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Upper bounds to atomic electron densities in position and momentum spaces

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Modified functions $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$ of the spherically averaged electron densities $\rho(r)$ in position space and $\Pi(p)$ in momentum space are found to be convex (i.e., the second derivatives are nonnegative everywhere) for all the 103 ground-state atoms from hydrogen (atomic number $Z = 1$) to lawrencium ($Z = 103$), if the parameters are chosen to be $\alpha \geqslant 0.6$ and $\beta \geqslant 1.4$. The convex property of $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$ is used to derive upper bounds to the density functions $\rho(r)$ and $\Pi(p)$ in terms of their radial moments $\langle r^s\rangle$ and $\langle p^s\rangle$ or frequency moments $\langle\rho^t\rangle$ and $\langle\Pi^t\rangle$. In most cases, the present bounds are shown to be more general and more accurate than those reported in the literature.

KEY WORDS: electron position and momentum densities, local bounds, convex densities, analytic inequalities

1. Introduction

With the progress of density functional methods [1–3], the electron densities $\rho(\mathbf{r})$ in position space and $\Pi(\mathbf{p})$ in momentum space play a more significant role in modern quantum theory of atoms and molecules. Accordingly, our knowledge on the general properties of electron density functions $\rho(\mathbf{r})$ and $\Pi(\mathbf{p})$ becomes more important.

For atomic systems the information of the three-dimensional position density $\rho(\mathbf{r})$ may be condensed into its spherical average $\rho(r)$ defined by

$$\rho(r) \equiv (4\pi)^{-1}\int \mathrm{d}\Omega_r\,\rho(\mathbf{r}), \tag{1a}$$

where (r, Ω_r) with $\Omega_r \equiv (\theta_r, \phi_r)$ are the spherical coordinates of the three-dimensional vector $\mathbf{r}$. For the spherically averaged density $\rho(r)$ of atoms, some structural properties are known either theoretically or numerically. In addition to its nonnegativity, the behaviors of $\rho(r)$ near [4,5] and far [6] from the nucleus were rigorously proved. It is known numerically that $\rho(r)$ is a monotonically decreasing function for all the neutral

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atoms with atomic number $Z \leqslant 103$ [7–9] and for all the singly-charged ions with the number of electrons $N \leqslant 54$ [10] in their experimental ground states. For some neutrals and ions, $\rho(r)$ has been found [11–13] to be convex, i.e., the second derivative $\rho''(r)$ of the density $\rho(r)$ is nonnegative for any r. The monotonicity of a function $r^{-\alpha}\rho(r)$ with $\alpha \geqslant 0$ has been also studied [14,15] for some neutral atoms.

The spherical average $\Pi(p)$ of the momentum density $\Pi(\mathbf{p})$ is defined by

$$\Pi(p) \equiv (4\pi)^{-1} \int \mathrm{d}\Omega_p \Pi(\mathbf{p}), \tag{1b}$$

where $\mathbf{p} = (p, \Omega_p)$ with $\Omega_p \equiv (\theta_p, \phi_p)$. The density $\Pi(p)$ is nonnegative, and its asymptotic behavior for large momentum is known [16] rigorously. There are several numerical studies on the monotonicity of $\Pi(p)$ for atoms (see [17] for a review), and the co-existence of monotonic and nonmonotonic momentum densities for atoms and atomic ions in their ground states has been established recently [17,18] within the Hartree–Fock framework. The monotonicity and convexity of a function $p^{-\beta}\Pi(p)$ with $\beta \geqslant 0$ has also been examined [19] for neutral atoms with $Z \leqslant 54$.

