Spatial generalizations of Kato’s cusp condition for atoms: Applications

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Two functions built from the spherically averaged atomic density, i.e., \( f(r) = \rho(r) + \rho'(r)/(2Z) \) and \( g(r) = \rho_s(r) + \rho'(r)/(2Z) \), are studied in the Hartree-Fock framework for atoms in the range \( Z = 2 \text{–} 54 \) and in their ground state. These studies and previous ones show that \( f(r) \) is a positive function for all these atoms, and \( g(r) \) is also a positive function for all atoms whose least-bounded electron is s-type. For these atoms the upper bound \( \rho(0) \leq Z(r^{-2})_s/2\pi \), which improves the accuracy of the bound of Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [J. Phys. B 11, L371 (1978)], is found. In addition we obtain sharp lower bounds to \( \rho(0) \) and inequalities between total and s-state radial expectation values, \( \langle r^a \rangle \) and \( \langle r^a \rangle_s \), respectively.

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I. INTRODUCTION

The information about the single-particle density \( \rho(r) \) of an atom in its ground state is very important for the understanding of the atomic structure and properties, which, as the density-functional-theory [1] states, can all be expressed as functionals of \( \rho(r) \). Also, relations among density-dependent quantities are useful for the knowledge of the atomic properties when \( \rho \) is unknown. Results of this type are frequently found in the recent literature (see Refs. [2–8]). In particular, the radial expectation values \( \langle r^a \rangle \) defined by

\[
\langle r^a \rangle = \int r^a \rho(r) \, dr
\]

play a special role [2,3,6–10], some of them being related to fundamental and/or experimentally measurable averaged atomic quantities.

In a previous work [11], it was conjectured that the function (atomic units are used throughout)

\[
f(r) = \rho(r) + \frac{\rho'(r)}{2Z}
\]

(2)

where \( \rho(r) \) is the spherically averaged single-particle density of a neutral atom of nuclear charge \( Z \) in its ground state, and \( \rho' \) denotes its first derivative is positive for any value of \( r \), which can be considered as a spatial generalization of Kato’s cusp condition [12]:

\[
\rho(0) + \frac{\rho'(0)}{2Z} = 0 . \tag{3}
\]

From this spatial property, interesting inequalities between \( \rho(0) \) and some radial expectation values \( \langle r^a \rangle \), and among \( \langle r^a \rangle_s \) values themselves, were found. In the present work a more detailed study of \( f(r) \) is done.

The following relationship [13] for closed-shell atoms in a bare Coulomb field is also known:

\[
\rho_s(r) + \frac{\rho'(r)}{2Z} = 0 . \tag{4}
\]

Here, \( \rho_s(r) \) denotes the contribution from the s-type electrons to the spherically averaged density

\[
\rho_s(r) = \sum_n N_{ns} |\phi_{ns}(r)|^2 , \tag{5}
\]

\( N_{ns} \) being the number of electrons in the \( ns \) state. Equation (4) suggests the study, in a more realistic model, of the function

\[
g(r) = \rho_s(r) + \frac{\rho'(r)}{2Z} . \tag{6}
\]

Some applications of the properties of these functions will produce interesting inequalities involving the atomic density at the nucleus, \( \rho(0) \), radial expectation values \( \langle r^a \rangle \) and s-state radial expectation values \( \langle r^a \rangle_s \), defined by

\[
\langle r^a \rangle_s = \int r^a \rho_s(r) \, dr . \tag{7}
\]

The structure of this paper is the following. In Sec. II some results about the \( f(r) \) function are presented. A lower bound to \( \rho(0) \) will be found in Sec. III. The function \( g(r) \) will be studied in Sec. IV, and some relationships between \( \rho(0) \), \( \langle r^a \rangle \), and \( \langle r^a \rangle_s \) values will be found in Sec. V. Finally, some concluding remarks will be made.

II. STUDY OF THE FUNCTION \( f(r) \)

Here we shall be concerned with the properties of the function \( f(r) \) defined by Eq. (2) for atoms in their ground state. In a previous work [11] several results concerning \( f(r) \) were shown. The main conclusion was the conjecture \( f(r) \geq 0 \) everywhere for real atoms (this is true in the Hartree-Fock framework). This property allowed us to obtain several accurate inequalities among \( \rho(0) \) and radial expectation values \( \langle r^a \rangle \), by applying a Stieltjes theorem [14].

