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LETTER TO THE EDITOR

# Improved lower bounds for the atomic charge density at the nucleus

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**Abstract.** Lower bounds $F(\alpha, \beta)$ to the electronic charge density of atomic systems with $N$ electrons at the nucleus, $\rho(0)$, are given by means of any two radial expectation values $\langle r^{\alpha}\rangle$ and $\langle r^{\beta}\rangle$, for real $\alpha \neq \beta$, in a rigorous and simple way. In particular, $\rho(0) \geqslant (N/8\pi)\langle r^{-2}\rangle^2/\langle r^{-1}\rangle$ which improves bounds found previously. An interesting property of these bounds is that they are equal to the exact value $\rho(0)$ in the limit $\beta \to -3$ for any fixed $\alpha$ value.

The electronic charge density of $N$-electron systems with nuclear charge $Z$ at the nucleus $\rho(0)$ is an important ingredient in the study of isotope shifts of atomic spectra, particularly field shifts (Blundell *et al* 1984, 1987, Otten 1987). Also it plays a relevant role in various physical problems (Thirring 1981) such as parity violation (Bouchiat and Bouchiat 1974, Henley and Wilets 1976) and the determination of the average electron density $\langle\rho\rangle$ (Tal and Levy 1980, Gadre and Chakravorty 1986a), a quantity recently found to be experimentally measurable from the form factor of scattered x-rays (Hyman *et al* 1978, 1984).

In addition, $\rho(0)$ has been shown to be related to the atomic binding energy (Hoffmann-Ostenhof *et al* 1978), the total electron–nucleus attraction energy (Sen 1984) and the Thomas–Fermi kinetic and Dirac exchange energy density functionals (Pathak and Bartolotti 1985). Nevertheless, to our knowledge, no exact expression of $\rho(0)$ is available for light and heavy atoms although some approximate calculations and parametrisations are often mentioned (Blundell *et al* 1984, 1987, Otten 1987).

There exist rigorous upper bounds to $\rho(0)$ due to Hoffmann-Ostenhof *et al* (1978) in terms of the radial expectation value $\langle r^{-2}\rangle$ of the electronic charge density $\rho(\boldsymbol{r})$ and, for S-state atoms and ions, to King (1984) by means of $\langle r_1^{-2}\rangle$ and $\langle r_{12}^{-2}\rangle$. Also Tal and Levy (1980) found additional approximate upper bounds in terms of $\langle r^{\alpha}\rangle$, with $\alpha > -3$ and $\langle \rho^{\alpha}\rangle$, with $\alpha > 1$. Lower bounds to $\rho(0)$ are even more scarce in the literature. The only rigorous result has been found for S-state atomic systems by King (1984).

Recently Gálvez and Dehesa (1988) have derived rigorous lower bounds to $\rho(0)$ by means of $\langle r^{\alpha}\rangle$ for any real $\alpha > -3$ as

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

of which that corresponding to $\alpha = -2$, i.e.

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

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is sharper than those with $\alpha > -2$. The quality of the last bound monotonically decreases with $N$ for neutral atoms. For clarity, let us state that $\langle r^\alpha \rangle$ refers to

$$\langle r^\alpha \rangle = \frac{1}{N} \int r^\alpha \rho(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}. \tag{3}$$

Here we will improve the quality of these bounds by generalising the bounds given by (1) and essentially conserving their simplicity. We have found that $\rho(0)$ may be bounded from below in terms of any two expectation values $\langle r^\alpha \rangle$ and $\langle r^\beta \rangle$ as

$$\rho(0) \geq F(\alpha, \beta) = f(\alpha, \beta) N \left( \frac{\langle r^\beta \rangle^{\alpha+3}}{\langle r^\alpha \rangle^{\beta+3}} \right)^{1/(\alpha-\beta)} \tag{4a}$$

where $\alpha$ and $\beta$ are real numbers, $\alpha > \beta$, and

$$f(\alpha, \beta) = \frac{(\alpha-\beta)^2}{4\pi B[(\beta+3)/(\alpha-\beta), 2]} \left( \frac{(\beta+3)^{\beta+3}}{(\alpha+3)^{\alpha+3}} \right)^{1/(\alpha-\beta)}. \tag{4b}$$

