PHYSICAL REVIEW A VOLUME 46, NUMBER 1 1 JULY 1992

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

I. Porras and F. J. Gálvez

Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain

(Received 9 October 1991; revised manuscript received 28 January 1992)

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 $Z=2$–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 $\rho(0)\le Z\langle r^{-2}\rangle_s/2\pi$, which improves the accuracy of the bound of Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [J. Phys. B **11**, L571 (1978)], is found. In addition we obtain sharp lower bounds to $\rho(0)$ and inequalities between total and s-state radial expectation values, $\langle r^\alpha\rangle$ and $\langle r^\alpha\rangle_s$, respectively.

PACS number(s): 31.10.+z, 31.90.+s

I. INTRODUCTION

The information about the single-particle density $\rho(\mathbf{r})$ 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 $\rho(\mathbf{r})$. Also, relations among density-dependent quantities are useful for the knowledge of the atomic properties when ρ is unknown. Results of this type are frequently found in the recent literature (see Refs. [2–8]). In particular, the radial expectation values $\langle r^\alpha\rangle$ defined by

$$\langle r^\alpha\rangle=\int r^\alpha\rho(\mathbf{r})d\mathbf{r} \tag{1}$$

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)

$$f(r)=\rho(r)+\frac{\rho'(r)}{2Z}\ , \tag{2}$$

where $\rho(r)$ is the spherically averaged single-particle density of a neutral atom of nuclear charge Z in its ground state, and ρ' 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 $\langle r^\alpha\rangle$, and among $\langle r^\alpha\rangle$ 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

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

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 $\langle r^\alpha\rangle$ and s-state radial expectation values $\langle r^\alpha\rangle_s$, defined by

$$\langle r^\alpha\rangle_s=\int r^\alpha\rho_s(\mathbf{r})d\mathbf{r}\ . \tag{7}$$

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 $\rho(0)$, $\langle r^\alpha\rangle$, and $\langle r^\alpha\rangle_s$ 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 $f(r)\ge 0$ 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 $\langle r^\alpha\rangle$, 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 maxima 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

$$\rho(r)=\rho(0)e^{-2Zr}+2Ze^{-2Zr}\int_0^r e^{2Zt}f(t)dt \ . \tag{8}$$

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

$$\rho(r)\geq\rho(0)e^{-2Zr} \ , \tag{9}$$

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

$$f_{nl}(r)=\rho_{nl}(r)+\frac{\rho'_{nl}(r)}{2Z} \ , \tag{10}$$

where

$$\rho_{nl}(r)=\frac{1}{4\pi}\int N_{nl}|\phi_{nl}(\mathbf{r})|^2 d\Omega \ . \tag{11}$$

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 $n>1$, $f_{ns}(r)\leq 0$ 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]:

$$f^B_{1s}(r)=0 \ , \tag{12}$$

$$f^B_{ns}(r)=-\frac{Z^4}{3\pi n^3}e^{-2Zr/n}\left[\left[1-\frac{1}{n}\right]r+O(r^2)\right] \quad \text{if } n>1 \ , \tag{13}$$

and

$$f^B_{nl}(r)=C_{nl}\left[\frac{2Zr}{n}\right]^{2l-1}e^{-2Zr/n}\left[\frac{2l}{n}+O(r)\right] \tag{14}$$

for $l>0$, where C_{nl} is a positive constant.

