Bounds to some local electron-pair properties with application to two-electron ions

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(Received 1 July 1993)

New bounds to the maximum characteristics u_{max} and $h_{max}=h(u_{max})$ of the spherically averaged electron-pair density $h(u)$ and to the electron-electron coalescence $h(0)=\langle\delta(\mathbf{u})\rangle$ of a many-electron system are shown in a rigorous manner (i.e., no approximate wave functions were used). The resulting rigorous inequalities also allow one to bound a given interelectronic moment $\langle u^{\beta}\rangle$ from above and from below. In particular, an interesting inequality is obtained for the electron-electron repulsion energy E_{ee} of an N-electron system: $2\pi h(0)u_{max}^2 \le E_{ee} \le 3N(N-1)/4u_{max}$. For completeness, just to have an idea of the worth of these results, some of the rigorous inequalities are numerically studied for two-electron ions with nuclear charge $Z=1$, 2, 3, 4, 5, and 10 using a highly accurate electron-pair density $h(u)$ constructed from the 204-term Hylleraas wave functions. The accuracy is found to increase, generally, with increasing Z and decreasing order β of the involved moments.

PACS number(s): 31.10.+z, 31.20.Tz, 71.10.+x

The structural features of the three-dimensional electron-pair density [1,2] $I(\mathbf{u})$ and its spherical average $h(u)\equiv(4\pi)^{-1}\int I(\mathbf{u})d\Omega_{\mathbf{u}}$, $\mathbf{u}=(u,\Omega_{\mathbf{u}})$, u being the interelectronic coordinate, strongly condition the electron correlation properties in atoms and molecules. We may cite Ref. [3] for a comprehensive review of the general properties of $h(u)$ up to 1986. Therein one realizes that the only known rigorous analytical characteristics of $h(u)$ are non-negativity and unimodality [4] (i.e., it displays a single maximum often away from the origin). However, we have recently shown in a Hylleraas-type framework that a related interelectronic function $h(u)/u^{\alpha}$, $\alpha>0$, is not only monotonically decreasing from the origin [5,6] but is also convex [5,6] and, even more importantly, log-convex [7] for some specific α values.

In this paper, we investigate in a rigorous manner (i.e., no approximate wave functions are used) some local properties of the spherically averaged electron-pair density $h(u)$, namely its central value $h(0)$ and the coordinates $[u_{max},h_{max}=h(u_{max})]$ of its maximum, in a rigorous inequality framework by means of the so-called interelectronic moments defined by

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

where $\{\mu_k;\ k=0,1,2,\ldots\}$ denotes the moments around the origin of the one-dimensional probability density $h(u)$. The former local quantity has a special physical significance: the electron-electron quantity $h(0)$ appears in the calculation of the relativistic [8] and radiative [9] corrections to the ground-state energy of atoms and ions as well as in the realization of the correlation cusp condition [4]; moreover, $h(0)=\langle\delta(\mathbf{u})\rangle$, i.e., it is a measure of the electron-electron coalescence [4,10,11].

The main results of this paper are (i) upper bounds to $h(0)$ and to the location u_{max} of the maximum of $h(u)$, and (ii) lower bounds to the intensity h_{max} of that maximum. The upper bounds are obtained by applying the Stieltjes theorem to any N-particle system with a unimodal particle-particle density $h(u)$, and the lower bounds are variationally found based only on the nonnegativity. Then, for completeness, the quality of some of these analytically rigorous bounds is numerically studied for two-electron atoms by means of the recent 204-term Hylleraas wave functions [12].