We have studied the shape of \( f(r) \) by using the Hartree-Fock data mentioned above [15]. This is illustrated in Figs. 1(a) and 1(b) for two representative atoms. We have found that for all atoms \( f(r) \) has only one maximum except in the cases \( Z = 4 \) and 11, where two maxi-
ma appear. The magnitude of the absolute maximum in all cases is much smaller than the maximum of \( \rho(r) \), i.e., \( \rho(0) \), the ratio between them being of the order of \( 10^{-2} \).

From the differential equation (2) we can write that

\[
\rho(r) = \rho(0) e^{-2Zr} + 2Ze^{-2Zr} \int_0^r e^{2Zt} f(t) dt .
\]

(8)

And because of \( f(r) \geq 0 \) one can obtain

\[
\rho(r) \geq \rho(0) e^{-2Zr} ,
\]

(9)
a result previously checked by Tal and Levy [3].

A more detailed study of \( f(r) \) can be made by means of the contributions from the \( nl \) orbitals to this function, i.e., by studying the functions defined by

\[
f_{nl}(r) = \rho_{nl}(r) + \frac{\rho'_{nl}(r)}{2Z} ,
\]

(10)

where

\[
\rho_{nl}(r) = \frac{1}{4\pi} \int N_{nl} |\phi_{nl}(r)|^2 d\Omega .
\]

(11)

Using the Hartree-Fock data of Clementi and Roetti [15], we have found that the functions \( f_{nl}(r) \) for all \( n,l \) have similar properties for all atoms in our range of study (\( Z = 2 \)–54). These are the following: (a) For all \( n, l \neq 0 \), \( f_{nl}(r) \geq 0 \) everywhere except small regions far from the origin, where it takes insignificant values; (b) \( f_{1s}(r) \geq 0 \) everywhere except small regions far from the origin; (c) for all \( n > 1 \), \( f_{nl}(r) \leq 0 \) for small values of \( r \). These features are illustrated in Fig. 2 for \( Z = 36 \), where the special behavior of \( f_{1s} \) is noticeable.

The contributions near the origin can be explained from the noninteracting electrons or bare-Coulomb-field model. In this model we find, from the hydrogenic-type wave functions [16]:

\[
f_{1s}^B(r) = 0 ,
\]

(12)

\[
f_{nl}^B(r) = -\frac{Z^4}{3\pi n^3} e^{-2Zr/n} \left[ \frac{1}{r} - \frac{1}{n} \right] r + O(r^2)
\]

if \( n > 1 \),

(13)

and

\[
f_{nl}^B(r) = C_{nl} \left( \frac{2Zr}{n} \right)^{2l-1} e^{-2Zr/n} \left[ \frac{2l}{n} + O(r) \right]
\]

(14)

for \( l > 0 \), where \( C_{nl} \) is a positive constant.

---

FIG. 1. Plot of the function \( f(r) \) defined by Eq. (2) for (a) the neon atom and (b) the xenon atom, both evaluated from the Hartree-Fock wave functions of Ref. [15]. A small negative zone at the origin appears in (a) because of the error of this model in the verification of the cusp condition.

FIG. 2. Plot of the single-orbital contributions to \( f(r) \) for the krypton atom evaluated from the Hartree-Fock wave functions of Ref. [15].
Therefore, for small values of \( r \), \( f_{\text{BCF}}^B(r) \leq 0 \) \( (n > 1) \), \( f_{\text{BCF}}^B(r) \geq 0 \) \( (l > 0) \), and \( f_{\text{BCF}}^B(r) = 0 \) everywhere. Then we find that the Hartree-Fock values of \( f_{\text{HF}}^B(r) \), which will also be called \( f_{\text{HF}}^B(r) \), do not present qualitative discrepancies for \( r \rightarrow 0 \) with those of \( f_{\text{BCF}}^B(r) \) except in the case 1s, where \( f_{\text{HF}}^B(r) \) take values above zero. For all values of \( r \), and except in the case of 1s, \( f_{\text{HF}}^B(r) \) can be seen as a smoothing of \( f_{\text{BCF}}^B \), which is illustrated in Fig. 3 for two representative orbitals \((2s, 2p)\) of the krypton atom. All these effects can be qualitatively explained if we think that the electronic repulsion (which is taken into account in the Hartree-Fock calculations) produces a dispersion on \( \rho_{\text{HF}}(r) \) along space.

