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Study of some interelectronic properties in helium-like atoms

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Abstract. By means of the optimum M-term Hylleraas-type wavefunctions with $1 \leqq M \leqq 6$ we study various interelectronic properties of the Helium-like atoms with nuclear charge $Z=1$, 2, 3, 5 and 10. Let $h(u)$ denote the spherically averaged electron-pair density of a finite many-electron system. Firstly we found that the intracule function $h(u)/u^\alpha$ of the above-mentioned atoms is (i) monotonically decreasing from the origin for $\alpha \geqslant \alpha_1$ and (ii) convex for $\alpha \geqslant \alpha_2$, where α_1 and α_2 are positive constants which depend on Z and M. Then we show that the electron-electron cusp condition, i.e. that $h'(0)=h(0)$, may be extended in the sense that the inequality $h(u)-h'(u) \geqq 0$ is valid for any $u \geqslant 0$. Thirdly, it is shown that the inequalities involving three interelectronic moments $\langle u^n \rangle$ recently found by the authors are, at times, of great quality. Finally the goodness of some bounds to the characteristics of the maximum of $h(u)$ and to the total interelectronic repulsion energy is discussed in detail.

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I. Introduction and methodology

The spherical average of the intracule or electron-pair density $h(u)$, u being the modulus of the interelectronic separation vector $\mathbf{u}=\mathbf{r}_{12}$, has been shown to play the dominant role in the atomic electron-electron correlation problem [1, 2]. In particular, it is related to the electron-electron distribution function or radial electron-pair density [3, 4] $P(u)$ by $P(u)=4\pi u^2 h(u)$ and to the weighted pair distribution function [5, 6] $f(u)$ by $f(u)=4\pi u h(u)$.

Up to now, to the best of our information, the only known rigorous properties of $h(u)$ are as follows:

1. It is positive at the origin, everywhere non-negative and vanishes at infinity [7]. As any other density function, it may be fully characterized by means of its moments μ_m; these quantities represent, apart from a factor 4π, the interelectronic radial expectation values $\langle u^m \rangle$ since

$$\langle u^m \rangle = \int u^m h(u)\, d\mathbf{u} = \int_0^\infty u^m P(u)\, du$$
$$= 4\pi \int_0^\infty u^{m+2} h(u)\, du \equiv 4\pi \mu_{m+2} \tag{1}$$

for any real number $m > -3$. These interelectronic moments are physically meaningful (e.g. $\langle u^{-1} \rangle = 4\pi\mu_1$ gives the value of the interelectronic repulsion energy of atoms and molecules) and form in fact the building blocks of the electron-electron correlation problem.

Just from the non-negativity property of $h(u)$ one can obtain [8] the interelectronic inequalities

$$\langle u^{n-2} \rangle \langle u^n \rangle \geqq \langle u^{n-1} \rangle^2, \qquad n > -1 \tag{2}$$

2. It satisfies the Kato electron-electron or correlation cusp condition [7]

$$\lim_{u \to 0} \frac{h'(u)}{h(u)} = 1 \tag{3}$$

3. Contrary to the atomic charge density $\rho(r)$, which is a monotonically decreasing function of r, $h(u)$ is not monotonic [7]. Indeed it is, at least, unimodal with the maximum at $u=u_{\max} \neq 0$. Let us call $h_{\max}=h(u_{\max})$. Recently [8] rigorous bounds to the characteristics $(u_{\max}, h_{\max})$ of the maximum of an unimodal intracule density $h(u)$ of a N-electronic system have been found by means of the interelectronic moments. They are given by:

(a) Upper bounds to the maximum location:

$$u_{\max} \leqq U_1 \leqq U_0 \tag{4}$$

with

$$U_0 = 2\frac{\langle u^{-1} \rangle}{\langle u^{-2} \rangle} \tag{5}$$

$$U_1 = \frac{2\langle u^{-2} \rangle \langle u \rangle - \frac{3}{2}N(N-1)\langle u^{-1} \rangle - A}{\frac{3}{2}N(N-1)\langle u^{-2} \rangle - 4\langle u^{-1} \rangle^2} \tag{6}$$

where

$$A=\left[-\frac{27}{4}N^2(N-1)^2\langle u^{-1}\rangle^2+4\langle u^{-2}\rangle^2\langle u\rangle^2\right.$$
$$-18N(N-1)\langle u^{-2}\rangle\langle u^{-1}\rangle\langle u\rangle$$
$$\left.+32\langle u^{-1}\rangle^3\langle u\rangle+\frac{27}{8}N^3(N-1)^3\langle u^{-2}\rangle\right]^{\frac{1}{2}}.$$

(b) Lower bounds to the maximum intensity:

$$h_{\max}\geqq h(s,t)\equiv\frac{1}{4\pi}\left\{\frac{[(t+3)\langle u^t\rangle]^{s+3}}{[(s+3)\langle u^s\rangle]^{t+3}}\right\}^{\frac{1}{s-t}} \tag{7}$$

where s and t are real numbers, $s>t$. This inequality may be used in both senses: to bound $h_{\max}$ in terms of the interelectronic moments and to bound these moments by means of $h_{\max}$. In the latter sense one has, e.g. if $s=0$ and $t=-1$

$$E_{ee}=\langle u^{-1}\rangle\leqq\left[\frac{9\pi}{8}N^2(N-1)^2h_{\max}\right]^{\frac{1}{3}} \tag{8}$$

which gives an upper bound to the total electron-electron repulsion energy E_{ee} of an N-electron system via $h_{\max}$.

