Atomic systems with a completely monotonic electron density

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For a many-particle system with a spherically averaged single-particle density $\rho(r)$ of a kth-order monotonic nature (i.e., a function whose successive derivatives up to that of order k alternate in sign), rigorous inequalities that involve the central values of $\rho(r)$ and its derivatives as well as the radial expectation values are derived. These inequalities become optimal in the completely monotonic case, that is for $k \to \infty$. Then, it is argued that for atomic systems the electron density is completely monotone to quite a good approximation except in hydrogen, where it is rigorous. In this approximation, the corresponding atomic inequalities produce the following: (i) the famous tight upper bound to the electron density at the nucleus $\rho(0) \leq (Z/2\pi)\langle r^{-2}\rangle$ obtained by Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [J. Phys. B **11**, L571 (1978)] by assuming an infinite nuclear mass, (ii) the lower bound $\rho(0) \geq \langle r^{-2}\rangle^2/(4\pi\langle r^{-1}\rangle)$, (iii) lower bounds to the values of any kth-order derivative of the electron density at the nucleus, and (iv) some inequalities involving two and/or three radial expectation values. These bounds and/or inequalities improve all the corresponding ones known at present. Finally, for completeness, the accuracy of these atomic bounds and/or inequalities are analyzed in the framework of the Hartree-Fock approximation.

I. INTRODUCTION

The single-particle density $\rho(\mathbf{r})$ is the fundamental quantity of the density-functional theory of many-body systems [1–5]. However, rigorous information about this quantity is very scarce, almost unexisting. Even for the ground state of electronic systems, which is the best studied case, the only known rigorous property of the electron density is its behavior near the origin [6] and at large distances [7]. Indeed, still today there is no rigorous proof of any structural properties (e.g., monotonically decreasing, convexity) of the ground-state electron density, although some numerical hints are known [8–11]. This situation is especially striking since the density-functional theory is presently one of the fundamental theories of matter that has been used to explain successfully numerous ground-state properties of fermionic systems (atoms, molecules, solids, nuclei) [1–5,12,13] and is being extended to excited states [14–17].

Here we will first describe some rigorous conditions that the spherically averaged single-particle density $\rho(r)$, $0 \leq r < \infty$, defined by

$$\rho(r) = \frac{1}{4\pi}\int_{\Omega} \rho(\mathbf{r}) d\Omega \ ,$$

must necessarily fulfill to be a monotone function of kth order, that is, a function whose successive derivatives up to that of order k alternate in sign, i.e.,

$$(-1)^n \rho^{(n)}(r) \geq 0 \quad \text{for } n = 0,1,2,\ldots,k \ .$$

For $k \to \infty$, one says that $\rho(r)$ is completely monotonic in agreement with the same definition in the mathematical literature [18,19]. Notice that for $k = 0$, 1, and 2 this property indicates that the density function is nonnegative definite, monotonically decreasing, and convex, respectively. Let us also say that $\rho(\mathbf{r})$, as well as $\rho(r)$, is normalized to the number of particles N of the system.

This paper is structured as follows. In Sec. II we explain how the above-mentioned conditions will be given and we state the "Stieltjes-moment-problem technique," which is the mathematical basis of our approach. This technique is applied in Sec. III to any density function $\rho(r)$ with a monotonicity of kth degree, from zero through infinite. Therein, specific inequalities among radial expectation values and/or central values of $\rho(r)$ and its derivatives are given in a simple, rigorous, and compact way, starting (i) only from the positivity property or monotonicity of zero degree of $\rho(r)$, (ii) from the monotonically decreasing behavior or monotonicity of first degree, (iii) from the convexity property or monotonicity of second degree, and so on. All these inequalities apply to any physical system provided that the corresponding monotonicity condition is satisfied. Particularly remarkable are those inequalities corresponding to the completely monotonic case, i.e., for $k \to \infty$.

In Sec. IV, the latter inequalities are applied to atomic systems and their accuracy is analyzed in a Hartree-Fock framework. We found that, although complete monotonicity is not a rigorous property for ground-state neutral atoms, it is however a reasonably good approximation, except for hydrogen, where it is rigorous. Then, numerous and interesting atomic relationships are encountered within such an approximation. Finally, some concluding remarks are given.

