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Analytical Hartree-Fock electron densities for singly charged cations and anions

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Abstract. The Hartree-Fock (HF) electron density has an important property that it is identical to the unknown exact density to the first order in the perturbation theory. We generate the spherically averaged HF electron density $\rho(r)$ by using the numerical HF method for the singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^- in their ground state. The resultant density is then accurately fitted into an analytical function $F(r)$, which is expressed by a linear combination of basis functions $r^{n_i}\exp(-\zeta_i r)$. The present analytical approximation $F(r)$ has the following properties: (1) $F(r)$ is nonnegative, (2) $F(r)$ is normalized, (3) $F(r)$ reproduces the HF moments $\langle r^k \rangle$ ($k = -2$ to $+6$), (4) $F(0)$ is equal to $\rho(0)$, (5) $F'(0)$ satisfies the cusp condition and (6) $F(r)$ has the correct exponential decay in the long-range asymptotic region. The present results together with our previous ones for neutral atoms provide a compilation of accurate analytical approximations of the HF electron densities for all the neutral and singly charged atoms with the number of electrons $N \leq 54$.

Key words: Electron density – Hartree-Fock – Singly-charged atoms

1 Introduction

Many important physical and chemical properties of atoms and molecules are derived [1, 2] in quantum mechanics from spin-reduced one-electron densities, which are a "condensation" of N-electron wave functions into the one-electron space. However, since many-electron Schrödinger equations can not be solved exactly, the exact wave functions and hence the exact electron densities are in general not obtained. This is not the case when we work within the Hartree-Fock (HF) framework. If an HF determinantal wave function is used as the zero-order wave function, the first-order perturbation theory shows that the exact wave function does not contain any singly substituted determinants due to the Brillouin's theorem. This results that the first-order correction to the electron density is zero according to the Condon-Slater rules. In other words, the HF electron density is identical to the exact density to the first order in the perturbation theory.

For atoms and atomic ions, the HF wave functions and the associated electron densities are accurately obtained by the numerical HF (NHF) method [3, 4]. However, the resultant HF densities are inconveniently given in the form of numerical tables as a function of discrete radial values. Thus the recent progress (for a review see, e.g. [5]) on the properties of the spherically averaged HF electron densities is based on analytical but approximate density functions constructed (see, e.g. [6]) from the Roothaan-Hartree-Fock (RHF) wave functions of Clementi and Roetti [7] and McLean and McLean [8]. As a consequence, some of the new findings [5] on the electron density are not very rigid, since they have been deduced from approximate RHF densities that do not satisfy the rigorous HF requirements such as the electron-nucleus cusp condition and the long-range asymptotic behaviour. Moreover, it has been recently pointed out [9–12] that the RHF wave functions of Clementi and Roetti [7] and McLean and McLean [8] include nontrivial errors and inaccuracies.

Analytical HF densities, that combine both the accuracy of NHF densities and the analytical convenience of RHF densities, have been very recently reported by Koga [13] for the ground-state neutral atoms from He ($Z = 2$) to Lr ($Z = 103$). He first generated the HF electron density $\rho(r)$ by the NHF method, and then fitted the discrete density $\rho(r)$ very accurately into an analytical function $F(r)$ which is a linear combination of density basis functions $r^{n_i}\exp(-\zeta_i r)$. In addition to nonnegativity and normalization, the function $F(r)$ has been designed to reproduce the NHF moments $\langle r^k \rangle$ with $k = -2$ to $+6$, have the NHF $\rho(0)$ value at the nucleus, satisfy the cusp relation and have the correct exponential decay in the long-range asymptotic r region. Some of these properties are difficult to be realized in the tradi-

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tional method of deriving electron densities from RHF wave functions. High accuracy, analytical tractability and sufficient compactness are characteristics of the analytical HF density $F(r)$. In the case of the Lr atom ($Z = 103$), for example, the function $F(r)$ consists of only 30 density basis functions, while the RHF density with the total energy errors of about 0.0005 hartrees requires more than 300 such functions.

In the present paper, we report analytical HF electron density functions $F(r)$ for 96 atomic ions using the method developed previously [13] for the neutral atoms. The singly charged 53 cations from Li^+ to Cs^+ and 43 anions from H^- to I^-, with the number of electrons $N \leq 54$, are considered in their ground state. To our knowledge, no analytical and accurate HF electron densities have been reported in the literature for these ions. Since many studies on the atomic electron density have hitherto concentrated on neutral species, the present results are expected to provide a reliable basis for their further extension to ionic species. The next section outlines our computational methods of generating NHF density $\rho(r)$ and constrained fitting of $\rho(r)$ to analytical functions $F(r)$. The results are presented and discussed in Sect. 3 and simple applications are given in Sect. 4. Hartree atomic units are used throughout this paper.

2 Computational method

NHF calculations have been performed for the singly charged cations from Li^+ to Cs^+ and anions from H^- to I^- in their ground state, using a modified and enhanced version of the MCHF72 program [14]. The experimental ground electronic configurations and terms [15, 16] are summarized in Table 1 for the cations and in Table 2 for the anions. There are two exceptions, however. For the anions Sc^- and Pd^-, the experimental ground states are reported [16] to be $[\mathrm{Ar}]4s(2)3d(1)4p(1)$, ^{1}D and $[\mathrm{Kr}]5s(1)4d(10)$, ^{2}S, but we could not obtain meaningful solutions to these states in NHF (and RHF) computations. Thus the second-lowest states as shown in Table 2 have been examined for these anions.

In the NHF calculations, the radial variable r has been transformed to a set of discrete radial values r_j by the formula

$$r_j = \frac{1}{Z}\exp[x_{\min} + h(j-1)], \quad (j = 1, 2, \ldots, N_p) \tag{1}$$

where Z is the atomic number. The discretization parameters have been chosen to be $x_{\min} = -6.0$, $h = 0.03$ and $N_p = 512$ based on a careful examination of the stability of numerical procedures involved in MCHF72. The present NHF results are reliable in ten significant figures for the total E, kinetic T and potential V energies and seven or more significant figures for other quantities such as the orbital energies ε_i and moments $\langle r^k \rangle$. The virial ratios V/T do not deviate from the exact value -2 by more than 1×10^{-10}. The local error of any occupied orbital at any r_j dose not exceed 1×10^{-10}, and the same accuracy holds for the resultant electron density $\rho(r_j)$. The NHF density satisfies the electron-nucleus cusp relation [17, 18] $\rho'(0) = -2Z\rho(0)$, because the orbital cusp condition [19] has been imposed on in the construction of NHF orbitals.

