Electron correlation in momentum space: The beryllium-atom isoelectronic sequence

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Various momentum-space properties are computed for the Be atom and its isoelectronic sequence from highly accurate configuration-interaction wave functions that include more than 90% of the correlation energy. We assess the effects of electron correlation in momentum space by making a comparison with the results obtained from the Hartree-Fock level. The results reveal differences that indicate that the inclusion of electron correlation is necessary if one is to obtain highly accurate momentum space quantities. Additionally, our results show that the sum of the position and momentum-space entropies increases in going from the Hartree-Fock to the configuration-interaction level, supporting the argument that this sum may be used in assessing the quality of a basis set. The observation that the entropy sum and the other calculated properties remain stable with the inclusion of more electron correlation suggests that these properties are not sensitive to the amount of electron correlation and that density convergence criteria may be more useful in obtaining an accurate electronic distribution than criteria based solely on the amount of correlation energy.

I. INTRODUCTION

It is well known that an accurate description of one-electron properties must include both momentum and position space densities, and that in combination, these two complementary avenues of analyses leads to a much better understanding of the electronic structure of atoms and molecules [1].

In the past, Benesch and co-workers [2–4] have examined the importance of electron correlation on momentum densities and other density related properties using then available correlated wave functions. With the increasing use of $(e,2e)$ spectroscopy [5] and Compton scattering [6] in recent years, as probes for the study of electron momentum distributions, it is desirable to obtain accurate momentum densities and Compton profiles using the highly accurate configuration-interaction (CI) atomic wave functions that are now available.

Bunge [7] has obtained a CI wave function for the beryllium atom that accounts for 99.55% of the correlation energy (CE). Such a wave function should produce essentially *exact* properties in position and momentum space. More recently, Esquivel and Bunge [8] obtained an accurate analytical density for Be by systematically improving the CI wave functions so that the density converges towards a definite expression as a function of r [9]. The result was a CI expansion built in a very compact basis set which accounts for 93% of the CE. Nevertheless, the agreement between the Esquivel-Bunge (EB) and Bunge's densities was shown to be impressive, both in the point by point analysis and in the results for one-electron expectation values. Moreover, both densities produce excellent values for the electron-nucleus cusp ratio and obey the asymptotic behavior.

An electron correlation study in momentum space is indeed necessary since it has been shown that the amount of CE included in the wave function is not in direct rela-

tionship to the reliability of the corresponding position space density. Thus it is important to address whether fully converged position space densities are fully able to produce momentum properties with the same accuracy as in position space. Besides, obtaining CI wave functions which account for over 99% of CE is by no means an easily accomplished task while fully converged densities may be obtained with much less effort [9].

In the present work, we report our study of the accurate momentum density, Compton profile, moments of the momentum density, information entropies in position and momentum spaces, and quantities related to the momentum density, for Be and its isoelectronic sequence using the CI wave functions constructed by Esquivel and co-workers [8,10]. Furthermore, we have also calculated these properties for Be with the use of Bunge's CI wave function [7]. Our aim is to examine and compare the momentum density related properties we obtain to calculations done at the Hartree-Fock level, to ascertain the sensitivity of these physically significant properties to the inclusion of electron correlation in the basis set. We also examine the change in these properties with the addition of more electron correlation to the wave function. Lastly, we compute the position and momentum-space information entropies [11] and their sums to analyze any trends in the isoelectronic sequence and also to examine the ability of these entropies in assessing the quality of a particular wave function. We discuss briefly in the next section our methodology for calculating the various properties and their physical significance. In the last section the results are presented and discussed.

II. THEORETICAL METHODOLOGY

The momentum distribution may be calculated by two distinct methods. The first involves the approximate solution of the Schrödinger equation in momentum space

to obtain the momentum-space wave function. Although attempts have been made in this direction [12], this area remains in its infancy. The second and by far the most predominant method involves the Dirac-Fourier transform of a position space wave function. However, we follow here a method suggested by Benesch and Smith [2,3]. First, the spin-traced one-particle density matrix,

$$\gamma(\mathbf{r},\mathbf{r}')=N \int \psi^*(\mathbf{r}'\sigma,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N)$$

$$\times \psi(\mathbf{r}\sigma,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N)d\sigma \, d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N \, , \tag{1}$$

is obtained in its natural form

$$\gamma(\mathbf{r},\mathbf{r}')= \sum_k \lambda_k \chi_k(\mathbf{r})\chi_k^*(\mathbf{r}') \tag{2}$$

and then transformed into momentum space

$$\gamma(\mathbf{p},\mathbf{p}')=(2\pi)^{-3} \int \exp(-i\mathbf{p}\cdot\mathbf{r}+i\mathbf{p}'\cdot\mathbf{r}')\gamma(\mathbf{r},\mathbf{r}')$$