The symbol $B$ denotes the beta function defined by

$$B(x, y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)} = \int_0^1 t^{x-1}(1-t)^{y-1}\, \mathrm{d}t. \tag{4c}$$

For a fixed $\alpha$, the sharper these lower bounds $F(\alpha, \beta)$, the smaller is $\beta$. Then, the lower bound $F(\alpha, \beta)$ of highest quality is obtained when $\beta \to -3$ for a fixed $\alpha$ value since expectation values $\langle r^\beta \rangle$ with $\beta \leq -3$ are not physical. Furthermore, the lower bounds $F(\alpha, \beta)$ have the following interesting property:

$$\rho(0) = \lim_{\beta \to -3} F(\alpha, \beta). \tag{5}$$

Before proving all these results, let us note that the inequality (4) for $\alpha = -1$ and $\beta = -2$ gives

$$\rho(0) \geq F(-1, -2) = \frac{N}{8\pi} \frac{\langle r^{-2} \rangle^2}{\langle r^{-1} \rangle} \tag{6}$$

and that $F(0, \alpha)$ is exactly the bound given by the inequality (1).

It can be shown that this bound $F(-1, -2)$ is sharper than any other $F(-1, \beta)$, $\beta > -2$. The quality of this bound is analysed in table 1 for some ground-state atoms

**Table 1.** Comparison between the lower bounds $F(0, -2)$ and $F(-1, -2)$ given by (2) and (6) respectively, and the values of $\rho(0)$ calculated with non-relativistic Hartree-Fock wavefunctions for several neutral atoms. Atomic units are used everywhere. The last two columns give the ratios $F(0, -2)/\rho(0)$ and $F(-1, -2)/\rho(0)$ respectively.

| $Z$ | $\langle r^{-2} \rangle$ | $\langle r^{-1} \rangle$ | $\rho(0)$ | $F(0, -2)$ | $F(-1, -2)$ | $R_{0,-2}(\%)$ | $R_{-1,-2}(\%)$ |
|---|---|---|---|---|---|---|---|
| 2 | 5.99 | 1.687 | 3.6 | 1.35 | 1.69 | 37.5 | 46.9 |
| 4 | 14.42 | 2.102 | 35 | 10.06 | 15.74 | 28.7 | 44.9 |
| 7 | 27.71 | 2.614 | 206 | 46.91 | 81.81 | 22.8 | 39.7 |
| 10 | 41.49 | 3.111 | 620.1 | 122.78 | 220.16 | 19.8 | 35.5 |
| 14 | 61.16 | 3.517 | 1 766 | 307.65 | 592.45 | 17.4 | 33.5 |
| 18 | 81.39 | 3.870 | 3 840 | 607.24 | 1 225.92 | 15.8 | 31.9 |
| 36 | 175.86 | 5.097 | 32 235 | 3 857.29 | 8 686.14 | 12.0 | 26.9 |
| 54 | 274.44 | 5.870 | 111 217 | 11 279.62 | 27 568.34 | 10.1 | 24.8 |
| 86 | 453.83 | 7.030 | 457 897 | 38 200.39 | 100 251.22 | 8.3 | 21.9 |

where also a comparison is made with the bound $F(0, -2)$ given by the inequality (2). The non-relativistic values of $\langle r^{-1}\rangle$ and $\langle r^{-2}\rangle$ are quoted by Desclaux (1973) and those of $\rho(0)$ are based on non-relativistic atomic wavefunctions as quoted by Tal and Levy (1980), Gadre and Chakravorty (1986b) and Ghosh and Parr (1987). One should notice that although the bound $F(-1, -2)$ is not yet sharp, it is of much better quality than $F(0, -2)$, and its decreasing behaviour against $Z$ is slower.

