Fermi and Coulomb Correlations in the 2^1S State of the Helium Isoelectronic Sequence

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The Fermi and Coulomb holes of the 2^1S state of the helium isoelectronic sequence are investigated. Several interesting differences between the results obtained and those which might be expected on the basis of the corresponding 2^3S state are pointed out and discussed.

Key words: Fermi and Coulomb correlations – Helium isoelectronic sequence, 2^1S state

1. Introduction

Although the majority of quantum chemical calculations are made within the self-consistent field formalism in which only the averaged (rather than instantaneous) interactions between electrons are included, much effort has been devoted to the incorporation of electron correlation [1] and to the attainment of a better understanding of its consequences. For the latter objective, much has been learned through the use of hole formalisms according to which the Coulomb and Fermi correlations between electrons are described as functions of the interelectronic separation. Explicitly evaluated Coulomb holes are available for the ground state of the He sequence [2], for the 2^3S state [3], as well as for larger atomic and molecular systems [4].

In this paper we present such a study for the first excited singlet state of the helium isoelectronic sequence. We begin with a discussion of the Hartree and Hartree-Fock wavefunctions, which are used for the study of the Fermi hole. This is followed by the results obtained by use of correlated wavefunctions for the determination of the Coulomb hole.

2. The Roothaan-Hartree-Fock Calculations

Hartree-Fock wavefunctions for the 2^1S state of He, Li^+ and Be^{2+} were computed using the self-consistent field equations previously described [5]. The two-electron wavefunction is:

$$\psi = 1s(1)2s(2) + 2s(1)1s(2).$$

$1s$ and $2s$ are linear combinations of N_1 and N_2 primitive Slater functions, respectively. The exponential parameters of the basis functions for each orbital were expressed in even-tempered form [6], reducing the number of non-linear parameters to be optimized to four. In order to converge to the first excited ^1S state the second lowest eigenvalue and eigenvector were iterated on in the SCF equation for the $2s$ orbital, following Coolidge and James [7]. The corresponding Hartree functions were discussed in Ref. [8].

The $1s$ and $2s$ orbitals are non-orthogonal to one another in both the Hartree and the Hartree-Fock wavefunctions for the 2^1S state. The overlap integral $\langle 1s|2s \rangle$ is plotted in Fig. 1. It vanishes both at $Z \to \infty$, where the orbitals become hydrogen-like and therefore orthogonal, and at $Z = 1$, where the outer orbital becomes infinitely diffuse. The maximum in the overlap at $1/Z \simeq 0.6$–0.7 can be used to quantify the distinction between the high Z and low Z members of the isoelectronic sequence, which is relevant to the discussion of convergence of $1/Z$ perturbation theory, behaviour of bound states close to the minimal Z necessary for binding, etc.

Table 1 lists the energies and some expectation values. By comparison with the virtually exact results [9], it is clear that the correlation corrections to the interelectronic repulsion, interelectronic distance and the square of this distance
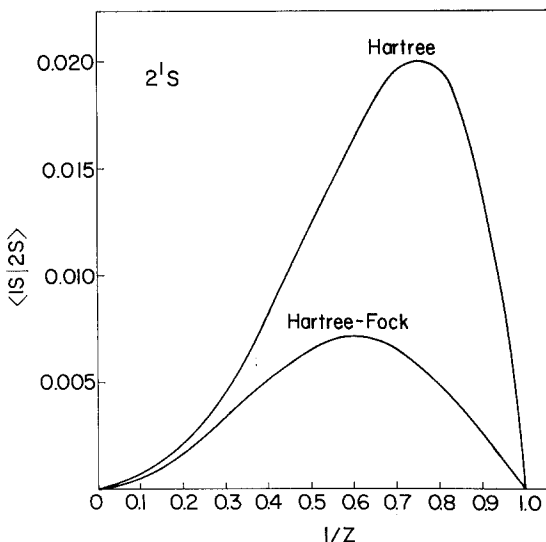

Fig. 1. The overlap integral between the inner and outer orbitals in the Hartree and Hartree-Fock wavefunctions for the 2^1S state of the He sequence

Table 1. Energies and expectation values for the 2^1S state[a]

