

Bounds on the atomic electronic density at the nucleus

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A lower bound estimate for the electron density at the nucleus $\rho(0)$ for S state atoms and ions is derived. A refinement is made to the best upper bound estimate for $\rho(0)$ for atomic systems available in the literature. A numerical test of the quality of the bounds is presented for members of the helium isoelectronic sequence.

INTRODUCTION

In the last problem set of his recent book, Thirring¹ poses the following question: "The upper bound (4.3.43) for $\rho(0)$ is the exact value if there is only one particle, while the lower bound is too small by a factor of 3/16. With more electrons the upper bound degrades somewhat and the lower bound gets much worse. Find better lower bounds". The equation referred to in the above quote is

$$\frac{1}{2\pi} |E_1|(E_2 - E_1) + \alpha \rho_{12}(0) \leq \rho(0) \leq \frac{1}{2\pi} \langle \Psi_1 | r_1^{-2} | \Psi_1 \rangle, \quad (1)$$

where

$$\rho(0) = \int d^3 x_1 d^3 x_2 |\Psi_1(\mathbf{x}_1, \mathbf{x}_2)|^2 \delta^3(\mathbf{x}_1), \quad (2)$$

$$\rho_{12}(0) = \int d^3 x_1 d^3 x_2 |\Psi_1(\mathbf{x}_1, \mathbf{x}_2)|^2 \delta^3(\mathbf{x}_1 - \mathbf{x}_2), \quad (3)$$

$$H\Psi_1 = E_1\Psi_1, \quad (4)$$

and $\alpha = Z^{-1}$, where Z is the nuclear charge. The upper bound estimate in Eq. (1) was derived by Hoffmann-Ostenhof *et al.*² A generalization of this upper bound has been suggested by Tal and Levy.³

The lower bound expression given by Thirring applies to two electron atoms. For the case of N electrons, Eq. (1) can be recast into the form (using atomic units)

$$\frac{1}{Z} \left[2P(0) + \frac{1}{\pi} E_1(E_1 - E_2) \right] \leq \rho(0) \leq \frac{ZN}{2\pi} \langle \Psi | r_1^{-2} | \Psi \rangle, \quad (5)$$

where $P(0)$ is the electron-electron distribution function evaluated at $r_{12} = 0$, i.e.,

$$P(0) = \left\langle \Psi \left| \sum_{i < j}^N \delta(\mathbf{r}_i - \mathbf{r}_j) \right| \Psi \right\rangle \\ = \frac{N(N-1)}{2} \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}_2) | \Psi \rangle. \quad (6)$$

In Eq. (5) and below $\rho(\mathbf{r}_1)$ is given by

$$\rho(\mathbf{r}_1) = N \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N. \quad (7)$$

To the author's knowledge, Eq. (1) is the only published lower bound for $\rho(0)$. A lower bound is available for the asymptotic behavior of $\rho(r)$.^{4,5}

The purpose of this note is to consider Thirring's question for S state atoms and ions. A slightly improved upper bound for general atomic systems is also given.

LOWER BOUND FOR $\rho(0)$

An improved lower bound for $\rho(0)$ can be derived following the line of argument used by Hoffmann-Ostenhof *et al.*² to obtain the upper bound for $\rho(0)$ given in Eq. (5). If the following substitutions are employed:

$$u(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = r_1 \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (8)$$

$$W = r_1^{-2} L_1^2 - \sum_{i=2}^N \nabla_i^2 + 2 \left(\sum_{i < j}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \frac{Z}{r_i} - E \right), \quad (9)$$

where $r_1^{-2} L_1^2$ is the angular part of $-\nabla_1^2$ and Ψ will be assumed real, then the Schrödinger equation takes the form

$$-\frac{\partial^2 u}{\partial r_1^2} + Wu = 0. \quad (10)$$

On combining the expression

$$\rho(0) = \frac{-N}{2\pi} \int \frac{\partial u}{\partial r_1} \frac{\partial^2 u}{\partial r_1^2} r_1^{-2} d\mathbf{x}_1 \dots d\mathbf{x}_N \quad (11)$$

