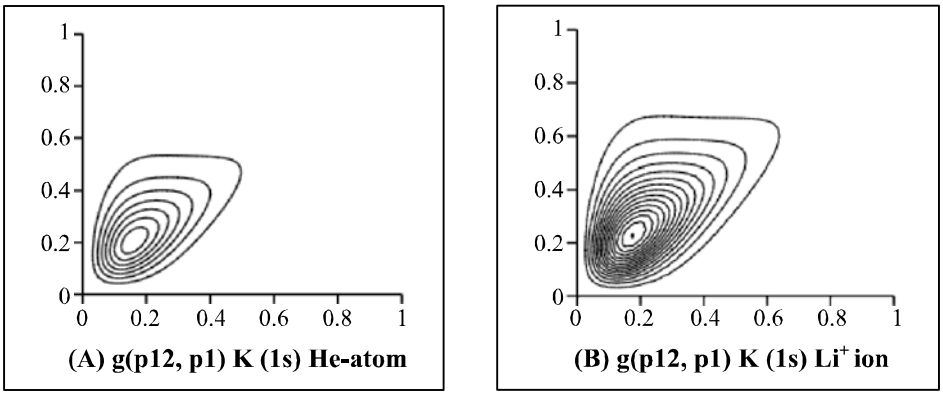


Fig. 1: The partial Coulomb holes $g(p_{12}; p_1)$, as a surface diagrams for (A) He-atom, (B) Li^+ ion, (C) Be^{2+} ion, (D) B^{3+} ion. Momentum correlated description of each state, with expectation of $1s^2$ was obtained from Hartree-Fock (HF) wave function



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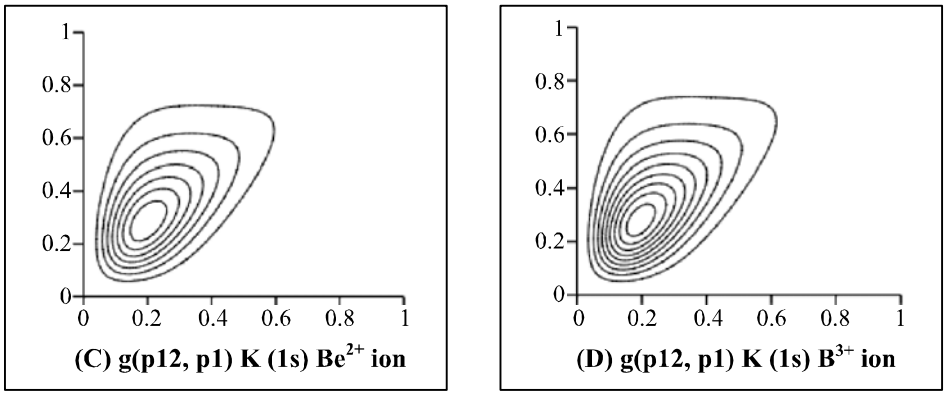

Fig. 2: The partial Coulomb holes $g(p_{12}; p_1)$, as a contour diagrams for (A) He-atom, (B) Li^+ ion, (C) Be^{2+} ion, (D) B^{3+} ion. Momentum correlated description of each state, with expectation of $1s^2$ was obtained from Hartree-Fock (HF) wave function

