Atomic-charge convexity and the electron density at the nucleus

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The convexity of the spherically averaged electron density $\rho(r)$ of neutral atoms with $Z \leq 54$ is numerically studied in a Hartree-Fock framework. It is found that $\rho(r)$ is convex for $Z=1$, 2, 7–15, and 33–44, while for the rest of the atoms it presents a small "nonconvex" region. Second, rigorous relationships between the values of the single-particle density and its first derivative at the origin and the radial expectation values $\langle r^k \rangle$ for a convex $\rho(r)$ are derived. These conditions are valid for any many-body system whose spherically averaged single-particle density is convex. Finally, for atomic systems, these determinantal conditions together with the electron-nucleus cusp condition are used to obtain novel upper and lower bounds to $\rho(0)$ by means of two or more expectation values. The quality of the new lower bounds is better than that of the corresponding ones known up to now. In particular, the convexity bound $(1/6\pi)(\langle r^{-2} \rangle^2 / \langle r^{-1} \rangle)$ to $\rho(0)$ improves by a factor of $\frac{4}{3}$ the accuracy of the corresponding bound obtained from the property of monotonic decrease of $\rho(r)$.

The spherically averaged electron density $\rho(r)$ of atomic systems, defined by

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

is one of the most useful quantum-mechanical concepts not only because of its physical meaning (i.e., the probability density of finding an electron at a radius r from the nucleus) and because it allows a more convenient and transparent interpretation of physical and chemical phenomena but also it is the cornerstone of modern atomic density-functional theories.[1,2] The electron density is given as

$$\rho(\mathbf{r}) = N \sum_{\sigma_i=1}^{2} \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N; \sigma_1, \sigma_2, \ldots, \sigma_N)|^2 \times d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \ ,$$

where $\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N; \sigma_1, \sigma_2, \ldots, \sigma_N)$ is the normalized wave function of the N-electron atomic system which is antisymmetric in the pairs $(\mathbf{r}_i, \sigma_i)$ of position-spin electronic coordinates. Both $\rho(\mathbf{r})$ and $\rho(r)$ are normalized to the number of electrons of the system.

However, it is hard to prove any mathematical properties of this quantity in a rigorous way apart possibly from its behavior near the origin and at large distances.[3] Numerical nonrelativistic self-consistent calculations suggest that the electron density $\rho(r)$ of the ground state of neutral atoms, hydrogen through uranium, is unimodal at the origin, i.e., it is monotonically decreasing.[4,5] Furthermore, it is known[6] that within the frame of the infinite nuclear mass approximation, the atomic $\rho(r)$ is a convex monotonically decreasing function outside a sphere whose radius depends on the ionization energy I and the electron-nucleus attraction, as the Hoffman-Ostenhof radius $r_{HO} = Z/I$ atomic units. This radius is very large for atoms; for example, its value goes from 2.0 a.u. (H) to 230.2 a.u. (In).

Here we will study the convexity of the atomic electron density $\rho(r)$ both formally and numerically. In a geometrical sense, the property of convexity indicates that each arc of the function $\rho(r)$ lies nowhere above the chord joining the end points of the arc. If the second derivative $\rho''(r)$ exists at each point of the interval $[0, \infty)$, then a necessary and sufficient condition that $\rho(r)$ be convex is that we have[7]