An analysis of the spherically averaged electron density $\rho(r)$ for atoms has shown [13] that $\rho(r)$ can be expanded as

$$\rho(r) \cong F(r) = f_0(r) + \sum_{i=1}^{N_f} c_i f_i(r) \ , \tag{2}$$

where

$$f_0(r) = \rho(0)\exp(-2Zr), \quad f_i(r) = r^{n_i}\exp(-\zeta_i r) \ , \tag{3}$$

and $F(r)$ is an analytical approximation to $\rho(r)$. The function $F(r)$ contains linear $\{c_i\}$ and nonlinear $\{n_i, \zeta_i\}$ parameters. They are so determined that $F(r)$ satisfies the following six conditions at least:

1. Nonnegativity: $F(r) \geq 0$ for $0 \leq r < \infty$. (4a)

2. Normalization: $4\pi \int_0^\infty F(r) r^2 dr = N$. (4b)

3. Moments: $4\pi \int_0^\infty F(r) r^{k+2} dr = \langle r^k \rangle$, $(k = -2, \ldots, +6)$ (4c)

where $\langle r^k \rangle$ are NHF moment values. A special case of $k = 0$ includes the normalization [Eq. (4b)], i.e. $\langle r^0 \rangle = N$.

4. Value at the nucleus: $F(0) = \rho(0)$. (4d)

5. Cusp relation: $F'(0) = -2Z\, F(0)$. (4e)

6. Long-range behaviour: $F(r) \approx \exp(-\sqrt{-8\varepsilon_h r})$, (4f)

for a large r, where ε_h is the orbital energy of the highest occupied orbital h. Equation (4f) follows from the long-range asymptotic behaviour of the HF orbital [20–22].

For the conditions in Eqs. (4b) and (4c) to be fulfilled, we define a function $\tilde{\Delta}$ following the Lagrange method of undetermined multipliers,

$$\tilde{\Delta} \equiv \Delta - \sum_{k=-2}^{+6} \lambda_k \left\{ 4\pi \int_0^\infty F(r) r^{k+2} dr - \langle r^k \rangle \right\} \ , \tag{5}$$

in which

$$\Delta \equiv 4\pi \int_0^\infty [\delta(r)]^2 \, r^2 dr \ , \tag{6}$$

$$\delta(r) \equiv F(r) - \rho(r) \ , \tag{7}$$

and $\{\lambda_k\}$ are the undetermined multipliers. From $\partial\tilde{\Delta}/\partial c_i = 0$ and $\partial\tilde{\Delta}/\partial\lambda_k = 0$, we obtain a set of $N_f + 9$ linear equations [13], which determine $\{c_i\}$. Following the discretization of the radial variable in the NHF method, all the integrals in Eqs. (5) and (6) are replaced with the corresponding summations over discrete N_p radial points. Although the powers $\{n_i\}$ in the basis function [Eq. (3)] can be any nonnegative real numbers,

Table 1. Numerical Hartree-Fock (NHF) results for singly charged cations. Note that $N = Z - 1$

