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# A study of the atomic momentum density by means of radial expectation values <sup>\*†</sup>

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**Abstract.** It is shown how the knowledge of a few low order radial momentum expectation values  $\langle p^k \rangle$  and the central value  $\gamma(0)$  of the electron momentum density in atomic systems allows to bound from below and from above the momentum density  $\gamma(p)$  for any value of the linear momentum, as well as the cumulative density and the cumulative radial density of any atom. The bounds are obtained by using Chebyshev inequalities and moment-theoretic methods. A knowledge of a greater number of expectation values results in an improvement of the accuracy of the above mentioned bounds. A numerical study of this accuracy is carried out in a Hartree-Fock framework.

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## 1. Introduction

The electron distribution of atomic systems in momentum space, described in terms of the monoparticle density  $\gamma(\mathbf{p})$ , allows an easy interpretation of numerous physical and chemical phenomena [21]. Specially interesting is the study of that distribution by means of the radial expectation values  $\langle p^k \rangle$  defined by

$$\langle p^k \rangle \equiv \int p^k \gamma(\mathbf{p}) d\mathbf{p} = 4\pi \int_0^\infty p^{k+2} \gamma(p) dp, \quad (k > -3) \quad (1)$$

where  $\gamma(p)$  denotes the spherically averaged electronic momentum density, i.e.

$$\gamma(p) \equiv \frac{1}{4\pi} \int \gamma(\mathbf{p}) d\Omega_{\mathbf{p}} \quad (2)$$

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Some of the expectation values  $\langle p^k \rangle$  can be indirectly calculated from measurements in  $X$  or  $\gamma$  ray Compton scattering processes, as well as from electron scattering experiments [7, 9, 25, 27].

We should remark the physical meaning [11] of quantities like  $\langle p^2 \rangle$  (twice the electron kinetic energy),  $\langle p^4 \rangle$  (proportional to the relativistic correction to the kinetic energy, due to the mass variation),  $\langle p^{-1} \rangle$  (twice the height of the peak of the Compton profile) and  $\langle p^0 \rangle$  (the number of electrons of the system). Also, it is known [14] the semiclassical relation between  $\langle p^3 \rangle$  and the mean charge density  $\langle \rho \rangle$ , as well as between  $\langle p \rangle$  and the Dirac-Slater exchange energy  $K_0$ . Many other rigorous relationships among these quantities have been provided in the last years (see eg. [22]).

The well-known asymptotic behavior [6]

$$\gamma(p) \sim p^{-8}$$

valid for high  $p$ -values, is of great importance to determine the range of orders for which the expectation values  $\langle p^\alpha \rangle$  exist. It is easy to show that only those with  $-3 < \alpha < 5$  are finite.

Moreover, it is also known [24] that the atomic momentum density at the origin,  $\gamma(0)$ , plays a relevant role describing the long-range behavior of the atomic charge density  $\rho(\mathbf{r})$ . Some lower bounds to  $\gamma(0)$  have been published [1, 15]. They are usually expressed in terms of one or more radial expectation values  $\langle p^\alpha \rangle$ . Numerical approximations and calculations of  $\gamma(0)$  have been also reported [12, 13].

Not so many other properties of  $\gamma(p)$  are known. For atoms with nuclear charge  $Z$  up to  $Z = 54$ , it has been numerically shown [26] that monotonicity (i.e. the negativity of the first derivative) only occurs for  $Z = 1 - 7, 11 - 13, 19 - 26, 31, 37 - 42, 49 - 50$ . For the rest of atoms in this region of the periodic table, some of them ( $Z = 27 - 30, 43 - 45, 47 - 48$ ) present their absolute maximum at the origin, i.e.  $\gamma_{max} = \gamma(0)$ , while for those with  $Z = 8 - 10, 14 - 18, 32 - 36, 46, 51 - 54$  this maximum is located at positions  $p \neq 0$ .

The aim of this work is to obtain rigorous upper and lower bounds to the spherically averaged atomic momentum density  $\gamma(p)$  in terms of the aforementioned quantities  $\gamma(0)$  and  $\langle p^\alpha \rangle$ . So, we cover the range of intermediate values of  $p$  for which rigorous results are very scarce. This kind of results allows one to check numerical approximations and theoretical computations on  $\gamma(p)$  or related quantities.

The only existing result in this field is that of Yue and Janmin [28], who extended a previous work of King and Dykema [18]. They obtained upper bounds on  $\gamma(p)$  in terms of the momentum expectation values  $\langle p^{-2} \rangle$  and  $\langle p^{-1} \rangle$ , and the quantity  $\langle r^2 \rangle$  (related to the diamagnetic susceptibility [20]).