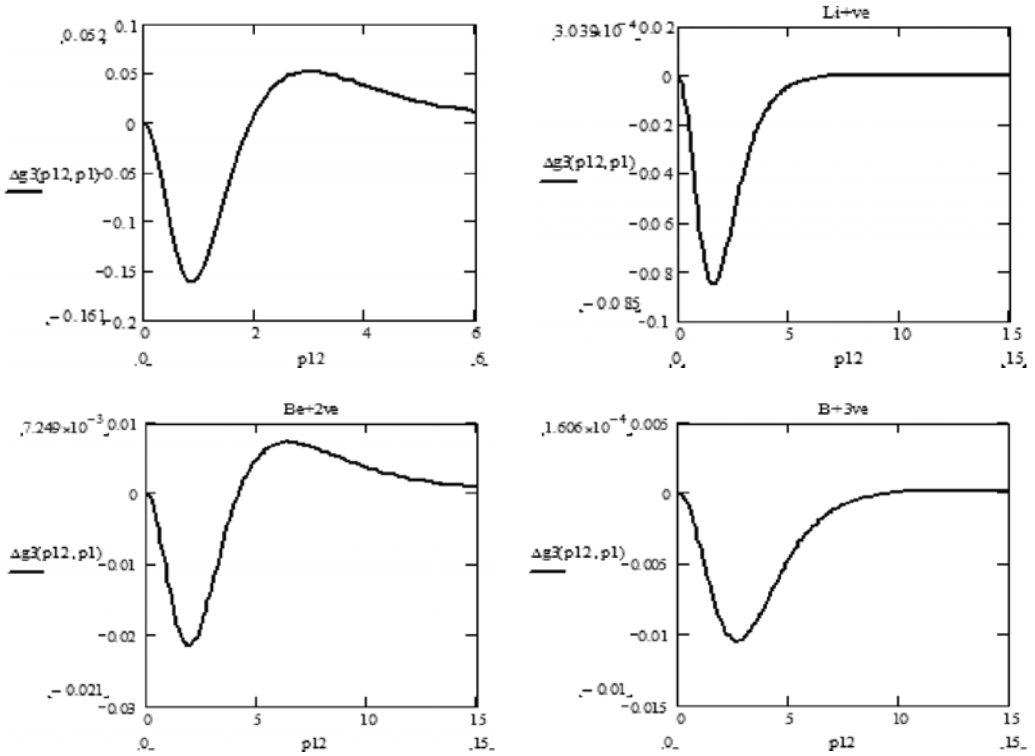

Fig. 3: The partial Coulomb holes $\Delta\, g(p_{12}; p_1)$, as a surface diagrams for (A) He-atom, (B) Li^+ ion, (C) Be^{2+} ion, (D) B^{3+} ion. Momentum correlated description of each state, with expectation of $1s^2$ was obtained from Hartree-Fock (HF) wave function

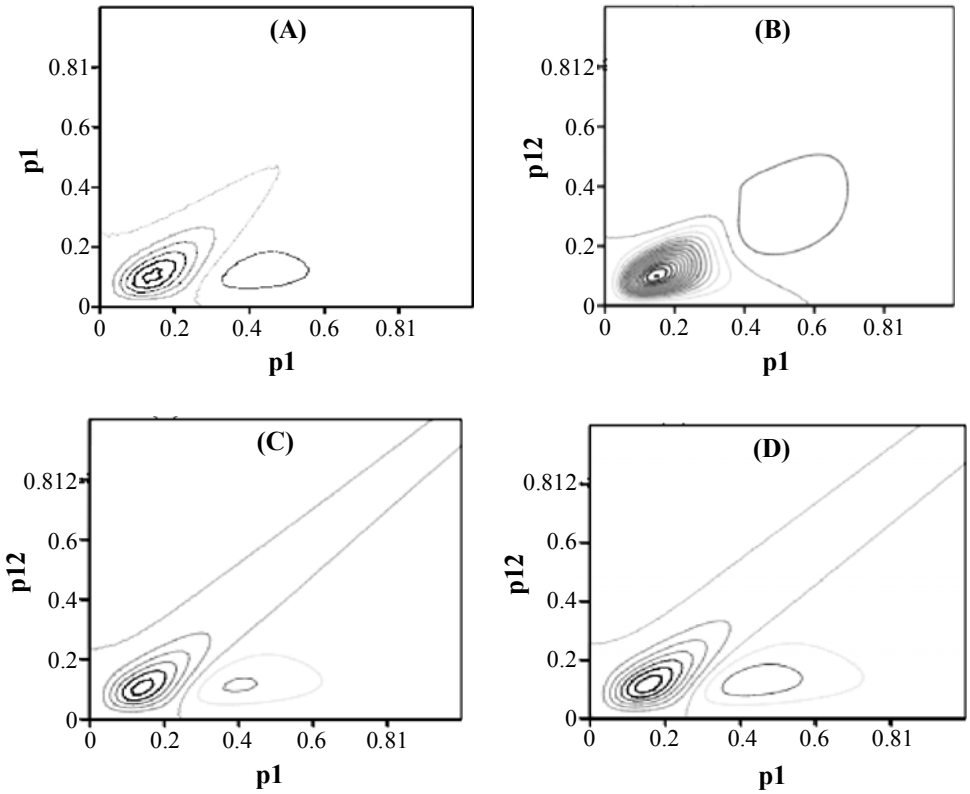

Fig. 4: The partial Coulomb holes $\Delta g(p_{12}; p_1)$, as a contour diagrams for (A) He-atom, (B) Li^+ ion, (C) Be^{2+} ion, (D) B^{3+} ion. Momentum correlated description of each state, with expectation of $1s^2$ was obtained from Hartree-Fock (HF) wave function

CONCLUSIONS

From the present work, it was noted that as Z increases, partial distribution function decreases in momentum treatment for both approximations. The results of partial distribution function for configuration interaction is larger than that for Hartree-Fock because each electrons move independently of each other, so this hypothesis neglectes the details of the electronic repulsion, which will reduce the HF results.

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