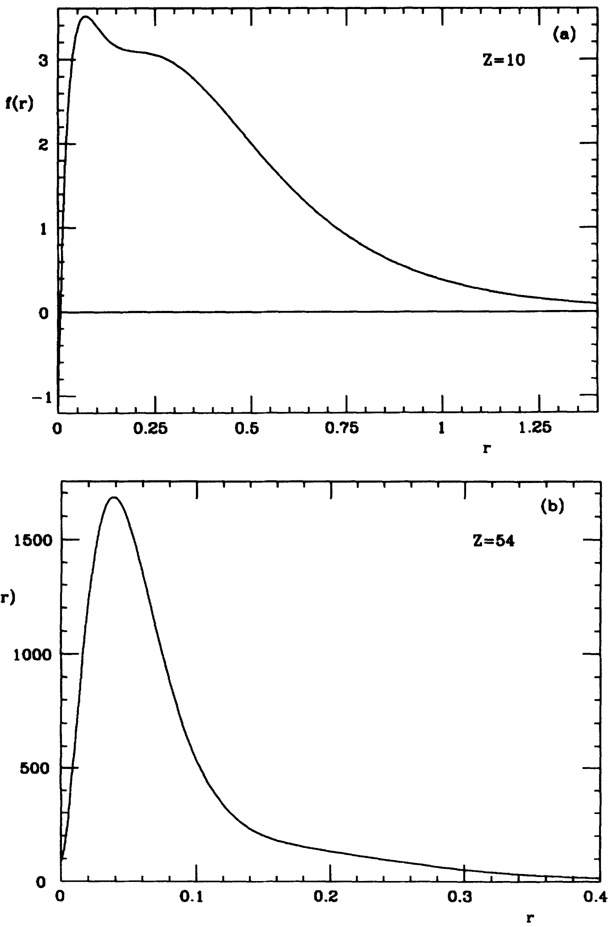

FIG. 1. Plot of the function $f(r)$ defined by Eq. (2) for (a) the neon atom and (b) the xenon atom, both evaluated from the Hartree-Fock wave functions of Ref. [15]. A small negative zone at the origin appears in (a) because of the error of this model in the verification of the cusp condition.

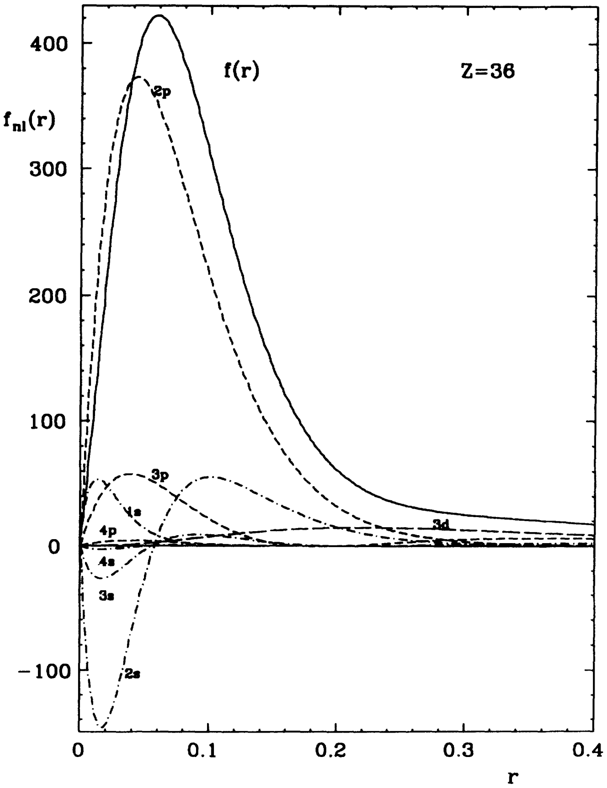

FIG. 2. Plot of the single-orbital contributions to $f(r)$ for the krypton atom evaluated from the Hartree-Fock wave functions of Ref. [15].

