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Charge monotonicity of atomic systems and radial expectation values

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Abstract. A function $f(r)$ is monotone of order p if its pth-derivative $f^{(p)}(r)$ fulfils that $(-1)^p f^{(p)}(r) \geqq 0$. So, e.g. the monotonicity properties of order $p=0, 1, 2$ describe the non-negativity ($p=0$), the monotonic decreasing from the origin ($p=1$) and the convexity ($p=2$) of the function, respectively. Here, the monotonicity properties of the electron function $g_n(r; \alpha) = (-1)^n \rho^{(n)}(r) r^{-\alpha}$, $\alpha \geqq 0$, of the ground state of atomic systems are analysed both analytically and numerically. The symbol $\rho(r)$ denotes the spherically averaged electron density. First of all, the condition which specifies, if exists, a value α_{np} such that $g_n(r; \alpha_{np})$ be monotone of order p is obtained. In particular, it is found that $\alpha_{01} = \max\{r\rho'(r)/\rho(r)\}$, $\alpha_{02} = \max\{q_0(r)\}$, $\alpha_{11} = \max\{r\rho''(r)/\rho'(r)\}$ and $\alpha_{12} = \max\{q_1(r)\}$, where $q_0(r)$ and $q_1(r)$ are simple combinations of the first few derivatives of $\rho(r)$. Secondly, numerical calculations of the first few values α_{np} in a Hartree-Fock framework for all ground-state atoms with nuclear charge $Z \leqq 54$ are performed. In doing so, the pioneering work of Weinstein, Politzer and Srebrenik about the monotonically decreasing behavior of $\rho(r)$ is considerably extended. Also, it is found that Hydrogen and Helium are the only two atoms having the functions $\rho(r)$, $-\rho'(r)$ and $\rho''(r)$ with the property of convexity. Thirdly, it is analytically shown that the charge function $r^{-\alpha}\rho(r)$ with $\alpha \geqq [(1+4Z^2/I)^{1/2}-1]/2$, I being the first ionization potential, is convex everywhere. Finally, the above mentioned monotonicity properties are used to obtain rigorous, simple and universal inequalities involving three radial expectation values which generalize all the similar ones known up to now. These inequalities allow to correlate various statical and dynamical quantities of the atomic system under study, due to the physical meaning of the radial expectation values. It is worth to remember that some of these expectation values may be experimentally measured in experiments of $(e, 2e)$-type.

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I. Introduction

The knowledge of structural properties of the single-fermion density $\rho(\mathbf{r})$ is playing an increasingly important role for the practical realization of the modern density-functional methods in the physics of many-fermion systems (Parr and Yang [1], Kryachko and Ludeña [2], Dreizler and Gross [3]). The monotonicity properties of the spherically averaged electron density $\rho(r)$ of the ground state of atomic systems, i.e. the non-negativity of the electron function

$$f_n(r) = (-1)^n \rho^{(n)}(r) \quad \text{for} \quad n = 0, 1, 2, \ldots \tag{1}$$

are specially relevant, due to the smooth character and the hidden structure of $\rho(r)$.

However, not so much is known apart from the positivity (monotonicity of zeroth-degree; $n=0$) and the numerical observation of the monotonically decreasing behavior (monotonicity of first degree) of $\rho(r)$ due to Sperber (Sperber [4]) and Weinstein et al. (Weinstein et al. [5]) for some atoms in the seventies, later corroborated and extended to the whole periodic table by other authors (Simas et al. [6], Angulo [7]).

Recently, we have numerically realized (Angulo et al. [8]) that convexity (monotonicity of second degree) is also a characteristic of the ground state density $\rho(r)$ of numerous neutral atoms (e.g. $Z=1$, 2, 7–15, 33–44). For the rest of atoms up to $Z=54$, $\rho(r)$ presents a extremely small *non-convex* region whose physical origin is not yet well understood. Furthermore, we have investigated (Angulo and Dehesa [9]) both rigorously and numerically the monotonicity property of nth-degree of $\rho(r)$ with n going zero (positivity) through infinite (complete monotonicity). We found, in particular, that the only neutral atom with a $\rho(r)$ completely monotone ($n \to \infty$) is hydrogen. Several effects of these monotonicity properties on some atomic quantities such as the electron density and its derivatives at the nucleus, $\rho^{(n)}(0)$, and the radial expectation values

$$\langle r^m \rangle = \int r^m \rho(\mathbf{r})\, d\mathbf{r}, \quad \text{for } m \geqq -3 \tag{2}$$

were also analysed.

Simultaneously, we have investigated both rigorous and numerically the property of logarithmic convexity (Angulo and Dehesa [10]) of the atomic charge density, showing that H and He are the only two atoms with a log-convex $\rho(r)$.

