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Analytical Hartree–Fock electron densities for atoms He through Lr

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Abstract. The Hartree–Fock electron density has an important property that it is identical to the exact density to first order in the perturbation theory. For the neutral atoms from He ($Z = 2$) to Lr ($Z = 103$) in their ground state, we report an accurate analytical approximation $F(r)$ to the spherically averaged electron density $\rho(r)$ obtained by the numerical Hartree–Fock method. The present density function $F(r)$ is expressed by a linear combination of reasonable number (not more than 30) of basis functions $r^{n_i} \exp(-\zeta_i r)$, and has the following properties: (i) $F(r)$ is nonnegative, (ii) $F(r)$ is normalized, (iii) $F(r)$ reproduces the Hartree–Fock moments $\langle r^k \rangle$ ($k = -2$ to $+6$), (iv) $F(0)$ is equal to $\rho(0)$, (v) $F'(0)$ satisfies the cusp condition, and (vi) $F(r)$ has the correct exponential decay in the long-range asymptotic region.

Key words: Electron density – Hartree–Fock – Neutral atoms

1 Introduction

An N-electron wave function $\Psi(\{r_i, \sigma_i\})$ involves $3N$ spatial $\{r_i\}$ and N spin $\{\sigma_i\}$ coordinates of the electrons, and hence the direct interpretation of the wave function is clearly formidable. However, the essential physical content of a wave function can be embodied by the spin-reduced one-electron density function $\rho(\boldsymbol{r})$, which has only three spatial variables (see e.g. Ref. [1]). For this reason, many researchers have studied the properties of $\rho(\boldsymbol{r})$ and explored its applications to physical and chemical problems (see e.g. Ref. [2]). Also there are continued efforts in developing the density functional theory, which bypasses the wave function and tries to determine the electron density directly (see e.g. Ref. [3]).

When we work within the Hartree–Fock framework, the associated density (i.e. Hartree–Fock electron density) has a special significance. If a Hartree–Fock determinantal wave function is used as the zeroth-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 fact results in that the first-order correction to the electron density is zero for the Condon–Slater rules. In other words, the Hartree–Fock electron density is identical to the exact density to first order in the perturbation theory.

In recent years, various new properties of the spherically averaged electron density $\rho(r)$ have been reported (see e.g. Ref. [4] for a review) for ground-state neutral atoms, based on the systematic examination of approximate density functions constructed from Roothaan–Hartree–Fock wave functions of Clementi and Roetti [5] and of McLean and McLean [6]. However, it has been unfortunately pointed out that these Roothaan–Hartree–Fock wave functions include nontrivial errors and inaccuracies [7–10].

In view of the theoretical significance of the Hartree–Fock electron densities and their demand in various studies, we have decided to construct accurate and reliable approximations $F(r)$ to the Hartree–Fock densities $\rho(r)$ for the neutral atoms from He ($Z = 2$) to Lr ($Z = 103$) in their ground state. We have employed the numerical Hartree–Fock method, and the resultant Hartree–Fock densities, in the form of numerical tables, have been fitted into simple analytical functions subject to several constraints. Compared to the traditional method (see e.g. Ref. [11]) of deriving electron density functions from Roothaan–Hartree–Fock wave functions, the present method avoids some problems inherent to the use of one-electron basis functions. An obvious difference is the number of terms required to represent the electron density: In the case of Lr ($Z = 103$), for example, the Roothaan–Hartree–Fock method needs approximately $15s12p11d8f$ Slater-type functions to achieve the accuracy of 0.0005 hartrees in the total energy. Then the associated density function is given by a linear combination of 300 different terms of the form of $r^{n_i}\exp(-\zeta_i r)$. On the other hand, the present study shows that only 30 such terms are sufficient for Lr to describe the electron density of the Hartree–Fock quality. Moreover, the present analytical electron densities are designed to fulfill six conditions, some of which are difficult to realize in the Roothaan–Hartree–Fock procedure. The conditions imposed are (i) nonnegativity, (ii) normalization, (iii) moments $\langle r^k \rangle$ with $k = -2$ to $+6$, (iv) value at the nucleus, (v) electron–nucleus cusp relation, and (vi) long-range asymptotic behavior. The next section summarizes the theoretical ground of our constrained fitting procedure, and Sect. 3 gives the computational details. The results are presented and discussed in Sect. 4, and simple applications are given in Sect. 5. Hartree atomic units are used throughout this paper.

2 Theoretical ground

2.1 Spherically-averaged electron density

For a normalized N-electron wave function $\Psi(\{x_i\})$, the (spin-reduced) three-dimensional electron density $\rho(\boldsymbol{r})$ is defined by

$$\rho(\boldsymbol{r}) \equiv N \int |\Psi(\boldsymbol{r}, \sigma, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)^2| \, d\sigma \, d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N, \tag{1}$$

$$\boldsymbol{x}_i = (\boldsymbol{r}_i, \sigma_i), \quad \boldsymbol{r}_i = (r_i, \Omega_i).$$

Then the spherically averaged electron density $\rho(r)$ is obtained by integrating $\rho(\boldsymbol{r})$ over the angular variable Ω,

$$\rho(r) \equiv \frac{1}{4\pi} \int \rho(\boldsymbol{r}) \, d\Omega. \tag{2}$$

By definitions (1) and (2), $\rho(r)$ is normalized to the number of electrons N,

$$4\pi \int_0^\infty \rho(r)\, r^2\, \mathrm{d}r = N. \tag{3}$$

For atomic Hartree–Fock wave functions composed of one-electron orbitals

$$\psi_{n\ell m}(r) = R_{n\ell}(r)\, Y_{\ell m}(\Omega), \tag{4}$$

the spherically averaged density $\rho(r)$ can be written, due to the orthonormality of the spherical harmonics $Y_{\ell m}(\Omega)$, as

$$\rho(r) = \frac{1}{4\pi} \sum_{n\ell} N_{n\ell} |R_{n\ell}(r)|^2, \tag{5}$$

where $N_{n\ell}$ denotes the number of electrons in the subshell specified by the quantum numbers n and ℓ, and $\sum_{n\ell} N_{n\ell} = N$.

For a neutral atom with nuclear charge $Z(=N)$, we define a function $g(r)$ by

$$g(r) \equiv \rho(r) + \frac{1}{2Z}\, \rho'(r), \tag{6}$$

where the prime ($'$) means differentiation with respect to r. The function $g(r)$ satisfies $g(0) = 0$ and $g(\infty) = 0$, where the first relation is nothing but the electron–nucleus cusp condition [12, 13] and the second relation comes from the long-range asymptotic behavior [14–16] of the Hartree–Fock orbitals which leads that $\rho(r) \approx \exp(-\sqrt{-8\varepsilon_\mathrm{h}}\, r)$ for a large r, with ε_h being the orbital energy of the highest occupied Hartree–Fock orbital.

