Monotonicity Properties of the Atomic Charge Density Function

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ABSTRACT

The present knowledge of the monotonicity properties of the spherically averaged electron density $\rho(r)$ and its derivatives, which comes mostly from Roothan–Hartree–Fock calculations, is reviewed and extended to all Hartree–Fock ground-state atoms from hydrogen ($Z = 1$) to uranium ($Z = 92$). In looking for electron functions with universal (i.e., valid in the whole periodic table) monotonicity properties, it is found that there exist positive values of α so that the function $g_0(r;\alpha) = \rho(r)/r^\alpha$ is convex, and $g_1(r;\alpha) = -\rho'(r)/r^\alpha$ is not only monotonically decreasing from the origin but also convex. This is, however, not the case for the function $g_2(r;\alpha) = \rho''(r)/r^\alpha$. Additionally, the conditions which specify values for β such that the function $g_n(r;\beta) = (-1)^n p^{(n)}(r)/r^\beta$ is logarithmically convex are obtained and numerically calculated for $n = 0, 1$ in all neutral atoms below uranium. The last property is used to obtain inequalities of general validity involving three radial expectation values which generalize all the similar ones known to date, as well as other relationships among these quantities and the values of the electron density and its derivatives at the nucleus.

Introduction

The one-electron density of an N-electron system in a physical state described by the quantum-mechanical wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N; \sigma_1, \ldots, \sigma_N)$, where $(\mathbf{r}_n, \sigma_n)$ denotes the spatial-spin coordinates of the nth-electron, is the fundamental cornerstone between the chemical and physical properties of the system at that state. However, the analytical features of this density are almost fully unknown from a general and rigorous point of view. Even in the ground state, where the one-electron density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = N \sum_{\sigma_i = -1/2}^{+1/2} \int |\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N; \sigma_1, \ldots, \sigma_N)|^2 \, d\mathbf{r}_2 \times \ldots d\mathbf{r}_N$$

(Ψ_0 denotes the normalized-to-unity ground-state wave function), the structural properties of $\rho(\mathbf{r})$

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and its spherical average ($\rho(r) = (4\pi)^{-1}\int\rho(\mathbf{r})\,d\Omega_r$, are very poorly known in spite of the fact that it is the basic variable for the modern density functional theory (DFT) initiated by Hohenberg and Kohn [1].

Rigorously, apart from the quantum-mechanical nonnegativity and the Hoffmann–Ostenhof's differential inequality [2,3], the only known analytical properties of $\rho(r)$ are as follows:

(i) The cusp condition, which gives the logarithmic derivative of $\rho(r)$ at the nucleus [4],

$$\rho'(0) = -2Z\rho(0). \tag{1}$$

(ii) The behavior at large distances [5–8],

$$\rho(r) \simeq r^{2b}e^{-2ar} \tag{2}$$

where $b = (Z - N + 1)/a - 1$, $a = \sqrt{2\epsilon}$, ϵ and Z being the negative of the highest occupied orbital energy and the nuclear charge of the atom under consideration, respectively.

(iii) The function $\rho(r)$ is monotonically decreasing and convex for values of $r \geq Z/\epsilon$ [2].

(iv) The one-electron function $\rho(r)/r^{\alpha}$ is convex everywhere [9] with

$$\alpha \geq \tfrac{1}{2}\left[(1 + 4Z^2/\epsilon)^{1/2} - 1\right].$$

Numerical calculations, which use Roothan–Hartree–Fock atomic wave functions [10,11], have led to the identification of a few other properties:

(v) Monotone decreasing or first-order monotonicity (see Appendix A) of $\rho(r)$, i.e., $\rho'(r) < 0$ everywhere. This property was recognized only in the early 1970s [12,13] and carefully studied in the late 1980s by the Kingston group [14] and others [15]. The rigorous proof of this property is an amazingly open problem.

Moreover, it has been shown [16,17] that the electron cusp inequality

$$\rho'(r) \geq -2Z\rho(r), \qquad r \geq 0, \tag{3}$$

holds in all neutral atoms with $1 \leq Z \leq 92$, which generalizes Kato's condition at the nucleus (1) and its (rigorously proven) spatial generalization for the bare Coulomb field model [18].

(vi) *Convexity of* $\rho(r)$, *i.e,* $\rho''(r) \geq 0$. It has been shown that the atoms with Z values of 1–2, 7–15, and 33–44 (group 1) have a convex (i.e., monotonic of second order) electron density [19]. The remaining atoms of the periodic table with nuclear charge Z of 3–6, 16–32, and 45–92 (group 2) have a $\rho(r)$ with a small but physically significant radial region wherein $\rho''(r) < 0$ [19,20]. Moreover, it appears that the electron density is strictly convex in the atoms of group 1 and strictly pseudoconvex (see Appendix A) in the atoms of group 2 [20]. Then, since strict convex functions are also strict pseudoconvex, it seems that strict pseudoconvexity is a general structural property of the one-electron density of all neutral atoms [21].

