

Shifts in fermi hole: individual zones analysis

Haneen A. Lafi¹, Wissam A. Ameen^{1,2*}

¹Physics Department, College of Science, University of Anbar, Anbar, Iraq

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Corresponding author

Wissam A. Ameen
wissam.ameen@uoanbar.edu.iq

ABSTRACT

Zones in the vicinity of the Fermi hole were studied for the $1S^22S^2$ state over the atomic-number range $4 \leq z \leq 12$. Calculations were performed using the Hartree–Fock method. The results showed that the hole becomes narrower and deeper as the atomic number increases. The shift in the Fermi hole for neighboring elements in the series shows a significant shrinkage due to increasing nuclear charge. The investigation also revealed the existence of a second hole, and the results show that a shift occurs in this second hole as well. Similarly, the second hole decreased in size as the nuclear charge increased. Across the series, the shifts in both holes were reduced. In addition, the electron–electron repulsion energy was reported for each shell.

Keywords: *Fermi hole, Fermi hole Shift, Hartree-Fock method*

1 INTRODUCTION

Although classical electrodynamics requires electrons to repel each other, creating exclusion regions in a system, quantum mechanics introduces an additional level of exclusion [1]. It requires the wavefunction to obey antisymmetry, which is embedded in the mathematical description of the quantum state. This condition prevents electrons with the same spin from occupying the same state [2, 3], leading to the formation of a Fermi hole [4]. While electrons with different spins are not subject to the Pauli exclusion principle, Coulomb repulsion still drives the system to form a Coulomb hole [5–8]. In their seminal paper, Coulson and Nielson argued that electron correlation reduces the probability of finding two electrons close together in position space [8]. However, J. K. Pearson and coworkers reported counterintuitive results, suggesting that electron correlation can bring electrons closer [5]. Moreover, they reported the existence of a second hole, associated with a higher probability of finding an electron pair at a relatively large separation compared with the case of the first hole.

The concept of the Fermi hole was discussed by Wigner and Seitz [9]. Slater also studied it in the analysis of free electrons [10]. McWeeny utilized density-matrix theory to approach the Fermi hole [11], and Maslen extended Slater’s work on the exchange hole [12]. Later, additional results were reported by Sperber [13]. However, these approaches did not define the Fermi hole in terms of the interparticle density distribution function [14]. Boyd and Coulson later introduced a definition of the Fermi hole in terms of the interparticle density distribution function [14]. More recently, the effects of both Fermi and Coulomb correlations have been investigated in position space [15, 16]. Jose M. Mercero et al. reported that the emergence of the Fermi hole reduces the size of the Coulomb hole at small electron–electron distances [17]. Bultinck and coworkers studied the effects of the Fermi hole on the nature of bonds and orbital geometry [18]. Recently, an algorithm was investigated to determine the information content in the electron–electron density function, and the authors reported reduced computational cost compared with older

versions [19]. Bader and Heard showed that the Fermi hole can be significantly localized in space [20]. The effects of localization were also investigated by Rincon et al., who studied bonding through the localization of the Fermi hole and the separation of information content [21, 22]. They showed that the Fermi hole is not a side effect of interparticle interactions; rather, it exists because particles are fermions.

Although many attempts have been made to investigate the Fermi hole in many-electron systems, the shift in holes due to increasing nuclear charge has not, to the best of our knowledge, been investigated. Therefore, this work reports the estimated size of the Fermi holes and shifts in the Fermi hole due to increasing nuclear charge throughout the Be-isoelectronic series in its ground state.

