

Bounds for the atomic electronic density and related functions

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Simple upper bounds for the spherical average of the atomic electronic density $\rho(r)$ in terms of different negative powers of r , and depending on some average quantities, such as either radial expectation values or other relevant functionals of $\rho(r)$, are obtained. The procedure used to get these results also enables us to find bounds for other atomic relevant functions, such as the number of electrons inside a sphere of radius r , i.e., $Q(r)$, the isotropic atomic form factor $F(q)$, the spherically averaged momentum density $\gamma(p)$, and the atomic Compton profile $J(q)$.

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I. INTRODUCTION

In recent literature, the interest in finding bounds for the electronic density of an atom has been pointed out, because of its special role in atomic physics and the lack of rigorous information about it. Different results have been found [1–8].

It is also interesting to bound other related functions of an atom, such as

(i) the number of electrons enclosed within a sphere of radius r , i.e.,

$$Q(r) = \int_0^r 4\pi r^2 \rho(r) dr, \quad (1)$$

where $\rho(r)$ denotes the spherically averaged electronic density;

(ii) the isotropic form factor

$$F(q) = \frac{4\pi}{q} \int_0^\infty r \sin qr \rho(r) dr; \quad (2)$$

(iii) the spherically averaged momentum density $\gamma(p)$; and

(iv) the Compton profile [9]

$$J(q) = 2\pi \int_q^\infty p \gamma(p) dp. \quad (3)$$

However, the results that can be found in the literature for these functions are more scarce [8,10–13].

Bounds for these functions are interesting when they depend only on quantities which have a physical meaning and/or are experimentally measurable. Some quantities of this type are the moments or radial expectation values of the function, which are physically interesting in many problems [14]. They are defined by

$$\langle r^\alpha \rangle = \int r^\alpha \rho(\vec{r}) d\vec{r} \quad (4)$$

for electronic density and in a similar form for the other quantities $Q(r)$, $F(q)$, $\gamma(p)$, and $J(q)$.

For electronic density, other relevant average quantities are those functionals of the type

$$\omega_t = \int [\rho(\vec{r})]^t d\vec{r} \quad (5)$$

which, e.g., for $t = 5/3$, $t = 4/3$ and $t = 2$, are related to the Thomas-Fermi kinetic energy, the Dirac-Slater exchange energy, and the average radial density, respectively.

The corresponding quantities in momentum space, i.e.,

$$U_t = \int [\gamma(\vec{p})]^t d\vec{p}, \quad (6)$$

are also of interest, e.g., the average momentum density $\langle \gamma \rangle = U_2$ which is an experimentally measurable quantity [15]. There exist not only inequalities between U_t and the momentum expectation values $\langle p^\alpha \rangle$ [16], but also between U_t and the radial expectation values $\langle r^\beta \rangle$ [14].

Two main types of bounds for the functions defined above can be found in the literature. Bounds of the first type are those which may be written by analytical and often simple expressions [1–7,10] which can be applied in analytical procedures, such as bounding expectation values of one-electron operators.

Recently, bounds of a different type have been found [8,11,12]. These bounds need to solve numerically a set of equations starting from numerical information about some average values such as the radial expectation ones. The accuracy of these bounds can be continuously improved by getting to know more of these quantities, but general analytical expressions cannot be given for them.

The aim of this work is to formulate upper bounds of the former type, of the functions mentioned above, in terms of their moments and functionals ω_t (U_t in momentum space). The only assumption used to obtain these bounds is that the function to be bounded must be monotone. This is a feature that has been found in different calculations for the electronic density [17,18] and for the atomic form factor [19]. Besides, it is trivially verified by the functions $Q(r)$ and $J(q)$ because of their definitions as integrals of positive functions. The bounds obtained here will be compared with similar analytical results which have been found in the literature.

II. UPPER BOUNDS FOR A MONOTONICALLY DECREASING FUNCTION

In order to find upper bounds for a monotonically decreasing and non-negative function $f(x)$ [i.e. $f(x) \geq 0, f'(x) \leq 0$], we define for a particular value of x the following function:

$$\hat{f}(y) = \begin{cases} f(x) & y \leq x \\ f(y) & y > x. \end{cases} \tag{7}$$

Then, for any positive function g and any positive and nondecreasing function F , it is verified that

$$\int_0^\infty g(y)F(\hat{f}(y))dy \leq \int_0^\infty g(y)F(f(y))dy, \tag{8}$$

provided that the right-hand side is finite. The left-hand side is bounded from below by

$$\begin{aligned} \int_0^\infty g(y)F(\hat{f}(y))dy &\geq \int_0^x g(y)F(\hat{f}(y))dy \\ &= F[f(x)] \int_0^x g(y)dy \end{aligned} \tag{9}$$

which leads to

$$f(x) \leq F^{-1} \left(\frac{\int_0^\infty g(y)F(f(y))dy}{\int_0^x g(y)dy} \right). \tag{10}$$

If we define $G(x)$ by

$$G(x) = \int_0^x g(y)dy, \tag{11}$$

then, for any $G(x)$ such that $G(0) = 0, G'(x) \geq 0$, it is verified that

$$f(x) \leq F^{-1} \left(\frac{\int_0^\infty G'(y)F(f(y))dy}{G(x)} \right). \tag{12}$$

This is the general basic result which will be applied later on. Here, F is an arbitrary function such that $F \geq 0$ and $F' \geq 0$. The particular case $F(f) = f$ leads to

$$f(x) \leq \frac{\int_0^\infty G'(y)f(y)dy}{G(x)}. \tag{13}$$

This result can also be derived from the Markov inequality [20].