In the present paper, we report new upper bounds with improved accuracy for the electron densities $\rho(r)$ and $\Pi(p)$ of atoms in terms of the radial moments

$$\langle r^s \rangle \equiv 4\pi \int_0^\infty \mathrm{d}r\, r^{s+2}\rho(r), \qquad \langle p^s \rangle \equiv 4\pi \int_0^\infty \mathrm{d}p\, p^{s+2}\Pi(p), \tag{2}$$

and the frequency moments,

$$\mu_t \equiv 4\pi \int_0^\infty \mathrm{d}r\, r^2\big[\rho(r)\big]^t, \qquad \nu_t \equiv 4\pi \int_0^\infty \mathrm{d}p\, p^2\big[\Pi(p)\big]^t, \tag{3}$$

in both position and momentum spaces, based on the convexity of the auxiliary functions $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$. In the literature [20–23], several bounds of this type are known. However, the literature bounds [20–22] are restrictive in the sense that one or two particular moments such as $\langle r^{-2} \rangle$, $\langle r^0 \rangle$, $\langle r^2 \rangle$, and $\langle p^2 \rangle$ are involved. On the other hand, the present bounds are general, and any of the radial and frequency moments can be employed to bound the electron densities $\rho(r)$ and $\Pi(p)$ from the above. Our bounds will be also shown to be more applicable and more accurate than those given in [23]. In the next section, we present our theoretical results in a general form, starting from an integral inequality derived by Volkov [24]. In section 3, we first discuss the convexity of the functions $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$. The present upper bounds are then applied to the ground-state neutral atoms with $1 \leqslant Z \leqslant 103$ and the accuracy of the new bounds is compared with that given in the literature. Hartree atomic units are used throughout.

2. Rigorous bounds to electron densities

For a nonnegative, decreasing function $f(x)$ defined over $(0, \infty)$, Volkov [24] derived an inequality

$$r^{n-1} \int_r^\infty \mathrm{d}x\, f(x) \leqslant \left(\frac{n-1}{n}\right)^{n-1} \int_0^\infty \mathrm{d}x\, x^{n-1} f(x), \quad n > 1, r > 0, \tag{4}$$

where the two integrals are assumed to exist.

For atomic systems, it is known [14,15,19] that the functions $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$ are convex, whenever the values of the parameters α ($\geqslant 0$) and β ($\geqslant 0$) be appropriately chosen. In order to derive new bounds to the electron density functions in terms of their radial and frequency moments, we fully use the fact that if $g''(x) \geqslant 0$ and $g'(x)$ is integrable over $(0, \infty)$, then a function $-g'(x)$ or $-([g(x)]^t)'$ with $t > 1$ is nonnegative and decreasing, where the prime ($'$) means a differentiation with respect to x and $g(x)$ is either $x^{-\alpha}\rho(x)$ or $x^{-\beta}\Pi(x)$.

We first consider a function $f(x) = -[x^{-\alpha}\rho(x)]'$ with a nonnegative α such that $x^{-\alpha}\rho(x)$ is convex. Since

$$\int_0^\infty \mathrm{d}x\, x^{n-1} f(x) = \frac{n-1}{4\pi} \langle r^{n-\alpha-4} \rangle \tag{5}$$

for $0 \leqslant \alpha < n-1$, we obtain from equation (4) a general bound to the density $\rho(r)$ in terms of the radial moments $\langle r^s \rangle$,

$$\rho(r) \leqslant \frac{(s+\alpha-1)^{s+\alpha}}{(s+\alpha)^{s+\alpha-1}} \frac{\langle r^{s-4} \rangle}{4\pi r^{s-1}}, \tag{6}$$

for $s > 1$. Some particular cases of equation (6) are

$$s = 2: \quad \rho(r) \leqslant \frac{(\alpha+1)^{\alpha+2}}{(\alpha+2)^{\alpha+1}} \frac{\langle r^{-2} \rangle}{4\pi r}, \tag{7a}$$

$$s = 3: \quad \rho(r) \leqslant \frac{(\alpha+2)^{\alpha+3}}{(\alpha+3)^{\alpha+2}} \frac{\langle r^{-1} \rangle}{4\pi r^2}, \tag{7b}$$

$$s = 4: \quad \rho(r) \leqslant \frac{(\alpha+3)^{\alpha+4}}{(\alpha+4)^{\alpha+3}} \frac{N}{4\pi r^3}, \tag{7c}$$

where we have used $\langle r^0 \rangle = N$, the number of electrons.