Z	Cation	Configuration	Term	$-E$	h	$-\varepsilon_h$	$\rho(0)/N$
3	Li^+	1*s*(2)	$^1\mathrm{S}$	7.236415201	1*s*	2.7923644	6.836071799
4	Be^+	[He]2*s*(1)	$^2\mathrm{S}$	14.27739481	2*s*	0.6661462	11.69163823
5	B^+	[He]2*s*(2)	$^1\mathrm{S}$	24.23757518	2*s*	0.8738233	18.15737151
6	C^+	[He]2*s*(2)2*p*(1)	$^2\mathrm{P}$	37.29222377	2*p*	0.9047596	25.69020429
7	N^+	[He]2*s*(2)2*p*(2)	$^3\mathrm{P}$	53.88800501	2*p*	1.1100685	34.54915571
8	O^+	[He]2*s*(2)2*p*(3)	$^4\mathrm{S}$	74.37260568	2*p*	1.3269095	44.73290389
9	F^+	[He]2*s*(2)2*p*(4)	$^3\mathrm{P}$	98.83172020	2*p*	1.4441222	56.27209769
10	Ne^+	[He]2*s*(2)2*p*(5)	$^2\mathrm{P}$	127.8178141	2*p*	1.6065983	69.13439701
11	Na^+	[He]2*s*(2)2*p*(6)	$^1\mathrm{S}$	161.6769626	2*p*	1.7971924	83.31980151
12	Mg^+	[Ne]3*s*(1)	$^2\mathrm{S}$	199.3718097	3*s*	0.5414396	99.35829457
13	Al^+	[Ne]3*s*(2)	$^1\mathrm{S}$	241.6746705	3*s*	0.6522984	116.9820162
14	Si^+	[Ne]3*s*(2)3*p*(1)	$^2\mathrm{P}$	288.5731311	3*p*	0.5858718	135.9052880
15	P^+	[Ne]3*s*(2)3*p*(2)	$^3\mathrm{P}$	340.3497759	3*p*	0.7199781	156.2658922
16	S^+	[Ne]3*s*(2)3*p*(3)	$^4\mathrm{S}$	397.1731828	3*p*	0.8617881	178.0632202
17	Cl^+	[Ne]3*s*(2)3*p*(4)	$^3\mathrm{P}$	459.0485907	3*p*	0.9387851	201.3085476
18	Ar^+	[Ne]3*s*(2)3*p*(5)	$^2\mathrm{P}$	526.2745343	3*p*	1.0453382	225.9894556
19	K^+	[Ne]3*s*(2)3*p*(6)	$^1\mathrm{S}$	599.0175794	3*p*	1.1705466	252.1057672
20	Ca^+	[Ar]4*s*(1)	$^2\mathrm{S}$	676.5700126	4*s*	0.4163189	279.9303398
21	Sc^+	[Ar]4*s*(1)3*d*(1)	$^3\mathrm{D}$	759.5391440	4*s*	0.4492774	309.0597792
22	Ti^+	[Ar]4*s*(1)3*d*(2)	$^4\mathrm{F}$	848.2034008	4*s*	0.4756649	339.6203335
23	V^+	[Ar]4*s*(0)3*d*(4)	$^5\mathrm{D}$	942.6707837	3*d*	0.5842464	371.4036466
24	Cr^+	[Ar]4*s*(0)3*d*(5)	$^6\mathrm{S}$	1043.139393	3*d*	0.6492315	404.8250876
25	Mn^+	[Ar]4*s*(1)3*d*(5)	$^7\mathrm{S}$	1149.649383	4*s*	0.5443657	439.9443654
26	Fe^+	[Ar]4*s*(1)3*d*(6)	$^6\mathrm{D}$	1262.213012	4*s*	0.5603010	476.2758404
27	Co^+	[Ar]4*s*(0)3*d*(8)	$^3\mathrm{F}$	1381.128750	3*d*	0.7346465	513.7852450
28	Ni^+	[Ar]4*s*(0)3*d*(9)	$^2\mathrm{D}$	1506.591099	3*d*	0.7692822	552.9901657
29	Cu^+	[Ar]4*s*(0)3*d*(10)	$^1\mathrm{S}$	1638.728242	3*d*	0.8101422	593.6351087
30	Zn^+	[Ar]4*s*(1)3*d*(10)	$^2\mathrm{S}$	1777.567545	4*s*	0.6117058	636.0063014
31	Ga^+	[Ar]4*s*(2)3*d*(10)	$^1\mathrm{S}$	1923.059722	4*s*	0.6880693	679.9778070
32	Ge^+	[Ar]4*s*(2)3*d*(10)4*p*(1)	$^2\mathrm{P}$	2075.086491	4*p*	0.5645233	725.2411434
33	As^+	[Ar]4*s*(2)3*d*(10)4*p*(2)	$^3\mathrm{P}$	2233.888335	4*p*	0.6734106	771.9860262
34	Se^+	[Ar]4*s*(2)3*d*(10)4*p*(3)	$^4\mathrm{S}$	2399.558574	4*p*	0.7864043	820.2114295
35	Br^+	[Ar]4*s*(2)3*d*(10)4*p*(4)	$^3\mathrm{P}$	2572.045211	4*p*	0.8378824	869.9239131
36	Kr^+	[Ar]4*s*(2)3*d*(10)4*p*(5)	$^2\mathrm{P}$	2751.567394	4*p*	0.9155539	921.1147950
37	Rb^+	[Ar]4*s*(2)3*d*(10)4*p*(6)	$^1\mathrm{S}$	2938.219931	4*p*	1.0085999	973.7836908
38	Sr^+	[Kr]5*s*(1)	$^2\mathrm{S}$	3131.373777	5*s*	0.3788875	1028.139480
39	Y^+	[Kr]5*s*(2)	$^1\mathrm{S}$	3331.472882	5*s*	0.4355508	1084.062701
40	Zr^+	[Kr]5*s*(1)4*d*(2)	$^4\mathrm{F}$	3538.809305	5*s*	0.4444511	1141.077994
41	Nb^+	[Kr]5*s*(0)4*d*(4)	$^5\mathrm{D}$	3753.389513	4*d*	0.5411126	1199.556803
42	Mo^+	[Kr]5*s*(0)4*d*(5)	$^6\mathrm{S}$	3975.333703	4*d*	0.6102590	1259.690059
43	Tc^+	[Kr]5*s*(1)4*d*(5)	$^7\mathrm{S}$	4204.594360	5*s*	0.5098361	1321.542961
44	Ru^+	[Kr]5*s*(0)4*d*(7)	$^4\mathrm{F}$	4441.321956	4*d*	0.6814328	1384.405929
45	Rh^+	[Kr]5*s*(0)4*d*(8)	$^3\mathrm{F}$	4685.664172	4*d*	0.7259596	1448.980515
46	Pd^+	[Kr]5*s*(0)4*d*(9)	$^2\mathrm{D}$	4937.675930	4*d*	0.7721779	1515.033571
47	Ag^+	[Kr]5*s*(0)4*d*(10)	$^1\mathrm{S}$	5197.481334	4*d*	0.8253211	1582.563530
48	Cd^+	[Kr]5*s*(1)4*d*(10)	$^2\mathrm{S}$	5464.878609	5*s*	0.5483328	1651.831707
49	In^+	[Kr]5*s*(2)4*d*(10)	$^1\mathrm{S}$	5739.978392	5*s*	0.6070558	1722.690852
50	Sn^+	[Kr]5*s*(2)4*d*(10)5*p*(1)	$^2\mathrm{P}$	6022.678323	5*p*	0.5075173	1794.866155
51	Sb^+	[Kr]5*s*(2)4*d*(10)5*p*(2)	$^3\mathrm{P}$	6313.165941	5*p*	0.5969990	1868.538734
52	Te^+	[Kr]5*s*(2)4*d*(10)5*p*(3)	$^4\mathrm{S}$	6611.503394	5*p*	0.6889556	1943.708694
53	I^+	[Kr]5*s*(2)4*d*(10)5*p*(4)	$^3\mathrm{P}$	6917.627273	5*p*	0.7264343	2020.381061
54	Xe^+	[Kr]5*s*(2)4*d*(10)5*p*(5)	$^2\mathrm{P}$	7231.708947	5*p*	0.7862694	2098.549984
55	Cs^+	[Kr]5*s*(2)4*d*(10)5*p*(6)	$^1\mathrm{S}$	7553.810329	5*p*	0.8587594	2178.215408

we employ $n_i = 2$ for all i based on the examination and discussion of the previous study [13]. Consequently, the function $F(r)$ exactly satisfies the conditions given by Eqs. (4d) and (4e). The smallest exponent $\zeta_{\min}$ of the basis functions in Eq. (3) is taken to be $\sqrt{-8\varepsilon_h}$ for the requirement in Eq. (4f). We also added a condition that the exponents constitute a geometrical series,

