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Electron-pair densities of group 2 atoms in their ^{1}P and ^{3}P terms

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Abstract. Electron-pair intracule (relative motion) and extracule (center-of-mass motion) densities are studied in both position and momentum spaces for the ^1P and ^3P 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 ($Z = 88$). In position space, the $^1P - {}^3P$ difference in the intracule densities shows that the probability of a small interelectronic distance is larger in the triplet for all the six atoms, as reported for the lightest Be atom in the literature. The position-space extracule density clarifies that the triplet electrons are more likely to be at opposite positions with respect to the nucleus than the singlet electrons for all the atoms. In momentum space, the singlet generally has a larger probability of a small relative momentum between two electrons as a naïve manifestation of the Fermi hole in the triplet. 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.

PACS. 32.10.+z Theory of electronic structure, electronic transitions, and chemical binding – 31.15.-p Calculations and mathematical techniques in atomic and molecular physics

1 Introduction

The ^1P and ^3P terms of the Be atom and its isoelectronic analogs with $1s^22s2p$ electronic configuration were examined in the literature [1–7]. In relation to the interpretation (see [8–12] for a review) of Hund's empirical rules (see, *e.g.*, [13,14]), it was pointed out [4,5] for the Be atom that the average interelectronic distance is smaller in the triplet than in the singlet. As a result, the ^3P term has a larger electron repulsion energy [4,5], against a simple perturbative consideration or an intuitive expectation based on the Fermi hole in the ^3P term. The $2s$ and $2p$ orbitals of the two terms were also found [1–5] to be nontrivially different and in particular the $2p$ orbital is quite diffuse in the singlet. Based on these results, as well as those (see references in [8–12]) on He and some light atoms, it is generally considered [8–12] that high spin state has more compact electron density distribution than low spin state, and the stability of high spin state is due to a decrease in the electron-nucleus attraction energy which is more than an increase in the electron-electron repulsion energy.

In the present paper, we study electron-pair intracule (relative motion) density $h(u)$ and extracule (center-of-mass motion) density $d(R)$ in position space, together with their counterparts $\bar{h}(v)$ and $\bar{d}(P)$ in momentum space, for the $nsnp$ ^1P and ^3P terms of the group 2 atoms, where n is the principal quantum number of the outermost shell. All the six atoms Be ($Z = 4$), Mg ($Z = 12$), Ca ($Z = 20$), Sr ($Z = 38$), Ba ($Z = 56$), and Ra ($Z = 88$), where Z is the atomic number, are examined to see whether the same physical picture of the $^1P - {}^3P$ difference is valid for heavier atoms as reported in the literature for the lightest Be atom [1–5]. To our knowledge, the extracule densities $d(R)$ and $\bar{d}(P)$ have not been previously examined in $nsnp$ multiplet studies. The present momentum-space densities $\bar{h}(v)$ and $\bar{d}(P)$ are also first calculations for the analysis of the $^1P - {}^3P$ difference of the $nsnp$ electronic configuration. The next section summarizes the definitions of the electron-pair intracule and extracule densities and the associated moments. One-electron densities and moments are also defined since they are used in our analysis of the singlet-triplet difference. In Section 3, we describe our computational procedures based on the numerical Hartree-Fock method. The results are presented and discussed in Section 4. It will be found that fortunately the $^1P - {}^3P$ difference observed for the Be atom is essentially common to all the group 2 atoms. The present study based on both the intracule and extracule densities and in both position and momentum spaces increases our knowledge on the different electronic structures of the atomic multiplet. Hartree atomic units are used throughout this paper.

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2 Definitions

For an N-electron system ($N \geq 2$), the (spherically averaged) intracule density $h(u)$ is defined [15,16] by

$$h(u) \equiv (4\pi)^{-1} \int \mathrm{d}\Omega_u \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \delta[\mathbf{u} - (\mathbf{r}_1 - \mathbf{r}_2)] \Gamma(\mathbf{r}_1, \mathbf{r}_2), \tag{1}$$

where $\mathbf{u} \equiv (u, \Omega_u)$ with $\Omega_u \equiv (\theta_u, \phi_u)$, $\delta(\mathbf{r})$ is the three-dimensional Dirac delta-function, and $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the spin-reduced two-electron density function [17],