Here, we will extend the study of monotonicity properties of atomic systems far beyond this situation. Indeed, first of all we will investigate both analytically (see Sect. II) and numerically (see Sect. III) the monotonicity properties of the atomic charge density function

$$g_n(r;\alpha) = r^{-\alpha} f_n(r), \quad \text{for } \alpha \geqq 0. \tag{3}$$

Then, in Sect. IV we will give rigorous conditions to be fulfilled by the electron density $\rho(r)$ so that the atomic electron function $g_n(r;\alpha)$ is monotone of order p, i.e. the non-negativity condition

$$G_{np}(r;\alpha) = (-1)^p g_n^{(p)}(r;\alpha) \geqq 0, \tag{4}$$

where p is any, but fixed, non-negative integer number, and $g_n^{(p)}(r;\alpha)$ denotes the pth-derivative of the g_n-function. These conditions will be obtained by means of the so-called Stieltjes moment-problem technique (Shohat and Tamarkin [11]), already used by the authors in atomic physics (Angulo and Dehesa [9], Angulo et al. [12]), and they will be expressed in terms of the radial expectation values $\langle r^m \rangle$. Also, in Sect. III it is numerically shown that there actually exists a value $\alpha = \alpha_{np}$ from which the condition (4) is satisfied, that is the electron function $g_n(r;\alpha)$ is monotone of pth-order for each atom at the ground state.

II. Analytical study of charge monotonicity

In this section, we investigate the monotonicity of pth-order of the atomic charge function $g_n(r;\alpha)$ in an analytical way. First we give the conditions to be fulfilled by the α-values so that $g_n(r;\alpha)$ be p-monotonic, and then we found analytical bounds for some α-values via the nuclear charge Z and the first ionization potential I of the atomic system under consideration.

- Let us begin with the assumption that the condition (4) is fulfilled. Working out the pth-derivation of $g_n(r;\alpha)$ one has

$$G_{np}(r;\alpha) = (-1)^{p+n} \frac{p!}{\Gamma(\alpha)} \sum_{k=0}^{p} \times (-1)^k \frac{\Gamma(\alpha+k)}{k!(p-k)!} r^{-\alpha-k} \rho^{(n+p-k)}(r) \tag{5}$$

for each $n, p = 0, 1, 2, \ldots$, and any $\alpha \geqq 0$. Remark that all the nth to the $(n+p)-$th derivatives of $\rho(r)$ appear in the expression of the function $G_{np}(r;\alpha)$. Let us examine only the cases corresponding to the first three lowest values of n.

1. Case $n=0$. Since $f_0(r) = \rho(r)$ and $g_0(r;\alpha) = r^{-\alpha}\rho(r)$, then

$$G_{0p}(r;\alpha) = (-1)^p \frac{d^p}{dr^p}\left[\frac{\rho(r)}{r^\alpha}\right]. \tag{6}$$

The non-negativity of this function fully describes the monotonicity properties of the charge function $r^{-\alpha}\rho(r)$. According to the inequality (4) and (5), one realizes that the condition

$$(-1)^p \frac{p!}{\Gamma(\alpha)} \sum_{k=0}^{p} \times (-1)^k \frac{\Gamma(\alpha+k)}{k!(p-k)!} \frac{1}{r^{\alpha+k}} \frac{d^{p-k}\rho(r)}{dr^{p-k}} \geqq 0 \tag{7}$$

defines a value α_{0p} such that for $\alpha \geqq \alpha_{0p}$ the charge function $r^{-\alpha}\rho(r)$ is monotone of order p. It is interesting to notice that the inequality (7) reduces to

$$p=0, \quad \rho(r) \geqq 0,$$
$$p=1, \quad \alpha\rho(r) - r\rho'(r) \geqq 0,$$
$$p=2, \quad r^2\rho''(r) - 2\alpha r\rho'(r) + \alpha(\alpha+1)\rho(r) \geqq 0,$$

and so on. These expressions show that

$$\alpha_{00} = 0, \quad \alpha_{01} = \max\left\{\frac{r\rho'(r)}{\rho(r)}\right\}, \quad \alpha_{02} = \max\{q_0(r)\}, \tag{8}$$

where

$$q_0(r) = \begin{cases} \dfrac{1}{2\rho(r)}\{2r\rho'(r) - \rho(r) + \lambda_0^{\frac{1}{2}}\}, & \text{if } \lambda_0 \geqq 0, \\ 0, & \text{if } \lambda_0 < 0, \end{cases} \tag{9}$$

and $\lambda_0 \equiv [2r\rho'(r) - \rho(r)]^2 - 4r^2\rho(r)\rho''(r)$. Then, apart from the well-known quantum-mechanical non-negativity character of $r^{-\alpha}\rho(r)$, one obtains two important characteristics of the charge density $\rho(r)$:

- The function $r^{-\alpha}\rho(r)$ with $\alpha \geqq \alpha_{01}$ is monotone of first order, i.e. unimodal with mode at the origin. This tells us that it is monotonically decreasing from the origin.
- The function $r^{-\alpha}\rho(r)$ with $\alpha \geqq \alpha_{02}$ is monotone of second order, i.e. it has the property of convexity.