with Eq. (10) and carrying out the partial integrations involved, Hoffmann-Ostenhof *et al.*² obtained the result

$$\rho(0) = \frac{N}{2\pi} \left(Z \langle \Psi | r_1^{-2} | \Psi \rangle + \sum_{i=2}^N \left\langle \Psi \left| \mathbf{r}_1 \cdot \frac{(\mathbf{r}_i - \mathbf{r}_1)}{r_1 r_{i1}^3} \right| \Psi \right\rangle - \left\langle \Psi \left| \frac{L_1^2}{r_1^3} \right| \Psi \right\rangle \right). \quad (12)$$

If the discussion is restricted to S state atoms and ions, the problem of bounding $\rho(0)$ from below reduces to one of finding a suitable upperbound for

$$\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle,$$

since Eq. (12) can be put in the form

$$(N-1) \left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle + \frac{2\pi}{N} \rho(0) = Z \langle \Psi | r_1^{-2} | \Psi \rangle. \quad (13)$$

If θ denotes the angle between the vectors \mathbf{r}_1 and \mathbf{r}_{12} , then for the matrix element on the left-hand side of Eq. (13) we obtain the following (where the caret denotes a vector of unit magnitude):

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$$\begin{aligned}
\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle &= \left\langle \Psi \left| \frac{\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12} |\mathbf{r}_1 - \mathbf{r}_2|}{r_{12}^3} \right| \Psi \right\rangle \\
&= \left\langle \Psi \left| \frac{\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12}}{r_{12}^2} \right| \Psi \right\rangle \\
&= \left\langle \Psi \left| \frac{\cos \theta}{r_{12}^2} \right| \Psi \right\rangle \\
&< \left\langle \Psi \left| \frac{1}{r_{12}^2} \right| \Psi \right\rangle. \quad (14)
\end{aligned}$$

Combining Eqs. (14) and (13) leads to the lower bound estimate

$$\rho(0) \geq \frac{N}{2\pi} \{ Z \langle \Psi | r_1^{-2} | \Psi \rangle - (N-1) \langle \Psi | r_{12}^{-2} | \Psi \rangle \}. \quad (15)$$

For a number of accurate wave functions, matrix elements of r_{12}^{-2} are readily available. An upper bound estimate for $\langle \Psi | r_{12}^{-2} | \Psi \rangle$ in terms of the ground state energy is available,⁶ i.e.,

$$\langle \Psi | r_{12}^{-2} | \Psi \rangle \leq 8|E|/N \quad (16)$$

but this bound is rather rough and not useful for numerical estimates for $\rho(0)$.

An alternative upperbound for

$$\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle,$$

which is sharper than the result given in Eq. (14), at least for some of the systems tested (see below), and which requires no additional information, can be obtained as follows:

$$\begin{aligned}
\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle &= \frac{1}{2} \left\langle \Psi \left| \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}^3} \right| \Psi \right\rangle \\
&= \frac{1}{2} \left\langle \Psi \left| \frac{1}{r_1 r_{12}} \right| \Psi \right\rangle \\
&\quad - \frac{1}{2} \left\langle \Psi \left| \frac{(r_1 - r_2)^2}{r_1 r_{12}^3} \right| \Psi \right\rangle. \quad (17)
\end{aligned}$$

Since the second matrix element on the right-hand side of Eq. (17) is obviously positive,

$$\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle < \frac{1}{2} \left\langle \Psi \left| \frac{1}{r_1 r_{12}} \right| \Psi \right\rangle. \quad (18)$$

The matrix element appearing on the right-hand side of the inequality Eq. (18) can be found in the literature, e.g., Ref. 7, but is usually not tabulated. On using the Schwarz-Bunjakowski inequality, inequality (18) can be written

$$\begin{aligned}
\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle \\
< \frac{1}{2} [\langle \Psi | r_1^{-2} | \Psi \rangle \langle \Psi | r_{12}^{-2} | \Psi \rangle]^{1/2}. \quad (19)
\end{aligned}$$