4. The intracule function $h(u)/u^{\alpha_1}$ with $\alpha_1=\max\{uh'(u)/h(u)\}$ is monotonically decreasing from the origin [8]. This property may be used to obtain [8]

$$\langle u^{n-2}\rangle\langle u^n\rangle\geqq\frac{(n+\alpha_1+2)^2}{(n+\alpha_1+2)^2-1}\langle u^{n-1}\rangle^2,\quad n>-1 \tag{9}$$

which improves the inequality (2), since $\alpha_1>0$ due to the first property of $h(u)$.

5. The intracule function $h(u)/u^{\alpha_2}$, $\alpha_2=\max\{f(u)\}$, where

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

is convex [8]. Using this property one obtains

$$\langle u^{n-2}\rangle\langle u^n\rangle\geqq\frac{(n+\alpha_2+2)(n+\alpha_2+3)}{(n+\alpha_2+2)(n+\alpha_2+3)-2}\langle u^{n-1}\rangle^2,\quad n>-1 \tag{10}$$

which further improves the inequality (9), since $\alpha_2>\alpha_1$.

From a numerical point of view, several properties of $h(u)$ have been studied for different wavefunctions, specially in two-electron ions [9-16]. Emphasis has been made to check the correlation cusp condition (3) and to evaluate the interelectronic values $\langle u^m\rangle$, $m=-2$, -1, 1, 2, 3 and 4.

In this paper we will use the optimum Hylleraas M-term wavefunctions, $1\leqq M\leqq 6$, developed by one of us [17, 18] to carry out a numerical analysis in the helium-like atoms having a nuclear charge $Z=1$, 2, 3, 5 and 10 for five purposes:

- To calculate some characteristics of the intracule density $h(u)$. See Sect. II.
- To extend the validity of the correlation cusp condition to any $u\neq 0$. See Sect. III.
- To evaluate the interelectronic moments $\langle u^m\rangle$ for any real m between -3 and 4, and to study the accuracy of the inequalities I [Eq. (2)], II [Eq. (9)] and III [Eq. (10)] among three of these quantities. See Sect. IV.
- To analyse the accuracy of the bounds (4) and (7) to the location and intensity of the maximum of the intracule density $h(u)$. See Sect. V.
- To investigate the goodness of the upper bound (8) to the total interelectronic repulsion energy. See Sect. V.

II. Some characteristics of the electron-pair density

Though there exists discussion [10] that it cannot be a formal solution to the Schrödinger equation, the Hylleraas function provides us with physical quantities of practical accuracy. We start with the comparison of the near exact values [11] of several quantities related to the intracule density $h(u)$ with those calculated by the optimum Hylleraas wavefunctions. This comparison is done for the helium-like atoms with $Z=1(\mathrm{H}^-)$, $2(\mathrm{He})$, $3(\mathrm{Li}^+)$, $5(\mathrm{B}^{3+})$ and $10(\mathrm{Ne}^{8+})$. The involved quantities are: the total ground state energy E, several interelectronic radial expectation values $\langle u^m\rangle$ of integer and fractional orders, the value of $h(u)$ at the origin $h(0)$, the location $u_{\max}$ and the intensity $h_{\max}$ of the maximum of the density, and the values α_1 and α_2 for which the intracule function $h(u)/u^\alpha$ is monotonically decreasing from the origin and convex, respectively.

The results of this comparison are shown in Tables 1-5 for the five atoms taken into consideration. A few observations are in order:

(i) The energy E and the interelectronic moments $\langle u^m\rangle$, which are globally averaged quantities, are much better determined for a given number of terms of the variational wavefunctions than local properties of $h(u)$ such as $h(0)$, the maximum characteristics $u_{\max}$ and $h_{\max}$, and the values α_1 and α_2.

(ii) The convergence of the quantities taken in this study when the number of terms of the wavefunction is increased, is very nice for the averaged quantities and nonuniform for the interelectronic local properties.

(iii) There where it is possible (i.e., for E, some values of $\langle u^m\rangle$ and $h(0)$), the comparison between our Rayleigh-Ritz variational values (specially when one uses the 6-term wavefunctions) and the near exact ones [11] is very good.

The first two observations should not be surprising because in a Rayleigh-Ritz variational calculation the approximate wavefunction can be locally much less accurate than for some globally averaged quantities in which local errors of opposite sign have been partially cancelled in the integration process.