2. Case $n=1$. Here $f_1(r) = -\rho'(r)$ and $g_1(r;\alpha) = -r^{-\alpha}\rho'(r)$. Then, one has that

$$G_{1p}(r;\alpha) = (-1)^p \frac{d^p}{dr^p}\left[\frac{-\rho'(r)}{r^\alpha}\right] \geqq 0. \tag{10}$$

This condition or equivalently, according to (5), the inequality

$$(-1)^{p+1} \frac{p!}{\Gamma(\alpha)} \sum_{k=0}^{p} \times (-1)^k \frac{\Gamma(\alpha+k)}{k!(p-k)!} \frac{\rho^{(p-k+1)}(r)}{r^{\alpha+k}} \geqq 0$$

allows to calculate the value α_{1p} so that for $\alpha \geqq \alpha_{1p}$ the charge function $-r^{-\alpha}\rho'(r)$ is monotone of order p. For the first lowest values of p, this inequality reduces as

$$p=0, \quad -\rho'(r) \geqq 0,$$
$$p=1, \quad r\rho''(r)-\alpha\rho'(r) \geqq 0,$$
$$p=2, \quad -r^2\rho'''(r)+2\alpha r\rho''(r)-\alpha(\alpha+1)\rho'(r) \geqq 0,$$

and so on. These expressions show that

$$\alpha_{10}=0, \quad \alpha_{11}=\max\left\{-\frac{r\rho''(r)}{\rho'(r)}\right\},$$
$$\alpha_{12}=\max\{q_1(r)\}, \tag{11}$$

where

$$q_1(r)=\begin{cases}\dfrac{1}{2\rho'(r)}\{2r\rho''(r)-\rho'(r)-\lambda_1^{\frac{1}{2}}\}, & \text{if } \lambda_1 \geqq 0,\\ 0, & \text{if } \lambda_1<0,\end{cases} \tag{12}$$

and $\lambda_1 \equiv [2r\rho''(r)-\rho'(r)]^2-4r^2\rho'(r)\rho'''(r)$. Then, one has two additional properties of the charge density $\rho(r)$:

- The function $-r^{-\alpha}\rho'(r)$ with $\alpha \geqq \alpha_{11}$ is monotonically decreasing from the origin, and
- The function $-r^{-\alpha}\rho'(r)$ with $\alpha \geqq \alpha_{12}$ is convex everywhere.

3. Case $n=2$. Now, $f_2(r)=\rho''(r)$ and $g_2(r;\alpha)=r^{-\alpha}\rho''(r)$. Then one has that

$$G_{2p}(r;\alpha)=(-1)^p\frac{d^p}{dr^p}\left[\frac{\rho''(r)}{r^\alpha}\right] \geqq 0. \tag{13}$$

Equation (5) shows that this condition transforms into

$$(-1)^p\frac{p!}{\Gamma(\alpha)}\sum_{k=0}^{p}$$
$$\times(-1)^k\frac{\Gamma(\alpha+k)}{k!(p-k)!}\frac{\rho^{(p-k+2)}(r)}{r^{\alpha+k}} \geqq 0,$$

which allows to find, for those atoms having a convex $\rho(r)$, the value α_{2p} such that for $\alpha \geqq \alpha_{2p}$ the charge function $r^{-\alpha}\rho''(r)$ is monotone of pth-order. This inequality simplifies for the first lowest values of p as follows:

$$p=0, \quad \rho''(r) \geqq 0,$$
$$p=1, \quad \alpha\rho''(r)-r\rho'''(r) \geqq 0,$$
$$p=2, \quad r^2\rho^{\mathrm{IV}}(r)-2\alpha r\rho'''(r)+\alpha(\alpha+1)\rho''(r) \geqq 0,$$

and so on. These expressions show that, for convex atoms,

$$\alpha_{20}=0, \quad \alpha_{21}=\max\left\{\frac{r\rho'''(r)}{\rho''(r)}\right\},$$
$$\alpha_{22}=\max\{q_2(r)\}, \tag{14}$$

where

$$q_2(r)=\begin{cases}\dfrac{1}{2\rho''(r)}\{2r\rho'''(r)-\rho''(r)-\lambda_2^{\frac{1}{2}}\}, & \text{if } \lambda_2 \geqq 0,\\ 0, & \text{if } \lambda_2<0,\end{cases} \tag{15}$$

and $\lambda_2 \equiv [2r\rho'''(r)-\rho''(r)]^2-4r^2\rho''(r)\rho^{\mathrm{IV}}(r)$. Then, two new properties of the charge density are found: the function $r^{-\alpha}\rho''(r)$ is (i) monotonically decreasing from the origin for $\alpha \geqq \alpha_{21}$ and (ii) convex everywhere for $\alpha \geqq \alpha_{22}$.

