Rigorous lower bounds to average electron radial and momentum densities for atomic systems

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Rigorous lower bounds to the average electron radial density $\langle \rho \rangle$ in terms of any two moments of the charge density have been found for N-electron systems. Similar bounds to the average electron momentum density $\langle \gamma \rangle$ are also given by means of any two momentum expectation values. These bounds allow us to establish rigorous inequalities to $\langle \rho \rangle$ and $\langle \gamma \rangle$ (which have been recently found to be experimentally measurable) and other fundamental and/or measurable quantities such as the electronic energy, the diamagnetic susceptibility, and the Compton profile peak height $J(0)$. The quality of the bounds is analytically discussed and numerically studied within the Hartree-Fock framework. Best bounds turn out to be (1) $\langle \rho \rangle \geq \langle r^{-1} \rangle^3 / 9\pi N$, (2) $\langle \gamma \rangle \geq 8[J(0)]^3 / 9\pi N$.

I. INTRODUCTION

In 1978 Hyman, Yaniger, and Liebman[1] showed that the average electron radial density (henceforth to be denoted by $\langle \rho \rangle$) of a many-electron system is an experimentally measurable quantity related to the intensity of x rays elastically scattered by the system. Since then, much useful work has been done with this quantity.[2-11] It has been found to be related to (i) the total electronic energy[1-3,8,10,12] E (then, to the total kinetic energy T because of the virial theorem), (ii) the electrostatic self-energy of the electron density $\rho(\mathbf{r})$ of the system or Coulomb energy[4,6,12] J, (iii) the total electron-electron repulsion energy[4] V_{ee}, (iv) the electron density of the system at the nucleus[2,10] $\rho(0)$, (v) the Weizsacker term of the total kinetic energy functional[10,12] T_W, (vi) a ratio of the Thomas-Fermi kinetic energy T_0 and the Dirac exchange energy K_0,[9,10] and to (vii) the electron-nucleus potential energy[7,12] V_{ne}. Most of these relationships are either semiempirical or have a semiclassical origin, although some rigorous inequalities are also known.

More recently, Gadre and Chakravorty[12] pointed out that the average electron momentum density, to be denoted by $\langle \gamma \rangle$, is also experimentally measurable and showed that it can be determined from the Compton profile via the reciprocal form factor. Here again, there already exist a few known relationships[12,13] which involve $\langle \gamma \rangle$ together with various fundamental quantities of the system, such as the second moment of the electron density $\langle r^2 \rangle$ (then, to the diamagnetic susceptibility), the third moment $\langle r^3 \rangle$, the peak height of the Compton profile $J(0)$, as well as with the total energy E and the ionization potential via the inequalities among $\langle r^2 \rangle$ and the last two quantities.[14]

This paper is structured as follows. Section II contains a brief review of the known relationships which involve $\langle \rho \rangle$ or $\langle \gamma \rangle$ and some fundamental quantities of an N-electron system. Later, in Secs. III and IV we show rigorous lower bounds to $\langle \rho \rangle$ and $\langle \gamma \rangle$, in terms of any two moments of the electron density $\rho(\mathbf{r})$ and the momentum density $\gamma(\mathbf{p})$ of the system, respectively. There will be found four types of bounds according to the different procedures used to obtain them. The proof of these bounds is the object of Sec. V. Finally, some concluding remarks are made.

II. REVIEW OF PREVIOUS RESULTS

Here, we will briefly review the known results (or better those published in the literature, to the best of our knowledge) about the spherically averaged electron radial density $\langle \rho \rangle$ and momentum density $\langle \gamma \rangle$ of an N-electron system. Atomic units are used.