Upper bounds to $h(0)$. The only existing upper bounds are those of Ref. [10], which are given in terms of u_{max} and one or more interelectronic moments. Among these, the one-moment bound is given by

$$h(0)\le U_0\equiv\frac{1}{4\pi}\frac{\langle u^{-2}\rangle}{u_{max}}\,, \tag{1}$$

whose quality is very poor. Here we find that

$$h(0)\le U_k^{(q)}\,,\quad q\ge 0\ \text{ and }\ k=0,1,2,\ldots$$

with

$$U_k^{(q)}\equiv\frac{1}{u_{max}^q}\frac{q}{4\pi}\langle u^{q-3}\rangle+\frac{1-\delta_{k,0}}{A_0}\sum_{j=1}^{k}\xi_j(q)A_j\,, \tag{2}$$

where $\delta_{k,0}$ is the Kronecker delta, and A_j is the cofactor of $\xi_j(q)$ in the determinant Δ_k given by

$$\Delta_k=\begin{vmatrix}\xi_0(q) & \xi_1(q) & \cdots & \xi_k(q)\\ \xi_1(q) & \xi_2(q) & \cdots & \xi_{k+1}(q)\\ \vdots & \vdots & \ddots & \vdots\\ \xi_k(q) & \xi_{k+1}(q) & \cdots & \xi_{2k}(q)\end{vmatrix}\,,$$

where the quantities $\xi_j(q)$ are given by

$$\xi_j(q)=\begin{cases}\dfrac{q}{4\pi}\langle u^{q-3}\rangle-h(0)u_{max}^q\,, & j=0\\ \dfrac{j+q}{4\pi}\langle u^{j+q-3}\rangle-\dfrac{j}{4\pi}\langle u^{j-3}\rangle u_{max}^q\,, & j>0\,.\end{cases} \tag{3}$$

For a given many-particle system, the higher the k value, the more involved becomes the bound. Since we are looking for analytically simple bounds, let us fix our attention to the subcase $k=0$. Then, Eq. (2) reduces to

$$U_0^{(q)} = \frac{1}{u_{\max}^q} \frac{q}{4\pi} \langle u^{q-3} \rangle \ , \quad q \geq 0 \ , \tag{4}$$

which considerably extends the inequality (1). Indeed, apart from the fact that $U_0^{(1)} = U_0$, the first few cases $q = 0$, 2, and 3 produce the following interesting expressions:

$$h(0) = \lim_{q \to 0} \frac{q}{4\pi} \langle u^{q-3} \rangle \ , \tag{5}$$

$$h(0) \leq U_0^{(2)} = \frac{2}{4\pi} \frac{\langle u^{-1} \rangle}{u_{\max}^2} = \frac{1}{2\pi} \frac{E_{ee}}{u_{\max}^2} \ , \tag{6}$$

$$h(0) \leq U_0^{(3)} = \frac{3}{4\pi} \frac{\langle u^0 \rangle}{u_{\max}^3} = \frac{3}{8\pi} \frac{N(N-1)}{u_{\max}^3} \ , \tag{7}$$

respectively. Equation (5) gives the exact value of the electron-electron coalescence in a limiting form, which has been recently found by different means [11]. The inequality (6) allows the correlation of the total electron-electron repulsion energy $E_{ee} = \langle u^{-1} \rangle$, $h(0)$ and the location $u_{\max}$ of the electron-pair maximum. The inequality (7) gives an upper bound to $h(0)$, which depends only on $u_{\max}$ and the number N of constituent electrons. At this point, it is worth remarking that the local properties $h(0)$, $u_{\max}$, and $h_{\max}$ of $h(u)$ which are being considered in this paper provide rigorous bounds to the repulsion energy E_{ee} of an N-electron system from above and from below as

$$2\pi h(0) u_{\max}^2 \leq E_{ee} \leq \left[\frac{9\pi}{8} N^2 (N-1)^2 h_{\max} \right]^{1/3} \ , \tag{8}$$

where we have taken into account the upper bound to E_{ee} recently reported [5].

Upper bounds to the maximum location $u_{\max}$. We have recently found [5] a simple upper bound to $u_{\max}$ by means of the moments $\langle u^{-1} \rangle$ and $\langle u^{-2} \rangle$ as

$$u_{\max} \leq H_0 \equiv 2 \frac{\langle u^{-1} \rangle}{\langle u^{-2} \rangle} \ , \tag{9}$$

which is valid for any many-electron system with a unimodal electron-pair density $h(u)$. Bounds including these two moments and others of different order are also known [5]; however, they are much less analytically tractable, although more accurate [6] than H_0.

