Electron correlation in momentum space for the neon-atom isoelectronic sequence from F^- through Ar^{8+}

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Accurate momentum-space properties for the neon-atom isoelectronic sequence from F^- through Ar^{8+} are calculated from highly accurate configuration-interaction wave functions that were constructed according to a density convergence criteria. These results should provide a benchmark to which calculations of momentum-space properties derived from other methods may be compared. Our results show that the inclusion of electron correlation has a smaller effect on these properties for the Ne sequence than on other isoelectronic sequences. The entropy sum is observed to increase with the inclusion of electron correlation which further substantiates the claim of its use as a measure of basis set or density quality. [S1050-2947(96)03007-7]

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I. INTRODUCTION

In recent years, electron momentum density (EMD) and other density related properties for atomic and molecular systems have been the subject of a number of investigations [1–4]. In all of these studies, the central theme was a focus of attention on the impact of the inclusion of electron correlation in the wave function. This was due in part to the availability of highly correlated bound state wave functions for a number of atoms and their isoelectronic sequences. Furthermore, such studies are also motivated because of the increasing use of $(e,2e)$ spectroscopy and Compton scattering of photons and high-energy electrons as powerful new techniques for obtaining the EMD [5].

Studies of atoms have played an important role both in the development of experimental techniques and in testing the validity of theoretical approximations such as the plane wave and distorted wave impulse ones. In particular, the noble gases have been studied due to their chemical and physical properties such as (i) gaseous at room temperature, (ii) their relative chemical inertness, and (iii) closed shell electronic structure.

Among the noble gases, the neon atom is an ideal test target and hence a large number of studies, both theoretical and experimental, have been carried out on the EMD. On the experimental side, several measurements for the Compton profile [6–9] and similarly for orbital momentum densities [10–13] are available. On the theoretical side, a number of authors have calculated momentum densities and Compton profiles within the impulse approximation, using bound state wave functions of varying degrees of sophistication [14–19].

Recently, Bunge and Esquivel [20] and Esquivel [21] have obtained a set of charge density optimized configuration-interaction (CI) wave functions with a high degree of induced correlation ($\geqslant 92\%$ of the correlation energy) for neon and its isoelectronic sequence from F^- through Ar^{8+}. The purpose of this paper is to report calculations for the EMD and other density related properties made from CI wave functions of Esquivel, which are substantially better than those used in earlier calculations.

II. THEORETICAL METHODOLOGY

The details of the theoretical methodology are well described in earlier papers [1,2], however, for the sake of clarity, we outline the approach briefly [22,23]. First, the spin-traced one-particle density matrix,

$$\rho(\mathbf{r},\mathbf{r}') = N \int \psi^*(\mathbf{r}'\sigma,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N) \times \psi(\mathbf{r}\sigma,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N) d\sigma d\mathbf{x}_2 d\mathbf{x}_3,\ldots,d\mathbf{x}_N \quad (2.1)$$

is obtained in its natural form

TABLE I. Calculated total energies for the Ne isoelectronic sequence at the HF and CI levels. All energies are given in hartrees.

Ion	CI	HF
F^-	−99.809149	−99.459366
Ne	−128.892006	−128.54705
Na^{1+}	−162.034760	−161.67692
Mg^{2+}	−199.192643	−198.83077
Al^{3+}	−240.365029	−240.00032
Si^{4+}	−285.545715	−285.18091
P^{5+}	−334.739982	−334.36963
S^{6+}	−387.937119	−387.56458
Cl^{7+}	−445.137788	−444.76439
Ar^{8+}	−506.343528	−505.96808

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$$\rho(\mathbf{r},\mathbf{r}')=\sum_k \lambda_k \chi_k(\mathbf{r})\chi_k^*(\mathbf{r}') \tag{2.2}$$

and then transformed into momentum space

$$\pi(\mathbf{p},\mathbf{p}')=(2\pi)^{-3}\int \exp(-i\mathbf{p}\cdot\mathbf{r}-i\mathbf{p}'\cdot\mathbf{r}')\rho(\mathbf{r},\mathbf{r}')d\mathbf{r}\, d\mathbf{r}'. \tag{2.3}$$