- Now we are going to show how to obtain analytical bounds to the α-values. To extend an important result of Hoffmann-Ostenhof and Hoffman-Ostenhof [13] according to which the charge density $\rho(r)$ is convex outside a sphere of radius Z/I (I being the first ionization potential), our attention is centered around the value of α_{02}. We have found that

$$\alpha_{02} \leqq \tfrac{1}{2}\left[\left(1+\frac{4Z^2}{I}\right)^{1/2}-1\right]. \tag{16}$$

To obtain this upper bound we start from the known inequation (Hoffmann-Ostenhof and Hoffman-Ostenhof [13])

$$-\tfrac{1}{2}u''+\left(I-\frac{Z}{r}\right)u \leqq 0,$$

for $u(r)=r[\rho(r)]^{1/2}$, which is valid in the infinite nuclear-mass approximation. We rewrite it in terms of the charge function $g_0(r;\alpha) \equiv r^{-\alpha}\rho(r)$ as

$$2r^2g_0g_0'' \geqq r^2g_0'^2+8Ir^2g_0^2-8Zrg_0^2$$
$$-\alpha(\alpha+2)g_0^2-2(\alpha+2)rg_0g_0'.$$

Then, taking into account that $\rho'(r) \leqq 0$, i.e. that $0 \leqq \alpha g_0 \leqq -rg_0'$, one reduces this inequality to

$$r^2\frac{g_0''}{g_0} \geqq 4Ir^2-4Zr+\alpha(\alpha+1),$$

so that g_0'' is positive for any value of r for α-values bigger than $[(1+4Z^2/I)^{1/2}-1]/2$. Since α_{02} is by definition, the minimum α-value from which $r^{-\alpha}\rho(r)$ is convex everywhere, then the inequality (16) follows.

Therefore, the charge function $r^{-\alpha}\rho(r)$ is, indeed, convex everywhere for any $\alpha \geqq [(1+4Z^2/I)^{1/2}-1]/2$. We should emphasize that much more effort should be spent to bound analytically other values of α_{np}. This woul help to gain much more insight into the charge monotonicity of the atomic systems, thus into their internal structure.

III. Numerical study of atomic charge monotonicity

The performance of numerical calculations based on the near Hartree-Fock wavefunctions of Clementi-Roetti [14] for all ground-state atoms, Hydrogen through Xenon, allows to find not only that $\alpha_{01} = \alpha_{10} = 0$ for all atoms (what indicates the monotonicity of first degree studied by many authors (Sperber [4], Weinstein et al. [5], Simas et al. [6], Angulo [7]) as already mentioned) but also the values of α_{02}, α_{11}, α_{12}, α_{21} and α_{22}. They are given in Table 1. A few observations may be readily made:

Table 1. Values of α_{02}, α_{11}, α_{12}, α_{21} and α_{22} for all neutral atoms, $1 \leqq Z \leqq 54$, obtained with Clementi-Roetti near-Hartree-Fock wavefunctions. The atomic density function $g_n(r;\alpha) = (-1)^n \rho^{(n)}(r) r^{-\alpha_{np}}$ is monotone of order p

Z	α_{02}	α_{11}	α_{12}	α_{21}	α_{22}
1	0.00000	0.00000	0.00000	0.00000	0.00000
2	0.00000	0.00000	0.00000	0.00000	0.00000
3	0.24820	0.76950	2.62566		
4	0.36165	1.22097	3.19750		
5	0.17110	0.52396	2.23153		
6	0.02016	0.05745	1.58678		
7	0.00000	0.00000	1.18589	8.35102	13.31590
8	0.00000	0.00000	0.91417	4.44487	7.85389
9	0.00000	0.00000	0.73114	3.01519	5.86426
10	0.00000	0.00000	0.59913	2.25093	4.78672
11	0.00000	0.00000	0.55849	2.04399	4.49240
12	0.00000	0.00000	0.57471	2.09190	4.53863
13	0.00000	0.00000	0.65869	2.12023	5.20914
14	0.00000	0.00000	1.26988	6.03374	10.54796
15	0.00000	0.00000	1.83298	26.23035	38.90220
16	0.49656	1.62042	4.12545		
17	0.18169	0.51373	2.58432		
18	0.28710	0.85423	3.02874		
19	0.34115	1.02885	3.28163		
20	0.37310	1.12608	3.43595		
21	0.35476	1.06745	3.35030		
22	0.32055	0.95563	3.19568		
23	0.28570	0.84317	3.03528		
24	0.21465	0.61551	2.71845		
25	0.21130	0.60288	2.69828		
26	0.17429	0.49506	2.53588		
27	0.13341	0.37334	2.36802		
28	0.09668	0.26645	2.22206		
29	0.04397	0.11944	2.01390		
30	0.03084	0.08273	1.96008		
31	0.01626	0.04366	1.91781		
32	0.00504	0.01343	1.87374		
33	0.00000	0.00000	1.85052	95.75753	159.56496
34	0.00000	0.00000	1.81100	33.97675	53.29167
35	0.00000	0.00000	1.84148	42.80330	70.13453
36	0.00000	0.00000	1.84652	46.24841	68.20616
37	0.00000	0.00000	1.77375	24.89784	34.87495
38	0.00000	0.00000	1.81469	27.90172	42.21412
39	0.00000	0.00000	1.77261	22.28058	33.03348
40	0.00000	0.00000	1.76633	20.52939	29.75565
41	0.00000	0.00000	1.73982	17.57648	25.95925
42	0.00000	0.00000	1.70677	15.25819	22.98737
43	0.00000	0.00000	1.93390	14.43761	22.50102
44	0.00000	0.00000	2.24874	78.33496	112.73189
45	0.08691	0.22837	2.55888		
46	0.17695	0.48156	2.86983		
47	0.24287	0.67307	3.12267		
48	0.31717	0.90145	3.44484		
49	0.36752	1.06153	3.64821		
50	0.40826	1.19324	3.83024		
51	0.44508	1.31973	4.00670		
52	0.47967	1.42030	4.16121		
53	0.50337	1.51612	4.28040		
54	0.53624	1.62106	4.43827		