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) \equiv \binom{N}{2} \int \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}\mathbf{x}_3 \ldots \mathrm{d}\mathbf{x}_N |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2, \tag{2}$$

in which $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ is the combined position-spin coordinate of the electron i and $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is the electronic wave function of a system under consideration. The intracule density $h(u)$ is the probability density functions for the *relative* distance $|\mathbf{r}_i - \mathbf{r}_j|$ of any pair of electrons i and j to be u. On the other hand, the (spherically averaged) extracule density $d(R)$ is defined [15,16] by

$$d(R) \equiv (4\pi)^{-1} \int \mathrm{d}\Omega_R \times \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \delta[\mathbf{R} - (\mathbf{r}_1 + \mathbf{r}_2)/2] \Gamma(\mathbf{r}_1, \mathbf{r}_2), \tag{3}$$

where $\mathbf{R} \equiv (R, \Omega_R)$ with $\Omega_R \equiv (\theta_R, \phi_R)$. The extracule density $d(R)$ represents the probability density function for the *center-of-mass* distance $|\mathbf{r}_i + \mathbf{r}_j|/2$ of any pair of electrons i and j to be R. The intracule $\langle u^k \rangle$ and extracule $\langle R^k \rangle$ moments are defined by

$$\langle u^k \rangle \equiv 4\pi \int_0^\infty \mathrm{d}u\, u^{k+2} h(u), \tag{4a}$$

$$\langle R^k \rangle \equiv 4\pi \int_0^\infty \mathrm{d}R\, R^{k+2} d(R). \tag{4b}$$

Exactly analogous definitions apply to the momentum-space intracule $\bar{h}(v)$ and extracule $\bar{d}(P)$ densities and the associated two-electron moments $\langle v^k \rangle$ and $\langle P^k \rangle$, if we start from the momentum-space N-electron wave function $\Phi(\mathbf{y}_1, \ldots, \mathbf{y}_N)$, where $\mathbf{y}_i \equiv (\mathbf{p}_i, \sigma_i)$ is the combined momentum-spin coordinate of the electron i. The momentum-space electron-pair densities $\bar{h}(v)$ and $\bar{d}(P)$ are probability density functions for the relative momentum $|\mathbf{p}_i - \mathbf{p}_j|$ to be v and the center-of-mass momentum $|\mathbf{p}_i + \mathbf{p}_j|/2$ to be P, respectively.

The spherical average $\rho(r)$ of the one-electron position density is obtained [17] from the two-electron density function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ by

$$\rho(r) = (4\pi)^{-1} \int \mathrm{d}\Omega_r \left[\frac{2}{N-1} \int \mathrm{d}\mathbf{r}_2 \Gamma(\mathbf{r}, \mathbf{r}_2) \right]. \tag{5a}$$

Within the Hartree-Fock framework, the density $\rho(r)$ for an atom is a sum of contributions $\rho_{nl}(r)$ from occupied subshells nl,

$$\rho(r) = \sum_{nl} \rho_{nl}(r). \tag{5b}$$

The position moments $\langle r^k \rangle$ and $\langle r^k \rangle_{nl}$, associated with the total $\rho(r)$ and subshell $\rho_{nl}(r)$ densities, are defined, respectively, by

$$\langle r^k \rangle \equiv 4\pi \int_0^\infty \mathrm{d}r\, r^{k+2} \rho(r), \tag{6a}$$

$$\langle r^k \rangle_{nl} \equiv 4\pi \int_0^\infty \mathrm{d}r\, r^{k+2} \rho_{nl}(r). \tag{6b}$$

Exactly the same procedure defines the one-electron momentum density $\Pi(p)$ and the one-electron momentum moments $\langle p^k \rangle$, and their subshell components $\Pi_{nl}(p)$ and $\langle p^k \rangle_{nl}$.

By definition, the one-electron density functions $\rho(r)$ and $\Pi(p)$ are normalized to the number of electrons N, and the subshell densities $\rho_{nl}(r)$ and $\Pi_{nl}(p)$ to the number of subshell electrons N_{nl}, where $\sum_{nl} N_{nl} = N$. On the other hand, all the two-electron density functions are normalized to the number of electron pairs $N(N-1)/2$. In Section 4, however, we will use a modified normalization scheme, which normalizes *all* the one- and two-electron densities to *unity*, in order to avoid large numbers and to facilitate the mutual comparison of results for different atoms.