In the above ψ is the position space representation of the N-electron wave function and $\chi_i=(\mathbf{r}_i,\sigma_i)$ 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). As in position space, $\pi(\mathbf{p},\mathbf{p}')$ may be expanded in terms of its orthonormal eigenfunctions (the momentum space NO's), $\phi_i(\mathbf{p})$

$$\pi(\mathbf{p},\mathbf{p}')=\sum_k \lambda_k \phi_k(\mathbf{p})\phi_k^*(\mathbf{p}'). \tag{2.4}$$

Given the NO, $\chi_i(\mathbf{r})$, in position space, Eq. (2.4) can be evaluated by computing the Fourier transform (FT),

$$\phi_k(\mathbf{p})=(2\pi)^{-3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}}\chi_k(\mathbf{r})d\mathbf{r}. \tag{2.5}$$

Evaluation of the FT of the kth NO is carried out in a standard manner [24]. The spherically averaged momentum density may be obtained as

$$\overline{\Pi}(p)=\int p^2\pi(\mathbf{p},\mathbf{p})d\Omega. \tag{2.6}$$

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

$$\overline{J(q)}=2\pi\int_q^\infty p\overline{\Pi}(p)dp. \tag{2.7}$$

The moments of the electron momentum density are defined by

TABLE II. The momentum density for Ne and its isoelectronic sequence.

p (a.u.)	F^-	Ne	Na^{1+}	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	Ar^{8+}
0.00000	0.41387	0.25073	0.15422	0.10318	0.07223	0.05254	0.03940	0.03032	0.02382	0.01907
0.04000	0.42044	0.25137	0.15434	0.10321	0.07223	0.05254	0.03940	0.03032	0.02382	0.01907
0.10000	0.45297	0.25460	0.15496	0.10334	0.07226	0.05254	0.03939	0.03031	0.02382	0.01906
0.20000	0.54519	0.26485	0.15700	0.10379	0.07233	0.05253	0.03936	0.03028	0.02379	0.01904
0.30000	0.63667	0.27799	0.15981	0.10439	0.07243	0.05249	0.03930	0.03022	0.02374	0.01900
0.40000	0.68467	0.28970	0.16267	0.10500	0.07249	0.05242	0.03921	0.03014	0.02368	0.01895
0.50000	0.67741	0.29632	0.16479	0.10540	0.07245	0.05229	0.03908	0.03003	0.02359	0.01888
0.60000	0.62697	0.29571	0.16550	0.10540	0.07225	0.05207	0.03890	0.02989	0.02348	0.01880
0.70000	0.55314	0.28750	0.16432	0.10483	0.07184	0.05175	0.03865	0.02970	0.02334	0.01870
0.80000	0.47261	0.27265	0.16103	0.10357	0.07114	0.05130	0.03834	0.02948	0.02318	0.01858
0.90000	0.39570	0.25290	0.15569	0.10154	0.07013	0.05069	0.03794	0.02920	0.02298	0.01843
1.00000	0.32733	0.23016	0.14852	0.09875	0.06878	0.04993	0.03746	0.02888	0.02276	0.01827
1.20000	0.22031	0.18238	0.13021	0.09106	0.06507	0.04788	0.03622	0.02807	0.02220	0.01788
1.40000	0.14761	0.13868	0.10944	0.08131	0.06015	0.04517	0.03460	0.02704	0.02151	0.01739
1.60000	0.09943	0.10289	0.08903	0.07054	0.05437	0.04190	0.03264	0.02579	0.02068	0.01682
1.80000	0.06766	0.07537	0.07073	0.05975	0.04815	0.03823	0.03039	0.02435	0.01972	0.01615
2.00000	0.04665	0.05496	0.05530	0.04964	0.04187	0.03435	0.02793	0.02275	0.01865	0.01541
2.20000	0.03265	0.04014	0.04282	0.04064	0.03586	0.03043	0.02537	0.02105	0.01748	0.01459
2.40000	0.02325	0.02949	0.03300	0.03292	0.03033	0.02663	0.02280	0.01929	0.01626	0.01373
2.60000	0.01687	0.02186	0.02542	0.02649	0.02540	0.02307	0.02028	0.01752	0.01501	0.01283
2.80000	0.01248	0.01638	0.01962	0.02123	0.02112	0.01981	0.01788	0.01578	0.01375	0.01191
3.00000	0.00942	0.01244	0.01522	0.01699	0.01748	0.01690	0.01566	0.01411	0.01251	0.01099
3.20000	0.00725	0.00957	0.01189	0.01361	0.01442	0.01434	0.01362	0.01254	0.01132	0.01008
3.40000	0.00569	0.00746	0.00936	0.01094	0.01188	0.01213	0.01180	0.01109	0.01018	0.00920
3.60000	0.00454	0.00590	0.00743	0.00882	0.00979	0.01023	0.01018	0.00975	0.00911	0.00836
3.80000	0.00369	0.00473	0.00596	0.00715	0.00808	0.00862	0.00875	0.00855	0.00813	0.00756
4.00000	0.00304	0.00385	0.00483	0.00583	0.00669	0.00726	0.00751	0.00748	0.00722	0.00682
4.50000	0.00198	0.00241	0.00298	0.00361	0.00424	0.00476	0.00512	0.00530	0.00531	0.00519
5.00000	0.00137	0.00162	0.00195	0.00234	0.00277	0.00317	0.00351	0.00374	0.00387	0.00390
6.00000	0.00073	0.00083	0.00096	0.00112	0.00131	0.00151	0.00172	0.00191	0.00206	0.00218
7.00000	0.00042	0.00047	0.00054	0.00061	0.00070	0.00080	0.00091	0.00103	0.00113	0.00123
8.00000	0.00025	0.00029	0.00032	0.00037	0.00041	0.00047	0.00053	0.00059	0.00066	0.00073
9.00000	0.00015	0.00018	0.00020	0.00023	0.00026	0.00029	0.00033	0.00036	0.00040	0.00045
10.00000	0.00009	0.00011	0.00013	0.00015	0.00017	0.00019	0.00021	0.00024	0.00026	0.00029