		Energy	$\langle 1/r_{12} \rangle$	$\langle r_{12} \rangle$	$\langle r_{12}^2 \rangle$
	$N=3$	-2.14295	0.2491	5.3911	34.08
	$N=4$	-2.14338	0.2496	5.3332	33.05
He	$N=5$	-2.14346[c]	0.2495[d]	5.3456	33.33
	Pekeris[b]	-2.14597	–	5.2697	33.30
	Correlation	-0.00251	–	-0.0759	-0.03
	$N=3$	-5.03515	0.481	2.84	9.7
	$N=4$	-5.03615	0.481	2.85	9.52
Li$^+$	$N=5$	-5.03620	0.480	2.85	9.54
	Pekeris[b]	-5.04087	–	2.84	9.44
	Correlation	-0.00467	–	-0.01	-0.10
	$N=3$	-9.17742	0.715	1.96	4.53
	$N=4$	-9.17878	0.715	1.95	4.44
Be^{++}	$N=5$	-9.17884	0.713	1.95	4.45
	Pekeris[b]	-9.18487	–	1.95	4.44
	Correlation	-0.00603	–	-0.00	0.01

[a] Atomic units are used throughout this paper.   [b] Ref. [9].
[c] Davidson's [J. Chem. Phys. **42**, 4199 (1965)] Hartree-Fock result
is -2.14344 a.u.
[d] Davidson's result is 0.2496.

have the opposite sign to what is expected on the basis of the more conventional effect of correlation, as observed in the helium ground state [2] and in the ground state of the hydrogen molecule [10]. As the nuclear charge increases, this reversed correlation effect decreases, in agreement with the suggestion that it is a consequence of the coupling of radial and angular correlations, which is a third-order effect in a $1/Z$ expansion [11]. Furthermore, the more diffuse the outer orbital, the smaller the effective nuclear charge, and the stronger the coupling. Therefore, the reversed correlation effect is expected to be stronger in the 2^1S state than in the 2^3S state since the outer orbital is more diffuse in the former, in agreement with the computed results. A similar situation also exists in the 2^3P and 2^1P states [11].

3. Fermi correlation in the $1s2s$ states

The Fermi hole may be defined as the difference between the Hartree-Fock and Hartree pair distributions [12]. Obviously, there is no Fermi hole for a closed shell (singlet) in a two electron system, but there is one for both the triplet and corresponding open-shell singlet.

If the orbitals in the singlet and triplet states are taken to be identical and orthogonal, then the "Fermi hole" of the singlet state is the mirror image of the triplet state one. Thus,

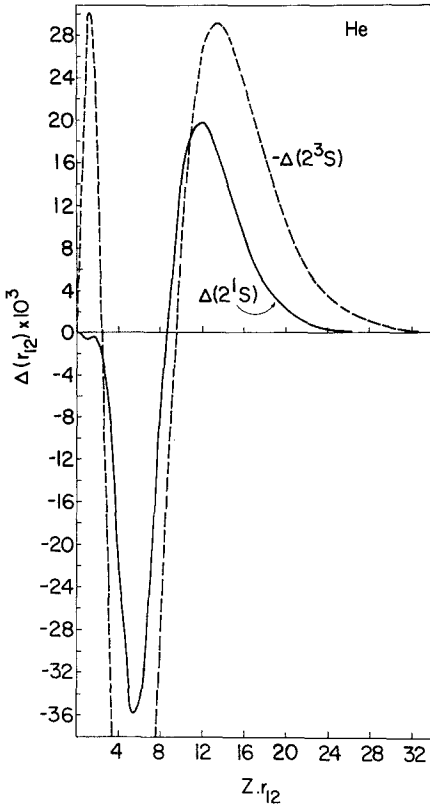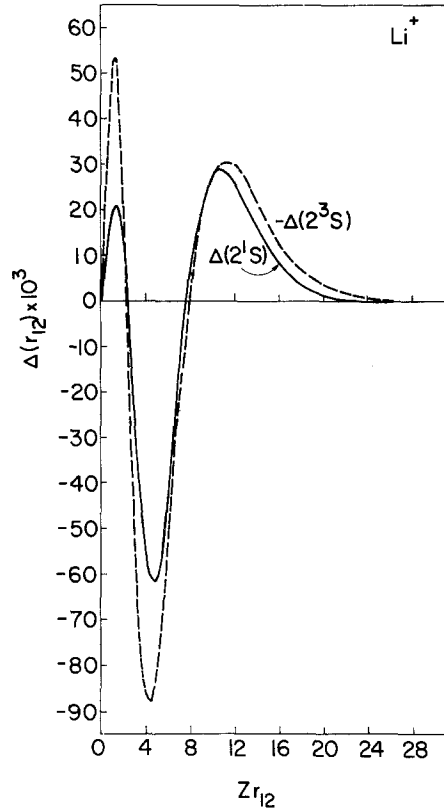$$^3f_{HF}(r_{12}) - f_H(r_{12}) = -[^1f_{HF}(r_{12}) - f_H(r_{12})] \tag{2}$$

Fig. 2. The Fermi hole for He

Fig. 3. The Fermi hole for Li$^+$

where the superscripts 3 and 1 refer to the triplet and singlet states respectively. However, with the $1s$ and $2s$ orbitals of the Hartree-Fock (HF) wavefunctions obtained variationally for each state, the Fermi holes are no longer mirror images of one another. The results are shown in Figs. 2 and 3.