Here, we are interested in obtaining rigorous upper and lower bounds to  $\gamma(p)$  in terms of  $\gamma(0)$  and the first few lowest order expectation values  $\langle p^\alpha \rangle$ , using a procedure based on Chebyshev inequalities [10, 23]. The same procedure allows also to obtain upper and lower bounds on (i) the integrated momentum density  $\Psi(p) = \int_0^p \gamma(p) dp$ , and (ii) the number of electrons with linear momentum lower than  $p$ ,  $B(p) = 4\pi \int_0^p p^2 \gamma(p) dp$ .

This technique has been also applied to find [4] upper and lower bounds to the atomic charge density  $\rho(r)$ , its first derivative  $\rho'(r)$ , the integrated charge density  $\Psi(r) = \int_0^r \rho(r)dr$  and the number of electrons enclosed in a sphere of radius  $r$ ,  $Q(r) = 4\pi \int_0^r r^2 \rho(r)dr$ , as well as in a variety of fields such as particle physics [2, 3], thermodynamics [17] and solid state physics [16, 19].

In Section II, a review of the technique used is given. In Section III, the results of the previous section are applied to the physical cases represented by the aforementioned atomic functions  $\gamma(p)$ ,  $\Psi(p)$  and  $B(p)$  (i.e. momentum density, integrated momentum density and integrated radial momentum density, respectively). Finally, some concluding remarks are given in Section IV.

## 2. Chebyshev upper and lower bounds

Let  $g(p)$  be a non-negative function related to  $\gamma(p)$ , which moments around the origin can be expressed in terms of  $\gamma(0)$  and the radial expectation values  $\langle p^\alpha \rangle$ . We construct the Stieltjes function

$$H(z) = \int_0^\infty \frac{g(p)}{1-zp} dp$$

The non-negativity of the weight function  $g(p)$  allows to obtain, via moment theory, approximations or rigorous bounds on  $H(z)$  by using the properties of the orthogonal polynomials associated with the weight  $g(p)$ .

A formal series expansion of  $H(z)$  can be obtained in terms of the moments

$$\mu_k = \int_0^\infty p^k g(p) dp \quad (k = 0, 1, 2, \dots)$$

in the form

$$H(z) = \sum_{i=0}^{\infty} \mu_i z^i$$

The bounding rigorous properties of the Padé approximants for this kind of functions are the consequence [4, 10] of bounding the cumulative weight  $G(p) \equiv \int_0^p g(p)dp$ . The residues and poles of the Padé approximants are easily related to the quadrature parameters  $\delta_i^{(n)} > 0$ ,  $p_i^{(n)} \in [0, \infty)$  which satisfy the extremely non linear moment equations

$$\mu_k = \sum_{i=1}^n \delta_i^{(n)} [p_i^{(n)}]^k, \quad k = 0, 1, \dots, 2n-1 \quad (3)$$

and yield bounds on  $G(p)$  at the points  $p_i^{(n)}$  in terms of  $\delta_i^{(n)}$  as follows:

$$\sum_{j=1}^{i-1} \delta_j^{(n)} \leq G(p_i^{(n)}) \leq \sum_{j=1}^i \delta_j^{(n)}, \quad i = 1, 2, \dots, n \quad (4)$$

It is possible to obtain bounds at any point  $p \in [0, \infty)$ , and not only at the fixed points  $p_i^{(n)}$ , by reducing the order of the moment equations (3) in the form

$$\mu_k = \sum_{i=1}^n \delta_i^{(n)}(p) [p_i^{(n)}(p)]^k, \quad k = 0, 1, \dots, 2n-2 \quad (5)$$

where now we can impose to have a quadrature point at an arbitrary position  $p \equiv p_i^{(n)}$  for some value of  $i$  [3, 5, 10]. A more detailed description of the method can be found in the above mentioned references, as well as in [4]. It should be pointed out that, due to the procedure used to obtain the bounds, the arithmetic mean of the upper and the lower bound obtained for a given number of moments is a convergent approximation to  $\gamma(p)$ . This type of approximations can be compared to other techniques which build up densities from moments [2].