3 Computational outline

For the six group 2 atoms from Be to Ra in their $nsnp$ ^1P and ^3P terms, the Hartree-Fock orbitals were numerically generated by using an enhanced version of the MCHF72 code [18,19]. The one-electron position densities $\rho(r)$ and $\rho_{nl}(r)$ and the associated moments $\langle r^k \rangle$ and $\langle r^k \rangle_{nl}$ were obtained directly from the numerical radial functions. The one-electron momentum densities $\Pi(p)$ and $\Pi_{nl}(p)$ and the associated moments $\langle p^k \rangle$ and $\langle p^k \rangle_{nl}$ were determined by incorporating the numerical Hankel transformation [20] of the Hartree-Fock radial functions into the MCHF72 code, as described in reference [21]. The intracule densities $h(u)$ in position space and $\bar{h}(v)$ in momentum space as well as their moments $\langle u^k \rangle$ and $\langle v^k \rangle$ were obtained by the method developed recently [22,23]. The extracule densities $d(R)$ and $\bar{d}(P)$ and moments $\langle R^k \rangle$ and $\langle P^k \rangle$ were determined by the procedure given in references [23,24]. We note that six states of the ^3P term can be expressed by a single determinant, but all the three states of the ^1P term require a linear combination of two Slater determinants.

4 Results and discussion

Summarized in Table 1 are the total E, electron-nucleus attraction V_{en}, and electron-electron repulsion V_{ee} energies for the ^1P and ^3P terms of the group 2 atoms, obtained from our numerical Hartree-Fock calculations. The

Table 1. The Hartree-Fock total E, electron-nucleus attraction $V_{\rm en}$, and electron-electron repulsion $V_{\rm ee}$ energies (in hartrees) of the *nsnp* ^1P and ^3P terms of the six group 2 atoms. The values in parentheses are experimental energies.

Z	Atom	Energy	^1P	^3P	^1P-^3P
4	Be	E	−14.39474	−14.51150	0.11676(0.0938)
		$V_{\rm en}$	−32.91210	−33.41128	0.49918
		$V_{\rm ee}$	4.12263	4.38827	−0.26564
12	Mg	E	−199.47113	−199.54671	0.07558(0.0600)
		$V_{\rm en}$	−477.35489	−478.28793	0.93304
		$V_{\rm ee}$	78.41262	79.19450	−0.78188
20	Ca	E	−676.65634	−676.71877	0.06243(0.0382)
		$V_{\rm en}$	−1601.36517	−1602.42554	1.06037
		$V_{\rm ee}$	248.05250	248.98800	−0.93550
38	Sr	E	−3131.45490	−3131.51075	0.05585(0.0319)
		$V_{\rm en}$	−7466.65519	−7468.34879	1.69360
		$V_{\rm ee}$	1203.74538	1205.32729	−1.58191
56	Ba	E	−7883.46710	−7883.51877	0.05167(0.0227)
		$V_{\rm en}$	−18670.18150	−18672.29371	2.11221
		$V_{\rm ee}$	2903.24729	2905.25615	−2.00886
88	Ra	E	−23094.23244	−23094.28150	0.04906(0.0243)
		$V_{\rm en}$	−54824.73271	−54827.76619	3.03348
		$V_{\rm ee}$	8636.26780	8639.20315	−2.93535

kinetic energy T is not given there, since the virial error $|V/T+2|$was no more than 1×10^{-9} in any of the present calculations, where $V = V_{\rm en} + V_{\rm ee}$ is the potential energy. For all the atoms, Hund's rule is valid and the triplet is found to have a total energy lower than the singlet by an amount ranging from 0.12 hartrees for Be to 0.05 hartrees for Ra. The corresponding experimental energy differences, calculated from Moore's tables [25], are given in the parentheses. The Hartree-Fock method predicts a singlet-triplet separation larger than the experimental one for all the cases. Of the two potential energy components, the electron-nucleus attraction is found to contribute to stabilize the ^3P term relative to the ^1P term, while the electron-electron repulsion works oppositely.