At small interelectronic distances the Fermi hole of the 2^1S state of He is negative, in contradiction to what one might expect on the basis of the results for the 2^3S state.

To account for the difference in the behaviour for small r_{12} we shall show that in the triplet state the Fermi hole is always negative for very small interelectronic distances. For s-type orbitals Coulson and Neilson [2] derived the pair distribution function:

$$f(r_{12}) = 8\pi^2 r_{12} \left[\int_{r_{12}}^{\infty} r_1 \, dr_1 \int_{r_1-r_{12}}^{r_1+r_{12}} r_2 \, dr_2 \Psi^2 + \int_{0}^{r_{12}} r_1 \, dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} r_2 \, dr_2 \Psi^2 \right] \qquad (3)$$

For very small interelectronic distances $r_1 \simeq r_2$ and consequently,

$$f(r_{12}) \sim r_{12}^2 \cdot \int_{0}^{\infty} r_1^2 \Psi^2(r_1, r_1+r_{12}) \, dr_1 \qquad (4)$$

In the Hartree approximation, $\psi_H = 1s(1) \cdot 2s(2)$ one obtains

$$\psi_H(r_1, r_1 + r_{12}) \simeq 1s(1) \cdot 2s(1) \tag{5}$$

Therefore the Hartree pair distribution function for very small r_{12} is proportional to the interelectronic distance squared

$$f_H(r_{12}) \sim r_{12}^2$$

The HF wavefunction of the triplet state is:

$$^3\Psi_{HF} = 1s(1) \cdot 2s(2) - 2s(1) \cdot 1s(2) \tag{6}$$

hence,

$$\begin{aligned}
^3\Psi_{HF}(r_1, r_1 + r_{12}) &\simeq [1s(1)2s(1) + r_{12}1s(1) \cdot \partial 2s(1)/\partial r_1] \\
&\quad - [2s(1) \cdot 1s(1) + r_{12} \cdot 2s(1) \cdot \partial 1s(1)/\partial r_1] \\
&= r_{12} \cdot [1s(1) \cdot \partial 2s(1)/\partial r_1 - 2s(1)/\partial 1s(1)/\partial r_1]
\end{aligned} \tag{7}$$

By substituting this result in Eq. (4) one obtains:

$$^3f_{HF}(r_{12}) \sim r_{12}^4$$

Therefore,

$$^3\Delta(r_{12}) = {}^3f_{HF}(r_{12}) - f_H(r_{12}) \sim -r_{12}^2 < 0 \tag{8}$$

which is what we wanted to prove.
However, in the singlet state

$$^1\Psi_{HF}(r_1, r_1 + r_{12}) \simeq 2 \cdot 1s(1) \cdot 2s(1) + r_{12} \, \partial[1s(1)2s(1)]/\partial r_1 \tag{9}$$

and

$$^1f_{HF}(r_{12}) \sim r_{12}^2$$

The corresponding Fermi hole at small r_{12} is equal to the difference of two terms containing the same power of r_{12}, and can therefore be either negative or positive.

In order to account for the shape of the singlet Fermi hole at large r_{12} we first point out that using the same orbitals for the Hartree and the Hartree-Fock wavefunctions a maximum should appear at large r_{12}, for high nuclear charges but not for low ones. The analogous result for the triplet state has been discussed in Ref. (8).

The calculations with full optimization yield, for large r_{12}, an opposite picture to the one discussed. This difference indicates that the low Z Fermi hole is not a direct manifestation of the exchange term, but rather has a significant contribution due to the Coulomb term; see Fig. 4.

