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Lower bounds on the electronic charge and momentum densities of atomic systems at the origin

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Rigorous lower bounds to the electronic charge and momentum densities of an atomic system at the origin, $\rho(0)$ and $\gamma(0)$, respectively, by the expectation values $\langle r^{\alpha}\rangle$ and $\langle p^{\alpha}\rangle$, respectively, are given for positive and negative values of α in both cases, provided that the charge and momentum densities have a monotone decrement behavior, respectively. They allow one to give rigorous bounds to $\rho(0)$ and $\gamma(0)$ in terms of experimentally measurable atomic quantities such as the diamagnetic susceptibility, the Compton profile peak, and the electronic energy. In particular it is shown that $\rho(0)\geq(4\sqrt{3}\pi)^{-1}N\langle r^{-2}\rangle^{3/2}$ with the charge density normalized to N, the number of electrons of the system. The quality and the asymptotic Z behavior of the bounds for neutral atoms ($N=Z$) are studied.

The determination of rigorous bounds to charge and momentum densities of atomic systems at the origin, henceforth to be denoted by $\rho(0)$ and $\gamma(0)$, respectively, has a great interest in various physical problems[1] (parity nonconservation,[2,3] isomer- and field-shift effects[4] etc.) and is an important ingredient in the density-functional theories[5–11] of atoms and ions which treat the electron density $\rho(\mathbf{r})$ or the electron momentum density $\gamma(\mathbf{p})$ as the basic variable.

Rigorous bounds to $\rho(0)$ are very scarce in the literature. To the best of our knowledge, the only ones are those of Hoffmann-Ostenhof *et al.*[3] and King.[12] The first authors found an upper bound by means of the expectation value $\langle r^{-2}\rangle$, and King gave for S state atoms and ions lower and upper bounds in terms of $\langle r_1^{-2}\rangle$ and $\langle r_{12}^{-2}\rangle$. In addition, Tal and Levy[6] have nonrigorously proved upper bounds by the expectation values $\langle r^{\alpha}\rangle$, $\alpha>-3$, and $\langle p^{\alpha}\rangle$, $\alpha>1$. Also, implicit lower and upper bounds have been recently given by Pathak and Bartolotti[8] in estimating the ratio $\rho(0)K_0/T_0^2$, where $T_0(\rho)$ is the Thomas-Fermi kinetic energy functional and $-K_0(\rho)$ is the Dirac exchange energy density functional. The last authors point out that their bounds for some member of the helium isoelectronic series are of less quality as those of King. On the other hand, we have not seen any published work dealing with bounds to $\gamma(0)$.

Here we shall prove that the electronic charge density at the nucleus and the momentum density at the origin of an N-electron system are bounded from below by any positive or negative radial expectation value as

$$\rho(0)\geq\frac{3}{4\pi}\left[\frac{3}{3+\alpha}\right]^{3/\alpha}N\langle r^{\alpha}\rangle^{-3/\alpha} \tag{1}$$

and

$$\gamma(0)\geq\frac{3}{4\pi}\left[\frac{3}{3+\alpha}\right]^{3/\alpha}N\langle p^{\alpha}\rangle^{-3/\alpha} \tag{2}$$

for any real $\alpha>-3$. In these two infinite sets of lower bounds, those corresponding to the value $\alpha=-2$ are sharper than those with $\alpha>-2$. The quality of the bounds

$$\rho(0)\geq\frac{1}{4\sqrt{3}\pi}N\langle r^{-2}\rangle^{3/2}\ , \tag{3}$$

$$\gamma(0)\geq\frac{1}{4\sqrt{3}\pi}N\langle p^{-2}\rangle^{3/2}\ , \tag{4}$$

is analyzed in Tables I and II, respectively, for some ground-state atoms. In Table I the values of $\langle r^{-2}\rangle$ and $\rho(0)$ are based on Clementi-Roetti's atomic wave functions[13] as quoted in Refs. 6 and 9. In Table II, the values of $\langle p^{-2}\rangle$ and $\gamma(0)$ are also based on the same near Hartree-Fock wave functions of Clementi-Roetti as quoted in Refs. 14 and 15 and Refs. 7 and 9–11, respectively. All the atoms considered in this table have been shown to

TABLE I. Comparison between the lower bound given by Eq. (3) and the values of $\rho(0)$ calculated with Clementi-Roetti wave functions for several neutral atoms. Atomic units are used.

