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

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<th>著者</th>
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<tr>
<td>誌名</td>
<td>The journal of chemical physics</td>
</tr>
<tr>
<td>巻数</td>
<td>116</td>
</tr>
<tr>
<td>号数</td>
<td>15</td>
</tr>
<tr>
<td>発行日</td>
<td>2002-04-15</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10258/814">http://hdl.handle.net/10258/814</a></td>
</tr>
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doi: info:doi/10.1063/1.1462614
Correlated electron-pair properties of the Be atom in position and momentum spaces

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(Received 11 December 2001; accepted 29 January 2002)

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.

DOI: 10.1063/1.1462614

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,

\[
H(u) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(u - |\mathbf{r}_i - \mathbf{r}_j|),
\]

\[
D(R) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(R - |\mathbf{r}_i + \mathbf{r}_j|/2),
\]

have been introduced and studied, 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 \((N \geq 2)\) wave function \(\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\) with \(\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)\) 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

\[
\langle u^n \rangle = \int_0^\infty du u^n H(u), \quad \langle R^n \rangle = \int_0^\infty dR R^n D(R),
\]

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 \(\tilde{H}(\nu)\) and extracule \(\tilde{D}(P)\) densities in momentum space, as well as their moments \(\langle \nu^n \rangle\) and \(\langle P^n \rangle\), have also been studied:

\[
\tilde{H}(\nu) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(\nu - |\mathbf{p}_i - \mathbf{p}_j|),
\]

\[
\tilde{D}(P) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(P - |\mathbf{p}_i + \mathbf{p}_j|/2),
\]

\[
\langle \nu^n \rangle = \int_0^\infty d\nu \nu^n \tilde{H}(\nu), \quad \langle P^n \rangle = \int_0^\infty dP P^n \tilde{D}(P),
\]

where \(\mathbf{p}_i\) is the momentum vector of the electron \(i\). The densities \(\tilde{H}(\nu)\) and \(\tilde{D}(P)\) 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, 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, to satisfy rigorous sum rules

\[
\delta_{\text{pos}} = 4\langle R^2 \rangle + \langle u^2 \rangle - 2\langle N - 1 \rangle \langle r^2 \rangle = 0,
\]

\[
\delta_{\text{mom}} = 4\langle P^2 \rangle + \langle \nu^2 \rangle - 2\langle N - 1 \rangle \langle p^2 \rangle = 0,
\]

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 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 and Li atoms. In the case of the Be atom, several correlated calculations were reported for the intracule and extracule properties in position space. On the other hand, correlated studies are extremely limited in momentum space: Only Sarsa et al. 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...
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 em-
ployed by Froese Fischer and Saxena,27 we obtained a 30
configuration MCHF function, which consists of 1s2n2s2(n =
2, 3), 1s23s4s, 1sn2p2(n=2,6), 1s2p4p, 1s32d2, 1s22f2,
2s2ns2(n=4–6), 2s2np2(n=3–5), 2s22p4p, 2s2nd2(n=4,5),
2s2nf2(n=4,6), 2s2g2, 2p24f1(l =s,p,d), 1s2s4p2, 1s2sn2p2(n=2,3), 1s2s2pn2p(n =
3,4), 1s2s1s3p3p4p, and 1s2s1s3s3p4p electron configura-
tions. Our MCHF total energy \( E \) is -14.66253 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 \( 1 \times 10^{-9} \), 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
algorithm29 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 values9,10,17–23 in Table I, where the col-
umns are arranged in the decreasing order of the total ener-
gies of the parent wave functions. When the intracule mo-
mments \( \langle u^3 \rangle \) 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 Galvaz 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 values9 in all the calculations.
Clearly, the electron correlation increases the average inter-
electronic separation \( \langle u \rangle \). These changes in \( \langle u^n \rangle \) from
their Hartree–Fock values are consistent with the electron corre-
lation effects 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 sym-
bol \( \Delta \) 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
Galvaz 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 results21–23 in view of the accuracy observed in the
partner intracule moments. The correlated moments \( \langle R^n \rangle \)

<table>
<thead>
<tr>
<th></th>
<th>Hartree–Fock (^a)</th>
<th>Sarsa et al. (^b)</th>
<th>Banyard–Mashat (^c)</th>
<th>Galvaz et al. (^d)</th>
<th>Present</th>
<th>Banyard–Mobb (^e)</th>
<th>Galvaz et al. (^f)</th>
<th>Komasa et al. (^g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlated</td>
<td>( E )</td>
<td>( -E/T )</td>
<td>( \langle u^2 \rangle )</td>
<td>( \langle u^{-1} \rangle )</td>
<td>( \langle u \rangle )</td>
<td>( \langle u^3 \rangle )</td>
<td>( \langle u^4 \rangle )</td>
<td>( \langle u^5 \rangle )</td>
</tr>
<tr>
<td>Intracule moments</td>
<td>(-1.0000)</td>
<td>(-0.99676)</td>
<td>(-0.99676)</td>
<td>(-0.99649)</td>
<td>(-1.0000)</td>
<td>(-1.0000)</td>
<td>(-1.0000)</td>
<td>(-1.0000)</td>
</tr>
</tbody>
</table>