Let us start with $\langle \rho \rangle$. Several semiempirical fits of the form $\langle \rho \rangle = C|E|^n$ are known;[2,3] in particular, Tal and Levy[2] showed that the relationship $\langle \rho \rangle = 0.21|E|^{1.38}$ is valid for neutral atoms with $4 \leq Z \leq 54$. Also, Gadre and Bendale[4] have tested numerically the constancy of the ratios $J/(N^4\langle \rho \rangle)^{1/3}$ and $V_{ee}/(N^4\langle \rho \rangle)^{1/3}$ by employing the ground-state electron densities of Clementi and Roetti[15] for atoms with $Z=3$ through $Z=36$. Also several semiclassical and approximate bounds to $\langle \rho \rangle$ have been found;[1,2,8,12] in particular,

$$\langle \rho \rangle \leq 0.205|E|^{3/2} \text{ and } \langle \rho \rangle \geq 0.034|E|^{3/2}$$

due to Hyman *et al.*,[1,8] and

$$\langle \rho \rangle \geq \frac{2^{5/2}}{3\pi^2}|E|^{3/2} \simeq 0.191|E|^{3/2}$$

given by Gadre and Chakravorty,[12] and

$$\langle \rho \rangle \geq \frac{\pi}{8Z^3}\rho(0)^2$$

according to Tal and Levy.[2] Rigorous lower and upper bounds to $\langle \rho \rangle$ are given in Refs. 6, 9, 10, and 12. In particular let us mention the lower bound[9,10]

$$\langle \rho \rangle \geq \frac{5}{2\pi(3\pi^2)^{1/3}}\frac{T_0^2}{K_0}$$

and the upper bound[10,12]

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$$\langle\rho\rangle \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2}(NT_W^3)^{1/2} \le \frac{1}{2\pi^2}\left[\frac{8}{3}\right]^{3/2}(NT^3)^{1/2} = 0.2206(NT^3)^{1/2}$$

which improves the first semiclassical inequality. Also it is worthy to point out here that[12]

$$\langle\rho\rangle \ge (\tfrac{3}{4})^3\tfrac{3}{2}\frac{J^3}{N^4} \quad \text{with } J=\tfrac{1}{2}\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' ,$$

which considerably improves a similar lower bound encountered by Thulstrup and Linderberg.[6] Also, the following upper bound is known for spherically symmetric densities:[12]

$$\langle\rho\rangle \le \frac{1}{2\pi}T_W\langle r^{-1}\rangle \le \frac{1}{2\pi}T\langle r^{-1}\rangle = \frac{1}{2\pi}\frac{ZT}{V_{ne}} .$$

Some approximate upper bounds to $\langle\rho\rangle$ are also given in Ref. 7 as well as various rigorous inequalities among the average electron radial densities corresponding to three successive members of an isoelectronic series of atoms have been pointed out.[11]

With respect to $\langle\gamma\rangle$, the main results known up to now are due to Gadre and Chakravorty.[12] These authors point out (i) the semiclassical relation $\langle\gamma\rangle = 2\langle r^3\rangle/3\pi^2$ and the semiempirical fit $\langle\gamma\rangle \simeq 0.0035N^{1/2}\langle r^2\rangle^{3/2}$, and (ii) the two following rigorous upper bounds:

$$\langle\gamma\rangle \le \frac{4}{3\sqrt{3}\pi^2}N^{1/2}\langle r^2\rangle^{3/2}$$

and

$$\langle\gamma\rangle \le \frac{1}{4\pi}\langle r^2\rangle\langle p^{-1}\rangle ,$$

which relate $\langle\gamma\rangle$ with the diamagnetic susceptibility via $\langle r^2\rangle$ and the peak height $J(0)$ of the Compton profile by means of $\langle p^{-1}\rangle = 2J(0)$.

III. LOWER BOUNDS TO $\langle\rho\rangle$

Let us consider the electron density $\rho(\mathbf{r})$ of an N-electron system which is normalized to N. Then, the αth moment around the origin of $\rho(\mathbf{r})$ is

$$\langle r^\alpha\rangle = \int r^\alpha\rho(\mathbf{r})d\mathbf{r} , \tag{1}$$

where α is a real number. In particular, $\langle r^0\rangle = N$.

Here we will show four different types of lower bounds to the quantity

$$\langle\rho\rangle = \int\rho^2(\mathbf{r})d\mathbf{r}$$

in terms of two moments or radial expectation values of the form (1). As it is known, these moments (specially those of low orders) are either directly measurable or related to measurable quantities.

A. Bounds of type 1

Two sets of lower bounds of this type to $\langle\rho\rangle$ are found.