TABLE III. The Compton profile for Ne and its isoelectronic sequence.

q (a.u.)	F^-	Ne	Na^{1+}	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	Ar^{8+}
0.00000	3.46914	2.73912	2.28799	1.97514	1.74077	1.55777	1.41034	1.28895	1.18709	1.10039
0.04000	3.46704	2.73786	2.28721	1.97462	1.74040	1.55751	1.41014	1.28879	1.18697	1.10029
0.10000	3.45551	2.73118	2.28313	1.97189	1.73850	1.55612	1.40910	1.28800	1.18634	1.09979
0.20000	3.40820	2.70669	2.26843	1.96213	1.73168	1.55117	1.40539	1.28514	1.18410	1.09799
0.30000	3.31454	2.66399	2.24354	1.94578	1.72031	1.54292	1.39921	1.28039	1.18037	1.09500
0.40000	3.16799	2.60145	2.20806	1.92275	1.70438	1.53139	1.39058	1.27375	1.17515	1.09083
0.50000	2.97424	2.51841	2.16173	1.89300	1.68388	1.51658	1.37951	1.26524	1.16847	1.08548
0.60000	2.74817	2.41590	2.10460	1.85656	1.65888	1.49855	1.36604	1.25489	1.16034	1.07897
0.70000	2.50710	2.29660	2.03719	1.81361	1.62945	1.47734	1.35020	1.24272	1.15078	1.07131
0.80000	2.26582	2.16447	1.96047	1.76448	1.59575	1.45306	1.33206	1.22878	1.13982	1.06253
0.90000	2.03466	2.02406	1.87583	1.70969	1.55801	1.42582	1.31169	1.21311	1.12749	1.05265
1.00000	1.81971	1.87990	1.78499	1.64989	1.51655	1.39579	1.28918	1.19577	1.11384	1.04169
1.20000	1.44792	1.59584	1.59225	1.51857	1.42396	1.32815	1.23823	1.15640	1.08276	1.01671
1.40000	1.15292	1.33545	1.39682	1.37777	1.32164	1.25211	1.18036	1.11138	1.04705	0.98790
1.60000	0.92423	1.10986	1.21042	1.23480	1.21372	1.17003	1.11698	1.06158	1.00728	0.95565
1.80000	0.74876	0.92143	1.04064	1.09592	1.10430	1.08446	1.04967	1.00803	0.96413	0.92044
2.00000	0.61444	0.76754	0.89111	0.96574	0.99700	0.99788	0.98006	0.95181	0.91833	0.88276
2.20000	0.51134	0.64343	0.76253	0.84708	0.89465	0.91250	0.90977	0.89403	0.87067	0.84318
2.40000	0.43163	0.54389	0.65376	0.74125	0.79926	0.83016	0.84022	0.83578	0.82192	0.80226
2.60000	0.36937	0.46406	0.56268	0.64839	0.71199	0.75224	0.77264	0.77801	0.77282	0.76055
2.80000	0.32013	0.39981	0.48684	0.56787	0.63333	0.67966	0.70799	0.72158	0.72406	0.71860
3.00000	0.28061	0.34776	0.42381	0.49861	0.56325	0.61293	0.64698	0.66717	0.67625	0.67689
3.20000	0.24843	0.30525	0.37138	0.43932	0.50136	0.55225	0.59006	0.61532	0.62988	0.63587
3.40000	0.22180	0.27020	0.32763	0.38869	0.44704	0.49752	0.53746	0.56639	0.58535	0.59591
3.60000	0.19945	0.24100	0.29094	0.34547	0.39957	0.44851	0.48925	0.52063	0.54297	0.55731
3.80000	0.18041	0.21642	0.25998	0.30852	0.35818	0.40483	0.44536	0.47815	0.50295	0.52032
4.00000	0.16400	0.19550	0.23369	0.27686	0.32213	0.36603	0.40560	0.43895	0.46541	0.48513
4.50000	0.13128	0.15488	0.18308	0.21548	0.25090	0.28732	0.32258	0.35472	0.38257	0.40558
5.00000	0.10669	0.12545	0.14719	0.17205	0.19974	0.22924	0.25922	0.28813	0.31478	0.33835
6.00000	0.07213	0.08559	0.10015	0.11619	0.13395	0.15332	0.17400	0.19532	0.21658	0.23711
7.00000	0.04947	0.05996	0.07087	0.08243	0.09488	0.10831	0.12276	0.13805	0.15391	0.16998
8.00000	0.03419	0.04254	0.05116	0.06011	0.06951	0.07947	0.09006	0.10129	0.11310	0.12535
9.00000	0.02380	0.03043	0.03735	0.04453	0.05198	0.05976	0.06792	0.07650	0.08552	0.09494
10.00000	0.01671	0.02192	0.02748	0.03331	0.03937	0.04565	0.05218	0.05899	0.06611	0.07352

