Electron-momentum densities of singly charged ions

Toshikatsu Koga,[1,2] Hisashi Matsuyama,[2] E. Romera,[1] J. S. Dehesa,[1] and Ajit J. Thakkar[3]
[1]*Instituto Carlos I de Física Teórica y Computacional, Facultad de Ciencias, Universidad de Granada, Granada E-18071, Spain*
[2]*Department of Applied Chemistry, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan*
[3]*Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2*
(Received 8 September 1998; revised manuscript received 21 December 1998)

Spherically averaged electron momentum densities $\Pi(p)$ are constructed by the numerical Hartree-Fock method for 54 singly charged atomic cations from He^+ (atomic number $Z=2$) to Cs^+ ($Z=55$) and 43 anions from H^- ($Z=1$) to I^- ($Z=53$) in their experimental ground state. As in the case of neutral atoms, the Hartree-Fock momentum densities for all these ions can be classified into three types; 28 cations and 10 anions have a unimodal density with a maximum at $p=0$, 22 cations and 21 anions have a unimodal density with a maximum at $p>0$, and 4 cations and 12 anions have a bimodal density with a primary maximum at $p=0$ and a secondary maximum at $p>0$. [S1050-2947(99)04006-8]

PACS number(s): 31.90.+s, 32.80.Cy, 31.10.+z

I. INTRODUCTION

In contrast to spherically averaged electron densities $\rho(r)$ in position space [1–3], it is known [4–17] that spherically averaged electron densities $\Pi(p)$ in momentum space for neutral atoms are not always monotonically decreasing functions even in their ground state. As reviewed in Ref. [17], however, the literature classification [4–16] of atoms with monotonic and nonmonotonic momentum densities has been contradictory for some cases, mainly due to inaccuracies of the Roothaan-Hartree-Fock or basis-set-expansion wave functions employed [18,19]. Very recently [17], precise modality assignments of momentum densities have been made using numerical Hartree-Fock wave functions; the coexistence of monotonic and nonmonotonic momentum densities was confirmed for the ground states of the neutral atoms from H ($Z=1$) to Lr ($Z=103$), where Z denotes atomic number. The Hartree-Fock momentum densities $\Pi(p)$ of the 103 neutral atoms were separated into three categories according to their modalities [11,17].

Type I. Unimodal $\Pi(p)$ with a maximum at $p=0$.

Type II. Unimodal $\Pi(p)$ with a local minimum at $p=0$ and a maximum at $p_{max}>0$.

Type III. Bimodal $\Pi(p)$ with a primary maximum at $p=0$, a secondary maximum at $p_{max}>0$, and a local minimum at p_{min} with $0<p_{min}<p_{max}$.

Moreover, subshell analysis of the momentum density clarified [11,17] that the three modalities originate from competing contributions of the outermost *s*, *p*, and *d* subshells. The contribution from *f* subshells is not significant. The results were summarized by six simple rules [17].

In the present paper, we study properties of the Hartree-Fock momentum densities $\Pi(p)$ for the experimental ground states of 97 singly charged ions with fewer than 55 electrons ($N<55$), i.e., 54 cations from He^+ ($Z=2$) to Cs^+ ($Z=55$) and 43 anions from H^- ($Z=1$) to I^- ($Z=53$). The corresponding position densities $\rho(r)$ were shown [20] numerically to be monotonically decreasing functions for all these ions. The momentum densities of the cations were examined by Westgate *et al.* [11], but unfortunately they relied on the Roothaan-Hartree-Fock wave functions of Clementi and Roetti [18] and McLean and McLean [19], which are now known [21–24] to suffer from nontrivial errors and inaccuracies. To our knowledge, momentum densities of the anionic species have not been reported in the literature. As in our previous work [17], we remove basis-set artifacts by using numerical Hartree-Fock wave functions to construct electron momentum densities for all the atomic ions. The next section outlines our computational procedures. In Sec. III, the results are presented and discussed. We will find that the Hartree-Fock momentum densities for the 97 ions again fall into the three distinct categories observed for the neutral atoms. Hartree atomic units are used throughout this paper.