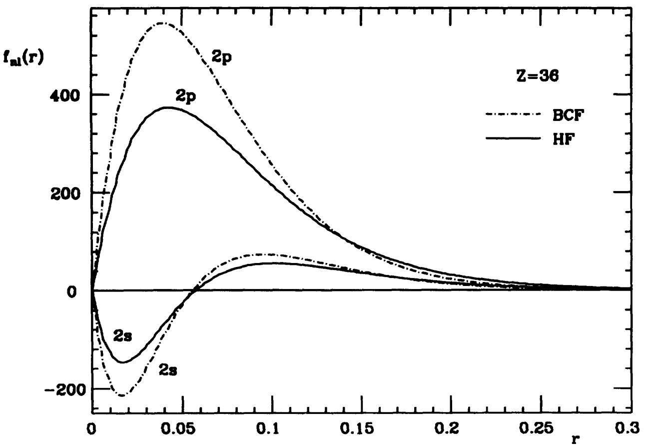

FIG. 3. Comparison between the bare-Coulomb-field values (BCF) and the Hartree-Fock values (HF, from Ref. [15]) of the single-orbital contributions $f_{2s}(r)$ and $f_{2p}(r)$ for the krypton atom. The smoothing effect of the Coulombic repulsion can be noticed.

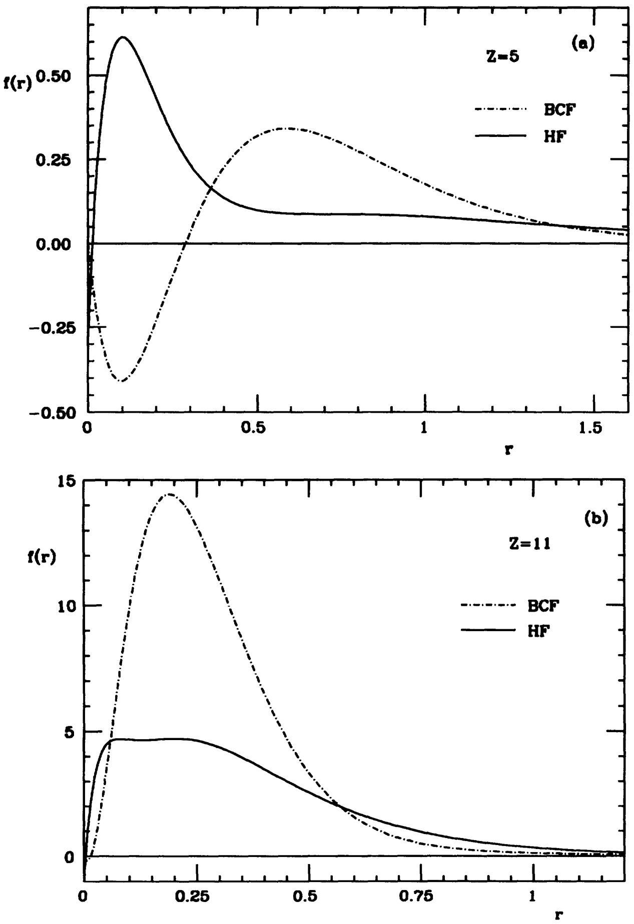

FIG. 4. Comparison between the bare-Coulomb-field values (BCF) and the Hartree-Fock values (HF, from Ref. [15]) of the function $f(r)$, (a) for the boron atom, for which the HF maximum is greater than the BCF one, and (b) for the sodium atom, which is representative for all $Z \geq 7$, for which the HF maximum is smaller than the BCF one, and the smoothing effect mentioned in the text is noticeable.

Therefore, for small values of r, $f^B_{ns}(r) \leq 0$ $(n>1)$, $f^B_{nl}(r) \geq 0$ $(l>0)$, and $f^B_{1s}(r)=0$ everywhere. Then we find that the Hartree-Fock values of $f_{nl}(r)$, which will also be called $f^H_{nl}(r)$, do not present qualitative discrepancies for $r \to 0$ with those of $f^B_{nl}(r)$ except in the case 1*s*, where $f^H_{1s}(r)$ take values above zero. For all values of r, and except in the case of 1*s*, f^H_{nl} can be seen as a smoothing of f^B_{nl}, which is illustrated in Fig. 3 for two representative orbitals (2*s*,2*p*) 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 $\rho_{nl}(r)$ 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 1*s* states is important for $f(r)$, we expect f^H to be greater than f^B near the origin (which is the region where it is more important) because of the effect of the electronic repulsion on the 1*s* state noted above. However, for high-Z atoms where the contribution of the 1*s* orbital is less important, the opposite can be expected. This is so because of the smoothing on $f_{nl}(r)$ produced by all the states different from 1*s*, which would imply that $f^H_{\max} \leq f^B_{\max}$. 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 $f^B(r)$ can take important negative values for some atoms, $f^H(r)$ 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,