To prove the main inequality (4) we start from the fact that the spherically averaged charge density $\rho(r)$ decreases monotonically in atomic systems (Sperber 1971, Weinstein *et al* 1975). Then, one may write for any positive $q$ that

$$\rho(0) \geqslant \left(\frac{1}{N}\int [\rho(\boldsymbol{r})]^{q+1}\,\mathrm{d}\boldsymbol{r}\right)^{1/q} \equiv \left(\frac{w_{q+1}}{N}\right)^{1/q} \tag{7}$$

where $w_q$ is the so-called frequency moment of order $q$ of the density function $\rho(\boldsymbol{r})$. Recently, it has been shown (Dehesa *et al* 1988) that $w_n$ (with $n$ not necessarily integer but greater than one) is bounded from below as

$$w_n \geqslant C(\alpha, \beta, n)N^n\left(\frac{\langle r^{\beta}\rangle^{n(\alpha+3)-3}}{\langle r^{\alpha}\rangle^{n(\beta+3)-3}}\right)^{1/(\alpha-\beta)} \tag{8a}$$

provided $\alpha > \beta > 3(1-n)/n$ and with

$$C(\alpha, \beta, n) = n^n(\alpha-\beta)^{2n-1}\left[4\pi B\left(\frac{n(\beta+3)-3}{(\alpha-\beta)(n-1)}, \frac{2n-1}{n-1}\right)\right]^{-(n-1)} \times\left(\frac{[n(\beta+3)-3]^{n(\beta+3)-3}}{[n(\alpha+3)-3]^{n(\alpha+3)-3}}\right)^{1/(\alpha-\beta)}. \tag{8b}$$

The combination of both inequalities (7) and (8) produces a set of lower bounds which have an increasing behaviour with $q$. Then, the best lower bound is for $q \to \infty$. This lower bound turns out in a straightforward manner to be that given by the inequality (4).

Let us now prove equation (5). We start with the expression of $F(\alpha, \beta)$ given by (4). For a fixed $\alpha$ value, we will investigate the limit

$$\lim_{\beta\to-3} F(\alpha, \beta) = \lim_{\varepsilon\to 0} F(\alpha, -3+\varepsilon). \tag{9}$$

To do that, we note that

$$\langle r^{-3+\varepsilon}\rangle = \frac{4\pi}{N}\int_0^{\infty} r^{\varepsilon-1}\,\rho(r)\,\mathrm{d}r \xrightarrow[\varepsilon\to 0]{} \frac{4\pi}{N}(\delta^{\varepsilon}/\varepsilon)\rho(0) \tag{10}$$

where $\delta$ is a very small positive finite number so that $\rho(\boldsymbol{r}) \simeq \rho(0)$ in the interval $0 \leqslant r \leqslant \delta$. On the other hand, operating in a similar manner and taking into account (4*b*) one has that

$$B\left(\frac{\varepsilon}{\alpha+3}, 2\right) \xrightarrow[\varepsilon\to 0]{} \frac{\alpha+3}{\varepsilon}\,\delta^{\varepsilon/(\alpha+3)}. \tag{11}$$

The combination of (9)–(11) leads to the required limiting equation (5).

In conclusion, we have found an infinite set of lower bounds $F(\alpha, \beta)$ to the charge density of atoms and ions at the nucleus in terms of any pair of radial expectation values in a fully rigorous way. They have two valuable characteristics: simplicity and exactness in the limit $\beta \to -3$. In addition, the value $F(-1, -2)$ gives the sharpest lower bound to $\rho(0)$ known up to now. However, one should point out that its quality is not very high. So, there still exists space for further improvements.

Finally, for the sake of completeness, let us indicate that a possible way to achieve lower bounds of higher quality is by improving $\rho(\boldsymbol{r}) \leqslant \rho(0)$, which is the main ingredient of the inequality (4). This may be done by using better upper bounds to the atomic electronic density, as, e.g., those found by King (1983). In particular, the use of the inequality

$$\rho(r) \leqslant \begin{cases} \rho(0)(1-ar) & r \leqslant r_0 \\ T/2\pi r & r \geqslant r_0 \end{cases}$$

(where $T$ denotes the atomic kinetic energy, and $r_0$ and $a$ are determined so that $\rho(0)(1-ar) = T/2\pi r$ has a unique solution) leads with the procedure shown in this paper to a lower bound to $\rho(0)$ which is similar (although not so simple and involving $T$) to that given by inequality (4). The new lower bound is of higher quality than (4). Indeed, its ratio with the exact value of $\rho(0)$ is 57% for He, 41% for Ne and 36% for Ar. These ratios are to be compared with 47%, 36% and 32% respectively as shown in table 1. One notices that a substantial improvement, especially for light atoms, is obtained.

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