II. COMPUTATIONAL OUTLINE

The theoretical background for the computation of atomic Hartree-Fock electron momentum densities $\Pi(p)$ and their subshell components $\Pi_{nl}(p)$, specified by the principal n and azimuthal l quantum numbers, has been given in a previous paper [17]. For the singly charged cations He^+ through Cs^+ and anions H^- through I^-, we performed numerical Hartree-Fock calculations using a modified and enhanced version of the MCHF72 program [25]. The experimental ground states [26,27] (see Ref. [28] for an explicit tabulation) were considered for all the species except for two anions. For Sc^- and Pd^-, the experimental ground states were reported [27] to be $[Ar]4s^2 3d 4p$, ^1D and $[Kr]5s 4d^{10}$, ^2S, respectively, but we could not obtain meaningful solutions for these states in numerical (and Roothaan-) Hartree-Fock calculations. Thus the second lowest states, $[Ar]4s^2 3d^2$, ^3F for Sc^- and $[Kr]5s^2 4d^9$, ^2D for Pd^-, were examined instead in the present work. The details of our numerical procedures were the same as those employed before for the neutral atoms [17], except that the increment h was halved and the number of mesh points N_p was doubled, because anionic species include very diffuse position-space orbitals compared to neutral and cationic species.

III. MODALITIES OF MOMENTUM DENSITIES

Examination of the Hartree-Fock momentum densities $\Pi(p)$ for the 97 singly charged ions shows that the modalities of the $\Pi(p)$ fall into one of the three categories found [11,17] for neutral atoms and summarized in the Introduction. No new types of modality were observed even for anions.

Type I. The 28 cations with $Z=2-9$, 12–16, 20–22, 25, 26, 32–34, 38–40, 43, 50–52 and the 10 anions with $Z=1$, 3, 11, 19, 21–23, 37, 40, 41 have unimodal $\Pi(p)$ with a maximum at $p=0$.

Type II. The 22 cations with $Z=10$, 11, 17–19, 23, 24, 27–29, 35–37, 41 42, 44–47, 53–55 and the 21 anions with $Z=5-9$, 13–17, 31–35, 39, 49–53 have unimodal $\Pi(p)$ with a local minimum at $p=0$ and a maximum at $p_{\max}>0$.

Type III. The four cations with $Z=30$, 31, 48, 49, and the 12 anions with $Z=24-29$ and 42–47 have bimodal $\Pi(p)$ with a primary maximum at $p=0$, a secondary maximum at $p_{\max}>0$, and a local minimum at $p_{\min}$ between the two maxima: $0<p_{\min}<p_{\max}$.

The present classification for the cations is the same as that of Westgate *et al.* [11] except for two species V^+ ($Z=23$) and Fe^+ ($Z=26$). Westgate *et al.* [11] found that V^+ has a type-I, instead of type-II, momentum density and Fe^+ has a type-II, instead of type-I, momentum density, but this is because they examined the Hartree-Fock ground states whereas we examine the experimental ground states.

Based on the analysis of $\Pi(p)$ of neutral atoms, we have previously proposed [17] three primary rules: (i) the overall behavior of $\Pi(p)$ is essentially determined by the contributions of the outermost *s*, *p*, *d* subshells; (ii) the maximum at $p=0$ in the type-I and -III modalities is essentially due to the outermost *s* subshell; (iii) the maximum away from $p=0$ in the type-II and -III modalities originates from the outermost *p* and *d* subshells; and three secondary rules: (iv) when only the outermost *s* contribution is dominant, the type-I modality results; (v) when the outermost *p* contribution is large enough relative to the outermost *s* contribution, a type-II momentum density appears; (vi) when the *p* and *d* contributions are small, relative to the *s* contribution, but work cooperatively, the secondary maximum in a type-III momentum density appears.

These six rules are found to hold also for the 97 singly charged ions with a small modification to rule (v). Our study of subshell momentum densities $\Pi_{nl}(p)$ has confirmed the validity of the rules (i)–(iii). Further, examination of the electronic configuration and the modality of $\Pi(p)$ clarifies that common to the cations and anions, the type-I modality appears when $n_s>n_p,n_d$ [rule (iv)], where n_l is the principal quantum number of the highest occupied subshell with symmetry l ($=s, p,$ or d). The type-II modality arises if $n_s=n_p>n_d$ and there is a sufficient *p* contribution [rule (v)]. For cations, we need at least five electrons in the outermost *p* subshell to have a type-II momentum density, but for anions only two electrons are sufficient. For some cations of the transition atoms, a type-II modality also appears when $n_s=n_p=n_d$, as found for the neutral Pd atom. In these cases, both the *p* and *d* contributions are required to create a maximum at $p>0$. Thus rule (v) should be modified as follows. (v′) When the sum of the outermost *p* and *d* contributions overwhelms the opposing contribution of the outermost *s* subshell, a type-II momentum density appears.