Using the function $g(r)$, we can express [17, 18] the electron density $\rho(r)$ as

$$\rho(r) = \rho(0) \exp(-2Zr) + \tilde{\rho}(r), \tag{7a}$$

$$\tilde{\rho}(r) = 2Z \exp(-2Zr) \int_0^r g(t) \exp(2Zt)\, \mathrm{d}t. \tag{7b}$$

Equations (7a, b) are equivalent to Eq. (6) and do not add new information mathematically. Nevertheless, Eq. (7) is useful for us to infer approximate functional forms of $\rho(r)$. Equation (7b) and the properties $\tilde{\rho}(0) = \tilde{\rho}(\infty) = 0$ suggest that the *unknown* part $\tilde{\rho}(r)$ of the electron density $\rho(r)$ may be adequately expanded by a set of "density basis" functions

$$f_i(r) = r^{n_i} \exp(-\zeta_i r), \quad (i = 1, \dots, N_f) \tag{8}$$

where $n_i > 0$ and $\zeta_i > 0$. Apart from the terms arising from $1s$ type functions, the form of Eq. (8) also appears in approximate electron densities constructed (see, e.g., Ref. [11]) by the Roothaan procedure with Slater-type or hydrogenic basis functions for one-electron orbitals.

2.2 *Analytical approximation*

We wish to approximate a numerically determined Hartree–Fock electron density $\rho(r)$ by an analytical function $F(r)$,

$$\rho(r) \cong F(r) = f_0(r) + \sum_{i=1}^{N_f} c_i f_i(r), \tag{9a}$$

where

$$f_0(r) = \rho(0)\exp(-2Zr), \tag{9b}$$

$f_i(r)$ is given by Eq. (8), and $\{c_i\}$ are mixing coefficients. The approximation (9a) consists of $N_f + 1$ terms and includes linear $\{c_i\}$ and nonlinear $\{n_i, \zeta_i\}$ parameters to be determined.

We impose the following conditions on the function $F(r)$:
(i) Non-negativity:

$$F(r) \geqslant 0 \text{ for } 0 \leqslant r < \infty. \tag{10a}$$

(ii) Normalization:

$$4\pi \int_0^\infty F(r) r^2 \, \mathrm{d}r = N. \tag{10b}$$

(iii) Moments:

$$4\pi \int_0^\infty F(r) r^{k+2} \, \mathrm{d}r = \langle r^k \rangle, \tag{10c}$$

where

$$\langle r^k \rangle \equiv 4\pi \int_0^\infty \rho(r) r^{k+2} \, \mathrm{d}r \quad (k = -2, \ldots, +6)$$

are the Hartree–Fock moment values. A special case of $k = 0$ includes the normalization (10b), i.e., $\langle r^0 \rangle = N$.
(iv) Value at the nucleus:

$$F(0) = \rho(0). \tag{10d}$$

This condition is automatically fulfilled since we have chosen $n_i > 0$ in our density basis function (8).
(v) Cusp:

$$F'(0) = -2ZF(0). \tag{10e}$$

The cusp condition is exactly satisfied if we restrict $n_i > 1$ in Eq. (8).
(vi) Long-range behavior:

$$F(r) \approx \exp(-\sqrt{-8\varepsilon_h}\, r) \tag{10f}$$

for a large r. This requirement is satisfied, if the smallest exponent $\zeta_{\min} = \min\{\zeta_i\}_{i=1}^{N_f}$ of the functions (8) is taken to be $\zeta_{\min} = \sqrt{-8\varepsilon_h}$.

Since the conditions (iv)–(vi) can be satisfied by an adjustment of some parameters in our basis functions (8), we determine the mixing coefficients $\{c_i\}$ and the remaining parameters in the analytical expansion (9a) by minimizing an error measure Δ,

$$\Delta \equiv 4\pi \int_0^\infty [\delta(r)]^2 r^2 \, \mathrm{d}r, \tag{11a}$$

$$\delta(r) \equiv \rho(r) - F(r) = \tilde{\rho}(r) - \sum_{i=1}^{N_f} c_i f_i(r), \tag{11b}$$

$$\tilde{\rho}(r) \equiv \rho(r) - f_0(r) \tag{11c}$$

subject to the constraints (10c). Following the Lagrange method of undermined multipliers, we now define a function

$$\tilde{\Delta} \equiv \Delta - \sum_{k=-2}^{+6} \lambda_k \left\{ 4\pi \int_0^\infty F(r) r^{k+2}\, dr - \langle r^k \rangle \right\}. \tag{12}$$

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 which determines the optimum values of the mixing coefficients (linear parameters) $\{c_i\}$ for a given set of values $\{n_i, \zeta_i; \langle r^k \rangle\}$ and a given number N_f of expansion terms:

$$2 \sum_{j=1}^{N_f} c_j \int_0^\infty f_i(r) f_j(r) r^2\, dr - \sum_{k=-2}^{+6} \lambda_k \int_0^\infty f_i(r) r^{k+2}\, dr = 2 \int_0^\infty \tilde{\rho}(r) f_i(r) r^2\, dr$$

$$(i = 1, 2, \ldots, N_f), \tag{13a}$$

$$\sum_{j=1}^{N_f} c_j \int_0^\infty f_j(r) r^{k+2}\, dr = \frac{\langle r^k \rangle}{4\pi} - \frac{\rho(0)(k+2)!}{(2Z)^{k+3}} \tag{13b}$$

$$(k = -2, -1, \ldots, +6).$$

Since we used 9 moment values as constraints, Eqs. (13a,b) in general will give meaningful solutions $\{c_i\}$ only when $N_f \geqslant 9$. We need a specification of the remaining nonlinear parameters $\{n_i, \zeta_i\}$. Details of the present determination of these parameters will be described in the next section.

3 Computational details

Numerical Hartree–Fock calculations have been performed for the neutral atoms from He ($Z = 2$) to Lr ($Z = 103$) in their ground state, using a modified and enhanced version of MCHF72 program [19]. The electronic configurations and terms examined in this study are summarized in Table 1 together with the associated total energies E, the highest occupied orbital energies ε_h, and the $\rho(0)$ values. Based on Eq. (5), the Hartree–Fock density $\rho(r_j)$ at the radius r_j has been generated, where the radial variable r was first transformed to a new variable x,

$$r = \frac{1}{Z} \exp(x), \tag{14a}$$

and then discretized into N_p points according to the formula

$$r_j = \frac{1}{Z} \exp[x_{\min} + h(j-1)] \quad (j = 1, 2, \ldots, N_p). \tag{14b}$$

The discretization parameters were taken to be $N_p = 2^9 = 512$, $x_{\min} = -6.0$, and $h = 0.03$, based on a careful examination of the stability of the numerical procedures involved in MCHF72. The above choice of the parameter values covers the r range of $1.2 \times 10^{-3} \leqslant r \leqslant 5.6 \times 10^3$ for He and of $2.4 \times 10^{-5} \leqslant r \leqslant 1.1 \times 10^2$ for Lr, for example. Other Hartree–Fock properties, such as orbital energies ε_i, moments $\langle r^k \rangle$, densities $\rho(0)$, $\rho'(0)$, and $\rho''(0)$, were calculated as well. The present density exactly satisfies the cusp relation $\rho(0) = -2Z\rho'(0)$, since the orbital cusp

Table 1. Ground electronic configurations, terms, numerical Hartree–Fock total energies E, orbital energies ε_h of the highest occupied atomic orbital h, and density values $\rho(0)$ (divided by the number of electrons N) of the 102 atoms examined in this study.