$$\zeta_i = \zeta_{\min}\alpha^{i-1}, \quad \zeta_{\min} = \sqrt{-8\varepsilon_h} \quad (i = 1, 2, \ldots, N_f) \tag{8}$$

in order to avoid numerical linear dependence among the basis functions [Eq. (3)] and to reduce the number of exponent parameters. The optimum spacing parameter α between two neighbouring exponents is determined by the conjugate directions method [23] so as to minimize Δ defined by Eq. (6). The number of basis functions N_f is chosen to be the minimal value that satisfies our accuracy criterion $\Delta \leq 5 \times 10^{-10}$. The nonnegativity of $F(r)$ was checked for all the r_j radial values during the optimization of the parameter α. We have recorded the maximum local deviation $\delta_{\max} = \max\{|\delta(r_j)|\}_{j=1}^{N_p}$, its location $r_{\max}$ and the relative deviation $R_{\max} = \delta_{\max}/\rho(r_{\max})$.

Table 2. NHF results for singly charged anions. Note that $N = Z + 1$

Z	Anion	Configuration	Term	$-E$	h	$-\varepsilon_h$	$\rho(0)/N$
1	H^-	$1s(2)$	^1S	0.487929734	$1s$	0.0462224	0.154596680
3	Li^-	$[He]2s(2)$	^1S	7.428232061	$2s$	0.0145377	3.452906259
5	B^-	$[He]2s(2)2p(2)$	^3P	24.51922137	$2p$	0.0264677	11.93724474
6	C^-	$[He]2s(2)2p(3)$	^4S	37.70884362	$2p$	0.0770517	18.13119049
7	N^-	$[He]2s(2)2p(4)$	^3P	54.32195889	$2p$	0.0937069	25.67571706
8	O^-	$[He]2s(2)2p(5)$	^2P	74.78974593	$2p$	0.1297733	34.53734596
9	F^-	$[He]2s(2)2p(6)$	^1S	99.45945391	$2p$	0.1809868	44.71847211
11	Na^-	$[Ne]3s(2)$	^1S	161.8551260	$3s$	0.0133513	69.47923107
13	Al^-	$[Ne]3s(2)3p(2)$	^3P	241.8782653	$3p$	0.0201838	100.1721426
14	Si^-	$[Ne]3s(2)3p(3)$	^4S	288.8896602	$3p$	0.0618071	117.6599167
15	P^-	$[Ne]3s(2)3p(4)$	^3P	340.6988736	$3p$	0.0772184	136.5995309
16	S^-	$[Ne]3s(2)3p(5)$	^2P	397.5384302	$3p$	0.1077993	156.9713241
17	Cl^-	$[Ne]3s(2)3p(6)$	^1S	459.5769253	$3p$	0.1503032	178.7763095
19	K^-	$[Ar]4s(2)$	^1S	599.1619170	$4s$	0.0103206	226.9326532
21	Sc^-	$[Ar]4s(2)3d(2)$	^3F	759.6887738	$4s$	0.0160318	280.8819398
22	Ti^-	$[Ar]4s(2)3d(3)$	^4F	848.3725498	$4s$	0.0159223	309.9902165
23	V^-	$[Ar]4s(2)3d(4)$	^5D	942.8631322	$4s$	0.0163431	340.5416797
24	Cr^-	$[Ar]4s(2)3d(5)$	^6S	1043.337097	$4s$	0.0166366	372.5302493
25	Mn^-	$[Ar]4s(2)3d(6)$	^5D	1149.729110	$4s$	0.0179248	405.9830790
26	Fe^-	$[Ar]4s(2)3d(7)$	^4F	1262.367074	$4s$	0.0188610	440.8722997
27	Co^-	$[Ar]4s(2)3d(8)$	^3F	1381.351810	$4s$	0.0197091	477.2035309
28	Ni^-	$[Ar]4s(2)3d(9)$	^2D	1506.821133	$4s$	0.0204936	514.9771395
29	Cu^-	$[Ar]4s(2)3d(10)$	^1S	1638.964145	$4s$	0.0210826	554.1890995
31	Ga^-	$[Ar]4s(2)3d(10)4p(2)$	^3P	1923.260381	$4p$	0.0180267	637.3801388
32	Ge^-	$[Ar]4s(2)3d(10)4p(3)$	^4S	2075.394742	$4p$	0.0593390	681.1685154
33	As^-	$[Ar]4s(2)3d(10)4p(4)$	^3P	2234.222940	$4p$	0.0736591	726.4544059
34	Se^-	$[Ar]4s(2)3d(10)4p(5)$	^2P	2399.904726	$4p$	0.1014659	773.2170400
35	Br^-	$[Ar]4s(2)3d(10)4p(6)$	^1S	2572.536273	$4p$	0.1393301	821.4571167
37	Rb^-	$[Kr]5s(2)$	^1S	2938.354900	$5s$	0.0095321	922.5693825
39	Y^-	$[Kr]5s(2)4d(1)5p(1)$	^1D	3331.683116	$5p$	0.0031494	1029.710532
40	Zr^-	$[Kr]5s(2)4d(3)$	^4F	3538.994500	$5s$	0.0174304	1085.344371
41	Nb^-	$[Kr]5s(2)4d(4)$	^5D	3753.578216	$5s$	0.0173953	1142.538015
42	Mo^-	$[Kr]5s(2)4d(5)$	^6S	3975.526268	$5s$	0.0172352	1201.205155
43	Tc^-	$[Kr]5s(2)4d(6)$	^5D	4204.764631	$5s$	0.0182856	1261.365231
44	Ru^-	$[Kr]5s(2)4d(7)$	^4F	4441.528477	$5s$	0.0188343	1322.998001
45	Rh^-	$[Kr]5s(2)4d(8)$	^3F	4685.875582	$5s$	0.0192304	1386.107486
46	Pd^-	$[Kr]5s(2)4d(9)$	^2D	4937.891544	$5s$	0.0195268	1450.694089
47	Ag^-	$[Kr]5s(2)4d(10)$	^1S	5197.700050	$5s$	0.0196384	1516.755557
49	In^-	$[Kr]5s(2)4d(10)5p(2)$	^3P	5740.175141	$5p$	0.0214043	1653.687889
50	Sn^-	$[Kr]5s(2)4d(10)5p(3)$	^4S	6022.972657	$5p$	0.0606191	1724.372175
51	Sb^-	$[Kr]5s(2)4d(10)5p(4)$	^3P	6313.481518	$5p$	0.0723568	1796.565917
52	Te^-	$[Kr]5s(2)4d(10)5p(5)$	^2P	6611.827949	$5p$	0.0964576	1870.253868
53	I^-	$[Kr]5s(2)4d(10)5p(6)$	^1S	6918.075883	$5p$	0.1291594	1945.437357

3 Results and discussion

The NHF results for the total energy E, the orbital energy ε_h of the highest occupied orbital h and the density at nucleus $\rho(0)$ divided by N are tabulated in Table 1 for the 53 cations and in Table 2 for the 43 anions.