### 3. Applications to atomic systems

In the previous section, a model-independent method to obtain lower and upper pointwise bounds to a given quantity  $G(p)$  has been derived in terms of the moments of  $g(p)$ . Here this method can be applied in a straightforward manner to the following atomic quantities: the momentum density  $\gamma(p)$ , the integrated momentum density  $\Psi(p)$ , and the number of electrons with linear momentum lower than  $p$ ,  $B(p)$  taking into account the following observations.

a)  $\underline{g(p) = -\gamma'(p)}$

The non-negativity of this function occurs for many atomic systems, as previously pointed out. We can bound the cumulative weight

$$\int_0^p g(p) dp = \gamma(0) - \gamma(p)$$

in terms of the moments

$$\mu_k = \int_0^\infty p^k g(p) dp = \begin{cases} \gamma(0) & k = 0 \\ \frac{k \langle p^{k-3} \rangle}{4\pi} & k = 1, 2, \dots, 7 \end{cases}$$

which results in upper and lower bounds to  $\gamma(p)$  in terms of  $\gamma(0)$ ,  $\langle p^{-2} \rangle$ ,  $\langle p^{-1} \rangle, \dots$

b)  $\underline{g(p) = \gamma(p)}$

The quantum-mechanical non-negativity of the electron momentum density allows to bound the function

$$\Psi(p) = \int_0^p g(p) dp$$

in terms of the moments

$$\nu_k = \int_0^\infty p^k g(p) dp = \frac{\langle p^{k-2} \rangle}{4\pi} \quad k = 0, 1, \dots, 6$$

c)  $\underline{g(p) = 4\pi p^2 \gamma(p) \equiv I(p)}$

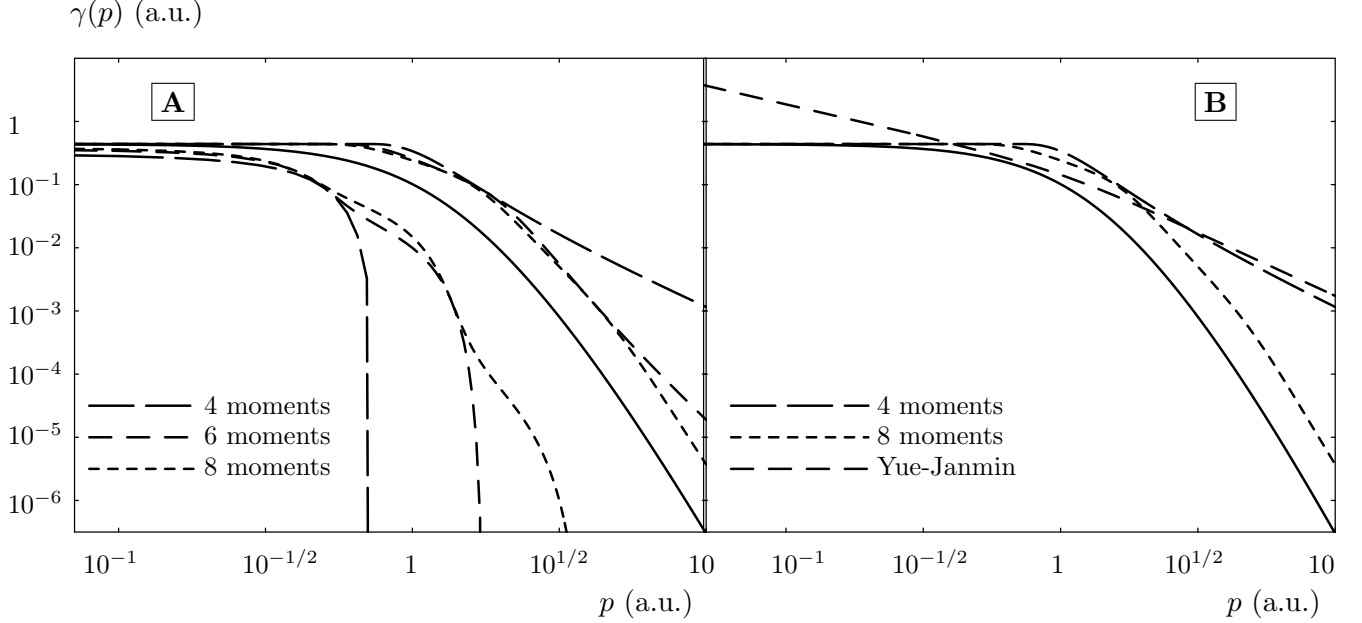
The non-negativity of the radial momentum density makes possible to bound the function

$$B(p) = \int_0^p I(p) dp$$

(which represents the number of electrons with linear momentum lower than  $p$ ) in terms of the radial expectation values

$$\xi_k = \int_0^\infty p^k I(p) dp = \langle p^k \rangle \quad k = 0, 1, 2, 3, 4$$