Combining Eqs. (19) and (13) leads to the lower bound estimate

$$\begin{aligned}
\rho(0) \geq \frac{N}{2\pi} \left\{ Z \langle \Psi | r_1^{-2} | \Psi \rangle \right. \\
\left. - \frac{1}{2} (N-1) [\langle \Psi | r_1^{-2} | \Psi \rangle \langle \Psi | r_{12}^{-2} | \Psi \rangle]^{1/2} \right\}. \quad (20)
\end{aligned}$$

There are two points to note about the lower bound estimates given in Eqs. (15) and (20). They both become exact for one particle systems, which is not the circumstance for Eq. (1). Secondly, only ground state information is required, in contrast to the situation for Eq. (1).

Numerical tests for the three lower bound estimates, Eq. (5), Eq. (15), and Eq. (20) are presented in Table I for some members of the helium isoelectronic series.

UPPER BOUND FOR $\rho(0)$

The upper bound given in Eq. (1) is fairly sharp, although, as noted by Thirring, would be expected to become weaker as the number of electrons increases. The upper bound estimate for $\rho(0)$ for a general atomic system can be strengthened by bounding the matrix element

$$\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle$$

from below.

Denote the angle between the vectors \mathbf{r}_1 and \mathbf{r}_2 by θ_{12} , then it follows that:

$$\begin{aligned}
\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle &= \left\langle \Psi \left| \frac{(r_1 + r_2) \sin^2(\theta_{12}/2)}{r_{12}^3} \right| \Psi \right\rangle \\
&\geq \left\langle \Psi \left| \frac{\sin^2(\theta_{12}/2)}{r_{12}^2} \right| \Psi \right\rangle. \quad (21)
\end{aligned}$$

TABLE I. Lower bound estimates for some members of the helium isoelectronic series.*

Species	Lower bounds for $\rho(0)$			
	Eq. (5)	Eq. (15)	Eq. (20)	"Exact" $\rho(0)$
He	0.4565	3.3645	3.3583	3.6209
Li ⁺	2.0854	1.2955 × 10 ¹	1.3012 × 10 ¹	1.3704 × 10 ¹
Be ²⁺	5.6205	3.2891 × 10 ¹	3.3067 × 10 ¹	3.4392 × 10 ¹
B ³⁺	1.1778 × 10 ¹	6.6991 × 10 ¹	6.7343 × 10 ¹	6.9516 × 10 ¹
C ⁴⁺	2.1276 × 10 ¹	1.1907 × 10 ²	1.1966 × 10 ²	1.2288 × 10 ²
N ⁵⁺	3.4831 × 10 ¹	1.9296 × 10 ²	1.9383 × 10 ²	1.9832 × 10 ²
O ⁶⁺	5.3158 × 10 ¹	2.9247 × 10 ²	2.9369 × 10 ²	2.9964 × 10 ²
F ⁷⁺	7.6974 × 10 ¹	4.2142 × 10 ²	4.2305 × 10 ²	4.3069 × 10 ²
Ne ⁸⁺	1.0700 × 10 ²	5.8363 × 10 ²	5.8572 × 10 ²	5.9523 × 10 ²
Na ⁹⁺	1.4385 × 10 ²	7.8294 × 10 ²	7.8554 × 10 ²	7.9721 × 10 ²
Mg ¹⁰⁺	1.8852 × 10 ²	1.0231 × 10 ³	1.0263 × 10 ³	1.0403 × 10 ³

* The necessary matrix elements, energies, and exact values for $\rho(0)$ have been taken from Refs. 7-9. All results are in atomic units.