\(^a\) References 9, 10.  
\(^b\) References 20, 23.  
\(^c\) Reference 17.  
\(^d\) Reference 21.  
\(^e\) Reference 19.  
\(^f\) Reference 18.  
\(^g\) Reference 22.
with \( n < 0 \) are larger, while those with \( n > 0 \) are smaller than their Hartree–Fock values. These changes correctly reflect the correlation contribution in the intracule 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 \( \rho \) to the intracule density \( \rho \) 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\(^{32} \) \( \pi[\mathbf{r}] \). Their values are similar among the correlated studies, except that the \( \langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle \) value of Banyard and Mashal\(^{17} \) is nontrivially smaller than the others. The last entry of Table I gives a sum rule check \( \delta_{\text{pos}} \) defined by Eq. (5a). The vanishing \( \delta_{\text{pos}} \) value in the present and Hartree–Fock\(^{9,10} \) calculations shows that the present and extracule properties are consistently obtained. However, we find nonzero \( \delta_{\text{pos}} \) 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 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 \( \langle \nu^m \rangle \) 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 \( \Delta \tilde{H}(\nu) \) to the intracule density \( \tilde{H}(\nu) \) in momentum space is depicted in Fig. 2(a). The difference \( \Delta \tilde{H}(\nu) \) 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-\( \nu \) to a small-\( \nu \) region, in accord with the change in the intracule moments \( \langle \nu^m \rangle \) 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 \( \langle \nu \rangle \) in position space.

On the other hand, Table II shows that the electron correlation decreases the extracule moments \( \langle P^m \rangle \) with \( n < 0 \) and increases \( \langle P^m \rangle \) with \( n > 0 \) in all the calculations. The correlation effect \( \Delta \tilde{D}(P) \) on the extracule density \( \tilde{D}(P) \) 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

<table>
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<th>Energies</th>
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<th>Sarsa et al.</th>
<th>Gálvez et al.</th>
<th>Present</th>
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<tr>
<td>( E )</td>
<td>-14.573 02</td>
<td>-14.6523(1)</td>
<td>-14.661 29(4)</td>
<td>-14.662 53</td>
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<tr>
<td>( -E/T )</td>
<td>1.000 00</td>
<td>0.996 76</td>
<td>0.998 49</td>
<td>1.000 00</td>
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<table>
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<tr>
<th>Intracule moments</th>
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<th>Sarsa et al.</th>
<th>Gálvez et al.</th>
<th>Present</th>
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<tr>
<td>( \langle \nu^2 \rangle )</td>
<td>6.755 57</td>
<td>6.915</td>
<td>7.1294</td>
<td>6.963 98</td>
</tr>
<tr>
<td>( \langle \nu^3 \rangle )</td>
<td>3.809 40</td>
<td>3.834</td>
<td>3.8761</td>
<td>3.843 12</td>
</tr>
<tr>
<td>( \langle \nu \rangle )</td>
<td>18.4571</td>
<td>18.422</td>
<td>18.428</td>
<td>18.4538</td>
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<tr>
<td>( \langle \nu^3 \rangle )</td>
<td>87.4381</td>
<td>87.30</td>
<td>87.115</td>
<td>87.0550</td>
</tr>
<tr>
<td>( \langle \nu^4 \rangle )</td>
<td>610</td>
<td>630</td>
<td>602</td>
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<table>
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<th>Gálvez et al.</th>
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<td>( \langle P^2 \rangle )</td>
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<td>21.46</td>
<td>21.065</td>
<td>20.7799</td>
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<tr>
<td>( \langle P^3 \rangle )</td>
<td>7.618 81</td>
<td>7.079</td>
<td>7.057</td>
<td>7.041 04</td>
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<tr>
<td>( \langle P \rangle )</td>
<td>9.228 55</td>
<td>9.372</td>
<td>9.2294</td>
<td>9.351 71</td>
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<tr>
<td>( \langle P^3 \rangle )</td>
<td>21.8595</td>
<td>22.2545</td>
<td>22.162</td>
<td>22.2238</td>
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<tr>
<td>( \langle P^4 \rangle )</td>
<td>76.2</td>
<td>77.1</td>
<td>...</td>
<td>77.6</td>
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<th>Other two-electron properties</th>
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<th>Sarsa et al.</th>
<th>Gálvez et al.</th>
<th>Present</th>
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<tr>
<td>( \langle S(1) \rangle )</td>
<td>19.4306</td>
<td>...</td>
<td>...</td>
<td>20.1634</td>
</tr>
<tr>
<td>( \pi[\mathbf{P}] )</td>
<td>0</td>
<td>0.445(4)</td>
<td>...</td>
<td>0.4601</td>
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<th>Sum rule check</th>
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<th>Sarsa et al.</th>
<th>Gálvez et al.</th>
<th>Present</th>
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<tr>
<td>( \delta_{\text{fl}} )</td>
<td>29.1460</td>
<td>29.400</td>
<td>29.367</td>
<td>29.3251</td>
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<tr>
<td>( \delta_{\text{nn}} )</td>
<td>0.0000</td>
<td>-0.082</td>
<td>-0.439</td>
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</table>

\( \text{References 9, 10.} \)
\( \text{References 23, 24.} \)
\( \text{Reference 25.} \)
moments 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 \( \langle P \rangle \). The correlation effect \( \Delta \bar{D}(P) \) 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 \( \langle p_1 \cdot p_2 \rangle \) of the dipole oscillator strength density,\(^{23,31} \) and the momentum-space statistical angular correlation coefficient\(^{22} \) \( \pi_{\mathbf{p}} \). 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 \( \delta_{\text{mom}} \) [Eq. (5b)], we find that \( \delta_{\text{mom}} \) 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 \( \delta_{\text{mom}} \) 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.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

\( ^{30} \) M. Inokuti, Rev. Mod. Phys. 43, 297 (1971).
\( ^{32} \) W. Kutzelnigg, G. Del Re, and G. Berthier, Phys. Rev. 172, 49 (1968).