(i) If $\alpha > \beta > -\frac{3}{2}$,

$$\langle\rho\rangle \ge C_1(\alpha,\beta)\left[\frac{\langle r^\beta\rangle^{2\alpha+3}}{\langle r^\alpha\rangle^{2\beta+3}}\right]^{1/(\alpha-\beta)} , \tag{2}$$

where C_1 is given as

$$C_1(\alpha,\beta) = \frac{(\alpha-\beta)^3}{\pi B((2\beta+3)/(\alpha-\beta),3)} \times\left[\frac{(2\beta+3)^{2\beta+3}}{(2\alpha+3)^{2\alpha+3}}\right]^{1/(\alpha-\beta)} . \tag{2a}$$

(ii) If $\beta < \alpha < -\frac{3}{2}$,

$$\langle\rho\rangle \ge C_2(\alpha,\beta)\left[\frac{\langle r^\alpha\rangle^{-2\beta-3}}{\langle r^\beta\rangle^{-2\alpha-3}}\right]^{1/(\alpha-\beta)} , \tag{3}$$

with

$$C_2(\alpha,\beta) = \frac{(\alpha-\beta)^3}{B((-2\alpha-3)/(\alpha-\beta),3)} \times\left[\frac{(-2\alpha-3)^{-2\alpha-3}}{(-2\beta-3)^{-2\beta-3}}\right]^{1/(\alpha-\beta)} . \tag{3a}$$

The B symbol denotes the β function defined by

$$B(x,y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)} = \int_0^1 t^{x-1}(1-t)^{y-1}dt .$$

Particular cases of the inequalities (2) are

$$\langle\rho\rangle \ge \frac{1}{9\pi}\frac{\langle r^{-1}\rangle^3}{N} = F(0,-1) , \tag{4a}$$

$$\langle\rho\rangle \ge \frac{3}{10\pi\sqrt{5}}\left[\frac{\langle r^{-1}\rangle^5}{\langle r\rangle}\right]^{1/2} = F(1,-1) , \tag{4b}$$

$$\langle\rho\rangle \ge \frac{2}{7^{4/3}\pi}\left[\frac{\langle r^{-1}\rangle^7}{\langle r^2\rangle}\right]^{1/3} = F(2,-1) , \tag{4c}$$

$$\langle\rho\rangle \ge \frac{2}{\pi}\left[\frac{3}{5}\right]^4\frac{N^5}{\langle r\rangle^3} = F(1,0) , \tag{4d}$$

$$\langle\rho\rangle \ge \frac{5}{2\pi}\left[\frac{3}{7}\right]^{5/2}\frac{N^{7/2}}{\langle r^2\rangle^{3/2}} = F(2,0) , \tag{4e}$$

$$\langle\rho\rangle \ge \frac{3}{\pi}\left[\frac{5}{7}\right]^6\frac{\langle r\rangle^7}{\langle r^2\rangle^5} = F(2,1) . \tag{4f}$$

The inequalities (2) and (3) are valid for any many-electron system. It is worthy to point out that the corresponding lower bounds do not explicitly depend on N (the number of electrons of the system) unless α or β vanish, which may occur in the inequality (2) only.

These bounds have been obtained by means of a new lower bound variational method due to the first two authors[16–20] extended[21] so that we minimize any quantity of the form $\omega_n = \int\rho^n d\mathbf{r}$ in terms of any two arbitrary radial expectation values of $\rho(\mathbf{r})$, as indicated in Sec. V. Therein, one can also see that the best bound to $\langle\rho\rangle$ for atoms is given by the two involved moments $\langle r^\alpha\rangle$ of lowest order, that is, by the inequality (4a). This fact is also numerically observed in Table I, where a comparison of several lower bounds $F(\alpha,\beta)$ among themselves and

with the Hartree-Fock value of $\langle\rho\rangle$ is made in a broad region of neutral atoms ($N=Z$). The expectation values $\langle r^{-1}\rangle$, $\langle r\rangle$, and $\langle r^2\rangle$ needed to calculate the various lower bounds were taken from Ref. 22. The last column of the table corresponds to the ratio between the best lower bound, namely, $F(0,-1)$, and the Hartree-Fock value[9,15] of $\langle\rho\rangle$; it shows that the quality of the bound goes down from He (88.5%) to Xe (47.8%).