TABLE II. Upper bound estimates for some members of the helium isoelectronic series.^a

Species	Exact $\rho(0)$	Upper bounds for $\rho(0)$	
		Eq. (5)	Eq. (24)
H ⁻	0.3291	0.3573	0.3498
He	3.6209	3.8308	3.7950
Li ⁺	1.3704×10^1	1.4255×10^1	1.4161×10^1
Be ²⁺	3.4392×10^1	3.5446×10^1	3.5269×10^1
B ³⁺	6.9516×10^1	7.1227×10^1	7.0939×10^1
C ⁴⁺	1.2288×10^2	1.2541×10^2	1.2499×10^2
N ⁵⁺	1.9832×10^2	2.0183×10^2	2.0124×10^2
O ⁶⁺	2.9964×10^2	3.0429×10^2	3.0351×10^2
F ⁷⁺	4.3069×10^2	4.3662×10^2	4.3563×10^2
Ne ⁸⁺	5.9523×10^2	6.0264×10^2	6.0140×10^2
Na ⁹⁺	7.9721×10^2	8.0617×10^2	8.0466×10^2
Mg ¹⁰⁺	1.0403×10^3	1.0510×10^3	1.0490×10^3

^a The necessary matrix elements and exact values for $\rho(0)$ have been taken from Refs. 7–9. All results are in atomic units.

Applying the Schwarz–Buniakowski inequality to $\langle \Psi | \sin^2(\theta_{12}/2) | \Psi \rangle$ leads to

$$\begin{aligned} & \langle \Psi | \sin^2(\theta_{12}/2) | \Psi \rangle^2 \\ & \leq \left\langle \Psi \left| \frac{\sin^2(\theta_{12}/2)}{r_{12}^2} \right| \Psi \right\rangle \langle \Psi | r_{12}^2 \sin^2(\theta_{12}/2) | \Psi \rangle \\ & < \left\langle \Psi \left| \frac{\sin^2(\theta_{12}/2)}{r_{12}^2} \right| \Psi \right\rangle \langle \Psi | r_{12}^2 | \Psi \rangle. \end{aligned} \quad (22)$$

Combining Eqs. (21) and (22) leads to

$$\begin{aligned} & \frac{1}{4} \frac{[1 - \langle \Psi | \cos \theta_{12} | \Psi \rangle]^2}{\langle \Psi | r_{12}^2 | \Psi \rangle} < \left\langle \Psi \left| \frac{\sin^2(\theta_{12}/2)}{r_{12}^2} \right| \Psi \right\rangle \\ & < \left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle. \end{aligned} \quad (23)$$

Substituting Eq. (23) into Eq. (12) leads to the improved upper bound

$$\begin{aligned} \rho(0) & \leq \frac{N}{2\pi} \left\{ Z \langle \Psi | r_1^{-2} | \Psi \rangle \right. \\ & \left. - \frac{1}{4} \frac{(N-1)[1 - \langle \Psi | \cos \theta_{12} | \Psi \rangle]^2}{\langle \Psi | r_{12}^2 | \Psi \rangle} \right\}. \end{aligned} \quad (24)$$

Matrix elements of r_{12}^2 , $\cos \theta_{12}$, and r_1^{-2} are accessible for a number of accurate wave functions. Lower bound estimates for

$$\left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle$$

can be derived in terms of different matrix elements than those given in Eq. (23), e.g.,

$$\frac{\langle \Psi | (1 - \cos \theta_{12}) | \Psi \rangle^3}{8 \langle \Psi | r_{12}^2 | \Psi \rangle^2} < \left\langle \Psi \left| \frac{\mathbf{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_1 r_{12}^3} \right| \Psi \right\rangle, \quad (25)$$

but these results were not as tight as the bound given in Eq. (23) for the systems examined. The bound given in Eq. (24)

remains exact for one particle systems. A numerical test of the upper bound estimates given in Eqs. (5) and (24) is presented in Table II for several members of the helium isoelectronic series.

From the numerical results displayed in Table I, the lower bound estimates represented by both Eqs. (15) and (20) are observed to be fairly sharp and much superior to the lower bound estimate given in Eq. (1). If the inequality in Eq. (18) had been employed, the lower bound estimates for $\rho(0)$ for the 1S state of He becomes 3.5251.

The upper bound given in Eq. (24) represents only a minor improvement over Eq. (5) for the cases examined in Table II. This situation prevails in part because Eq. (5) represents a fairly sharp bound for two-electron systems. For larger electron systems, the correction term in Eq. (24) is likely to be more significant.

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