$$\rho''(r) \geq 0 \quad \text{for } 0 \leq r < \infty \ . \tag{2}$$

The first purpose of this paper is to investigate numerically the convexity property (2) of all neutral atoms with $Z \leq 54$ by means of the nonrelativistic self-consistent wave functions of Clementi and Roetti.[8] The evaluation of $\rho''(r)$ has been done up to the radius of Hoffmann-Ostenhof r_{HO}, from which $\rho''(r)$ is rigorously positive as said before. This Hartree-Fock study shows that the atoms with $Z=1$, 2, 7–15, and 33–44 have a convex electron density $\rho(r)$ since the second derivative $\rho''(r)$ is positive everywhere. The rest of atoms considered in this study have a function $\rho''(r)$ which is positive with the only exception of a small radial region of negativity as shown in Table I, where it is also given the greatest negative value within this region, i.e., the minimum of $\rho''(r)$ in such a region, $\rho''_{\min}$, and its position r_0, as well as the value of $\rho''(r)$ at the origin, $\rho''(0)$, for the sake of comparison. Notice that the absolute value of the ratio $\rho''_{\min}/\rho''(0)$ is always much less than 10^{-5}. For completeness and transparency, we represent in Fig. 1 the function $\rho''(r)$ of carbon ($Z=6$) which typically illustrates how small its value is in the negativity region.

Besides, from Table I one observes that the width Δ of the negativity region decreases from 0.56 to 0.07 a.u. in the first block of atoms with $Z=3$–6 and from 0.31 to 0.01 a.u. in the second block of atoms with $Z=16$–32, and it remains almost constant (0.13 a.u.) in the third atomic block with $Z=45$–54. The very small values of the extension of this region as well as of the $\rho''(r)$ in it al-

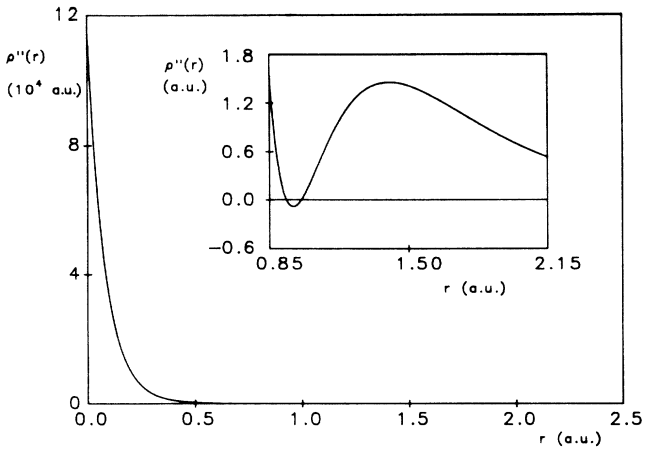

FIG. 1. Second derivative of the charge density, $\rho''(r)$, of carbon. The region of negative $\rho''(r)$ is shown separately to illustrate its small width and magnitude.

low to say that convexity is, also for these three blocks of atoms, to a good degree of approximation, a property of the ground-state electron density. Nevertheless, further research to understand the physical origin of the negativity region of $\rho''(r)$ should be done for these atoms by using other self-consistent wave functions of higher quality.

Secondly, we will study the convexity property (2) from a rigorous point of view. A theorem of Stieltjes[9] allows one to say that if $\rho''(r)$ is a density function (i.e., is positive definite), then its moments ν defined by

$$\nu_k \equiv \int_0^\infty r^k \rho''(r) dr = \begin{cases} -\rho'(0), & k=0 \\ \rho(0), & k=1 \\ \dfrac{1}{4\pi} k(k-1)\langle r^{k-4}\rangle, & k>1 \end{cases} \tag{3}$$

satisfy the determinantal inequalities

$$\Delta_m \geq 0, \quad \Delta'_m \geq 0, \quad m=0,1,\ldots \tag{4}$$

where the Hadamard determinants are given by

TABLE I. Values of $\rho''(r)$ at the origin, $\rho(0)$, and at the minimum r_0 of the negativity region, $\rho''_{\min}=\rho''(r_0)$, and their mutual ratio are given for all the atoms with $Z \leq 54$ which are not strictly convex. Also, the width Δ of that region is shown. Numbers in square brackets denote the corresponding power of 10, i.e., 1.5880[+3] means 1.5880×10^3. Atomic units are used throughout. See text for further details.

