Electron-pair logarithmic convexity and interelectronic moments in atoms: Application to heliumlike ions

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The electron-pair function $h(u)$ of a finite many-electron system is not monotonic, but the related quantity $h(u)/u^\alpha$, $\alpha>0$, is not only monotonically decreasing from the origin but also convex for the values α_1 and α_2, respectively, as has been recently found. Here, it is first argued that this quantity is also logarithmically convex for any $\alpha \geq \alpha'$ with $\alpha'=\max\{-u^2 d^2[\ln h(u)]/du^2\}$. Then this property is used to obtain a general inequality which involves three interelectronic moments $\langle u^t \rangle$. Particular cases of this inequality involve relevant characteristics of the system such as the number of electrons and the total electron-electron repulsion energy. Second, the logarithmic-convexity property of $h(u)$ as well as the accuracy of this inequality are investigated by the optimum 20-term Hylleraas-type wave functions for two-electron atoms with nuclear charge $Z=1$, 2, 3, 5, and 10. It is found that (i) $14<\alpha'<20$ for these atomic cases (we remark that $\alpha' \gg \alpha_2 \gg \alpha_1$) and (ii) the accuracy of the inequality which involves moments of contiguous orders oscillates between 62.4% and 96.7% according to the specific He-like atom and the moments involved. Finally, the importance of the logarithmic-convexity effects on the interelectronic moments relative to those coming from other monotonicity properties of $h(u)/u^\alpha$ are analyzed in the same numerical Hylleraas framework.

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The electron correlation properties of atomic and molecular systems require [1,2] a deep knowledge of the structural properties of the spherically averaged electron-pair density $h(u)$, u being the interelectronic distance, i.e.,

$$h(u)=\frac{1}{4\pi}\int I(\mathbf{u})d\Omega_u ,$$

where $I(\mathbf{u})$ is the three-dimensional electron-pair density [2] and $\mathbf{u}=(u,\Omega_u)$. This univariate density function is positive and displays a global maximum located away from the origin [3], generally speaking. No other monotonicity property of $h(u)$ is known, to the best of our information. Recently, the monotonicity properties of the related function

$$g_\alpha(u)=\frac{h(u)}{u^\alpha} , \quad \alpha>0 \tag{1}$$

have been explored [4]. It has been found that this function is monotonically decreasing from the origin and convex for some α values α_1 and α_2, respectively, given by

$$\alpha_1=\max\left\{u\frac{h'(u)}{h(u)}\right\} , \quad \alpha_2=\max\{f(u)\} , \tag{2}$$

where

$$f(u)=\frac{1}{2h(u)}(2uh'(u)-h(u)+\{[h(u)-2uh'(u)]^2 -4u^2h''(u)h(u)\}^{1/2}) .$$

Here, we will *first* study the logarithmic convexity of $h(u)$, which is a property much stronger than convexity. That property requires the following non-negativity condition:

$$\frac{d^2\ln g_\alpha(u)}{du^2}\geq 0 .$$

This inequality together with Eq. (1) allows us to show that there always exists a minimal value $\alpha'\geq 0$ such that the interelectronic function $g_\alpha(u)$ with $\alpha\geq\alpha'$ is logarithmically convex and that

$$\alpha'=\max\left\{-u^2\frac{d^2\ln h(u)}{du^2}\right\} . \tag{3}$$

To have an idea about the value of α', we have numerically evaluated it for several He-like atoms with nuclear charge $Z=1$, 2, 3, 5, and 10. We have used the optimum 20-term Hylleraas-like wave functions [5], which have been shown to describe various global [5,6] and local [7,8] interelectronic properties with sufficiently high accuracy. In Table I we give the values of not only α' but also, for comparison, α_1 and α_2. One notices that in this atomic sample it is fulfilled that

$$14<\alpha'<20 , \quad 0.0016<\alpha_1<0.1658, \quad 0.10<\alpha_2<0.39 .$$

That is, $\alpha'\gg\alpha_2\gg\alpha_1$ for each atom. It is worthy to point out that here the 20-term Hylleraas wave functions of Ref. [4] were optimized in the sense detailed in Ref. [5]. This is why there are some slight differences in the values of α_1 and α_2 when compared with those found in Ref. [4].

TABLE I. Values α_1, α_2, and α' of the α parameter for which the interelectronic function $h(u)/u^\alpha$ is monotonically decreasing from the origin, convex and logarithmically convex, respectively. The optimum 20-term Hylleraas-type wave functions for the two-electron atoms with nuclear charge $Z=1$, 2, 3, 5, and 10 were used.