A. Bounds in terms of moments

For $F(f) = f$ and $G(x) = x^k$, for any $k > 0$, Eq. (12) leads to

$$f(x) \leq \frac{k\mu_{k-1}}{x^k} \equiv f_k^*(x), \tag{14}$$

where μ_k denotes the moment of order k of the function f , i.e.,

$$\mu_k = \int_0^\infty x^k f(x) dx. \tag{15}$$

In the limit $k \rightarrow 0$ this inequality is fulfilled because of the monotonic decreasing of f , as

$$f(x) \leq f(0) \equiv f_0^*(x). \tag{16}$$

Equation (14) gives a set of pointwise upper bounds for $f(x)$ provided we have information about the average quantities μ_k . From now on, unless explicitly stated, we will restrict ourselves to integer values of k .

We now ask ourselves, for a given value of x , which of the bounds $f_k^*(x), k = 0, 1, \dots$, is the best one? To answer this question let us define the points

$$x_1 = \frac{\mu_0}{f(0)} \tag{17}$$

and

$$x_k = \frac{k\mu_{k-1}}{(k-1)\mu_{k-2}} \tag{18}$$

for $k > 1$.

Here, each x_k is the cut between $f_{k-1}^*(x)$ and $f_k^*(x)$. It is clear that for $x < x_k$ the relation $f_{k-1}^*(x) < f_k^*(x)$ is fulfilled and otherwise if $x > x_k$.

In addition, the sequence $\{x_1, x_2, \dots, x_k, \dots\}$ increases with k , as we will prove below. Then, for a fixed x , the best bound for $f(x)$ in $x_k < x < x_{k+1}$ is $f_k^*(x)$. Then we can build a continuous function which is the best bound among $f_k^*(x)$ for every x , as:

$$f^*(x) = \begin{cases} f_0^*(x) = f(0) & \text{if } 0 \leq x \leq x_1 \\ f_1^*(x) = \mu_0 x^{-1} & \text{if } x_1 \leq x \leq x_2 \\ \vdots & \vdots \\ f_k^*(x) = k\mu_{k-1}x^{-k} & \text{if } x_k \leq x \leq x_{k+1} \\ \vdots & \vdots \end{cases} \tag{19}$$

In order to prove that $x_k \leq x_{k+1}$ for every k , we recall Stieltjes' theorem [21] which states that, if μ'_k are the moments of a positive function $p(x)$, the following determinant inequalities hold:

$$\begin{vmatrix} \mu'_k & \mu'_{k+1} & \cdots & \mu'_{k+m} \\ \mu'_{k+1} & \mu'_{k+2} & \cdots & \mu'_{k+m+1} \\ \vdots & \vdots & \ddots & \vdots \\ \mu'_{k+m} & \mu'_{k+m+1} & \cdots & \mu'_{k+2m} \end{vmatrix} \geq 0 \tag{20}$$

for any $k \geq 0$ and any $m \geq 0$, provided that all the moments involved exist. If we apply this theorem, when $m = 1$, to $p(x) = -f'(x)$, whose moments are related to those of $f(x)$ by

$$\mu'_k = - \int_0^\infty x^k f'(x)dx = \begin{cases} k\mu_{k-1} & \text{if } k > 0 \\ f(0) & \text{if } k = 0 \end{cases} \tag{21}$$

we find that

$$x_k \leq x_{k+1} \tag{22}$$

for any $k \geq 1$.

Let us analyze the asymptotic behavior of these upper bounds. If $f(x)$ vanishes at infinity as $x^{-\alpha}$, its moments μ_k do exist if and only if $k < \alpha + 1$, which means that the bound given by Eq. (19) will be applicable from $k = 0$ to the integer part of α , if α is not an integer, or to $k = \alpha - 1$ otherwise. If we apply Eq. (14) for noninteger values of k , we can find bounds with an asymptotic behavior like $x^{-\alpha+\epsilon}$, with ϵ being a positive arbitrary small number.