The extremum characteristics of the type-II momentum densities are summarized in Table I. For cations with regular electronic configurations, both the local minimum $\Pi(0)$ and maximum $\Pi(p_{\max})$ values decrease while the location $p_{\max}$ of the maximum increases, when the number of outermost *p* or *d* electrons increases. The same is true for the type-II momentum densities of anions. When two or more isoelectronic species have a type-II momentum density, we invariably observe inequalities $\Pi^+(x)<\Pi^0(x)<\Pi^-(x)$, in which x is either 0 or $p_{\max}$, and the superscripts +, 0, and − refer to the cationic, neutral, and anionic properties respectively; with some exceptions, we also find $p^-_{\max}<p^0_{\max}<p^+_{\max}$. Type-III momentum densities of the cations and anions obey the rule (vi), and emerge when $n_s=n_p+1=n_d+1$, the outermost *p* subshell is fully occupied, and the *d* contribution is large. For anions, five or more *d* electrons induce the type-III modality, but for cations ten *d* electrons are required. The extremum characteristics of the 16 type-III momentum densities are given in Table II. As we have seen in Table I for the type-II momentum density, the five characteristic quantities in Table II show a definite trend according to the change in the numbers of the outermost *s* electrons for the four cations and of the outermost *d* electrons for the 12 anions. For isoelectronic series, the extremum characteristic of the type-III momentum densities always satisfy the inequalities $\Pi^+(0)<\Pi^0(0)<\Pi^-(0)$, $\Pi^+(x)<\Pi^0(x)<\Pi^-(x)$, and $x^-<x^0<x^+$, for $x=p_{\min}$ and $p_{\max}$.

The modality of the momentum density $\Pi(p)$ depends strongly on the atomic number Z within an isoelectronic series. Smith and co-workers [13,29] observed that monotonically decreasing type-I densities become more common as Z increases. For the Ne isoelectronic series, they reported that $\Pi(p_{\max})/\Pi(0)$ approaches unity and $p_{\max}$ approaches 0 as Z increases; for $Z>14$, type-II nonmonotonicity is completely replaced by type-I monotonicity. This behavior can be understood with the help of a $1/Z$ perturbation expansion [29,30]. Smith *et al.* [29] showed that the momentum density of any closed-shell atomic species is monotonically decreasing if the bare Coulomb potential model [31] is assumed, and this monotonic density constitutes the leading component of the $1/Z$ expansion.

The results of this study conform with the discussion of Smith and co-workers [13,30]. The simplest case we met is the $N=6$ isoelectronic systems with the $1s^22s^22p^2$ electronic configuration: N^+ and C have a type-I momentum density, while B^- has a type-II density. In general, we observed a remarkable difference between anions and cations in the relative frequency with which monotonic (type I) versus nonmonotonic (types II and III) momentum densities appear. About 50% of the 54 neutral atoms and 54 singly charged cations have monotonic densities as opposed to 23% of the 43 anions. The relative frequency of type-III momentum densities steadily decreases from 28% in anions, via 19% in neutral atoms, to only 7% in singly charged cations.

In summary, the present results for 97 singly charged ions and previous ones for neutral atoms with $Z\leqslant 103$ [17] strongly suggest the general rule that, within the Hartree-

TABLE I. Extremum characteristics of type-II momentum densities of singly charged atoms.