From the previous discussion, it seems natural to think that a lower bound to $\langle\rho\rangle$ better than $F(0,-1)$ could be $F(-1,-2)$, i.e., would depend on $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$, but such a bound is not possible to be obtained with the use of the above-mentioned variational method only. However, procedures exist in which the combination of this variational principle with some other inequalities allows to obtain lower bounds to $\langle\rho\rangle$ involving $\langle r^{-1}\rangle$, $\langle r^{-2}\rangle$ that are less accurate than those given by (2). Three of these procedures are used to show the bounds of types 2, 3, and 4 which are indicated below.

B. Bounds of type 2

For N-electron systems and any real n greater than 2, it is satisfied that

$$\langle\rho\rangle \geq C(n)\left[\frac{1}{N^{n+2}}\frac{\langle r^{-1}\rangle^{3n+2}}{\langle r^{-2}\rangle^{4}}\right]^{1/(n-2)} = F_2(-1,-2)\,, \quad (5)$$

where

$$C(n)=\frac{\left[\frac{3}{2}-\frac{1}{n}\right]^{(3n-2)/(n-2)}\left[\frac{2}{n}\right]^{4/(n-2)}}{4\pi B\left[\frac{4}{n-2},\frac{4n-4}{n-2}\right]\left[\frac{3}{2}+\frac{1}{n}\right]^{(3n+2)/(n-2)}}\,. \quad (5a)$$

The best of these bounds is obtained for an optimal n which depends on the system under consideration. For this optimal n and for neutral atoms, this bound usually lies in between the values of $F(2,-1)$ and $F(1,0)$ shown in Table I. Its derivation makes use of the Holder's inequality[23] to bound $\langle\rho\rangle$ by means of a ω-frequency moment and then one bounds from below this ω moment in terms of the expectation values $\langle r^{-1}\rangle$,$\langle r^{-2}\rangle$ following the lower bound variational method of the authors.[20,21]

C. Bounds of type 3

For ions and atoms with a nuclear charge Z, we find

$$\langle\rho\rangle \geq \left[\frac{2\pi}{Z}\right]^{q-2} C_q \frac{\langle r^{-2}\rangle^{q-1}}{\langle r^{-1}\rangle^{q-3}}\,, \quad (6)$$

where q is any real number greater than 3, and

$$C_q=\frac{q^q}{\left[4\pi B\left[\frac{q-3}{q-1},\frac{2q-1}{q-1}\right]\right]^{q-1}}\frac{(q-3)^{q-3}}{(2q-3)^{2q-3}}\,. \quad (6a)$$

TABLE I. Comparison of various lower bounds $F(\alpha,\beta)$ given by expressions (4a)–(4f) with themselves and with the Hartree-Fock values of $\langle\rho\rangle$ for several neutral atoms. Atomic units are used everywhere. The last column gives the ratio $F(0,-1)/\langle\rho\rangle_{\rm HF}$.

Z	Atom	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$	$F(0,-1)$	$F(1,-1)$	$F(2,-1)$	$F(1,0)$	$F(2,0)$	$F(2,1)$	$\langle\rho\rangle_{\rm HF}$	Ratio (%)
2	He	3.374	1.854	2.330	0.679	0.656	0.61	0.41	0.30	0.14	0.76	89.37
6	C	15.00	7.188	14.05	19.894	13.881	10.93	1.73	0.96	0.23	31.7	62.76
10	Ne	31.11	7.89	9.38	106.490	82.073	68.62	16.80	10.53	3.33	170.5	62.46
14	Si	49.24	14.55	32.77	301.565	190.487	132.01	14.42	5.24	0.46	525.3	57.41
18	A	69.66	16.00	26.06	664.180	432.373	320.16	38.05	17.79	2.83	1205.5	55.10
22	Ti	91.41	21.60	50.16	1227.910	734.013	485.23	42.17	13.45	0.88	2335.2	52.58
36	Kr	183.5	26.24	39.53	6069.555	3802.021	2670.27	276.00	107.78	11.27	11 622.0	52.22
54	Xe	317.0	39.04	62.59	20 859.779	12 226.450	8203.48	636.59	223.62	18.26	43 606.0	47.84

Even for the optimal q, these lower bounds are smaller than that given by (4a) and those of type 2. The reason is that the procedure used for its derivation needs three different inequalities: (i) $\langle\rho\rangle \geq \langle\rho^{q-1}\rangle/[\rho(0)]^{q-2}$, (ii) the Hoffmann-Ostenhof *et al.*'s upper bound[24] $\rho(0) \geq Z\langle r^{-2}\rangle/2\pi$, and (iii) the lower bound[21] to $\langle\rho^{q-1}\rangle$ in terms of $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$ for $q>3$.