N	$\langle r^{-2}\rangle$	Lower bound	$\rho(0)$
2	5.99	1.35	3.6
4	14.42	10.06	35.0
7	27.71	46.91	206.0
10	41.49	122.78	620.1
14	61.16	307.65	1766.0
18	81.39	607.24	3840.0

TABLE II. Comparison between the lower bound given by Eq. (4) and the values of $\gamma(0)$ calculated with Clementi-Roetti wave functions for several neutral atoms. Atomic units are used.

Atom	$\langle p^{-2}\rangle$	Lower bound	$\gamma(0)$
Be	6.32	2.92	5.95
B	3.25	1.35	2.54
C	1.96	0.75	1.34
N	1.30	0.48	0.80
Al	2.14	1.87	4.94
Co	1.35	1.95	9.02
Cu	0.82	0.99	5.8
Zn	1.05	1.49	7.15
Ga	0.88	1.18	4.30

have a spherically-averaged momentum density $\gamma(p)$ with the property of strictly decreasing monotony.[11,14–16] One notices that the inequality given by Eq. (3) is quite crude while the lower bound (4) to $\gamma(0)$ is relatively accurate.

The basic idea of our proof is the decreasing monotonicity of the electronic charge density $\rho(r)$ given by

$$\rho(\mathbf{r})=N\int |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3\cdots d\mathbf{r}_N\ ,$$

and that the electron momentum density $\gamma(\mathbf{p})$ defined by

$$\gamma(\mathbf{p})=N\int |\Phi(\mathbf{p},\mathbf{p}_2,\ldots,\mathbf{p}_N)|^2 d\mathbf{p}_2 d\mathbf{p}_3\cdots d\mathbf{p}_N$$

has the property $\gamma(0)\geq\gamma(\mathbf{p})$ for any $\mathbf{p}$ in a variety of atoms. Here $\Phi(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)$ is the momentum-space normalized wave function of the N-electron system, i.e., the Fourier transformation of the configuration-space normalized wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ of the system.

One should immediately see that while the spherically-averaged charge density decreases monotonically in atomic systems, the same is not systematically true for the momentum density. Indeed, although there is not a rigorous proof of the monotone decrement of $\rho(r)$, all the numerical calculations show it.[17] In addition, the nonmonotonic nature of $\gamma(\mathbf{p})$ is also known[11,14,16,18] at least for atoms with their outer p shells occupied by two or more electrons. Nevertheless, there exist other atoms (e.g., in the first row from He to N; in the second row Na, Mg, and Al; in the third row Co, Cu, and Zn; in the fourth row Ga) which exhibit[11,14,16] a monotonically decreasing momentum density.

Firstly let us prove the inequalities (1)–(3). Starting from the fact that $\rho(0)\geq\rho(\mathbf{r})$ for all $\mathbf{r}$ in a closed-shell atom and that $\rho(0)$ is not smaller than the spherically-averaged charge density $\rho(r)$ for an arbitrary atom, one may write for any positive q that

$$\rho(0)\geq\left[\frac{1}{N}\int[\rho(r)]^{q+1}d\mathbf{r}\right]^{1/q}\equiv\left[\frac{\omega_{q+1}}{N}\right]^{1/q}\ , \tag{5}$$

where ω_q is the so-called frequency moment of order q of the density function $\rho(r)$. Recently, the authors[19] have shown for an N-fermion system that the frequency moment of order q (not necessarily integer but ≥ 1) of the one-fermion density $\rho(r)$ is bounded from below as