II. METHOD

The above-mentioned conditions will be given by means of the radial expectation values

$$\langle r^{\alpha}\rangle = \int r^{\alpha}\rho(\mathbf{r}) d\mathbf{r}$$

and to find them we will apply the so-called "Stieltjes moment problem" technique [20] to the function

$$f_m^{(k)}(r)=(-1)^k\rho^{(k)}(r)r^m\ , \tag{1}$$

where m is any non-negative integer. A straightforward calculation shows that the moments of this function, defined by

$$\nu_\alpha(k,m)=\int_0^\infty r^\alpha f_m^{(k)}(r)dr$$

have the values

$$\nu_\alpha(k,m)=\begin{cases}(-1)^{k-\alpha-m-1}\rho^{(k-\alpha-m-1)}(0)(\alpha+m)! & \text{if } \alpha=-m,-m+1,\ldots,k-m-1\ , \\ \dfrac{\Gamma(\alpha+m+1)}{4\pi\Gamma(\alpha+m-k+1)}\langle r^{\alpha+m-k-2}\rangle & \text{if } \alpha>k-m-1\ . \end{cases} \tag{2}$$

A Stieltjes theorem [20] states that, since $f_m^{(k)}(r)\geq 0$, the quantities $\{\nu_\alpha(k,m),\ \alpha=0,1,2,\ldots\}$ must necessarily fulfill the following two types of inequalities:

$$\Delta_j^{(i)}\geq 0 \quad \text{for } i=0,1 \quad \text{and } j=0,1,\ldots\ , \tag{3}$$

where $\Delta_j^{(i)}$ denotes

$$\Delta_j^{(i)}=\begin{vmatrix} \nu_i & \nu_{i+1} & \cdots & \nu_{i+j} \\ \nu_{i+1} & \nu_{i+2} & \cdots & \nu_{i+j+1} \\ & & \cdots & \\ \nu_{i+j} & \nu_{i+j+1} & \cdots & \nu_{i+2j} \end{vmatrix}\ ,$$

which is the so-called Hadamard determinant associated to the moments given by Eq. (2).

III. GENERAL RESULTS

Here the Stieltjes theorem shown in the preceding section is applied to the function $f_m^{(k)}(r)$ for various choices of the parameter m. This application produces several rigorous inequalities to be fulfilled by a kth-order monotone function, which involve radial expectation values and/or the central values of the function and its derivatives. We will only shown those inequalities coming from the non-negativity of the Hadamard determinants $\Delta_1^{(0)}$ and/or $\Delta_1^{(1)}$ because they are nontrivial, physically interesting, and specially simple.

First: $m=k-1$. The single-particle density at the origin is bounded from below as

$$\rho(0)\geq\frac{1}{4\pi}\frac{k}{k+1}\frac{\langle r^{-2}\rangle^2}{\langle r^{-1}\rangle}\ ,\quad k=1,2,\ldots\ . \tag{4}$$

This inequality reduces to the known lower bounds [11,21,22] to the central single-particle density $\rho(0)$ for the cases $k=1$ (monotonically decreasing density) and $k=2$ (convex density). Even more, such lower bounds get naturally improved for higher values of k in (4).

Second: $m=k-2$. The value of the first derivative of the single-particle density at the origin satisfies the inequality

$$-\rho'(0)\geq 4\pi\frac{k-1}{k}\frac{[\rho(0)]^2}{\langle r^{-2}\rangle}\ ,\quad k=2,3,\ldots\ . \tag{5}$$

In particular, for $k=2$ one has that

$$-\rho'(0)\geq 2\pi\frac{[\rho(0)]^2}{\langle r^{-2}\rangle} \tag{6}$$

for a convex single-particle density, as recently shown by Ref. [11].

Third: $m=k-n-1$, $n\geq 2$. The central value of the nth derivative of the single-particle density is bounded from below by means of the corresponding values of the derivatives of the two previous orders as

$$\rho^{(n-2)}(0)\rho^{(n)}(0)\geq\frac{k-n}{k-(n-1)}[\rho^{(n-1)}(0)]^2\ ,$$

$$n=2,3,\ldots\ ,\quad k=n+1,n+2,\ldots\ . \tag{7}$$

It is worthwhile to remark that the combination of inequalities (4), (5), and (7) allows one to find rigorous bounds to any central derivative $\rho^{(n)}(0)$ in terms of the radial expectation values $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$.

Fourth: $m=k+n$ and $n>-1$. The radial expectation values $\langle r^\alpha\rangle$ with $\alpha=n$, $n-1$, and $n-2$ fulfill

$$\langle r^n\rangle\langle r^{n-2}\rangle\geq\frac{(k+n+1)(n+2)}{(k+n+2)(n+1)}\langle r^{n-1}\rangle^2$$

$$\text{with } n>-1,\quad k=0,1,\ldots\ . \tag{8}$$

These inequalities considerably generalize and improve all the corresponding ones known up to now [23–27]. Let us show some particular cases.