It is worthy noting that in the atoms belonging to group 2 the second derivative of $\rho(r)$ presents pairs of local maxima and minima [15,17] so that (a) the number of which never decreases with increasing nuclear charge and (b) the occurrence of new local minima and maxima always corresponds to the addition of an electron in a new subshell. Furthermore, it seems [20] that electron correlation does not seriously affect the curvature of $\rho(r)$ and that the bare Coulomb field of the nucleus is the main element responsible for the appearance of nonconvex regions in atoms. However, this point needs further investigation.

Also, let us mention that plausible arguments [21] and numerical results [20] indicate that the total electron density of an arbitrary number of closed shells is convex in the bare Coulomb field model.

(vii) *Higher order monotonicity of* $\rho(r)$. The maximal order k of monotonicity of $\rho(r)$ in each atom of group 1 is not known. Numerically it depends on the approximate wave functions that you use. Indeed, in helium one obtains $k = 15$ with the near-Hartree–Fock wave functions of Clementi–Roetti and $k = 6$ [22] with the highly accurate 204-term Hylleras wave functions of Koga et al. [23]. Should k be known, (a) one can represent the electron

density as [22].

$$\rho(r) = \frac{1}{k!}\int_r^\infty (s-r)^k \, dv(s)$$

where $v(s)$ is a nonnegative measure, and (b) simple compact and (at times) accurate relationships among local and global quantities can be derived.

Complete monotonicity of $\rho(r)$, i.e., monotonicity with $k \to \infty$ (see Appendix A), has also been investigated [24] within the near-Hartree–Fock framework of Clementi–Roetti. It was found that, apart from hydrogen, in which it is rigorous, there is no neutral atom which has a completely monotonic electron density. However, the assumption of this property allows us to obtain very good approximate expressions for and among local and global properties such as, e.g., the electron density at the nucleus and various radial expectation values [24, 25].

(viii) *Log-convexity of* $\rho(r)$. This property has been investigated in all neutral atoms with nuclear charge $Z \leq 54$ [26]. This study is extended in the second section to the region $55 \leq Z \leq 92$ of the periodic table. Briefly, it is found that hydrogen, in which it is rigorous, and helium are the only two atoms with a log-convex electron density.

Additionally, in searching for electron density functions of a universal nature (i.e., valid for all ground-state atoms) with a degree of monotonicity higher than that of $\rho(r)$ but keeping its simplicity and being physically meaningful, we have investigated [9] in a Hartree–Fock framework the monotonicity properties of the function

$$g_n(r;\alpha) = \frac{(-1)^n \rho^{(n)}(r)}{r^\alpha} \tag{4}$$

as well as the log-convexity property of the function [26]

$$g_0(r;\beta) = \frac{\rho(r)}{r^\beta} \tag{5}$$

Specifically, we have indicated [9] how to calculate the minimal values α_{np} and β_0 of the positive parameters α and β, respectively, so that the function $g_n(r,\alpha)$ is pth-order monotone, i.e.,

$$(-1)^p \frac{d^p g_n(r;\alpha)}{dr^p} \geq 0 \qquad \text{for all } r \text{ and } \alpha \geq \alpha_{np} \tag{6}$$

and the function $g_0(r;\beta)$ is logarithmically convex (shortly, log-convex), i.e.,

$$\frac{d^2 \log g_0(r;\beta)}{dr^2} \geq 0 \qquad \text{for all } r \text{ and } \beta \geq \beta_0. \tag{7}$$

Then, the functions $g_n(r,\alpha_{np})$ and $g_0(r;\beta_0)$ are monotone of pth-order and log-convex, respectively. A physical analysis of the g_0-like electron functions and its corresponding function in momentum space has been recently carried out [27]. The values of α_{02}, α_{11}, α_{12}, α_{21}, and α_{22} as well as the value of β_0 have been recently tabulated [9, 27] for all Hartree–Fock ground-state neutral atoms with nuclear charge $1 \leq Z \leq 54$.

The study of these kinds of monotonicity properties has been proven [9, 16, 19, 24, 26] to be very useful in the theoretical determination, estimation, and correlation of several physically relevant and/or experimentally measurable quantities (e.g., local values of the density or radial expectation values, as defined in the fourth section) as well as in setting up rigorous bounds to numerous functionals to the one- and two-particle densities, which play an important role in the modern density functional theory. Additionally, some of these properties allow us to also reveal the atomic shell structure and other physical and chemical phenomena [17, 20, 21].

Here we want to extend the work done in [9] and [26] by calculating the values of α_{02}, α_{11}, α_{12}, α_{21}, and α_{22} as well as β_0 and β_1 in all Hartree–Fock ground-state neutral atoms with nuclear charge $1 \leq Z \leq 92$. Notice, then, that the log-convexity property [28] of the function $g_n(r;\beta)$ will be considered. In doing all this, we will use the Clementi–Roetti wave functions [10] for all atoms up to xenon ($Z = 54$), and the similar McLean–McLean atomic wave functions [11] for the atoms with nuclear charge $55 \leq Z \leq 92$. Additionally, we compare these values with those obtained with the improved Roothan–Hartree–Fock wave functions of Koga et al. [29] and Bunge et al. [30] in a few atoms.

At this point we should mention that the Clementi–Roetti wave function for $Z = 45$ [31, 32] and McLean-McLean wave functions for $Z = 67$,

68 [33] are erratic, so more accurate calculations of those atomic functions and consequently of the associated monotonicity parameters α_{np} and β_n need to be done.