What can we say about the comparison between both models for the total \( f(r) \)? For small-\( Z \) atoms, where the effect of the 1s states is important for \( f(r) \), we expect \( f_{\text{HF}}^B \) to be greater than \( f_{\text{BCF}}^B \) near the origin (which is the region where it is more important) because of the effect of the electronic repulsion on the 1s state noted above. However, for high-\( Z \) atoms where the contribution of the 1s orbital is less important, the opposite can be expected. This is so because of the smoothing on \( f_{\text{HF}}(r) \) produced by all the states different from 1s, which would imply that \( f_{\text{HF}}^B \geq f_{\text{BCF}}^B \). This fact is numerically found to happen for \( Z \geq 7 \). In Figs. 4(a) and 4(b) the two main behaviors are illustrated, for \( Z = 5 \) and 11. The interesting effect of the electronic interaction that, although \( f_{\text{HF}}^B(r) \) can take important negative values for some atoms, \( f_{\text{HF}}^B(r) \) is always positive, can also be seen.

III. A LOWER BOUND TO \( \rho(0) \)

In a previous work [11], the positivity of \( f(r) \) allowed us to find inequalities among its moments,

\[
\nu_k = \int_0^\infty r^k f(r) dr
\]

\[
= \begin{cases} 
\frac{\langle r^{-2} \rangle}{4\pi} - \frac{\rho(0)}{2Z} & \text{if } k = 0 \\
\frac{1}{4\pi} \left( \frac{\langle r^{k-2} \rangle}{2Z} - \frac{k}{2Z} \langle r^{k-3} \rangle \right) & \text{if } k \geq 1
\end{cases}
\]

(15)

Now we will perform another application of this property which will lead to a lower bound to the atomic density at the origin \( \rho(0) \). We start from a lower bound [8] to the maximum value of any positive function defined in \([0, \infty)\):

\[
\max \{ f(r) \} \geq \frac{1}{2} \nu_1
\]

(16)

Using Eq. (15) for the moments, we can bound the maximum of \( f(r) \), \( f_{\text{max}} \). After some manipulation we find

\[
\rho(0) \geq 2Z \left[ \frac{\langle r^{-2} \rangle}{4\pi} - \frac{1}{2\pi} \left( \frac{\langle r^{-1} \rangle - \langle r^{-2} \rangle}{2Z} \right) f_{\text{max}}^{1/2} \right]
\]

\[
\equiv \text{L}_1
\]

(17)

For high-\( Z \) atoms \((Z \geq 7)\) we have seen that \( f_{\text{max}}^B \) is smaller than \( f_{\text{max}}^B \), which can be expected theoretically. When
TABLE I. Values of the different lower bounds to \( \rho(0) \), i.e., \( L_1 \), \( L_2 \), and \( L_3 \) given by Eqs. (17), (18), and (41) compared to those of \( \rho(0) \) by means of their respective ratios \( R_1 = L_1 / \rho(0) \), \( R_2 = L_2 / \rho(0) \), and \( R_3 = L_3 / \rho(0) \) for several atoms in the range \( Z = 2 \text{--} 54 \). All these quantities are calculated from the Hartree-Fock wave functions of Clementi and Roetti [15], and the values of \( f_{\text{max}}^B \) have been calculated numerically from the hydrogenic-type wave functions. The values of \( L_1 \) have been displayed only for those atoms for which \( g(r) \) is numerically found to be positive everywhere (see text for further details).

<table>
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<tr>
<th>( Z )</th>
<th>( \rho(0) )</th>
<th>( f_{\text{max}} )</th>
<th>( f_{\text{max}}^B )</th>
<th>( L_1 )</th>
<th>( R_1 )</th>
<th>( L_2 )</th>
<th>( R_2 )</th>
<th>( L_3 )</th>
<th>( R_3 )</th>
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<td>1016.92</td>
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</table>

Z increases, the difference is so high that we expect the exact \( f_{\text{max}} \) to be smaller than \( f_{\text{max}}^B \), which leads us to write the weaker bound

\[
\rho(0) \geq 2Z \left\{ \frac{\langle r^{-2} \rangle}{4\pi} - \frac{1}{2\pi} \left[ \langle r^{-1} \rangle - \frac{\langle r^{-2} \rangle}{2Z} \right] f_{\text{max}}^B \right\}^{1/2}
\]

\( \equiv L_2 \)  \hspace{1cm} (18)

valid for \( Z \geq 7 \).