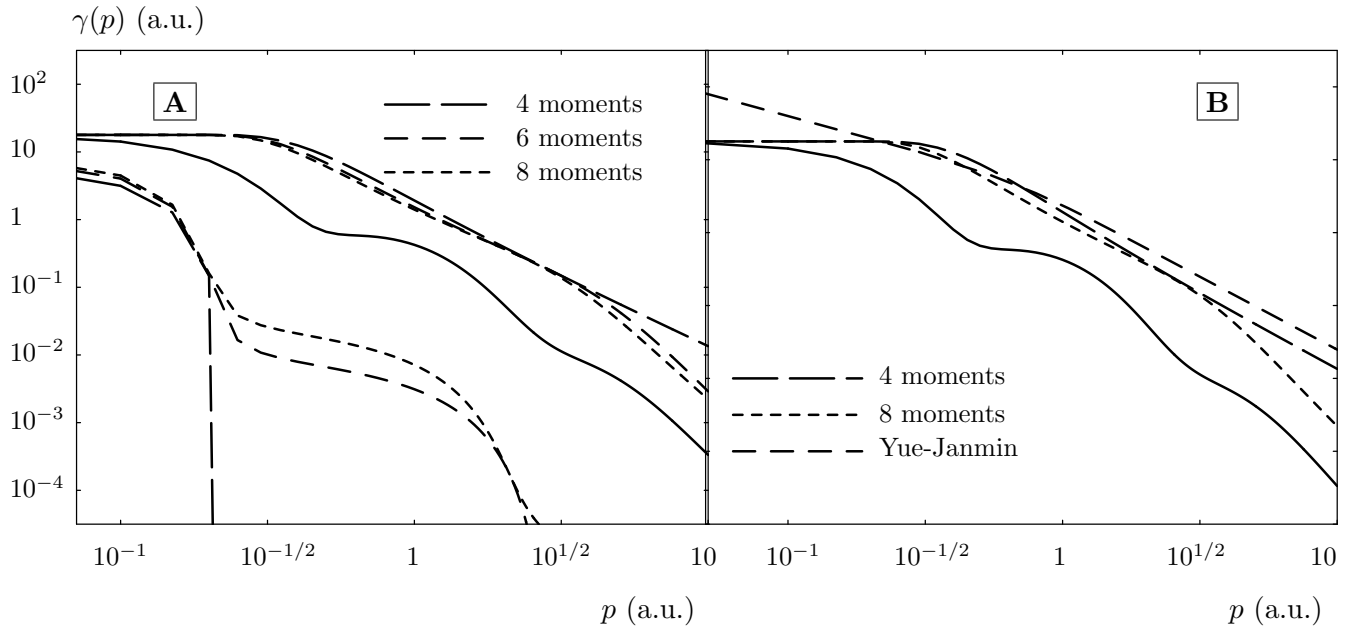
Then, the method provides rigorous pointwise lower and upper bounds to  $\gamma(p)$ ,  $\Psi(p)$  and  $B(p)$  in the whole periodic table by means of  $\gamma(0)$  and the momentum expectation values  $\langle p^k \rangle$ . To have an idea of the quality of these bounds, we have numerically analyzed them in three different atoms (Helium, Potassium, Rubidium) within the framework of a realistic model.