As mentioned in Sect. 2, the ε_h value determines the smallest exponent $\zeta_{\min} = \sqrt{-8\varepsilon_h}$ in the analytical density expression, and governs the manner of electron distribution in an atom. In Fig. 1a, we plot the $\zeta_{\min}$ values for the cations as a function of Z. Within a period, the group 1 cation with a closed shell has the largest $\zeta_{\min}$ and therefore the most tight electron density. The opposite is true for the group 2 cations with singly occupied s-orbitals; they have the smallest $\zeta_{\min}$ values and the most diffuse density distributions. An analogous discussion holds for the anions as depicted in Fig.1b: a group 17 anion has the largest $\zeta_{\min}$, whereas a group 1 anion has the smallest compared to the other anions in the same period. An exception is found for Y^- in the fifth period, which has the highest occupied $5p$ orbital (see Table 2). All $\zeta_{\min}$ values of the anions are smaller than those of the cations, reflecting the more diffuse nature of the electron densities in anions.

For singly charged ions, the HF $\rho(0)$ values have been reported [24] in five significant figures based on the improved RHF wave functions. A comparison of these with the present NHF values shows that the RHF $\rho(0)$ values are insufficiently accurate at the last figure. However, the observation [24] $\rho_Z^0(0) \cong \rho_Z^+(0) \cong \rho_Z^-(0) \propto Z^3$ is correct particularly for a large Z, where ρ_Z^0, ρ_Z^+ and ρ_Z^- denote respectively the electron densities of neutral, cationic and anionic species with atomic number Z. In Tables 1 and 2, we additionally find an approximate and empirical relation $\rho_Z^+(0)/N \cong \rho_{Z+1}^-(0)/N$, which can be roughly explained by the Z^3 dependence of the $\rho_Z(0)$ value.

The performance of our analytical HF electron density construction is summarized in Table 3. We note that

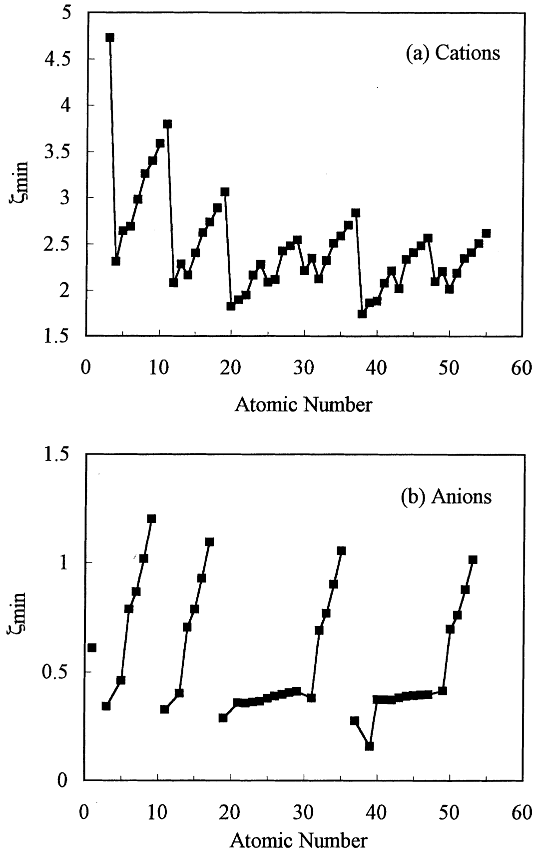

Fig. 1a, b. The smallest exponents ζ_{min} as a function of Z: **a** cations **b** anions

the normalization $\langle r^0 \rangle = 1$, instead of N, is used in Table 3 in order to assign the same relative accuracies to species with different N.

The number N_f of expansion terms, required to satisfy $\Delta < 5 \times 10^{-10}$, increases generally as we go down the periodic table from the first to the fifth period. The N_f values are approximately independent of Z within a period. The second-, third-, fourth- and fifth-period cations require roughly 13, 17, 20 and 22 expansion terms, respectively, though there are exceptions. For the group 1 cations with closed shells, their $F(r)$ are described by fewer terms than those of the remaining cations of that period, as expected from the examination of the ζ_{min} values. In the case of anions, the N_f values are again roughly equal within a period, and the second-, third-, fourth- and fifth-period anions require about 12, 14, 18 and 23 expansion terms, respectively. The maximum N_f values for the cations and anions are respectively 25 (Sc^+) and 24 (Y^-, Ag^- and In^-). The compactness of the present analytical HF electron densities is clearly seen. From the analysis of ζ_{min} values, we have anticipated that the anions will need more expansion terms than the cations, but this has been found to be true only for a limited number of ions.

However, the optimum spacing parameters α show a marked difference between the cations and anions. For cations, the optimum α-value ranges from 1.07 to 1.27, while for anions it ranges from 1.27 to 1.39. The larger values for anions are needed to cover a wide range of exponent values which describe both the tight and diffuse parts of anionic electron densities.

For all the ions examined, the radius r_{max}, where δ_{max} appears, is very small (in the order of 10^{-3}–10^{-2} bohr) and the largest local deviation in $F(r)$ appears in the vicinity of the nucleus. However, the relative errors R_{max} are very small, in the order of 10^{-7}–10^{-5}. Thus the functions $F(r)$ are concluded to be highly accurate analytical approximations to the NHF electron densities.