		Local minimum	Maximum				Local minimum	Maximum	
Z	Cation	$\Pi(0)$	p_{max}	$\Pi(p_{max})$	Z	Anion	$\Pi(0)$	p_{max}	$\Pi(p_{max})$
10	Ne^+	0.2047	0.3906	0.2079	5	B^-	3.7572	0.1574	5.0207
11	Na^+	0.1537	0.5830	0.1632	6	C^-	1.8848	0.2203	2.2219
17	Cl^+	0.8529	0.2719	0.8686	7	N^-	1.0329	0.2882	1.4144
18	Ar^+	0.6584	0.4017	0.7061	8	O^-	0.6357	0.3545	0.9409
19	K^+	0.5205	0.4945	0.5909	9	F^-	0.4214	0.4249	0.6552
23	V^+	0.2221	0.8077	0.3180	13	Al^-	6.7901	0.1403	10.1140
24	Cr^+	0.1888	0.8732	0.2747	14	Si^-	3.9222	0.1984	4.9219
27	Co^+	0.1212	1.0240	0.1990	15	P^-	2.4628	0.2467	3.4476
28	Ni^+	0.1064	1.0737	0.1801	16	S^-	1.6804	0.2972	2.4715
29	Cu^+	0.0940	1.1252	0.1632	17	Cl^-	1.2097	0.3504	1.8345
35	Br^+	1.1190	0.2965	1.1627	31	Ga^-	5.7089	0.1419	9.7489
36	Kr^+	0.9200	0.3922	1.0172	32	Ge^-	3.8206	0.2037	5.0625
37	Rb^+	0.7687	0.4631	0.9047	33	As^-	2.6825	0.2442	3.9042
41	Nb^+	0.3727	0.7388	0.5759	34	Se^-	2.0018	0.2878	3.0322
42	Mo^+	0.3251	0.7994	0.5087	35	Br^-	1.5532	0.3333	2.4137
44	Ru^+	0.2526	0.8958	0.4213	39	Y^-	31.2602	0.0633	46.1702
45	Rh^+	0.2253	0.9451	0.3841	49	In^-	8.0820	0.1377	11.4319
46	Pd^+	0.2022	0.9943	0.3514	50	Sn^-	5.5658	0.1823	6.7485
47	Ag^+	0.1824	1.0449	0.3218	51	Sb^-	4.0496	0.2210	5.4218
53	I^+	1.7920	0.2447	1.8431	52	Te^-	3.1154	0.2590	4.3815
54	Xe^+	1.5109	0.3340	1.6474	53	I^-	2.4828	0.2978	3.6124
55	Cs^+	1.2913	0.3964	1.4971					

Fock approximation, electron momentum densities for ground-state atoms and atomic ions have exactly three types of modalities. The physical origin of the three different modalities in $\Pi(p)$ of the neutral atoms and singly charged ions can be commonly explained by six rules obtained previously from a subshell analysis of contributions to $\Pi(p)$. In the literature (see, e.g., [16] and references therein), the monotonicity of $\Pi(p)$ and related functions has been successfully

TABLE II. Extremum characteristics of type-III momentum densities of singly charged atoms.

		Primary maximum	Local minimum		Secondary maximum	
Z	Atom	$\Pi(0)$	p_{min}	$\Pi(p_{min})$	p_{max}	$\Pi(p_{max})$
			Cations			
30	Zn^+	2.1206	1.1360	0.1207	1.3095	0.1214
31	Ga^+	3.1872	1.2978	0.0942	1.5069	0.0951
48	Cd^+	2.8709	0.9249	0.2506	1.1783	0.2579
49	In^+	4.4403	1.0564	0.2078	1.3095	0.2137
			Anions			
24	Cr^-	85.1381	0.7545	0.2914	0.8077	0.2916
25	Mn^-	75.1373	0.7945	0.2621	0.8356	0.2621
26	Fe^-	68.6851	0.8055	0.2338	0.8955	0.2342
27	Co^-	63.4852	0.8211	0.2093	0.9498	0.2103
28	Ni^-	59.1569	0.8383	0.1881	1.0017	0.1898
29	Cu^-	56.0311	0.8522	0.1687	1.0583	0.1714
42	Mo^-	85.1414	0.6533	0.5422	0.7497	0.5448
43	Tc^-	76.9679	0.6678	0.4898	0.7975	0.4947
44	Ru^-	72.5273	0.6767	0.4375	0.8531	0.4471
45	Rh^-	69.2893	0.6872	0.3913	0.9066	0.4056
46	Pd^-	66.8099	0.6986	0.3507	0.9584	0.3694
47	Ag^-	65.3879	0.7096	0.3137	1.0116	0.3368

applied to derive various inequality relations among important physical properties such as momentum moments $\langle p^k \rangle$, Compton peak height $J(0)$, average position density $\langle \rho \rangle$, interelectronic repulsion energy $\langle 1/r_{12} \rangle$, and so on. The precise knowledge of the modality of $\Pi(p)$ for atomic ions, obtained in the present work, would be useful for such studies.