4.1 Position-space electron-pair densities

Figure 1(a) plots the singlet-triplet difference of the radial intracule density $4\pi u^2 h(u)$ in position space. For all the six atoms, the effect of Fermi hole $^3h(0) = 0$ in the ^3P term is found to appear only in a small u region, as pointed out previously for the lightest Be atom [4,5]. The predominant aspect in the singlet-triplet difference is that the ^1P terms have larger probability density in a large u region than the ^3P terms. When we go down the column of group 2 atoms in the periodic table, the difference in the intracule density decreases and the u values where the minimum and maximum of the density difference occur become larger. Corresponding to the $^1P - {}^3P$ density difference in Figure 1(a), the intracule moments $\langle u^k \rangle$ summarized in Table 2 are larger when $k < 0$ and smaller when $k > 0$ in the ^3P term than in the ^1P term. In particular, the average electron-electron distance $\langle u \rangle$ is smaller and the electron repulsion energy $\langle u^{-1} \rangle$ is larger in ^3P than in ^1P. The difference in the moments is most remarkable for the lightest Be atom.

The singlet-triplet difference of the radial extracule density $4\pi R^2 d(R)$ in position space is given in Figure 1(b). Common to the six group 2 atoms, the ^3P extracule density is larger than the ^1P density for a small R and smaller for a large R, though the magnitude decreases with increasing Z. In the triplet, there is a higher probability for finding the center-of-mass radius R of two electrons to be small. In other words, two electrons in ^3P are more likely than in ^1P to be on opposite sides of the nucleus, as suggested [5] for the Be atom and observed [23] for the He atom in its $1s2p$ ^1P and ^3P terms. The extracule moments $\langle R^k \rangle$ compared in Table 2 for the singlet and triplet terms are consistent with the difference in the extracule density plotted in Figure 1(b).

In the one-electron densities $\rho(r)$ and $\rho_{nl}(r)$, the $^1P - {}^3P$ difference appears mainly in the outermost s and p subshells. Table 2 also compares the one-electron subshell moments $\langle r^k \rangle_s$ and $\langle r^k \rangle_p$, associated with the outermost s and p orbitals, of the ^1P and ^3P terms. The distributions of the outermost s orbitals are slightly more diffuse in the triplet than in the singlet, but the differences are not large. In contrast, the outermost p orbital is markedly condensed in the ^3P term compared to the ^1P term. These aspects,

Table 2. Position-space moments for the ^1P and ^3P terms of group 2 atoms. All the parent densities are normalized to unity.

			Two-electron moments				One-electron subshell moments			
			$\langle u^k \rangle$		$\langle R^k \rangle$		$\langle r^k \rangle_s$		$\langle r^k \rangle_p$	
Z	Atom	k	^1P	^3P	^1P	^3P	^1P	^3P	^1P	^3P
4	Be	-2	1.69282	1.71884	6.73300	7.04836	1.42561	1.14493	0.112148	0.284015
		-1	0.687106	0.731379	1.35402	1.51596	0.600361	0.543632	0.267973	0.449232
		$+1$	3.44091	2.67473	1.77357	1.23913	2.31016	2.53657	5.02551	2.88310
		$+2$	18.5148	9.95422	4.86092	2.09987	6.25253	7.64747	31.2381	10.2389
12	Mg	-2	3.69239	3.69897	16.6059	16.6407	1.09712	0.864254	0.0632848	0.203999
		-1	1.18807	1.19992	2.50159	2.52951	0.459357	0.416117	0.189694	0.312825
		$+1$	2.13510	1.79775	1.05790	0.873765	2.81454	3.10777	6.50706	4.06892
		$+2$	10.5448	6.04042	2.64532	1.43940	9.05649	11.2268	49.5610	19.4070
20	Ca	-2	5.23792	5.24025	23.9154	23.9262	0.752710	0.572062	0.0467953	0.146982
		-1	1.30554	1.31046	2.72963	2.74064	0.343383	0.308977	0.155680	0.243239
		$+1$	2.04697	1.83396	1.01400	0.900313	3.67910	4.07262	7.71966	5.10132
		$+2$	9.92571	6.52188	2.47817	1.58029	15.2116	18.9022	68.3777	29.7212
38	Sr	-2	8.59707	8.59801	39.4646	39.4689	0.682881	0.511640	0.0410027	0.130266
		-1	1.71230	1.71455	3.55314	3.55793	0.306754	0.275701	0.142108	0.216965
		$+1$	1.54730	1.43065	0.767704	0.707271	4.05118	4.49152	8.33687	5.62903
		$+2$	6.55391	4.54724	1.63407	1.11729	18.3348	22.8409	79.0542	35.8731
56	Ba	-2	11.3605	11.3610	52.0573	52.0595	0.573178	0.421429	0.0352833	0.111606
		-1	1.88523	1.88653	3.89084	3.89357	0.266130	0.238656	0.128766	0.192990
		$+1$	1.45469	1.37210	0.722733	0.680325	4.61235	5.11772	9.10275	6.24666
		$+2$	5.83313	4.28037	1.45364	1.05654	23.6044	29.4124	93.5186	43.7789
88	Ra	-2	16.0061	16.0064	72.8864	72.8875	0.539441	0.393023	0.0328105	0.104431
		-1	2.25608	2.25685	4.62961	4.63119	0.248431	0.222680	0.122206	0.181289
		$+1$	1.21048	1.15660	0.602315	0.574901	4.89840	5.43818	9.52924	6.59663
		$+2$	4.35153	3.29241	1.08487	0.816075	26.5381	33.0895	102.064	48.6177