Z	α_1	α_2	α'
1	0.165 765 502 0	0.387 816 835 1	16.830 232 50
2	0.042 242 671 68	0.208 200 497 1	16.000 000 00
3	0.018 789 978 58	0.160 957 513 1	14.048 862 47
5	0.006 907 329 203	0.128 499 932 4	19.680 477 01
10	0.001 628 679 058	0.106 181 220 8	16.375 684 17

Second, we will consider the effects of the aforementioned logarithmic-convexity property on some correlated dynamical quantities such as the interelectronic moments or radial expectation values defined by

$$\langle u^\beta \rangle = \int u^\beta I(\mathbf{u}) d\mathbf{u} = 4\pi \int_0^\infty u^{\beta+2} h(u) du \ , \quad \beta > -3 \ .$$

To do that we use a theorem pointed out by Karlin, Proschan, and Barlow [9] and we operate in a similar manner as indicated in Ref. [10]. One obtains the following general inequality:

$$[\langle u^{n+2m-2} \rangle]^a [\langle u^{n-2} \rangle]^{1-a} \geq F(a,m,n,\alpha') \langle u^{n+2am-2} \rangle \ , \tag{4}$$

where $m \geq 0$, $0 < a < 1$, $n > -1$, and

$$F(a,m,n,\alpha') = \frac{[\Gamma(n+\alpha'+2m+1)]^a [\Gamma(n+\alpha'+1)]^{1-a}}{\Gamma(n+\alpha'+2am+1)} \ .$$

Some particular cases are

$$[\langle u^n \rangle]^a [\langle u^{n-2} \rangle]^{1-a} \geq F(a,1,n,\alpha') \langle u^{n+2a-2} \rangle \quad (m=1) \ ,$$
$$[\langle u^{n+2} \rangle]^a [\langle u^{n-2} \rangle]^{1-a} \geq F(a,2,n,\alpha') \langle u^{n+4a-2} \rangle \quad (m=2) \ . \tag{5}$$

From inequality (4) one can extract a lot of physically useful information; e.g., the values $a=\frac{1}{2}$, $m=1$, and $n=1$ lead to

$$\langle u \rangle \langle u^{-1} \rangle \geq \frac{1}{4} \frac{\alpha'+3}{\alpha'+2} [N(N-1)]^2 \ , \tag{6}$$

which is the correlation inequality corresponding to the celebrated charge inequality $\langle r \rangle \langle r^{-1} \rangle \geq \frac{9}{8} N^2$ valid for any N-electron atom [11]. In writing (6) we have used the value $\langle u^0 \rangle = \frac{1}{2} N(N-1)$, which is the usual normalization of the electron-pair density $I(\mathbf{u})$. Besides, this inequality allows us to relate three important quantities of the system (the centroid of the electron-pair density $\langle u \rangle$, the total electron-electron repulsion energy $E_{ee} = \langle u^{-1} \rangle$,

TABLE II. Accuracy in percent of the inequality (4) with the integer $0 \leq n \leq 10$ for the two-electron atoms with nuclear charge $Z=1$, 2, 3, 5, and 10 and the four indicated sets of values (a,m). The optimum 20-term Hylleraas-type atomic wave functions were used.

