Bounds to the central electron-pair density with applications to two-electron atoms

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The local electron-electron quantity $\langle\delta(\mathbf{r}_{12})\rangle$ of atomic systems, which plays an important role in the realization of the so-called correlation cusp condition, as well as in the description of the relativistic and radiative corrections to the ground-state energy, is investigated by means of the interelectronic radial expectation values $\langle r_{12}^{\alpha}\rangle$, $\alpha>-3$. Starting from the unimodal character of the spherically averaged electron-pair density $h(r_{12})$ and the recently found inequality $h(r_{12})>h'(r_{12})$, upper U_k and lower L_k bounds, $k=0,1,2,\ldots$, to the electron-pair density at the origin or central electron-pair density $h(0)$, which is equal to the quantity $\langle\delta(\mathbf{r}_{12})\rangle$, are found analytically. For the two-electron atoms with $Z=1$, 2, 3, 5, and 10, the quality of these bounds is analyzed by means of the optimum 20-term Hylleraas-type wave functions recently obtained by two of us [T. Koga and K. Matsui, Z. Phys. D (to be published)]. It is shown that the accuracy of both types of bounds increases with k for fixed Z, being greater for the lower bounds than for the upper bounds when k is small. Both bounds are of similar quality for big values of k. Moreover, any desired accuracy may be reached by increasing the k value.

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Here we consider the electron-electron property $\langle\delta(\mathbf{u})\rangle$, $\mathbf{u}\equiv\mathbf{r}_{12}$ being the interelectronic vector, of atomic and molecular systems. This quantity appears in the calculation of the relativistic [1] and radiative [2] corrections to the ground-state energy of atoms and ions as well as in the realization of the electron-electron or correlation cusp condition [3]. Moreover, (i) it is a very sensitive probe of the behavior of the wave function at small values of $\mathbf{r}_{12}$, and (ii) it is an important local property of the electron-pair density $I(\mathbf{u})$; namely, the value $h(0)$ at the origin of the spherically averaged electron-pair density $h(u)$ given by

$$h(u)=\frac{1}{4\pi}\int I(\mathbf{u})d\Omega_{\mathbf{u}}\ . \tag{1}$$

Indeed, one has [3]

$$\langle\delta(\mathbf{u})\rangle\equiv\int I(\mathbf{u})\delta(\mathbf{u})d\mathbf{u}=h(0)\ ,$$

where we have used the formulas

$$\delta(\mathbf{u})=(2\pi)^{-1}u^{-2}\delta(u),\quad \int_0^{\infty}\delta(u)h(u)du=\tfrac{1}{2}h(0)$$

as well as Eq. (1). Then, $\langle\delta(\mathbf{u})\rangle$ is a measure of probability of electron-electron coalescence. Our purpose is to study this property by means of the so-called interelectronic moments or radial expectation values $\langle u^{\alpha}\rangle$ defined as

$$\langle u^{\alpha}\rangle\equiv\int u^{\alpha}I(\mathbf{u})d\mathbf{u}=4\pi\int_0^{\infty}u^{\alpha+2}h(u)du\equiv 4\pi\mu_{\alpha+2}\ ,\qquad \alpha>-3\ ,$$

where $\{\mu_k;k=0,1,2,\ldots\}$ denote the moments about the origin of the one-dimensional probability density $h(u)$. In doing so, we continue the research of correlation properties of atomic systems using the interelectronic moments $\langle u^{\alpha}\rangle$ which we have recently initiated [4,5]. Although all the observations in this paper are related to the He-like systems, the method used and the results found in it may be extended to any other atomic and molecular system in a straightforward manner. We have found analytically upper and lower bounds to $h(0)$ in terms of the moments $\langle u^{\alpha}\rangle$ by making use of one of the following properties of $h(u)$: unimodality and the inequality $h(u)>h'(u)$ valid for any $u\geq 0$. Moreover, the accuracy of the resulting bounds is analyzed by means of the optimum 20-term Hylleraas-type wave functions of Koga and Matsui [6].

To obtain lower bounds to $h(0)$ we use the nonnegativity of the function $g_0(u)=h(u)-h'(u)$, which extends the known correlation cusp condition [3] to any u value as recently shown by the authors [5]. Stieltjes's theorem [7,8] applied to the density function $g_0(u)$ leads to the following determinantal inequalities:

$$\Delta_k=\begin{vmatrix}\nu_0 & \nu_1 & \cdots & \nu_k\\ \nu_1 & \nu_2 & \cdots & \nu_{k+1}\\ \vdots & \vdots & \ddots & \vdots\\ \nu_k & \nu_{k+1} & \cdots & \nu_{2k}\end{vmatrix}>0 \tag{2}$$

for all $k=0,1,2,\ldots$. The symbol ν_{α} denotes the moment around the origin of order α of the function $g_0(u)$, whose value is

$$\nu_{\alpha}=\int_0^{\infty}u^{\alpha}g_0(u)du=h(0)\delta_{\alpha 0}+\mu_{\alpha}+\alpha\mu_{\alpha-1}$$
$$=h(0)\delta_{\alpha 0}+\frac{1}{4\pi}[\langle u^{\alpha-2}\rangle+\alpha\langle u^{\alpha-3}\rangle]$$

for any $\alpha\geq 0$. Remark that

$$\nu_0=h(0)+\frac{1}{4\pi}\langle u^{-2}\rangle,\quad \nu_1=\frac{1}{4\pi}[\langle u^{-1}\rangle+\langle u^{-2}\rangle],\ldots .$$