noted in the literature for the Be atom [1–5], are seen to be common to all the group 2 atoms.

Combination of the above results for the one- and two-electron densities and the associated moments in position space clarifies the following physical picture of the singlet-triplet difference in the group 2 atoms: Compared to the singlet, the outermost p orbital is much condensed in the triplet, leading to a greater electron-nucleus attraction energy. At the same time, the tight p orbital decreases the interelectronic distance and increases the electron repulsion energy in the triplet. However, the electrons in the triplet have a tendency to be at the opposite positions with respect to the nucleus to reduce the increased electron repulsion energy.

4.2 Momentum-space electron-pair densities

The singlet-triplet difference of the radial intracule density $4\pi v^2 \bar{h}(v)$ in momentum space is given in Figure 2(a). For all the six atoms, the ^3P density is smaller for a small v and larger for a large v than the ^1P density. Namely, there is more probability in the ^3P term for two electrons to have different momenta. Thus the effect of the Fermi hole $^3\bar{h}(0) = 0$ for the triplet term appears naturally in momentum space. The intracule moments $\langle v^k \rangle$ in momentum space are compared in Table 3. Corresponding to the density difference in Figure 2(a), the moments $\langle v^k \rangle$ are larger in the singlet when $k < 0$, whereas in the triplet when $k > 0$.

The $^1P - {}^3P$ difference in the momentum-space radial extracule density $4\pi P^2 \bar{d}(P)$ is shown in Figure 2(b). The major profile of the difference is similar to its position-space counterpart, and the ^3P density is larger for a small P and smaller for a large P than the ^1P density. This implies that there is greater probability for electrons to have opposite momenta and the center of momenta of two electrons distributes more around the origin $\mathbf{p} = \mathbf{0}$ in the triplet than in the singlet. The extracule moments $\langle P^k \rangle$ tabulated in Table 3 reflect this difference. In Figure 2(b), the extracule density difference shows a secondary peak at a large P value for heavier atoms except for Be. A finer