$$\times d\mathbf{r}\, d\mathbf{r}' \, . \tag{3}$$

In the above ψ is the position space representation of the N-electron wave function and $x_i=(\mathbf{r}_i,\sigma_i)$ is a combined space-spin coordinate for electron i. The χ_k are the natural orbitals which give the density matrix in diagonal form and λ_k are interpreted as the occupation numbers of the respective natural orbitals (NO's). Using the natural expansion $\gamma(\mathbf{p},\mathbf{p}')$ may be written as

$$\gamma(\mathbf{p},\mathbf{p}')= \sum_k \lambda_k \chi_k(\mathbf{p})\chi_k^*(\mathbf{p}') \, . \tag{4}$$

Here $\chi_k(\mathbf{p})$ is the NO in the momentum space. Thus, given the NO, $\chi_k(\mathbf{r})$, in the position space, Eq. (4) can be evaluated by computing the Fourier transform (FT), i.e.,

$$\chi_k(\mathbf{p})=(2\pi)^{-3/2} \int e^{-i\mathbf{p}\cdot\mathbf{r}}\chi_k(\mathbf{r})d\mathbf{r} \, . \tag{5}$$

Evaluation of the FT of the kth NO is described in detail in the review article of Kaijser and Smith [13]. The spherically averaged momentum density may thus be obtained as

$$\overline{\Pi}(p)= \int p^2 \gamma(\mathbf{p},\mathbf{p})d\Omega \, . \tag{6}$$

The isotropic Compton profile (ICP), $\overline{J}(q)$, is related to the spherically averaged momentum density, $\overline{\Pi}(p)$, i.e.,

$$\overline{J}(q)=2\pi \int_{|q|}^\infty p\overline{\Pi}(p)dp \, . \tag{7}$$

The moments of the electron momentum density are defined by

$$\langle p^n \rangle =4\pi \int_0^\infty p^{n+2}\overline{\Pi}(p)dp, \quad -2\leq n \leq 4 \tag{8}$$

where the limits on n arise from the fact that $\overline{\Pi}(p)$ does not vanish at the origin and decays as p^{-8} at large p [2]. These moments have physical meaning: $\langle p^2 \rangle$ is proportional to the nonrelativistic kinetic energy and $\langle p^{-1} \rangle$ is simply the peak value of $\overline{J}(q=0)$ of the ICP. $\langle p \rangle$ is proportional to the Slater-Dirac exchange energy to a high degree of accuracy and $\langle p^3 \rangle$ is roughly proportional to the initial value of the Patterson function in x-ray crystallography [14]. The expectation values E_4 and H_0 are the quasirelativistic energy

$$E_4=\langle p^2 \rangle /2m_e - \langle p^4 \rangle /8m_e^3 c^2 \tag{9}$$

and the complete relativistic kinetic-energy operator

$$H_0=m_e c^2\{[1+p^2/(m_e^2 c^2)]^{1/2}-1\} \, , \tag{10}$$

where m_e is the mass of the electron and c is the speed of light in a vacuum (for details see Ref. [15]). We have also computed the small-p MacLaurin and large-p asymptotic coefficients of $\overline{\Pi}(p)$ which may prove useful in the analysis of experimental Compton profiles. The general expressions for the asymptotic expansions of $\overline{\Pi}(p)$ [16] are

$$\overline{\Pi}(p)= A_0 + A_2 p^2 + A_4 p^4 + O(p^6) \, , \tag{11}$$

for small p, and

$$\overline{\Pi}(p)= B_8 p^{-8} + B_{10} p^{-10} + B_{12} p^{-12} + O(p^{-14}) \, , \tag{12}$$

for large p. These coefficients as obtained from Hartree-Fock wave functions [17] have been tabulated [15,16].

In addition to the properties above, we have computed the momentum-space information entropy [11]

$$S_\Pi = - \int \gamma(\mathbf{p},\mathbf{p})\ln\gamma(\mathbf{p},\mathbf{p})d\mathbf{p} \, . \tag{13}$$

TABLE I. Calculated total energies in hartrees at the HF and CI levels for (a) the Be atom and (b) the Be isoelectronic sequence.