$$\nu_k = \int_0^\infty r^k f(r)\,dr = \begin{cases} \dfrac{\langle r^{-2}\rangle}{4\pi} - \dfrac{\rho(0)}{2Z} & \text{if } k=0 \\[2ex] \dfrac{1}{4\pi}\left[\langle r^{k-2}\rangle - \dfrac{k}{2Z}\langle r^{k-3}\rangle\right] & \text{if } k \geq 1 \;. \end{cases} \tag{15}$$

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 $[0,\infty)$:

$$\max\{f(r)\} \geq \frac{1}{2}\frac{\nu_0^2}{\nu_1} \;. \tag{16}$$

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

$$\rho(0) \geq 2Z\left\{\frac{\langle r^{-2}\rangle}{4\pi} - \left[\frac{1}{2\pi}\left[\langle r^{-1}\rangle - \frac{\langle r^{-2}\rangle}{2Z}\right] f_{\max}\right]^{1/2}\right\}$$
$$\equiv L_1 \;. \tag{17}$$

For high-Z atoms $(Z \geq 7)$ we have seen that $f^H_{\max}$ is smaller than $f^B_{\max}$, 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 $Z=2-54$. All these quantities are calculated from the Hartree-Fock wave functions of Clementi and Roetti [15], and the values of $f^B_{\max}$ have been calculated numerically from the hydrogenic-type wave functions. The values of L_3 have been displayed only for those atoms for which $g(r)$ is numerically found to be positive everywhere (see text for further details).

Z	$\rho(0)$	$f_{\max}$	$f^B_{\max}$	L_1	R_1	L_2	R_2	L_3	R_3
10	620.146	3.503	10.77	612.295	0.987	576.022	0.929		
11	833.833	4.696	14.42	825.361	0.990	775.218	0.930	799.76	0.959
12	1 093.73	6.834	18.87	1 079.30	0.987	1 016.92	0.930	1 044.58	0.955
18	3 840.22	35.53	81.01	3 735.91	0.973	3 500.48	0.911		
19	4 538.46	43.80	95.35	4 408.21	0.971	4 139.50	0.912	4 304.38	0.948
22	7 133.88	75.55	149.1	6 889.19	0.966	6 496.52	0.911	6 755.01	0.947
25	10 559.5	119.1	221.0	10 144.8	0.961	9 584.45	0.908	10 015.70	0.948
28	14 942.5	176.5	313.4	14 290.3	0.956	13 510.8	0.904	14 193.99	0.950
30	18 448.6	223.6	388.0	17 588.1	0.953	16 637.9	0.902	17 545.50	0.951
36	32 228.2	422.0	728.5	30 520.7	0.947	28 718.0	0.891		
37	35 023.8	468.6	791.3	33 131.1	0.946	31 222.7	0.891	33 250.10	0.949
40	44 466.8	607.8	1004	41 968.2	0.944	39 596.9	0.890	42 160.96	0.948
43	55 451.6	777.8	1253	52 183.3	0.941	49 290.1	0.889	52 686.94	0.950
45	63 716.0	907.4	1441	59 833.2	0.939	56 560.4	0.888	60 565.98	0.951
48	77 609.1	1129	1757	72 668.5	0.936	68 761.8	0.886	73 696.69	0.950
54	111 164	1682	2601	103 567	0.932	97 814.5	0.880		

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

$$\rho(0)\geq 2Z\left\{\frac{\langle r^{-2}\rangle}{4\pi}-\left[\frac{1}{2\pi}\left[\langle r^{-1}\rangle-\frac{\langle r^{-2}\rangle}{2Z}\right]f^B_{\max}\right]^{1/2}\right\}$$
$$\equiv L_2 \qquad (18)$$

valid for $Z\geq 7$.