D. Bounds of type 4

For N-electron ions of nuclear charge Z, we find

$$\langle\rho\rangle \geq \frac{1}{2^9\pi Z^3}\frac{\langle r^{-2}\rangle^4}{\langle r^{-1}\rangle^2}\ , \tag{7}$$

which is also of poorer quality than $F(0,-1)$ and $F_2(-1,-2)$ but is better than the bounds of type 3. The reason is that its derivation requires (i) the bound[12] $\langle\rho\rangle \leq \pi[\rho(0)]^2/8Z^3$, where $\rho(0)$ is the electronic charge density at the nucleus, and (ii) a lower bound to $\rho(0)$ recently found by the authors[25] in terms of $\langle r^{-1}\rangle$, $\langle r^{-2}\rangle$.

IV. LOWER BOUNDS TO $\langle\gamma\rangle$

Operating as in Sec. III, one may obtain lower bounds to $\langle\gamma\rangle$ in the momentum space similar to those given in Eqs. (2)–(6) in the position space. In particular, by replacing $\langle\rho\rangle \leftrightarrow \langle\gamma\rangle$ and $\langle r^\alpha\rangle \leftrightarrow \langle p^\alpha\rangle$ in the bounds $F(\alpha,\beta)$ to $\langle\rho\rangle$ one obtains the new bounds $G(\alpha,\beta)$ to $\langle\gamma\rangle$.

The new inequalities allow us to relate $\langle\gamma\rangle$ with various experimentally measurable quantities and/or fundamental quantities of the many-electron system due to the physical meaning of the expectation values $\langle p^\alpha\rangle$ for some α's. For illustration, one obtains by using $\langle p^{-1}\rangle = 2J(0)$ and $\langle p^2\rangle = 2T$ in $G(0,-1)$, $G(2,-1)$, and $G(2,0)$ that the average momentum density is bounded from below by the peak height of the Compton profile and the total kinetic energy of the system as

$$\begin{aligned}
\langle\gamma\rangle &\geq \frac{8}{9\pi}\frac{[J(0)]^3}{N}\ , \\
\langle\gamma\rangle &\geq \frac{8}{7^{4/3}\pi}\left[\frac{[J(0)]^7}{T}\right]^{1/3}\ , \\
\langle\gamma\rangle &\geq \frac{5}{\pi}\left[\frac{3}{14}\right]^{5/2}\frac{N^{7/2}}{T^{3/2}}\ ,
\end{aligned} \tag{8}$$

respectively.

Here again, all the bounds $G(\alpha,\beta)$ are valid for any many-electron system. Even more, one may notice that they do not show any explicit dependence on N unless α or β are equal to zero. The proof of these bounds is fully analogous to that discussed in Sec. V for $\langle\rho\rangle$. Also, the best bound to $\langle\gamma\rangle$ is given by the two moments of lowest order, that is, by $G(0,-1)$. This fact is also numerically illustrated in Table II where a comparison of several lower bounds $G(\alpha,\beta)$ with themselves and with the Hartree-Fock value of $\langle\gamma\rangle$ is made in a large region of neutral atoms. The necessary expectation values $\langle p^{-1}\rangle$, $\langle p\rangle$, and $\langle p^2\rangle$ were taken from Ref. 26. The last column of the table corresponds to the ratio between the best