Z	Atom	Electronic configuration	Term	$-E$	h	$-\varepsilon_h$	$\rho(0)/N$
2	He	$1s(2)$	^{1}S	2.861679996	$1s$	0.9179556	1.797959132
3	Li	[He]$2s(1)$	^{2}S	7.432726931	$2s$	0.1963228	4.604939957
4	Be	[He]$2s(2)$	^{1}S	14.57302317	$2s$	0.3092696	8.846929184
5	B	[He]$2s(2)2p(1)$	^{2}P	24.52906073	$2p$	0.3098564	14.38427415
6	C	[He]$2s(2)2p(2)$	^{3}P	37.68861896	$2p$	0.4333405	21.24299539
7	N	[He]$2s(2)2p(3)$	^{4}S	54.40093421	$2p$	0.5675889	29.42404962
8	O	[He]$2s(2)2p(4)$	^{3}P	74.80939847	$2p$	0.6319062	38.95761157
9	F	[He]$2s(2)2p(5)$	^{2}P	99.40934939	$2p$	0.7300175	49.81358631
10	Ne	[He]$2s(2)2p(6)$	^{1}S	128.5470981	$2p$	0.8504097	61.99220741
11	Na	[Ne]$3s(1)$	^{2}S	161.8589116	$3s$	0.1821027	75.79613936
12	Mg	[Ne]$3s(2)$	^{1}S	199.6146364	$3s$	0.2530526	91.14315277
13	Al	[Ne]$3s(2)3p(1)$	^{2}P	241.8767073	$3p$	0.2099507	107.9112005
14	Si	[Ne]$3s(2)3p(2)$	^{3}P	288.8543625	$3p$	0.2971145	126.1147821
15	P	[Ne]$3s(2)3p(3)$	^{4}S	340.7187810	$3p$	0.3917083	145.7542765
16	S	[Ne]$3s(2)3p(4)$	^{3}P	397.5048959	$3p$	0.4373687	166.8418559
17	Cl	[Ne]$3s(2)3p(5)$	^{2}P	459.4820724	$3p$	0.5064001	189.3641386
18	Ar	[Ne]$3s(2)3p(6)$	^{1}S	526.8175128	$3p$	0.5910174	213.3212127
19	K	[Ar]$4s(1)$	^{2}S	599.1647868	$4s$	0.1474752	238.8765238
20	Ca	[Ar]$4s(2)$	^{1}S	676.7581859	$4s$	0.1955297	265.9803569
21	Sc	[Ar]$4s(2)3d(1)$	^{2}D	759.7357180	$4s$	0.2101088	294.3954435
22	Ti	[Ar]$4s(2)3d(2)$	^{3}F	848.4059970	$4s$	0.2207882	324.2377398
23	V	[Ar]$4s(2)3d(3)$	^{4}F	942.8843377	$4s$	0.2305790	355.5197988
24	Cr	[Ar]$4s(1)3d(5)$	^{7}S	1043.356376	$4s$	0.2220504	388.0722378
25	Mn	[Ar]$4s(2)3d(5)$	^{6}S	1149.866252	$4s$	0.2478710	422.4030969
26	Fe	[Ar]$4s(2)3d(6)$	^{5}D	1262.443665	$4s$	0.2581808	458.0270811
27	Co	[Ar]$4s(2)3d(7)$	^{4}F	1381.414553	$4s$	0.2674207	495.0882164
28	Ni	[Ar]$4s(2)3d(8)$	^{3}F	1506.870908	$4s$	0.2762506	533.5917342
29	Cu	[Ar]$4s(1)3d(10)$	^{2}S	1638.963742	$4s$	0.2384935	573.2847524
30	Zn	[Ar]$4s(2)3d(10)$	^{1}S	1777.848116	$4s$	0.2925071	614.9225269
31	Ga	[Ar]$4s(2)3d(10)4p(1)$	^{2}P	1923.261010	$4p$	0.2084998	657.9742694

32	Ge	[Ar]4*s*(2)3*d*(10)4*p*(2)	^{3}P	2075.359734	4*p*	0.2873539	702.5036848
33	As	[Ar]4*s*(2)3*d*(10)4*p*(3)	^{4}S	2234.238654	4*p*	0.3694824	748.5133243
34	Se	[Ar]4*s*(2)3*d*(10)4*p*(4)	^{3}P	2399.867612	4*p*	0.4028547	796.0115867
35	Br	[Ar]4*s*(2)3*d*(10)4*p*(5)	^{2}P	2572.441333	4*p*	0.4570858	844.9876499
36	Kr	[Ar]4*s*(2)3*d*(10)4*p*(6)	^{1}S	2752.054977	4*p*	0.5241867	895.4414047
37	Rb	[Kr]5*s*(1)	^{2}S	2938.357454	5*s*	0.1378667	947.5034314
38	Sr	[Kr]5*s*(2)	^{1}S	3131.545686	5*s*	0.1784564	1001.126660
39	Y	[Kr]5*s*(2)4*d*(1)	^{2}D	3331.684170	5*s*	0.1961428	1056.135465
40	Zr	[Kr]5*s*(2)4*d*(2)	^{3}F	3538.995065	5*s*	0.2072933	1112.606440
41	Nb	[Kr]5*s*(1)4*d*(4)	^{6}D	3753.597728	5*s*	0.2155945	1170.417031
42	Mo	[Kr]5*s*(1)4*d*(5)	^{7}S	3975.549500	5*s*	0.2227290	1229.825807
43	Tc	[Kr]5*s*(2)4*d*(5)	^{6}S	4204.788737	5*s*	0.2312744	1290.862809
44	Ru	[Kr]5*s*(1)4*d*(7)	^{5}F	4441.539488	5*s*	0.2224282	1353.068375
45	Rh	[Kr]5*s*(1)4*d*(8)	^{4}F	4685.881704	5*s*	0.2216183	1416.904641
46	Pd	[Kr]4*d*(10)	^{1}S	4937.921024	4*d*	0.3360020	1482.075190
47	Ag	[Kr]5*s*(1)4*d*(10)	^{2}S	5197.698473	5*s*	0.2199798	1549.009409
48	Cd	[Kr]5*s*(2)4*d*(10)	^{1}S	5465.133143	5*s*	0.2648559	1617.532476
49	In	[Kr]5*s*(2)4*d*(10)5*p*(1)	^{2}P	5740.169156	5*p*	0.1972834	1687.472759
50	Sn	[Kr]5*s*(2)4*d*(10)5*p*(2)	^{3}P	6022.931695	5*p*	0.2650404	1758.905600
51	Sb	[Kr]5*s*(2)4*d*(10)5*p*(3)	^{4}S	6313.485321	5*p*	0.3347114	1831.834695
52	Te	[Kr]5*s*(2)4*d*(10)5*p*(4)	^{3}P	6611.784059	5*p*	0.3598323	1906.267021
53	I	[Kr]5*s*(2)4*d*(10)5*p*(5)	^{2}P	6917.980896	5*p*	0.4031805	1982.195097
54	Xe	[Kr]5*s*(2)4*d*(10)5*p*(6)	^{1}S	7232.138364	5*p*	0.4572901	2059.619220
55	Cs	[Xe]6*s*(1)	^{2}S	7553.933658	6*s*	0.1236683	2138.644636
56	Ba	[Xe]6*s*(2)	^{1}S	7883.543827	6*s*	0.1575277	2219.229692
57	La	[Xe]6*s*(2)5*d*(1)	^{2}D	8221.066703	6*s*	0.1704049	2301.222631
58	Ce	[Xe]6*s*(2)4*f*(1)5*d*(1)	^{1}G	8566.872681	6*s*	0.1714320	2384.517790
59	Pr	[Xe]6*s*(2)4*f*(3)	^{4}I	8921.181028	6*s*	0.1639242	2469.115121
60	Nd	[Xe]6*s*(2)4*f*(4)	^{5}I	9283.882945	6*s*	0.1657826	2555.363921
61	Pm	[Xe]6*s*(2)4*f*(5)	^{6}H	9655.098969	6*s*	0.1675935	2643.094227
62	Sm	[Xe]6*s*(2)4*f*(6)	^{7}F	10034.95255	6*s*	0.1693198	2732.302870