$$\langle p^n\rangle = 4\pi\int_0^\infty p^{n+2}\pi(p)dp, \quad -2\leqslant n\leqslant 4, \tag{2.8}$$

where the limits on n arise from the p^{-8} asymptotic behavior of $\overline{\Pi}(p)$ and the fact that $\overline{\Pi}(p)$ is finite and nonzero at $p=0$ [25]. $\langle p\rangle$ 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 [25]. $\langle p^{-1}\rangle$ is simply the peak value of $J(q=0)$ of the ICP. $\langle p^2\rangle$ is proportional to the nonrelativistic kinetic energy. The expectation values, E_4 and H_0 are the quasirelativistic energy

$$E_4 = \langle p^2\rangle/(2m_e) - \langle p^4\rangle/(8m_e c^2) \tag{2.9}$$

and the complete relativistic kinetic-energy operator

$$H_0 = m_e c^2\{[1+p^2/(m_e^2c^2)]^{1/2}-1\}. \tag{2.10}$$

In Eq. (2.9), the first term is the nonrelativistic kinetic energy and the second one is the Breit-Pauli mass velocity correction. m_e is the mass of the electron and c is the speed of light in vacuum (for details see Ref. [26]). 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 [26]. The general expressions for the asymptotic expansions of $\overline{\Pi}(p)$ [27] are

$$\overline{\Pi}(p) = A_0 + A_2p^2 + A_4p^4 + O(p^6) \tag{2.11}$$

for small p, and

$$\overline{\Pi}(p) = B_8p^{-8} + B_{10}p^{-10} + B_{12}p^{-12} + O(p^{-14}) \tag{2.12}$$

for large p. These coefficients have been tabulated for Hartree-Fock wave functions [26].