Now, this bound only involves the values of $\langle r^{-2}\rangle$, $\langle r^{-1}\rangle$, and $f^B_{\max}$, 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 $f_{\max}$ can be much smaller than $f^B_{\max}$, 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

$$g(r)=\rho_s(r)+\frac{\rho'(r)}{2Z}\ . \qquad (19)$$

The first conclusion we can extract is that

$$g(r)\leq f(r) \qquad (20)$$

everywhere.

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

$$g(r)=f(r)=0\ . \qquad (21)$$

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

$$g(0)=f(0)=0\ . \qquad (22)$$

In addition, for small values of r, one has

$$g(r)=f(r)+O(r^2)\ . \qquad (23)$$

We have studied the positivity of $g(r)$ with the Hartree-Fock data of Ref. [15] for atoms in the range $Z=2-54$ finding that $g(r)$ is positive everywhere for all of them except those with $Z=6-10$, $13-18$, $31-36$, 46, and $49-54$, i.e., those whose least-bounded electron is not s 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 s type,

$$g(r)\sim\left[1-\frac{\sqrt{2I}}{Z}\right]r^{2\beta}e^{-2\sqrt{2I}r}\geq 0 \qquad (24)$$

and

$$g(r)\sim-\frac{\sqrt{2I}}{Z}r^{2\beta}e^{-2\sqrt{2I}r}\leq 0\ . \qquad (25)$$

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

$$I=\int_0^\infty g(r)dr \tag{26}$$

which will be called

$$I_-=-\int_{r_0}^\infty g(r)dr \tag{27}$$

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

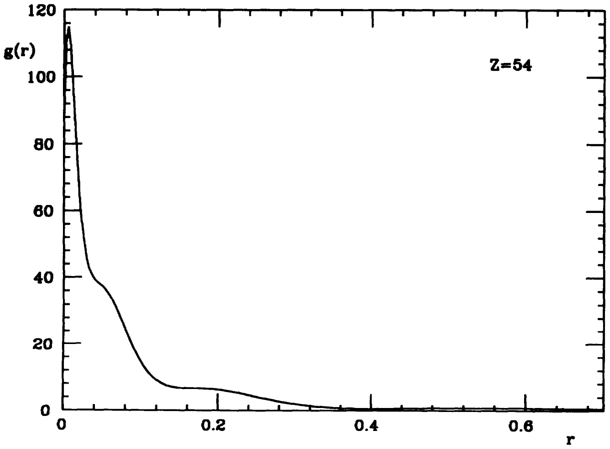

FIG. 5. Plot of the function $g(r)$ defined by Eq. (19) for the xenon atom evaluated from the Hartree-Fock wave functions of Ref. [15].

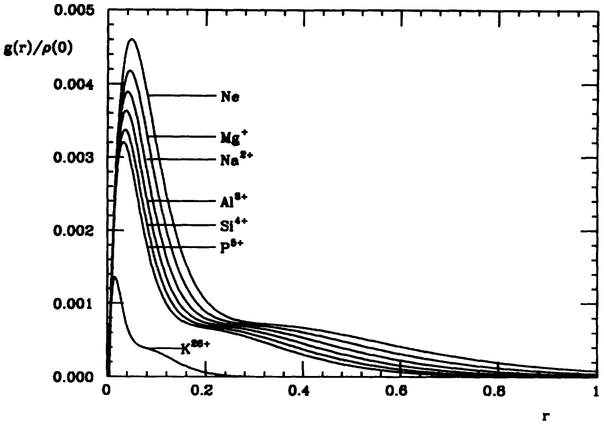

FIG. 6. Plot of the function $g(r)/\rho(0)$ for some ions in the isoelectronic sequence of ten electrons, evaluated from the Hartree-Fock wave functions of Ref. [15].