(i) $k=0$. Then, any single-particle density, because of its positive definiteness, satisfies

$$\langle r^n\rangle\langle r^{n-2}\rangle\geq\langle r^{n-1}\rangle^2\ . \tag{9}$$

(ii) $k=1$. A monotonically decreasing single-particle density, that is, a density-function unimodal with mode at the origin, satisfies not only (9) but also

$$\langle r^n\rangle\langle r^{n-2}\rangle\geq\frac{(n+2)^2}{(n+1)(n+3)}\langle r^{n-1}\rangle^2\ . \tag{10}$$

(iii) $k=2$. A single-particle density with the convexity property satisfies

$$\langle r^n\rangle\langle r^{n-2}\rangle\geq\frac{(n+2)(n+3)}{(n+1)(n+4)}\langle r^{n-1}\rangle^2\ , \tag{11}$$

which is better than the inequalities (9) and (10).

(iv) $n=0$. Then, a kth-order monotonic density fulfills

TABLE I. Comparison of the upper bound (UB), $U=(Z/2\pi)\langle r^{-2}\rangle$, and the lower bound (LB), $L=(1/4\pi)(\langle r^{-2}\rangle^2/\langle r^{-1}\rangle)$, of Hoffmann-Ostenhof *et al.* with the value of $\rho(0)$ for all neutral atoms with $Z\leq 54$ in the Hartree-Fock approximation. Ratios between bounds and $\rho(0)$ are given in percent. Numbers in parentheses denote the corresponding power of 10, i.e., 3.1831(−1) means 3.1831×10^{-1}. Atomic units are used throughout.