Now, this bound only involves the values of \( \langle r^{-2} \rangle \), \( \langle r^{-1} \rangle \), and \( f_{\text{max}}^B \), and the latter can be calculated exactly from the Hydrogenic-type wave functions. These bounds are found to be very sharp, when tested by using Hartree-Fock values of \( \langle r^{-2} \rangle \), \( \langle r^{-1} \rangle \), and \( \rho(0) \), as illustrated in Table I by means of the ratios \( R_1 = L_1 / \rho(0) \) and \( R_2 = L_2 / \rho(0) \). We can notice how, although \( f_{\text{max}} \) can be much smaller than \( f_{\text{max}}^B \), the bound does not lose much accuracy. The improvement of the bound given by (18) with respect to previous lower bounds [8,17] is important.

The bounds given by Eqs. (17) and (18) have a similar structure to those found by King [18]. The first term is the upper bound of Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [2] and the second a slight negative quantity.

IV. STUDY OF THE FUNCTION \( g(r) \)

The result given by Eq. (4) for closed-shell atoms in a bare Coulomb field suggests the interest of the study for more realistic atoms of the function defined by

\[
g(r) = \rho_1(r) + \frac{p^2(r)}{2Z}.
\]

The first conclusion we can extract is that

\[
g(r) \leq f(r)
\]

everywhere.

Some properties of this function can be obtained from the properties of \( f(r) \). For one-electron atoms, we have

\[
g(r) = f(r) = 0.
\]

(21)

From Kato’s cusp condition, and \( \rho(0) = 0 \), we also know that

\[
g(r) = f(r) = 0.
\]

(22)

In addition, for small values of \( r \), one has

\[
g(r) = f(r) + O(r^2).
\]

(23)

We have studied the positivity of \( g(r) \) with the Hartree-Fock data of Ref. [15] for atoms in the range \( Z = 2 \text{--} 54 \) finding that \( g(r) \) is positive everywhere for all of them except those with \( Z = 6 \text{--} 10, 13 \text{--} 18, 31 \text{--} 36, 46, \text{and} 49 \text{--} 54 \), i.e., those whose least-bounded electron is not a type, with the exception of boron (\( Z = 5 \)). For these atoms \( g(r) \) is positive except for large values of \( r \), where it takes negative values, very small in magnitude, up to infinity.

This asymptotic negative behavior can be explained by means of the theoretical results of Handy, Marron, and Silverstone [19] and Handler, Smith, and Silverstone [20] which predicts, for the atoms whose least-bounded electron is of a type,

\[
g(r) \sim \left( 1 - \frac{\sqrt{2I}}{Z} \right) r^{3/2} e^{-2\sqrt{2I}r} \geq 0
\]

(24)

and

\[
g(r) \sim - \frac{\sqrt{2I}}{Z} r^{3/2} e^{-2\sqrt{2I}r} \leq 0.
\]

(25)

when the least-bounded electron has \( l > 0 \). Nevertheless, the negative part of \( g(r) \) for these atoms
is found to have very little importance compared to the whole function. For a given number of \( np \) subshells in the atom it is found that the negative part of \( g(r) \) is more important when the number of electrons in the last \( p \) subshell is greater. In addition its importance decreases when the number of \( np \) subshells increases. Then the most unfortunate case is \( Z = 10 \), for which the ratio between the minimum of the negative part and the maximum of the positive part is \( \approx 10^{-4} \). For the atom whose negative part is the least important (\( Z = 49 \)) this ratio has the value of \( 10^{-12} \). Also, if we estimate numerically the contribution of the negative part to the integral

\[
I = \int_0^\infty g(r)dr
\]

which will be called

\[
I_- = -\int_0^\infty g(r)dr
\]  

[here \( r_0 \) denotes the point from which \( g(r) < 0 \), we find that \( I_- / I = 5 \times 10^{-4} \) for \( Z = 10 \) and \( 3 \times 10^{-10} \) for \( Z = 49 \).]

The shape of \( g(r) \) is illustrated in Fig. 5 for a representative atom (\( Z = 54 \)), for which \( g(r) \) is negative from \( r = 6.5 \), which cannot be seen in the plot. The main result of this study is that \( g(r) \geq 0 \) in the zone where it is most significant in the range \( Z = 2-54 \) and everywhere for the atoms whose least bounded electron is of \( s \) type.