Table 1. (Conitnued)

Z	Atom	Electronic configuration	Term	$-E$	h	$-\varepsilon_h$	$\rho(0)/N$
63	Eu	[Xe]$6s(2)4f(7)$	^{8}S	10423.54302	$6s$	0.1709643	2822.989217
64	Gd	[Xe]$6s(2)4f(7)5d(1)$	^{9}D	10820.66121	$6s$	0.1833833	2915.345835
65	Tb	[Xe]$6s(2)4f(9)$	^{6}H	11226.56837	$6s$	0.1744915	3008.839804
66	Dy	[Xe]$6s(2)4f(10)$	^{5}I	11641.45260	$6s$	0.1761480	3103.983473
67	Ho	[Xe]$6s(2)4f(11)$	^{4}I	12065.28980	$6s$	0.1777807	3200.610210
68	Er	[Xe]$6s(2)4f(12)$	^{3}H	12498.15278	$6s$	0.1793920	3298.720147
69	Tm	[Xe]$6s(2)4f(13)$	^{2}F	12940.17440	$6s$	0.1809546	3398.310302
70	Yb	[Xe]$6s(2)4f(14)$	^{1}S	13391.45619	$6s$	0.1824625	3499.379679
71	Lu	[Xe]$6s(2)4f(14)5d(1)$	^{2}D	13851.80800	$6s$	0.1988558	3602.131880
72	Hf	[Xe]$6s(2)4f(14)5d(2)$	^{3}F	14321.24981	$6s$	0.2090020	3706.375505
73	Ta	[Xe]$6s(2)4f(14)5d(3)$	^{4}F	14799.81260	$6s$	0.2174897	3812.117702
74	W	[Xe]$6s(2)4f(14)5d(4)$	^{5}D	15287.54637	$6s$	0.2248086	3919.358085
75	Re	[Xe]$6s(2)4f(14)5d(5)$	^{6}S	15784.53319	$6s$	0.2306728	4028.093787
76	Os	[Xe]$6s(2)4f(14)5d(6)$	^{5}D	16290.64860	$6s$	0.2387670	4138.339560
77	Ir	[Xe]$6s(2)4f(14)5d(7)$	^{4}F	16806.11315	$6s$	0.2453734	4250.079445
78	Pt	[Xe]$6s(1)4f(14)5d(9)$	^{3}D	17331.06996	$6s$	0.2228296	4363.100953
79	Au	[Xe]$6s(1)4f(14)5d(10)$	^{2}S	17865.40008	$6s$	0.2207775	4477.813899
80	Hg	[Xe]$6s(2)4f(14)5d(10)$	^{1}S	18408.99149	$6s$	0.2610460	4594.276760
81	Tl	[Xe]$6s(2)4f(14)5d(10)6p(1)$	^{2}P	18961.82482	$6p$	0.1923974	4712.156504
82	Pb	[Xe]$6s(2)4f(14)5d(10)6p(2)$	^{3}P	19524.00804	$6p$	0.2556974	4831.539815
83	Bi	[Xe]$6s(2)4f(14)5d(10)6p(3)$	^{4}S	20095.58643	$6p$	0.3201046	4952.430397
84	Po	[Xe]$6s(2)4f(14)5d(10)6p(4)$	^{3}P	20676.50091	$6p$	0.3414671	5074.834320
85	At	[Xe]$6s(2)4f(14)5d(10)6p(5)$	^{2}P	21266.88171	$6p$	0.3798654	5198.745088
86	Rn	[Xe]$6s(2)4f(14)5d(10)6p(6)$	^{1}S	21866.77224	$6p$	0.4280068	5324.162994
87	Fr	[Rn]$7s(1)$	^{2}S	22475.85871	$7s$	0.1179115	5451.183536
88	Ra	[Rn]$7s(2)$	^{1}S	23094.30367	$7s$	0.1487712	5579.766697
89	Ac	[Rn]$7s(2)6d(1)$	^{2}D	23722.19206	$7s$	0.1610132	5709.774708