(a) The Be atom

HF	$-14.573\,021$
CI_{ex}	$-14.666\,902$
CI_{EB}	$-14.661\,017$
CI_K	$-14.610\,111$
CI_L	$-14.619\,026$
CI_{KL}	$-14.578\,660$

(b) The Be isoelectronic sequence

Level	B^+	C^{2+}	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
HF	$-24.237\,566$	$-36.408\,489$	$-51.082\,311$	$-68.257\,705$	$-87.934\,048$	$-110.111\,005$
CI	$-24.343\,379$	$-36.529\,551$	$-51.217\,415$	$-68.406\,070$	$-88.095\,490$	$-110.285\,012$

TABLE II. A comparison between various momentum densities for the Be atom.

p (a.u.)	$\Pi_{ex}(p)$	$\Pi_{EB}(p)$	$\Pi_K(p)$	$\Pi_L(p)$	$\Pi_{KL}(p)$	$\Pi_{HF}(p)$
0.0	4.840 64	4.853 63	5.950 60	4.895 15	5.948 97	5.950 81
0.1	4.507 00	4.516 34	5.491 16	4.521 92	5.489 64	5.491 34
0.3	2.620 37	2.618 74	2.996 88	2.623 19	2.996 01	2.996 93
0.5	1.010 79	1.010 52	1.045 60	1.012 16	1.045 33	1.045 63
0.7	0.314 15	0.314 75	0.286 67	0.314 90	0.286 68	0.286 73
1.0	0.060 46	0.060 42	0.046 77	0.060 28	0.046 81	0.046 79
1.5	0.020 16	0.020 18	0.018 70	0.020 14	0.018 71	0.018 70
2.0	0.012 87	0.012 86	0.012 71	0.012 86	0.012 73	0.012 72
3.0	0.004 43	0.004 43	0.004 44	0.004 44	0.004 45	0.004 44
4.0	0.001 45	0.001 45	0.001 45	0.001 45	0.001 45	0.001 45
5.0	0.000 50	0.000 50	0.000 50	0.000 50	0.000 50	0.000 50
7.0	0.000 08	0.000 08	0.000 08	0.000 07	0.000 07	0.000 07

We have also calculated S_ρ, the analogous quantity in position space, so that we may compute the sum, $S_\Pi + S_\rho$. These entropies are of interest since it has been suggested that [11] their sum increases with an enhancement of the quality of the basis as well as with electron correlation for ground-state atoms. Hence these measures could be of importance in the assessment of basis set and wave function quality.

All integrals pertaining to the respective properties were numerically calculated by dividing the interval $[0, \infty]$ into a number of subintervals, each of which was treated with an eight point Gauss-Lobatto quadrature.

III. RESULTS AND DISCUSSION

The orbital and total $\overline{\Pi}(p)$ and $\overline{J}(q)$ and related moments for Be and its isoelectronic sequence were calculated both from the Hartree-Fock wave functions of Clementi and Roetti [17] and the CI wave function of Bunge [7] and those of Esquivel and Bunge [8] and Esquivel, Smith, and Bunge [10] using Eqs. (6)–(8). For the beryllium atom the corresponding quantities were analyzed by means of Bunge's wave function with a 650 term expansion in a $[10s, 9p, 8d, 7f, 5g, 3h, 1i]$ Slater-type orbitals (STO) basis that represents 99.55% of the CE [7]. This function was reproduced and the natural orbitals

and occupation numbers were calculated [8]. The EB wave function was also employed for the present analysis. This CI expansion contains 508 terms in a $[9s, 6p, 4d, 1f]$ basis including 93% of the CE [8].

Furthermore, in order to study correlation effects of the core, valence, and intershell electrons, CI wave functions were specifically calculated in the K-, L-, and intershell regions by promoting electrons in the $1s$, $2s$, and $1s2s$ configurations, respectively. The CI expansion contains 68 terms for the K and L shells and 103 terms for the intershell. These CI expansions are built in the same basis set as the EB wave function.

For all other ions along the isoelectronic sequence, fully converged analytical charge densities were employed. The corresponding nonrelativistic CI wave functions were calculated in a systematic manner, i.e., all single and double excited configurations obtained by promoting K and L electrons in the Hartree-Fock configuration are included in the wave function. No triple and quadruple excitations are included. The final CI expansions contain 289 terms in $[8s, 6p, 6d, 3f, 3g]$ STO basis sets yielding energies which approximately represent 95% of the CE (see Table I). Position space information for CI densities of these ions are planned to be published elsewhere [10].