Z	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\rho(0)$	LB	UB	LB(%)	UB(%)
1	2.0000	1.0000	3.1831(−1)	3.1831(−1)	3.1831(−1)	100.0	100.0
2	1.1992(+1)	3.3747	3.5973	3.3911	3.8172	94.3	94.2
3	3.0217(+1)	5.7156	1.3834(+1)	1.2713(+1)	1.4428(+1)	91.9	95.9
4	5.7624(+1)	8.4087	3.5428(+1)	3.1424(+1)	3.6685(+1)	88.7	96.6
5	9.3663(+1)	1.1379(+1)	7.1985(+1)	6.1351(+1)	7.4535(+1)	85.2	96.6
6	1.3877(+2)	1.4689(+1)	1.2756(+2)	1.0433(+2)	1.3252(+2)	81.8	96.3
7	1.9322(+2)	1.8336(+1)	2.0613(+2)	1.6203(+2)	2.1526(+2)	78.6	95.8
8	2.5726(+2)	2.2260(+1)	3.1197(+2)	2.3660(+2)	3.2755(+2)	75.8	95.2
9	3.3107(+2)	2.6519(+1)	4.4871(+2)	3.2891(+2)	4.7422(+2)	73.3	94.6
10	4.1490(+2)	3.1113(+1)	6.2015(+2)	4.4029(+2)	6.6033(+2)	71.0	93.9
11	5.0949(+2)	3.5430(+1)	8.3383(+2)	5.8303(+2)	8.9197(+2)	69.9	93.5
12	6.1482(+2)	3.9920(+1)	1.0937(+3)	7.5352(+2)	1.1742(+3)	68.9	93.1
13	7.3035(+2)	4.4500(+1)	1.4029(+3)	9.5388(+2)	1.5111(+3)	68.0	92.8
14	8.5623(+2)	4.9243(+1)	1.7657(+3)	1.1847(+3)	1.9078(+3)	67.1	92.6
15	9.9256(+2)	5.4148(+1)	2.1863(+3)	1.4478(+3)	2.3696(+3)	66.2	92.3
16	1.1409(+3)	5.9497(+1)	2.6701(+3)	1.7410(+3)	2.9053(+3)	65.2	91.9
17	1.2967(+3)	6.4372(+1)	3.2180(+3)	2.0786(+3)	3.5084(+3)	64.6	91.7
18	1.4650(+3)	6.9725(+1)	3.8402(+3)	2.4495(+3)	4.1969(+3)	63.8	91.5
19	1.6442(+3)	7.4894(+1)	4.5385(+3)	2.8724(+3)	4.9720(+3)	63.3	91.3
20	1.8344(+3)	8.0159(+1)	5.3199(+3)	3.3406(+3)	5.8391(+3)	62.8	91.1
21	2.0343(+3)	8.5709(+1)	6.1836(+3)	3.8423(+3)	6.7991(+3)	62.1	90.9
22	2.2446(+3)	9.1420(+1)	7.1339(+3)	4.3856(+3)	7.8593(+3)	61.5	90.8
23	2.4655(+3)	9.7273(+1)	8.1783(+3)	4.9729(+3)	9.0251(+3)	60.8	90.6
24	2.6960(+3)	1.0346(+2)	9.3152(+3)	5.5906(+3)	1.0298(+4)	60.0	90.5
25	2.9391(+3)	1.0941(+2)	1.0560(+4)	6.2829(+3)	1.1694(+4)	59.5	90.3
26	3.1922(+3)	1.1565(+2)	1.1912(+4)	7.0117(+3)	1.3209(+4)	58.9	90.2
27	3.4560(+3)	1.2205(+2)	1.3371(+4)	7.7875(+3)	1.4851(+4)	58.2	90.0
28	3.7305(+3)	1.2858(+2)	1.4943(+4)	8.6129(+3)	1.6624(+4)	57.6	89.9
29	4.0144(+3)	1.3548(+2)	1.6627(+4)	9.4658(+3)	1.8528(+4)	56.9	89.7
30.	4.3120(+3)	1.4206(+2)	1.8449(+4)	1.0415(+4)	2.0588(+4)	56.5	89.6
31	4.6200(+3)	1.4865(+2)	2.0388(+4)	1.1426(+4)	2.2794(+4)	56.0	89.4
32	4.9396(+3)	1.5533(+2)	2.2470(+4)	1.2500(+4)	2.5157(+4)	55.6	89.3
33	5.2704(+3)	1.6209(+2)	2.4690(+4)	1.3637(+4)	2.7681(+4)	55.2	89.2
34	5.6128(+3)	1.6892(+2)	2.7061(+4)	1.4841(+4)	3.0372(+4)	54.8	89.1
35	5.9662(+3)	1.7584(+2)	2.9572(+4)	1.6109(+4)	3.3234(+4)	54.5	89.0
36	6.3305(+3)	1.8285(+2)	3.2228(+4)	1.7441(+4)	3.6271(+4)	54.1	88.9
37	6.7057(+3)	1.8967(+2)	3.5024(+4)	1.8866(+4)	3.9488(+4)	53.9	88.7
38	7.0936(+3)	1.9657(+2)	3.8009(+4)	2.0371(+4)	4.2901(+4)	53.6	88.6
39	7.4917(+3)	2.0362(+2)	4.1153(+4)	2.1935(+4)	4.6501(+4)	53.3	88.5
40	7.9002(+3)	2.1090(+2)	4.4462(+4)	2.3550(+4)	5.0294(+4)	53.0	88.4
41	8.3206(+3)	2.1817(+2)	4.7949(+4)	2.5253(+4)	5.4295(+4)	52.7	88.3
42	8.7521(+3)	2.2552(+2)	5.1613(+4)	2.7029(+4)	5.8503(+4)	52.4	88.2
43	9.1956(+3)	2.3281(+2)	5.5466(+4)	2.8903(+4)	6.2932(+4)	52.1	88.1
44	9.6488(+3)	2.4046(+2)	5.9491(+4)	3.0810(+4)	6.7569(+4)	51.8	88.0
45	1.0114(+4)	2.4805(+2)	6.3716(+4)	3.2817(+4)	7.2436(+4)	51.5	88.0
46	1.0589(+4)	2.5590(+2)	6.8129(+4)	3.4868(+4)	7.7523(+4)	51.2	87.9
47	1.1078(+4)	2.6350(+2)	7.2755(+4)	3.7062(+4)	8.2867(+4)	50.9	87.8
48	1.1579(+4)	2.7111(+2)	7.7609(+4)	3.9354(+4)	8.8457(+4)	50.7	87.7
49	1.2090(+4)	2.7880(+2)	8.2644(+4)	4.1721(+4)	9.4285(+4)	50.5	87.7
50	1.2612(+4)	2.8651(+2)	8.7899(+4)	4.4179(+4)	1.0036(+5)	50.3	87.6
51	1.3146(+4)	2.9427(+2)	9.3371(+4)	4.6734(+4)	1.0670(+5)	50.1	87.5
52	1.3692(+4)	3.0208(+2)	9.9074(+4)	4.9386(+4)	1.1332(+5)	49.8	87.4
53	1.4250(+4)	3.0995(+2)	1.0501(+5)	5.2135(+4)	1.2020(+5)	49.6	87.4
54	1.4818(+4)	3.1787(+2)	1.1116(+5)	5.4969(+4)	1.2735(+5)	49.5	87.3