This article is structured so that, first, in the second section, the aforementioned monotonicity properties of $g_n(r;\alpha)$ are investigated and then, in the third section, the log-convexity of the similar function $g_n(r;\beta)$ is examined. Finally, some log-convexity effects on the radial expectation values are discussed in the fourth section, and then some concluding remarks are given.

Monotonicity Properties of the Electron Function $g_N(R;\alpha)$

In this section, the monotonicity properties of the general electron density function $g_n(r;\alpha)$ given by Eq. (4) will be studied. That is, the minimal value α_{np} of the parameter α so that the inequality (6) is fulfilled will be numerically investigated for a given order of monotonicity p by use of the Clementi–Roetti and McLean–McLean (CR and ML heretoforth) ground-state wave functions in all atoms with nuclear charge $1 \le Z \le 92$. Then, to know how confident the subsequent results are, we compare then with the corresponding values obtained by use of the Roothan–Hartree–Fock wavefunctions of Koga et al. [29] and Bunge et al. [30] in a number of atoms. The expressions of the first few α_{np} are [9]

$$\alpha_{01} = \max\left\{\frac{r\rho'(r)}{\rho(r)}\right\}, \qquad \alpha_{02} = \max\{q_0(r)\},$$

$$\alpha_{11} = \max\left\{-\frac{r\rho''(r)}{\rho'(r)}\right\}, \qquad \alpha_{12} = \max\{q_1(r)\},$$

$$\alpha_{21} = \max\left\{\frac{r\rho'''(r)}{\rho''(r)}\right\}, \qquad \alpha_{22} = \max\{q_2(r)\},$$

where the functions $q_i(r)$, $i = 0,1,2$, are given by

$$q_i(r) = \begin{cases} \dfrac{1}{2\rho^{(i)}(r)}\{2r\rho^{(i+1)}(r) - \rho^{(i)}(r) + \lambda_i^{1/2}\} \\ \qquad \text{if } \lambda_i \ge 0, \\ 0 \\ \qquad \text{if } \lambda_i < 0, \end{cases}$$

with

$$\lambda_i := [2r\rho^{(i+1)}(r) - \rho^{(i)}(r)]^2 - 4r^2\rho^{(i)}(r)\rho^{(i+2)}(r).$$

A finite value of α_{np} indicates that the function $g_n(r;\alpha_{np}) = (-1)^n\rho^{(n)}(r)/r^{\alpha_{np}}$ is monotone of pth order. Extensive use of the near-Hartree–Fock ground-state wave function of Clementi–Roetti [10] and McLean–McLean [11] have allowed us to calculate the values of the parameters α_{np}, with $n = 0,1,2$ and $p = 1,2$, in all neutral atoms with nuclear charge $Z \le 92$. First, we find that $\alpha_{01} = 0$ everywhere, which means that the electron density $g_0(r;0) \equiv \rho(r)$ is monotonically decreasing from the origin in all atoms. This is a well-known fact pointed out by Sperber [12] and Weinstein et al. [13] for $Z \le 54$ and by Simas et al. [14] and Angulo [15] for the remaining atoms up to uranium.

The values that we obtain for the rest of parameters α_{np} considered in this work are shown in Figures 1–5, which are to be discussed in the following. The values of α_{02} shown in Figure 1 indicate that $0 \le \alpha_{02} < 0.6$ in all atoms, hydrogen through uranium. Then the electron function $g_0(r;\alpha_{02}) = r^{-\alpha_{02}}\rho(r)$ is convex everywhere. Such a small value of α_{02} shows that the electron density $\rho(r)$ is "almost" convex in all atoms. In fact, the only atoms with a strictly convex $\rho(r)$ are the members of the aforementioned group 1 (i.e., Z values of 1–2, 7–15, and 33–44), since then α_{02} vanishes. It is observed that the main peaks of the

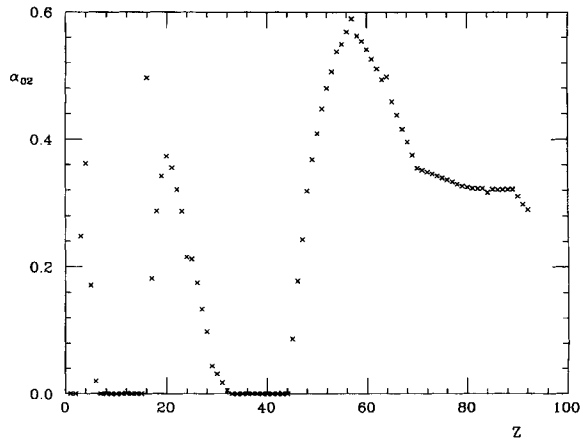

FIGURE 1. Values of the parameter α_{02} obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\alpha \ge \alpha_{02}$ the electron function $g_0(r;\alpha) = \rho(r)/r^{\alpha}$ is convex.