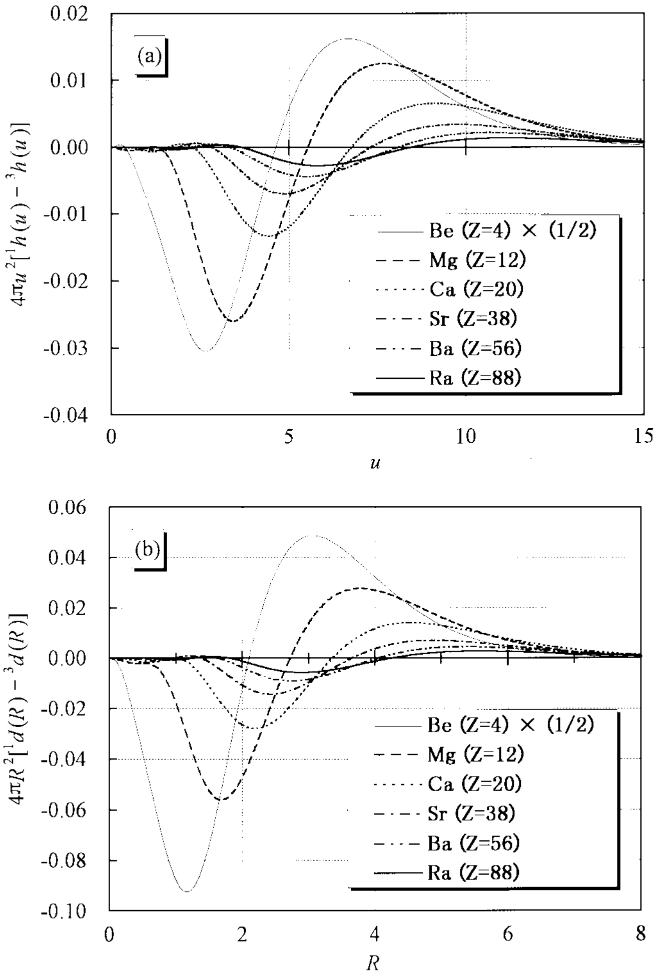

Fig. 1. The position-space difference of the radial electron-pair density for the ^1P and ^3P terms of the group 2 atoms. (a) Intracule density. (b) Extracule density.

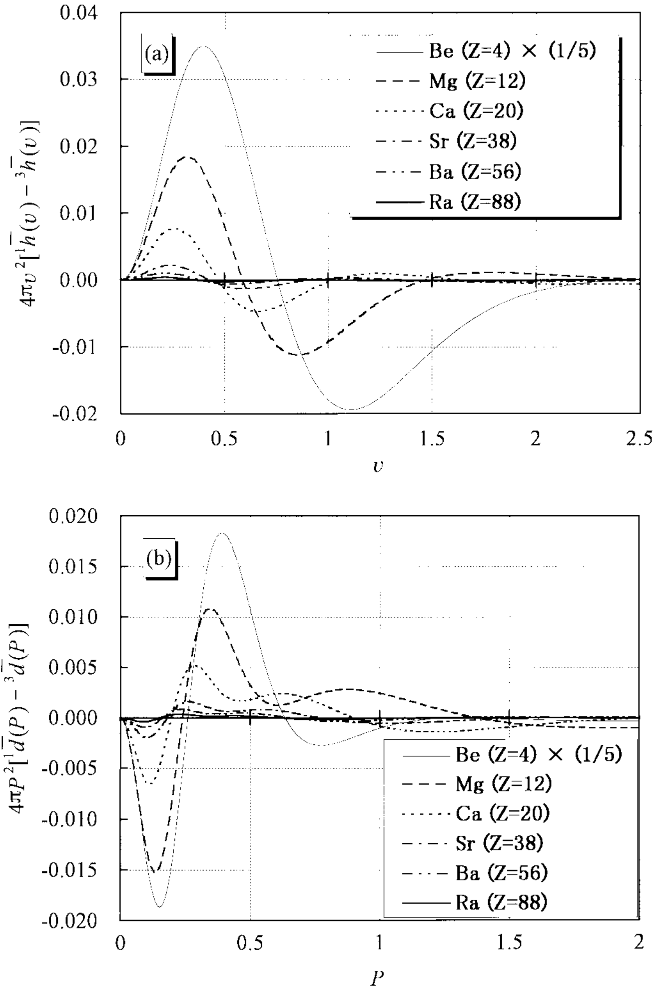

Fig. 2. The momentum-space difference of the radial electron-pair density for the ^1P and ^3P terms of the group 2 atoms. (a) Intracule density. (b) Extracule density.

analysis clarified that this peak comes from the pair of electrons in np and $(n-1)p$ subshells.

Table 3 also includes a comparison of the one-electron momentum moments $\langle p^k \rangle_s$ and $\langle p^k \rangle_p$ associated with the outermost s and p orbitals. Common to the six group 2 atoms, the outermost s orbital in momentum space is more condensed in the ^3P term than in the ^1P term. The $^1P - {}^3P$ difference in the s orbital is larger in momentum moments (Tab. 3) than in position moments (Tab. 2). On the contrary, the ^3P term has more diffuse outermost p orbital in momentum space than the ^1P term.

In momentum space, the picture of the singlet-triplet difference of the group 2 atoms may be summarized as follows: In the ^3P term, the outermost s orbital is contracted while the outermost p orbital is expanded compared to the ^1P term. These changes help to increase the relative momentum distance of two electrons with parallel spins in the triplet. In fact, the intracule density in Figure 2(a) shows that the probability for electrons to have a small v value is larger in the singlet. Thus the effect of Fermi hole reveals itself intuitively in momentum space. The extracule density also clarifies that electrons in ^3P term have a trend to have opposite momenta than those in the ^1P term, which also increases the momentum distance between the electrons in the triplet. At present, however, we do not know how these changes in electron-pair momentum densities for two electrons in *different* subshells affect the total energy of an atom, though it has been proved [26] that when electrons belong to the *same* subshell nl, the electron-pair second moments $\langle v^2 \rangle_{nl}$ and $\langle P^2 \rangle_{nl}$ in momentum space are exactly related to the total energy.