In addition to the properties above, we have computed the momentum space information entropy [28]

$$S_\Pi = -\int \pi(\mathbf{p},\mathbf{p})\ln\pi(\mathbf{p},\mathbf{p})d\mathbf{p}. \tag{2.13}$$

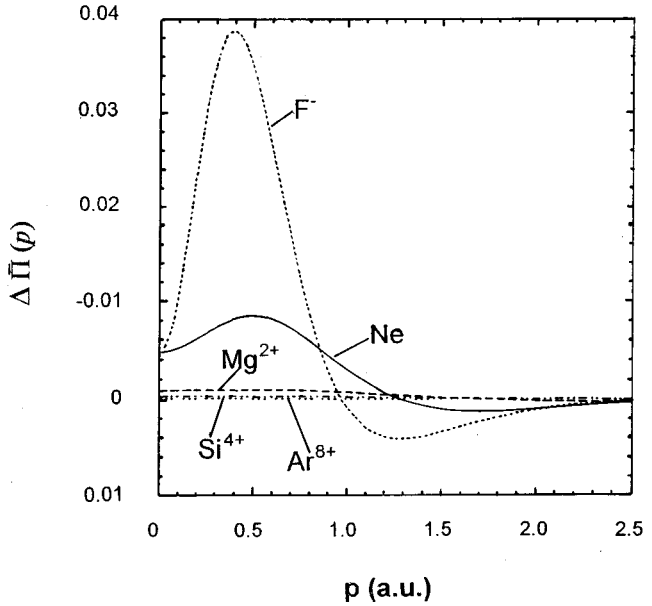

FIG. 1. Momentum-density differences for some members of the neon isoelectronic sequence.

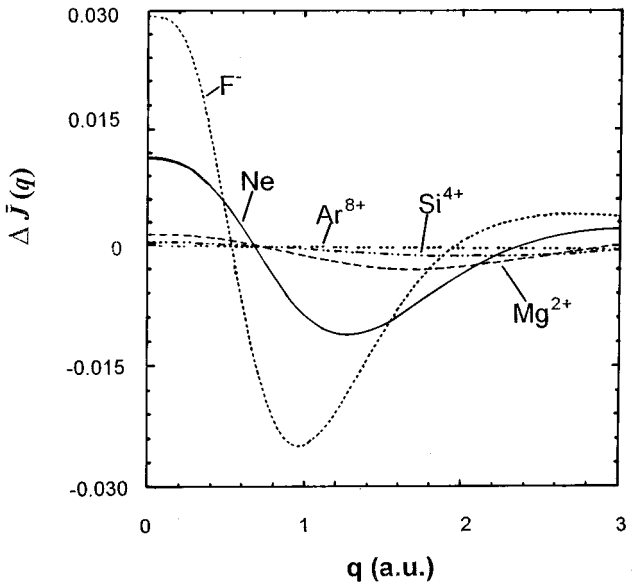

FIG. 2. Compton profile differences for some members of the neon isoelectronic sequence.

We have also calculated S_ρ, the analgous 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 [28] 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 quality. Such studies have been performed on a variety of atoms and molecular systems [29]. All integrals pertaining to the respective properties were calculated numerically 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 momentum-space properties of neon and its isoelectronic sequence were calculated from Hartree-Fock (HF) [30] and CI wave functions [21,22] using Eqs. (2.6)–(2.8). The CI expansion of the neon wave function contains 486 terms in a $[6s,7p,3d,2f,$ and $1f]$ Slater-type orbital (STO) basis set and are distributed among the K, L, and intershell regions. These terms include all single and double excitations, of the K and L shells and intershell ($1s2s$ and $1s2p$ excitations), into the virtual orbitals. This procedure yields energies that approximately represent 93% of the correlation energy (see Table I). No triple and quadruple excitations

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 F^- through Al^{3+} at the CI level. All numbers are in atomic units; numbers in brackets indicate powers of 10.