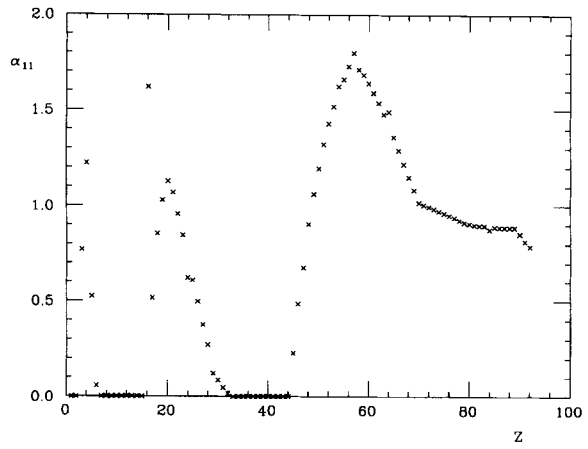

FIGURE 2. Values of the parameter α_{11} obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\alpha \geq \alpha_{11}$ the electron function $g_1(r;\alpha) = -\rho'(r)/r^{\alpha}$ is monotonically decreasing from the origin.

figure correspond to $Z = 4, 16, 20, 57$. So, it seems that there is no apparent connection between the values of α_{02} and shell structure, although further investigation is needed at this point. A similar comment about the location of the peaks should be done for the rest of the figures.

The values of α_{11} given in Figure 2 show that $0 \leq \alpha_{11} \leq 1.8$ in all neutral atoms below uranium. Then, the electron function $g_1(r;\alpha_{11}) = -r^{-\alpha_{11}}\rho'(r)$ is monotonically decreasing from the origin. Notice that α_{11} vanishes for the atoms

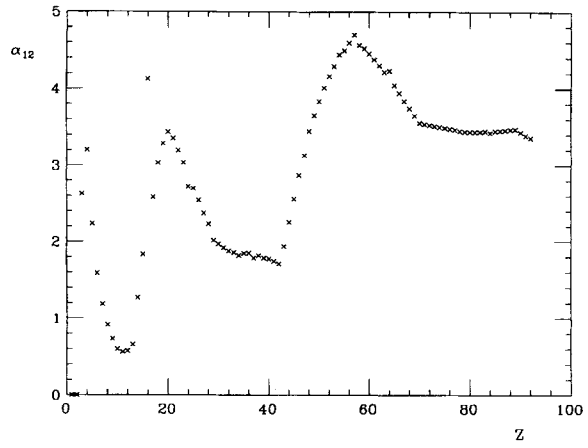

FIGURE 3. Values of the parameter α_{12} obtained by use of the Clementi–Roetti and McLean–McLean wave function in all atoms, hydrogen through uranium. Recall that for $\alpha \geq \alpha_{12}$ the electron function $g_1(r;\alpha) = -\rho'(r)/r^{\alpha}$ is convex.

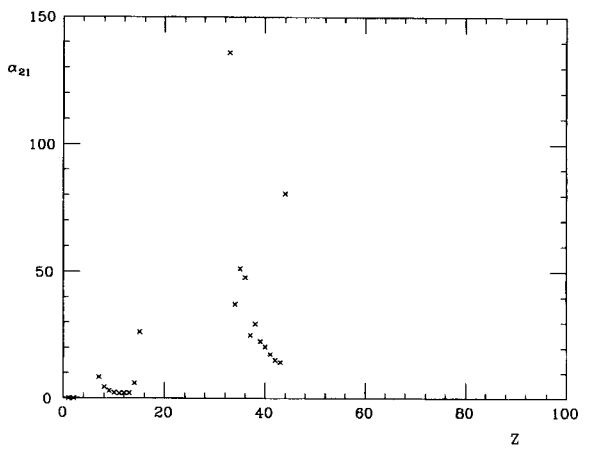

FIGURE 4. Values of the parameter α_{21} obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\alpha \geq \alpha_{21}$ the electron function $g_2(r;\alpha) = \rho''(r)/r^{\alpha}$ is monotonically decreasing from the origin. Notice that most atoms do not present finite values for α_{21}, which indicates lack of this monotonicity property.

belonging to group 1, which again shows the convexity of the electron density $\rho(r)$ of these atoms. It seems clear that the convexity property (see Appendix) of the ground-state electron density $\rho(r)$ is too strong for all neutral atoms. Therefore, the electron density $\rho(r)$ of all atoms might have a certain analyticity property stronger than the first-order monotonicity and weaker than the second-

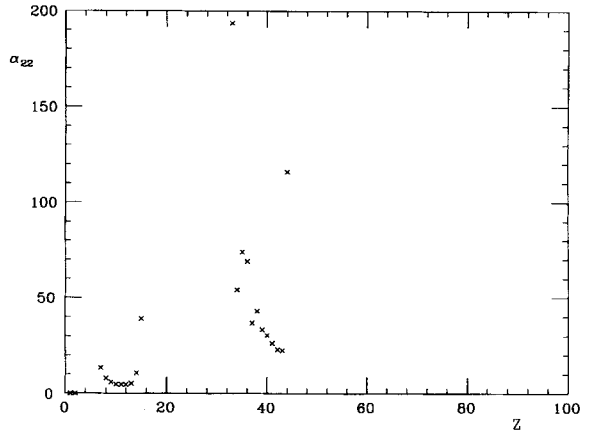

FIGURE 5. Values of the parameter α_{22} obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\alpha \geq \alpha_{22}$ the electron function $g_2(r;\alpha) = \rho''(r)/r^{\alpha}$ is convex. Notice that most atoms do not have finite values for α_{22} (or they are too large), which indicates lack of convexity.

order monotonicity (i.e., convexity); that property, which cannot be expressed in the differential form (A1), has been recently found: It is pseudoconvexity (see Appendix) [20, 21].