The momentum density and Compton profile for Be are tabulated in Tables II and III for a few selected points

TABLE III. A comparison between various ICP $[\overline{J}(q)]$ values for the Be atom.

| q (a.u.)	$\overline{J}_{ex}(q)$	$\overline{J}_{EB}(q)$	$\overline{J}_K(q)$	$\overline{J}_L(q)$	$\overline{J}_{KL}(q)$	$\overline{J}_{HF}(q)$
0.0	2.953 79	2.954 54	3.158 87	2.957 40	3.158 50	3.159 13
0.1	2.807 03	2.807 43	2.979 25	2.810 12	2.978 94	2.979 51
0.3	1.936 31	1.936 21	1.949 44	1.937 60	1.949 42	1.949 67
0.5	1.098 07	1.098 66	1.031 91	1.098 59	1.032 15	1.032 12
0.7	0.658 75	0.658 99	0.600 26	0.658 38	0.600 58	0.600 44
1.0	0.432 20	0.432 13	0.408 49	0.431 67	0.408 74	0.408 60
1.5	0.312 41	0.312 37	0.309 23	0.312 24	0.309 42	0.309 36
2.0	0.223 90	0.223 84	0.223 72	0.223 80	0.223 84	0.223 81
3.0	0.102 31	0.102 26	0.102 48	0.102 19	0.102 44	0.102 43
4.0	0.045 26	0.045 21	0.045 31	0.045 12	0.045 23	0.045 22
5.0	0.020 70	0.020 68	0.020 71	0.020 60	0.020 64	0.020 64
7.0	0.005 10	0.005 10	0.005 10	0.005 06	0.005 07	0.005 07
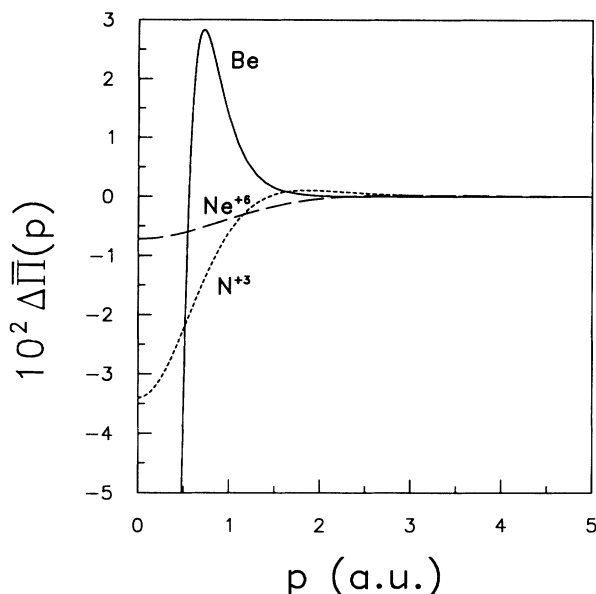
FIG. 1. A plot of the momentum density difference function for a few members of the Be isoelectronic sequence.
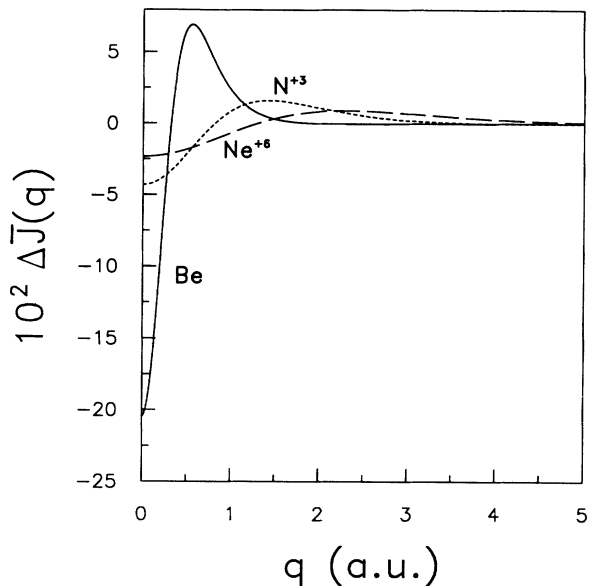

FIG. 2. A plot of the Compton profile difference function for a few members of the Be isoelectronic sequence.

in order to compare these quantities obtained from the wave functions of Bunge [7], EB [8], and Hartree-Fock [17]. A point by point comparison of $\overline{\Pi}_{ex}, \overline{\Pi}_{EB}$, and $\overline{\Pi}_L$ [defined, respectively, as the momentum densities obtained from the wave functions of Bunge (ex), Esquivel and Bunge (EB) and that obtained from the L-shell region of Be (L)] shows a good resemblance. Both $\overline{\Pi}_{EB}$ and $\overline{\Pi}_L$ agree within 0.3% and 0.5% with $\overline{\Pi}_{ex}$ at $p=0$ and within less than 0.1% at all subsequent values of p. The other densities, i.e., $\overline{\Pi}_K$, $\overline{\Pi}_{KL}$, and $\overline{\Pi}_{HF}$ are in general too high (approximately 30%) at $p=0$ but tend to converge gradually to the exact densities $(\overline{\Pi}_{ex}, \overline{\Pi}_{EB}, \overline{\Pi}_L)$ for p values greater than 1.5 a.u., although they exhibit a remarkably

good agreement among themselves. This feature may be rationalized by noting that due to the near degeneracy between the $2s$ and $2p$ states of the Be atom, the singly and doubly excited configurations from the core and the intershell are not effective in introducing electron correlations. All correlations originating from these configurations come from the valence shell.

