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Atomic configuration-interaction electron-electron counterbalance densities

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The atomic electron-electron counterbalance density $d(0)$ represents the probability density of finding any two electrons exactly at mirror positions with respect to the nucleus. We have computed these densities from accurate configuration interaction and Hartree-Fock-like wave functions for the isoelectronic series of He and first-row atoms. Our calculations demonstrate that the electron correlation decreases the value of $d(0)$, and thus indicate that the radial correlation effects dominate over the angular effects. We have also found that inclusion of dynamical correlation is crucial for a realistic description of the electron-electron counterbalance density. [S1050-2947(99)07405-3]

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I. INTRODUCTION

The electronic relative-motion (intracule) $I(\mathbf{u})$ and the center-of-mass-motion (extracule) $E(\mathbf{R})$ densities are reductions of the second-order density matrix that still retain a genuine two-electron character and have been widely recognized [1,2] as useful tools to learn more about the interaction among electrons in both atomic and molecular systems. In particular, their corresponding radial functions $h(u)$ and $d(R)$ give, respectively, the probability density for the relative distance $|\mathbf{r}_i-\mathbf{r}_j|$ to be $|\mathbf{u}|=u$ and the probability density that the center of mass $|(\mathbf{r}_i+\mathbf{r}_j)|/2$ of any electron pair be $|\mathbf{R}|=R$.

Special cases of these probability densities correspond to their values at the origin. Thus, the intracule density $h(u)$ for $u=0$ gives the electron-electron coalescence density $h(0)$, which is the probability density of any two electrons to have identical space coordinates. This quantity, which appears in the evaluation of both the relativistic [3] and radiative [4] corrections in the electronic structure calculations, has recently been studied extensively [5–9].

However, the electron-electron counterbalance density $d(0)$ is far less familiar and has only been studied systematically for atomic ground state Hartree-Fock wave functions [8–10]. In particular it has been shown that for atoms, $d(0)$ can be expressed exactly in terms of the electron-density function, with a form depending on the electronic configuration and the LS multiplet state of the atom under consideration [8,9]. Also, Koga [10] has demonstrated that within the Hartree-Fock approximation there exists an *electron-electron counterbalance hole,* between any two electrons in spin orbitals with the same spin and spatial inversion symmetry. These two electrons *cannot* be at opposite positions with respect to the nucleus. Nevertheless, in spite of its importance, the properties of the electron-electron counterbalance density are scarcely known.

One fact that seriously inhibits progress in this field is the lack of accurate correlated data for $d(0)$. Indeed, one important point which needs to be clarified is the effect of electron correlation on the electron-electron counterbalance density. Therefore, in this paper, we shall discuss the results from our calculations of $d(0)$ using configuration interaction wave functions for the ground states of the atoms of the first row.

II. METHODS

The electron-electron coalescence densities discussed in the present work have been obtained from the corresponding Hartree-Fock (HF), configuration interaction [both full configuration interaction (FCI) and single and double configuration interaction (SDCI)] and the multiconfiguration self-consistent-field (MCSCF) wave functions of each system studied, as prescribed earlier [11]. In the MCSCF calculations, all the electrons of the actual atom, except the inner $1s^2$ ones, have been correlated in the $2s$, $2p$, $3s$, $3p$, and $3d$ active orbitals. The details of the procedures used to obtain the wave functions can be found elsewhere [12].

For the calculations of the isoelectronic series of He we have used a previously built 7/7/5 basis set [13], which is identified by its number of *s*-, *p*-, and *d*-type sets of basis functions, respectively. It was constructed starting from the standard 311G($3pd$) basis [14], 3/3/1 according to our notation, and then the exponents of the complementary basis functions were chosen to form an even-tempered set with ratio 3.0, until reaching the 7/7/5 size. This basis set has been found to perform accurately in FCI calculations not only for the ground state of He but also for the excited states [15].

The double-ζ (DZ), double-ζ plus polarization (DZP), triple-ζ (TZ), and triple-ζ plus polarization (TZP) basis sets used for these calculations, correspond with the 6-31G, 6-31G(d), 6-311G, and 6-311G(d) standard basis sets of Hehre *et al.* [16], respectively. The DZ2P and DZ3P, and TZ2P and TZ3P basis sets have been constructed from the DZP and TZP bases adding one and two extra *d*-type functions, respectively, whose exponents have been optimized by Frisch *et al.* [17]. Notice that the exponents of the added functions were chosen to form an even tempered set with ratio 4.0 with respect to the most diffuse *d*-type function of each set.