Here we find that

$$u_{\max} \leq G(\alpha,\beta) \equiv \left[\frac{(\alpha+3)\langle u^{\alpha} \rangle}{(\beta+3)\langle u^{\beta} \rangle} \right]^{1/(\alpha-\beta)} \ , \quad \alpha > \beta > -3 \ , \tag{10}$$

which substantially generalizes the inequality (9). Indeed, one can check not only that $G(-1,-2) = H_0$ but also that

$$u_{\max} \leq G(\alpha,\beta \to -3) = \left[\frac{(\alpha+3)\langle u^{\alpha} \rangle}{4\pi h(0)} \right]^{1/(\alpha+3)} \ , \quad \alpha > -3 \ , \tag{11}$$

which can also be derived from the inequality $h(0) \leq U_0^{(q)}$ shown in Eq. (4).

Some other interesting cases of the inequality (10) are

$$G(\alpha,-1) = \left[\frac{(\alpha+3)\langle u^{\alpha} \rangle}{2\langle u^{-1} \rangle} \right]^{1/(\alpha+1)} \ , \quad \alpha > -1 \ , \tag{12}$$

TABLE I. Various ground-state properties of the 204-term Hylleraas wave functions used in the present numerical study. Atomic units are used throughout.

	$Z=1$		$Z=2$		$Z=3$		$Z=4$		$Z=5$		$Z=10$	
	Present	Thakkar-Smith	Present	Thakkar-Smith	Present	Thakkar-Smith	Present	Thakkar-Smith	Present	Thakkar-Smith	Present	Thakkar-Smith
$-E$	0.527 751	0.527 751	2.903 72	2.903 72	7.279 91	7.279 91	13.655 6	13.655 6	22.031 0	22.031 0	93.906 8	93.906 8
$h(0)$	0.002 739 78	0.002 740	0.106 353	0.106 352	0.533 747	0.533 808	1.522 95	1.524 587	3.312 53	3.314 78	32.620 8	32.643 2
$h_{\max}$	0.004 039 96		0.116 535		0.555 786		1.558 05		3.361 30		32.741 1	
$u_{\max}$	0.927 042		0.193 674		0.083 438 0		0.046 485 0		0.029 646 4		0.007 405 69	
α_1	0.178 899		0.044 465 2		0.019 941 8		0.011 293 7		0.007 263 55		0.001 837 75	
α_2	0.396 100		0.209 365		0.161 976		0.140 838		0.128 947		0.106 905	
$\langle u^{-5/2} \rangle$	0.158 904		2.783 28		10.216 3		24.009 7		45.386 9		299.246	
$\langle u^{-2} \rangle$	0.155 106	0.155 108	1.464 77	1.464 77	4.082 24	4.082 25	8.028 81	8.029 19	13.307 1	13.307 5	59.691 9	59.694 6
$\langle u^{-3/2} \rangle$	0.203 071		1.080 20		2.314 81		3.832 23		5.587 49		17.160 0	
$\langle u^{-1} \rangle$	0.311 022	0.311 022	0.945 818	0.945 818	1.567 72	1.567 72	2.190 87	2.190 87	2.814 70	2.814 70	5.937 24	5.937 24
$\langle u^{-1/2} \rangle$	0.532 972		0.930 221		1.196 46		1.413 69		1.601 89		2.325 14	
$\langle u^0 \rangle$	1	1	1	1	1	1	1	1	1	1	1	1
$\langle u^{1/2} \rangle$	2.028 586		1.156 14		0.899 950		0.762 162		0.672 893		0.463 963	
$\langle u \rangle$	4.412 67	4.412 69	1.422 07	1.422 07	0.862 315	0.862 315	0.618 756	0.618 757	0.482 436	0.482 436	0.229 492	0.229 492
$\langle u^{3/2} \rangle$	10.234 3		1.846 56		0.872 657		0.530 710		0.365 500		0.120 002	
$\langle u^2 \rangle$	25.201 3	25.202 0	2.516 44	2.516 44	0.927 065	0.927 064	0.477 947	0.477 947	0.290 791	0.290 791	0.065 917 4	0.065 917 4
$\langle u^{5/2} \rangle$	65.669 2		3.582 48		1.028 95		0.449 763		0.241 773		0.037 848 3	
$\langle u^3 \rangle$	180.583	180.601	5.308 01	5.308 00	1.188 57	1.188 56	0.440 530	0.440 530	0.209 245	0.209 243	0.022 625 4	0.022 625 4
$\langle u^{7/2} \rangle$	522.759		8.159 94		1.424 34		0.447 667		0.187 894		0.014 035 2	
$\langle u^4 \rangle$	1589.37	1590.0	12.981 3	12.981 2	1.766 04	1.766 0	0.470 699	0.470 69	0.174 581	0.174 58	0.009 009 85	0.009 010 0