Then, in Figure 3, the property of convexity of the function $g_1(r;\alpha)$ is investigated by plotting the parameter α_{12} against Z; it is found that $0 \leq \alpha_{12} < 4.8$. One observes that the only atoms with vanishing α_{12} are H and He; so, they are the only neutral atoms with a Hartree–Fock ground-state electron density $\rho(r)$ of monotonicity of third order.

Finally, in Figures 4 and 5, the first- and second-order monotonicity properties of the electron function $g_2(r;\alpha) = r^{-\alpha}\rho''(r)$ are investigated, respectively. It is observed that $\alpha_{21} = \alpha_{22} = 0$ occurs only in H and He. In addition, the remaining atoms of the periodic table seem not to have these two properties except those of the regions with nuclear charge Z values of 7–15 and 33–44. Thus, the atoms of group 1 are the only ones which have a convex electron function $g_2(r;\alpha_{22})$.

To know how much we should trust in the calculated CR and ML α values, we compare them with the corresponding ones obtained by use of other Roothan–Hartree–Fock atomic wave functions, such as those of Koga et al. [29] and Bunge et al. [30]. This is done in Table I for a number of atoms. It is observed that the α values obtained with the three sets of wave functions are very similar except in the case of α_{21} and α_{22} of the Rb atom ($Z = 37$), which is in the atomic region with $33 \leq Z \leq 44$.

To understand the relative behavior of the resulting values α_{np} represented in Figures 1–5, we have done a simple and analytical study of the monotonic condition (A1) of the electron function $g_n(r;\alpha)$ given by Eq. (4). We obtain [9]

$$\alpha_{np} \leq \alpha_{n,p+1} \leq \alpha_{n+1,p},$$

which gives, in particular, $0 \leq \alpha_{02} \leq \alpha_{12}$ (notice that the results shown in Figs. 1 and 2 are consis-

TABLE I

Comparison of values for monotonicity parameters α_{02}, α_{11}, α_{12}, α_{21}, and α_{22} and log-convexity parameters β_0 and β_1, obtained by use of three sets of ground-state wave functions (CR = Clementi and Roetti [10]; KOG = Koga et al. [29]; BUN = Bunge et al. [30]) in atoms with nuclear charge $Z = 3, 6, 11, 18, 26, 37, 47, 54$.

Set	Z	α_{02}	α_{11}	α_{12}	α_{21}	α_{22}	β_0	β_1
CR	3	0.24823	0.76968	2.62585			2.74310	8.26814
KOG	3	0.24616	0.76257	2.61746			2.73377	8.24917
BUN	3	0.24318	0.75237	2.60341			2.72376	8.20967
CR	6	0.02018	0.05747	1.58718			1.99999	5.62091
KOG	6	0.01758	0.05000	1.57572			2.00000	5.58460
BUN	6	0.01695	0.04822	1.57273			2.00000	5.57105
CR	11	0.00000	0.00000	0.56060	2.04749	4.49399	4.00000	4.56483
KOG	11	0.00000	0.00000	0.56384	2.06294	4.51727	4.00000	4.50779
BUN	11	0.00000	0.00000	0.56016	2.04562	4.49117	4.00000	4.45202
CR	18	0.28743	0.85459	3.03137			6.00000	10.88796
KOG	18	0.29574	0.88185	3.07966			6.00000	11.09183
BUN	18	0.29582	0.88208	3.07930			4.00000	11.09031
CR	26	0.17517	0.49588	2.54223			6.00000	9.78024
KOG	26	0.16864	0.47634	2.51571			6.00000	9.69990
BUN	26	0.16943	0.47876	2.52011			6.00000	9.71040
CR	37	0.00000	0.00000	1.78299	24.94840	36.69819	8.00000	8.50316
KOG	37	0.00000	0.00000	1.85460	50.42587	72.62506	8.00000	8.45182
BUN	37	0.00000	0.00000	1.84437	41.76212	60.40800	8.00000	8.38922
CR	47	0.24300	0.67511	3.12643			8.00000	13.16918
KOG	47	0.24603	0.68502	3.12595			8.00000	13.06106
BUN	47	0.24835	0.69123	3.14234			8.00000	13.19799
CR	54	0.53712	1.62176	4.43855			8.00000	17.85890
KOG	54	0.53081	1.59963	4.39790			8.00000	17.67016
BUN	54	0.52489	1.57862	4.37665			8.00000	17.62283

tent with these bounds) and $\alpha_{02} \leq \alpha_{03} \leq \alpha_{12}$, which predicts that all atoms have a Hartree–Fock ground-state electron function $g_0(r; \alpha_{03}) = r^{-\alpha_{03}}\rho(r)$ which is monotone of third order. Taking into account the values of α_{02} and α_{12} given by Figures 1 and 2, respectively, one already knows that $0 \leq \alpha_{03} \leq 4.8$.