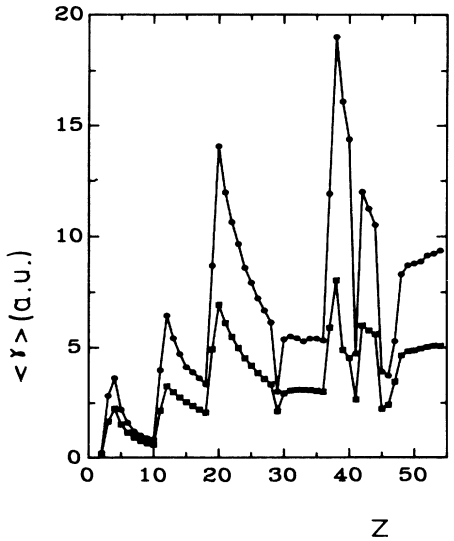

FIG. 1. Plot of the Hartree-Fock values of $\langle\gamma\rangle$, ●, and the lower bound $G(0,-1)$, given by (8), ■, vs the atomic number Z for the neutral atoms helium through xenon. Atomic units are used.

lower bound, namely, $G(0,-1)$, and the Hartree-Fock value[12] of $\langle\gamma\rangle$.

One notices that, contrary to the corresponding bound $F(0,-1)$ for $\langle\rho\rangle$, the quality of the bound $G(0,-1)$ has no monotonic behavior with Z. This is also illustrated in Fig. 1 where the Hartree-Fock values[12,27] of $\langle\gamma\rangle$ and the lower bound $G(0,-1)$ are compared between each other. It may be observed from this figure that the bound exhibits the same characteristics as the Hartree-Fock quantity. This should not be surprising once one realizes that $G(0,-1)$ is directly proportional to a positive power of $J(0)$ and both Hartree-Fock values of $J(0)$ and $\langle\gamma\rangle$ behave versus Z in the same manner.[12]

V. PROOFS

Let us start with the proofs of bounds of type 1 to $\langle\rho\rangle$ shown in Sec. III. To do that we minimize the quantity

$$\langle f\rangle = \int [f(\mathbf{r})]^2 d\mathbf{r}$$

subject to the conditions

$$\langle r^\alpha\rangle = \int r^\alpha f(\mathbf{r})d\mathbf{r}\ , \tag{8a}$$

$$\langle r^\beta\rangle = \int r^\beta f(\mathbf{r})d\mathbf{r}\ , \tag{8b}$$

where α and β are arbitrary real numbers and $\alpha>\beta$. Then, we take variations in the form

$$\delta\left[\langle f\rangle - \lambda\int r^\alpha f(\mathbf{r})d\mathbf{r} - \mu\int r^\beta f(\mathbf{r})d\mathbf{r}\right] = 0\ ,$$

λ,μ being Lagrange multipliers. One finds that

$$f(r) = \tfrac{1}{2}(\lambda r^\alpha + \mu r^\beta)\ .$$

Since λ and μ cannot be both negative or positive, there only remain two possible cases. For each of these two cases, the last expression transforms with an appropriate change of scale as the following.

TABLE II. Comparison of various lower bounds $G(\alpha,\beta)$ (see Sec. IV) among themselves and with the Hartree-Fock values of $\langle\gamma\rangle$ for several neutral atoms. Atomic units are used everywhere. The last column gives the ratio $G(0,-1)/\langle\gamma\rangle_{HF}$.