In order to study the differences in the momentum density and Compton profile obtained from the EB and HF functions, we have displayed difference functions, defined as

$$\Delta\overline{\Pi}(p)=\overline{\Pi}_{EB}(p)-\overline{\Pi}_{HF}(p), \quad \Delta\overline{J}(q)=\overline{J}_{EB}-\overline{J}_{HF}, \quad (14)$$

TABLE IV. The expectation values of the momentum density, the quasirelativistic kinetic-energy operator, the relativistic kinetic-energy operator, the information entropies, and asymptotic coefficients for the Be atom. Note that the large-p asymptotic coefficients have been scaled by powers of Z. All numbers are in atomic units; numbers in square brackets indicate powers of 10.

Property	CI(ex)	CI(EB)	CI(K)	CI(L)	CI(KL)	HF
$\langle p^{-2} \rangle$	21.9387	21.9590	25.2896	21.9877	25.2833	25.2906
$\langle p \rangle$	7.53298	7.53042	7.44043	7.52088	7.43514	7.43418
$\langle p^2 \rangle$	29.3329	29.3143	29.2152	29.2327	29.1503	29.1458
$\langle p^3 \rangle$	186.351	186.210	186.289	185.427	185.613	185.586
$\langle p^4 \rangle$	2165.03	2163.63	2166.67	2157.06	2161.09	2160.95
E_4	$-1.4413[-2]$	$-1.4402[-2]$	$-1.4422[-2]$	$-1.4358[-2]$	$-1.4385[-2]$	$-1.4384[-2]$
$\langle H_0 \rangle$	$8.9461[-4]$	$8.9402[-4]$	$8.9637[-4]$	$8.9977[-4]$	$9.0192[-4]$	$9.0210[-4]$
S_Π	11.6944	11.6911	11.2218	11.6747	11.2181	11.2155
S_ρ	8.7543	8.7576	8.9529	8.7661	8.9508	8.9503
$S_\Pi + S_\rho$	20.4486	20.4487	20.1747	20.4407	20.1688	20.1658
A_0	4.84064	4.85363	5.95060	4.85915	5.94897	5.95077
A_2	-34.7775	-35.1855	-48.1532	-35.1757	-48.1411	-48.1560
A_4	145.883	150.476	229.125	150.080	229.069	229.079
B_8/Z^5	1.40906	1.40778	1.41183	1.41939	1.42298	1.42329
B_{10}/Z^7	-6.30111	-6.11045	-6.27276	-7.18668	-7.31205	-7.31701
B_{12}/Z^9	-51.0219	8.05658	11.3897	24.8216	30.6749	29.3135

TABLE V. The expectation values of the momentum density, the quasirelativistic kinetic-energy operator, the relativistic kinetic-energy operator, the information entropies, and asymptotic coefficients for the Be-atom isoelectronic sequence. All numbers are in atomic units; numbers in square brackets indicate powers of 10.

Property	B^+	C^{2+}	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
$\langle p^{-2} \rangle$	10.0801	5.84443	3.82402	2.70182	2.01241	1.55751
$\langle p \rangle$	9.91742	12.3010	14.6996	17.0885	19.4770	21.8648
$\langle p^2 \rangle$	48.6784	73.0600	102.441	136.820	176.205	220.578
$\langle p^3 \rangle$	386.923	698.097	1143.91	1748.45	2536.71	3531.92
$\langle p^4 \rangle$	5591.88	12076.6	23046.8	40193.0	65545.1	101286.0
E_4	$-3.7222[-2]$	$-8.0387[-2]$	$-1.5341[-1]$	$-2.6754[-1]$	$-4.3630[-1]$	$-6.7421[-1]$
$\langle H_0 \rangle$	$2.8290[-3]$	$7.2001[-3]$	$1.5775[-2]$	$3.0971[-2]$	$5.6036[-2]$	$9.4925[-2]$
S_Π	15.3956	18.2051	20.4588	22.3477	23.9753	25.4056
S_ρ	4.8960	2.0296	$-2.5955[-1]$	-2.1723	-3.8172	-5.2604
$S_\Pi + S_\rho$	20.2915	20.2347	20.1993	20.1754	20.1581	20.1453
A_0	1.46540	0.65489	0.33892	0.20052	0.12856	0.08733
A_2	-4.40971	-1.12800	-0.38395	-0.15909	-0.07554	-0.03949
A_4	7.2507	1.1123	0.24413	0.07056	0.02477	0.00994
B_8/Z^5	1.47663	1.52709	1.56459	1.59299	1.61615	1.63428
B_{10}/Z^7	-6.39233	-6.67210	-6.57037	-6.79260	-6.63746	-6.86642
B_{12}/Z^9	-2.32092	18.4346	10.51319	17.53192	9.69505	17.89817