We next consider another nonnegative and decreasing function

$$f(x) = -\left(\left[x^{-\alpha}\rho(x)\right]^t\right)',$$

where $t > 1$ and α is nonnegative. Using equation (4) again with $n = \alpha t + 4$ and

$$\int_0^\infty \mathrm{d}x\, x^{\alpha t+3} f(x) = \frac{\alpha t + 3}{4\pi} \mu_t, \tag{8}$$

we obtain another general bound to the density $\rho(r)$,

$$\rho(r) \leqslant \left(\frac{\alpha t + 3}{\alpha t + 4}\right)^{(\alpha t+3)/t} \left[\frac{(\alpha t + 3)\mu_t}{4\pi r^3}\right]^{1/t}, \tag{9}$$

in terms of the frequency moment μ_t, where $\alpha \geqslant 0$, $t > 1$. A special case of equation (9) for $t = 2$ reads

$$\rho(r) \leqslant \left(\frac{2\alpha + 3}{2\alpha + 4}\right)^{(2t+3)/2} \left[\frac{(2\alpha + 3)\langle\rho\rangle}{4\pi r^3}\right]^{1/2}, \tag{10}$$

where $\mu_2 = \langle\rho\rangle$ is the average electron density in position space.

An exactly analogous procedure with the functions $f(x) = -[x^{-\beta}\Pi(x)]'$ and $f(x) = -([x^{-\beta}\Pi(x)]^t)'$ allows us to obtain from equation (4) the corresponding bounds to the electron density $\Pi(p)$ in momentum space,

$$\Pi(p) \leqslant \frac{(s + \beta - 1)^{s+\beta}}{(s + \beta)^{s+\beta-1}} \frac{\langle p^{s-4}\rangle}{4\pi p^{s-1}}, \tag{11}$$

with the condition $1 < s < 9$, and

$$\Pi(p) \leqslant \left(\frac{\beta t + 3}{\beta t + 4}\right)^{(\beta t+3)/t} \left[\frac{(\beta t + 3)\nu_t}{4\pi p^3}\right]^{1/t}, \tag{12}$$

with the conditions $\beta \geqslant 0$ and $t > 1$. The condition $s < 9$ for equation (11) originates from the p^{-8} decay of $\Pi(p)$ for large p [16].

We note that a function $x^{x+1}/(x + 1)^x$ is an increasing function on x. Therefore, the bounds (6) and (11) are better for smaller values of α and β; the best bounds are found when $\alpha = 0$ and $\beta = 0$, which means that the electron densities $\rho(r)$ and $\Pi(p)$ are convex.

3. Numerical results and discussion

A function $x^{-\alpha} f(x)$ is convex for any value of α which satisfies $\alpha \geqslant \alpha_0$, where α_0 is given by [14]

$$\alpha_0 = \max_{0 \leqslant x < \infty} \big[q_0(x)\big], \tag{13a}$$

in which

$$q_0(x) = \begin{cases} \dfrac{1}{2f(x)}\big\{2xf'(x) - f(x) + \lambda_0^{1/2}\big\}, & \text{if } \lambda_0 \geqslant 0, \\ 0, & \text{if } \lambda_0 < 0, \end{cases} \tag{13b}$$

and $\lambda_0 = [2xf'(x) - f(x)]^2 - 4x^2 f(x) f''(x)$.

Previously [14,15], the value of α_0, which makes the position-space density function $r^{-\alpha}\rho(r)$ with $\alpha \geqslant \alpha_0$ convex, was examined for the atoms with $Z \leqslant 92$ based on different sets of Roothaan–Hartree–Fock wave functions [25–29]. Moreover, the function $r^{-\alpha}\rho(r)$ in atomic systems was proved [14] to be convex everywhere if $\alpha \geqslant [(1+4Z^2/I)^{1/2}-1]/2$, where I is the first ionization potential of an atom. In momentum space, the value of β_0 which makes the density function $p^{-\beta}\Pi(p)$ with $\beta \geqslant \beta_0$ convex was reported [19] for the atoms with $Z \leqslant 54$, using more accurate wave functions [30].

However, the wave functions due to Clementi and Roetti [25] and McLean and McLean [26], used in previous studies [14,15], are now known [27–29] to suffer from nontrivial errors and inaccuracies. Therefore, we have re-evaluated the values of α_0 and β_0 for all the atoms with $Z \leqslant 103$ using the accurate wave functions constructed very recently by Koga et al. [30,31]. The α_0 values for the atoms with $93 \leqslant Z \leqslant 103$ and the β_0 values for the atoms with $55 \leqslant Z \leqslant 103$ are determined here for the first time.