Z \ n	0	1	2	3	4	5	6	7	8	9	10
					$a=\frac{1}{2}$, $m=1$						
1	81.12	87.64	90.22	91.70	92.85	93.97	95.09	96.15	97.06	97.79	98.35
2	80.41	88.59	91.97	93.85	95.05	95.88	96.49	96.96	97.33	97.63	97.89
3	80.12	88.65	92.15	94.07	95.29	96.13	96.75	97.21	97.58	97.87	98.11
5	79.00	87.77	91.42	93.44	94.73	95.63	96.30	96.81	97.22	97.55	97.83
10	79.02	87.97	91.66	93.70	94.99	95.88	96.53	97.03	97.42	97.73	97.99
					$a=\frac{1}{2}$, $m=2$						
1	56.22	65.41	70.44	74.29	77.97	81.70	85.32	88.57	91.29	93.43	95.06
2	58.04	70.33	77.01	81.31	84.33	86.56	88.29	89.67	90.81	91.78	92.63
3	58.02	70.81	77.71	82.13	85.20	87.47	89.21	90.58	91.69	92.62	93.40
5	55.64	68.54	75.61	80.19	83.44	85.86	87.75	89.26	90.51	91.55	92.44
10	56.05	69.25	76.44	81.05	84.29	86.69	88.53	90.00	91.18	92.15	92.96
					$a=\frac{1}{4}$, $m=2$						
1	60.83	70.88	75.72	79.04	81.99	84.94	87.84	90.49	92.73	94.53	95.89
2	61.25	74.29	80.71	84.63	87.29	89.21	90.67	91.82	92.75	93.53	94.21
3	61.03	74.59	81.23	85.25	87.96	89.91	91.38	92.52	93.44	94.19	94.82
5	58.93	72.66	79.49	83.67	86.53	88.62	90.21	91.47	92.49	93.34	94.06
10	59.16	73.21	80.14	84.36	87.21	89.27	90.83	92.05	93.02	93.82	94.48
					$a=\frac{3}{4}$, $m=2$						
1	67.64	74.16	77.93	81.00	83.97	86.91	89.65	92.03	93.97	95.47	96.60
2	70.07	78.71	83.41	86.46	88.61	90.21	91.45	92.45	93.28	93.99	94.61
3	70.19	79.16	84.01	87.12	89.30	90.92	92.16	93.15	93.95	94.62	95.18
5	68.19	77.35	82.37	85.64	87.96	89.71	91.07	92.17	93.07	93.83	94.47
10	68.63	77.97	83.05	86.32	88.63	90.34	91.66	92.71	93.57	94.27	94.86

and the number N of electrons); this is something which is extremely difficult to obtain otherwise.

To investigate the quality of the general inequality (4), we show in Table II the accuracy in percent of the inequalities corresponding to the cases

$$(a,m)=(\tfrac{1}{2},1)\ ,\quad (\tfrac{1}{2},2),\quad (\tfrac{1}{4},2)\ ,\quad (\tfrac{3}{4},2)$$

for the two-electron atoms with nuclear charge $Z=1$, 2, 3, 5, and 10, calculated in the aforementioned numerical Hylleraas framework. From this table, one observes that (i) for a given atom the accuracy increases with increasing n, oscillating between 55.64% and 98.35% in taking into account all the atoms of this work; (ii) the inequalities which involve moments of only non-negative order are specially accurate; (iii) the inequalities associated to the case $(a,m)=(\frac{1}{2},1)$ are more accurate than the others for the whole atomic sample considered in this work, being always bigger than 79% and smaller than 98.5%; and (iv) the accuracy of the important inequality (6) is around 88% for all the atoms examined.

Third, to give an idea to the reader about the importance of the logarithmic-convexity effects relative to those effects coming from the positivity, monotone decreasing from the origin, and the convexity properties of $g_\alpha(u)$, we have analyzed the quality of the inequalities

$$\langle u^n\rangle\langle u^{n-2}\rangle \ge F_p\langle u^{n-1}\rangle^2\ ,\quad n>-1\ ,\quad p=1,2,3,4\ , \tag{7}$$

which may be obtained from each of the four previously mentioned monotonicity properties as proven in Ref. [4] for the cases $p=1$ (positivity), $p=2$ (monotonically decreasing), and $p=3$ (convexity), and in this work for the case $p=4$ (logarithmic convexity). In the following, these inequalities will be referred to as inequalities I, II, III, and IV, respectively. It is known that

$$F_1=1\ ,\quad F_2=\frac{(n+\alpha_1+2)^2}{(n+\alpha_1+2)^2-1}\ ,$$

$$F_3=\frac{(n+\alpha_2+2)(n+\alpha_2+3)}{(n+\alpha_2+2)(n+\alpha_2+3)-1}\ ,\quad F_4=\frac{n+\alpha'+2}{n+\alpha'+1}\ .$$

We remark that $F_4=F(\frac{1}{2},1,n,\alpha')$, so that inequality (7) for $p=4$ is exactly the inequality (5) with $a=\frac{1}{2}$. In Table III the accuracy in percent of the inequalities I–IV measured by

$$100\frac{\langle u^{n-1}\rangle^2F_p}{\langle u^{n-2}\rangle\langle u^n\rangle}$$

is shown in the two-electron atoms with $Z=1$, 2, 3, 5,

TABLE III. Accuracy in percent of the inequalities I–IV with the integer values $0\le n\le 10$ for the two-electron atoms with nuclear charge $Z=1$, 2, 3, 5, and 10. The optimum 20-term Hylleraas-type atomic wave functions were used.