Property	F^-	Ne	Na^{1+}	Mg^{2+}	Al^{3+}
$\langle p^{-2}\rangle$	9.0105	5.5527	3.8497	2.8657	2.2237
$\langle p^{-1}\rangle$	6.9383	5.4782	4.5760	3.9503	3.4815
$\langle p\rangle$	30.0142	35.2412	40.4205	45.5635	50.6920
$\langle p^2\rangle$	199.607	257.751	324.045	398.369	480.722
$\langle p^3\rangle$	2.5501[3]	3.5915[3]	4.8968[3]	6.4966[3]	8.4209[3]
$\langle p^4\rangle$	6.3741[4]	9.8719[4]	1.4669[5]	2.1060[5]	2.9371[5]
E_4	−4.2429[−1]	−6.5712[−1]	−9.7645[−1]	−1.4018	−1.9551
$\langle H_0\rangle$	5.4376[−2]	9.2007[−2]	1.4794[−1]	2.2806[−1]	3.3962[−1]
S_Π	35.7927	41.3815	45.9644	49.8711	53.2952
S_γ	4.23488	−2.33118	−7.41906	−11.64297	−15.29224
$S_\Pi + S_\gamma$	40.0276	39.0503	38.5453	38.2281	38.0030
A_0	4.1387[−1]	2.5073[−1]	1.5422[−1]	1.0318[−1]	7.2227[−2]
A_2	4.1496	3.9881[−1]	7.5809[−2]	1.6373[−2]	3.0622[−3]
A_4	−2.4743[1]	−1.2119	−1.6375[−1]	−3.4493[−2]	−9.5991[−3]
B_8/Z^5	0.92770	1.58615	2.57670	4.01193	6.03624
B_{10}/Z^7	−3.37434	−6.99489	−13.55977	−24.70429	−43.44633
B_{12}/Z^9	9.93360	22.36282	51.56557	106.97828	222.77527

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 Si^{4+} through Ar^{8+} at the CI level. All numbers are in atomic units; numbers in brackets indicate powers of 10.

Property	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	Ar^{8+}
$\langle p^{-2}\rangle$	1.7795	1.4577	1.2169	1.0316	0.8861
$\langle p^{-1}\rangle$	3.1156	2.8207	2.5779	2.3742	2.2008
$\langle p\rangle$	55.8101	60.9250	66.0345	71.1408	76.2449
$\langle p^{2}\rangle$	571.075	669.462	775.856	890.254	1012.66
$\langle p^{3}\rangle$	1.0700[4]	1.3364[4]	1.6444[4]	1.9970[4]	2.3973[4]
$\langle p^{4}\rangle$	3.9944[5]	5.3167[5]	6.9448[5]	8.9225[5]	1.1298[6]
E_4	−2.6588	−3.5390	−4.6228	−5.9392	−7.5206
$\langle H_0\rangle$	4.9031[−1]	6.8975[−1]	9.4826[−1]	1.2776	1.6915
S_Π	56.3486	59.1096	61.6289	63.9472	66.0952
S_γ	−18.51572	−21.41063	−24.03863	−26.44711	−28.67109
$S_\Pi+S_\gamma$	37.8329	37.6990	37.5903	37.5001	37.4241
A_0	5.2544[−2]	3.9403[−2]	3.0322[−2]	2.3825[−2]	1.9068[−2]
A_2	−2.8867[−4]	−1.0139[−3]	−1.0501[−3]	−8.8852[−4]	−7.1229[−4]
A_4	−3.1830[−3]	−1.2037[−3]	−4.9096[−4]	−2.1843[−4]	−1.0299[−4]
B_8/Z^5	8.80188	12.50608	17.36188	23.61799	31.57162
B_{10}/Z^7	−72.90073	−118.21104	−185.37078	−282.45076	−420.94214
B_{12}/Z^9	446.45674	793.46597	1398.93423	2378.15380	3935.91610

were included. The importance of these excitations was examined but it was noticed that the effects were always less than 0.01% in all of the space. For the ions of the isoelectronic sequence, the corresponding nonrelativistic CI wave functions were calculated in a systematic manner, i.e., all singly and doubly excited configurations obtained by promoting K and L electrons in the Hartree-Fock configuration are included in the wave function. The final CI expansions contain 723 terms in $[7s,7p,4d,4f,2g]$ STO basis sets allowing for over 92% of the correlation energy.

These compact CI wave functions for neon and its isoelectronic sequence represent the final stage of a convergent sequence, both in the charge density and its derivative. These densities satisfy the cusp condition [31] and asymptotic behavior [32]. Fully converged results for one-electron properties in position space have been reported [33].

The momentum density and Compton profile for neon and its isoelectronic sequence are tabulated in Tables II and III. In order to study the differences in the momentum density and Compton profile obtained from HF and CI wave func-

TABLE VI. The expectation values of the momentum density, the quasirelativistic kinetic-energy operator, the relativistic kinetic-energy operator, the information entropies, and asymptotic coefficients for F^- through Al^{3+} at the HF level. All numbers are in atomic units; numbers in brackets indicate powers of 10.