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:

$$\Delta_m^{(k)}=\begin{vmatrix} \nu_k & \nu_{k+1} & \cdots & \nu_{k+m} \\ \nu_{k+1} & \nu_{k+2} & \cdots & \nu_{k+m} \\ \vdots & \vdots & \vdots & \vdots \\ \nu_{k+m} & \nu_{k+m+1} & \cdots & \nu_{k+2m} \end{vmatrix} \geq 0 \tag{28}$$

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

$$\nu_k=\int_0^\infty r^k g(r)dr$$
$$=\begin{cases} \dfrac{\langle r^{-2}\rangle_s}{4\pi}-\dfrac{\rho(0)}{2Z} & \text{if } k=0 \\ \dfrac{1}{4\pi}\left[\langle r^{k-2}\rangle_s-\dfrac{k}{2Z}\langle r^{k-3}\rangle\right] & \text{if } k\geq 1. \end{cases} \tag{29}$$

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

$$\nu_k \geq 0 \tag{30}$$

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 $k=0$:

$$\rho(0) \le \frac{Z\langle r^{-2}\rangle_s}{2\pi} \equiv B_0 \ , \tag{31}$$

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]:

$$\rho(0) \le \frac{Z\langle r^{-2}\rangle}{2\pi} \equiv B_{\mathrm{HO}} \ . \tag{32}$$

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

$$\langle r^{-1}\rangle_s \ge \frac{\langle r^{-2}\rangle}{2Z} \equiv B_1 \ . \tag{33}$$

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

$$\langle r^{-1}\rangle \ge \frac{\langle r^{-2}\rangle}{2Z} \tag{34}$$

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

$$\langle r^{\alpha}\rangle_s \ge \frac{\alpha+2}{2Z}\langle r^{\alpha-1}\rangle \tag{35}$$

for $\alpha \ge -1$. One interesting particular case is

$$\langle r^{-1}\rangle \le Z N_s \equiv B_2 \ , \tag{36}$$

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

$$\langle r^{-1}\rangle \le Z^2 \tag{37}$$

found by using $f(r) \ge 0$ [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

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

For $m=1$ and $k=1$, the following inequality is obtained:

$$\langle r^{-2}\rangle \le 2Z\left[\langle r^{-1}\rangle_s - \frac{(N_s - \langle r^{-1}\rangle/Z)^2}{\langle r\rangle_s - \frac{3}{2}}\right] \equiv A_1 \ . \tag{39}$$

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 II. Test of the upper bound B_0 given by Eq. (31) to $\rho(0)$ in terms of $\langle r^{-2}\rangle_s$, when the values of this quantity and those of $\rho(0)$ are calculated from the Hartree-Fock wave functions of Ref [15]. A comparison with the Hartree-Fock values of the upper bound of Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [2], B_{HO} [Eq. (32)], is also included.

Z	$\rho(0)$	B_0	B_{HO}	$\rho(0)/B_0$	$\rho(0)/B_{\mathrm{HO}}$
2	3.60	3.82	3.82	0.942	0.942
6	127.56	130.82	132.52	0.975	0.962
10	620.15	631.13	660.33	0.983	0.939
12	1 093.73	1 111.55	1 174.22	0.984	0.931
14	1 765.71	1 791.67	1 907.82	0.986	0.926
18	3 840.22	3 887.55	4 196.94	0.988	0.915
22	7 133.88	7 210.88	7 859.21	0.989	0.908
26	11 911.58	12 023.07	13 209.51	0.991	0.902
30	18 448.59	18 605.66	20 588.32	0.992	0.896
34	27 060.83	27 275.62	30 372.14	0.992	0.891
38	38 008.70	38 312.68	42 901.04	0.992	0.886
42	51 612.88	51 993.22	58 503.72	0.993	0.882
46	68 128.53	68 594.17	77 525.70	0.993	0.879
48	77 609.10	78 112.54	88 455.89	0.994	0.877
50	87 898.96	88 460.34	100 366.72	0.994	0.876
54	111 163.94	111 834.82	127 351.77	0.994	0.873

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).