Log-convexity Properties of the Electron Function $g_N(R;\beta)$

Here the logarithmic convexity of the electron function $g_n(r; \beta)$ given by Eq. (4) will be investigated. That is, we will look for the minimal value β_n of the parameter β so that the nonnegativity condition

$$\frac{d^2}{dr^2} \log g_n(r; \beta) \geq 0 \qquad \text{for all } r \text{ and } \beta \geq \beta_n$$

is fulfilled for a given n by use of the CR and ML atomic wave functions in all atoms with nuclear charge $Z \leq 92$.

Straightforwardly one obtains

$$\beta_n = \max\left\{-r^2 \frac{d^2}{dr^2} \log\left[(-1)^n \rho^{(n)}(r)\right]\right\}$$

$$= \max\left\{(-1)^{n+1} r^2 \frac{\rho^{(n+2)}(r)\rho^{(n)}(r) - [\rho^{(n+1)}(r)]^2}{[\rho^{(n)}(r)]^2}\right\}.$$

In particular, for $n = 0$ and $n = 1$ one has

$$\beta_0 = \max\left\{-r^2 \frac{\rho''(r)\rho(r) - [\rho'(r)]^2}{[\rho(r)]^2}\right\},$$

$$\beta_1 = \max\left\{r^2 \frac{\rho'''(r)\rho'(r) - [\rho''(r)]^2}{[\rho'(r)]^2}\right\}.$$

A finite value of β_n indicates that the function $\log g_n(r; \beta_n)$ is monotone of second order, i.e., convex. In particular, the existence of the values β_0 and β_1 would mean that the electron functions $g_0(r; \beta_0) = \rho(r)/r^{\beta_0}$ and $g_1(r; \beta_1) = -\rho'(r)/r^{\beta_1}$ are logarithmically convex.

The resulting values β_0 and β_1 obtained by the use of the CR and ML wave functions are plotted against the atomic nuclear charge Z in Figures 6 and 7, respectively. Note that the values of β_0 are

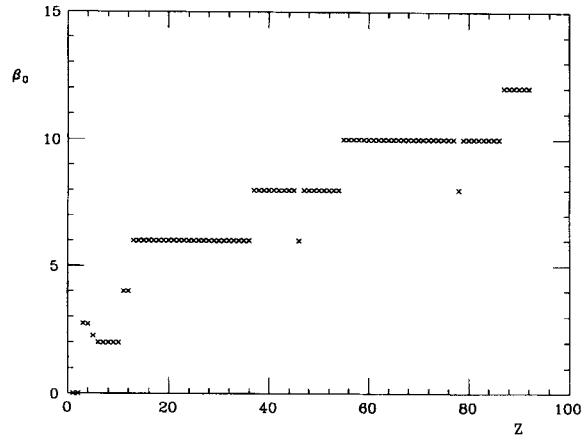

FIGURE 6. Values of the parameter β_0 obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\beta \geq \beta_0$ the electron function $g_0(r; \beta) = \rho(r)/r^{\beta}$ is logarithmically convex.

piecewise constant. This can be understood theoretically because the asymptotic behavior of $\rho(r)$ is determined by the most diffuse Slater basis function of the given atom and then the asymptotic behavior of the CR and ML $\rho(r)$ is given by $\rho(r) \simeq r^{2m}e^{-2\gamma r}$ (with m integer), which differs from the theoretical one given by Eq. (2), i.e., the values of the parameters m and γ are different, respectively, from those of the parameters a and b appearing in Eq. (2). When calculating β_0, it happens that the maximum of the function appearing

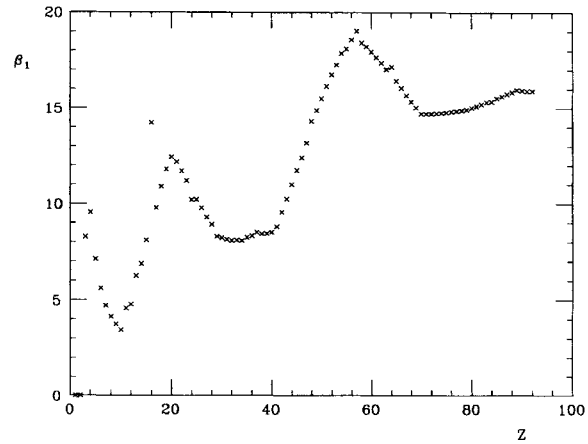

FIGURE 7. Values of the parameter β_1 obtained by use of the Clementi–Roetti and McLean–McLean wave functions in all atoms, hydrogen through uranium. Recall that for $\beta \geq \beta_1$ the electron function $g_1(r; \beta) = -\rho'(r)/r^{\alpha}$ is logarithmically convex.

in the definition of β_0 usually occurs at large r, so that the asymptotic behavior of $\rho(r)$ is strongly important in the determination of the parameter β_0. In Figure 7 we observe that the values of β_1 are in the range 0–19 with a Z behavior similar to that of α_{12} as given in Figure 3. Again, the highest peaks are located at $Z = 4$, 16, 20, 57, 64, and 89.