2 MATERIALS AND METHODS

The wavefunction in fermionic systems is supposed to be antisymmetric, where electrons with similar spins are kept apart. This is the key cause of the emergence of the Fermi hole:

$$\Delta f(r_{12}) = f(r_{12})_{KL(^3S)} - f(r_{12})_{KL(^1S)}, \quad (1)$$

where, $f(r_{12})_{KL(^3S)}$ and $f(r_{12})_{KL(^1S)}$, refers to the interparticle probability density distribution for triplet $KL(^3S)$ and singlet $KL(^1S)$ states respectively [14]. Following Coulson and Nielson, the interparticle probability density distribution is defined as [8]:

$$f(r_{12}) = \frac{r_{12}}{2} \left(\int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_1-r_{12}}^{r_1+r_{12}} r_2 \Gamma''_{HF}(r_1, r_2) dr_2 + \int_0^{r_{12}} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} r_2 \Gamma''_{HF}(r_1, r_2) dr_2 \right). \quad (2)$$

The interparticle distance is given in terms of $r_{12} = |r_2 - r_1|$. The term $\Gamma''_{HF}(r_1, r_2)$ defines the reduced two-electron density, where the integration is carried upon both the spin and angular parts, as follows:

$$\Gamma''_{HF}(r_1, r_2) = \binom{N}{2} \int \mathcal{O}_{HF}^*(x_1, x_2, x_p, \dots, x_q) \times \mathcal{O}_{HF}(x_1, x_2, x_p, \dots, x_q) dx_p \dots dx_q d\Omega_1 d\Omega_2 d\sigma_1 d\sigma_2 \quad (3)$$

Here, N is the number of electrons and $d\Omega_k$ represents the angular part of the volume element, whereas $d\sigma_k$

indicates the spin element. And r_i represents the distance between the i^{th} electron and the nucleus. The term $\mathcal{O}_{HF}(1, 2, \dots, N)$ represents the Hartree-Fock wavefunction [23–25]. To estimate the Fermi-hole numerically, the modified version of strength, S^{zone} is introduced:

$$S^{\text{zone}} = \int_{u_1}^{u_2} \Delta f(r_{12}) dr_{12} \quad (4)$$

Here, u_k refers to the k^{th} root in the $\Delta f(r_{12})$ plot for a given atom (or ion) [5]. Moreover, the strength density shift, $\Delta S^{\text{zone}}_{i,i+1}$, is introduced to determine the partial probability shift in $\Delta f(r_{12})$ in a given ion at position $i+1$ in the Be-isoelectronic series relative to another ion at the i^{th} position. The shift occurs due to the rise in atomic number by one unit, i.e., $|Z_i - Z_{i+1}| = 1$. The strength shift, $\Delta S^{\text{zone}}_{i,i+1}$, is considered for nearest neighbor pairs of atomic systems within the same isoelectronic series:

$$\Delta S^{\text{zone}}_{i,i+1} = \int_{p_1}^{p_2} |\Delta f(r_{12})_i - \Delta f(r_{12})_{i+1}| dr_{12} \quad (5)$$

Both $f(r_{12})_i$ and $f(r_{12})_{i+1}$ represent the electron-electron radial density distribution for an atom (or ion) at position i and $i+1$ in the series, respectively [8, 26]. The absolute value ensures that the difference is expressed as a positive value. Here, p_k are the roots of the overlapped $\{\Delta f(r_{12})_i, \Delta f(r_{12})_{i+1}\}$ plots that define the beginning and end of each zone. The shift, $\Delta S^{\text{zone}}_{i,i+1}$ is manifested in the first Fermi-hole and at least three other zones. The electron-electron repulsion potential energy is determined using the following formula:

$$V_{ee} = \int_0^{\infty} f(r_{12}) r_{12} dr_{12} \quad (6)$$

All calculations are conducted using Roothan-Hartree-Fock basis functions provided by Clementi and Roetti [27].