If $f(x)$ vanishes at infinity faster than any inverse power of x , all μ_k exist. The sequence in Eq. (19) can be continued to arbitrary large values of k . Therefore, $f^*(x)$ will also vanish at infinity faster than any inverse power of x . We can compare the asymptotic behavior of f and f^* in the following example: if f is a function which behaves asymptotically as

$$f(x) \sim x^b \exp(-ax^p) \quad (23)$$

its moments in the k large limit are given by

$$\mu_k \sim \frac{\Gamma\left(\frac{k+b+1}{p}\right)}{p a^{(k+b)/p}} \quad (24)$$

which allows us to calculate $f^*(x_k)$, which in this limit behaves asymptotically as

$$f^*(x_k) \sim x_k^{b+p/2} \exp(-ax_k^p), \quad (25)$$

a behavior which is closer to that of f than one of any negative power of x .

B. Bounds in terms of functionals ω_t

For $g(x) = 4\pi x^2$ and $F(f) = f^t$, being $t > 0$, Eq. (10) leads to

$$f(x) \leq \left(\frac{3}{4\pi}\right)^{1/t} \frac{\hat{\omega}_t^{1/t}}{x^{3/t}} \quad (26)$$

where $\hat{\omega}_t$ is defined by

$$\hat{\omega}_t = 4\pi \int_0^\infty x^2 [f(x)]^t dx \quad (27)$$

which is equal to ω_t in Eq. (5) for a three-dimensional isotropic function. If $f(r)$ denotes the spherical average of a nonisotropic $f(\vec{r})$, it is easy to prove by means of the Hölder inequality, that

$$\left[\int d\Omega f(r, \Omega) \right]^t \leq (4\pi)^{t-1} \int d\Omega [f(r, \Omega)]^t. \quad (28)$$

It can then be proved straightforwardly that

$$\hat{\omega}_t \leq \int [f(\vec{r})]^t d\vec{r} \equiv \omega_t \quad (29)$$

which allows us to replace $\hat{\omega}_t$ by ω_t in Eq. (26).

In the limit $t \rightarrow \infty$, Eq. (26) reduces to

$$f(x) \leq f(0). \quad (30)$$

For $t = 1$ we find

$$f(x) \leq \frac{3\mu_2}{x^3}. \quad (31)$$

which can also be obtained from Eq. (14) when $k = 3$.

III. APPLICATIONS

A. Upper bounds for the atomic electronic density

We shall now apply the previous results to the spherically averaged atomic electronic density

$$\rho(r) = \frac{1}{4\pi} \int \rho(\vec{r}) d\Omega. \quad (32)$$

When $f = \rho$, Eq. (14) leads to the following inequality:

$$\rho(r) \leq \frac{k \langle r^{k-3} \rangle}{4\pi r^k} \equiv \rho_k^*(r), \quad (33)$$

where the bounds are written in terms of the radial expectation values defined in Eq. (4)

Some particular cases of Eq. (33) are the following:

$$\rho(r) \leq \frac{\langle r^{-2} \rangle}{4\pi r} \equiv \rho_1^*(r), \quad (34)$$

$$\rho(r) \leq \frac{\langle r^{-1} \rangle}{2\pi r^2} \equiv \rho_2^*(r), \quad (35)$$

$$\rho(r) \leq \frac{3N}{4\pi r^3} \equiv \rho_3^*(r), \quad (36)$$

$$\rho(r) \leq \frac{\langle r \rangle}{\pi r^4} \equiv \rho_4^*(r). \quad (37)$$

Here, N stands for the number of electrons. As shown in Sec. II, each of these bounds is the best of all of them in a particular range of r values. Therefore, if several $\langle r^k \rangle$ values were known, we could build the optimum upper bound [Eq. (19)] which in this case is written as

$$\rho^*(r) = \begin{cases} \rho(0) & r \leq r_1 \\ \frac{\langle r^{-2} \rangle}{4\pi r} & r_1 \leq r \leq r_2 \\ \vdots & \vdots \\ \frac{k \langle r^{k-3} \rangle}{4\pi r^k} & r_k \leq r \leq r_{k+1} \\ \vdots & \vdots \end{cases} \quad (38)$$

where the values of r_k are given by

$$r_1 = \frac{\langle r^{-2} \rangle}{4\pi \rho(0)} \quad (39)$$

when $k = 1$ and

$$r_k = \frac{k \langle r^{k-3} \rangle}{(k-1) \langle r^{k-4} \rangle} \quad (40)$$

for $k > 1$.

Just as an illustration, we have performed a numerical test of some of the upper bounds $\rho_k^*(r)$ given by Eq. (33). These bounds are plotted in Fig. 1 for the neon atom, where the $\langle r^k \rangle$ values have been evaluated from the Hartree-Fock data of Clementi and Roetti [22]. A comparison of the values of $\rho(r)$ (dot-dashed line) evaluated within the same model is included. The solid line represents the values of the optimum bound [Eq. (38)], which proves to be adequate in a wide range of r .

We will now discuss briefly the asymptotic behavior of this bound when the sequence is continued to infinity. From Eq. (25) and the knowledge of the asymptotic behavior [23] of $\rho(r)$,

$$\rho(r) \sim r^\beta e^{-2(2I)^{1/2}r}, \quad (41)$$

we can state that for large k

$$\rho^*(r_k) \sim r_k^{1/2} \rho(r_k). \quad (42)$$

We can also obtain bounds in terms of other density functionals by applying Eqs. (26) and (29) to $\rho(r)$, which leads to the upper bounds

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{1/t} \frac{\omega_t^{1/t}}{r^{3/t}}, \quad (43)$$

where ω_t is defined in Eq. (5).