To shed light on the behaviors of β_0 and β_1, as shown in Figures 6 and 7, one should remember that (i) the logarithmic convexity of $\rho(r)$ is a property stronger than convexity and weaker than complete monotonicity, which implies that $\alpha_{n2} \leq \beta_n \leq \alpha_{n\infty}$ and, in particular, $\beta_1 \geq \alpha_{12}$; and (ii) the asymptotic behavior of $\rho(r)$ is given by Eq. (2), so that $\beta_0 \geq \max\{b, 0\}$.

Log-convexity Effects on Radial Expectation Values

To identify analyticity properties in the electron density $\rho(r)$ or any related function is of great physical relevance because those properties may often be used to calculate or to correlate local and/or global quantities of the system under consideration, which would be very difficult, if not impossible, to obtain otherwise. In this section, the log-convexity of the electron function

$$g_n(r;\beta) = \frac{(-1)^n \rho^{(n)}(r)}{r^\beta} \tag{8}$$

is used to derive relationships among radial expectation values $\langle r^m \rangle$, i.e.,

$$\langle r^m \rangle = \int r^m \rho(\mathbf{r})\, d\mathbf{r} = 4\pi \int_0^\infty r^{m+2} \rho(r)\, dr$$

and/or the values of the electron density and its derivatives at the nucleus $\rho^{(m)}(0)$. To obtain these relationships, we employ the property (A5) of the log-convex function $g_n(r;\beta = \beta_n)$. The modified moments $\lambda_p \equiv \lambda_{p,n}$ of this function are

$$\begin{aligned}\lambda_p &= \frac{1}{\Gamma(p+1)} \int_0^\infty r^p g_n(r;\beta_n)\, dr \\ &= \frac{\Gamma(p-\beta_n+1)}{\Gamma(p+1)} \\ &\quad \times \begin{cases} (-1)^{n-p+\beta_n-1} \rho^{(n-p+\beta_n+1)}(0) & \text{if } p = \beta_n, \beta_n+1, \ldots, \beta_n+n-1, \\ \dfrac{\langle r^{p-\beta_n-n-2} \rangle}{4\pi\Gamma(p-\beta_n-n+1)} & \text{if } p > \beta_n + n - 1. \end{cases}\end{aligned} \tag{9}$$

Then, property (A5) allows us to find, in particular, the following three-term recurrence relations among the radial expectation values:

$$\frac{\langle r^{ap+bq-\beta_n-n-2} \rangle}{\Gamma(ap+bq+1)} \leq C \left[\frac{\langle r^{p-\beta_n-n-2} \rangle}{\Gamma(p+1)} \right]^a \times \left[\frac{\langle r^{q-\beta_n-n-2} \rangle}{\Gamma(q+1)} \right]^b, \tag{10}$$

which is valid for $p, q \geq \beta + n - 1$ and $a, b \geq 0$ provided that $a + b = 1$, and the symbol C denotes the constant

$$\begin{aligned} C = &\frac{\Gamma(ap+bq-\beta_n-n+1)}{\Gamma(ap+bq-\beta_n+1)} \\ &\times \left[\frac{\Gamma(p-\beta_n+1)}{\Gamma(p-\beta_n-n+1)} \right]^a \\ &\times \left[\frac{\Gamma(q-\beta_n+1)}{\Gamma(q-\beta_n-n+1)} \right]^b. \end{aligned} \tag{11}$$

This general relationship extends considerably similar and simpler inequalities previously encountered [26–28, 34–36]. In particular, notice that for $n = 0$ the constant C is equal to unity and the relation (10) reduces as

$$\frac{\langle r^{ap+bq-\beta_0-2} \rangle}{\Gamma(ap+bq+1)} \leq \left[\frac{\langle r^{p-\beta_0-2} \rangle}{\Gamma(p+1)} \right]^a \left[\frac{\langle r^{q-\beta_0-2} \rangle}{\Gamma(q+1)} \right]^b, \tag{12}$$

which was previously obtained and thoroughly discussed by the authors [26]. The cases with $n > 0$ of relationship (10) are fully new. Here we will study these cases comparatively with the case $n = 0$, although, for simplicity, only for $a = b = \frac{1}{2}$ and $q = p + 2$. Then, relation (10) with the change $p \rightarrow$

$s: s = p - \beta_n - n$ transforms into

$$\langle r^s\rangle\langle r^{s-2}\rangle \geq \frac{(s+2)(s+n+1)(s+\beta_n+n+2)}{(s+1)(s+n+2)(s+\beta_n+n+1)} \times \langle r^{s-1}\rangle^2 \quad (13)$$

for $s \geq -\beta_n - n$. Some subcases are

$$N\langle r^{-2}\rangle \geq \frac{2(n+1)(\beta_n+n+2)}{(n+2)(\beta_n+n+1)}\langle r^{-1}\rangle^2, \quad (14)$$

$$\langle r\rangle\langle r^{-1}\rangle \geq \frac{3(n+2)(\beta_n+n+3)}{2(n+3)(\beta_n+n+2)}N^2, \quad (15)$$

$$\langle r^2\rangle N \geq \frac{4(n+3)(\beta_n+n+4)}{3(n+4)(\beta_n+n+3)}\langle r\rangle^2. \quad (16)$$

We have seen in the previous Hartree–Fock calculations that $\beta_1 \geq \beta_0$ (compare Figures 6 and 7); so, the bounds given by Eqs. (14)–(16) with $n = 1$ obtained from the log-convexity property of the electron function $g_1(r;\beta_1) = -\rho'(r)/r^{\beta_1}$ are more accurate than the corresponding ones known up to now [26, 36] in all Hartree–Fock ground-state neutral atoms below uranium, at least within the aforementioned Hartree–Fock framework.