90	Th	[Rn]7*s*(2)6*d*(2)	$^{3}\mathrm{F}$	24359.62244	7*s*	0.1699892	5841.281055
91	Pa	[Rn]7*s*(2)5*f*(2)6*d*(1)	$^{4}\mathrm{K}$	25007.10987	7*s*	0.1637330	5974.043114
92	U	[Rn]7*s*(2)5*f*(3)6*d*(1)	$^{5}\mathrm{L}$	25664.33827	7*s*	0.1651763	6108.411940
93	Np	[Rn]7*s*(2)5*f*(4)6*d*(1)	$^{6}\mathrm{L}$	26331.45496	7*s*	0.1665675	6244.275933
94	Pu	[Rn]7*s*(2)5*f*(6)	$^{7}\mathrm{F}$	27008.71944	7*s*	0.1599292	6381.504691
95	Am	[Rn]7*s*(2)5*f*(7)	$^{8}\mathrm{S}$	27695.88722	7*s*	0.1613092	6520.353009
96	Cm	[Rn]7*s*(2)5*f*(7)6*d*(1)	$^{9}\mathrm{D}$	28392.77117	7*s*	0.1715765	6660.841308
97	Bk	[Rn]7*s*(2)5*f*(8)6*d*(1)	$^{8}\mathrm{H}$	29099.83161	7*s*	0.1738858	6802.699202
98	Cf	[Rn]7*s*(2)5*f*(10)	$^{5}\mathrm{I}$	29817.41892	7*s*	0.1655472	6945.902657
99	Es	[Rn]7*s*(2)5*f*(11)	$^{4}\mathrm{I}$	30544.97219	7*s*	0.1668423	7090.743786
100	Fm	[Rn]7*s*(2)5*f*(12)	$^{3}\mathrm{H}$	31282.77760	7*s*	0.1681040	7237.081993
101	Md	[Rn]7*s*(2)5*f*(13)	$^{2}\mathrm{F}$	32030.93297	7*s*	0.1693171	7384.915616
102	No	[Rn]7*s*(2)5*f*(14)	$^{1}\mathrm{S}$	32789.51214	7*s*	0.1704816	7534.244159
103	Lr	[Rn]7*s*(2)5*f*(14)6*d*(1)	$^{2}\mathrm{D}$	33557.95041	7*s*	0.1832965	7685.242507

condition [20] is imposed on in the construction of the numerical Hartree–Fock orbitals. However, the present $\rho''(0)$ values have been found to include the maximum 0.05% inaccuracy, when hydrogenic species were used as benchmark.

As a consequence of the discretization of the radial variable r in the numerical Hartree–Fock method, all the integrals over r in Eqs. (13a,b) are replaced with the corresponding summations over discrete N_p radial points. For example, the first integral in Eq. (13a) becomes

$$\int_0^\infty f_i(r) f_j(r) r^2 \, dr \cong h \sum_{k=1}^{N_p} f_i(r_k) f_j(r_k) r_k^3, \tag{15}$$

where $\{r_k\}$ are given by Eq. (14b). Note that $dr = r \, dx$.

The powers $\{n_i\}$ in the density basis functions (8) can be either integer or noninteger numbers, but we restricted them to be a *common* integer for the simplicity of our fitting procedure and for the greater tractability of resultant analytical approximations. For a few selected atoms, we tested three choices $n_i = 1, 2$, and 3. A small error (about 0.01%) appeared in the cusp relation when we used $n_i = 1$, while a large exponent appeared when we used $n_i = 3$. Thus, we adopted and fixed $n_i = 2$ for all i in the present work, and therefore the resultant function $F(r)$ exactly satisfies the cusp condition (10e).

For the exponents $\{\zeta_i\}$ of the basis functions (8), we restricted that the minimum value $\zeta_{\min}$ is equal to $\sqrt{-8\varepsilon_h}$ for the long-range requirement (10f). Moreover, we added a condition that the exponents constitute a geometrical series in order to avoid numerical linear dependence among the basis functions. Thus,

$$\zeta_i = \zeta_{\min} \alpha^{i-1} \quad (i = 1, 2, \ldots, N_f) \tag{16a}$$

$$\zeta_{\min} = \sqrt{-8\varepsilon_h}, \tag{16b}$$

where α is the spacing parameter of the two neighboring exponents. By this choice for the exponent values, we have only *one* nonlinear parameter α to be determined, and we employed the conjugate directions method [21] to obtain the optimum α which minimizes Δ.

Finally, we note that the nonnegativity of the $F(r)$ function was checked for all the $\{r_j\}$ radial values during the optimization of the parameter α. We have also recorded the maximum absolute deviation $\delta_{\max} = \max\{|\delta(r_j)|\}_{j=1}^{N_p}$ and its location $r_{\max}$ for the optimum $F(r)$.

4 Results and discussion

Following the procedure described in the previous sections, the optimum linear $\{c_i\}$ and nonlinear α parameters have been determined for the analytical approximation $F(r)$ of the numerical Hartree–Fock density $\rho(r)$. In order to avoid large numbers and to assign the same relative accuracies to all the 102 atoms from He to Lr, the normalization $\langle r^0 \rangle = 1$, instead of N, is applied to all the quantities discussed in this section. The number N_f of expansion terms has been taken to be the minimum value which satisfies the criterion $\Delta < 1 \times 10^{-10}$. Several different initial values have been examined for the parameter α.

Table 2 exemplifies the final result for the Cs atom ($Z = 55$), which approximately occupies the center of the 102 atoms examined in this study and yet involves

Table 2. Analytical Hartree–Fock electron density for the Cs atom. $F(r)$ and $\rho(r)$ are normalized to unity

$$Z = 55$$

$$N_f = 26$$

$$\alpha = 1.224798108\text{d} + 000$$

$$\Delta = 6.128660785\text{d} - 011$$

$$\delta_{\max} = 9.751466567\text{d} - 004$$

$$r_{\max} = 3.820655840\text{d} - 003$$

$$\delta_{\max}/\rho(r_{\max}) = 6.938796398\text{d} - 007$$

i	$c_i/\rho(0)$	n_i	ζ_i
0	1.000000000d +000	0	1.100000000d +002
1	7.568725643d −008	2	9.946589365d −001
2	−2.496571994d −007	2	1.218256384d +000
3	1.434597444d −006	2	1.492118114d +000
4	−1.080391408d −005	2	1.827543442d +000
5	6.246205057d −005	2	2.238371750d +000
6	−2.620180803d −004	2	2.741553485d +000
7	1.219741477d −003	2	3.357849521d +000
8	−3.691941653d −003	2	4.112687740d +000
9	1.022050760d −002	2	5.037212163d +000
10	−3.134609636d −002	2	6.169567927d +000
11	9.318892188d −002	2	7.556475124d +000
12	−1.154370496d −001	2	9.255156435d +000
13	2.576536190d −001	2	1.133569809d +001
14	−1.264433315d +000	2	1.388394157d +001
15	1.768140754d +000	2	1.700502537d +001
16	6.774677143d +000	2	2.082772290d +001
17	−1.447161158d +001	2	2.550975560d +001
18	5.461208312d +000	2	3.124430039d +001
19	−1.692428476d +001	2	3.826796001d +001
20	1.078346367d +002	2	4.687052501d +001
21	−1.089350638d +001	2	5.740693036d +001
22	−2.116646042d +001	2	7.031189969d +001
23	−4.042828753d +001	2	8.611788170d +001
24	−2.778205573d +001	2	1.054770186d +002
25	4.518080514d +001	2	1.291880528d +002
26	−2.130846007d +001	2	1.582292826d +002

$F(0) = 2138.644636$ (error = 0.00000%)
$F'(0) = -235250.9099$ (error = 0.00000%)
$F''(0) = 25933170.49$ (error = 0.04582%)

the density contributions both from the tight ($\varepsilon_{1s} = -1272.768831$) and loose ($\varepsilon_{6s} = -0.123668$) atomic orbitals. For the Cs atom, we need 27 (=26 + 1) expansion terms for $F(r)$. The largest local deviation $\delta_{\max} = 9.8 \times 10^{-4}$ is observed at $r_{\max} = 3.8 \times 10^{-3}$, which is very close to the nucleus. At a first glance, the $\delta_{\max}$ value may not appear enough small, but when compared with the value of the original electron density $\rho(r_{\max})$ at this point, the relative error is only $R_{\max} \equiv \delta_{\max}/\rho(r_{\max}) = 6.9 \times 10^{-7}$. The values $F(0)$, $F'(0)$, and $\langle r^k \rangle$ ($k = -2$ to $+6$) coincide exactly with those from the numerical Hartree–Fock method. The $F''(0)$ value has an error of 0.046%, but it is within the uncertainty of the numerical Hartree–Fock value.