Z \ n	0	1	2	3	4	5	6	7	8	9	10
					Positivity ($p=1$)						
1	62.32	72.94	77.49	80.23	82.44	84.60	86.78	88.86	90.69	92.20	93.38
2	61.06	74.35	80.36	83.89	86.24	87.24	89.23	90.25	91.09	91.79	92.40
3	60.20	73.97	80.21	83.85	86.28	88.03	89.35	90.40	91.25	91.96	92.56
5	59.53	73.64	80.04	83.77	86.25	88.03	89.39	90.46	91.33	92.06	92.68
10	59.05	73.39	79.90	83.68	86.19	88.00	89.36	90.44	91.31	92.03	92.63
					Monotonicity ($p=2$)						
1	79.20	81.02	82.22	83.35	84.67	86.28	88.11	89.93	91.58	92.94	94.01
2	80.32	83.85	85.60	87.32	88.67	89.75	90.63	91.37	92.00	92.55	93.04
3	79.77	83.09	85.50	87.32	88.73	89.85	90.77	91.53	92.17	92.72	93.21
5	79.19	82.80	85.35	87.25	88.70	89.86	90.80	91.59	92.25	92.83	93.33
10	78.69	82.55	85.22	87.17	88.65	89.83	90.78	91.57	92.23	92.79	93.28
					Convexity ($p=3$)						
1	82.78	84.28	84.65	85.18	86.09	87.42	89.05	90.72	92.25	93.52	94.52
2	85.08	87.28	88.43	89.42	90.28	91.02	91.66	92.21	92.71	93.15	93.56
3	85.12	87.24	88.45	89.48	90.38	91.15	91.81	92.39	92.89	93.33	93.73
5	85.09	87.14	88.39	89.46	90.38	91.18	91.86	92.46	92.98	93.45	93.86
10	85.05	87.04	88.32	89.42	90.36	91.16	91.85	92.44	92.96	93.42	93.82
					Logarithmic convexity ($p=4$)						
1	65.81	76.81	81.39	84.08	86.22	88.31	90.43	92.44	94.20	95.63	96.73
2	64.65	78.48	84.59	88.08	90.35	91.94	93.11	94.01	94.73	95.32	95.82
3	64.20	78.58	84.91	88.50	90.81	92.42	93.60	94.50	95.21	95.78	96.26
5	62.41	77.04	83.57	87.31	89.74	91.46	92.74	93.73	94.52	95.16	95.70
10	62.45	77.39	84.02	87.79	90.23	91.93	93.18	94.15	94.90	95.51	96.02

and 10. We have used the aforementioned Hylleraas framework. The values of the interelectronic moments calculated in this numerical framework were tabulated by the authors in Ref. [8]. The values of the calculated accuracies are given Table III when n goes from 0 to 10. Table III allows us to make the following observations, among others.

(i) All the inequalities I–IV have for a given atom an accuracy which increases with increasing n. This indicates that the higher the order of the moments involved in an inequality, the greater is its quality.

(ii) For a specific atom and a given value of n, the inequality III is systematically much more accurate than the inequality II; something similar can be stated for the inequality II with respect to the inequality I. All this is understandable since (a) convexity is a property stronger than monotonic decreasing from the origin and this is itself stronger than positivity, and (b) both values α_1 and α_2 are small. The latter assumes the existence of monotonic decreasing and convexity effects already in the neighborhood of the origin.

(iii) The inequality IV is, for a specific atom, systematically more accurate than inequality III only in the cases that $n \geq 5$ (i.e., when the involved moments are of order higher than 3). This is because $\alpha' \gg \alpha_2$, as already found in this work, and then, in spite of that logarithmic-convexity is a property stronger than convexity, the manifestation of logarithmic-convexity effects is produced in a region far away from the origin. This region is mostly taken care by the moments of higher order.

(iv) The accuracy of the inequality III (convexity) oscillates between 82.8% ($H^-; n=0$) and 94% ($n=10$), while that of inequality IV (logarithmic-convexity) is always higher than 88% for $n \geq 5$ and can reach the value of 96% for all members of the atomic sample considered in this study.

In summary, we have studied the logarithmic-convexity of the interelectronic function $h(u)/u^{\alpha}$, $\alpha > \alpha'$ in comparison with its positivity, monotonicity, and convexity properties. The logarithmically-convex property has been shown to provide us with new and important information about the electron-pair density and the electron correlation problem in atoms and molecules. The inequalities developed from the logarithmic-convexity have a greater accuracy than the other known ones in general.

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