Correlated electron-pair properties of the Be atom in position and momentum spaces

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Based on multiconfiguration Hartree–Fock calculations, correlated electron-pair intracule (relative motion) and extracule (center-of-mass motion) properties are reported for the Be atom in position and momentum spaces. Particularly in the latter space, the present results are more accurate and consistent than those in the literature. © *2002 American Institute of Physics.*
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I. INTRODUCTION AND DEFINITIONS

For an explicit examination of the electron–electron interaction in many-electron atoms, the electron-pair intracule (relative motion) $H(u)$ and extracule (center-of-mass motion) $D(R)$ densities,

$$H(u)\equiv\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\delta(u-|\mathbf{r}_i-\mathbf{r}_j|)\right\rangle,$$
$$D(R)\equiv\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\delta(R-|\mathbf{r}_i+\mathbf{r}_j|/2)\right\rangle, \tag{1}$$

have been introduced[1] and studied,[2–5] where $\delta(x)$ is the one-dimensional Dirac delta function and the angular brackets $\langle\ \rangle$ stand for the expectation value over the N-electron ($N\geqslant 2$) wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ with $\mathbf{x}_i\equiv(\mathbf{r}_i,\sigma_i)$ being the combined position-spin coordinates of the electron i. The intracule $H(u)$ and extracule $D(R)$ densities are the probability density functions for the interelectronic distance $|\mathbf{r}_i-\mathbf{r}_j|$ and the center-of-mass radius $|\mathbf{r}_i+\mathbf{r}_j|/2$ of any pair of electrons i and j to be u and R, respectively, and are normalized to $N(N-1)/2$, the number of electron pairs. The moments associated with the electron-pair densities $H(u)$ and $D(R)$ are defined by

$$\langle u^n\rangle\equiv\int_0^\infty du\, u^n H(u),\quad \langle R^n\rangle\equiv\int_0^\infty dR\, R^n D(R), \tag{2}$$

and characterize the distributions of the parent densities. In particular, $\langle u^{-1}\rangle$ is nothing but the electron repulsion energy, $\langle u\rangle$ is the average interelectronic distance, and $\langle R\rangle$ is the average distance of electron pairs from the nucleus. The corresponding intracule $\overline{H}(\nu)$ and extracule $\overline{D}(P)$ densities in momentum space, as well as their moments $\langle\nu^n\rangle$ and $\langle P^n\rangle$, have also been studied:[5]

$$\overline{H}(\nu)\equiv\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\delta(\nu-|\mathbf{p}_i-\mathbf{p}_j|)\right\rangle,$$
$$\overline{D}(P)\equiv\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\delta(P-|\mathbf{p}_i+\mathbf{p}_j|/2)\right\rangle, \tag{3}$$

$$\langle\nu^n\rangle\equiv\int_0^\infty d\nu\,\nu^n\overline{H}(\nu),\quad \langle P^n\rangle\equiv\int_0^\infty dP\,P^n\overline{D}(P), \tag{4}$$

where $\mathbf{p}_i$ is the momentum vector of the electron i. The densities $\overline{H}(\nu)$ and $\overline{D}(P)$ and moments $\langle\nu^n\rangle$ and $\langle P^n\rangle$ have the physical meanings analogous to those of their position-space counterparts, but in momentum space.

In a recent paper,[6] it was shown that the precise and consistent knowledge of the electron-pair moments is important, because in addition to their own significance, the four types of the second electron-pair moments $\langle u^2\rangle$, $\langle R^2\rangle$, $\langle\nu^2\rangle$, and $\langle P^2\rangle$ are directly related to several physical properties, which have been hitherto studied independently. Examples are diamagnetic susceptibility, form factor, incoherent scattering function, dipole polarizability, mass polarization correction, nuclear momentum squared, and moments of oscillator strength density. Moreover, the second moments were demonstrated,[7] to satisfy rigorous sum rules

$$\delta_{\rm pos}\equiv 4\langle R^2\rangle+\langle u^2\rangle-2(N-1)\langle r^2\rangle=0, \tag{5a}$$
$$\delta_{\rm mom}\equiv 4\langle P^2\rangle+\langle\nu^2\rangle-2(N-1)\langle p^2\rangle=0, \tag{5b}$$

for any exact and approximate wave functions of atoms and molecules, where $\langle r^2\rangle$ and $\langle p^2\rangle$ are the second single-electron moments in position and momentum spaces, respectively.