TABLE II. Hartree-Fock study of inequalities (22) and (23) as well as the cusp condition for all neutral atoms with $Z \leq 54$. The ratios $C_{01}=(-2Z)\rho(0)/\rho'(0)$, $C_{02}=(-2Z)^2\rho(0)/\rho''(0)$, and $C_{12}=(-2Z)\rho'(0)/\rho''(0)$ are given. See text for further details. Atomic units are used throughout.

Z	$\rho(0)$	$-\rho'(0)$	$\rho''(0)$	C_{01}	C_{02}	C_{12}
1	3.1831(−1)	6.3662(−1)	1.2732	1.000 00	1.000 00	1.000 00
2	3.5973	1.4420(+1)	6.1251(+1)	0.997 85	0.939 69	0.941 72
3	1.3834(+1)	8.3479(+1)	5.2892(+2)	0.994 32	0.941 61	0.946 98
4	3.5428(+1)	2.8479(+2)	2.3778(+3)	0.995 19	0.953 56	0.958 17
5	7.1985(+1)	7.2260(+2)	7.4775(+3)	0.996 19	0.962 69	0.966 37
6	1.2756(+2)	1.5357(+3)	1.8968(+4)	0.996 70	0.968 37	0.971 57
7	2.0613(+2)	2.8950(+3)	4.1581(+4)	0.996 85	0.971 66	0.974 72
8	3.1197(+2)	5.0099(+3)	8.2180(+4)	0.996 35	0.971 84	0.975 40
9	4.4871(+2)	8.1019(+3)	1.4907(+5)	0.996 91	0.975 26	0.978 29
10	6.2015(+2)	1.2425(+4)	2.5299(+5)	0.998 22	0.980 49	0.982 25
11	8.3383(+2)	1.8365(+4)	4.1023(+5)	0.998 88	0.983 78	0.984 88
12	1.0937(+3)	2.6274(+4)	6.3933(+5)	0.999 05	0.985 39	0.986 32
13	1.4029(+3)	3.6511(+4)	9.6168(+5)	0.999 02	0.986 16	0.987 12
14	1.7657(+3)	4.9490(+4)	1.4029(+6)	0.998 99	0.986 72	0.987 72
15	2.1863(+3)	6.5638(+4)	1.9911(+6)	0.999 25	0.988 26	0.989 00
16	2.6701(+3)	8.5545(+4)	2.7691(+6)	0.998 81	0.987 39	0.988 56
17	3.2180(+3)	1.0942(+5)	3.7530(+6)	0.999 92	0.991 22	0.991 31
18	3.8402(+3)	1.3837(+5)	5.0320(+6)	0.999 09	0.989 05	0.989 95
19	4.5385(+3)	1.7254(+5)	6.6136(+6)	0.999 56	0.990 92	0.991 35
20	5.3199(+3)	2.1294(+5)	8.5922(+6)	0.999 33	0.990 66	0.991 32
21	6.1836(+3)	2.5995(+5)	1.1016(+7)	0.999 07	0.990 22	0.991 14
22	7.1339(+3)	3.1411(+5)	1.3934(+7)	0.999 29	0.991 17	0.991 87
23	8.1783(+3)	3.7653(+5)	1.7464(+7)	0.999 12	0.990 90	0.991 77
24	9.3152(+3)	4.4745(+5)	2.1638(+7)	0.999 29	0.991 89	0.992 60
25	1.0560(+4)	5.2813(+5)	2.6576(+7)	0.999 71	0.993 34	0.993 63
26	1.1912(+4)	6.1997(+5)	3.2480(+7)	0.999 09	0.991 65	0.992 55
27	1.3371(+4)	7.2271(+5)	3.9319(+7)	0.999 05	0.991 63	0.992 57
28	1.4943(+4)	8.3728(+5)	4.7190(+7)	0.999 40	0.993 01	0.993 60
29	1.6627(+4)	9.6482(+5)	5.6296(+7)	0.999 51	0.993 53	0.994 02
30	1.8449(+4)	1.1073(+6)	6.6813(+7)	0.999 61	0.994 04	0.994 43
31	2.0388(+4)	1.2633(+6)	7.8596(+7)	1.000 59	0.997 15	0.996 57
32	2.2470(+4)	1.4373(+6)	9.2300(+7)	1.000 55	0.997 17	0.996 63
33	2.4690(+4)	1.6286(+6)	1.0782(+8)	1.000 61	0.997 48	0.996 87
34	2.7061(+4)	1.8401(+6)	1.2564(+8)	1.000 03	0.995 95	0.995 92
35	2.9572(+4)	2.0701(+6)	1.4549(+8)	0.999 98	0.995 96	0.995 98
36	3.2228(+4)	2.3199(+6)	1.6761(+8)	1.000 24	0.996 77	0.996 52
37	3.5024(+4)	2.5877(+6)	1.9167(+8)	1.001 56	1.000 65	0.999 10
38	3.8009(+4)	2.8844(+6)	2.1942(+8)	1.001 47	1.000 52	0.999 05
39	4.1153(+4)	3.2053(+6)	2.5025(+8)	1.001 43	1.000 51	0.999 08
40	4.4462(+4)	3.5521(+6)	2.8444(+8)	1.001 37	1.000 40	0.999 04
41	4.7949(+4)	3.9267(+6)	3.2231(+8)	1.001 30	1.000 31	0.999 01
42	5.1613(+4)	4.3300(+6)	3.6408(+8)	1.001 26	1.000 27	0.999 01
43	5.5466(+4)	4.7643(+6)	4.1014(+8)	1.001 20	1.000 21	0.999 00
44	5.9491(+4)	5.2288(+6)	4.6057(+8)	1.001 22	1.000 28	0.999 07
45	6.3716(+4)	5.7280(+6)	5.1604(+8)	1.001 13	1.000 12	0.999 00
46	6.8129(+4)	6.2610(+6)	5.7659(+8)	1.001 09	1.000 09	0.998 99
47	7.2755(+4)	6.8316(+6)	6.4281(+8)	1.001 07	1.000 09	0.999 02
48	7.7609(+4)	7.4448(+6)	7.1568(+8)	1.000 76	0.999 40	0.998 64
49	8.2664(+4)	8.0979(+6)	7.9519(+8)	1.000 39	0.998 38	0.997 99
50	8.7899(+4)	8.7822(+6)	8.7919(+8)	1.000 88	0.999 77	0.998 90
51	9.3371(+4)	9.5153(+6)	9.7156(+8)	1.000 90	0.999 87	0.998 97
52	9.9074(+4)	1.0295(+7)	1.0718(+9)	1.000 85	0.999 78	0.998 93
53	1.0501(+5)	1.1122(+7)	1.1802(+9)	1.000 79	0.999 68	0.998 88
54	1.1116(+5)	1.1996(+7)	1.2970(+9)	1.000 80	0.999 73	0.998 93