The present results for α_0 are shown in figure 1(a). For the atoms with $Z \leqslant 92$, the present values are found to be little different from those reported previously [14,15].

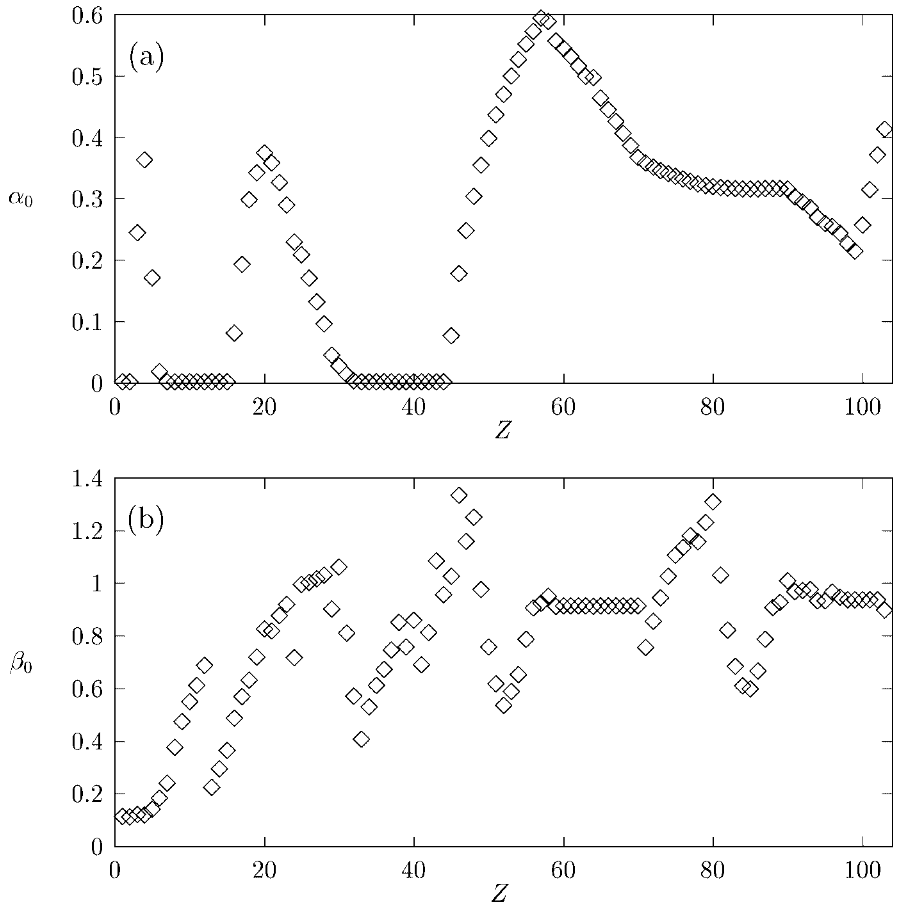

Figure 1. Convexity parameters α_0 and β_0 as a function of Z. (a) Values of the parameter α_0 such that $r^{-\alpha}\rho(r)$ is convex for $\alpha \geqslant \alpha_0$. (b) Values of the parameter β_0 such that $p^{-\beta}\Pi(p)$ is convex for $\beta \geqslant \beta_0$. All values in atomic units.

For the 103 atoms, the α_0 values distribute between 0 and 0.6. In particular, the 23 atoms with $Z = 1$, 2, 7–15 and 33–44 have $\alpha_0 = 0$, which implies that these atoms have a convex position density $\rho(r)$. In position space, we can conclude that the density function $r^{-0.6}\rho(r)$, and $r^{-1}\rho(r)$ for simplicity, is always convex for all the atoms with $Z \leqslant 103$ in their ground state. The β_0 values for the momentum density are plotted in figure 1(b). The value ranges from 0.1 to 1.4, and an atom with a convex $\Pi(p)$ does not exist among the 103 atoms. Instead, we can say that a momentum-space density function $p^{-1.4}\Pi(p)$, and $p^{-2}\Pi(p)$ simply, is convex for all the 103 atoms.