Table 1. Comparison, there where it is possible, between the values of various average and local ground-state quantities of *the H^- ion* calculated by means of the optimum M-term Hylleraas-type wavefunctions, $1 \leqq M \leqq 6$, and the near-exact ones [11]. The symbols E, $\langle u^k \rangle$, $h(0)$, $u_{\max}$, α_1 and α_2 denote the total energy, the kth-interelectronic radial expectation value, the electron-pair density at the origin, the location of the maximum, the intensity of the electron-pair density at its maximum, and the values of α for which the electron-pair function $h(u)/u^\alpha$ is monotonically decreasing from the origin and convex, respectively. Atomic units are used throughout

$Z=1$	Hylleraas wave function						Near exact
	1-term	2-term	3-term	4-term	5-term	6-term	
$-E$	0.472656	0.512293	0.525851	0.526927	0.527362	0.527570	0.527751
$\langle u^{-5/2} \rangle$	0.429784	0.223858	0.168747	0.158996	0.165523	0.163628	–
$\langle u^{-2} \rangle$	0.315104	0.183743	0.163226	0.155173	0.157118	0.156883	0.155108
$\langle u^{-3/2} \rangle$	0.334896	0.220930	0.212578	0.204119	0.204142	0.204330	–
$\langle u^{-1} \rangle$	0.429688	0.323526	0.322849	0.313345	0.312119	0.312388	0.311022
$\langle u^{0} \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	3.18182	4.28989	4.08521	4.31960	4.34221	4.34748	4.41269
$\langle u^{2} \rangle$	12.6942	23.1821	20.4881	23.9225	23.8716	23.9516	25.2020
$\langle u^{3} \rangle$	60.5860	149.482	120.973	164.709	159.753	160.197	180.601
$\langle u^{4} \rangle$	335.715	1111.31	817.663	1371.14	1264.56	1259.15	1590.0
$h(0)$	0.0129294	0.00608770	0.00305538	0.00288526	0.00322725	0.00306420	0.002740
$u_{\max}$	0.000000	0.000000	0.923985	0.967835	0.812928	0.876085	–
$h_{\max}$	0.0129294	0.00608770	0.00420245	0.00389237	0.00404550	0.00405284	–
α_1	0.000000	0.000000	0.150071	0.142292	0.106942	0.132288	–
α_2	0.0871262	0.0785974	0.372100	0.373125	0.305717	0.347517	–

Table 2. Comparison, there where it is possible, between the values of various average and local ground-state quantities of *the He atom* calculated by means of the optimum M-term Hylleraas-type wavefunctios, $1 \leqq M \leqq 6$, and the near-exact ones [11]. The symbols E, $\langle u^k \rangle$, $h(0)$, $u_{\max}$, $h_{\max}$, α_1 and α_2 are as explained in caption of Table 1 or text. Atomic units are used throughout

$Z=2$	Hylleraas wave function						Near exact
	1-term	2-term	3-term	4-term	5-term	6-term	
$-E$	2.847656	2.891121	2.902432	2.902772	2.903385	2.903453	2.903724
$\langle u^{-5/2} \rangle$	4.05674	3.01033	2.87320	2.87723	2.80702	2.80851	–
$\langle u^{-2} \rangle$	1.89844	1.55270	1.48305	1.48388	1.46917	1.46959	1.46477
$\langle u^{-3/2} \rangle$	1.28785	1.12815	1.08513	1.08484	1.08152	1.08162	–
$\langle u^{-1} \rangle$	1.05469	0.974297	0.947174	0.946498	0.946387	0.946409	0.945818
$\langle u^{0} \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	1.29630	1.37242	1.42058	1.42497	1.42091	1.42002	1.42207
$\langle u^{2} \rangle$	2.10700	2.32730	2.50449	2.52594	2.51166	2.50433	2.51644
$\langle u^{3} \rangle$	4.09694	4.66983	5.24207	5.32757	5.29172	5.24976	5.30800
$\langle u^{4} \rangle$	9.24882	10.7844	12.6608	12.9921	12.9258	12.7116	12.9812
$h(0)$	0.191202	0.119912	0.116122	0.116240	0.109425	0.109444	0.106352
$u_{\max}$	0.000000	0.162781	0.140105	0.142180	0.177457	0.177793	–
$h_{\max}$	0.191202	0.127021	0.120845	0.121239	0.117174	0.117358	–
α_1	0.000000	0.0283162	0.0196774	0.0207758	0.0335512	0.0342107	–
α_2	0.0871262	0.183845	0.163095	0.165021	0.194323	0.194757	–

Table 3. Comparison, there where it is possible, between the values of various average and local ground-state quantities of *the Li^+ ion* calculated by means of the optimum M-term Hylleraas-type wavefunctios, $1 \leqq M \leqq 6$, and the near-exact ones [11]. The symbols E, $\langle u^k \rangle$, $h(0)$, $u_{\max}$, $h_{\max}$, α_1 and α_2 are as explained in caption of Table 1 or text. Atomic units are used throughout

