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Original contributions

New bounds for the atomic charge and momentum densities at the origin

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Abstract. The "Stieltjes moment problem" technique together with the positivity and monotonic decreasing properties of the electronic density of an atom is used to find new and more accurate lower bounds for the charge density at the nucleus and the momentum density at the origin, in terms of radial and momentum expectation values, respectively. Bounds depending on two and three expectation values are given explicitly and a Hartree-Fock study of their quality is carried out. Also, the behavior of the new bounds at large Z's is discussed. The Stieltjes technique allows to find lower bounds of better accuracy by including expectation values of higher order.

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The electronic charge and momentum densities of N-electron systems with nuclear charge Z (heretoforth to be denoted by $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ respectively) at the origin are quantities which play a fundamental role in many problems of atomic physics (Otten [1], Gálvez and Dehesa [2], Gálvez et al. [3]). No exact expressions are known for these quantities except in the hydrogenic case, but a rigorous upper bound (Hoffmann-Ostenhof et al. [4]) and an estimated value (Cioslowski [5]) to $\rho(0)$ of high accuracy have been recently derived in terms of radial expectation values $\langle r^\alpha \rangle$ with $\alpha = -1$ and -2.

Also, we have found lower bounds to $\rho(0)$ in terms of one (Gálvez and Dehesa [2]) and two (Gálvez et al. [3]) expectation values $\langle r^\alpha \rangle$ for any real $\alpha > -3$ provided that max $\rho(r) = \rho(0)$, $\rho(r)$ being the spherically averaged charge density of an atom, i.e.

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

what has been numerically shown to be true for all atoms studied (Sperber [6], Weinstein et al. [7], Simas et al. [8], Angulo [9]). To obtain these bounds, a variational technique was used. The most accurate lower bound in terms of expectation values of integer order turns out to be

$$\rho(0) \geqq \frac{1}{8\pi} \frac{\langle r^{-2} \rangle^2}{\langle r^{-1} \rangle} \equiv C_2 \qquad (1)$$

For neutral atoms this bound, as studied in a Hartree-Fock framework, has a quality which worsens with high Z, and its accuracy is always less than 50% (Gálvez et al. [3]).

In the $\gamma(0)$ case, the only published results are lower bounds given by means of the momentum expectation value $\langle p^\alpha \rangle$ for any real α with $-3 < \alpha < 5$ (Gálvez and Dehesa [2], Gálvez [10]). Best bound for integer α's is obtained for $\alpha = -2$, as

$$\gamma(0) \geqq \frac{1}{4\sqrt{3}\pi} \frac{\langle p^{-2} \rangle^{3/2}}{N^{1/2}} \equiv M' \qquad (2)$$

provided that max $\gamma(p) = \gamma(0)$, where $\gamma(p)$ is the spherically averaged momentum density of an atom. For spherical atoms, there is a slightly better bound, namely

$$\gamma(0) \geqq \frac{\sqrt{2}}{3\pi^2} \frac{\langle p^{-2} \rangle^{3/2}}{N^{1/2}}.$$

The behavior and Hartree-Fock properties of these two bounds have been discussed in the last two previously mentioned papers. One should also quote that inequalities involving *(i)* $\rho(0)$, $\langle r^\alpha \rangle$ and the average charge density, $\langle \rho \rangle$, *(ii)* $\rho(0)$, $\langle r^\alpha \rangle$ and the indirect Coulomb energy, $J(\rho)$, *(iii)* $\gamma(0)$, $\langle p^\alpha \rangle$ and the average momentum density, $\langle \gamma \rangle$, have been derived for spherical atoms (Gálvez [10]).

Here, we will use the so-called "Stieltjes moment problem" technique to find in a rigorous way that:

1. The charge density at the nucleus, $\rho(0)$, is bounded from below both by C_2 and by

$$\rho(0) \geqq \frac{1}{\pi} \frac{2\langle r^{-1}\rangle^3 + \langle r^{-2}\rangle^2 \langle r\rangle - 3N\langle r^{-2}\rangle\langle r^{-1}\rangle}{8\langle r^{-1}\rangle\langle r\rangle - 9N^2} \equiv C_3 \tag{3}$$

for all atoms which fulfil that $\rho'(r) \leqq 0$.