Z	$\rho''(0)$	$-\rho''_{\min}$	$-\dfrac{\rho''_{\min}}{\rho''(0)}$	r_0	Δ
3	1.5880[+3]	1.3082[−3]	8.2[−7]	2.500	0.56
4	9.5266[+3]	4.1281[−2]	4.3[−6]	1.590	0.44
5	3.7426[+4]	1.4616[−1]	3.9[−6]	1.195	0.24
6	1.1397[+5]	8.3965[−2]	7.4[−7]	0.960	0.07
16	4.4306[+7]	2.6820	6.1[−8]	1.315	0.31
17	6.3801[+7]	2.0596	3.2[−8]	1.205	0.18
18	9.0577[+7]	6.4402	7.1[−8]	1.080	0.21
19	1.2909[+8]	1.4320[+1]	1.1[−7]	0.980	0.20
20	1.7559[+8]	2.7525[+1]	1.6[−7]	0.895	0.19
21	2.3581[+8]	4.2429[+1]	1.8[−7]	0.835	0.18
22	3.1270[+8]	6.0299[+1]	1.9[−7]	0.780	0.15
23	4.1029[+8]	8.2155[+1]	2.0[−7]	0.730	0.14
24	5.3256[+8]	8.9912[+1]	1.7[−7]	0.695	0.12
25	6.8509[+8]	1.3216[+2]	1.9[−7]	0.655	0.11
26	8.5479[+8]	1.5668[+2]	1.8[−7]	0.620	0.10
27	1.0761[+9]	1.6899[+2]	1.6[−7]	0.590	0.08
28	1.3356[+9]	1.7214[+2]	1.3[−7]	0.565	0.07
29	1.6443[+9]	1.0377[+2]	6.3[−8]	0.540	0.04
30	2.0205[+9]	1.0121[+2]	5.0[−8]	0.515	0.04
31	2.4381[+9]	7.6290[+1]	3.1[−8]	0.495	0.02
32	2.9638[+9]	2.9818[+1]	1.0[−8]	0.470	0.01
45	2.2771[+10]	3.2250[+1]	1.4[−9]	0.910	0.08
46	2.6007[+10]	8.4860[+1]	3.3[−9]	0.875	0.11
47	2.9647[+10]	1.5306[+2]	5.2[−9]	0.835	0.12
48	3.3644[+10]	2.6355[+2]	7.8[−9]	0.805	0.13
49	3.8324[+10]	3.9468[+2]	1.0[−8]	0.770	0.14
50	4.3055[+10]	5.6318[+2]	1.3[−8]	0.740	0.14
51	4.8553[+10]	7.8288[+2]	1.6[−8]	0.710	0.13
52	5.4596[+10]	1.0584[+3]	1.9[−8]	0.685	0.13
53	6.1274[+10]	1.3940[+3]	2.3[−8]	0.665	0.13
54	6.8563[+10]	1.8379[+3]	2.7[−8]	0.640	0.13

$$\Delta_m \equiv \begin{vmatrix} \nu_0 & \nu_1 & \cdots & \nu_m \\ \nu_1 & \nu_2 & & \nu_{m+1} \\ \cdots & & & \cdots \\ \nu_m & \nu_{m+1} & \cdots & \nu_{2m} \end{vmatrix} ,$$

$$\Delta'_m \equiv \begin{vmatrix} \nu_1 & \nu_2 & \cdots & \nu_{m+1} \\ \nu_2 & \nu_3 & & \nu_{m+2} \\ \cdots & & & \cdots \\ \nu_{m+1} & \nu_{m+2} & \cdots & \nu_{2m+1} \end{vmatrix} .$$

Also, in writing (3) we have assumed that $\langle r^k \rangle$, defined as

$$\langle r^k \rangle \equiv \int r^k \rho(\mathbf{r}) d\mathbf{r} = 4\pi \int_0^\infty r^{k+2} \rho(r) dr ,$$

exist for any k, what is known to be true at least for atomic systems because $\rho(r)$ decays exponentially at large distances.[3]

We remark that the inequalities (4) involve the electron density and its first derivative at the nucleus, $\rho(0)$ and $\rho'(0)$, respectively and the radial expectation values. For atomic systems, since $\rho'(0) = -2Z\rho(0)$ because of the electron-nucleus cusp condition,[10] they involve $\rho(0)$ and the $\langle r^k \rangle$ values only.