$Z=3$	Hylleraas wave function						Near exact
	1-term	2-term	3-term	4-term	5-term	6-term	
$-E$	7.222656	7.268157	7.278030	7.278505	7.279446	7.279567	7.279913
$\langle u^{-5/2} \rangle$	12.9849	10.7544	10.5224	10.4723	10.3291	10.2661	–
$\langle u^{-2} \rangle$	4.81510	4.22792	4.13508	4.12432	4.09944	4.08982	4.08225
$\langle u^{-3/2} \rangle$	2.58836	3.37173	2.32651	2.32412	2.31814	2.31641	–
$\langle u^{-1} \rangle$	1.67969	1.59244	1.56994	1.56987	1.56831	1.56807	1.56772
$\langle u^{0} \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	0.813953	0.848217	0.863889	0.861540	0.862006	0.862488	0.862315
$\langle u^{2} \rangle$	0.830719	0.894956	0.931239	0.923405	0.925262	0.927877	0.927064
$\langle u^{3} \rangle$	1.01425	1.12288	1.19678	1.17617	1.18221	1.19127	1.18856
$\langle u^{4} \rangle$	1.43770	1.62778	1.78088	1.72888	1.74683	1.77421	1.7660
$h(0)$	0.772335	0.580883	0.572786	0.568445	0.549727	0.541255	0.533808
$u_{\max}$	0.000000	0.0622761	0.0525144	0.0541871	0.0700142	0.0767448	–
$h_{\max}$	0.772335	0.592966	0.581090	0.576954	0.564646	0.559181	–
α_1	0.000000	0.0102183	0.00715835	0.00738766	0.0132510	0.0161001	–
α_2	0.0871262	0.139287	0.129530	0.129871	0.145984	0.154302	–

Table 4. Comparison, there where it is possible, between the values of various average and local ground-state quantities of *the* B^{3+} *ion* calculated by means of the optimum M-term Hylleraas-type wavefunctios, $1 \leqq M \leqq 6$, and the near-exact ones [11]. The symbols E, $\langle u^k \rangle$, $h(0)$, $u_{\max}$, $h_{\max}$, α_1 and α_2 are as explained in caption of Table 1 or text. Atomic units are used throughout

$Z=5$	Hylleraas wave function						Near exact
	1-term	2-term	3-term	4-term	5-term	6-term	
$-E$	21.972656	22.019544	22.028354	22.029268	22.030305	22.030504	22.030970
$\langle u^{-5/2} \rangle$	52.1700	46.8555	46.3999	45.8604	45.7293	45.6576	–
$\langle u^{-2} \rangle$	14.6484	13.5843	13.4461	13.3688	13.3488	13.3375	13.3075
$\langle u^{-3/2} \rangle$	5.96229	5.66319	5.61227	5.59961	5.59408	5.59217	–
$\langle u^{-1} \rangle$	2.92969	2.83781	2.81865	2.81765	2.81565	2.81547	2.81470
$\langle u^0 \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	0.466667	0.478975	0.483346	0.481795	0.482473	0.482382	0.482436
$\langle u^2 \rangle$	0.273067	0.286590	0.292395	0.289678	0.290747	0.290706	0.290791
$\langle u^3 \rangle$	0.191147	0.204575	0.211368	0.207602	0.209031	0.209152	0.209243
$\langle u^4 \rangle$	0.155345	0.169169	0.177263	0.172225	0.174112	0.174525	0.17458
$h(0)$	4.09811	3.49671	3.47628	3.39860	3.37455	3.36700	3.314478
$u_{\max}$	0.000000	0.0199600	0.0171867	0.0212889	0.241119	0.0238086	–
$h_{\max}$	4.09811	3.51851	3.49204	3.42234	3.40595	3.39689	–
α_1	0.000000	0.00310052	0.00225749	0.00346966	0.00461195	0.00440319	–
α_2	0.0871262	0.113730	0.109172	0.115710	0.119673	0.119841	–

Table 5. Comparison, there where it is possible, between the values of various average and local ground-state quantities of *the* Ne^{8+} *ion* calculated by means of the optimum M-term Hylleraas-type wavefunctios, $1 \leqq M \leqq 6$, and the near-exact ones [11]. The symbols E, $\langle u^k \rangle$, $h(0)$, $u_{\max}$, $h_{\max}$, α_1 and α_2 are as explained in caption of Table 1 or text. Atomic units are used throughout