2. The atomic momentum density at the origin, $\gamma(0)$, has similar bounds M_2 and M_3, with $\langle r^\alpha\rangle$ replaced by $\langle p^\alpha\rangle$, provided that $\gamma'(p) \leqq 0$.

To prove the above mentioned bounds we invoke the following corollary of a Stieltjes theorem (Shohat and Tamarkin [11]): A necessary condition which the sequence of moments $\{v_0, v_1, \ldots, v_n\}$ must satisfy in order that a density function $\phi(x)$, $0 \leqq x < \infty$, having these moments

$$v_\alpha = \int_0^\infty x^\alpha \phi(x)\,dx, \qquad \alpha = 0, 1, \ldots, n$$

may exist is that the following inequalities hold:

$$\begin{vmatrix} v_0 \, v_1 \ldots v_m \\ v_1 \, v_2 \ldots v_{m+1} \\ \ldots\ldots\ldots\ldots \\ v_m \, v_{m+1} \ldots v_{2m} \end{vmatrix} \geqq 0, \qquad m = 0, 1, \ldots, [n/2]$$

where $[z]$ denotes the greatest integer less than or equal to z.

Assuming that $\phi(x)$ is unimodal at the origin, i.e., monotically decreasing from the origin, then $f(x) \equiv -\phi'(x)$ is a positive-definite function with moments

$$\int_0^\infty x^\alpha f(x)\,dx = \phi(0)\,\delta_{\alpha,0} + \alpha v_{\alpha-1}$$

The application of the previous corollary to the function $f(x)$ leads to the new inequalities

$$\begin{vmatrix} \phi(0) & v_0 & 2v_1 \ldots m v_{m-1} \\ v_0 & 2v_1 & 3v_2 \ldots (m+1)v_m \\ \ldots & \ldots & \ldots \\ m v_{m-1} & (m+1)v_m & (m+2)v_{m+1} \ldots 2m v_{2m-1} \end{vmatrix} \geqq 0,$$

$$m = 1, 2, \ldots, [n/2] \tag{4}$$

which allow to bound the value of the density function $\phi(x)$, $0 \leqq x < \infty$, at the origin, $\phi(0)$, in terms of any given number of its moments. Furthermore, they supply lower bounds to $\phi(0)$ since the principal minor of $\phi(0)$ in this matrix is indeed positive as it is indicated by the Stieltjes moment problem associated to the function $-x^2\phi'(x)$.

In particular, for $m = 1, 2$ one has

$$\phi(0) \geqq \frac{v_0^2}{2v_1} \tag{4a}$$

and

$$\phi(0) \geqq \frac{4v_0^2 v_3 - 12 v_0 v_1 v_2 + 8 v_1^3}{8 v_1 v_3 - 9 v_2^2} \tag{4b}$$

respectively.

In case that the function ϕ represents the spherically averaged charge density of an atom, $\rho(r)$, its moments are

$$v_\alpha = \int_0^\infty r^\alpha \rho(r)\,dr = \frac{1}{4\pi}\int r^{\alpha-2}\rho(\mathbf{r})\,d^3r \equiv \frac{1}{4\pi}\langle r^{\alpha-2}\rangle \tag{5}$$

for $\alpha > -1$. It is assumed that the charge density $\rho(r)$ is normalized to the number of electrons of the system, i.e.

$$\int \rho(\mathbf{r})\,d^3r = N.$$

On the other hand, the condition $\rho'(r) \leqq 0$, which expresses the monotically decreasing of the electron density $\rho(r)$, has been numerically shown to be true for all atoms studied (Simas et al. [8], Angulo [9]); then, the inequalities given by (4) are valid. Now, taking the values of v_α with $\alpha = 0, 1, 2$ and 3 to (4a and b) one has in a straightforward manner the searched lower bounds C_2 and C_3 to $\rho(0)$ as given by the inequalities (1) and (3) respectively.

In momentum space, the application of the same procedure to the spherically averaged momentum density of an atom, $\gamma(p)$, easily leads to the above mentioned lower bounds M_2 and M_3 to $\gamma(0)$, provided that $\gamma'(p) \leqq 0$. The latter condition, which indicates the unimodality at the origin of the atomic momentum density, is not universally true. Indeed, the condition $\gamma'(p) \leqq 0$ is only fulfilled for $Z = 1$–7, 11–13, 19–26, 31, 37–42 and 49–50 in the $1 \leqq Z \leqq 54$ region of the periodic table (Angulo[9]).