Special cases of interest of Eq. (43) are

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{3/5} \frac{\omega_{5/3}^{3/5}}{r^{9/5}}, \quad (44)$$

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{3/4} \frac{\omega_{4/3}^{3/4}}{r^{9/4}}, \quad (45)$$

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{1/2} \frac{\omega_2^{1/2}}{r^{3/2}}, \quad (46)$$

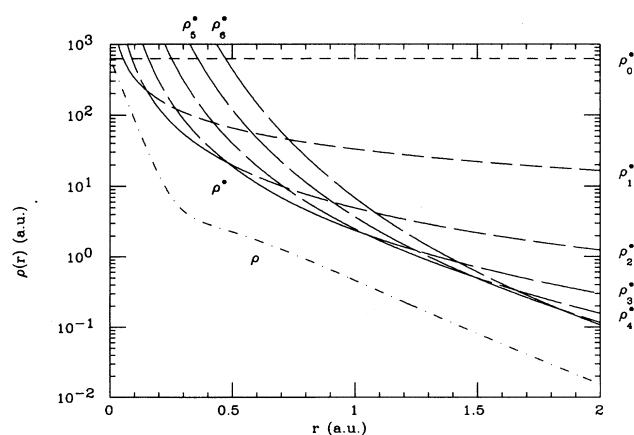


FIG. 1. Plot of the bounds ρ_k^* (dashed lines), given by Eq. (33), for ρ (dot-dashed line) and for the neon atom. The optimum bound, i.e., ρ^* [Eq. (38)] is shown by the solid line. The HF data of Clementi and Roetti [22] have been used.

since in these cases the functionals ω_t are related to the Thomas-Fermi kinetic energy, the exchange energy in Dirac-Slater form, and the average radial density, respectively, by means of the following expressions (atomic units will be used throughout):

$$T_0 = \frac{3}{10} (3\pi^2)^{2/3} \omega_{5/3}, \quad (47)$$

$$K_0 = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \omega_{4/3}, \quad (48)$$

$$\langle \rho \rangle = \omega_2, \quad (49)$$

which allow us to write

$$\begin{aligned} \rho(r) &\leq \frac{5}{2\pi} \left(\frac{2}{15\pi}\right)^{2/5} \frac{T_0^{3/5}}{r^{9/5}} \\ &\leq \frac{5}{2\pi} \left(\frac{2}{15\pi}\right)^{2/5} \frac{T^{3/5}}{r^{9/5}}, \end{aligned} \quad (50)$$

where T is the exact kinetic energy. For the last step we have made use of Lieb's conjecture [24], $T \geq T_0$. For the other cases,

$$\rho(r) \leq \frac{1}{3^{1/4}\pi^{1/2}} \frac{(-K_0)^{3/4}}{r^{9/4}}, \quad (51)$$

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{1/2} \frac{\langle \rho \rangle^{1/2}}{r^{3/2}}. \quad (52)$$

These bounds depend on different noninteger powers of r , and they improve, in some regions, the quality of the bounds in terms of the moments described above. This is illustrated in Fig. 2 for the neon atom by using the same Hartree-Fock (HF) data, where the bounds given by Eqs. (44)–(46) are compared to the optimum bound given by Eq. (38) and the values of $\rho(r)$.

From this comparison we realize that the bounds given

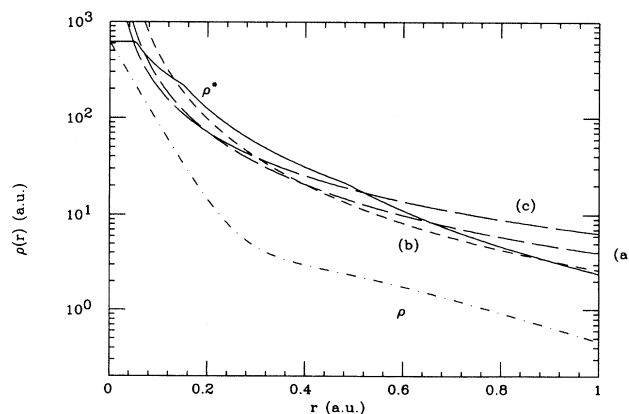


FIG. 2. Plot of the bounds given by Eqs. (44), (45), and (46) denoted, respectively, by (a), (b), and (c), compared to the optimum bound given by Eq. (38) (dot-dashed line), and to the HF value of ρ (dot-dashed line). The same HF data as in Fig. 1 are used.

by Eqs. (44)–(46) improve the one given by Eq. (38) for small values of r (in the case of neon for r values between 0.15 and 0.6 a.u.). The last bound in Eq. (50) would lie slightly above that corresponding to Eq. (44) by a factor of 1.054.