At the Hartree–Fock limit level, the electron-pair properties in both position and momentum spaces were established[8–14] for all the 102 neutral atoms from He to Lr in their ground states. At the correlated level, however, the electron-pair properties were not known in a consistent manner except for the He[15] and Li[16] atoms. In the case of the Be atom, several correlated calculations were reported for the intracule[17–22] and extracule[21–23] properties in position space. On the other hand, correlated studies are extremely limited in momentum space: Only Sarsa *et al.*[23–25] published correlated electron-pair data of the Be atom based on Monte Carlo calculations. However, a closer examination shows that the results of Sarsa *et al.* are insufficiently accurate in that the statistical uncertainty is large in the sum rule, the total energy of the parent wave function is rather poor, and the virial error is nontrivial. Therefore, we have performed correlated calculations of the momentum-space electron-pair properties of

TABLE I. Electron-pair properties of the Be atom in position space. For the Monte Carlo results, the statistical error in the last digit is given in parentheses.

		Correlated						
	Hartree–Fock[a]	Sarsa *et al.*[b]	Banyard–Mashat[c]	Gálvez *et al.*[d]	Present	Banyard–Mobbs[e]	Gálvez *et al.*[f]	Komasa *et al.*[g]
Energies								
E	−14.573 02	−14.6523(1)	−14.660 90	−14.661 29(4)	−14.662 53	−14.664 19	−14.6647(1)	−14.667 36
$-E/T$	1.000 00	0.996 76	⋯	0.998 49	1.000 00	⋯	⋯	1.000 00
Intracule moments								
$\langle u^{-2}\rangle$	10.5366	9.66(2)	⋯	9.59(1)	9.642 32	⋯	9.55(1)	9.536 92
$\langle u^{-1}\rangle$	4.489 14	7.3958(3)	⋯	4.3590(6)	4.380 13	4.3632	4.375(1)	4.374 70
$\langle u\rangle$	15.1205	15.163(2)	15.3930	15.364(3)	15.2804	15.4404	15.305(3)	15.2717
$\langle u^2\rangle$	51.9563	52.27(2)	53.6556	53.27(2)	52.9295	⋯	53.15(3)	52.8490
$\langle u^3\rangle$	218.118	220.9(1)	⋯	224.1(2)	223.015	⋯	224.7(2)	222.431
$\langle u^4\rangle$	1074.83	⋯	⋯	1098(1)	1094.42	⋯	1098(1)	1090.11
Extracule moments								
$\langle R^{-2}\rangle$	42.1465	43.28(6)	⋯	43.7(6)	42.9430	⋯	43.14(8)	⋯
$\langle R^{-1}\rangle$	8.978 29	9.2736(4)	⋯	9.241(1)	9.269 95	⋯	9.280(2)	⋯
$\langle R\rangle$	7.560 26	7.0776(5)	⋯	7.099(1)	7.076 75	⋯	7.083(2)	⋯
$\langle R^2\rangle$	12.9891	11.253(2)	⋯	11.198(4)	11.1826	⋯	11.228(7)	⋯
$\langle R^3\rangle$	27.2647	21.821(8)	⋯	21.23(1)	21.2990	⋯	21.53(2)	⋯
$\langle R^4\rangle$	67.1767	49.89(3)	⋯	46.68(4)	47.1047	⋯	48.10(9)	⋯
Other two-electron properties								
$\langle \mathbf{r}_1\cdot\mathbf{r}_2\rangle$	0	⋯	−2.3834	⋯	−2.0498	−2.0316	−2.058(2)	⋯
$S(-1)$	11.5459	⋯	⋯	⋯	8.1181	⋯	⋯	⋯
$\tau[\mathbf{r}]$	0	⋯	⋯	⋯	−0.0840	−0.0827	−0.0840(1)	⋯
Sum rule check								
$\langle r^2\rangle$	17.3188	16.215(5)	⋯	16.348(7)	16.2767	16.3724	16.343(9)	16.2459
δ_{pos}	0.0000	−0.008(58)	⋯	−0.026(78)	0.0000	⋯	0.004(112)	⋯