5 Concluding remarks

The electron-pair intracule and extracule densities, in both position and momentum spaces, have been examined for the $nsnp$ ^1P and ^3P terms of the six group 2 atoms from Be ($Z = 4$) to Ra ($Z = 88$) using the numerical Hartree-Fock wave functions. The position-space intracule density has shown that the Fermi hole effect is not significant and the average interelectronic distance is shorter in the triplet than in the singlet. On the contrary,

Table 3. Momentum-space moments for the ^1P and ^3P terms of group 2 atoms. All the parent densities are normalized to unity.

			Two-electron moments				One-electron subshell moments			
			$\langle v^k \rangle$		$\langle P^k \rangle$		$\langle p^k \rangle_s$		$\langle p^k \rangle_p$	
Z	Atom	k	^1P	^3P	^1P	^3P	^1P	^3P	^1P	^3P
4	Be	−2	1.46556	0.470818	2.61569	3.88538	8.27978	10.8531	9.81622	3.27050
		−1	0.685576	0.519972	1.15283	1.22166	2.22581	2.53172	2.75841	1.58865
		+1	3.04025	3.11644	1.53085	1.53303	0.754766	0.661556	0.469150	0.798641
		+2	14.3934	14.5815	3.59903	3.61036	1.37223	1.09454	0.303879	0.813517
12	Mg	−2	0.298716	0.170494	0.844572	1.08081	11.0832	15.0980	14.9736	5.90122
		−1	0.305309	0.288064	0.612152	0.623998	2.56369	2.97461	3.47200	2.16088
		+1	6.27671	6.28479	3.07518	3.07677	0.685937	0.589574	0.357686	0.616122
		+2	67.3254	67.3555	16.4138	16.4189	1.52137	1.18357	0.216072	0.745457
20	Ca	−2	0.232224	0.166891	0.806509	0.925700	16.9040	23.5209	20.1275	8.60569
		−1	0.264983	0.257652	0.541083	0.545558	3.12170	3.67847	4.04461	2.61616
		+1	8.56692	8.56996	4.22257	4.22347	0.609275	0.511703	0.309368	0.526229
		+2	136.701	136.715	33.4903	33.4932	1.39455	1.04809	0.196733	0.686816
38	Sr	−2	0.0994624	0.0791996	0.376350	0.413948	19.5518	27.5570	22.9562	10.1659
		−1	0.168681	0.166559	0.346088	0.347346	3.33479	3.96271	4.32674	2.84288
		+1	13.1431	13.1441	6.50061	6.50093	0.591990	0.491764	0.290074	0.491893
		+2	332.108	332.115	81.7863	81.7877	1.55298	1.15013	0.199580	0.721362
56	Ba	−2	0.0737682	0.0626568	0.294595	0.314216	23.9315	34.0920	26.7627	12.0837
		−1	0.143102	0.142028	0.293375	0.293918	3.66110	4.38508	4.67709	3.09720
		+1	16.7981	16.7986	8.33126	8.33144	0.560773	0.460125	0.270468	0.460610
		+2	566.413	566.417	139.949	139.950	1.56333	1.13644	0.199353	0.730499
88	Ra	−2	0.0409271	0.0360586	0.167737	0.176216	26.2309	37.6213	28.9679	13.2393
		−1	0.104100	0.103648	0.212827	0.213040	3.81763	4.59385	4.86858	3.23995
		+1	22.7488	22.7490	11.3058	11.3059	0.549987	0.448233	0.260867	0.445353
		+2	1054.32	1054.32	261.290	261.290	1.70111	1.22501	0.208442	0.778937

the momentum-space intracule density has clarified that the average momentum distance between a pair of electrons is larger in the triplet as a naïve manifestation of the Fermi hole effect. The extracule densities in position and momentum spaces have demonstrated that in both spaces, the triplet electrons have more tendency to be at opposite positions with respect to the origin ($\mathbf{r} = \mathbf{0}$ or $\mathbf{p} = \mathbf{0}$) than the singlet ones. All these features have been found to be essentially common to the six atoms.