The position-space density $r^{-\alpha}\rho(r)$ with $\alpha = 1$ is convex for any of the 103 ground-state atoms. Then, equations (6) and (9) with $\alpha = 1$ give upper bounds

$$\rho(r) \leqslant \frac{s^{s+1}}{(s+1)^s}\frac{\langle r^{s-4}\rangle}{4\pi r^{s-1}}, \quad s > 1 \tag{14}$$

and

$$\rho(r) \leqslant \left(\frac{t+3}{t+4}\right)^{(t+3)/t}\left[\frac{(t+3)\mu_t}{4\pi r^3}\right]^{1/t}, \quad t > 1 \tag{15}$$

to the electron density $\rho(r)$, respectively. Three particular cases resulting from equation (14) with $s = 3$, with $s = 6$, and equation (15) with $t = 2$, i.e.,

$$\rho(r) \leqslant \rho_1(r) \equiv \frac{3^4}{4^3}\frac{\langle r^{-1}\rangle}{4\pi r^2}, \tag{16a}$$

$$\rho(r) \leqslant \rho_2(r) \equiv \frac{6^7}{7^6}\frac{\langle r^{2}\rangle}{4\pi r^2}, \tag{16b}$$

$$\rho(r) \leqslant \rho_3(r) \equiv \left(\frac{5}{6}\right)^{5/2}\left[\frac{5\langle\rho\rangle}{4\pi r^3}\right]^{1/2}, \tag{16c}$$

are of our special interest, because $\langle r^{-1}\rangle$ in equation (16a) specifies the electron–nucleus attraction energy, $\langle r^2\rangle$ in equation (16b) is proportional to the Langevin–Pauli diamagnetic susceptibility [32], and $\langle\rho\rangle$ in equation (16c) is the average electron density.

Gálvez and Porras [23] reported an upper bound for a decreasing $\rho(r)$,

$$\rho(r) \leqslant (s-1)\frac{\langle r^{s-4}\rangle}{4\pi r^{s-1}}, \quad s > 1. \tag{17}$$

If we compare the coefficients, $s^{s+1}/(s+1)^s$ and $(s-1)$, on the right-hand sides of equations (14) and (17), we find that the former is always smaller than the latter; the ratio varies from 8/9 for $s = 2$ to 1/e for $s = \infty$. Thus, the present upper bound, equation (14), is more tight and accurate than that of [23], equation (17). Hoffmann-Ostenhof and Hoffmann-Ostenhof [20] gave a bound

$$\rho(r) \leqslant \frac{\sqrt{2NT}}{4\pi}\frac{1}{r^2}, \tag{18}$$

corresponding to equation (16a), where N is the number of electrons and $T = \langle p^2\rangle/2$ is the electronic kinetic energy. When the coefficient $\sqrt{2NT}/(4\pi)$ in equation (18) and $3^4\langle r^{-1}\rangle/(4^4\pi)$ in equation (16a) have been numerically examined with the accurate Hartree–Fock wave functions [30,31], we have found that equation (16a) always has a smaller coefficient for all the atoms with $4 \leqslant Z \leqslant 103$. King [21] reported upper bounds

$$\rho(r) \leqslant \frac{T}{2\pi}\frac{1}{r}, \tag{19a}$$

$$\rho(r) \leqslant \frac{T\sqrt{(2-\delta)\delta}}{2\pi}\frac{1}{r}, \tag{19b}$$

where $\delta = \langle r^{-2}\rangle/(4T)$ (if $\delta < 1$). Numerical examinations have shown that our bound, equation (14) with $s = 2$, i.e.,

$$\rho(r) \leqslant \frac{2^3}{3^2}\frac{\langle r^{-2}\rangle}{4\pi r}, \tag{20}$$

is better than equation (19a) for the atoms with $Z \geqslant 39$. However, equation (19b) is better than equation (20) for all the atoms, partly because equation (19b) employs the information of two moments $\langle r^{-2}\rangle$ and $\langle p^2\rangle$.