$$N\langle r^{-2}\rangle \geq 2\frac{k+1}{k+2}\langle r^{-1}\rangle^2 , \quad k=0,1,\ldots . \tag{12}$$

(v) $n=1$. In this case, the inequality

$$N\langle r^{-2}\rangle \geq \frac{4}{3}\frac{k+3}{k+4}\langle r\rangle^2 , \quad k=0,1,\ldots \tag{13}$$

is also valid for any monotone density of order k.

An important observation about inequalities (4)–(8) is that they are optimal in the completely monotonic case, i.e., for $k=\infty$. Then one obtains that for a completely monotone single-particle density, the following two sets of rigorous inequalities are satisfied.

(i) Inequalities involving $\rho(0)$ or $\rho^{(n)}(0)$:

$$\rho(0) \geq \frac{1}{4\pi}\frac{\langle r^{-2}\rangle^2}{\langle r^{-1}\rangle} , \tag{14}$$

$$-\rho'(0) \geq 4\pi\frac{[\rho(0)]^2}{\langle r^{-2}\rangle} , \tag{15}$$

$$\rho^{(n-2)}(0)\rho^{(n)}(0) \geq [\rho^{(n-1)}(0)]^2, \quad n\geq 2 . \tag{16}$$

(ii) Inequalities involving $\langle r^{\alpha}\rangle$:

$$\langle r^n\rangle\langle r^{n-2}\rangle \geq \frac{n+2}{n+1}\langle r^{n-1}\rangle^2 , \quad n>-1 . \tag{17}$$

Some particular cases are

$$N\langle r^{-2}\rangle \geq 2\langle r^{-1}\rangle^2 , \tag{18}$$

$$\langle r^{-1}\rangle\langle r\rangle \geq \tfrac{3}{2}N^2 , \tag{19}$$

$$N\langle r^2\rangle \geq \tfrac{4}{3}\langle r\rangle^2 . \tag{20}$$

Inequalities (4)–(20) can still be improved by taking into account Hadamard determinantal inequalities (3) of order $k\geq 2$. This implies that the resulting inequalities involve a higher number of radial expectation values and/or $\rho^{(n)}(0)$ values, making them much more complicated.