In the present study, we have concentrated our attention on accurate calculations of nonrelativistic Hartree-Fock electron-pair densities and associated moments. For the $1s2p$ ^1P and ^3P terms of the He atom, it is known [23] that the electron correlation contribution cancels out when the difference in the electron-pair densities is examined. In the present case, however, the Hartree-Fock and experimental $^1P - {}^3P$ energy separations in Table 1 show a nontrivial difference, which suggests that the correlation effect may modify the Hartree-Fock density differences. Correlated studies are awaited, since a method has been recently developed [23,27]. Nevertheless, the present Hartree-Fock results would be useful to clarify how the inclusion of electron correlation and/or relativistic corrections changes the two-electron properties accompanied by the ^1P and ^3P terms. Hartree-Fock and correlated analysis of the ^1P-^3P separation in $nsn'p$ configurations and of isoelectronic series may be interesting. In some cases, the energetic origins of the relative stability of terms in higher excited configurations and in cations are known to be different from those of lower configurations and of the isoelectronic neutral atom. For example, our numerical Hartree-Fock calculations show that *both* the electron-nucleus attraction V_{en} and electron-electron repulsion V_{ee} energies are smaller in the $2s2p$ ^3P term than in the 1^P term for the four-electron cations with $Z \geq 5$.

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References

1. D.R. Hartree, W. Hartree, Proc. Roy. Soc. (Lond.) A **154**, 588 (1936).
2. C. Froese, J. Chem. Phys. **47**, 4010 (1967).
3. H. Tatewaki, H. Taketa, F. Sasaki, Int. J. Quantum Chem. **5**, 335 (1971).
4. H. Tatewaki, K. Tanaka, J. Chem. Phys. **60**, 601 (1974).
5. I. Shim, J.P. Dahl, Theor. Chim. Acta **48**, 165 (1978).
6. J.L. Krause, R.S. Berry, J. Chem. Phys. **83**, 5153 (1985).
7. R.L. Graham, D.L. Yeager, J. Olsen, P. Jørgensen, R. Harrison, S. Zarrabian, R. Bartlett, J. Chem. Phys. **85**, 6544 (1986).
8. R.L. Snow, J.L. Bills, J. Chem. Educ. **51**, 585 (1974).
9. J. Katriel, R. Pauncz, Adv. Quantum Chem. **10**, 143 (1977).
10. R.J. Boyd, Nature **310**, 480 (1984).
11. J.D. Morgan III, W. Kutzelnigg, J. Phys. Chem. **97**, 2425 (1993).
12. W. Kutzelnigg, J. D. Morgan III, Z. Phys. D **36**, 197 (1996).
13. I.N. Levine, *Quantum Chemistry*, 4th edn. (Prentice Hall, Englewood Cliffs, NJ, 1991) p. 303.
14. F.L. Pilar, *Elementary Quantum Chemistry*, 2nd edn. (McGraw-Hill, New York, 1990) p. 228.
15. A.J. Coleman, Int. J. Quantum Chem. Symp. **1**, 457 (1967).
16. A.J. Thakkar, in *Density Matrices and Density Functionals*, edited by R.M. Erdahl, V.H. Smith, Jr. (Reidel, Dordrecht, 1987) pp. 553-581.
17. P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).
18. C. Froese Fischer, Comput. Phys. Commun. **4**, 107 (1972).
19. C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).
20. J.D. Talman, Comput. Phys. Commun. **30**, 93 (1983).
21. T. Koga, A.J. Thakkar, J. Phys. B **29**, 2973 (1996).
22. T. Koga, H. Matsuyama, J. Chem. Phys. **107**, 8510 (1997).
23. T. Koga, H. Matsuyama, J. Phys. B **31**, 3765 (1998).
24. T. Koga, H. Matsuyama, J. Chem. Phys. **108**, 3424 (1998).
25. C.E. Moore, Atomic Energy Levels. NSRDS-NBS 35, Vols. 1-3 (Nat. Bur. Stand. U.S., Washington, 1971).
26. T. Koga, H. Matsuyama, Theor. Chem. Acc. **99**, 320 (1998).
27. D.G. Ellis, Phys. Rev. A **53**, 3986 (1996).