In figure 2(a), the three typical upper bounds, equations (16a)–(16c), from the present study are explicitly exemplified and compared with the Hartree–Fock position density $\rho(r)$ for the Cs atom ($Z = 55$). This atom has been chosen since it approximately occupies the center of the 103 atoms examined in this work and yet includes the density contributions both from the tight and loose atomic orbitals; the 1s orbital energy is -1272.769 hartrees, while the 6s orbital energy is -0.124 hartrees. We see in figure 2(a) that the relative accuracies of the bounds depend on the r value. The bound $\rho_3(r)$ is best for $r < 0.6$ bohrs, whereas $\rho_2(r)$ is best for $r > 0.6$ bohrs among the three bounds. However, neither bound is still with enough accuracy for very small and large values of r, and these regions await improved bounds.

In momentum space, the density function $p^{-\beta}\Pi(p)$ with $\beta = 2$ is convex for any of the 103 ground-state atoms. For $\beta = 2$, the inequalities (11) and (12) are now:

$$\Pi(p) \leqslant \frac{(s+1)^{s+2}}{(s+2)^{s+1}}\frac{\langle p^{s-4}\rangle}{4\pi p^{s-1}}, \quad 1 < s < 9, \tag{21}$$

$$\Pi(p) \leqslant \left(\frac{2t+3}{2t+4}\right)^{(2t+3)/t}\left[\frac{(2t+3)\nu_t}{4\pi p^3}\right]^{1/t}, \quad t > 1. \tag{22}$$

The particular cases of equation (21) with $s = 3$, with $s = 6$, and equation (17) with $t = 2$, i.e.,

$$\Pi(p) \leqslant \Pi_1(p) \equiv \frac{4^5}{5^4}\frac{\langle p^{-1}\rangle}{4\pi p^2}, \tag{23a}$$

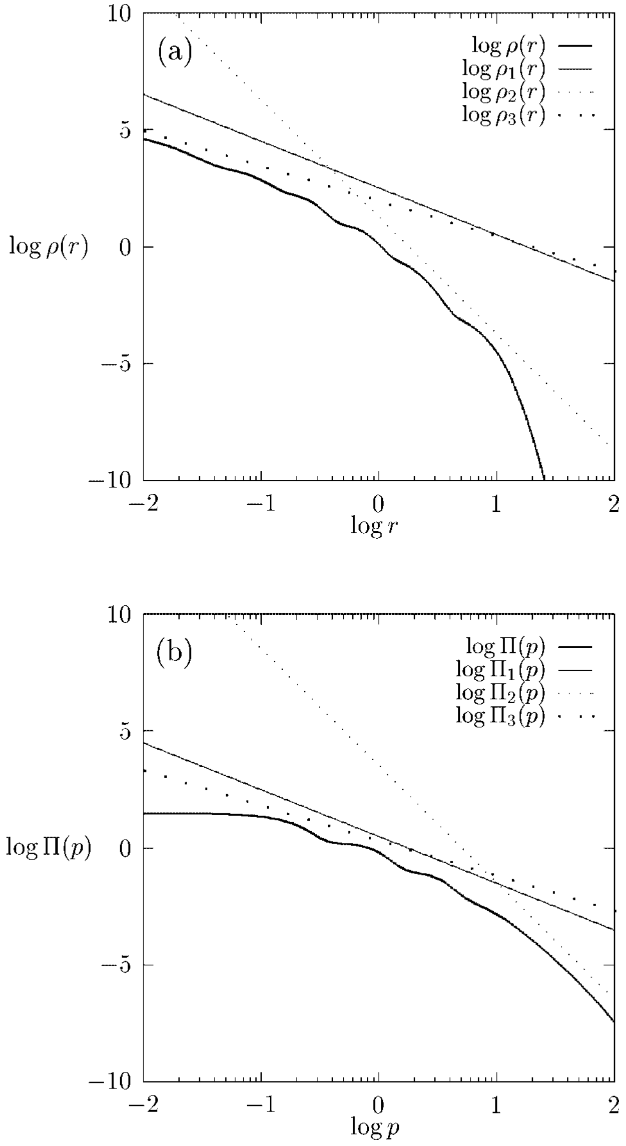

Figure 2. Illustration of the present upper bounds for the Cs atom ($Z = 55$). (a) Position density. (b) Momentum density. All values in atomic units.