$Z=10$	Hylleraas wave function						Near exact
	1-term	2-term	3-term	4-term	5-term	6-term	
$-E$	93.847656	93.895417	93.903482	93.904865	93.905927	93.906250	93.906802
$\langle u^{-5/2} \rangle$	320.033	304.264	303.078	300.993	300.510	300.273	–
$\langle u^{-2} \rangle$	62.5651	60.3198	60.0683	59.8484	59.8032	59.7739	59.6946
$\langle u^{-3/2} \rangle$	17.7141	17.2731	17.2087	17.1816	17.1731	17.1689	–
$\langle u^{-1} \rangle$	6.05469	5.95996	5.94311	5.94087	5.93876	5.93825	5.93724
$\langle u^0 \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	0.225806	0.228854	0.229751	0.229338	0.229501	0.229482	0.229492
$\langle u^2 \rangle$	0.0639334	0.0655776	0.0661534	0.0657928	0.0659171	0.0659081	0.0659174
$\langle u^3 \rangle$	0.0216549	0.0224573	0.0227831	0.0225376	0.0226184	0.0226192	0.0226254
$\langle u^4 \rangle$	0.00851583	0.00892190	0.00910982	0.00894928	0.00900124	0.00900677	0.0090100
$h(0)$	36.1739	33.5643	33.4908	33.0532	32.9429	32.9115	32.6432
$u_{\max}$	0.000000	0.00458808	0.00396024	0.00509340	0.00582351	0.00565712	–
$h_{\max}$	36.1739	33.6100	33.5245	33.1083	33.0161	32.9797	–
α_1	0.000000	0.000680507	0.000502641	0.000833109	0.00110861	0.00103482	–
α_2	0.0871262	0.0989632	0.0970888	0.100471	0.102300	0.102134	–

III. Extension of the correlation cusp condition

Here we have evaluated $h(u)$ and its derivative $h'(u)$ as well as their difference

$$g_0(u) = h(u) - h'(u)$$

for all the two-electron ions with $Z = 1, 2, 3, 5$ and 10 by means of the 6-term Hylleraas wavefunctions. The results are shown in Fig. 1. Therein we observe that in all cases,

1. The intracule density $h(u)$ is unimodal as was previously seen [9].
2. The intracule function $g_0(u)$ is positive at the origin and, up to 5 atomic units, non-negative and non-monotonic. Indeed, it possesses a single maximum whose characteristics $u_{\max}$ and $g_0(u_{\max})$ are given in Table 6, which also collects the coordinates $(u_{\min}, h'_{\min})$ of the minimum of $h'(u)$.

From Fig. 1 and Table 6 it is interesting to point out that the location of both extrema $u_{\max}$ and $u_{\min}$ get closer one to another with increasing Z, so that in Ne^{8+} $(Z=10)$ case they coincide up to 94 percent. Something similar occurs for the intensities $g_0(u_{\max})$ and $|h'_{\min}|$.

We may argue that $g_0(u) \geq 0$ not only at the origin, as the correlation cusp condition implies, but also for all positive values of u. This observation has important physical consequences, as e.g. for the atomic electron-electron coalescence, which will be discussed elsewhere [19].