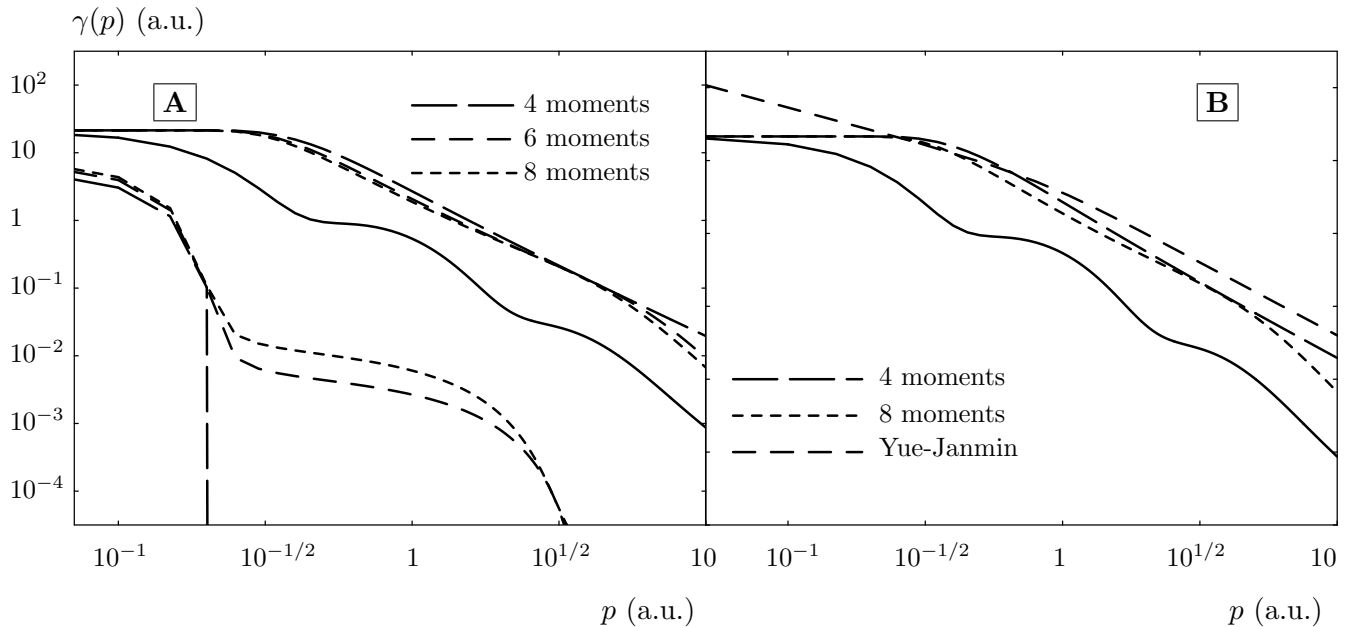
**Figure 1.-** (A) Spherically averaged momentum density  $\gamma(p)$  (solid line) and 4, 6 and 8 moments upper and lower bounds, and (B) comparison between the 4 and 8 moments upper bounds and Yue and Janmin upper bound (see Eq. (1) of (Yue and Janmin 1984)) for the Helium ground state atom. The solid line represents the spherically averaged momentum density. Atomic units are used.

In *Figures 1(A), 2(A) and 3(A)*, we compare the bounds obtained by using 4, 6 and 8 moments with the Hartree-Fock [8] momentum density  $\gamma(p)$  of the Helium ( $Z = 2$ ), Potassium ( $Z = 19$ ) and Rubidium ( $Z = 37$ ) atoms, respectively. It is observed that the accuracy of these bounds improves, for the three atoms here studied, when the number of moments considered increases, as we expected. This improvement is more evident for the lower bounds, specially in going from the 4-moment to the 6-moment case.

In *Figures 1(B), 2(B) and 3(B)*, our upper bounds are compared with the best (for intermediate and high momenta) upper bound of Yue and Janmin, i.e. Eq. (1) of [28], for each of the above mentioned atoms. Notice that our results are considerable better than that of Yue and Janmin at low and high momenta (specially for the case of 8 moments), while their upper bound is lower than ours for a narrow region around  $p = 1$  a.u.



**Figure 2.-** (A) Spherically averaged momentum density  $\gamma(p)$  (solid line) and 4, 6 and 8 moments upper and lower bounds, and (B) comparison between the 4 and 8 moments upper bounds and Yue and Janmin upper bound (see Eq. (1) of (Yue and Janmin 1984)) for the Potassium ground state atom. The solid line represents the spherically averaged momentum density. Atomic units are used.



**Figure 3.-** (A) Spherically averaged momentum density  $\gamma(p)$  (solid line) and 4, 6 and 8 moments upper and lower bounds, and (B) comparison between the 4 and 8 moments upper bounds and Yue and Janmin upper bound (see Eq. (1) of (Yue and Janmin 1984)) for the Rubidium ground state atom. The solid line represents the spherically averaged momentum density. Atomic units are used.

## 4. Concluding remarks

The knowledge of some radial momentum expectation values  $\langle p^k \rangle$  and the central value of the electron momentum density  $\gamma(0)$  allows to obtain rigorous upper and lower bounds not only to the momentum density  $\gamma(p)$  for those atoms having a  $\gamma(p)$  monotonically decreasing, but also to the cumulative momentum density  $\Psi(p)$  as well as the cumulative radial momentum density  $B(p)$  for any atom. These bounds require the knowledge of only the few radial expectation values  $\langle p^k \rangle$  of lowest orders, being their accuracy improved when the number of moments considered is increased.

It is remarkable that the arithmetic mean of the upper and lower bound to  $\gamma(p)$ ,  $\Psi(p)$  and  $B(p)$  for a given number of moments converges to the exact bounded function when this number increases.

Moreover, it should be pointed out that the procedure here described in order to obtain the bounds can be applied to many other interesting density functions.

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