[a]References 9, 10.
[b]References 20, 23.
[c]Reference 17.
[d]Reference 21.
[e]Reference 18.
[f]Reference 22.
[g]Reference 19.

the Be atom in a more accurate yet consistent manner, and the results are reported in this article. The position-space results are also compared with those in the literature. Hartree atomic units are used throughout.

II. COMPUTATIONAL OUTLINE

We first constructed a multiconfiguration Hartree–Fock (MCHF) wave function using a modified version of the MCHF88 program.[26] By referring to the configurations employed by Froese Fischer and Saxena,[27] we obtained a 30 configuration MCHF function, which consists of $1s^2ns^2(n=2,3)$, $1s^23s4s$, $1snp^2(n=2,6)$, $1s^22p4p$, $1s^23d^2$, $1s^25f^2$, $2s^2ns^2(n=4-6)$, $2s^2np^2(n=3-5)$, $2s^22p4p$, $2s^2nd^2(n=4,5)$, $2s^2nf^2(n=4,6)$, $2s^25g^2$, $2p^24l^2(l=s,p,d)$, $1s2s4s^2$, $1s2snp^2(n=2,3)$, $1s2s2pnp(n=3,4)$, $1s2s(^1S)3p4p$, and $1s2s(^3S)3p4p$ electron configurations. Our MCHF total energy E is −14.662 53 hartrees, which recovers 94.9% of the correlation energy in the Be atom.[19] The deviation in the virial ratio $-E/T$ from unity is 1×10^{-9}, where T is the electronic kinetic energy. All the electron-pair densities and moments were then calculated by the procedure described in Ref. 28. We used Talman's algorithm[29] for the required Hankel transformation from position- to momentum-space functions.

III. RESULTS AND DISCUSSION

To check the accuracy of the present MCHF calculations, we have first computed the electron-pair properties in position space. The results are summarized and compared with the literature values[9,10,17–23] in Table I, where the columns are arranged in the decreasing order of the total energies of the parent wave functions. When the intracule moments $\langle u^n\rangle$ are compared, the present values show satisfactory agreements with those of Komasa *et al.*[19] with the lowest total energy. Except for $\langle u^{-2}\rangle$ and $\langle u^{-1}\rangle$, the correlated Monte Carlo results of Gálvez *et al.*[22] have a larger deviation from Komasa *et al.* values than the present, though their total energy is lower. For $n<0$, the correlated $\langle u^n\rangle$ are smaller, while for $n>0$ the correlated moments are larger than the Hartree–Fock values[9] in all the calculations. Clearly, the electron correlation increases the average interelectronic separation $\langle u\rangle$. These changes in $\langle u^n\rangle$ from their Hartree–Fock values are consistent with the electron correlation effect appeared in the radial density $H(u)$ depicted in Fig. 1(a); $\Delta H(u)$ is positive in the regions $0.50<u<1.09$ and $3.44<u<7.87$, whereas $\Delta H(u)$ is negative mainly in the regions $0<u<0.50$ and $1.09<u<3.44$, where the symbol Δ stands for the correlated quantity subtracted by the corresponding Hartree–Fock quantity. Analogous correlation effects in $\Delta H(u)$ were reported by Banyard *et al.*[17,18] and by Gálvez *et al.*,[21] but the first positive region is missing in the result of the latter authors.