Although the expansion coefficients $\{c_i\}$ are not shown, we have confirmed that the coefficient of the term with the smallest exponent is positive for all the ions; this guarantees that the present density function $F(r)$ is positive for a very large r.

4 Simple applications

Using the analytical approximations $F(r)$, we have examined the sign of the first derivative of the HF density. At any discretized radial points r_j specified by Eq. (1) along with the parameter values given below it, we have confirmed that $\rho'(r) < 0$ holds for all the cations ($Z = 3$–55) and anions ($Z = 1$–53) as well as the neutral atoms ($Z = 2$–103). Thus the numerical results show that the ground-state HF densities have monotonicity of first order. According to Angulo et al. [5], however, rigorous theoretical proof of this property is still an open problem.

Galvez and Porras [25, 26] introduced a function

$$g(r) \equiv \rho(r) + \frac{1}{2Z}\rho'(r) \ , \tag{9}$$

which satisfies $g(0) = 0$ and $g(\infty) = 0$. The first equality is the electron-nucleus cusp condition [17, 18] and the second equality follows from the long-range asymptotic behaviour of the HF density. Assuming that $g(r) \geq 0$, Galvez and Porras [25] derived various inequalities among $\rho(0)$ and $\langle r^k \rangle$. A few examples are

$$\rho(0) \ \leq \ \frac{Z}{2\pi}\langle r^{-2} \rangle \ , \tag{10}$$

$$\langle r^{k-3} \rangle \ \leq \ \frac{2Z}{k}\langle r^{k-2} \rangle . \quad (k > 0) \ . \tag{11}$$

Previously [13], we have reported that $g(r) \geq 0$ holds for all the neutral atoms from He to Lr in their ground state. In addition, the examination of the present HF densities shows that the conjecture $g(r) \geq 0$ is again true for all singly charged cations and anions with $N \leq 54$. Thus the inequalities derived by Galvez and Porras [25] are confirmed to be valid for the neutrals ($Z = 2$–103), cations ($Z = 3$–55), and anions ($Z = 1$–53) within the HF framework.

For a convex electron density (i.e. $\rho(r)$ with non-negative second derivative $\rho''(r)$ for $0 \leq r < \infty$), Angulo et al. [27] derived another set of inequalities among $\rho(0)$ and $\langle r^k \rangle$. An example of their results is

$$\frac{1}{6\pi}\frac{\langle r^{-2} \rangle^2}{\langle r^{-1} \rangle} \ \leq \ \rho(0) \ \leq \ \frac{Z}{\pi}\langle r^{-2} \rangle \ . \tag{12}$$

Table 3. Analytical approximations for HF electron densities of singly charged cations and anions