TABLE I. Comparison, where it is possible, between the values of various ground-state quantities of the He-like atoms with $Z=1$, 2, 3, 5, and 10 calculated by means of the optimum 20-term Hylleraas-type wave functions and the near-exact ones. The symbols E, $h(0)$, $h_{\max}$, $u_{\max}$, and $\langle u^{\alpha}\rangle$ denote the total energy, the electron-pair density at the origin, the intensity, and the location of the maximum of the electron-pair density and the αth-order interelectronic moment. Atomic units are used throughout.

Quantity \ Z	1		2		3		5		10	
	Hylleraas	Near exact	Hylleraas	Near exact	Hylleraas	Near exact	Hylleraas	Near exact	Hylleraas	Near exact
$-E$	0.527 742	0.527 751	2.903 722	2.903 724	7.279 910	7.279 913	22.030 966	22.030 970	93.906 798	93.906 802
$h(0)$	0.002 82245	0.002 740	0.106 852	0.106 352	0.535 251	0.533 808	3.316 17	3.314 78	32.661 9	32.643 2
$h_{\max}$	0.0004 03015		0.116 518		0.556 017		3.362 56		32.768 6	
$u_{\max}$	0.926 347		0.191 818		0.081 9881		0.029 098 9		0.007021 38	
$\langle u^{-5/2}\rangle$	0.159 814		2.786 10		10.223 3		45.399 2		299.350	
$\langle u^{-2}\rangle$	0.155 344	0.155 108	1.465 10	1.464 77	4.082 91	4.082 25	13.308 0	13.307 5	59.697 5	59.694 6
$\langle u^{-3/2}\rangle$	0.203 191		1.080 24		2.314 88		5.587 58		17.160 3	
$\langle u^{-1}\rangle$	0.311 136	0.311 022	0.945 819	0.945 818	1.567 72	1.567 72	2.814 71	2.814 70	5.937 25	5.937 24
$\langle u^{-1/2}\rangle$	0.533 101		0.930 219		1.196 46		1.601 89		2.325 14	
$\langle u^{0}\rangle$	1	1	1	1	1	1	1	1	1	1
$\langle u^{1/2}\rangle$	2.027 57		1.156 14		0.899 952		0.6272 893		0.463 964	
$\langle u\rangle$	4.406 54	4.412 69	1.422 08	1.422 07	0.862 320	0.862 315	0.482 435	0.482 436	0.229 492	0.229 492
$\langle u^{3/2}\rangle$	10.203 9		1.846 58		0.872 666		0.365 498		0.120 002	
$\langle u^{2}\rangle$	25.059 5	25.202 0	2.516 49	2.516 44	0.927 083	0.927 064	0.290 790	0.290 791	0.065 917 3	0.065 917 4
$\langle u^{5/2}\rangle$	65.020 7		3.582 63		1.028 99		0.241 769		0.037 848 2	
$\langle u^{3}\rangle$	177.627	180.601	5.308 40	5.308 00	1.188 64	1.188 56	0.290 239	0.209 243	0.022 625 3	0.022 625 4
$\langle u^{7/2}\rangle$	509.244		8.160 95		1.424 49		0.187 886		0.014 035 2	
$\langle u^{4}\rangle$	1527.21	1590.0	12.983 9	12.981 2	1.766 33	1.766 0	0.174 568	0.174 58	0.009 009 84	0.009 010 0

TABLE II. Values of the central electron-pair density $h(0)$ and the three first lower bounds L_k, $k=1$, 2, and 3, calculated with the optimum 20-term Hylleraas-type wave functions in the heliumlike systems characterized by $Z=1$, 2, 3, 5, and 10. Atomic units are used throughout.

Z	L_1	L_2	L_3	$h(0)$
1	−0.001 688	0.000 622 3	0.001 513	0.002 822
2	0.043 37	0.078 27	0.090 89	0.106 9
3	0.289 5	0.424 4	0.473 5	0.535 3
5	2.061	2.750	3.001	3.316
10	21.88	27.78	29.93	32.66

From the inequality (2) one has that

$$\Delta_k=\sum_{j=0}^{k}\nu_j A_j=\nu_0 A_0+\sum_{j=1}^{k}\nu_j A_j>0\ ,$$

where A_j is the cofactor of ν_j, i.e., $(-1)^j$ times the determinant resulting from the elimination of the first row and $(j+1)$th column of Δ_k. From this equation one easily obtains that

$$h(0)>L_k\equiv-\left[\mu_0+A_0^{-1}\sum_{j=1}^{k}\nu_j A_j\right],\quad k=1,2,3,\ldots\ ,$$

which produces an infinite set of lower bounds L_k to $h(0)$. The bound $L_0=-\mu_0=-\langle u^{-2}\rangle/4\pi$ is useless since $\langle u^{-2}\rangle$ is always positive, but

$$L_1=\frac{1}{4\pi}\frac{\langle u^{-1}\rangle^2+\langle u^{-2}\rangle(\langle u^{-2}\rangle-\langle u^0\rangle)}{\langle u^0\rangle+2\langle u^{-1}\rangle}$$

and so on provide us with useful bounds as we will see later. One should keep in mind that $\langle u^0\rangle=1$ for two-electron atoms.