The four sets of the correlated extracule moments $\langle R^n\rangle$ in Table I are not very different, but we expect that the present MCHF values will be more reliable than the Monte Carlo results[21–23] in view of the accuracy observed in the partner intracule moments. The correlated moments $\langle R^n\rangle$

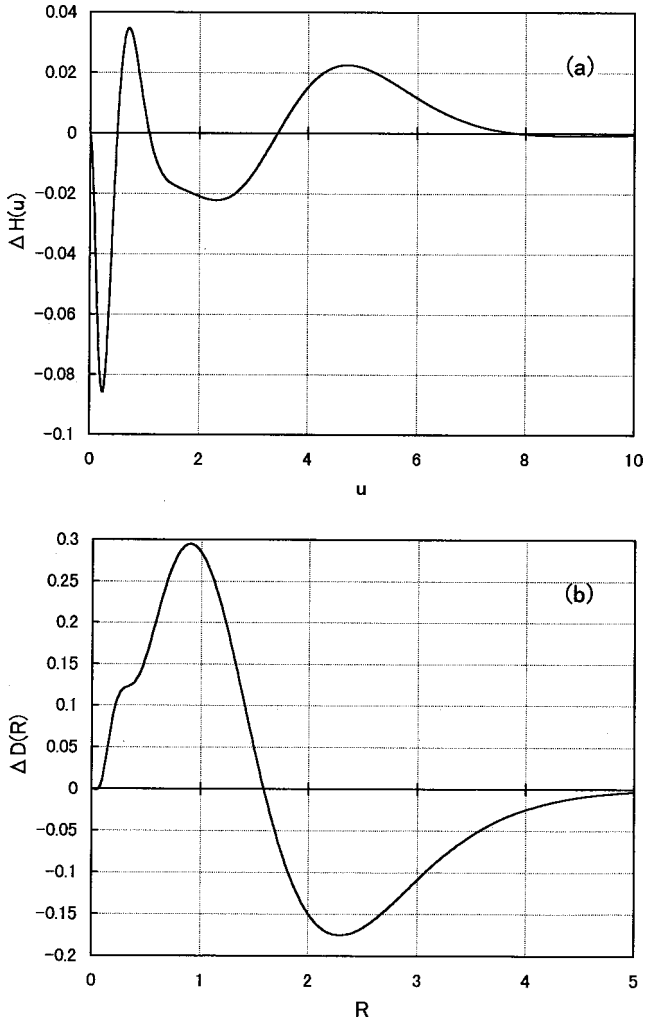

FIG. 1. The electron correlation effect on the electron-pair densities of the Be atom in position space. (a) Intracule density. (b) Extracule density.

with $n<0$ are larger, while those with $n>0$ are smaller than their Hartree–Fock values.[10] These changes correctly reflect the correlation contribution in the extracule density $D(R)$ that the density is shifted from a large-R ($R>1.58$) to a small-R ($0<R<1.58$) region, as shown in Fig. 1(b). Gálvez *et al.*[21,23] reported similar behavior for $\Delta D(R)$. The electron correlation in the Be atom reduces the average center-of-mass radius $\langle R\rangle$ of electron pairs.

Table I also lists the inner product $\langle \mathbf{r}_1\cdot\mathbf{r}_2\rangle$, the minus first moment $S(-1)$ of the dipole oscillator strength density[30,31] and the statistical angular correlation coefficient[32] $\tau[\mathbf{r}]$. Their values are similar among the correlated studies, except that the $\langle \mathbf{r}_1\cdot\mathbf{r}_2\rangle$ value of Banyard and Mashat[17] is nontrivially smaller than the others. The last entry of Table I gives a sum rule check $\delta_{\rm pos}$ defined by Eq. (5a). The vanishing $\delta_{\rm pos}$ value in the present and Hartree–Fock[9,10] calculations shows that the intracule and extracule properties are consistently obtained. However, we find nonzero $\delta_{\rm pos}$ for the Monte Carlo results,[20–23] though the value is within the sum of the statistical errors in the three relevant moments.