3 RESULTS AND DISCUSSION

The emergence of the first and secondary Fermi holes provides a deep understanding of the rule of exclusion principle. It seems that the exclusion principle has no fixed effect on the interparticle distance of electrons of the whole interval of r_{12} . According to Eq. 1, the electron pairs in the singlet state $KL(^1S)$ are allowed to come close to each other, as shown in the first Fermi hole, depicted as the grey zone in Figure 1. On the contrary, those in the triplet state $KL(^3S)$ are pushed apart to dominate the zone at intermediate r_{12} as shown in the green zone in Figure 1. The probability of $KL(^3S)$

electrons is slightly higher than those in the $KL(1S)$ state at intimate r_{12} interval. The probability of finding electrons with different spins is reduced at large r_{12} in favour of those with dissimilar spins again, which leads to the emergence of the secondary Fermi hole, as appears in the blue zone of Figure 1. The emergence of two Fermi holes seems reasonable since the first one indicates the existence of a shell with dissimilar spin, which is the K-shell, as depicted in Figure 1. Whereas, the second Fermi hole refers to the existence of the L-shell where dissimilar spins, again, dominate the shell. The existence of the first Fermi hole, the intermediate zone and the second Fermi hole seems to dominate the $\Delta f(r_{12})$ plots throughout the Be-isoelectronic series as shown in Figures 2 and 3. Once both probabilities are equated, $\Delta f(r_{12})_{KL(3S)} = \Delta f(r_{12})_{KL(1S)}$, the $\Delta f(r_{12})$ drops to zero as appeared in Figure 1. As the nucleus charge increases, the $\Delta f(r_{12})$ are shifted towards the nucleus as depicted in Figure 4.

The first Fermi hole becomes deeper throughout the series. The depth of the second hole increases more slowly than that of the first, as shown in Figure 2. The intermediate zone shows significant enlargement throughout the series, as shown in Figure 2. The present work also shows a reduction in the strength $\Delta S_{i,i+1}^{zone}$ throughout the series. The Fermi hole plots of $\{\Delta f(r_{12})_i, \Delta f(r_{12})_{i+1}\}$ for adjacent atoms are depicted in Figure 4, showing distinct zones. In this work, the colored zones represent the shift in Fermi hole density resulting from increasing nuclear charge. The shape of the shift in the three zones, depicted in Figure 1, is illustrated in Figure 4 for the first two pairs of adjacent atoms in the series. The pairing energy increases with increasing nuclear charge, as reported in Table 1.

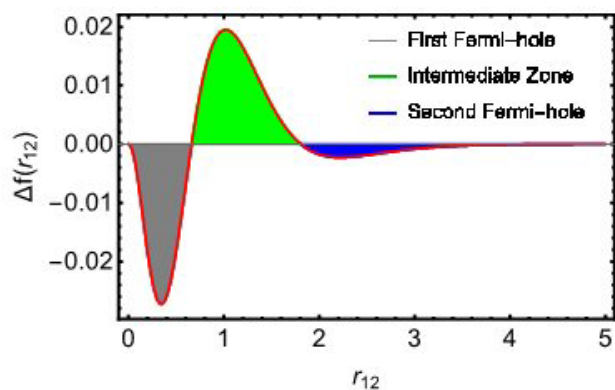


Fig. 1 Three identified zones in the Fermi-hole plot for Be atom. Atomic units have been used

The present work demonstrates how the zone-like approach can be applied to investigate shifts in the probability distributions.

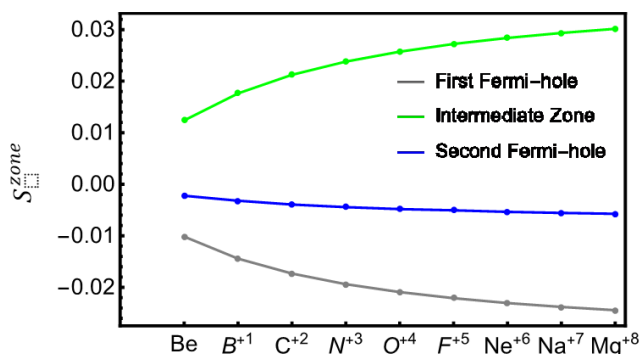


Fig. 2 The strength S^{zone} of the first and second Fermi holes in addition to the intermediate zone, for the Be-isoelectronic series. Atomic units have been used