$$\omega_q\geq\frac{qk}{q(3-k)-3}\left[k\frac{\left[\dfrac{q(3-k)-3}{3q-3}\right]^{3/k}}{4\pi B\left[\dfrac{3}{k}-\dfrac{1}{q-1},\dfrac{q}{q-1}\right]}\right]^{q-1}\times N^q\langle r^{-k}\rangle^{(3q-3)/k} \tag{6}$$

for $k=1,2,\ldots$, provided that $k<(3q-3)/q$. Alternatively, the moment ω_q can also be bounded from below by the expectation values $\langle r^k\rangle$ as[20]

$$\omega_q\geq\frac{qk}{q(3+k)-3}\left[k\frac{\left[\dfrac{3q-3}{q(k+3)-3}\right]^{3/k}}{4\pi B\left[\dfrac{3}{k},\dfrac{q}{q-1}\right]}\right]^{q-1}\times\frac{N^q}{\langle r^k\rangle^{(3q-3)/k}} \tag{7}$$

for $k=1,2,\ldots$. The symbol B in Eqs. (6) and (7) denotes the β function defined by

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

and $\langle r^\alpha\rangle$, $\alpha>-3$, are the αth moment around the origin of the normalized-to-N density $\rho(\mathbf{r})$, that is

$$\langle r^\alpha\rangle=N^{-1}\int r^\alpha\rho(\mathbf{r})d\mathbf{r}\equiv N^{-1}\langle r^\alpha\rangle_0\ . \tag{8}$$

From Eqs. (5) and (6) one obtains

$$\rho(0)\geq\left[\frac{(q+1)k}{(q+1)(3-k)-3}\right]^{1/q}\times\frac{k\left[\dfrac{(q+1)(3-k)-3}{3q}\right]^{3/k}}{4\pi B\left[\dfrac{3}{k}-\dfrac{1}{q},\dfrac{q+1}{q}\right]}N\langle r^{-k}\rangle^{3/k}\ , \tag{9}$$

which gives a lower bound for each q and k so that $k<(3q-3)/q$. This lower bound is an increasing function of q. So, the best lower bound is obtained for $q\to\infty$,

$$\rho(0)\geq\frac{3}{4\pi}(1-k/3)^{3/k}N\langle r^{-k}\rangle^{3/k},\ \ k<3\ .$$

Then, Eq. (1) is proved for $\alpha=-k$. From Eqs. (5) and (7), and operating in a similar way, one obtains Eq. (1) for $\alpha=+k$.

In a fully analogous way one easily shows the inequality (2) for $\gamma(0)$, provided that the electron momentum density $\gamma(\mathbf{p})\leq\gamma(0)$, for any $\mathbf{p}$ occurs at least for some atoms as already mentioned. With this hypothesis, one has an inequality similar to (5) for any positive q,

$$\gamma(0) \geq \left[\frac{1}{N} \int [\gamma(\mathbf{p})]^{q+1} d\mathbf{p} \right]^{1/q} \equiv \left[\frac{\omega'_{q+1}}{N} \right]^{1/q},$$

which together with the lower bounds of ω'_{q+1} by means of $\langle p^\alpha \rangle$, analogous to Eqs. (6) and (7), leads to the desired inequality (2) in a straightforward manner.

It is worthwhile to point out that for neutral atoms ($N=Z$) and as $Z \rightarrow \infty$, where the Thomas-Fermi becomes exact,[21] the lower bounds to $\rho(0)$ and $\gamma(0)$ defined by Eqs. (1) and (2), respectively, are denoted by $B_\alpha(\rho)$ and $B_\alpha(\gamma)$ have the following Z-behavior:

$$B_\alpha(\rho) \sim Z^2 , \tag{10a}$$

$$B_\alpha(\gamma) \sim Z^{-1} , \tag{10b}$$

for $-3/2 < \alpha < 3$. To show this behavior is enough to remark that

$$B_\alpha(\rho) \sim Z^{1+3/\alpha} \langle r^\alpha \rangle_0^{-3/\alpha}$$

because of Eqs. (1) and (8) and that $\langle r^\alpha \rangle_0 \sim Z^{1-\alpha/3}$ with $-\frac{3}{2} < \alpha < 3$ for atomic Thomas-Fermi densities;[6,22–26] in this way, one obtains relation (10a). Similarly one can find relation (10b) by taking into account that $B_\alpha(\gamma) \sim Z^{1+3/\alpha} \langle p^\alpha \rangle_0^{-3/\alpha}$ with $-3/2 < \alpha < 3$ for atomic Thomas-Fermi densities.[6,25]

One cannot extend the domain of validity, $-\frac{3}{2} < \alpha < 3$, of relations (10a) and (10b) in neutral atoms because the expectation values $\langle r^\alpha \rangle$ with $\alpha \leq -\frac{3}{2}$ and $\langle p^\alpha \rangle$ at $\alpha \geq 3$ depend on the electron density near the origin and on the atom periphery which are not correctly described within the Thomas-Fermi model.[25] In case of ions, the Thomas-Fermi model does not present this difficulty any longer and one can easily determine the expectation values $\langle r^\alpha \rangle_0$ at $\alpha \geq -\frac{3}{2}$ and $\langle p^\alpha \rangle_0$ at $-3 < \alpha < 3$ as discussed in Refs. 24 and 26 and Ref. 25, respectively; then, a simple Z,N behavior for the lower bounds $B_\alpha(\rho)$ and $B_\alpha(\gamma)$ follow in a straightforward manner at the so-called hydrogenic limit,[24,26] that is, for a system of N noninteracting electrons moving about a nucleus of charge Z, where both N and Z are infinitely large but the ratio N/Z is a vanishingly small constant.

For completeness, let us also mention that, for a neutral atom, it has been shown[25] that $\langle r^\alpha \rangle_0 \sim Z^{-\alpha}$, $-3 < \alpha < -\frac{3}{2}$ for large values of Z. Then, from Eqs. (8) and (9), one obtains that the electronic charge density of a very heavy atom at the nucleus is bounded from below by $B_{\delta-3}(\rho) \sim Z^{3-[\delta/(3-\delta)]}$ for $0 < \delta < \frac{3}{2}$. In particular, notice that $B_{-2}(\rho) \sim Z^{5/2}$ for very heavy neutral atoms. However, for light atoms, $B_{-2}(\rho)$ have the nice Z^3 behavior since in such a case the expectation value $\langle r^{-2} \rangle \sim Z^{7/3}$.[3] A similar discussion for the electronic momentum density of very heavy atoms at the origin can be made but taking into account that asymptotic estimates for $\langle p^\alpha \rangle$ are known only for $3 < \alpha < 5$, namely $\langle p^\alpha \rangle \sim Z^\alpha$.[25]

Summarizing, the inequalities (1) and (2) give rigorous lower bounds to the atomic charge density at the nucleus $\rho(0)$ in terms of the expectation values $\langle r^\alpha \rangle$ and to the atomic momentum density at the origin $\gamma(0)$ by means of $\langle p^\alpha \rangle$ for any real $\alpha > -3$, provided that the charge and momentum densities have a monotone decrement behavior, respectively. This behavior has been numerically shown to occur for the charge density in all the studied atoms but such is not the case for the momentum density. They allow us to obtain in a straightforward manner rigorous (although not accurate) bounds to $\rho(0)$ and $\gamma(0)$ by means of experimentally measurable quantities such as, for example, the diamagnetic susceptibility ($\sim \langle r^2 \rangle$), the electronic energy ($\sim \langle p^2 \rangle$), and the spherically-averaged Compton profile peak $J(0)$ ($\sim \langle p^{-1} \rangle$), respectively. However, as said before, the best bounds for $\rho(0)$ and $\gamma(0)$ are given by the radial and expectation values of order $\alpha = -2$ in the way shown by the inequalities (3) and (4).

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