1. From (7) and the second column of Table 1 which gives the values of α_{02}, one concludes that the charge density $\rho(r)$ is convex for atoms with $Z = 1, 2, 7$–15 and 33–44. For the rest of atoms with $Z \leqq 54$, one has that $r^{-\alpha_{02}} \rho(r)$, with $0 < \alpha_{02} < 0.54$, is convex. It indicates that, in such cases, convexity is violated, although very weakly. A detailed analysis of the corresponding non-convexity region of these atoms has been recently carried out (Angulo et al. [8]).
2. Equation (10) together with the values of α_{11} given in the third column of Table 1 once again show the convexity of $\rho(r)$ in the above mentioned atomic region of the periodic table since, in such a region, $G_{11}(r; \alpha_{11} = 0) = \rho''(r)$. For the rest of atoms with $Z \leqq 54$ one has that the charge function $-r^{-\alpha_{11}} \rho(r)$ is monotonically decreasing from the origin where the value of α_{11} varies from 0.01 (Ge) to 1.62 (S, Xe). In addition, the values of α_{12} in the fourth column allow to gain further insight into the structure of the atomic charge density. Indeed, α_{12} vanishes only for H and He; so, $G_{12}(r; \alpha_{12} = 0) = -\rho'''(r) \geqq 0$. Then, these two atoms are the only ones having a charge density $\rho(r)$ with the property of monotonicity of third degree. Furthermore, for the atoms with $Z \leqq 54$ the charge function $-r^{-\alpha_{12}} \rho'(r)$ is convex and the values of α_{12} varies from 0.558 (Na) to 4.438 (Xe).
3. The fifth and sixth columns give the values of α_{21} and α_{22}. These values together with (13) suggest a few comments. Since $\alpha_{21} = 0$ for the two lightest atoms and $G_{21}(r; 0) = -r\rho'''(r) \geqq 0$, then the monotonicity of third order of $\rho(r)$ of H and He is again found, coherently with the previous paragraph. Besides, $\alpha_{22} = 0$ for H and He. This indicates that the H and He have a charge density with the stronger property of monotonicity of fourth order. Additionally, the charge function $r^{-\alpha} \rho''(r)$ is not only (i) monotonically decreasing from the origin in the regions with $7 \leqq Z \leqq 15$ for α varying from 2.04 (Na) to 26.23 (P) and with $33 \leqq Z \leqq 44$ for α going from 14.44 (Tc) to 95.76 (As), but also (ii) convex with $7 \leqq Z \leqq 15$ for α varying from 4.49 (Na) to 38.90 (P) and with $33 \leqq Z \leqq 44$ for α much less than 100 except in the As and Ru cases. Finally, let us also say that in the atomic regions $3 \leqq Z \leqq 6$, $16 \leqq Z \leqq 32$ and $45 \leqq Z \leqq 54$ the charge function $r^{-\alpha} \rho''(r)$ cannot be neither convex nor monotonically decreasing from the origin.

IV Charge monotonicity effects: Inequalities among radial expectation values

Once we have seen that there really exist atomic systems with a charge function $g_n(r;\alpha)$ having the property of monotonicity of order $p = 0, 1, 2, \ldots$, i.e. satisfying (4), we will search its effects on the charge density $\rho(r)$ itself. This shall be done by means of the so-called Stieltjes moment-problem technique (Shohat and Tamarkin [11]) which has been recently (Angulo et al. [8], Angulo and Dehesa [9], Angulo et al. [12], Dehesa et al. [15]) proved to be very useful to gain physical insight in the internal structure of many-electron systems.