Z	Atom	$\langle p^{-1}\rangle$	$\langle p\rangle$	$\langle p^2\rangle$	$G(0,-1)$	$G(1,-1)$	$G(2,-1)$	$G(1,0)$	$G(2,0)$	$G(2,1)$	$\langle\gamma\rangle_{HF}$	Ratio (%)
2	He	2.141	2.799	5.723	0.174	0.171	0.157	0.120	0.079	0.028	0.266	65.24
3	Li	5.186	4.906	14.865	1.644	1.181	0.900	0.170	0.078	0.012	2.81	58.52
4	Be	6.318	7.434	29.146	2.230	1.572	1.140	0.206	0.078	0.008	3.61	61.77
5	B	5.980	10.649	49.058	1.513	1.144	0.843	0.214	0.078	0.007	2.18	69.39
6	C	5.755	14.462	75.376	1.124	0.892	0.668	0.212	0.077	0.007	1.60	70.22
7	N	5.597	18.863	108.80	0.886	0.729	0.554	0.207	0.077	0.007	1.20	73.82
8	O	5.553	23.721	149.62	0.757	0.637	0.489	0.203	0.076	0.007	1.02	74.22
9	F	5.503	29.166	198.82	0.655	0.562	0.436	0.196	0.075	0.007	0.88	74.00
10	Ne	5.456	35.197	257.09	0.574	0.501	0.392	0.189	0.073	0.008	0.84	68.38
11	Na	8.711	40.732	323.71	2.125	1.499	1.081	0.197	0.073	0.007	3.96	53.67
12	Mg	10.294	46.530	399.22	3.215	2.129	1.488	0.204	0.072	0.006	6.42	50.08
13	Al	10.298	52.724	483.74	2.971	2.002	1.397	0.209	0.071	0.005	5.31	55.95
14	Si	10.216	59.280	577.69	2.694	1.850	1.293	0.213	0.071	0.005	4.68	57.55
15	P	10.135	66.184	681.43	2.455	1.717	1.201	0.216	0.070	0.005	4.09	60.02
16	S	10.214	73.301	794.86	2.355	1.663	1.162	0.220	0.070	0.005	3.87	60.86
17	Cl	10.156	80.848	918.93	2.179	1.561	1.092	0.222	0.070	0.004	3.60	60.54
18	A	10.128	88.700	1053.6	2.041	1.480	1.037	0.223	0.069	0.004	3.33	61.30
19	K	13.769	96.221	1198.3	4.859	3.063	2.034	0.229	0.069	0.004	8.67	56.05
20	Ca	15.749	103.93	1353.5	6.908	4.123	2.672	0.235	0.069	0.004	14.07	49.10
21	Sc	15.323	112.73	1519.5	6.059	3.697	2.412	0.235	0.069	0.004	11.97	50.62
22	Ti	15.040	121.98	1696.8	5.469	3.392	2.226	0.234	0.068	0.004	10.63	51.45
36	Kr	14.744	281.41	5504.1	3.149	2.125	1.435	0.234	0.066	0.004	5.30	59.41

(i) $\lambda<0,\mu>0$

$$f_1(r)=\begin{cases} Cr^{\beta}(a^{\alpha-\beta}-r^{\alpha-\beta}) & \text{if } 0\le r\le a \\ 0 & \text{otherwise .} \end{cases} \tag{9}$$

(ii) $\lambda>0,\mu<0$

$$f_2(r)=\begin{cases} Cr^{\beta}(r^{\alpha-\beta}-a^{\alpha-\beta}) & \text{if } r\ge a \\ 0 & \text{otherwise ,} \end{cases}$$

where the parameters C and a are positive for both cases. These two parameters are to be determined by the restrictions (8a) and (8b).

One can easily obtain that

$$\langle r^{\alpha}\rangle=\frac{4\pi C}{\alpha-\beta}a^{2\alpha+3}B((2\beta+3)/(\alpha-\beta)+1,2) ,$$

$$\langle r^{\beta}\rangle=\frac{4\pi C}{\alpha-\beta}a^{\alpha+\beta+3}B((2\beta+3)/(\alpha-\beta),2)$$

for the first case. Then, the expectation value $\langle f_1\rangle$ turn out to be as

$$\langle f_1\rangle=C_1(\alpha,\beta)\left[\frac{\langle r^{\beta}\rangle^{2\alpha+3}}{\langle r^{\alpha}\rangle^{2\beta+3}}\right]^{1/(\alpha-\beta)} ,$$

where C_1 is given by (2a) and provided that $\alpha>\beta>-\frac{3}{2}$. The last condition assures finiteness of $\langle r^{\alpha}\rangle$, $\langle r^{\beta}\rangle$, and $\langle f_1\rangle$.

Operating in a fully analogous way one gets

$$\langle f_2\rangle=C_2(\alpha,\beta)\left[\frac{\langle r^{\alpha}\rangle^{-2\beta-3}}{\langle r^{\beta}\rangle^{-2\alpha-3}}\right]^{1/(\alpha-\beta)} ,$$

with C_2 given by (3a) and provided that $\beta<\alpha<-\frac{3}{2}$.