For closed-shell atoms in a bare Coulomb field it was shown by March \([13]\) that \( g(r) = 0 \). Then, for a real closed-shell atom, this function must carry the information about the importance of the Coulombic repulsion among the electrons. We have studied this function for the isoelectronic series of two and ten electrons. One can expect that when \( Z \) increases the effect of the Coulombian repulsion must decrease when compared to the nuclear attraction. This fact can be observed in Fig. 6 where we have plotted, for the sequence of ten electrons, the values of the function \( g(r)/\rho(0) \), which become smaller when \( Z \) increases.

**FIG. 5.** Plot of the function \( g(r) \) defined by Eq. (19) for the xenon atom evaluated from the Hartree-Fock wave functions of Ref. [15].

**FIG. 6.** Plot of the function \( g(r)/\rho(0) \) for some ions in the isoelectronic sequence of ten electrons, evaluated from the Hartree-Fock wave functions of Ref. [15].

**V. RELATIONSHIPS INVOLVING \( \rho(0) \)
AND RADIAL EXPECTATION VALUES**

The observed fact that \( g(r) \) is positive everywhere for some atoms and nearly positive for the rest of them makes interesting the application of the following Stieltjes theorem: if \( g(r) \) is a positive function, the following inequalities hold:

\[
\Delta_m^{(k)} = \begin{vmatrix} v_k & v_{k+1} & \cdots & v_{k+m} \\ v_{k+1} & v_{k+2} & \cdots & v_{k+m} \\ \vdots & \vdots & \ddots & \vdots \\ v_{k+m} & v_{k+m+1} & \cdots & v_{k+2m} \end{vmatrix} \geq 0 \]

for any \( k \geq 0 \) and any \( m \geq 0 \), \( v_k \) being the \( k \)th-order moment of \( g(r) \), i.e.,

\[
v_k = \int_0^\infty r^k g(r)dr
\]

\[
\Delta_m^{(k)} = \begin{cases} \left( \frac{\langle r^{-2} \rangle_s}{4\pi} - \frac{\rho(0)}{2Z} \right) & \text{if } k = 0 \\ \frac{1}{4\pi} \left( \frac{\langle r^{k-2} \rangle_s}{2Z} - \frac{k}{2Z} \langle r^{k-1} \rangle_s \right) & \text{if } k \geq 1. \end{cases}
\]

For \( m = 0 \), the inequalities obtained by Eq. (28) only mean the positivity of the moments \( v_k \),

\[
v_k \geq 0
\]

for any \( k \geq 0 \).

Inequalities (28) and (30) are verified for those atoms whose least bounded electron is of \( s \) type. For the rest of the atoms \( g(r) \) is not positive for all \( r \), but we can expect that inequalities (30) also hold for small values of \( k \) because the contribution of the negative part of \( g(r) \) to the integrals (29) is insignificant. This is not the case for large values of \( k \). Then for all atoms we can expect that the following result holds, obtained by (30) with \( k = 0 \):
\[ \rho(0) \leq \frac{Z \langle r^{-2} \rangle_s}{2\pi} \equiv B_0 , \]  
(31)

which improves the accuracy of the upper bound of Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [2] to \( \rho(0) \), also obtained by means of the positivity of \( f(r) \) [11]:

\[ \rho(0) \leq \frac{Z \langle r^{-2} \rangle_s}{2\pi} \equiv B_{HO} . \]  
(32)

The goodness of these upper bounds to \( \rho(0) \) is illustrated in Table II for 16 atoms. The improvement mentioned above can be noticed. In addition, the tightness of the bound given by Eq. (31) increases with \( Z \).

Also we can expect inequality (30) to hold for \( k = 1 \), because the effect of the negative part of \( g(r) \) is found to be less than 0.5\%, obtaining

\[ \langle r^{-1} \rangle_s \geq \frac{\langle r^{-2} \rangle_s}{2Z} \equiv B_1 . \]  
(33)

This inequality, which improves the one obtained by means of the positivity of \( f(r) \) [11],

\[ \langle r^{-1} \rangle \geq \frac{\langle r^{-2} \rangle}{2Z} \]  
(34)

is a particular case of the inequalities (30) valid for atoms whose least-bounded electron is of \( s \) type, i.e.,

\[ \langle r^\alpha \rangle_s \geq \frac{\alpha + 2}{2Z} \langle r^{\alpha-1} \rangle \]  
(35)

for \( \alpha \geq -1 \). One interesting particular case is

\[ \langle r^{-1} \rangle \leq ZN_s \equiv B_2 , \]  
(36)

where \( N_s = \langle r^0 \rangle_s \) is the number of \( s \) electrons. It also improves the accuracy of the analogue result

\[ \langle r^{-1} \rangle \leq Z^2 \]  
(37)

found by using \( f(r) \geq 0 \) [11].