The momentum-space electron-pair properties obtained from the present MCHF calculations are summarized and compared with the literature values[9,10,23–25] in Table II. The

TABLE II. Electron-pair properties of the Be atom in momentum space. For the Monte Carlo results, the statistical error in the last digit is given in parentheses, when reported.

		Correlated		
	Hartree–Fock[a]	Sarsa *et al.*[b]	Gálvez *et al.*[c]	Present
Energies				
E	−14.573 02	−14.6523(1)	−14.661 29(4)	−14.662 53
$-E/T$	1.000 00	0.996 76	0.998 49	1.000 00
Intracule moments				
$\langle\nu^{-2}\rangle$	6.755 57	6.915	7.1294	6.963 98
$\langle\nu^{-1}\rangle$	3.809 40	3.834	3.8761	3.843 12
$\langle\nu\rangle$	18.4571	18.422	18.428	18.4538
$\langle\nu^{2}\rangle$	87.4381	87.30	87.115	87.0550
$\langle\nu^{3}\rangle$	610	630	⋯	602
Extracule moments				
$\langle P^{-2}\rangle$	27.0223	21.46	21.065	20.7799
$\langle P^{-1}\rangle$	7.618 81	7.079	7.057	7.041 04
$\langle P\rangle$	9.228 55	9.372	9.2294	9.351 71
$\langle P^{2}\rangle$	21.8595	22.2545	22.162	22.2238
$\langle P^{3}\rangle$	76.2	77.1	⋯	77.6
Other two-electron properties				
$\langle \mathbf{P}_1\cdot\mathbf{P}_2\rangle$	0	0.445(4)	⋯	0.4601
$S(+1)$	19.4306	⋯	⋯	20.1634
$\tau[\mathbf{P}]$	0	⋯	0.0098	0.0105
Sum rule check				
$\langle p^{2}\rangle$	29.1460	29.400	29.367	29.3251
$\delta_{\rm mom}$	0.0000	−0.082	−0.439	0.0000

[a]References 9, 10.
[b]References 23, 24.
[c]Reference 25.

columns of the table are again arranged in the decreasing order of the associated total energies. When compared with the Hartree–Fock values[9] the intracule moments $\langle\nu^n\rangle$ are found to be increased if $n<0$ and decreased if $n>0$ upon the inclusion of the electron correlation. An exception is the previous calculation by Sarsa *et al.*,[24] where they obtained a correlated $\langle\nu^3\rangle$ value (630.) larger than the corresponding Hartree–Fock result (610). The correlation contribution $\Delta\overline{H}(\nu)$ to the intracule density $\overline{H}(\nu)$ in momentum space is depicted in Fig. 2(a). The difference $\Delta\overline{H}(\nu)$ is positive at $0<\nu<0.80$ and $1.79<\nu<7.37$, whereas it is negative at $0.80<\nu<1.79$ and $\nu>7.37$. An analogous correlation effect was previously observed by Gálvez *et al.*[25] The predominant contribution of the electron correlation is the density shift from a large-ν to a small-ν region, in accord with the change in the intracule moments $\langle\nu^n\rangle$ discussed previously. The electron correlation effect works to reduce the average distance $\langle\nu\rangle$ of two electrons in momentum space; an opposite result observed for $\langle u\rangle$ in position space.