Upper bounds in terms of either r^{-2} or r^{-1} can also be found from Eq. (43). They can be compared with those obtained by means of the moments and with other well known results in the literature. For $t = 3/2$ we obtain

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{2/3} \frac{\omega_{3/2}^{2/3}}{r^2}, \quad (53)$$

and for $t = 3$ we have

$$\rho(r) \leq \left(\frac{3}{4\pi}\right)^{1/3} \frac{\omega_3^{1/3}}{r}. \quad (54)$$

These bounds can be expressed in terms of other more interesting average quantities, such as the zeroth and second order of the gradient expansion of the kinetic energy, i.e., T_0 and T_2 ($T_2 = 9T_W$, T_W being the classical von Weizsäcker term).

(a) From the generalized Hölder inequality it can be found that

$$\omega_{3/2}^{2/3} \leq N^{1/6} \omega_{5/3}^{1/2} \quad (55)$$

which, in addition to Eqs. (47) and (53), allow us to obtain

$$\rho(r) \leq \left(\frac{125}{96\pi^8}\right)^{1/6} \frac{N^{1/6} T_0^{1/2}}{r^2}, \quad (56)$$

and a result in terms of T can be obtained by applying Lieb's conjecture

$$\rho(r) \leq \left(\frac{125}{96\pi^8}\right)^{1/6} \frac{N^{1/6} T^{1/2}}{r^2} \equiv \hat{\rho}_T(r). \quad (57)$$

(b) By means of the Sobolev inequality [25] it can be found that [26]

$$\omega_3 \leq \frac{2^7 3^3}{\pi^4} T_2^3 \quad (58)$$

which can be applied to Eq. (54), leading to

$$\rho(r) \leq \left(\frac{2^5 3^4}{\pi^5}\right)^{1/3} \frac{T_2}{r} \equiv \hat{\rho}_{T_2}(r). \quad (59)$$

Several analytical bounds with the behavior of r^{-1} and r^{-2} can be found in the literature. Let us mention a result of Hoffmann-Ostenhof and Hoffmann-Ostenhof

$$\rho(r) \leq \frac{(2NT)^{1/2}}{4\pi r^2} \equiv \hat{\rho}_H(r), \quad (60)$$

and the result found by King [7]

$$\rho(r) \leq \frac{T}{2\pi r} \equiv \hat{\rho}_{K_1}(r). \quad (61)$$

These two bounds correspond to the large and small r

expressions of the well known upper bound [1],

$$\rho(r) \leq \frac{1}{8\pi r^2} (1 - e^{-2\alpha r})(\alpha N + 2T/\alpha), \quad (62)$$

which is a very appropriate bound for most values of r when optimizing the free parameter α numerically for each r . The only cases where α can be determined analytically correspond to the limits mentioned above, and these are the cases that will be compared with our results.

Another bound in terms of r^{-1} , which improves Eq. (61), was found in Ref. [6]:

$$\rho(r) \leq \frac{T}{2\pi r} [(2 - \delta)\delta]^{1/2} \equiv \hat{\rho}_{K_2}(r), \quad (63)$$

this being $\delta = (r^{-2})/(4T)$. It is applicable only if $\delta < 1$. Other bounds with a similar dependence on r can be found [4,5], but they are worse than those mentioned here.

A comparison of the bounds in terms of r^{-1} , those given by Eqs. (34), (59), (61), and (63), has been performed by using Clementi and Roetti's Hartree-Fock data [22]. This is illustrated in Table I, where the values of the coefficients of r^{-1} in each bound have been displayed for several atoms. From these values we can conclude that the bound ρ_{T_2} given by Eq. (59) in the present work is smaller than the previous results for atoms with large Z . Let us also note that the accuracy of the bound ρ_1 , given by Eq. (34), approaches those of the other bounds when Z increases.

A direct comparison between the bounds in terms of r^{-2} , ρ_T , and ρ_H , given by Eqs. (57) and (60), can be performed since they have the same dependence on T . Equation (57) of this work gives a better bound than Eq. (60) for $Z \geq 9$. In order to include Eq. (35) in this comparison we have again made use of the Hartree-Fock data mentioned above and obtained the values displayed in Table II. We realize that this latter bound, i.e., ρ_2 , also lies below ρ_H for large atoms, but is always above ρ_T .

We must also mention here that the bounds in this work are unsatisfactory only in the very near nuclear region, because they are singular at the origin except for the trivial bound $\rho(r) \leq \rho(0)$. However, appropriate bounds for the very near nuclear region are known [7].

Let us finally comment that if we compare these bounds to others of a different type recently found [8],

TABLE I. Comparison among the bounds $\rho_1^*(r)$, $\hat{\rho}_{T_2}(r)$, $\hat{\rho}_K(r)$, and $\hat{\rho}_{K_2}(r)$ to $\rho(r)$, given respectively by Eqs. (34), (59), (61), and (63), by means of the coefficient of r^{-1} in the r.h.s. of these expressions, for some atoms. These coefficients have been evaluated from the Clementi and Roetti²² HF data. Numbers in square brackets denote powers of ten. Atomic units are used.