The overall performance of the present construction of analytical Hartree–Fock electron densities is summarized in Table 3. The required number N_f of expansion terms increases generally with increasing Z, but it is not regular. Apart from the $f_0(r)$ term, the first-, second-, third-, fourth-, fifth-, and sixth-row atoms require, roughly speaking, 15, 19, 22, 25, 27, and 29 expansion terms, respectively. We stress the compactness of the present expansion. Though a special exception is seen for $N_f = 18$ of the Rb atom ($Z = 37$), we could not find any reasonable explanation. When Z increases, the maximum local error $\delta_{\max}$ increases from the order of 10^{-5} to the order of 10^{-3}, but its relative value $R_{\max}$ is almost constant and of the order of 10^{-6}–10^{-7}. The radius $r_{\max}$ where $\delta_{\max}$ appears is very small. All the relative errors $\delta F''(0)$ (in percent) of the $F''(0)$ values are within the uncertainty of the numerical Hartree–Fock value except for He, Be, and C atoms. The optimum value of the spacing parameter α for the exponents is around 1.2 for all the atoms examined. The $\zeta_{\min}$ and $\zeta_{\max}$ values are also given in the table to show the distribution of exponents for each atom, where $\zeta_{\min}$ has been determined by Eq. (16b). The $\zeta_{\max}$ value is specified by α and N_f through Eq. (16a), but we observe an empirical relation $\zeta_{\max}/Z \cong 3$ except for the He atom. Though the expansion coefficients $\{c_i\}$ are not shown in the table, we have confirmed that the coefficient of the term with the smallest exponent is positive for all the atoms; this guarantees that the present density function $F(r)$ is positive for a very large r.

We have also compared the electron densities $F(r)$ and $\rho(r)$ as a function of r. Since the two density curves are essentially superimposed, we have plotted in Fig. 1 the difference $\delta(r) = F(r) - \rho(r)$ for the group 1 atoms Li, Na, K, Rb, Cs, and Fr. (The result for Li is superimposed on the horizontal axis in the present scale of the figure.) We observe that the deviation occurs mainly in a region close to the nucleus and is extremely small compared with the $\rho(0)/N$ value given in Table 1.

5 Simple applications

Using an approximate electron density constructed from the Clementi–Roetti wave functions [5], Galvez and Porras [17] examined the sign of the function $g(r)$ for the neutral atoms He through Xe. Since the Clementi–Roetti functions do not satisfy the cusp condition, a small region where $g(r) < 0$ was found in the vicinity of the nucleus for some atoms. However, Galvez and Porras have conjectured [17, 18] that $g(r) \geqslant 0$ for the Hartree–Fock electron density and employed the presumed nonnegative property of $g(r)$ to derive various inequalities among $\rho(0)$ and $\langle r^k \rangle$. As an application of the analytical Hartree–Fock electron density developed in this study, we have examined the sign of the function $g(r)$ derived from $F(r)$. We have confirmed that the above conjecture is correct for all the ground-state neutral atoms not only from He to Xe but also from Cs to Lr.

Angulo et al. [22] examined the convexity (i.e. nonnegativity of the second derivative $\rho''(r)$ for $0 \leqslant r < \infty$) of the spherically averaged electron density $\rho(r)$ for the neutral atoms with $Z \leqslant 54$, also using the approximate density functions constructed from the Clementi–Roetti wave functions. They concluded [22] that the atoms with $Z = 1, 2, 7$–15, and 33–44 have a convex electron density, whereas

Table 3. Summary of the analytical Hartree–Fock electron densities

Z	Atom	N_f	Δ	δ_{max}	r_{max}	R_{max}	$\delta F''(0)$	α	ζ_{min}	ζ_{max}
2	He	11	9.27d−11	1.83d−5	2.03d−1	2.25d−5	−0.093	1.143936	2.709916	10.398568
3	Li	14	5.49d−11	1.07d−5	1.44d−1	5.45d−6	0.056	1.165523	1.253229	9.179161
4	Be	13	3.03d−11	2.37d−5	4.80d−2	3.92d−6	0.068	1.182340	1.572945	11.738716
5	B	14	8.77d−11	2.16d−5	8.90d−2	3.63d−6	0.052	1.195015	1.574437	15.958057
6	C	13	4.31d−11	4.33d−5	3.30d−2	3.02d−6	0.061	1.209989	1.861914	18.337309
7	N	15	9.37d−11	5.68d−5	4.43d−2	3.58d−6	0.042	1.178172	2.130894	21.158480
8	O	15	1.30d−11	1.71d−5	5.40d−2	1.04d−6	0.048	1.187804	2.248388	25.020773
9	F	17	7.37d−11	1.17d−4	2.33d−2	3.56d−6	0.032	1.174441	2.416638	31.659999
10	Ne	15	2.27d−11	3.98d−5	3.83d−2	1.38d−6	0.046	1.193935	2.608309	31.195087
11	Na	19	3.14d−11	5.67d−5	5.30d−2	2.38d−6	0.051	1.200161	1.206989	32.211783
12	Mg	19	5.62d−11	8.52d−5	4.44d−2	2.70d−6	0.050	1.193295	1.422821	34.246256
13	Al	19	4.93d−11	7.97d−5	4.10d−2	2.13d−6	0.049	1.207525	1.295996	38.613239
14	Si	19	3.50d−11	7.55d−5	3.80d−2	1.73d−6	0.048	1.200433	1.541725	41.313423
15	P	19	1.55d−11	5.70d−5	3.66d−2	1.16d−6	0.048	1.196266	1.770216	44.558278
16	S	18	5.95d−11	1.32d−4	1.20d−2	1.16d−6	0.051	1.209806	1.870548	47.658238
17	Cl	19	4.64d−11	1.05d−4	3.04d−2	1.56d−6	0.047	1.194177	2.012759	49.093966
18	Ar	18	7.64d−11	1.52d−4	3.24d−2	2.27d−6	0.049	1.207379	2.174428	53.540666
19	K	21	7.87d−11	1.62d−4	3.16d−2	2.23d−6	0.049	1.217581	1.086187	55.701074
20	Ca	22	6.30d−11	1.67d−4	3.09d−2	2.14d−6	0.049	1.200113	1.250695	57.652231
21	Sc	22	7.92d−11	1.97d−4	2.86d−2	2.21d−6	0.048	1.200779	1.296484	60.463278
22	Ti	22	6.21d−11	2.30d−4	9.27d−3	1.07d−6	0.049	1.202181	1.329024	63.518102
23	V	22	7.66d−11	3.09d−4	2.32d−2	2.51d−6	0.046	1.204256	1.358172	67.305484
24	Cr	21	9.35d−11	2.48d−4	2.57d−2	2.19d−6	0.048	1.218297	1.332818	69.156542
25	Mn	22	9.89d−11	3.72d−4	2.20d−2	2.62d−6	0.046	1.206780	1.408179	72.919863
26	Fe	22	8.32d−11	2.88d−4	2.24d−2	2.00d−6	0.047	1.207895	1.437166	75.879294
27	Co	22	6.62d−11	2.58d−4	7.11d−3	7.64d−7	0.048	1.209158	1.462657	78.938594
28	Ni	22	5.94d−11	3.31d−4	2.02d−2	1.91d−6	0.046	1.211165	1.486608	83.074282
29	Cu	22	5.06d−11	3.65d−4	1.84d−2	1.84d−6	0.045	1.219316	1.381285	88.864126
30	Zn	22	5.83d−11	4.69d−4	7.44d−3	1.19d−6	0.048	1.212738	1.529724	87.845594
31	Ga	22	6.66d−11	2.78d−4	2.06d−2	1.50d−6	0.047	1.226491	1.291510	93.983736
32	Ge	23	2.49d−11	2.04d−4	6.00d−3	4.26d−7	0.046	1.206669	1.516190	94.557569