All the HF wave functions were obtained by use of GAUSSIAN [18] and all the post-HF ones with a locally modified version of GAMESS [19].

III. THE He ISOELECTRONIC SERIES

As pointed out by Koga and Matsuyama [9], beyond the Hartree-Fock approximation, the effect of the electron correlation on $d(0)$ in atomic system may be viewed as an overlap of its radial and angular contributions. The radial part aims to place any two electrons as far apart as possible.

TABLE I. The electron-electron counterbalance density for the ground state of the He isoelectronic series, at the HF and FCI levels of theory.

Atom	$1\,^1$S HF	$1\,^1$S FCI	$2\,^1$S FCI
He	1.523632	1.434339	0.110811
Li^{+1}	6.140993	5.932282	0.685418
Be^{+2}	15.83019	15.38916	2.089985
B^{+3}	32.34944	31.55047	4.681168
C^{+4}	57.27800	56.01082	8.802881
N^{+5}	91.97453	90.16356	14.76989
O^{+6}	137.5683	135.1876	22.85317
F^{+7}	194.9748	192.0632	33.27370
Ne^{+8}	264.9026	261.5810	46.19934

Thus, when one electron is close to the nucleus, the other will be pushed away and consequently $d(0)$ will be reduced with respect to the Hartree-Fock value. The angular correlation, on the other hand, increases the probability of those electron pairs with their electrons located on opposite sides of the nucleus [20]. These situations contribute to $d(0)$. Hence, the angular correlation may increase $d(0)$ with respect to its Hartree-Fock value. The end result is that the effect of the electron correlation on the atomic electron-electron counterbalance density consists of the superposition of the two opposite contributions.

The values of the electron-electron counterbalance density for the ground state of the He isoelectronic series, at the HF and FCI levels of theory, can be found in Table I. Our calculations indicate that inclusion of the electron correlation effects decreases the value of the counterbalance density for these simplest two-electron systems. It is worth noting at this point that our calculations are *not* exact, for we have used a truncated basis set. Nevertheless, our value for the HF $d(0)$ for He, 1.523 632, compares well with the HF limit value of Koga and Matsuyama [9], 1.524 832 1. Thus, our calculations deserve some confidence and give support to our statement on the reduction of $d(0)$ as a consequence of including electron correlation effects. We shall come back to this point in Sec. V, where the electron-electron counterbalance density of the first row atoms will be discussed.

Koga [10] has recently shown that within the Hartree-Fock framework, there exist an *electron-electron counterbalance hole* between two electrons in spin orbitals *i* and *j* with the same spin and spatial inversion symmetry. Namely, the center-of-mass vector of these electrons cannot be zero [21]. The $2\,^3$S state of the He isoelectronic series satisfies the inversion requirement, so that according to Koga the $d(0)$ must be zero at the HF level of theory. It should also be noted that for triplet states of two-electron systems with even total angular momentum quantum number, the spatial part of the wave function Ψ must be antisymmetric under exchange of electrons and of even parity with respect to the inversion of the coordinates of the electrons. Hence,

$$\Psi(\vec{r}_1,-\vec{r}_1)=0. \tag{1}$$

Since the electron-electron counterbalance density $d(0)$ is proportional to

$$\int d\vec{r}_1 |\Psi(\vec{r}_1,-\vec{r}_1)|^2, \tag{2}$$

it follows that $d(0)$ must vanish for these states. We have been able to check that $d(0)$ is exactly zero for the $2\,^3$S states of the He isoelectronic series.

IV. SELECTION OF A BASIS SET

Table II collects the values of the electron-electron counterbalance density of ground state of the atoms of the first row calculated from the nonrelativistic self-consistent-field Hartree-Fock wave functions (restricted for closed shells and unrestricted for open shells) with various selected basis sets. Results from the numerical Hartree-Fock limit calculations of Koga and Matsuyama [9] have been included for comparison.

Inspection of Table II reveals that comparing with the numerical Hartree-Fock limit results, on the overall, the triple-zeta basis sets perform remarkably better than their analogous double-zeta counterparts, as expected. Addition of *d*-type polarization functions to either double- or triple-zeta basis sets improves the poor unpolarized basis set estimation of $d(0)$, in both cases. Nevertheless, it is worth noting that the TZP and TZ3P are closer to each other than to the TZ2P values. This might indicate that the value of $d(0)$ oscillates with respect to the increase of the basis set size. However, to

TABLE II. The electron-electron counterbalance density for the ground state of the first row atoms at the Hartree-Fock level of theory.