Z	Cation	N_f	α	Δ	$r_{\max}$	$R_{\max}$	Anion	N_f	α	Δ	$r_{\max}$	$R_{\max}$
1							H^-	9	1.313232	9.60*d*-13	5.49*d*-1	9.68*d*-6
3	Li^+	9	1.073374	2.75*d*-10	2.06*d*-1	1.54*d*-5	Li^-	12	1.373404	6.75*d*-11	8.90*d*-2	5.16*d*-6
4	Be^+	12	1.155750	4.19*d*-10	1.33*d*-1	7.23*d*-6						
5	B^+	12	1.162272	3.94*d*-10	1.20*d*-1	1.14*d*-5	B^-	12	1.379201	2.22*d*-10	4.08*d*-2	6.82*d*-6
6	C^+	13	1.172405	5.01*d*-11	6.19*d*-2	2.48*d*-6	C^-	11	1.376158	4.38*d*-10	3.83*d*-2	7.88*d*-6
7	N^+	13	1.168937	2.61*d*-10	1.52*d*-1	1.32*d*-5	N^-	11	1.383331	2.28*d*-10	3.09*d*-2	5.62*d*-6
8	O^+	13	1.187348	1.53*d*-10	2.79*d*-2	3.05*d*-6	O^-	12	1.338395	2.18*d*-10	2.79*d*-2	5.83*d*-6
9	F^+	15	1.149864	1.63*d*-10	1.08*d*-1	8.94*d*-6	F^-	11	1.373529	1.85*d*-10	6.47*d*-2	6.22*d*-6
10	Ne^+	13	1.184996	2.59*d*-10	5.33*d*-2	4.19*d*-6						
11	Na^+	14	1.176399	3.03*d*-10	1.06*d*-1	1.20*d*-5	Na^-	16	1.384231	6.42*d*-11	2.03*d*-2	2.90*d*-6
12	Mg^+	14	1.246524	1.02*d*-10	1.65*d*-2	1.99*d*-6						
13	Al^+	17	1.183869	1.99*d*-10	4.62*d*-2	4.87*d*-6	Al^-	15	1.389301	3.54*d*-10	1.67*d*-2	4.62*d*-6
14	Si^+	17	1.196833	2.37*d*-10	3.92*d*-2	3.98*d*-6	Si^-	14	1.371518	4.58*d*-10	1.64*d*-2	5.45*d*-6
15	P^+	18	1.180059	4.69*d*-10	3.66*d*-2	4.99*d*-6	P^-	14	1.366854	4.31*d*-10	1.58*d*-2	5.46*d*-6
16	S^+	18	1.178828	2.81*d*-10	3.43*d*-2	3.93*d*-6	S^-	14	1.355395	4.68*d*-10	1.48*d*-2	5.50*d*-6
17	Cl^+	17	1.188869	3.10*d*-10	3.64*d*-2	5.28*d*-6	Cl^-	15	1.330589	4.96*d*-11	3.33*d*-2	1.12*d*-6
18	Ar^+	17	1.189237	3.74*d*-10	3.24*d*-2	5.14*d*-6						
19	K^+	17	1.194040	2.30*d*-10	1.25*d*-2	3.05*d*-6	K^-	18	1.367933	8.57*d*-11	1.14*d*-2	2.06*d*-6
20	Ca^+	21	1.179269	4.73*d*-10	1.12*d*-2	3.95*d*-6						
21	Sc^+	20	1.190191	4.94*d*-10	1.00*d*-2	3.16*d*-6	Sc^-	18	1.358662	6.04*d*-11	9.71*d*-3	1.38*d*-6
22	Ti^+	20	1.193975	2.00*d*-10	1.05*d*-2	3.43*d*-6	Ti^-	18	1.364585	1.22*d*-10	2.28*d*-2	1.06*d*-6
23	V^+	19	1.208848	1.15*d*-10	2.32*d*-2	2.49*d*-6	V^-	18	1.369925	2.44*d*-10	1.27*d*-2	2.25*d*-6
24	Cr^+	19	1.207531	1.16*d-10*	2.36*d*-2	1.92*d*-6	Cr^-	18	1.376855	3.15*d*-10	1.05*d*-2	3.63*d*-6
25	Mn^+	16	1.269299	2.65*d*-10	2.48*d*-2	4.30*d*-6	Mn^-	18	1.379513	2.69*d*-10	9.48*d*-3	3.29*d*-6
26	Fe^+	19	1.217891	3.49*d*-10	1.93*d*-2	3.66*d*-6	Fe^-	18	1.383051	2.33*d*-10	8.58*d*-3	2.49*d*-6
27	Co^+	19	1.212763	5.48*d*-11	2.22*d*-2	1.61*d*-6	Co^-	18	1.386525	2.78*d*-10	2.51*d*-2	3.39*d*-6
28	Ni^+	19	1.210720	2.70*d*-10	1.96*d*-2	2.90*d*-6	Ni^-	18	1.389965	4.59*d*-10	7.28*d*-3	7.80*d*-7
29	Cu^+	19	1.213489	1.04*d*-10	1.95*d*-2	1.96*d*-6	Cu^-	19	1.356832	8.47*d*-11	8.42*d*-3	1.29*d*-6
30	Zn^+	20	1.211300	2.54*d*-10	2.00*d*-2	3.43*d*-6						
31	Ga^+	21	1.194915	1.30*d*-10	1.94*d*-2	2.36*d*-6	Ga^-	19	1.374828	1.64*d*-10	6.99*d*-3	1.07*d*-6
32	Ge^+	20	1.218308	2.53*d*-10	2.05*d*-2	2.74*d*-6	Ge^-	18	1.346529	4.91*d*-11	2.39*d*-2	2.03*d*-6
33	As^+	21	1.200414	1.17*d*-10	1.77*d*-2	2.61*d*-6	As^-	17	1.375497	3.13*d*-10	6.00*d*-3	4.35*d*-7
34	Se^+	21	1.195000	1.29*d*-10	6.37*d*-3	1.54*d*-6	Se^-	17	1.359857	8.17*d*-11	6.18*d*-3	8.19*d*-7
35	Br^+	21	1.195057	1.23*d*-10	5.83*d*-3	1.15*d*-6	Br^-	17	1.344726	1.84*d*-10	1.82*d*-2	2.61*d*-6
36	Kr^+	21	1.193483	1.72*d*-10	1.72*d*-2	2.97*d*-6						
37	Rb^+	21	1.190864	2.86*d*-10	1.67*d*-2	3.02*d*-6	Rb^-	21	1.365614	4.60*d*-11	5.85*d*-3	9.00*d*-7
38	Sr^+	25	1.179372	4.14*d*-10	5.87*d*-3	2.44*d*-6						
39	Y^+	24	1.184936	4.22*d*-10	5.72*d*-3	2.48*d*-6	Y^-	24	1.341760	1.69*d*-10	6.45*d*-3	1.68*d*-6
40	Zr^+	23	1.198371	4.30*d*-10	5.92*d*-3	2.75*d*-6	Zr^-	21	1.347656	4.42*d*-10	5.58*d*-3	1.25*d*-6
41	Nb^+	21	1.219533	2.96*d*-10	4.97*d*-3	1.21*d*-6	Nb^-	22	1.325062	2.25*d*-10	6.14*d*-3	8.32*d*-7
42	Mo^+	21	1.217401	2.82*d*-10	1.52*d*-2	3.25*d*-6	Mo^-	22	1.328573	4.43*d*-10	5.64*d*-3	1.20*d*-6
43	Tc^+	21	1.223654	4.86*d*-10	5.51*d*-3	2.67*d*-6	Tc^-	23	1.306024	9.03*d*-11	1.00*d*-2	7.58*d*-7
44	Ru^+	21	1.216158	3.44*d*-10	1.45*d*-2	3.13*d*-6	Ru^-	23	1.307473	1.63*d*-10	7.49*d*-3	7.39*d*-7
45	Rh^+	21	1.215483	3.83*d*-10	1.42*d*-2	3.28*d*-6	Rh^-	23	1.309342	2.90*d*-10	1.80*d*-2	1.85*d*-6
46	Pd^+	22	1.205895	2.72*d*-10	1.31*d*-2	2.24*d*-6	Pd^-	23	1.311566	4.78*d*-10	1.66*d*-2	2.49*d*-6
47	Ag^+	21	1.214347	3.60*d*-10	1.32*d*-2	2.79*d*-6	Ag^-	24	1.292770	8.82*d*-11	1.04*d*-2	8.10*d*-7
48	Cd^+	18	1.283284	9.35*d*-11	1.14*d*-2	7.61*d*-7						
49	In^+	22	1.213731	4.39*d*-10	4.29*d*-3	1.45*d*-6	In^-	24	1.294143	2.04*d*-10	1.76*d*-2	1.36*d*-6
50	Sn^+	21	1.235059	2.20*d*-10	1.28*d*-2	2.56*d*-6	Sn^-	22	1.297041	3.87*d*-10	5.34*d*-3	1.33*d*-6
51	Sb^+	23	1.205682	2.41*d*-10	1.25*d*-2	2.48*d*-6	Sb^-	22	1.291653	3.08*d*-10	5.24*d*-3	8.07*d*-7
52	Te^+	23	1.200872	2.65*d*-10	1.30*d*-2	2.91*d*-6	Te^-	22	1.281126	1.32*d*-10	1.92*d*-2	8.82*d*-7
53	I^+	23	1.199340	4.59*d*-10	1.24*d*-2	3.68*d*-6	I^-	22	1.270799	5.94*d*-11	3.96*d*-3	5.77*d*-7
54	Xe^+	23	1.197883	4.16*d*-10	1.25*d*-2	3.55*d*-6						
55	Cs^+	24	1.188526	3.42*d*-10	1.16*d*-2	2.66*d*-6						