The Stieltjes technique allows for the inclusion of higher moments (expectation values), provided they exist, so improving the quality of the bounds.

That quality is numerically studied in Tables 1 and 2 and Fig. 1 for several ground-state atoms satisfying the required constraint. The radial and momentum expectation values as well as the values of $\rho(0)$ and $\gamma(0)$ used in the tables are based on non-relativistic atomic wavefunctions (Clementi and Roetti [12], Boyd [13], Gadre et al. [14]). In Table 1 we compare the two-, three- and five-moments bounds (i.e., C_2, C_3 and C_4 respectively) with the Hartree-Fock value of $\rho(0)$ for a few atoms. This comparison is extended to all atoms with $Z \leqq 54$ in Fig. 1. In Table 2, the one-, two-, three- and five-moments bounds (i.e., M', M_2, M_3 *and* M_4 respectively) are compared among themselves and with the Hartree-Fock value of $\gamma(0)$. One observes that sharpness is not yet obtained. The momentum M-bounds are of much better accuracy than the charge C-bounds. In both cases, one notices that the accuracy of the bounds gets substantially improved when a new expectation value is included. In addition, the quality of the charge C-bounds has a monoton decreasing behavior with increas-

Table 1. Comparison of the two-, three- and five-moments lower bounds (C_2, C_3 and C_4 respectively) with the Hartree-Fock value of $\rho(0)$ for a few neutral atoms. Ratios between bounds and $\rho(0)$ are given in percent. Atomic units are used everywhere

Z	$\rho(0)$	C_2	C_3	C_4	R_2	R_3	R_4
2	3.60	1.70	2.28	2.58	47.1	63.4	71.8
6	127.56	52.16	66.20	72.89	40.9	51.9	57.1
10	620.15	220.14	308.50	345.96	35.5	49.7	55.8
14	1765.71	592.36	733.81	364.45	33.5	41.6	49.0
18	3840.22	1224.77	1560.64	1833.07	31.9	40.6	47.7
27	13370.81	3893.83	4961.13	5569.79	29.1	37.1	41.7
36	32228.20	8720.68	11184.14	13188.25	27.1	34.7	40.9
42	51612.91	13514.35	16945.05	19168.98	26.2	32.8	37.1
48	77609.13	19676.69	24900.82	27920.37	25.4	32.1	36.0
54	111163.95	27484.77	34310.90	39920.39	24.7	30.9	35.9

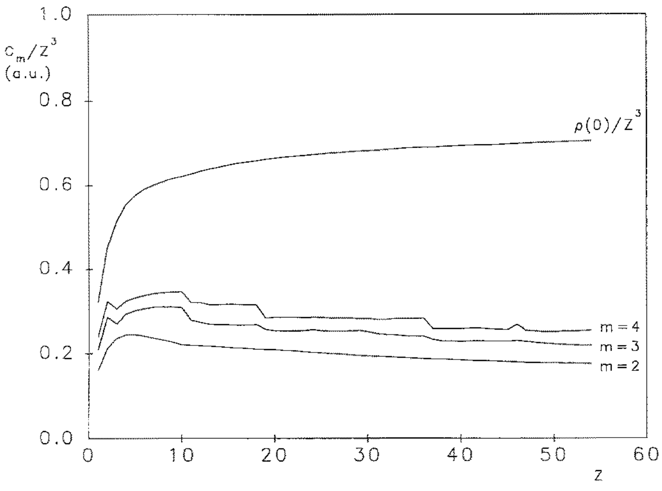

Fig. 1. Comparison of the two-, three- and five-moments lower bounds, C_2/Z^3, C_3/Z^3 and C_4/Z^3 respectively, with the Hartree-Fock value $\rho(0)/Z^3$ for all neutral atoms with $Z \leq 54$. Atomic units are used everywhere

ing Z's while that of the momentum M-bounds does not.