Let us apply the Stieltjes technique (Shohat and Tamarkin [11]) to the non-negative function $r^m G_{np}(r;\alpha)$ for any real m. It states that the moments of that function, i.e. the quantities

$$\nu_j \equiv \nu_j(\alpha,n,p,m) = \int_0^\infty r^{j+m} G_{np}(r;\alpha)\,\mathrm{d}r$$
$$= (-1)^{p+n} \int_0^\infty r^{j+m} \frac{\mathrm{d}^p}{\mathrm{d}r^p}\left(\frac{\rho^{(n)}(r)}{r^\alpha}\right)\mathrm{d}r \tag{17}$$

must satisfy the following Hadamard determinantal inequalities:

$$\Delta_k^{(i)} \geqq 0, \quad \text{for } i=0,\ 1 \quad\text{and}\quad k=0,\ 1,\ 2,\ldots, \tag{18}$$

where

$$\Delta_k^{(i)} = \begin{vmatrix} \nu_{m+i} & \nu_{m+i+1} & \cdots & \nu_{m+i+k} \\ \nu_{m+i+1} & \nu_{m+i+2} & \cdots & \nu_{m+i+k+1} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{m+i+k} & \nu_{m+i+k+1} & \cdots & \nu_{m+i+2k} \end{vmatrix}. \tag{19}$$

The moments ν_j given by (17) can be expressed in terms of the radial expectation values $\langle r^\beta \rangle$ as given by

$$\nu_j = \frac{p!\,\Gamma(n+t+3)\,\Gamma(n+t+\alpha+p+3)}{4\pi\Gamma(n+t+\alpha+3)\,\Gamma(t+3)}\langle r^t \rangle, \quad \text{if } t > -3, \tag{20}$$

where $t = j+m-\alpha-p-n-2$. The expressions (18) and (19) together with the values of the moments given by (20) lead to a huge variety of infinite new and rigorous relationships among various radial expectation values $\langle r^t \rangle$. Let us only consider the simplest case, i.e. $i=0$, $k=1$ and $m=0$. Then, one has that $\nu_0\nu_2 \geqq \nu_1^2$ which produces a fundamental inequality involving three radial expectation values as

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq F_n(q,\alpha_{np},p)\langle r^{q-1}\rangle^2, \quad q > -1, \tag{21}$$

with $n=0,\ 1,\ 2,\ldots$, $p=0,\ 1,\ 2,\ldots$ and

$$F_n(q,\alpha_{np},p) = \frac{(q+2)(n+q+1)(n+q+\alpha_{np}+2)(n+q+\alpha_{np}+p+1)}{(q+1)(n+q+2)(n+q+\alpha_{np}+1)(n+q+\alpha_{np}+p+2)}. \tag{22}$$

Also, the optimal value α_{np} (i.e. the minimal value of α which satisfies the inequality (4) for given n and p) has been taken into account. One should realize that α_{np} depends not only on n and p but also on the specific system that one is dealing with. It is interesting to point out that

$$\alpha_{np} \leqq \alpha_{n,p+1} \leqq \alpha_{n+1,p}, \tag{23}$$

and then

$$\alpha_{n,n+k} \leqq \alpha_{n+k,n} \quad \text{for} \quad k=0,\ 1,\ldots \tag{24}$$

In case that $\alpha_{np}\to\infty$ or when $p=0$, i.e. just using the positivity condition of $g_n(r;\alpha) = (-1)^n \rho^{(n)}(r)$, then the inequality (21) transforms into

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)(n+q+1)}{(q+1)(n+q+2)}\langle r^{q-1}\rangle^2. \tag{25}$$

Since the accuracy of this inequality increases with n for a fixed q, then the optimality will be obtained for $n\to\infty$, in which case one has

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{q+2}{q+1}\langle r^{q-1}\rangle^2, q > -1. \tag{26}$$

The relationships (4)–(15) as well as (21)–(22) and any inequality among a number of values $\langle r^t \rangle$ other than three obtained from (18)–(20), are universal in the sense that they are valid for both ground and excited states of any physical system. Furthermore, the inequality (21) strongly generalizes and improves all the similar ones (Angulo and Dehesa [9], Angulo and Dehesa [10], Tsapline [16], Blau et al. [17], Gadre [18], Gadre and Matcha [19], Gálvez [20]) which have appeared in the literature, to the best of our information.