in Figs. 1 and 2 for the Be the isoelectronic sequence. From Fig. 1 it is clear that there is a large deviation between the CI and HF densities up to $p \approx 1.5$ a.u. The difference decreases as one moves down the isoelectronic sequence, i.e., largest for Be ($\approx 30\%$) and smallest for Ne^{6+} ($\approx 8\%$). The large negative deviation of $\Delta\bar{\Pi}(p)$ near the valence shell region at small-p values can be understood intuitively. It is well known that in the HF description of the atom each electron obeying the exclusion principle moves in the average potential without disturbing the position of the other electrons. As soon as electron correlation is introduced, the electrons start avoiding each other. Consequently the expectation value of the kinetic-energy operator enhances. Furthermore the electron moves under an increased effective nuclear charge due to lesser screening. These effects together increase the mean radius of the electron distribution in momentum space (a decrease in the mean radius of the electron distribution in position space; for a detailed discussion see Benesch and Smith [3]). Further, the decreasing trend along the isoelectronic sequence reflects the result that the effect of electron correlation decreases near the valence shell region. A similar variation can be seen in Fig. 2 for $\Delta\bar{J}(q)$. Again we see here that the correlation effects on this quantity are appreciable but not as important as the case of $\Delta\bar{\Pi}(p)$. The fact that the relative differences are smaller in this case may be attributed to an averaging out of $\Delta\bar{\Pi}(p)$ due to the integration [see Eq. (7)].

On examination, a similar behavior is also noticed for the corresponding $\bar{J}(q)$ and the moments of the momentum density (see Tables IV and V). The corresponding trend in the asymptotic coefficients of $\bar{\Pi}(p)$ for the Be atom and its isoelectronic sequence (see Tables IV and V) is more similar to the case of $\bar{\Pi}(p)$ in that the differences from the Hartree-Fock level (see Ref. [16]) are relatively large. On comparison with the coefficients at the HF level (see Table VI), this seems to be also true for the remainder of the isoelectronic sequence with the largest differences occurring in the B_{12} coefficient. This should be expected since the parent momentum densities are themselves quite different. The excellent agreement between the results obtained by using Bunge's [7] 650 term and EB's [8] 508 term CI wave functions over the entire range of p and q values studied here leads us to conclude that $\bar{\Pi}(p)$ and $\bar{J}(q)$ and the moments of the momentum density depend on a good balance of the electronic distribution among the different atomic shells as it permits an

TABLE VI. The first three coefficients in the small-p MacLaurin and large-p asymptotic expansion of the spherically averaged momentum density for the Be-atom isoelectronic sequence computed from Hartree-Fock wave functions [17].

Coefficient	B^+	C^{2+}	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
A_0	1.69973	0.72045	0.37294	0.21883	0.13955	0.09453
A_2	-5.74565	-1.33968	-0.44015	-0.17970	-0.08453	-0.04405
A_4	11.2237	1.41186	0.29055	0.08206	0.02838	0.01136
B_8/Z^5	1.49163	1.54385	1.58138	1.61055	1.63102	1.65143
B_{10}/Z^7	-7.31787	-7.38988	-7.40211	-7.41116	-7.34279	-7.37392
$B_{12} Z^9$	27.5800	27.2074	26.5733	26.1364	24.9891	24.9539

appropriate representation of the density at the nucleus and at large distances and to a lesser extent on the amount of CE included in the wave function. We have tabulated in Tables VII and VIII values of $\bar{\Pi}(p)$ and $\bar{J}(q)$ at various values of p and q, which have been constructed from the wave functions of Esquivel, Smith, and Bunge [10].

The information entropies in Table IV for the Be atom reveal some interesting trends. First, the S_p values decrease from the HF to the CI quantities while S_{Π} increases. These trends are not in agreement with those of Gadre et al. [11] where the opposite behavior for S_p and S_{Π} was shown on going from a poor HF basis to a near Hartree-Fock one. Second, the sum $S_{\Pi} + S_p$ is a maximum for the CI functions and a minimum for the HF case. This agrees with the conjecture [11] that the entropy sum enhances with the quality of the wave function. It is interesting to note that although the CI wave function of Bunge [7] includes more correlation than that of the EB [8] function, the entropy sums are about the same. This observation may serve to further validate the

opinion [8] that a fairly balanced electronic distribution may be obtained by using a density convergence criterion instead of the usual approach based on the correlation energy. The results from the Be isoelectronic sequence in Table V show the same kinds of trends as those presented for the near Hartree-Fock case: (i) S_p decreases with increasing atomic number, Z; (ii) S_{Π} enhances as Z increases; (iii) the sum $S_p + S_{\Pi}$ decreases very slowly as Z increases.