Finally, property (A5) together with expression (9) of the modified moments λ_p can readily provide us with other important three-term recursion relations among the values of the atomic electron density and its derivatives at the nucleus, $\rho^{(k)}(0)$, and/or some radial expectation values which will be separately discussed.

Summary and Concluding Remarks

To summarize, the present knowledge of the monotonicity and log-convexity properties of the spherically averaged electron density $\rho(r)$ of the ground-state atomic system and of the related electron functions $g_n(r;\gamma) = (-1)^n\rho^{(n)}(r)/r^\gamma$ has been reviewed and extended from Xe ($Z = 54$) through U ($Z = 92$). The minimal values of γ necessary for the function $g_n(r;\gamma)$ and its logarithm to have a property of monotonicity of a given order p are numerically investigated within a Roothan–Hartree–Fock framework. In particular, it is argued that (i) H and He are the only two neutral atoms where the electron functions $\rho(r)/r^\gamma$ and $-\rho'(r)/r^\gamma$ are logarithmically convex and (ii) all neutral atoms have an electron function $g_0(r;\gamma) = \rho(r)/r^\gamma$ with a monotonicity property of third order, being $0 \leq \gamma \leq 5$. Then, the way to extract information from all these properties on local and global quantities of the system is illustrated by finding three-term recurrence relationships of global validity among radial expectation values $\langle r^k\rangle$. It is shown how to obtain other similar relationships among central values of the electron density and its derivatives and/or the quantities $\langle r^k\rangle$. Finally, let us emphasize that more accurate wave functions should be calculated in order to obtain more precise values of the parameters α_{np} and β_{np}, as it is revealed in Table I, in which, in particular, the values α_{21} and α_{22} seem to be very large for some atoms.

Appendix

Some mathematical notions used in the present work are summarized below.

- *Monotonicity of kth order.* A continuous function $f(x)$ on $(0,\infty)$ is monotone of order k if all its successive derivatives up to that of kth order alternate in sign, i.e.,

$$(-1)^n f^{(n)}(x) \geq 0, \quad x \in [0,\infty),\ n = 0,1,\ldots,k. \quad (A1)$$

Then, $f(x)$ is nonnegative if $k = 0$, monotonically decreasing if $k = 1$, convex if $k = 2$, etc., and it is called completely monotone [37] if $k \to \infty$.

For convenience, let us recall here another way to define convexity [21, 28]. A finite-valued $f(x)$ is convex on a set **C** if it satisfies the Jensen inequality

$$f(\lambda x_1 + (1-\lambda)x_2) \leq \lambda f(x_1) + (1-\lambda)f(x_2), \quad (A2)$$

where $x_1, x_2 \in \mathbf{C}$ are such that the real-valued $f(x)$ is also defined at $\lambda x_1 + (1-\lambda)x_2$ for all real values x_1 and x_2 with $0 \leq \lambda \leq 1$. For differentiable functions, this inequality can also be expressed as

$$f(x_1) - f(x_2) \geq (x_1 - x_2)f'(x_2). \quad (A3)$$

Moreover, the function $f(x)$ is said to be strictly convex if the inequalities in Eqs. (A2) and (A3) are strict for $x_1 \neq x_2$ or, equivalently, if $f''(x) > 0$.

- *Pseudoconvexity.* Several other classes of convexity have been defined in the mathematical literature [38, 39]. Here we consider only that which has been shown particularly relevant to atomic densities up to now: pseudoconvexity [20, 21].

  A function $f(x)$ is pseudoconvex if

$$f'(x_2)(x_1 - x_2) \geq 0 \Rightarrow f(x_1) \geq f(x_2). \quad \text{(A4)}$$

  In addition, $f(x)$ is said to be strictly pseudoconvex if the two inequalities in (A4) are strict.

  It is worth noting that if $f(x)$ is convex, then it is pseudoconvex but the converse is not true.

- *Log-convexity.* A continuous function $f(x)$, $0 \leq x < \infty$, is logarithmically convex [28] if its logarithm is convex, i.e., if

$$\frac{d^2}{dx^2} \log f(x) \geq 0.$$

  Karlin et al. [40] have shown that the modified moments λ_p of a function $f(x)$, i.e., the quantities

$$\lambda_p = \frac{1}{\Gamma(p+1)} \int_0^\infty x^p f(x)\, dx$$

  are also log-convex for $p \geq 0$, which means that they satisfy the inequality

$$\lambda_{ap+bq} \leq \lambda_p^a \lambda_q^b \quad \text{(A5)}$$

  for $p, q \leq 0$, $a, b \geq 0$, and $a + b = 1$.

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