Let us consider some particular cases of the inequality (21):

1. Case $n=0$. Then, $g_0(r;\alpha) = r^{-\alpha}\rho(r)$ is assumed to be monotone of order p. The inequality (21) simplifies as

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq F_0(q,\alpha_p,p)\langle r^{q-1}\rangle^2, q > -1, \tag{27}$$

with

$$F_0(q,\alpha_p,p) = \frac{(q+\alpha_p+2)(q+\alpha_p+p+1)}{(q+\alpha_p+1)(q+\alpha_p+p+2)}, \tag{28}$$

where $\alpha_p \equiv \alpha_{0p}$. Some particular subcases are

$$q=0, \quad N\langle r^{-2}\rangle \geqq \frac{(\alpha_p+2)(\alpha_p+p+1)}{(\alpha_p+1)(\alpha_p+p+2)}\langle r^{-1}\rangle^2, \tag{29}$$

$$q=1, \quad \langle r^{-1}\rangle\langle r\rangle \geqq \frac{(\alpha_p+3)(\alpha_p+p+2)}{(\alpha_p+2)(\alpha_p+p+3)}N^2, \tag{30}$$

$$q=2, \quad N\langle r^2\rangle \geqq \frac{(\alpha_p+4)(\alpha_p+p+3)}{(\alpha_p+3)(\alpha_p+p+4)}\langle r\rangle^2. \tag{31}$$

Notice that we have used $\langle r^0 \rangle = N$, the number of particles of the system.On the other hand, for $\alpha_p=0$, i.e. when $g_0(r;\alpha) = \rho(r)$, which corresponds to the case of a charge density $\rho(r)$ of monotonicity of order p, the inequality (27) reduces to

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)(q+p+1)}{(q+1)(q+p+2)}\langle r^{q-1}\rangle^2, \quad q > -1 \quad\text{and}\quad p=0,\ 1,\ 2,\ldots \tag{32}$$

This particular result has been recently found by the authors (Angulo and Dehesa [9]) and shown to generalize all the known inequalities involving three successive radial expectation values (Tsapline [16], Blau et al. [17], Gadre [18], Gadre and Matcha [19], Gálvez [20]).

It is important to remark that for completely monotonic electron densities, i.e. for $p\to\infty$, the inequality (32) takes on the form (26). This is a consequence of the fact that the requirement of positivity of $(-1)^n \rho^{(n)}(r)$ for all n's is equivalent to the assumption of complete monotonicity for $\rho(r)$. In addition one should say here that the inequality (26) has been discussed recently by the authors (Angulo and Dehesa [9]) in both theoretical and numerical senses.

2. *Case* $n=1$. Then $g_1(r;\alpha) = -r^{-\alpha}\rho'(r)$ is assumed to be monotone of order p. The inequality (21) reduces as

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq F_1(q,\alpha_{1p},p)\langle r^{q-1}\rangle^2, q>-1, \tag{33}$$

with

$$F_1(q,\alpha_{1p},p) = \frac{(q+2)^2(q+\alpha_{1p}+3)(q+\alpha_{1p}+p+2)}{(q+1)(q+3)(q+\alpha_{1p}+2)(q+\alpha_{1p}+p+3)}. \tag{34}$$

Some particular subcases are

$$q=0, \quad N\langle r^{-2}\rangle \geqq \frac{4(\alpha_{1p}+3)(\alpha_{1p}+p+2)}{3(\alpha_{1p}+2)(\alpha_{1p}+p+3)}\langle r^{-1}\rangle^2, \tag{35}$$

$$q=1, \quad \langle r^{-1}\rangle\langle r\rangle \geqq \frac{9(\alpha_{1p}+4)(\alpha_{1p}+p+3)}{8(\alpha_{1p}+3)(\alpha_{1p}+p+4)}N^2, \tag{36}$$

$$q=2, \quad N\langle r^2\rangle \geqq \frac{16(\alpha_{1p}+5)(\alpha_{1p}+p+4)}{15(\alpha_{1p}+4)(\alpha_{1p}+p+5)}\langle r\rangle^2. \tag{37}$$

Notice that with the only requirement of positivity for $-\rho'(r)$ or, what is equivalent, for monotonically decreasing densities $\rho(r)$, one is led to

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)^2}{(q+1)(q+3)}\langle r^{q-1}\rangle^2, \quad q>-1, \tag{38}$$

what was recently found by the authors (Angulo and Dehesa [9]).

On the other hand, for $\alpha_{1p}=0$, i.e. when $g_1(r;\alpha) = -\rho'(r)$ is monotone of order p, then the inequality (33) reduces as

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)(q+p+2)}{(q+1)(q+p+3)}\langle r^{q-1}\rangle^2, \quad q>-1. \tag{39}$$

This inequality was recently found (Angulo and Dehesa [9]) only for the particular value $p=1$, which corresponds to the first order monotonicity of $-\rho'(r)$ or, what is equivalent, to a convex $\rho(r)$. In addition, let us point out that the comparison between the inequalities (32) and (39) shows that the latter one is more accurate than the former one for fixed values of p and q. This is because the pth-order monotonicity for $-\rho'(r)$ is a requirement stronger than the corresponding one for $\rho(r)$. The improvement factor in going from (32) to (39) is

$$I_0 \equiv \frac{(q+p+2)^2}{(q+p+1)(q+p+3)} \geqq 1, \tag{40}$$

which varies from 1.333 for $q+p=0$ to 1 for $q+p=\infty$.