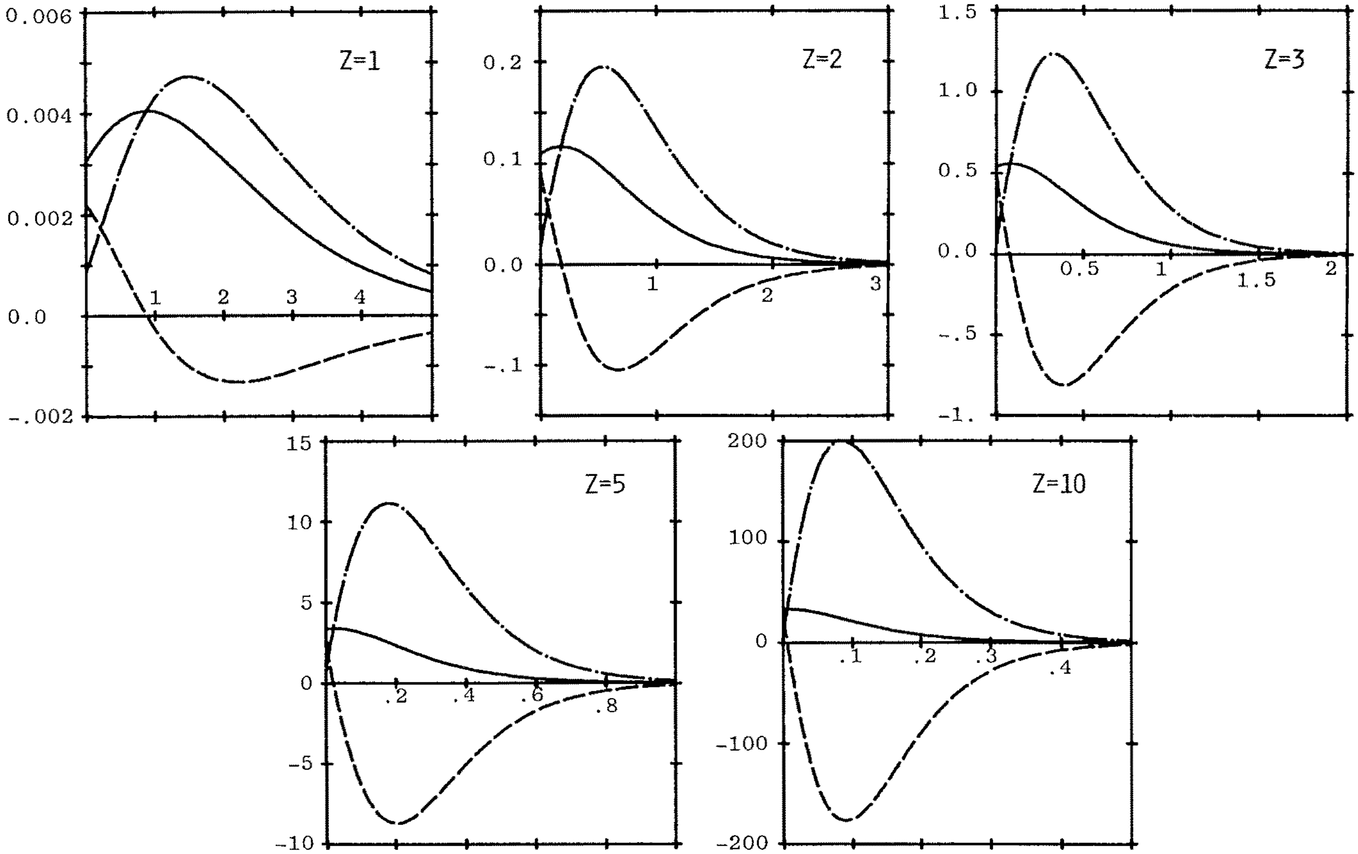

Fig. 1. The electron-pair density (solid line) $h(u)$, its derivative (dashed line) $h'(u)$ and the difference (dotted-dashed line) $g_0(u)=h(u)-h'(u)$ calculated by means of the optimum Hylleraas 6-term wavefunctions in the two-electron atoms with $Z=1$, 2, 3, 5 and 10. Remark that $g_0(u)$ is everywhere non-negative. Atomic units are used throughout

Table 6. Maximum characteristics of the interelectronic function $g_0(u)=h(u)-h'(u)$. The symbols $u_{\max}$ and $g_{0,\max}$ denote the location of the maximum and the intensity of $g_0(u)$ at its maximum. Corresponding meanings may be attributed to the minimum characteristics $(u_{\min}, h'_{\min})$ of $h'(u)$. Atomic units are used throughout

Z	Minimum of $h'(u)$		Maximum of $g_0(u)=h(u)-h'(u)$	
	$u_{\min}$	$h'_{\min}$	$u_{\max}$	$g_{0,\max}$
1	2.17564	− 0.00133111	1.49001	0.00471892
2	0.666966	− 0.105517	0.528974	0.195147
3	0.378406	− 0.817447	0.320436	1.23167
5	0.197513	− 8.73022	0.177229	11.1789
10	0.0896275	− 175.570	0.0846755	198.923

IV. Interelectronic moments: values and inequalities

Here we will evaluate the interelectronic radial expectation values $\langle u^{\mu}\rangle$ for all integer and non-integer orders μ between -3 and 4, and then we will use them to study the accuracy of the interelectronic three-moment inequalities I [Eq. (2)], II [Eq. (9)] and III [Eq. (10)] for all the two-electron atoms with $Z=1$, 2, 3, 5 and 10. The optimum 6-term Hylleraas wavefunctions are used.

The calculated values of the interelectronic moments $\langle u^{\mu}\rangle$ are shown in Table 7 and drawn as a function of μ

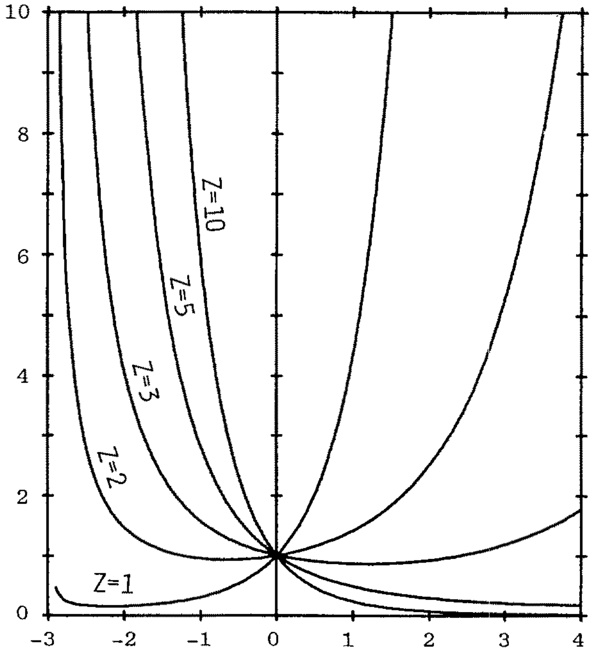

Fig. 2. Dependence of the calculated interelectronic moment $\langle u^{\mu}\rangle$ on the order μ, $-3<\mu\leq 4$, in the two-electron atoms with $Z=1$, 2, 3, 5 and 10. The optimum Hylleraas 6-term wavefunctions were used. Atomic units are used throughout

Table 7. Fractional and integer interelectronic moments $\langle u^{\mu} \rangle$, $-2.8 \leqq \mu \leqq 4.0$ of the electron-pair density $h(u)$ calculated by means of the optimum Hylleraas 6-term wavefunction. Atomic units are used throughout