ACKNOWLEDGMENTS

This work has been supported in part by Fundación de Banco Bilbao Vizcaya (BBV) of Spain, in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan, and in part by the Natural Sciences and Engineering Research Council of Canada.

[1] G. Sperber, Int. J. Quantum Chem. **5**, 189 (1971).
[2] H. Weinstein, P. Politzer, and S. Srebrenik, Theor. Chim. Acta **38**, 159 (1975).
[3] T. Koga, Theor. Chim. Acta **95**, 113 (1997).
[4] W. Weyrich, P. Pattison, and B. G. Williams, Chem. Phys. **41**, 271 (1979).
[5] A. J. Thakkar, A. M. Simas, and V. H. Smith, Jr., Chem. Phys. **63**, 175 (1981).
[6] A. J. Thakkar, J. Chem. Phys. **76**, 747 (1982).
[7] S. R. Gadre and R. L. Matcha, J. Chem. Phys. **76**, 748 (1982).
[8] S. R. Gadre, S. Chakravorty, and R. K. Pathak, J. Chem. Phys. **78**, 4581 (1983).
[9] A. Harmalkar, A. M. Simas, V. H. Smith, Jr., and W. M. Westgate, Int. J. Quantum Chem. **23**, 811 (1983).
[10] S. R. Gadre and S. Chakravorty, Chem. Phys. Lett. **120**, 101 (1985).
[11] W. M. Westgate, A. M. Simas, and V. H. Smith, Jr., J. Chem. Phys. **83**, 4054 (1985).
[12] W. M. Westgate, R. P. Sagar, A. Farazdel, V. H. Smith, Jr., A. M. Simas, and A. J. Thakkar, At. Data Nucl. Data Tables **48**, 213 (1991).
[13] R. P. Sagar, R. O. Esquivel, H. Schmider, A. N. Tripathi, and V. H. Smith, Jr., Phys. Rev. A **47**, 2625 (1993).
[14] A. J. Thakkar, A. L. Wonfor, and W. A. Pedersen, J. Chem. Phys. **87**, 1212 (1987).
[15] J. C. Angulo, Phys. Rev. A **48**, 4768 (1993).
[16] E. Romera, T. Koga, and J. S. Dehesa, Z. Phys. D **42**, 251 (1997).
[17] T. Koga, H. Matsuyama, H. Inomata, E. Romera, J. S. Dehesa, and A. J. Thakkar, J. Chem. Phys. **109**, 1601 (1998).
[18] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).
[19] A. D. McLean and R. S. McLean, At. Data Nucl. Data Tables **26**, 197 (1981).
[20] T. Koga and H. Matsuyama, Theor. Chem. Acc. **98**, 129 (1997).
[21] C. F. Bunge, J. A. Barrientos, A. V. Bunge, and J. A. Cogordan, Phys. Rev. A **46**, 3691 (1992).
[22] T. Koga, H. Tatewaki, and A. J. Thakkar, Phys. Rev. A **47**, 4510 (1993).
[23] T. Koga and A. J. Thakkar, Phys. Rev. A **48**, 4775 (1993); **50**, 891 (1994).
[24] T. Koga, S. Watanabe, K. Kanayama, R. Yasuda, and A. J. Thakkar, J. Chem. Phys. **103**, 3000 (1995).
[25] C. Froese-Fischer, Comput. Phys. Commun. **4**, 107 (1972).
[26] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, NSRDS-NBS 34 (National Bureau of Standards, Washington, D.C., 1970); *Atomic Energy Levels*, NSRDS-NBS 35. (National Bureau of Standards, Washington, D.C., 1971), Vols. 1–3.
[27] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).
[28] T. Koga, H. Tatewaki, and A. J. Thakkar, J. Chem. Phys. **100**, 8140 (1994).
[29] V. H. Smith, Jr., D. D. Robertson, and A. N. Tripathi, Phys. Rev. A **42**, 61 (1990).
[30] S. R. Singh and V. H. Smith, Jr., Z. Phys. **255**, 83 (1972).
[31] N. H. March, Phys. Rev. A **33**, 88 (1986).