On the other hand, Table II shows that the electron correlation decreases the extracule moments $\langle P^n\rangle$ with $n<0$ and increases $\langle P^n\rangle$ with $n>0$ in all the calculations. The correlation effect $\Delta\overline{D}(P)$ on the extracule density $\overline{D}(P)$ is plotted in Fig. 2(b), which shows that the extracule density mainly migrates from a small-P ($0<P<0.40$) to a large-P ($0.40<P<1.02$) region, when the electron correlation is incorporated. There are additional negative ($1.02<P<1.91$) and positive ($P>1.91$) regions, but their contributions are small. Thus, two electrons are less likely to have the opposite

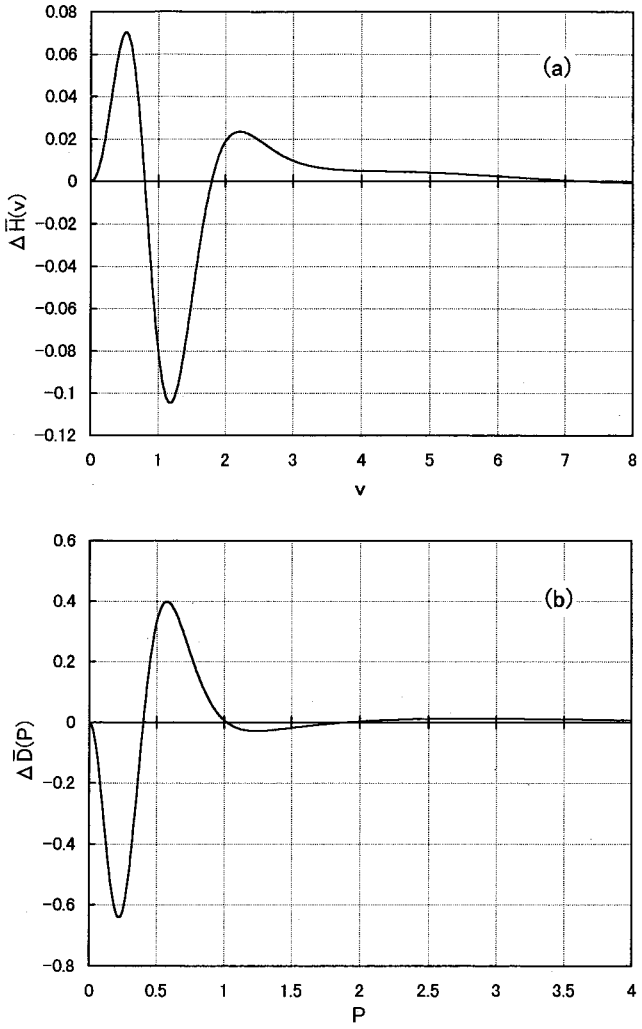

FIG. 2. The electron correlation effect on the electron-pair densities of the Be atom in momentum space. (a) Intracule density. (b) Extracule density.

momenta and the center-of-mass radius of an electron pair in momentum space is larger than the case of the Hartree–Fock approximation. The results are consistent with the correlation effect observed in the extracule moments $\langle P^n \rangle$. The correlation effect $\Delta\overline{D}(P)$ was also shown by Gálvez *et al.*[23,25] as a function of P, but their plots have an extra hump[23] around $P=1$ and an oscillatory feature[25] for $P>0.9$.

Table II also lists the inner product $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$, the first moment $S(+1)$ of the dipole oscillator strength density,[30,31] and the momentum-space statistical angular correlation coefficient[32] $\tau[\mathbf{p}]$. The present MCHF and Monte Carlo results[23–25] are analogous, when available. When the consistency of the momentum-space intracule and extracule properties is checked by means of δ_{mom} [Eq. (5b)], we find that δ_{mom} is zero for the present and Hartree–Fock results, whereas it is nonzero for the results of Sarsa *et al.*[23,24] and of Gálvez *et al.*[25] The statistical uncertainty was not reported for the electron-pair moments in momentum space. Judging from the total energies, virial errors, and δ_{mom} values, we consider that the present MCHF results are most accurate among the three sets of available data summarized in Table II.

IV. SUMMARY

For the Be atom, correlated electron-pair intracule (relative motion) and extracule (center-of-mass motion) properties in position and momentum spaces have been reported based on MCHF calculations.

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