μ	$Z=1$	$Z=2$	$Z=3$	$Z=5$	$Z=10$
−2.8	0.269063	6.94996	30.2630	163.743	1362.45
−2.6	0.178852	3.49652	13.5296	64.1578	456.081
−2.4	0.155520	2.35305	8.13354	33.9558	206.693
−2.2	0.151217	1.79324	5.55556	20.4784	106.902
−2.0	0.156883	1.46959	4.08982	13.3375	59.7739
−1.8	0.170164	1.26557	3.16891	9.15597	35.2564
−1.6	0.190897	1.13110	2.55131	6.53801	21.6443
−1.4	0.220067	1.04123	2.11766	4.81704	13.7168
−1.2	0.259588	0.982321	1.80269	3.64222	8.92453
−1.0	0.312388	0.946409	1.56807	2.81547	5.93825
−0.8	0.382673	0.928730	1.38998	2.21877	4.02926
−0.6	0.476380	0.926433	1.25298	1.77874	2.78182
−0.4	0.601853	0.937916	1.14672	1.44814	1.95082
−0.2	0.770850	0.962454	1.06406	1.19565	1.38763
0.0	1.00000	1.00000	1.00000	1.00000	1.00000
0.2	1.31296	1.05108	0.950936	0.846416	0.729404
0.4	1.74355	1.11674	0.914281	0.724438	0.538045
0.6	2.34048	1.19857	0.888156	0.626537	0.401089
0.8	3.17423	1.29873	0.871210	0.547210	0.301970
1.0	4.34748	1.42002	0.862488	0.482382	0.229482
1.2	6.01063	1.56600	0.861348	0.428992	0.175949
1.4	8.38533	1.74114	0.867401	0.384719	0.136046
1.6	11.8000	1.95100	0.880470	0.347782	0.106042
1.8	16.7443	2.20253	0.900567	0.316803	0.0832929
2.0	23.9516	2.50433	0.927877	0.290706	0.0659081
2.2	34.5270	2.86710	0.962755	0.268643	0.0525222
2.4	50.1437	3.30418	1.00573	0.249941	0.0421407
2.6	73.3486	3.83222	1.05750	0.234066	0.0340337
2.8	108.037	4.47204	1.11897	0.220585	0.0276608
3.0	160.197	5.24976	1.19127	0.209152	0.0226192
3.2	239.074	6.19822	1.27575	0.199486	0.0186063
3.4	359.010	7.35883	1.37409	0.191359	0.0153933
3.6	542.354	8.78398	1.48828	0.184585	0.0128062
3.8	824.080	10.5401	1.62070	0.179014	0.0107116
4.0	1259.15	12.7116	1.77421	0.174525	0.00900677

Table 8. Accuracy in percent of the inequalities I, II and III which involve three interelectronic moments $\langle u^{n} \rangle$. The optimum Hylleraas 6-term wave-functions were used. See text for details. Atomic units are used throughout

Z	$\langle n^{n-2} \rangle \langle u^{n} \rangle \geqq \langle u^{n-1} \rangle^2$					$\langle n^{n-2} \rangle \langle u^{n} \rangle \geqq F_2 \langle u^{n-1} \rangle^2$					$\langle u^{n-2} \rangle \langle u^{n} \rangle \geqq F_3 \langle u^{n-1} \rangle^2$				
	$n=0$	1	2	3	4	$n=0$	1	2	3	4	$n=0$	1	2	3	4
1	62.20	73.63	78.91	82.37	85.09	79.74	81.99	83.82	85.62	87.42	83.44	85.36	86.34	87.53	88.91
2	60.94	74.41	80.52	84.13	86.57	80.37	83.48	85.79	87.59	89.02	85.27	87.46	88.66	89.70	90.64
3	60.12	73.94	80.17	83.79	86.20	79.74	83.07	85.47	87.26	88.65	85.20	87.26	88.43	89.43	90.31
5	59.43	73.63	80.04	83.76	86.22	79.13	82.80	85.37	87.25	88.68	85.20	87.20	88.43	89.47	90.37
10	59.00	73.38	79.90	83.69	86.19	78.63	82.55	85.23	87.17	88.65	85.09	87.07	88.34	89.43	90.36

in Fig. 2. One observes that these quantities have a similar behavior in all cases. For a given Z and beginning at $\mu = -3$ they decrease down to a minimum and then they continously grow with increasing μ. The minimum lies at $\mu = -2.2$ in H^- case, and at -0.7 and 1.1 in He and Li^+ cases respectively. For the other two cases the minimum lies outside of the interval $-3 < \mu < 4$.