IV. CONCLUSIONS

The present calculation clearly demonstrates that the effects of electron correlation are very important in obtaining the accurate $\bar{\Pi}(p)$ and $\bar{J}(q)$ particularly in the valence region. The remarkable resemblance of the properties calculated using Bunge's [7] wave function with those of EB's [8] CI wave function for the Be atom clearly indicates that the Esquivel and Bunge wave function is

TABLE VII. The momentum density for Be and its isoelectronic sequence.

p (a.u.)	Be	B^+	C^{2+}	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
0.00	4.853 63	1.465 40	0.643 89	0.338 92	0.200 52	0.128 56	0.087 33
0.04	4.797 72	1.458 36	0.642 09	0.338 31	0.200 26	0.128 44	0.087 27
0.10	4.516 34	1.422 02	0.632 72	0.335 11	0.198 94	0.127 80	0.086 94
0.20	3.658 49	1.300 10	0.600 50	0.323 94	0.194 27	0.125 58	0.085 77
0.30	2.618 74	1.121 66	0.550 82	0.306 26	0.186 76	0.121 95	0.083 86
0.40	1.691 85	0.915 69	0.488 85	0.283 30	0.176 78	0.117 08	0.081 26
0.50	1.010 52	0.710 17	0.420 41	0.256 56	0.164 82	0.111 13	0.078 05
0.60	0.571 99	0.525 90	0.350 99	0.227 65	0.151 41	0.104 31	0.074 32
0.70	0.314 75	0.374 16	0.285 08	0.198 10	0.137 12	0.096 85	0.070 17
0.80	0.173 24	0.257 57	0.225 80	0.169 23	0.122 47	0.088 97	0.065 69
0.90	0.098 68	0.172 97	0.174 87	0.142 09	0.107 94	0.080 89	0.061 00
1.00	0.060 42	0.114 40	0.132 81	0.117 40	0.093 95	0.072 82	0.056 19
1.20	0.031 00	0.050 18	0.073 21	0.076 81	0.068 72	0.057 37	0.046 59
1.40	0.223 39	0.024 44	0.039 08	0.048 00	0.048 23	0.043 65	0.037 53
1.60	0.018 43	0.014 69	0.021 16	0.029 11	0.032 71	0.032 20	0.029 44
1.80	0.015 47	0.010 89	0.012 34	0.017 51	0.021 65	0.023 15	0.022 55
2.00	0.012 86	0.009 11	0.008 17	0.010 77	0.014 14	0.016 30	0.016 92
2.20	0.010 55	0.007 95	0.006 21	0.007 02	0.009 26	0.011 33	0.012 48
2.40	0.008 57	0.006 99	0.005 21	0.004 98	0.006 21	0.007 84	0.009 10
2.60	0.006 91	0.006 09	0.004 61	0.003 89	0.004 35	0.005 47	0.006 59
2.80	0.005 54	0.005 26	0.004 15	0.003 28	0.003 25	0.003 90	0.004 77
3.00	0.004 43	0.004 51	0.003 74	0.002 91	0.002 60	0.002 88	0.003 49
3.20	0.003 54	0.003 83	0.003 35	0.002 64	0.002 21	0.002 24	0.002 61
3.40	0.002 83	0.003 23	0.002 98	0.002 42	0.001 96	0.001 83	0.002 01
3.60	0.002 26	0.002 72	0.002 63	0.002 22	0.001 79	0.001 56	0.001 60
3.80	0.001 81	0.002 29	0.002 31	0.002 03	0.001 65	0.001 39	0.001 33
4.00	0.001 45	0.001 92	0.002 02	0.001 84	0.001 54	0.001 27	0.001 15
4.50	0.000 84	0.001 23	0.001 43	0.001 42	0.001 27	0.001 07	0.000 90
5.00	0.000 50	0.000 79	0.000 99	0.001 06	0.001 02	0.000 90	0.000 77
6.00	0.000 19	0.000 34	0.000 48	0.000 58	0.000 63	0.000 62	0.000 57
7.00	0.000 08	0.000 15	0.000 24	0.000 31	0.000 37	0.000 40	0.000 40
8.00	0.000 03	0.000 07	0.000 12	0.000 17	0.000 22	0.000 25	0.000 27
9.00	0.000 01	0.000 04	0.000 06	0.000 09	0.000 13	0.000 15	0.000 18
10.0	0.000 01	0.000 02	0.000 03	0.000 05	0.000 08	0.000 10	0.000 11