IV. APPLICATION TO ATOMIC SYSTEMS

Now let us apply some of the inequalities found in the preceding section to the atomic systems. First of all, one should say that among inequalities (4)–(20) the only rigorous one is (9). However, it is known from near Hartree-Fock calculations that $\rho(r)$ is not only monotonically decreasing [8,9] but also, to a very good approximation, convex [11]. Even more, these numerical calculations performed in neutral atoms with $Z\leq 54$ show [28] that the monotone behavior of order higher than 2 is only weakly violated, and the violation is so that its effects on measurable and/or fundamental quantities of the system are extremely small since the electron density always appears within an integral kernel in evaluating those quantities. So, although the only known many-electron system with a rigorous completely monotonic electron density is the hydrogen atom, one may assume that the electron density of any neutral atom is completely monotone to quite a good approximation.

To illustrate the goodness of this approximation, let us

TABLE III. Hartree-Fock study of inequalities (16), (17), and (18) for all neutral atoms with $Z\leq 54$. The ratios R_i, $i=0,1,2$, defined in text are given in percent. Atomic units are used throughout.

Z	$\langle r\rangle$	$\langle r^2\rangle$	R_0	R_1	R_2
1	1.50	3.00	100.0	100.0	100.0
2	1.85	2.37	95.0	95.9	96.8
3	5.02	18.63	72.1	47.1	60.1
4	6.13	17.32	61.4	46.6	72.3
5	6.81	15.85	55.3	48.4	78.0
6	7.14	13.79	51.8	51.5	82.2
7	7.35	12.08	49.7	54.5	85.2
8	7.61	11.17	48.2	56.7	86.4
9	7.78	10.24	47.2	58.9	87.5
10	7.89	9.38	46.7	61.1	88.6
11	10.84	27.15	44.8	47.2	52.5
12	12.25	29.57	43.2	44.2	56.4
13	13.72	33.45	41.7	41.5	57.7
14	14.48	32.25	40.5	41.2	61.9
15	14.97	30.26	39.4	41.6	65.8
16	15.36	28.98	38.8	42.0	67.8
17	15.82	27.64	37.6	42.6	71.1
18	16.07	26.04	36.9	43.4	73.5
19	19.45	51.19	35.9	37.2	51.9
20	21.25	56.58	35.0	35.2	53.2
21	21.48	53.16	34.4	35.9	55.1
22	21.60	50.18	33.8	36.8	56.3
23	21.68	47.52	33.4	37.6	57.3
24	20.48	37.62	33.1	40.8	61.9
25	21.79	43.08	32.6	39.3	58.8
26	21.86	41.14	32.2	40.1	59.6
27	21.91	39.41	31.9	40.9	60.2
28	21.95	37.80	31.7	41.7	60.7
29	21.06	32.28	31.5	44.2	63.2
30	22.00	34.99	31.2	43.2	61.5
31	23.40	40.91	30.9	41.5	57.5
32	24.20	41.57	30.5	40.9	58.7
33	24.78	41.05	30.2	40.7	60.4
34	25.40	41.15	29.9	40.4	61.5
35	25.87	40.50	29.6	40.4	62.9
36	26.24	39.52	29.3	40.5	64.5
37	29.80	68.19	29.0	36.3	46.9
38	31.81	76.05	28.7	34.6	46.7
39	32.35	73.22	28.4	34.6	48.9
40	31.49	61.23	28.2	36.1	54.0
41	31.69	58.49	27.9	36.5	55.9
42	31.85	56.13	27.7	36.8	57.4
43	33.32	63.15	27.4	35.8	54.5
44	32.37	53.88	27.2	37.3	58.9
45	32.56	52.67	27.0	37.6	59.6
46	31.37	42.08	26.9	39.5	67.8
47	32.88	50.44	26.7	38.3	60.8
48	33.99	54.34	26.4	37.5	59.1
49	35.51	61.43	26.2	36.4	55.9
50	36.47	63.04	26.0	35.9	56.3
51	37.20	63.06	25.8	35.6	57.4
52	37.96	63.75	25.6	35.4	58.0
53	38.57	63.45	25.4	35.2	59.0
54	39.06	62.64	25.3	35.2	60.1