Now we will study the accuracy of the inequalities I [Eq. (2)], II [Eq. (9)] and III [Eq. (10)] which are of the form

$$\langle u^{n-2} \rangle \langle u^{n} \rangle \geqq F_p \langle u^{n-1} \rangle^2, \qquad n > -1, p = 1, 2, 3$$

where F_p have the values

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

$$F_3 = \frac{(n+\alpha_2+2)(n+\alpha_2+3)}{(n+\alpha_2+2)(n+\alpha_2+3) - 1}$$

respectively. The accuracy is measured by the ratio of both sides of the inequality times a hundred. Its values in percent are shown in Table 8 for these three inequalities. This table allows to make several observations. The

Table 10. Calculated values of the intensity of the electron-pair density at its maximum, $h_{\max}$, and the lower bound $h(s, t)$ for the optimum value of t (which is given in parentheses) and several values of s, which differs from t by 0.01, 0.1, 0.5 and 1.0. The optimum Hylleraas 6-term wavefunctions were used. See text for details. Atomic units are used throughout

Z	$h_{\max}$	$h(s,t)$ $[s > t > -3]$			
		$s-t=0.01$	$s-t=0.1$	$s-t=0.5$	$s-t=1.0$
1	0.0041	0.0034 (−2.23)	0.0034 (−2.27)	0.0034 (−2.42)	0.0034 (−2.54)
2	0.1174	0.1100 (−2.72)	0.1100 (−2.76)	0.1098 (−2.88)	0.1095 (−2.97)
3	0.5592	0.5413 (−2.94)	0.5413 (−2.98)	0.5413 (−3.00)	0.5413 (−3.00)
5	3.3969	3.3670 (−3.00)	3.3670 (−3.00)	3.3670 (−3.00)	3.3670 (−3.00)
10	32.9797	32.9115 (−3.00)	32.9115 (−3.00)	32.9115 (−3.00)	32.9115 (−3.00)

accuracy of inequality I goes from 59% (for $Z=10$ and $n=0$) to 86% (for $Z=10$ and $n=4$). The other two inequalities are much more accurate. For a fixed n and a given atom, the inequality III (where the convexity of $h(u)/u^{\alpha}$ is required) is of higher accuracy than the corresponding inequalities II (where the monotonically decreasing from the origin of $h(u)/u^{\alpha}$ is required) and I (where only the non-negativity of $h(u)$ is used). Moreover, the inequality III is of great quality. Indeed, its accuracy is always higher than 83%, going up to 90.64% in the helium case when $n=4$. Also one should say that when the inequality involves interelectronic moments $\langle u^n \rangle$ of positive powers (i.e. for $n \geqq 0$) only, its accuracy is slightly higher than that having any moment of negative power.

Table 9. Calculated values of the maximum location $u_{\max}$ and two upper bounds U_0 and U_1 by means of the optimum Hylleraas 6-term wavefunction. See text for details. Atomic units are used throughout

Z	$u_{\max}$	U_1	U_0
1	0.8761	3.0709	3.9824
2	0.1778	0.9157	1.2880
3	0.0767	0.5355	0.7668
5	0.0238	0.2898	0.4222
10	0.0057	0.1352	0.1987

Table 11. Calculated values of the total interelectronic repulsion energy $E_{ee} = \langle u^{-1} \rangle$ and the upper bound given by (8). The optimum Hylleraas 6-term wavefunctions were used. See text for details. Atomic units are used throughout

Z	$\langle u^{-1} \rangle$	Bound
1	0.3124	0.3855
2	0.9464	1.1838
3	1.5681	1.9921
5	2.8155	3.6348
10	5.9383	7.7542

V. Bounding the maximum of the electron-pair density and the repulsion energy

First of all, we will analyse the goodness of the upper bounds U_0 and U_1 given by (4)–(6) to the location $u_{\max}$ of the maximum of the intracule density $h(u)$ as well as the lower bound $h(s, t)$ given by Eq. (7) of the intensity $h_{\max}$ of $h(u)$ at the maximum. This is done for the helium-like atoms with $Z=1$, 2, 3, 5 and 10 by means of the Hylleraas 6-term wavefunctions. The results are given in Tables 9 and 10. A glance to Table 9 allows to realize that both upper bounds U_0 and U_1 to $u_{\max}$ are of poor quality. However, Table 10 illustrates that the two-moments lower bounds $h(s, t)$ to $h_{\max}$ given by (7), i.e. depending on $\langle u^t \rangle$ and $\langle u^s \rangle$ where s and t are real numbers so that $s > t$, are very good.

In Table 10 we have given the values of $h_{\max}$ and the bound $h(s, t)$ calculated for the optimum value of t which is given in parentheses, and different values of s which differ from t in 0.01, 0.1, 0.5 and 1.0. One observes that the best bound is found when this difference is the smallest one, i.e. is 0.01. This bound is of great accuracy; indeed it is always higher than 84% and, at times, the bound is practically equal to $h_{\max}$.

Then, the quality of the upper bound to the total interelectronic repulsion energy $E_{ee} = \langle u^{-1} \rangle$, as given by (8), is studied in Table 11 for all the above mentioned He-like atoms by means of the Hylleraas 6-term wavefunction. Therein the values of $\langle u^{-1} \rangle$ and the bound (8) are explicitly given. We observe that the bound is reasonably accurate for all the two-electron ions taken into account. It differs from the calculated values less than thirty percent in all the atoms.

In brief, further effort should be done to improve these bounds.

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