3. *Case* $n=2$. Then $g_2(r;\alpha) = r^{-\alpha}\rho''(r)$ is assumed to be monotone of order p. The inequality (21) reduces as

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq F_2(q,\alpha_{2p},p)\langle r^{q-1}\rangle^2, q>-1, \tag{41}$$

with

$$F_2(q,\alpha_{2p},p) = \frac{(q+2)(q+3)(q+\alpha_{2p}+4)(q+\alpha_{2p}+p+3)}{(q+1)(q+4)(q+\alpha_{2p}+3)(q+\alpha_{2p}+p+4)}. \tag{42}$$

Some particular subcases are

$q=0$,

$$N\langle r^{-2}\rangle \geqq \frac{3(\alpha_{2p}+4)(\alpha_{2p}+p+3)}{2(\alpha_{2p}+3)(\alpha_{2p}+p+4)}\langle r^{-1}\rangle^2, \tag{43}$$

$q=1$,

$$\langle r^{-1}\rangle\langle r\rangle \geqq \frac{6(\alpha_{2p}+5)(\alpha_{2p}+p+4)}{5(\alpha_{2p}+4)(\alpha_{2p}+p+5)}N^2, \tag{44}$$

$q=2$,

$$N\langle r^2\rangle \geqq \frac{10(\alpha_{2p}+6)(\alpha_{2p}+p+5)}{9(\alpha_{2p}+5)(\alpha_{2p}+p+6)}\langle r\rangle^2. \tag{45}$$

With $p=0$ one has

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)(q+3)}{(q+1)(q+4)}\langle r^{q-1}\rangle^2, \quad q>-1, \tag{46}$$

which is satisfied by any convex density $\rho(r)$.

On the other hand, let us point out that for $\alpha_{2p}=0$, i.e. when $g_2(r;\alpha)=\rho''(r)$ is monotone of order p, the inequality (41) gets transformed into

$$\langle r^{q-2}\rangle\langle r^q\rangle \geqq \frac{(q+2)(q+p+3)}{(q+1)(q+p+4)}\langle r^{q-1}\rangle^2, \quad q>-1. \tag{47}$$

The particular case $p=0$ (which means to consider that $\rho''(r)$ is positive or, what is the same, that $\rho(r)$ is convex) has been recently found (Angulo and Dehesa [9]).

Let us now compare the inequalities (32), (39) and (47) for fixed values of p and q. The inequality (47) is more accurate than the inequality (32) by a factor

$$e_1 \equiv \frac{(q+p+2)(q+p+3)}{(q+p+1)(q+p+4)} \geqq 1,$$

which goes from 1.5 when $q+p=0$ down to 1 for $q+p$ And it is more accurate than inequality (39) by a factor

$$e_2 \equiv \frac{(q+p+3)^2}{(q+p+2)(q+p+4)} \geqq 1,$$

which varies from 1.125 for $q+p=0$ to 1 for $q+p=\infty$.

Finally, let us point out that the quality of the inequalities found in this section depends much on the specific atom and the order of monotonicity of its groundstate density taken into account in each case. To give an idea of it, we have calculated the accuracy of the inequalities (30), (36) and (44) for $p=2$ in all the atoms with nuclear charge $1 \leqq Z \leqq 54$. It is found that the accuracy is around 80% in H and He for all three inequalities and then it decreases with increasing Z but it is always bigger than 26.5%.

V. Concluding remarks

To summarize, the montonicity properties of the atomic electron density $(-1)^n \rho^{(n)}(r) r^{-\alpha}, \alpha \geqq 0$, are investigated. We find, as particular cases, the values α_{np} of α for which the functions $r^{-\alpha_{0p}} \rho(r)$, $-r^{-\alpha_{1p}} \rho'(r)$ and $r^{-\alpha_{2p}} \rho''(r)$ are monotonically decreasing from the origin (i.e. monotone of order $p=1$) and convex (i.e. monotone of order $p=2$). These values are numerically evaluated in a Hartree-Fock framework for all ground-state atoms with $Z \leqq 54$. It is found that $\alpha_{01}=0$, $0 \leqq \alpha_{02} \leqq 0.54$, $0 \leqq \alpha_{11} \leqq 1.63$, $0 \leqq \alpha_{12} \leqq 4.44$ and, if exist, $0 \leqq \alpha_{21} < 100$ and $0 \leqq \alpha_{22} < 100$ except for $Z=33$ and 44 where $\alpha_{22} > 100$.

Finally, we make use of the above mentioned monotonicity properties of order p to obtain simple, compact and universal inequalities among three radial expectation values of contiguous orders. These inequalities generalize all the previous published in the literature, to the best of our information. They are specially remarkable because these expectation values may be often experimentally measurable by means of, among others, experiments of $(e, 2e)$-type and represent some statical and dynamical quantities of the atomic system under consideration.

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