The accuracy of the bounds \( B_1 \) and \( B_2 \) is displayed in Table III for neutral atoms. The tightness of the relationship (33) can be noticed.

Relationships including a greater number of expectation values can be obtained from Eq. (28). In particular, setting \( m = 1 \) and \( k = 0 \) in this equation, we find

\[ \rho(0) \leq \frac{Z}{2\pi} \left[ \langle r^{-2} \rangle_s - \frac{(\langle r^{-1} \rangle_s - \langle r^{-2} \rangle_s / 2Z)^2}{N_s - \langle r^{-1} \rangle_s / Z} \right] \equiv A_0 . \]  
(38)

For \( m = 1 \) and \( k = 1 \), the following inequality is obtained:

\[ \langle r^{-2} \rangle \leq 2Z \left[ \langle r^{-1} \rangle_s - \frac{(N_s - \langle r^{-1} \rangle_s / Z)^2}{\langle r \rangle_s - \frac{1}{2}} \right] \equiv A_1 . \]  
(39)

These relations, which are equalities for closed-shell atoms in a bare Coulomb field and rigorous upper bounds for Clementi and Roetti’s Hartree-Fock values for all atoms whose least-bounded electron is of \( s \) type, are found to be very approximate for all atoms in the range \( Z = 2 - 54 \), as we can see in Table IV, where we compare the values of \( A_0 \) and \( A_1 \) to those of \( \rho(0) \) and \( \langle r^{-2} \rangle \), respectively. We also give the ratios \( \rho(0)/A_0 \) and \( \langle r^{-2} \rangle / A_1 \).

Another application of the positivity of \( g(r) \) for the atoms mentioned above can be performed in the same way as done for \( f(r) \) in Sec. III. This leads to a lower bound \( B_L \) for \( \rho(0) \):

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( \rho(0) )</th>
<th>( B_0 )</th>
<th>( B_{HO} )</th>
<th>( \rho(0)/B_0 )</th>
<th>( \rho(0)/B_{HO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.60</td>
<td>3.82</td>
<td>3.82</td>
<td>0.942</td>
<td>0.942</td>
</tr>
<tr>
<td>6</td>
<td>127.56</td>
<td>130.82</td>
<td>132.52</td>
<td>0.975</td>
<td>0.962</td>
</tr>
<tr>
<td>10</td>
<td>620.15</td>
<td>631.13</td>
<td>660.33</td>
<td>0.983</td>
<td>0.939</td>
</tr>
<tr>
<td>12</td>
<td>1093.73</td>
<td>1111.55</td>
<td>1174.22</td>
<td>0.984</td>
<td>0.931</td>
</tr>
<tr>
<td>14</td>
<td>1765.71</td>
<td>1791.67</td>
<td>1907.82</td>
<td>0.986</td>
<td>0.926</td>
</tr>
<tr>
<td>18</td>
<td>3840.22</td>
<td>3887.55</td>
<td>4196.94</td>
<td>0.988</td>
<td>0.915</td>
</tr>
<tr>
<td>22</td>
<td>7133.88</td>
<td>7210.88</td>
<td>7859.21</td>
<td>0.989</td>
<td>0.908</td>
</tr>
<tr>
<td>26</td>
<td>11911.58</td>
<td>12023.07</td>
<td>13209.51</td>
<td>0.991</td>
<td>0.902</td>
</tr>
<tr>
<td>30</td>
<td>18448.59</td>
<td>18605.66</td>
<td>20588.32</td>
<td>0.992</td>
<td>0.896</td>
</tr>
<tr>
<td>34</td>
<td>27060.83</td>
<td>27275.62</td>
<td>30372.14</td>
<td>0.992</td>
<td>0.891</td>
</tr>
<tr>
<td>38</td>
<td>38080.70</td>
<td>38312.68</td>
<td>42901.04</td>
<td>0.992</td>
<td>0.886</td>
</tr>
<tr>
<td>42</td>
<td>51612.88</td>
<td>51993.22</td>
<td>58503.72</td>
<td>0.993</td>
<td>0.882</td>
</tr>
<tr>
<td>46</td>
<td>68128.53</td>
<td>68594.17</td>
<td>77525.70</td>
<td>0.993</td>
<td>0.879</td>
</tr>
<tr>
<td>50</td>
<td>77609.10</td>
<td>78112.54</td>
<td>88455.89</td>
<td>0.994</td>
<td>0.877</td>
</tr>
<tr>
<td>54</td>
<td>111163.94</td>
<td>111834.82</td>
<td>127351.77</td>
<td>0.994</td>
<td>0.873</td>
</tr>
</tbody>
</table>
TABLE III. Hartree-Fock values (calculated from Ref. [15]) of the lower bound $B_1$ [Eq. (33)] compared to those of $\langle r^{-1} \rangle_s$ for some atoms in the range $Z = 2$–54 and values of the upper bound $B_2$ [Eq. (36)] compared to the Hartree-Fock values of $\langle r^{-1} \rangle$ for some atoms for which $g(r)$ is found to be positive everywhere (see text).