Property	F^-	Ne	Na^{1+}	Mg^{2+}	Al^{3+}
$\langle p^{-2}\rangle$	8.7972	5.4795	3.8269	2.8545	2.2176
$\langle p^{-1}\rangle$	6.8797	5.4558	4.5691	3.9474	3.4802
$\langle p\rangle$	29.9661	35.1964	40.3681	45.5127	50.6439
$\langle p^{2}\rangle$	198.9176	257.0936	323.3558	397.6597	479.9994
$\langle p^{3}\rangle$	2.5435[+3]	3.5843[+3]	4.8891[+3]	6.4876[+3]	8.4108[+3]
$\langle p^{4}\rangle$	6.3655[+4]	9.8596[+4]	1.4655[+5]	2.1040[+5]	2.9344[+5]
E_4	−4.2372[−1]	−6.5629[−1]	−9.7549[−1]	−1.4005	−1.9532
$\langle H_0\rangle$	5.4367[−2]	9.1929[−2]	1.4781[−1]	2.2783[−1]	3.3923[−1]
S_Π	35.7618	41.3451	45.9201	49.8322	53.2619
S_γ	3.96101	−2.47329	−7.48988	−11.68605	−15.32137
$S_\Pi+S_\gamma$	39.7228	38.8718	38.4302	38.1462	37.9405
A_0	4.0950[−1]	2.4592[−1]	1.5284[−1]	1.0233[−1]	7.1754[−2]
A_2	3.5287	3.6119[−1]	6.9937[−2]	1.5728[−2]	2.9831[−3]
A_4	−2.0409[+1]	−1.0761	−1.5052[−1]	−3.2970[−2]	−9.3002[−3]
B_8/Z^5	0.92776	1.58483	2.57421	4.00756	6.02836
B_{10}/Z^7	−3.39139	−6.99796	−13.49727	−24.61929	−43.22294
B_{12}/Z^9	9.22736	22.46007	50.33300	106.01984	218.45003

TABLE VII. The expectation values of the momentum density, the quasirelativistic kinetic-energy operator, the relativistic kinetic-energy operator, the information entropies, and asymptotic coefficients for Si^{4+} through Ar^{8+} at the HF level. All numbers are in atomic units; numbers in brackets indicate powers of 10.

Property	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	Ar^{8+}
$\langle p^{-2}\rangle$	1.7758	1.4560	1.2157	1.0309	0.8854
$\langle p^{-1}\rangle$	3.1148	2.8207	2.5779	2.3743	2.2008
$\langle p\rangle$	55.7662	60.8821	65.9947	71.1038	76.2105
$\langle p^2\rangle$	570.3601	668.7356	775.1270	889.5274	1011.9358
$\langle p^3\rangle$	1.0689[+4]	1.3351[+4]	1.6431[+4]	1.9957[+4]	2.3959[+4]
$\langle p^4\rangle$	3.9921[+5]	5.3127[+5]	6.9403[+5]	8.9180[+5]	1.1293[+6]
E_4	−2.6573	−3.5364	−4.6198	−5.9362	−7.5171
$\langle H_0\rangle$	4.9015[−1]	6.8903[−1]	9.4746[−1]	1.2769	1.6907
S_Π	56.3210	59.0850	61.6077	63.9291	66.0795
S_γ	−18.53749	−21.42539	−24.05067	−26.45698	−28.67953
$S_\Pi+S_\gamma$	37.7835	37.6596	37.5570	37.4721	37.3400
A_0	5.2265[−2]	3.9268[−2]	3.0239[−2]	2.3773[−2]	1.9026[−2]
A_2	−2.7936[−4]	−9.9414[−4]	−1.0450[−3]	−8.8448[−4]	−7.0670[−4]
A_4	−3.1071[−3]	−1.1883[−3]	−4.8207[−4]	−2.1509[−4]	−1.0190[−4]
B_8/Z^5	8.79898	12.49038	17.34433	23.60243	31.55259
B_{10}/Z^7	−72.81070	−117.48209	−184.50471	−281.75297	−420.00817
B_{12}/Z^9	425.30513	776.09342	1376.16551	2352.24972	3901.17946