Indeed, for $m = 1$, the inequalities $\Delta_1 \geq 0$ and $\Delta'_1 \geq 0$ together with the moment values (3) produce the upper bound

$$\rho(0) \leq \frac{Z}{\pi} \langle r^{-2} \rangle \tag{5}$$

and the lower bound

$$\rho(0) \geq C_1 \equiv \frac{1}{6\pi} \frac{\langle r^{-2} \rangle^2}{\langle r^{-1} \rangle} \tag{6}$$

to the atomic electron density at the nucleus, respectively. While the one-moment upper bound is of poor quality in comparison with that obtained by Hoffmann-Ostenhof *et al.*[11] for Coulombic systems, the bound (6) improves the best two-moments lower bound obtained up to now[12] by a factor of $\frac{4}{3} = 1.333$.

For $m = 2$ the positive values of the determinants Δ_2 and Δ'_2 lead to the inequality

$$b - (b^2 - c)^{1/2} \leq \rho(0) \leq b + (b^2 - c)^{1/2} , \tag{7}$$

with

$$b = \frac{1}{4\pi N} (2ZN \langle r^{-2} \rangle - 3Z \langle r^{-1} \rangle^2 + \langle r^{-2} \rangle \langle r^{-1} \rangle) ,$$

$$c = \frac{1}{24\pi^2 N} \langle r^{-2} \rangle^3 ,$$

and to the lower bound

$$\rho(0) \geq C_2 \equiv \frac{1}{12\pi} \frac{27\langle r^{-1} \rangle^3 + 10\langle r^{-2} \rangle^2 \langle r \rangle - 36N \langle r^{-2} \rangle \langle r^{-1} \rangle}{5\langle r^{-1} \rangle \langle r \rangle - 6N^2} , \tag{8}$$

respectively. The quality of the three-moments upper bound $b + (b^2 - c)^{1/2}$ given by (7) is better than the one given by equation (5) but still worse than the one-moment upper bound found by Hoffmann-Ostenhof *et al.*[11] by completely different methods. However, the three-moments lower bound (8) which is much better than the bound $b - (b^2 - c)^{1/2}$ given by (7), improves not only the two-moments bound (6) obtained above but also the best three-moments lower bound known up to now[12] by a factor which goes from 1.25 (H) to 1.34 (Xe). Here, we should mention that Cioslowski[13] has recently found a three-moments approximate expression for $\rho(0)$ which has a structure similar to our rigorous three-moment upper bound (7) and a higher accuracy. It is worthwhile to point out that the convexity condition gives better lower bounds to $\rho(0)$ than the property of monotonic decrease of the atomic electron density. Furthermore, for heavy neutral atoms both lower bounds C_1 and C_2 behave as $Z^{8/3}$ since $\langle r^{-2} \rangle \sim Z^2$, $\langle r^{-1} \rangle \sim Z^{4/3}$ and $\langle r \rangle \sim Z^{2/3}$ for large values of the nuclear charge.[14]

For the sake of completeness we study the accuracy of the best two- and three-moments lower bounds C_1 and C_2, given by (6) and (8), respectively, in Table II for all neutral atoms with $Z \leq 54$ whose ground-state electron density has been numerically shown above to be convex. Again, the Clementi-Roetti's atomic wave functions have been used to evaluate $\rho(0)$ an the required radial expectation values. Notice that (i) the accuracy of both bounds monotonically worsens for increasing values of Z, and (ii) the three-moments bound C_2 is more accurate than the two-moments bound C_1 by a factor of about 1.25.

We should mention here that the quantities C_1 and C_2 evaluated for atoms whose electron density is not convex, have a behavior similar to those obtained for atoms with a convex electron density. For example, the accuracy of C_1 and C_2 is 54.5% and 68.8% for carbon ($Z = 6$), 38.8% and 49.7% for iron ($Z = 27$), and 33.0% and 41.5% for xenon ($Z = 54$), respectively.