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$\langle r^{-1} \rangle_s$</th>
<th>$B_1$</th>
<th>$B_1/\langle r^{-1} \rangle_s$</th>
<th>$\langle r^{-1} \rangle$</th>
<th>$B_2$</th>
<th>$\langle r^{-1} \rangle/B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.375</td>
<td>2.998</td>
<td>0.888</td>
<td>3.38</td>
<td>4</td>
<td>0.84</td>
</tr>
<tr>
<td>6</td>
<td>13.122</td>
<td>11.564</td>
<td>0.881</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>22.501</td>
<td>20.745</td>
<td>0.922</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>28.210</td>
<td>25.618</td>
<td>0.908</td>
<td>39.92</td>
<td>72</td>
<td>0.55</td>
</tr>
<tr>
<td>14</td>
<td>33.549</td>
<td>30.580</td>
<td>0.912</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>44.140</td>
<td>40.695</td>
<td>0.922</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>55.535</td>
<td>51.013</td>
<td>0.919</td>
<td>91.42</td>
<td>176</td>
<td>0.52</td>
</tr>
<tr>
<td>26</td>
<td>66.242</td>
<td>61.389</td>
<td>0.927</td>
<td>115.66</td>
<td>208</td>
<td>0.56</td>
</tr>
<tr>
<td>30</td>
<td>76.922</td>
<td>71.867</td>
<td>0.934</td>
<td>142.06</td>
<td>240</td>
<td>0.59</td>
</tr>
<tr>
<td>34</td>
<td>88.130</td>
<td>82.541</td>
<td>0.937</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>99.922</td>
<td>93.336</td>
<td>0.934</td>
<td>196.57</td>
<td>380</td>
<td>0.52</td>
</tr>
<tr>
<td>42</td>
<td>110.925</td>
<td>104.192</td>
<td>0.939</td>
<td>225.52</td>
<td>378</td>
<td>0.60</td>
</tr>
<tr>
<td>46</td>
<td>121.775</td>
<td>115.101</td>
<td>0.945</td>
<td>255.90</td>
<td>368</td>
<td>0.69</td>
</tr>
<tr>
<td>50</td>
<td>134.005</td>
<td>126.125</td>
<td>0.941</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>145.593</td>
<td>137.204</td>
<td>0.942</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$\rho(0) \geq 2Z \left[ \frac{\langle r^{-2} \rangle_s}{4\pi} \right. $$

$$ - \left[ \frac{1}{2\pi} \left( \langle r^{-1} \rangle_s - \frac{\langle r^{-2} \rangle}{2Z} \right) \right] g_{\text{max}}^{1/2} \right]^{1/2} $$

$$ \equiv B_L. \quad (40) $$

$$ \rho(0) \geq 2Z \left[ \frac{\langle r^{-2} \rangle_s}{4\pi} \right. $$

$$ - \left[ \frac{1}{2\pi} \left( \langle r^{-1} \rangle_s - \frac{\langle r^{-2} \rangle}{2Z} \right) \right] f_B^{\text{max}} \right]^{1/2} \right] $$

$$ \equiv L_3. \quad (41) $$

For Hartree-Fock values of $\rho(0)$ and $B_L$, we obtain for all atoms between $Z = 2$–54 that $B_L/\rho(0) > 0.975$, which shows the tightness of this relationship.

Using the fact that $g_{\text{max}} \leq f_{\text{max}}$, and $f_{\text{max}} \leq f_B^{\text{max}}$ for $Z \geq 7$, we can write

$$ R_3 = L_3 / \rho(0). $$

TABLE IV. Comparison between the Hartree-Fock values of $\rho(0)$ and $\langle r^{-1} \rangle$ to those of $A_0$ [Eq. (38)] and $A_1$ [Eq. (39)], respectively.