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

$$\rho(0)\geq 2Z\left\{\frac{\langle r^{-2}\rangle_s}{4\pi}-\left[\frac{1}{2\pi}\left\{\langle r^{-1}\rangle_s-\frac{\langle r^{-2}\rangle}{2Z}\right\}g_{\max}\right]^{1/2}\right\}\equiv B_L\ . \tag{40}$$

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 $g_{\max}\leq f_{\max}$, and $f_{\max}\leq f^B_{\max}$ for $Z\geq 7$, we can write

$$\rho(0)\geq 2Z\left\{\frac{\langle r^{-2}\rangle_s}{4\pi}-\left[\frac{1}{2\pi}\left\{\langle r^{-1}\rangle_s-\frac{\langle r^{-2}\rangle}{2Z}\right\}f^B_{\max}\right]^{1/2}\right\}\equiv L_3 \tag{41}$$

for atoms whose least-bounded electron is of s type and $Z\geq 7$. This bound is found to be very tight when tested with Hartree-Fock values of $\rho(0)$, $\langle r^{-2}\rangle_s$, $\langle r^{-2}\rangle$, and $\langle r^{-1}\rangle_s$ calculated from Ref. [15], improving the accuracy of the bound L_2 [Eq. (18)] and even of L_1 [Eq. (17)] for high-Z atoms, as illustrated in Table I by means of $R_3=L_3/\rho(0)$.

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.

Z	$\rho(0)$	A_0	$\langle r^{-2}\rangle$	A_1	$\rho(0)/A_0$	$\langle r^{-2}\rangle/A_1$
2	3.597	3.673	11.992	12.395	0.979	0.968
6	127.555	129.321	138.773	144.425	0.986	0.961
10	620.146	625.603	414.900	423.677	0.991	0.979
14	1 765.707	1 783.759	856.227	898.880	0.990	0.953
18	3 840.215	3 871.556	1 465.009	1 519.531	0.992	0.964
22	7 133.884	7 192.254	2 244.585	2 370.278	0.992	0.947
26	11 911.575	11 995.633	3 192.222	3 354.866	0.993	0.952
30	18 448.586	18 568.276	4 312.007	4 512.831	0.994	0.956
34	27 060.826	27 219.844	5 612.758	5 832.216	0.994	0.962
38	38 008.696	38 258.334	7 093.557	7 446.281	0.994	0.953
42	51 612.876	51 909.746	8 752.136	9 129.739	0.994	0.959
46	68 128.534	68 460.367	10 589.311	10 862.655	0.995	0.975
50	87 898.961	88 344.612	12 612.454	13 115.467	0.995	0.962
54	111 163.943	111 687.797	14 818.052	15 350.114	0.995	0.965

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 $v_0/\rho(0)$ 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 $\langle r^{-2}\rangle_s$ for the sequence of ten electrons, for which the ratio $v_0/\rho(0)$ increases monotonically from 0.982 for $Z=10$ to 0.994 for $Z=54$.

VI. CONCLUSIONS

A numerical study of the functions $f(r)=\rho(r)+\rho'(r)/(2Z)$ and $g(r)=\rho_s(r)+\rho'(r)/(2Z)$, 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)].

ACKNOWLEDGMENTS

We are very grateful to Dr. Ajit J. Thakkar for useful suggestions. Also we acknowledge partial financial support from the Spanish Dirección General de Ciencia y Tecnología (DGCYT) and from the Junta de Andalucía.

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