$$G(\alpha,0)=\left[\frac{(\alpha+3)\langle u^{\alpha}\rangle}{3\langle u^{0}\rangle}\right]^{1/\alpha}, \quad \alpha>0, \tag{13}$$

and

$$G(\alpha,\alpha)=\exp\left[\frac{1}{\alpha+3}+\frac{\langle u^{\alpha}\ln u\rangle}{\langle u^{\alpha}\rangle}\right], \quad \alpha>-3. \tag{14}$$

To obtain Eq. (14) we have used the rigorous relation $d/dt\langle u^{t}\rangle=\langle u^{t}\ln u\rangle$. Since we use the normalization $\langle u^{0}\rangle=\frac{1}{2}N(N-1)$ for an N-electron system and $\langle u^{-1}\rangle=E_{ee}$, the above expressions produce the following important inequalities:

$$E_{ee}\le\frac{(\alpha+3)\langle u^{\alpha}\rangle}{2u_{\max}^{\alpha}}, \quad \alpha>-1, \tag{15}$$

$$\langle u^{\alpha}\rangle\ge\frac{3N(N-1)}{2(\alpha+3)}u_{\max}^{\alpha}, \quad \alpha>0,$$
$$\langle\ln u\rangle\ge\tfrac{1}{2}N(N-1)[\ln u_{\max}-\tfrac{1}{3}], \tag{16}$$

which explicitly show how various electron-electron properties of an N-electron system get conditioned by means of the knowledge of the maximum location $u_{\max}$ of the electron-pair density. A special value $\alpha=0$ in the inequality (15) leads to the following upper bound for the repulsion energy:

$$E_{ee}\le\frac{3N(N-1)}{4u_{\max}}, \tag{17}$$

which is to be compared with that originally obtained in Ref. [5] and shown in Eq. (8).

To prove the general upper bounds $U_k^{(q)}$ and $G(\alpha,\beta)$ given by Eqs. (2) and (10), respectively, we use the unimodality of the electron-pair density, according to which one can write that

$$\phi_q(u)\equiv(u_{\max}^{q}-u^{q})h'(u)\ge0, \quad q\ge0.$$

The moments of this univariate non-negative function, i.e., the quantities

$$\xi_j(q)\equiv\int_0^{\infty}u^{j}\phi_q(u)du,$$

can be easily shown to have the values given by Eq. (3). Then, a straightforward application of the Stieltjes theorem (which is valid for any non-negative density function) to $\phi_q(u)$ produces the following Hadamard determinantal inequalities [14,15]:

$$\Delta_k^{(m)}\equiv\begin{vmatrix}\xi_m(q) & \xi_{m+1}(q) & \cdots & \xi_{m+k}(q)\\ \xi_{m+1}(q) & \xi_{m+2}(q) & \cdots & \xi_{m+k+1}(q)\\ \vdots & \vdots & \ddots & \vdots\\ \xi_{m+k}(q) & \xi_{m+k+1}(q) & \cdots & \xi_{m+2k}(q)\end{vmatrix}\ge0,$$

for any real non-negative m and q, and $k=0,1,2,\ldots$. Now, setting $m=0$ and developing the resulting determinant $\Delta_k\equiv\Delta_k^{(0)}$ with respect to the first row, one can easily obtain the desired bounds $U_k^{(q)}$ to $h(0)$ given by Eq. (2). On the other hand, in the case $k=0$ the inequality $\Delta_0^{(m)}=\xi_m(q)>0$ produces

$$u_{\max}\le\left[\frac{(j+q)\langle u^{j+q-3}\rangle}{j\langle u^{j-3}\rangle}\right]^{1/q}, \quad j,q>0,$$

which gives rise to the second desired bounds $G(\alpha,\beta)$ given by Eq. (10) after a trivial change of variable. Moreover, one can obtain new, better, but more complicated upper bounds to $u_{\max}$ from the cases $k>0$.