tions, we have displayed difference functions defined as

$$\Delta\overline{\Pi}(p)=\overline{\Pi}_{eb}(p)-\overline{\Pi}_{\mathrm{HF}}(p) \quad \text{and} \quad \Delta\overline{J}(q)=\overline{J}_{eb}-\overline{J}_{\mathrm{HF}} \tag{3.1}$$

in Figs. 1 and 2 for the neon isoelectronic sequence. Figure 1 shows the electron correlation effect on $\overline{\Pi}(p)$: It is seen that there is a small deviation between the CI and HF densities up to 2.0 a.u. The deviations follow the general trend, i.e., decreasing with increasing nuclear charge. The largest difference occurs for F^- ($\approx$6%), Ne ($\approx$3%), and then decreases rapidly thereafter along the isoelectronic sequence becoming almost negligible for Ar^{8+}. This clearly shows that the impact of the inclusion of electron correlation is not significant for closed shell atoms such as neon and its isoelectronic ions. Obviously, this trend is different from that seen for the beryllium and lithium isoelectronic sequences [1,2]. These qualitative changes observed on going to closed shell systems may be understood intuitively. The main correlation effects for these atoms are promotions of electrons into $3s$ and $3p$ states, which are both more diffuse in position space than the orbitals occupied in the HF picture. Thus the overall effect is an expansion. Since more localized p orbitals get depopulated and more diffuse ones become populated, one may expect some nodal oscillations in the difference profile in both position and momentum spaces. This is what is observed in Fig. 1. A similar variation for the charge density, momentum density, and internally folded density has been observed [34].

A similar variation can be seen in Fig. 2 for $\Delta\overline{J}(q)$. Again, we see here that the correlation effects on this quantity are not as important as for the $\Delta\overline{\Pi}(p)$. The intensity of the correlation shift near the peak of the profile is about 1% for F^- and 0.5% for Ne. It is almost negligible for the rest of the isoelectronic sequence. The fact that the relative differences are smaller in this case may be due to an averaging out of $\overline{\Pi}(p)$ from the integration [see Eq. (2.7)].

Atomic properties $\langle p^n\rangle(-2\leqslant n\leqslant 4)$, E_4, H_0, information entropies, and both small and large p expansion coefficients of $\overline{\Pi}(p)$ are compiled in Tables IV and V and in Tables VI and VII for the CI and HF results, respectively. Note that $\langle p^2\rangle$ and $\langle p^4\rangle$ values for the neon atom have been reported previously [35] and used to test the accuracy of values obtained from a variational Monte Carlo method. It is observed that all properties obtained from CI and HF wave functions are in good agreement of the order of 1% except the small p coefficients, which differ as much as 10% for a few members of the sequence. This is expected as these coefficients depend on the low momentum region of $\overline{\Pi}(p)$, which is sensitive to electron correlation. This agreement is also seen on comparison of the asymptotic coefficients, which test the differences in the core regions. The behavior of the entropy sum further validates its use as a measure of density quality as there is an increase on going from the HF to the CI levels for all of the atoms of the sequence. S_π and S_γ are both seen to increase on going from HF to CI. This is unlike the beryllium atom sequence where S_γ was seen to decrease, and S_π increase, from HF to CI [1].

Inspection of $\overline{\Pi}(p)$ in Table II reveals that $\overline{\Pi}(p)$ is nonmonotonic for F^- through Al^{3+} and is monotonic for Si^{4+} and higher Z members of the sequence. This behavior has been noted previously for both HF and correlated wave functions [36]. Consistent with this is the fact that A_2 is positive for F^- through Al^{3+} and negative for the higher Z members of the sequence.

IV. SUMMARY AND CONCLUSIONS

Accurate calculations of various momentum-space quantities for the neon isoelectronic sequence are reported. These

calculations employed highly accurate configuration-interaction wave functions that were constructed using density convergence criteria. The values for the momentum-space properties when compared with those from Hartree-Fock calculations indicate that the effects of electron correlation are less than those of other closed shell isoelectronic sequences. It is noted that the entropy sum, $S_\pi + S_\gamma$, increases from the HF to the CI level, which gives further credibility to the argument of its use as a measure of basis set or density quality. The results presented here should provide a benchmark for testing valence properties of wave functions and densities obtained by other methods.

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