	Li	Be	B	C	N	O	F	Ne
DZ	6.292294	16.92430	35.63540	65.54525	109.7481	173.6667	261.9263	378.8843
DZP	6.300243	16.92942	35.62795	65.37797	109.4736	173.1470	261.1490	378.3765
DZ2P	6.274657	16.87712	35.54018	65.30426	109.9361	174.4434	262.0369	379.3837
DZ3P	6.274318	16.81094	35.58268	65.46264	109.4408	174.1566	261.7214	379.3837
TZ	6.272706	16.78849	35.50558	65.50646	110.2067	174.5501	262.9420	380.5357
TZP	6.272706	16.79124	35.50149	65.49247	110.1694	174.5340	262.9602	380.6172
TZ2P	6.271070	16.78788	35.50246	65.48178	110.1302	174.3984	262.6731	380.1138
TZ3P	6.272014	16.79020	35.49711	65.48804	110.1681	174.5461	262.9584	380.5762
Num[a]	6.274309	16.79252	35.50797	65.50878	110.2036	174.6705	263.1421	380.8466

[a] Taken from Ref. [9].

TABLE III. The electron-electron counterbalance density for the ground state of the first row atoms at various levels of theory with the TZP basis set.

	Li	Be	B	C	N	O	F	Ne
HF	6.272706	16.79124	35.50149	65.49247	110.1694	174.5340	262.9602	380.6172
SDCI	5.753903	15.94461	34.52467	63.36824	107.2059	170.6853	257.7956	373.9640
FCI	5.753893	15.85480	33.98779	63.24212	–	–	–	–
MCSCF	6.273351	16.82768	35.56544	65.59269	110.3520	174.7236	263.1192	380.7115

proceed we have to choose a basis set based on its computational cost and accuracy. Inspection of the data shown in Table II indicates that the TZP basis set represents such a choice. Thus, hereafter, subsequent calculations of the first row atoms were all carried out with this basis set.

V. ELECTRON-ELECTRON COUNTERBALANCE DENSITIES

Table III shows the electron-electron counterbalance densities for the atoms Li to Ne in their ground state, calculated with the TZP basis sets and various levels of theory. Our calculations clearly indicate that the radial contribution dominates over the angular contribution, for all the atoms investigated, so that the value of $d(0)$ decreases as a consequence of including the effects of the electron correlation. This becomes clear from the comparison of the HF with the FCI and SDCI values of Table III. Also from Table III one can observe that the FCI $d(0)$ values are smaller than their corresponding SDCI values. This indicates that as triple and further excitations are included in the wave function, the radial contribution to the electron-electron counterbalance density keeps growing relative to the angular contribution, so that on average, the electrons tend be as far apart from each other as possible rather than to arrange in pairs with each electron located on the opposite of the nucleus.

Our calculations also demonstrate the great importance of handling properly the *core-valence* correlation. Observe that the MCSCF $d(0)$ values are larger than their corresponding FCI ones and even larger than the HF values, for all the atoms investigated. This leads not only to a quantitatively but to a qualitatively *incorrect* picture of the balance between the radial and angular contributions of the electron correlation effects on the electron-electron counterbalance density. Related failures due to the lack of including dynamic electron correlation (i.e., correlation between the active and inactive electrons) have been reported recently [2]. In the particular case of $d(0)$, it is found that the major part of the electron-electron coalescence density comes from the inner core $1s$ electrons. This can be observed by comparing the FCI $d(0)$ values of the $1\,^1$S and the $2\,^1$S states of the He isoelectronic series shown in Table I. Therefore, not including them in the active space leads to unrealistic counterbalance density values.

VI. SUMMARY

We have calculated the atomic electron-electron counterbalance density $d(0)$ that represents the probability density of finding any two electrons exactly at mirror positions with respect to the nucleus, from accurate configuration interaction and Hartree-Fock-like wave functions for the isoelectronic series of He and first-row atoms. Our calculations demonstrate that the electron correlation decreases the value of $d(0)$, and thus indicate that the radial correlation effects dominate over the angular effects. We have also found that inclusion of dynamical correlation is crucial for a realistic description of the electron-electron counterbalance density.

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