Z	$r\rho_1^*(r)$	$r\hat{\rho}_{T_2}(r)$	$r\hat{\rho}_K(r)$	$r\hat{\rho}_{K_2}(r)$
10	0.33017[+02]	0.20527[+02]	0.20459[+02]	0.20074[+02]
18	0.11658[+03]	0.69857[+02]	0.83843[+02]	0.79854[+02]
36	0.50377[+03]	0.28917[+03]	0.43799[+03]	0.39649[+03]
54	0.11792[+04]	0.66408[+03]	0.11509[+04]	0.10048[+04]

TABLE II. Comparison among the bounds $\rho_2^*(r)$, $\hat{\rho}_T(r)$ and $\hat{\rho}_H(r)$, given respectively by Eqs. (35), (57), and (60), by means of the coefficient of r^{-2} in the r.h.s. of these expressions, for some atoms. These coefficients have been evaluated from the Clementi and Roetti²² HF data. Atomic units are used.

Z	$r^2\rho_2^*(r)$	$r^2\hat{\rho}_T(r)$	$r^2\hat{\rho}_H(r)$
2	0.537	0.431	0.269
10	4.952	3.780	4.035
18	11.097	8.439	10.959
36	29.101	21.650	35.423
54	50.591	37.549	70.329

both have a similar accuracy when few $\langle r^k \rangle$ are known. In the following sections, similar applications of the general results of Sec. II will be developed for other atomic relevant functions, which will be discussed with less detail.

B. Lower bounds for $Q(r)$

The results of Sec. II A can be applied in order to find lower bounds for the number of electrons enclosed within a sphere of radius r , i.e., $Q(r)$ defined by Eq. (1). If we define the function

$$f(r) = N - Q(r) = 4\pi \int_r^\infty s^2 \rho(s) ds \quad (64)$$

and apply Eq. (14) to this monotonically decreasing function $f(r)$, we find

$$f(r) \leq \frac{\langle r^k \rangle}{r^k}. \quad (65)$$

This implies that the function $Q(r)$ is bounded from below by

$$Q(r) \geq N - \frac{\langle r^k \rangle}{r^k} \equiv Q_k^*(r) \quad (66)$$

for any $k > 0$.

As was done for $\rho(r)$, we can build an optimum bound from $Q_k^*(r)$ by using the best choice of k in every r , which is given by

$$Q(r) \leq Q^* = N - \frac{\langle r^k \rangle}{r^k} \text{ for } r \in [r_k, r_{k+1}], \quad (67)$$

where

$$r_1 = \frac{\langle r \rangle}{N} \quad (68)$$

and

$$r_k = \frac{\langle r^k \rangle}{\langle r^{k-1} \rangle} \quad (69)$$

for $k > 1$. The limit $k \rightarrow 0$ gives, in this case, the trivial bound $Q(r) \geq 0$.

A plot of some of the lower bounds $Q_k^*(r)$ is given in Fig. 3 (dashed lines) where the values of $Q(r)$ (dot-dashed line) have been also plotted for the neon atom. The optimum bound, corresponding to Eq. (67), is plotted by the solid line. The function $Q(r)$ and the values $\langle r^k \rangle$ have been evaluated from the HF data of Clementi and Roetti [22].

C. Upper bounds for the atomic form factor

The isotropic atomic form factor, defined in Eq. (2), is a quantity that in numerical calculations is found to be a monotonically decreasing [19] function. To the best of the author's knowledge, there are no bounds for this function known in the literature, apart from a lower bound that was recently found [13].

Some of the moments of the atomic form factor defined by

$$\mu_k = \int_0^\infty q^k F(q) dq \quad (70)$$

are related to those of the electronic density and the value of $\rho(0)$ by means of the expressions [27–29]

$$\mu_0 = \frac{\pi \langle r^{-1} \rangle}{2}, \quad (71)$$

$$\mu_1 = \langle r^{-2} \rangle, \quad (72)$$

$$\mu_2 = 2\pi^2 \rho(0). \quad (73)$$

Therefore, starting from Eqs. (14) and (16), we can find upper bounds for $F(q)$ in terms of these quantities, in the form

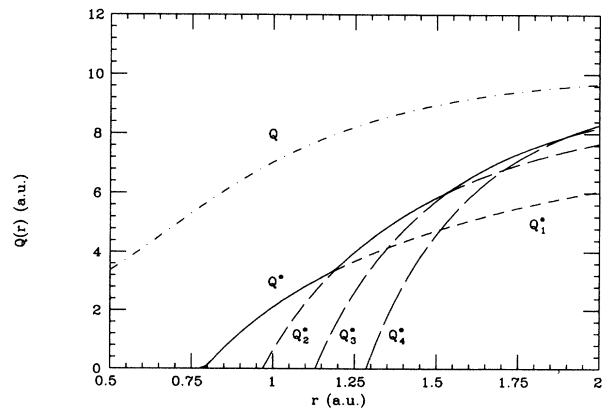


FIG. 3. Plot of the bounds Q_k^* (dashed lines), given by Eq. (66), for the function Q (dot-dashed line) and for the neon atom. The optimum bound, i.e., Q^* [Eq. (67)] is shown by the solid line. The HF data of Clementi and Roetti [22] are used.