$$\Pi(p) \leqslant \Pi_2(p) \equiv \frac{7^8}{8^7}\frac{\langle p^2\rangle}{4\pi p^5}, \tag{23b}$$

$$\Pi(p) \leqslant \Pi_3(p) \equiv \left(\frac{7}{8}\right)^{7/2}\left(\frac{7\langle\Pi\rangle}{4\pi p^3}\right)^{1/2}, \tag{23c}$$

are interesting, because they include physically important quantities; $\langle p^{-1}\rangle$ in equation (23a) is twice the peak height of the isotropic Compton profile in photon–electron interactions [16,33], $\langle p^2\rangle$ in equation (23b) is twice the nonrelativistic electronic kinetic energy, and $\langle \Pi\rangle$ in equation (23c) is the average momentum density.

A set of upper bounds analogous to equation (21) was derived by Gálvez and Porras [23] for a decreasing $\Pi(p)$:

$$\Pi(p) \leqslant (s-1)\frac{\langle p^{s-4}\rangle}{4\pi p^{s-1}}, \quad 1 < s < 9. \tag{24}$$

Comparison of the coefficients $(s+1)^{s+2}/(s+2)^{s+1}$ in equation (21) and $(s-1)$ in equation (24) immediately clarifies that equation (21) is more tight bound than equation (24) except for the case of $s = 2$. We note that equation (24) is applicable only when an atom has a monotonically decreasing momentum density, but equation (21) as well as equations (22) and (23) can be used for all the atoms. In fact, it is known [17] that 37 atoms among the 103 atoms with $1 \leqslant Z \leqslant 103$ do not have monotonically decreasing $\Pi(p)$. Yue and Janmin [22] gave a different upper bound:

$$\Pi(p) \leqslant \frac{\langle r^2\rangle}{4\pi p}. \tag{25}$$

Setting $s = 2$ in equation (21), the corresponding bound from this study is

$$\Pi(p) \leqslant \frac{3^4}{4^3}\frac{\langle p^{-2}\rangle}{4\pi p}. \tag{26}$$

Numerical examination of $\langle r^2\rangle$ and $\langle p^{-2}\rangle$ with the Hartree–Fock wave functions [30,31] has shown that the present bound (26) is better than equation (25) for the 67 atoms with $Z =$ 7–10, 14–18, 24, 29, 31–36, 41–55, 57, 64, and 71–103 among the 103 ground-state atoms.

In figure 2(b), we plot the present three upper bounds, equations (23a)–(23c), to the momentum density $\Pi(p)$ for the Cs atom. As was the bounds to the position density $\rho(r)$, we observe in figure 2(b) that each bound to $\Pi(p)$ has different accuracy depending on the value of p: $\Pi_3(p)$ is best for $p < 2.4$, $\Pi_1(p)$ is best for $2.4 < p < 10.2$, and $\Pi_2(p)$ is best for $p > 10.2$ among the three bounds. This aspect is more or less the same for all the atoms examined.

4. Summary

The present study has improved and extended our knowledge on the convex property of modified density functions $r^{-\alpha}\rho(r)$ and $p^{-\beta}\Pi(p)$ for all the 103 ground-state atoms with $1 \leqslant Z \leqslant 103$ in both position and momentum spaces. In particular, it has been found that the functions $r^{-1}\rho(r)$ and $p^{-2}\Pi(p)$ are always convex for all the 103 ground-state atomic systems. The convexity of these functions has enabled us to derive new upper bounds to the electron density functions $\rho(r)$ in position space and

$\Pi(p)$ in momentum space in terms of their radial moments $\langle r^s \rangle$ and $\langle p^s \rangle$ or frequency moments $\langle \rho^t \rangle$ and $\langle \Pi^t \rangle$. The results correlate local and global properties of the electron densities of atomic systems, which would not be easy to obtain otherwise. Since the present mathematical techniques are general, it may be interesting to apply them to other density functions such as the Compton profile and the form factor which are also important from both experimental and theoretical points of view.

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