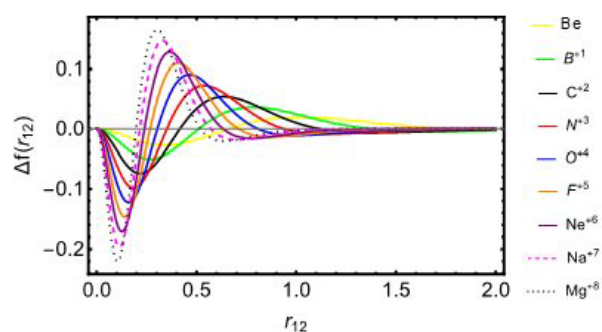


Fig. 3 Fermi-hole for Be-isoelectronic series. Atomic units have been used

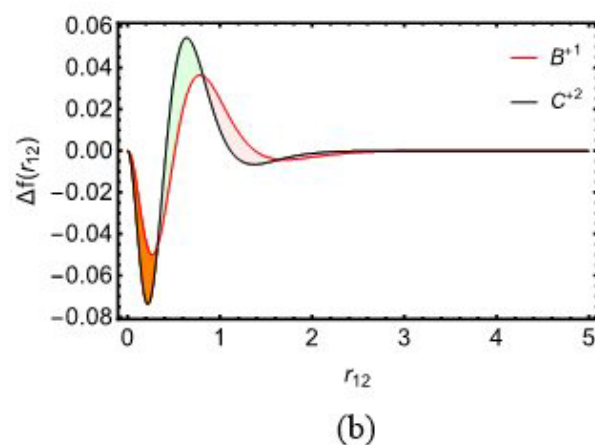
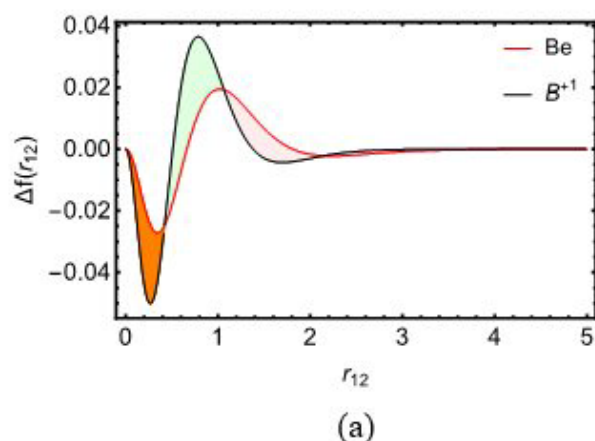


Fig. 4 Shift the first and second Fermi holes in addition to the intermediate zone for two pairs: (a) $Be, B^{(+1)}$ (b) $B^{(+1)}, C^{(+2)}$. Atomic units have been used

Table 1 The pairing energy V_{ee} for the Be-isoelectronic series. Atomic units have been used

Z	Atom	KK	KL ($\frac{1}{S}$)	KL ($\frac{3}{S}$)	LL
4	Be	2.27298	0.48088	0.45527	0.34323
5	B^{+1}	2.89619	0.70259	0.65645	0.50380
6	C^{+2}	3.51985	0.91877	0.85118	0.65935
7	N^{+3}	4.14386	1.13261	1.04331	0.81288
8	O^{+4}	4.76813	1.34520	1.23410	0.96535
9	F^{+5}	5.39253	1.55711	1.42412	1.11726
10	Ne^{+6}	6.01695	1.76850	1.61362	1.26876
11	Na^{+7}	6.64154	1.97957	1.80278	1.42005
12	Mg^{+8}	7.26625	2.19045	1.99171	1.57114

4 CONCLUSION

The present work reports an analysis of three distinct zones in the interparticle density distribution for the Be isoelectronic series. The first and third zones correspond to the first and second Fermi holes. The remaining zone is the intermediate zone, which lies between the first and second Fermi holes. The results show that the absolute value of the strength increase for all three zones as the nuclear charge increases. Moreover, shifts in the Fermi holes and the intermediate zone were estimated using the strength shift, which also decreases throughout the series. This behavior is attributed to compression of the electronic charge cloud in response to increasing nuclear charge. Finally, the pairing energy shows a steady increase for all shells throughout the series.

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N/A

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N/A

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