It is also interesting to remark that the consideration of determinantal inequalities (4) of order $m \geq 3$, would lead to more and more accurate bounds to $\rho(0)$ but to the price of including further radial expectation values, so making the corresponding bounds less useful and their evaluation more cumbersome.

Summarizing, we have shown numerically that the Hartree-Fock charge density of the ground states of atoms with $Z = 1$, 2, 7–15, and 33–44 is convex. Furthermore, the rest of atoms with $Z \leq 54$ also have a Hartree-Fock ground-state charge density with the convexity property, to a very good approximation. Indeed, for these atoms the second derivative $\rho''(r)$ is positive everywhere except in a small radial region of width between 0.55 (Li) and 0.01 (Ge) atomic units, where it has a small negative magnitude. Secondly, rigorous relation-

TABLE II. Comparison of the charge density at the nucleus, $\rho(0)$, with the two- and three-moment lower bounds, C_1 and C_2, given by the inequalities (6) and (8), respectively, for all neutral atoms with $Z \leq 54$ which have a convex ground-state charge density. Ratios R_1 and R_2 between bounds and $\rho(0)$ are given in percent. Atomic units are used throughout.

Z	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\rho(0)$	C_1	C_2	R_1	R_2
1	2.00	1.00	1.50	0.32	0.21	0.27	66.7	83.3
2	11.99	3.37	1.85	3.60	2.26	2.88	62.8	80.0
7	193.22	18.34	7.35	206.13	108.02	140.90	52.4	68.4
8	257.26	22.26	7.61	311.97	157.73	211.12	50.6	67.7
9	331.07	26.52	7.78	448.71	219.28	300.83	48.9	67.0
10	414.90	31.11	7.89	620.15	293.52	412.08	47.3	66.4
11	509.49	35.43	10.84	833.83	388.68	492.80	46.6	59.1
12	614.82	39.92	12.25	1 093.73	502.35	627.72	45.9	57.4
13	730.35	44.50	13.72	1 402.91	635.92	785.34	45.3	56.0
14	856.23	49.24	14.48	1 765.71	789.82	978.48	44.7	55.4
15	992.56	54.15	14.97	2 186.31	965.23	1 204.54	44.1	55.1
33	5 270.42	162.09	24.78	24 690.05	9 091.37	11 713.82	36.8	47.4
34	5 612.76	168.92	25.40	27 060.83	9 893.99	12 738.28	36.6	47.1
35	5 966.16	175.84	25.87	29 572.21	10 739.26	13 842.05	36.3	46.8
36	6 330.53	182.85	26.24	32 228.20	11 627.58	15 020.15	36.1	46.6
37	6 705.70	189.67	29.80	35 023.84	12 577.06	15 732.57	35.9	44.9
38	7 093.56	196.57	31.81	38 008.72	13 580.36	16 788.06	35.7	44.2
39	7 491.68	203.62	32.35	41 153.07	14 622.73	18 095.36	35.5	44.0
40	7 900.96	210.79	32.68	44 466.83	15 711.28	19 491.56	35.3	43.8
41	8 320.63	218.17	31.69	47 948.88	16 835.44	21 171.02	35.1	44.2
42	8 752.14	225.52	31.85	51 612.91	18 019.13	22 746.60	34.9	44.1
43	9 194.49	232.95	32.13	55 451.63	19 252.96	24 367.95	34.7	43.9
44	9 648.75	240.46	32.37	59 490.87	20 540.09	26 072.63	34.5	43.8

ships between the charge density at the nucleus, $\rho(0)$, and the radial expectation values, $\langle r^{\alpha} \rangle$, are given by means of determinantal inequalities. Due to the physical meaning of the moments ν_k they are extremely useful for correlating in a rigorous way various atomic quantities, provided that convexity is assured. Finally, some of these inequalities are used to find simple rigorous upper and lower bounds to $\rho(0)$ which depend on the two and three radial expectation values of lowest order. The latter bounds considerably improve the quality of the previously known ones, as it is shown in a Hartree-Fock framework.

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