Now, by means of a procedure carefully discussed in Ref. 16 one can show that both $\langle f_1\rangle$ and $\langle f_2\rangle$ are indeed lower bounds to $\langle\rho\rangle$. Then, inequalities (2) and (3) are proved. Working on a similar manner for the momentum density $\gamma(\mathbf{p})$, one could show the inequalities which involve $\langle\gamma\rangle$, $\langle p^{\alpha}\rangle$, and $\langle p^{\beta}\rangle$.

From Eq. (9) one may notice that $\alpha=0$ and $\beta=-1$ (among the allowed α and β values) give the closest f_1 function to the realistic electronic density. This is the reason that the inequality (4a) supplies the best lower bound to $\langle\rho\rangle$. A similar reason can be argued to state that the inequality $G(0,-1)$ gives the best bound to $\langle\gamma\rangle$.

To prove the bounds of type 2 we start from Holder's inequality[23]

$$\int\rho^{r+s}d\mathbf{r}\le\left[\int\rho^{rp}d\mathbf{r}\right]^{1/p}\left[\int\rho^{sq}d\mathbf{r}\right]^{1/q} ,$$

where r and s are real numbers and $1/p+1/q=1$. By taking $r+s=\frac{3}{2}-1/n$ (where n is an arbitrary real number bigger than $\frac{2}{3}$) and choosing $rp=2$, $sq=1$,

$$\langle\rho\rangle\ge\left[\frac{\omega_{3/2-1/n}}{N^{(n+2)/2n}}\right]^{2n/(n-2)} .$$

Now, for $n>2$ one can bound from below[21] $\omega_{3/2-1/n}$ by means of $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$, thus, obtaining the inequality (5). A similar procedure in the momentum space gives rise to a similar inequality for $\langle\gamma\rangle$.

To prove the bounds of type 3 to $\langle\rho\rangle$ we start from the observation

$$\omega_q=\int[\rho(\mathbf{r})]^q d\mathbf{r}\le[\rho(0)]^{q-2}\langle\rho\rangle$$

for any real $q>2$. Here one has also taken into account that the spherically averaged charge density decreases monotonically in atomic systems.[28] On the other hand, one knows[21] that for $q>3$,

$$\omega_q\ge C_q\frac{\langle r^{-2}\rangle^{2q-3}}{\langle r^{-1}\rangle^{q-3}}$$

where C_q is given by (6a). Combining the last two inequalities together with the Hoffmann-Ostenhof *et al.*'s lower bound[24] to $\rho(0)$ for atoms and ions,

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

one immediately gets the wanted lower bound (6) to $\langle\rho\rangle$.

Finally, the proof of the bounds of type 4 [Eq. (7)] may be easily done with the indications given in Sec. III and further taking into account the inequality[25]

$$\rho(0)\ge\frac{(\alpha-\beta)^2}{4\pi B((\beta+3)/(\alpha-\beta),2)}\left[\frac{(\beta+3)^{\beta+3}}{(\alpha+3)^{\alpha+3}}\right]^{1/(\alpha-\beta)}\times\left[\frac{\langle r^{\beta}\rangle^{\alpha+3}}{\langle r^{\alpha}\rangle^{\beta+3}}\right]^{1/(\alpha-\beta)}$$

for any real $\alpha>\beta>-3$.

VII. CONCLUSIONS

Summarizing, several types of lower bounds to the spherically averaged electron radial density $\langle\rho\rangle$ and momentum density $\langle\gamma\rangle$ have been found by means of any two moments of the corresponding densities in a fully rigorous way for arbitrary N-electron systems. They allow us to settle down rigorous relationships among various fundamental and/or measurable quantities of the system, e.g., the diamagnetic susceptibility, the Compton profile peak height, and the total kinetic energy (or the total electronic energy due to the virial theorem).

One should remark the bounds of type 1 and especially the lower bounds $F(0,-1)$ to $\langle\rho\rangle$ and $G(0,-1)$ to $\langle\gamma\rangle$ because of their better accuracy and their behaviors with respect to the Hartree-Fock value. Let us only point out that the bound $G(0,-1)$ has the same periodic behavior versus Z as the Hartree-Fock value of $\langle\gamma\rangle$ throughout the whole Periodic Table.

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