TABLE VIII. The Compton profile for Be and its isoelectronic sequence.

q (a.u.)	Be	B^+	C^{2+}	N^{3+}	O^{4+}	F^{5+}	Ne^{6+}
0.00	2.954 54	2.043 08	1.568 54	1.275 91	1.076 54	0.931 60	0.821 30
0.04	2.930 28	2.035 74	1.565 30	1.274 21	1.075 53	0.930 96	0.820 86
0.10	2.807 43	1.997 73	1.548 48	1.265 33	1.070 26	0.927 57	0.818 56
0.20	2.423 87	1.869 55	1.490 39	1.234 27	1.051 74	0.915 64	0.810 42
0.30	1.936 21	1.679 72	1.400 02	1.184 79	1.021 81	0.896 20	0.797 10
0.40	1.470 96	1.456 56	1.285 86	1.120 00	0.981 85	0.869 92	0.778 95
0.50	1.098 66	1.228 08	1.157 59	1.043 75	0.933 58	0.837 66	0.756 43
0.60	0.833 74	1.016 29	1.024 70	0.960 20	0.878 98	0.800 45	0.730 10
0.70	0.658 99	0.834 49	0.895 34	0.873 42	0.820 11	0.759 39	0.700 61
0.80	0.548 19	0.687 60	0.775 58	0.787 07	0.759 03	0.715 64	0.668 61
0.90	0.478 13	0.574 38	0.669 25	0.704 17	0.697 59	0.670 32	0.634 80
1.00	0.432 13	0.490 05	0.578 08	0.626 99	0.637 44	0.624 49	0.599 04
1.20	0.373 92	0.384 01	0.440 42	0.495 01	0.526 04	0.534 98	0.529 04
1.40	0.331 69	0.326 90	0.352 22	0.395 18	0.431 63	0.453 05	0.460 62
1.60	0.293 60	0.291 70	0.297 73	0.324 27	0.356 43	0.382 17	0.397 84
1.80	0.257 54	0.265 05	0.263 29	0.275 77	0.299 32	0.323 66	0.342 67
2.00	0.223 84	0.241 42	0.239 51	0.242 90	0.257 37	0.277 12	0.295 90
2.20	0.193 07	0.219 01	0.220 89	0.220 01	0.227 08	0.241 14	0.257 44
2.40	0.165 55	0.197 46	0.204 54	0.203 02	0.205 14	0.213 82	0.226 56
2.60	0.141 36	0.176 95	0.189 18	0.189 28	0.188 84	0.193 21	0.202 18
2.80	0.120 34	0.157 72	0.174 37	0.177 22	0.176 12	0.177 54	0.183 12
3.00	0.102 26	0.139 96	0.160 02	0.165 99	0.165 57	0.165 35	0.168 22
3.20	0.086 81	0.123 77	0.146 24	0.155 20	0.156 27	0.155 49	0.156 47
3.40	0.073 68	0.109 17	0.133 13	0.144 71	0.147 66	0.147 14	0.147 00
3.60	0.062 55	0.096 10	0.120 80	0.134 51	0.139 43	0.139 73	0.139 14
3.80	0.053 15	0.084 49	0.109 31	0.124 64	0.131 44	0.132 89	0.132 38
4.00	0.045 21	0.074 22	0.098 71	0.115 17	0.123 63	0.126 38	0.126 33
4.50	0.030 39	0.053 62	0.075 95	0.093 53	0.104 99	0.110 88	0.112 88
5.00	0.020 67	0.038 82	0.058 13	0.075 15	0.087 99	0.096 21	0.100 48
6.00	0.009 98	0.020 70	0.033 99	0.047 73	0.060 18	0.070 24	0.077 51
7.00	0.005 10	0.011 40	0.020 10	0.030 19	0.040 48	0.049 96	0.057 97
8.00	0.002 74	0.006 50	0.012 13	0.019 24	0.027 15	0.035 13	0.042 57
9.00	0.001 55	0.003 84	0.007 50	0.012 43	0.018 30	0.024 65	0.031 02
10.0	0.000 91	0.002 35	0.004 75	0.008 17	0.012 46	0.017 37	0.022 57

of the same quality and can be safely used to obtain accurate $\overline{\Pi}(p)$, $\overline{J}(q)$, and moments of the momentum density. Furthermore, the entropy sum $S_p + S_\Pi$ is shown to increase with the inclusion of electron correlation which lends credence to the argument that this quantity may be useful in judging the accuracy of a particular wave function. Based on this criterion, our results also suggest that the quality of the electronic charge distribution obtained from a particular basis depends to a lesser extent on the *amount* of electron correlation included with that basis. This study further validates the opinion that in the construction of accurate densities, density convergence criteria are superior to those based solely on the correlation energy.

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