Also, it is interesting to analyze the asymptotic behavior of the above mentioned bounds with the nuclear charge Z. Since the expectation values $\langle r^\alpha \rangle$ and $\langle p^\alpha \rangle$ of neutral atoms go for large Z as (Dmitrieva and Plindov [15])

$$\langle r^\alpha \rangle \sim \begin{cases} Z^{-\alpha}, & -3<\alpha<-3/2 \\ Z^{1-\alpha/3}, & -3/2<\alpha<3 \\ \ln Z, & \alpha=3 \end{cases}$$

$$\langle p^\alpha \rangle \sim \begin{cases} 1, & -3<\alpha<-3/2 \\ Z^{1+2\alpha/3}, & -3/2<\alpha<3 \\ Z^3 \ln Z, & \alpha=3 \end{cases}$$

then one can easily obtain that the encountered bounds C_m, $m=2, 3, 4$ to $\rho(0)$ and M_m, $m=2, 3, 4$, to $\gamma(0)$ have a $Z^{8/3}$- and $Z^{-1/3}$-behavior at large Z, respectively, while in the variational case (with only one moment) go as $Z^{5/2}$ (position space) and $Z^{-1/2}$ (momentum space).

For completeness, let us point out that contrary to the momentum case, where the only existing expectation values $\langle p^\alpha \rangle$ are those with $-3<\alpha<5$ due to the p^{-8}-decreasing behavior of $\gamma(p)$ at large momenta (Benesch and Smith [16], Thakkar [17]), in the position space the existence of all the radial expectation values $\langle r^\alpha \rangle$, $\alpha>-3$, and then all the moments v_α, $\alpha>-1$, of the charge density $\rho(r)$, is assured due to its known expontential behavior at large distances (Benesch and Smith [16]). So, in principle, one can obtain with the Stieltjes technique, by means of the determinantal inequalities (4), a lower bound of $\rho(0)$ with any given accuracy just by taking into account a sufficiently high number of moments v_α. However, the corresponding expressions are not analytically useful.

Summarizing, we have found two sets of rigorous lower bounds $\{C_m, m=2, 3, 4, \ldots\}$ and $\{M_m, m=2, 3$ and $4\}$ to the atomic charge and momentum densities at the origin, respectively, by means of the expectation values of the corresponding coordinate provided that such densities have a monotonically decreasing behavior. As already discussed, Hartree-Fock calculations seem to show such a behavior for a large portion of atoms in the momentum density and for the whole periodic table in the

Table 2. Comparison of the one-, two-, three- and five-moments lower bounds (M', M_2, M_3 and M_4 respectively) with the Hartree-Fock value $\gamma(0)$ for a few neutral atoms which have a monotonically decreasing momentum density. Ratios between bounds and $\gamma(0)$ are given in percent. Atomic units are used everywhere

Z	$\gamma(0)$	M'	M_2	M_3	M_4	R'	R_2	R_3	R_4
2	0.439	0.269	0.311	0.371	0.388	61.2	70.8	84.5	88.5
7	0.799	0.477	0.589	0.665	0.693	59.7	73.7	83.2	86.7
11	10.385	2.547	4.776	6.298	6.975	24.5	46.0	60.7	67.2
13	4.881	1.873	2.996	3.596	3.815	38.4	61.4	73.7	78.2
20	19.270	4.873	9.346	11.225	12.064	25.3	48.5	58.2	62.6
25	10.640	2.430	4.708	5.914	6.480	22.8	44.2	55.6	60.9
31	4.290	1.168	2.120	2.680	2.925	7.2	49.4	62.5	68.2
38	23.821	4.604	10.216	12.485	13.412	19.3	42.9	52.4	56.3
40	16.966	3.280	6.973	8.569	9.235	19.3	41.1	50.5	54.4
50	4.227	1.170	2.120	2.576	2.764	27.7	50.2	61.0	65.4

charge density. The first two bounds of each set have a simple and compact form which involve the expectation values of order $\alpha = -2$, -1 and $+1$. In general, the quality of the momentum M-bounds is better than that of the charge C-bounds, being much better for light atoms. Finally, let us only mention that the new bounds allow to correlate in a simple manner $\rho(0)$ and $\gamma(0)$ with fundamental and/or measurable quantities which are represented by the radial and momentum expectation values respectively, such as, for example, the diamagnetic susceptibility ($\sim \langle r^2 \rangle$), the electron-nucleus potential ($\sim \langle r^{-1} \rangle$), the spherically averaged Compton profile peak ($\sim \langle p^{-1} \rangle$), the Dirac-Slater exchange energy ($\sim \langle p \rangle$), the non-relativistic kinetic energy ($\sim \langle p^2 \rangle$) and the relativistic Breit-Pauli correction to the kinetic energy ($\sim \langle p^4 \rangle$).

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