analyze the quality of inequalities (14)–(20), which supply interesting relationships between values of the electron density and its derivatives at the nucleus and the radial expectation values for atomic systems. First, inequality (15) together with the so-called atomic cusp condition [6] $\rho'(0)=-2Z\rho(0)$, Z being the atomic number, produces

$$\rho(0)\leq\frac{Z}{2\pi}\langle r^{-2}\rangle \ . \tag{21}$$

This is the famous upper bound for the electron density at the nucleus obtained in 1978 by Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [29], in the electrostatic approximation for the atomic Hamiltonian, which assures that the nuclear mass is infinite. Just recently, an approximate expression for $\rho(0)$, which coincides with this bound, has also been found by Cioslowski [30] with assumptions on the electron density stronger than the complete monotonicity.

Second, the inequality (14) gives a lower bound to $\rho(0)$ that is better by a factor $\frac{3}{2}$ than the best corresponding one known up to now, namely that obtained with the convexity condition [11]. Other similar, but less accurate, lower bounds to $\rho(0)$ have been also published [21,27,31–33]. In Table I, the qualities of both the lower and upper bounds given by (14) and (21), respectively, are investigated by means of the near Hartree-Fock wave functions [34] for all neutral atoms with $Z\leq 54$. Here we should point out that the near Hartree-Fock values of $\rho(0)$ were previously calculated by Westgate *et al.* [35]. It is found that the upper bound (21) is very accurate not only for very light atoms, as is already known [25], but also for all the atoms up to Xe. The lower bound (14) is very accurate for light atoms but its quality decreases to about 50% in the region of atoms with $35\leq Z\leq 54$.

Third, inequality (16) with $n=2$ together with the above-mentioned cusp condition leads to the following two lower bounds for the central second derivative $\rho''(0)$ of atomic systems:

$$\rho''(0)\geq(-2Z)\rho'(0) \ , \tag{22}$$

$$\rho''(0)\geq(-2Z)^2\rho(0) \ . \tag{23}$$

The quality of these inequalities for all ground-state neutral atoms up to xenon is illustrated in Table II, where again the near Hartree-Fock atomic wave functions of Clementi-Roetti [34] have been used. Remark that in Table II the atomic cusp condition $\rho'(0)=-2Z\rho(0)$ is, for the sake of completeness, also numerically studied in the same Hartree-Fock framework. A careful examination of this table allows us to conclude that the accuracy of the two inequalities (22) and (23) is similar to that of the cusp condition. So, the lower bounds (22) and (23) may be considered as the computational value of $\rho''(0)$.

Finally, we study the quality of the atomic inequalities (18), (19), and (20) in Table III. Therein the Hartree-Fock values of the ratios

$$R_0=\frac{2}{N}\frac{\langle r^{-1}\rangle^2}{\langle r^{-2}\rangle} \ , \quad R_1=\frac{3N^2}{2}(\langle r^{-1}\rangle\langle r\rangle)^{-1} \ ,$$

$$R_2=\frac{4}{3N}\frac{\langle r\rangle^2}{\langle r^2\rangle}$$

are given for all the neutral atoms with $Z\leq 54$. One notices that the quality of inequality (20) is higher than that of the other two inequalities (18) and (19), being always bigger than $\sim 50\%$ for all atoms with $Z\leq 54$. Inequalities (18) and (19) are reasonably accurate only for atoms with $Z\leq 10$.

V. CONCLUDING REMARKS

To summarize, we have found several sets of rigorous inequalities that involve the values at the origin of the single-particle density $\rho(r)$ and its derivatives as well as the radial expectation values. They are valid for any many-particle system characterized by a single-particle density function $\rho(r)$ with a monotone nature of finite or infinite order.

The application of these inequalities to atomic systems in the approximation of complete monotonicity allows to extend considerably and improve the accuracy of the known inequalities among three expectation values as well as that of the bounds to the electron density $\rho(r)$ and its derivatives at the nucleus. Particularly remarkable are the upper bound given by (21) and the lower bound given by (14) of Hoffmann-Ostenhof *et al.* to the atomic electron density at the nucleus, $\rho(0)$, as well as the computational values for the second derivative of the electron density at the nucleus, $\rho''(0)$.

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