4. The Coulomb Hole

Fig. 5 illustrates the Coulomb hole for the 2^1S state of He, Li^+ and Be^{++}, computed by use of the Hartree-Fock pair distribution function discussed in the previous section, and the correlated pair distribution function evaluated by Boyd and Coulson [13] using Perkins' wavefunction [14].
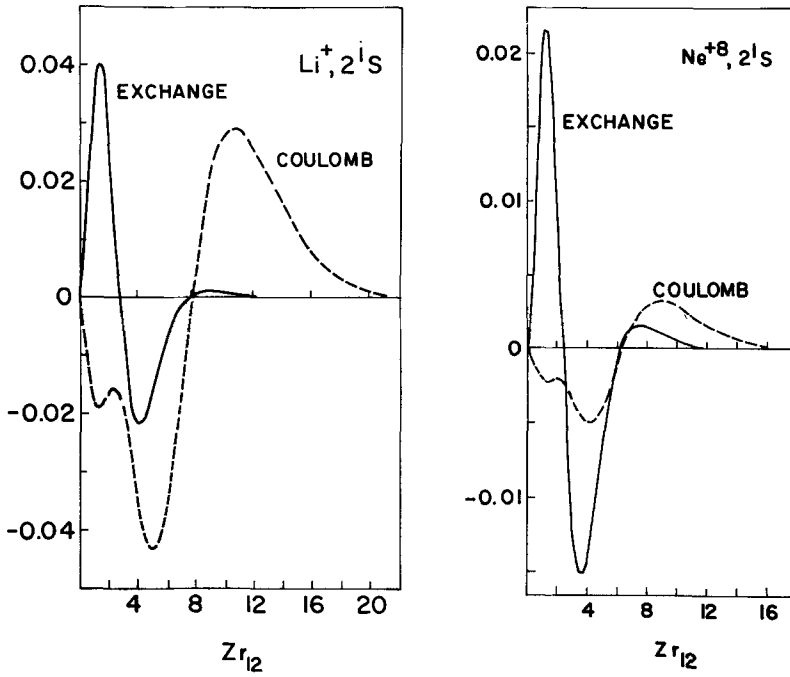
Fig. 4. Exchange vs. Coulomb contributions to the Fermi hole. a. Li$^+$, b. Ne^{+8}
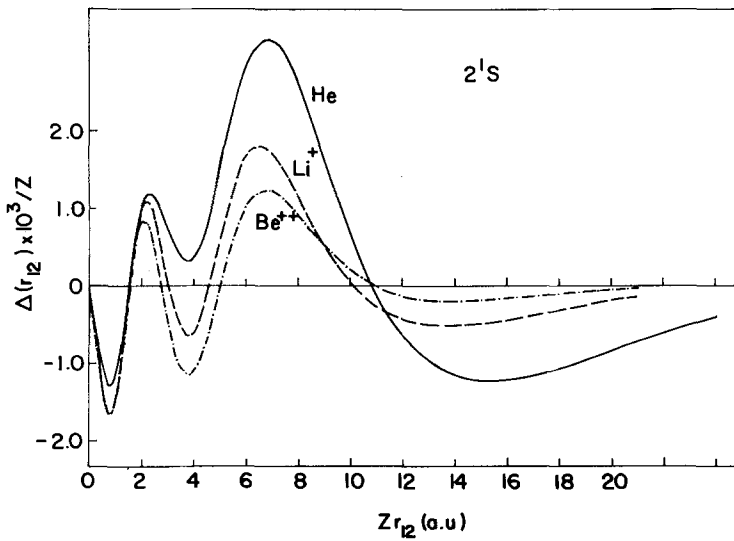

Fig. 5. The Coulomb hole

On the basis of a previous comparison [13] for He, the correlated wavefunctions of Perkins appear to be adequate for the determination of the Coulomb hole.

The accuracy of the Hartree-Fock pair distribution function is assessed by the comparative values in Table 2. The agreement among the results is excellent at low r_{12} and adequate at large r_{12}. As the nuclear charge increases the results for $N_1 = N_2 = 4$ and $N_1 = N_2 = 5$ get even closer.

Table 2. Dependence of the He 2^1S Coulomb hole on the choice of Hartree-Fock wavefunction

r_{12}	Value of $\Delta(r_{12})^a$		
	Davidson[b]	$N_1 = N_2 = 4$	$N_1 = N_2 = 5$
0.4	-0.0026	-0.0027	-0.0026
1.2	$+0.0023$	$+0.0023$	$+0.0023$
1.9	$+0.0004$	-0.0009	$+0.0006$
3.6	$+0.0067$	$+0.0077$	$+0.0062$
7.0	-0.0038	-0.0037	-0.0023
Energy	-2.14344	-2.14338	-2.14346

[a] $\Delta(r_{12})$ evaluated by use of the correlated wavefunction of Perkins (1963) and the SCF wavefunction indicated at the top of each column.
[b] J. Chem. Phys. **42**, 4199 (1965).

The gradual changes observed in Fig. 5 for the 2^1S state Coulomb hole as a function of the nuclear charge, Z, are in sharp contrast to the situation in the 2^3S state. For the latter, it has been observed [3] that the Coulomb hole changes distinctly between He and Li$^+$. Nevertheless, the Coulomb hole for He has some conspicuous differences from the larger Z Coulomb holes. Further increase in Z leads to a contraction of the Coulomb hole but retains the Li$^+$ form for the other isoelectronic ions.

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