$$F(q) \leq F(0) = N \equiv F_0^*(q), \quad (74)$$

$$F(q) \leq \frac{\pi \langle r^{-1} \rangle}{2q} \equiv F_1^*(q), \quad (75)$$

$$F(q) \leq \frac{2 \langle r^{-2} \rangle}{q^2} \equiv F_2^*(q), \quad (76)$$

and

$$F(q) \leq \frac{6\pi^2 \rho(0)}{q^3} \equiv F_3^*(q). \quad (77)$$

We can build again the optimum bound using the best $F_k^*(q)$ for any particular value of q . In Fig. 4 we have plotted for the neon atom the bounds given by Eqs. (75)–(77) (dashed line) and the optimum bound (solid line) compared to the function $F(q)$, by means of the same HF data of Clementi and Roetti [22].

We can also bound $F(q)$ from Eq. (26). In particular, for $t = 2$, we obtain

$$F(q) \leq \sqrt{\frac{3}{4\pi}} \frac{\int |F(\vec{q})|^2 d\vec{q}}{q^{3/2}} = \sqrt{6\pi^2} \frac{\langle \rho \rangle^{1/2}}{q^{3/2}}, \quad (78)$$

where in the last step we have used, $F(\vec{q})$ and $\rho(\vec{r})$ are the Fourier transforms of each other.

D. Lower bounds for the spherically averaged momentum density

Although the spherically averaged momentum density is not a monotonically decreasing function for all atoms, several results have been found in the literature under this assumption for those atoms for which the numerical calculations verify it [30], i.e., $Z = 1-7, 11-13, 19-25, 31,$

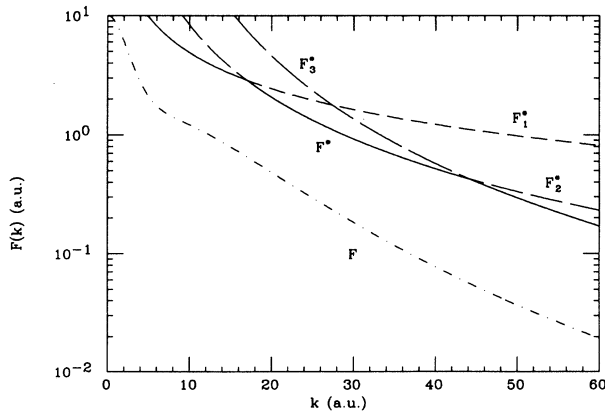


FIG. 4. Plot of the bounds F_1^* , F_2^* , and F_3^* (dashed lines) given, respectively, by Eqs. (75), (76), and (77), for the isotropic form factor F (dot-dashed line) and for the neon atom. The optimum bound, denoted by F^* (see text) is shown by the solid line. The HF data of Clementi and Roetti [22] are used.

37–42, 49–50, 55–74, 81–82, and 87–92. For these atoms, the application of the bounds given by Eq. (16) leads to

$$\gamma(p) \leq \frac{k \langle p^{k-3} \rangle}{4\pi p^k} \equiv \gamma_k^*(p). \quad (79)$$

When $k = 1$ we obtain

$$\gamma(p) \leq \frac{\langle p^{-2} \rangle}{4\pi p} \quad (80)$$

which can be compared to the following result [10] that is analogous to Eq. (61) in the momentum space:

$$\gamma(p) \leq \frac{\langle r^2 \rangle}{4\pi p}. \quad (81)$$

The former bound will lie below the latter provided that $\langle p^{-2} \rangle$ is smaller than $\langle r^2 \rangle$. A comparison of both values from the HF data of Clementi and Roetti shows up when this occurs, among the atoms above considered, for $Z = 6, 7, 13, 22-31,$ and $37-50$.

The optimum bound in every region from Eq. (79) is given by

$$\gamma^*(p) = \begin{cases} \gamma(0) & p \leq p_1 \\ \frac{\langle p^{-2} \rangle}{4\pi p} & p_1 \leq p \leq p_2 \\ \vdots & \vdots \\ \frac{k \langle p^{k-3} \rangle}{4\pi p^k} & p_k \leq p \leq p_{k+1} \\ \vdots & \vdots \end{cases} \quad (82)$$

for $k < 8$ (otherwise the moments do not exist) where

$$p_1 = \frac{\langle p^{-2} \rangle}{4\pi \gamma(0)} \quad (83)$$

and, for $k > 1$,

$$p_k = \frac{k \langle p^{k-3} \rangle}{(k-1) \langle p^{k-4} \rangle}. \quad (84)$$

The values of $\gamma^*(p)$ (solid line) are compared to those of $\gamma(p)$ (dot-dashed line) for the helium atom in Fig. 5, both calculated from the HF wave functions of Clementi and Roetti [22]. The particular bounds given by Eq. (79) which contribute to $\gamma^*(p)$ in the region displayed also appear in the figure (dashed lines).