Angulo et al. [27] examined the convexity of $\rho(r)$ for the neutral atoms with $Z \leq 54$ using approximate density functions constructed from the Clementi-Roetti wave functions [7]. They concluded [27] that the electron densities of the atoms with $Z = 1$, 2, 7–15 and 33–44 are convex, whereas those of the atoms with $Z = 3$–6, 16–32 and 45–54 are nonconvex. Our previous examination [13] of the HF densities of neutral atoms has shown that their classification is correct except that the Ge atom ($Z = 32$) has been found to have a convex density. (Note that there is a typographical error in [13].) Moreover, all the heavier neutral atoms with $Z = 55$–103 have been found [13] to have a nonconvex electron density in their ground state. For singly charged cations, an analysis of the present HF density shows that the cations with $Z = 3$, 7–15 and 32–44 have a convex density, while the cations with $Z = 4$–6, 16–31 and 45–55 have a nonconvex density. Similarly, we have found that the HF electron densities of the singly charged anions $Z = 1$, 6–15 and 32–44 are convex, while those with $Z = 3$, 5, 16–31 and 45–53 are nonconvex. To sum up, the convexity of the HF density is seen for the species with

$N = 1$ and 2, and $Z = 7$–15 and 32–44. For $Z = 6$, the HF density is convex only for the anion.

In order to study the extrema of the moment density $D_q(r) \equiv 4\pi r^q \rho(r)$, Schmider et al. [28] introduced the double-logarithmic derivative (DLD) $L(r)$ defined by

$$L(r) \equiv \frac{d \ln \rho(r)}{d \ln r} = \frac{r}{\rho(r)} \frac{d\rho(r)}{dr} \ . \tag{13}$$

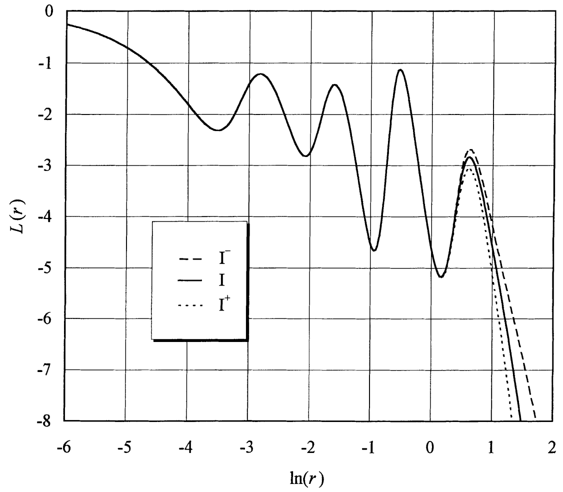

Fig. 2. The double-logarithmic derivative $L(r)$ for I (*solid line*), I^+ (*dotted line*), and I^- (*dashed line*)

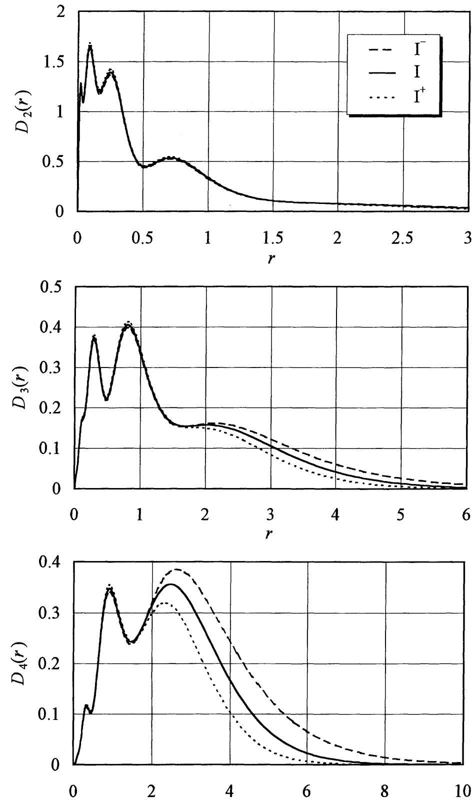

Fig. 3. Comparison of moment densities $D_q(r)$ with $q = 2$, 3, and 4 for I (*solid line*), I^+ (*dotted line*), and I^- (*dashed line*)

The locations of maxima and minima in $D_q(r)$, which provide insight on the shell structure of atoms and atomic ions, can be determined by an equation $L(r) = -q$. As an application of the HF densities constructed in this study, we plot DLDs in Fig. 2 for the iodine atom and its singly charged ions. We find in Fig. 2 that DLDs have four peaks (except the peak at $r = 0$ or $\ln r = -\infty$) and the essential difference among the three species appears around and beyond the last peak (observed at $r = 1.86$ or $\ln r = 0.62$) or in a very outer region of the density distribution. The different heights of this peak for I, I^+ and I^- mean different "strengths" to reveal the maximum corresponding to the O-shell. A finer analysis shows that the O-shell maximum in the moment density $D_q(r)$ can be detected if $q > 2.7$ for I^-, $q > 2.9$ for I and $q > 3.1$ for I^+. Thus the conventional radial density $D_2(r) = 4\pi r^2 \rho(r)$ does not find any peak corresponding to the O-shell. However, $D_q(r)$ with $q = 3$ shows an O-shell peak for I^- and I, but still not for I^+. Figure 3 explicitly compares the moment densities $D_q(r)$ with $q = 2$, 3 and 4 for the three species. The result suggests that the problem of atomic-shell structure (see, e.g. [28] for relevant references) may be more difficult for a cation than for the corresponding neutral and anion with the same Z.

5 Summary

For the singly charged cations Li^+–Cs^+ and anions H^-–I^- in their ground state, the HF electron densities have been constructed by using the NHF method and fitted into a simple analytical function subject to several physically important constraints. High accuracy of the resultant approximation has been confirmed. We hope the present analytical expression of the HF electron density will prove useful for studies on electron density and its applications. Full details of the present results for the 96 ions are available upon request to T.K. at the e-mail address: koga@muroran–it.ac.jp.

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