Table 3. (Continued)

Z	Atom	N_f	Δ	$\delta_{\max}$	$r_{\max}$	$R_{\max}$	$\delta F''(0)$	α	$\zeta_{\min}$	$\zeta_{\max}$
33	As	22	5.41d–11	3.17d–4	1.82d–2	1.40d–6	0.046	1.212303	1.719261	97.988847
34	Se	22	9.83d–11	5.97d–4	1.48d–2	2.04d–6	0.045	1.211381	1.795226	100.696673
35	Br	21	5.23d–11	6.75d–4	6.38d–3	1.25d–6	0.048	1.218755	1.912246	99.970064
36	Kr	22	6.71d–11	2.83d–4	5.18d–3	4.59d–7	0.046	1.206367	2.047802	105.282621
37	Rb	18	3.39d–11	3.15d–4	1.32d–2	8.77d–7	0.044	1.319985	1.050206	117.746394
38	Sr	25	4.51d–11	3.75d–4	1.58d–2	1.24d–6	0.046	1.206763	1.194844	108.701320
39	Y	25	3.76d–11	3.82d–4	1.54d–2	1.19d–6	0.045	1.205924	1.252654	112.074577
40	Zr	25	2.62d–11	5.13d–4	5.41d–3	7.10d–7	0.046	1.205745	1.287768	114.806693
41	Nb	24	5.75d–11	5.21d–4	1.42d–2	1.42d–6	0.045	1.218054	1.313300	122.657936
42	Mo	24	5.49d–11	4.88d–4	1.39d–2	1.26d–6	0.045	1.218603	1.334853	125.969471
43	Tc	25	2.74d–11	3.68d–4	1.36d–2	9.10d–7	0.045	1.207381	1.360219	125.277425
44	Ru	24	4.41d–11	4.17d–4	1.41d–2	1.05d–6	0.045	1.221511	1.333951	132.977224
45	Rh	24	7.27d–11	6.09d–4	1.29d–2	1.37d–6	0.045	1.222411	1.331520	135.002890
46	Pd	21	6.22d–11	3.05d–4	4.30d–3	3.06d–7	0.045	1.251126	1.639517	144.789808
47	Ag	24	9.65d–11	6.39d–4	1.40d–2	1.52d–6	0.046	1.223638	1.326589	137.642161
48	Cd	25	2.70d–11	4.45d–4	1.18d–2	8.47d–7	0.044	1.209984	1.455626	141.175668
49	In	24	7.17d–11	8.89d–4	4.29d–3	8.03d–7	0.046	1.228228	1.256291	142.071065
50	Sn	24	8.70d–11	9.49d–4	1.24d–2	1.85d–6	0.045	1.221721	1.456133	145.734313
51	Sb	25	3.44d–11	6.97d–4	9.83d–3	1.03d–6	0.044	1.206984	1.636365	149.525963
52	Te	25	2.77d–11	4.80d–4	3.81d–3	3.73d–7	0.045	1.205297	1.696661	149.916540
53	I	25	2.46d–11	3.72d–4	1.13d–2	6.18d–7	0.044	1.203566	1.795952	153.311239
54	Xe	24	5.37d–11	8.60d–4	4.01d–3	6.44d–7	0.046	1.211462	1.912674	157.674962
55	Cs	26	6.13d–11	9.75d–4	3.82d–3	6.94d–7	0.046	1.224798	1.218255	158.229283
56	Ba	27	3.97d–11	6.92d–4	9.80d–3	9.30d–7	0.044	1.211969	1.122596	166.343648
57	La	27	4.11d–11	6.64d–4	1.02d–2	9.20d–7	0.044	1.210434	1.167578	167.399612
58	Ce	27	3.72d–11	6.76d–4	1.00d–2	9.04d–7	0.044	1.211585	1.171092	172.105996
59	Pr	27	3.62d–11	6.00d–4	1.05d–2	8.31d–7	0.044	1.213600	1.145161	175.725530
60	Nd	27	4.60d–11	1.02d–3	3.61d–3	6.14d–7	0.045	1.212522	1.151634	172.681095
61	Pm	27	5.79d–11	1.01d–3	9.84d–3	1.26d–6	0.044	1.213383	1.157907	176.855816
62	Sm	26	9.40d–11	1.57d–3	3.49d–3	8.87d–7	0.046	1.220417	1.163855	169.280477
63	Eu	27	5.69d–11	9.89d–4	3.24d–3	5.25d–7	0.045	1.213245	1.169493	178.096313