Secondly, to obtain upper bounds to $h(0)$ we use the known unimodal character [3,9] of $h(u)$. Then, by construction the function

$$\phi(u)\equiv(u_{\max}-u)h'(u)$$

is always non-negative. Its moments around the origin are given by

$$\xi_j=\int_0^\infty u^j\phi(u)du=\begin{cases}\mu_0-u_{\max}h(0) & \text{if } j=0\\ (j+1)\mu_j-u_{\max}j\mu_{j-1}, & \text{if } j>0\ ,\end{cases}\tag{3}$$

where $u_{\max}$ denotes the location of the maximum of $h(u)$.

Then, Stieltjes's theorem applied to the density function $\phi(u)$ produces an infinite set of determinantal inequalities for the moments ξ_j similar to that given by (2). These new inequalities together with Eq. (3) lead to the new upper bounds U_k as

$$h(0)<U_k\equiv\frac{1}{u_{\max}}\left[\frac{1}{4\pi}\langle u^{-2}\rangle+\frac{1}{B_0}\sum_{j=1}^{k}\xi_j B_j\right]$$

for any $k=0,1,2,\ldots$ and where $\{B_j,\ j=0,1,2,\ldots\}$ have a meaning analogous to $\{A_j\}$. For illustration, let us point out that the explicit expression of the lowest-order upper bound is

$$U_0=\frac{1}{4\pi}\frac{\langle u^{-2}\rangle}{u_{\max}}\ .$$

Finally, for the sake of completeness, we study numerically the quality of the bounds L_k and U_k found here. To do that we use the optimum 20-term Hylleraas-type wave functions recently described in [9]. They are very appropriate for this purpose as it is shown in Table I where the values of various ground-state properties obtained with these wave functions are compared, where it is possible, with the near-exact ones [10] in the two-electron atoms with $Z=1$, 2, 3, 5, and 10. The properties considered are the total energy E, the central electron-pair density $h(0)$, various interelectronic moments $\langle u^\alpha\rangle$, and the intensity $h_{\max}$ and location $u_{\max}$ of the maximum of the electron-pair density. One observes that (i) the optimum Hylleraas-type 20-term wave functions are of sufficient accuracy except possibly for the $Z=1$ case, and (ii) there is not yet enough information available for $h(u)$ and $\langle u^\alpha\rangle$ at the near-exact level.

In Table II the quality of the lower bounds L_k, $k=1$, 2, and 3, is discussed for various two-electron atoms with $Z=1,2,3,5$, and 10. One notices that it increases with Z for fixed k and with k for fixed Z. Going He through Ne^{8+} one has that the accuracy of the bounds goes (i) from 41% up to 67% in the L_1 case, (ii) from 73% up to 85% in the L_2 case, and (iii) from 85% up to 92% in the L_3 case.

Similarly, the quality of the upper bounds U_k, $k=0$, 1, 2, and 3, is illustrated in Table III for the same aforementioned heliumlike ions. It is apparent that it decreases with Z for fixed k, contrary to what happens for the lower bounds, and it increases with k for fixed Z faster than for the lower bounds. In the He case, for example, the bound U_3 is 1.14 times the Hylleraas $h(0)$ value. In fact, for both lower and upper bounds one can get any

TABLE III. Values of the central electron-pair density $h(0)$ and the four first upper bounds U_k, $k=0,1,2,$and3, calculated with the optimum 20-term Hylleraas-type wave functions in the heliumlike systems characterized by $Z=1$, 2, 3, 5, and 10. Atomic units are used throughout.

Z	U_0	U_1	U_2	U_3	$h(0)$
1	0.013 44	0.005 233	0.004 008	0.003 643	0.002 822
2	0.607 8	0.199 7	0.137 8	0.121 6	0.106 9
3	3.963	1.187	0.745 2	0.625 2	0.535 3
5	36.39	9.896	5.486	4.236	3.316
10	676.6	166.7	78.71	52.86	32.66

desired accuracy by means of the inclusion of a high enough number of interelectronic moments, i.e., by taking into account a high enough value of k in the corresponding L_k and U_k expressions.

In summary, we have derived lower L_k and upper U_k bounds to the interelectronic quantity $h(0)=\langle \delta(\mathbf{u}) \rangle$ in terms of the moments $\langle u^\alpha \rangle$. Satisfactory accuracy of these bounds has been shown for several He-like atoms.

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