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$\rho(0)$</th>
<th>$A_0$</th>
<th>$\langle r^{-2} \rangle$</th>
<th>$A_1$</th>
<th>$\rho(0)/A_0$</th>
<th>$\langle r^{-2} \rangle/A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.597</td>
<td>3.673</td>
<td>11.992</td>
<td>12.395</td>
<td>0.979</td>
<td>0.968</td>
</tr>
<tr>
<td>6</td>
<td>127.555</td>
<td>129.321</td>
<td>138.773</td>
<td>144.425</td>
<td>0.986</td>
<td>0.961</td>
</tr>
<tr>
<td>10</td>
<td>620.146</td>
<td>625.603</td>
<td>414.900</td>
<td>423.677</td>
<td>0.991</td>
<td>0.979</td>
</tr>
<tr>
<td>14</td>
<td>1765.707</td>
<td>1783.759</td>
<td>856.227</td>
<td>898.880</td>
<td>0.990</td>
<td>0.953</td>
</tr>
<tr>
<td>18</td>
<td>3840.215</td>
<td>3871.556</td>
<td>1465.009</td>
<td>1519.531</td>
<td>0.992</td>
<td>0.964</td>
</tr>
<tr>
<td>22</td>
<td>7133.884</td>
<td>7192.254</td>
<td>2244.585</td>
<td>2370.278</td>
<td>0.992</td>
<td>0.947</td>
</tr>
<tr>
<td>26</td>
<td>11911.575</td>
<td>11995.633</td>
<td>3192.222</td>
<td>3354.866</td>
<td>0.993</td>
<td>0.952</td>
</tr>
<tr>
<td>30</td>
<td>18448.586</td>
<td>18568.276</td>
<td>4312.007</td>
<td>4512.831</td>
<td>0.994</td>
<td>0.956</td>
</tr>
<tr>
<td>34</td>
<td>27060.826</td>
<td>27219.844</td>
<td>5612.758</td>
<td>5832.216</td>
<td>0.994</td>
<td>0.962</td>
</tr>
<tr>
<td>38</td>
<td>38008.696</td>
<td>38258.334</td>
<td>7093.557</td>
<td>7446.281</td>
<td>0.994</td>
<td>0.953</td>
</tr>
<tr>
<td>42</td>
<td>51612.876</td>
<td>51909.746</td>
<td>8752.136</td>
<td>9129.739</td>
<td>0.994</td>
<td>0.959</td>
</tr>
<tr>
<td>46</td>
<td>68128.534</td>
<td>68460.367</td>
<td>10589.311</td>
<td>10862.655</td>
<td>0.995</td>
<td>0.975</td>
</tr>
<tr>
<td>50</td>
<td>87898.961</td>
<td>88344.612</td>
<td>12612.454</td>
<td>13115.467</td>
<td>0.995</td>
<td>0.962</td>
</tr>
<tr>
<td>54</td>
<td>111163.943</td>
<td>111687.797</td>
<td>14818.052</td>
<td>15350.114</td>
<td>0.995</td>
<td>0.965</td>
</tr>
</tbody>
</table>
Finally, let us think again about an isoelectronic sequence of closed-shell electrons. As we said above in Sec. IV, we expect $g(r)/\rho(0)$ to be less important when increasing $Z$. This suggests that the ratio $\nu_0/\rho(0)$ will also decrease and the bound given by Eq. (31) will be more accurate when increasing $Z$. This is found when we test Eq. (31) by using Hartree-Fock values of $\rho(0)$ and $\langle r^{-2} \rangle$, for the sequence of ten electrons, for which the ratio $\nu_0/\rho(0)$ increases monotonically from 0.982 for $Z = 10$ to 0.994 for $Z = 54$.

VI. CONCLUSIONS

A numerical study of the functions

\[ f(r) = \rho(r) + \rho'/(2Z) \]

and

\[ g(r) = \rho_s(r) + \rho'/(2Z), \]

by using Hartree-Fock data, shows that the former is positive for all atoms in the range $Z = 1 - 54$ and the latter is positive for the atoms whose least-bounded electron is of s type. The application of the positivity of $f(r)$ or $g(r)$ allows us to find tight lower and upper bounds to $\rho(0)$ [Eqs. (18), (31), (38), and (41)] and relationships between radial expectation values of $\rho(r)$ and $\rho_s(r)$ [Eqs. (33), (36), and (39)].

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