64	Gd	27	4.86d−11	1.13d−3	3.28d−3	5.90d−7	0.045	1.212313	1.211225	180.804279
65	Tb	27	5.96d−11	9.39d−4	1.01d−2	1.15d−6	0.045	1.214068	1.181496	183.124785
66	Dy	27	5.52d−11	1.00d−3	9.66d−3	1.14d−6	0.045	1.214710	1.187091	186.541273
67	Ho	27	4.65d−11	9.21d−4	2.95d−3	4.28d−7	0.045	1.215327	1.192579	189.893737
68	Er	27	5.32d−11	1.22d−3	3.18d−3	5.71d−7	0.045	1.215538	1.197972	191.613959
69	Tm	27	5.89d−11	1.12d−3	8.70d−3	1.09d−6	0.044	1.216514	1.203178	196.504575
70	Yb	27	6.82d−11	8.60d−4	2.83d−3	3.66d−7	0.044	1.216654	1.208180	197.914380
71	Lu	27	6.38d−11	8.88d−4	2.79d−3	3.68d−7	0.044	1.215245	1.261288	200.479471
72	Hf	27	4.59d−11	1.16d−3	8.34d−3	1.03d−6	0.044	1.215479	1.293065	206.563384
73	Ta	26	9.95d−11	1.37d−3	9.00d−3	1.32d−6	0.045	1.221470	1.319059	196.033440
74	W	26	7.67d−11	4.59d−4	7.64d−3	3.61d−7	0.044	1.225763	1.341070	217.577585
75	Re	26	8.92d−11	6.67d−4	6.69d−3	4.50d−7	0.043	1.226316	1.358449	222.896399
76	Os	26	9.01d−11	1.23d−4	5.85d−3	7.19d−7	0.043	1.226912	1.382077	229.545582
77	Ir	26	8.04d−11	3.05d−4	2.35d−3	1.03d−7	0.043	1.227752	1.401066	236.712472
78	Pt	25	7.07d−11	1.63d−3	8.42d−3	1.37d−6	0.045	1.235327	1.335154	212.958418
79	Au	25	7.32d−11	1.67d−3	8.07d−3	1.32d−6	0.044	1.236737	1.328992	217.860365
80	Hg	26	8.48d−11	1.03d−3	5.40d−3	5.29d−7	0.043	1.229845	1.445119	254.780285
81	Tl	25	8.74d−11	4.58d−4	6.98d−3	2.99d−7	0.043	1.244174	1.240637	234.848851
82	Pb	26	5.94d−11	1.91d−3	2.49d−3	5.94d−7	0.045	1.222328	1.430237	216.321848
83	Bi	26	6.64d−11	7.71d−4	5.86d−3	4.10d−7	0.043	1.225923	1.600261	260.477798
84	Po	26	9.15d−11	8.26d−4	5.46d−3	4.06d−7	0.043	1.224388	1.652797	260.732953
85	At	26	6.66d−11	6.87d−4	6.08d−3	3.70d−7	0.043	1.221688	1.743251	260.235987
86	Rn	26	7.43d−11	1.25d−3	5.49d−3	6.01d−7	0.043	1.217852	1.850420	255.348417
87	Fr	28	7.70d−11	2.78d−3	2.56d−3	7.96d−7	0.045	1.224428	1.189202	229.891498
88	Ra	27	8.59d−11	1.62d−3	6.83d−3	9.56d−7	0.044	1.231132	1.090949	243.066183
89	Ac	28	7.02d−11	2.34d−3	2.36d−3	6.24d−7	0.045	1.217801	1.134947	232.025709
90	Th	28	6.68d−11	2.34d−3	2.33d−3	6.08d−7	0.045	1.217003	1.166153	234.223343
91	Pa	28	6.20d−11	2.00d−3	2.24d−3	5.04d−7	0.045	1.218794	1.144493	239.182963
92	U	28	6.31d−11	1.84d−3	7.14d−3	1.11d−6	0.044	1.219330	1.149526	243.103069
93	Np	28	7.27d−11	1.65d−3	7.07d−3	9.71d−7	0.044	1.219882	1.154357	247.129474
94	Pu	28	8.81d−11	1.62d−3	6.58d−3	8.65d−7	0.044	1.221935	1.131121	253.401874

Table 3. (Continued)

Z	Atom	N_f	Δ	$\delta_{\max}$	$r_{\max}$	$R_{\max}$	$\delta F''(0)$	α	$\zeta_{\min}$	$\zeta_{\max}$
95	Am	29	4.95d–11	3.44d–3	2.35d–3	8.23d–7	0.045	1.210764	1.135990	240.457524
96	Cm	28	1.00d–10	1.25d–3	6.45d–3	6.41d–7	0.044	1.221475	1.171585	259.810716
97	Bk	29	4.31d–11	3.24d–3	2.30d–3	7.44d–7	0.045	1.210065	1.179443	245.651482
98	Cf	29	4.18d–11	2.47d–3	2.08d–3	5.34d–7	0.045	1.212092	1.150816	251.189859
99	Es	29	3.85d–11	2.34d–3	2.06d–3	4.95d–7	0.045	1.212563	1.155309	254.929754
100	Fm	29	3.76d–11	2.45d–3	2.10d–3	5.14d–7	0.045	1.213008	1.159669	258.533390
101	Md	29	3.87d–11	2.24d–3	2.02d–3	4.56d–7	0.044	1.213514	1.163846	262.511158
102	No	29	3.45d–11	1.92d–3	1.94d–3	3.78d–7	0.044	1.214091	1.167841	266.942954
103	Lr	29	3.72d–11	2.00d–3	1.92d–3	3.85d–7	0.044	1.212709	1.210938	268.103468

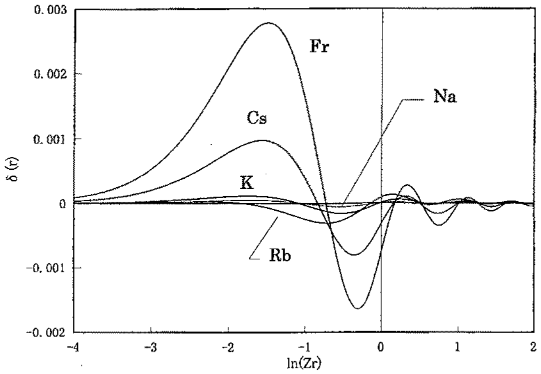

Fig. 1. Deviation $\delta(r)$ of the analytical density $F(r)$ from the numerical Hartree–Fock density $\rho(r)$ for the group 1 atoms Li, Na, K, Rb, Cs, and Fr. The parent densities are normalized to unity

the atoms with $Z = 3$–6, 16–32, and 45–54 have a nonconvex density. Since the second derivative is expected to be highly sensitive to the accuracy of the electron density employed, we have re-examined the convexity based on the present Hartree–Fock density $F(r)$. Fortunately, we have confirmed that the above-mentioned classification of the atoms with the convex and nonconvex densities is correct. Additionally, we have found that all the heavier atoms with $55 \leqslant Z \leqslant 103$ have a nonconvex electron density in their ground state. However, the details of the properties of the nonconvex densities summarized in Ref. [22] have been found to be insufficiently accurate.

6 Summary

For the neutral atoms from He ($Z = 2$) to Lr ($Z = 103$) in their ground state, the numerical Hartree–Fock electron density has been 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 Hartree–Fock electron density would be useful for various studies on the electron density and its applications. Full details of the present results for the 102 atoms are available upon request to the author at the e-mail address: koga@muroran-it.ac.jp.

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