The bounds of Sec. II B can be useful in this case because there are some relevant functionals U_t of $\gamma(p)$. They are quite analogous to those of $\rho(r)$, given by Eq. (43),

$$\gamma(p) \leq \left(\frac{3}{4\pi} \right)^{1/t} \frac{U_t^{1/t}}{p^{3/t}}, \quad (85)$$

where U_t is defined by Eq. (6). For example, U_2 is an experimentally measurable quantity [15] called the average momentum density and denoted by $\langle \gamma \rangle$. Besides, some functionals U_t of $\gamma(p)$ have been found to be bounded from above [14] by means of radial expectation values $\langle r^k \rangle$.

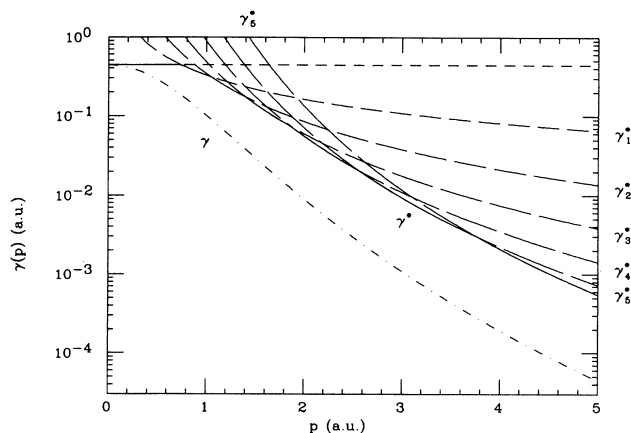


FIG. 5. Plot of the bounds γ_k^* (dashed lines), given by Eq. (79), for the momentum density γ (dot-dashed line) and for the neon atom. The optimum bound, i.e., γ^* [Eq. (82)] is shown by the solid line. The HF data of Clementi and Roetti [22] are used.

E. Upper bounds for the atomic Compton profile

The Compton profile, defined by Eq. (3), can be bounded from above in terms of expectation values $\langle p^k \rangle$ by using Eq. (14) and expressing the moments of $J(q)$ in terms of those of $\gamma(p)$ by means of a simple integration by parts. This leads to

$$J(q) \leq \frac{\langle p^{k-1} \rangle}{2q^k} \equiv J_k^*(q) \quad (86)$$

for $k \geq 0$.

The cuts between two successive bounds, J_{k-1}^* and J_k^* , are given by $q_k = \langle p^{k-1} \rangle / \langle p^{k-2} \rangle$ for $k > 0$. The optimum bound is $J_k^*(q)$ for those $q \in [q_k, q_{k+1}]$. An illustration of the values of some bounds $J_k^*(q)$ (dashed lines), as well as those of the optimum bound (solid line), is given in Fig. 6, where they have been compared to those of $J(q)$ (dot-dashed line) for the neon atom, evaluated from the data of Clementi and Roetti [22].

IV. CONCLUDING REMARKS

We have found that the knowledge of some average quantities of a function which is relevant in the study of

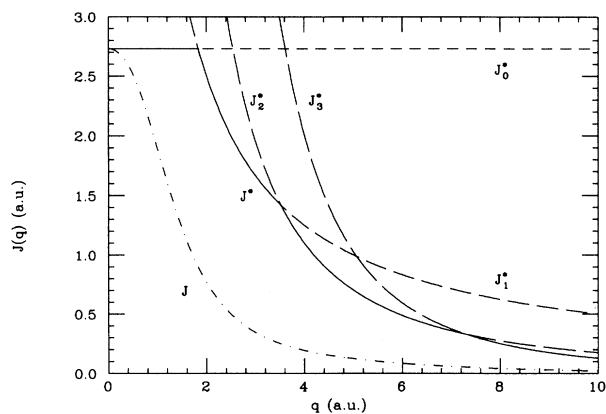


FIG. 6. Plot of the bounds J_k^* (dashed lines), given by Eq. (86), for the Compton profile J (dot-dashed line) and for the neon atom. The optimum bound, denoted by J^* (see text), is shown by the solid line. The HF data of Clementi and Roetti [22] are used.

an atomic system enables us to bound it for any value of its argument. The bounds are written by very simple analytical expressions, in terms of either the moments of the function or other simple functionals. We have restricted ourselves to some physically interesting functionals, but other different applications of the results of Sec. II can be performed which would lead to bounds with different powers of the argument than those appearing in this work.

The particular results found for the electronic density and the momentum density improve for different atoms, the accuracy of the previous results of the same type. Also, the general results allow us to find bounds for functions for which results of this type are scarce or unexisting (e.g., the atomic form factor). The construction of optimum bounds from particular simple expressions make us find bounds that can be appropriate both at short and larger distances from the origin.

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