Lower bounds to the maximum intensity $h_{\max}$. Recently [5] it has been variationally shown that the value $h_{\max}$ of the electron-pair density at its maximum is bounded from below as

$$h_{\max}\ge H(\alpha,\beta)\equiv\frac{1}{4\pi}\left\{\frac{[(\beta+3)\langle u^{\beta}\rangle]^{\alpha+3}}{[(\alpha+3)\langle u^{\alpha}\rangle]^{\beta+3}}\right\}^{1/(\alpha-\beta)}, \quad \alpha>\beta>-3.$$

This inequality was analytically proved and discussed in Ref. [5] and its accuracy was numerically analyzed in Ref. [6] for some heliumlike atoms. The use of a similar variational technique allows us to find (i) lower bounds which depend on three interelectronic moments, as, e.g.,

$$h_{\max}\ge\frac{5\sqrt{5}\langle u^{-1}\rangle^{3}}{54\pi^{2}}\left[\frac{\langle u^{0}\rangle\langle u^{-2}\rangle-\langle u^{-1}\rangle^{2}}{\langle u^{0}\rangle^{5}\langle u^{-2}\rangle}\right]^{1/2};$$

and (ii) a lower bound which depends on the interelectronic mean logarithmic radius $\langle\ln u\rangle$ as given by

$$h_{\max}\ge\frac{3\langle u^{0}\rangle}{4\pi}\exp\left[-1-3\frac{\langle\ln u\rangle}{\langle u^{0}\rangle}\right]. \tag{18}$$

Let us point out that the combination of the inequalities (16) and (18) allows us to bound, from above and from below, the interelectronic mean logarithmic radius $\langle\ln u\rangle$ in terms of the maximum characteristics of the electron-pair density as

$$\tfrac{1}{2}N(N-1)[\ln u_{\max}-\tfrac{1}{3}]\le\langle\ln u\rangle\le\tfrac{1}{6}N(N-1)\left[-1-\ln\frac{8\pi h_{\max}}{3N(N-1)}\right]$$

for any N-electron system.

Numerics. To give the reader an idea of the quality of the bounds found in this paper, we have numerically studied the accuracy of some of them in the two-electron ions with nuclear charge $Z=1$ (H^-), 2 (He), 3 (Li^+), 4 (Be^{2+}), 5 (B^{3+}), and 10 (Ne^{8+}). To do that we have used the most accurate electron-pair density $h(u)$ in the literature constructed from the 204-term Hylleraas wave functions. Various ground-state properties obtained from these wave functions are given in Table I. It lists the total energy E, the central electron-pair density $h(0)$, the intensity $h_{\max}$ and the location $u_{\max}$ of the maximum of the electron-pair density, the values α_1 and α_2 for which

TABLE II. Accuracy of the upper bound $U_0^{(q)}$, given in percents, to the central electron-pair density $h(0)$.

q	$Z=1$	$Z=2$	$Z=3$	$Z=4$	$Z=5$	$Z=10$
0.000 01	100.0	100.0	100.0	100.0	100.0	100.0
0.000 1	99.98	99.98	99.98	99.98	99.98	99.97
0.001	99.76	99.82	99.81	99.79	99.78	99.72
0.01	97.69	98.22	98.09	97.93	97.78	97.24
0.10	80.63	83.76	82.48	81.07	79.82	75.47
0.20	66.97	70.46	68.04	65.63	63.57	56.74
0.30	56.64	59.40	56.09	53.03	50.49	42.50
0.40	48.44	50.11	46.17	42.75	39.99	31.71
0.50	41.72	42.26	37.93	34.37	31.58	23.58
0.60	36.10	35.61	31.09	27.56	24.87	17.47
0.70	31.32	29.97	25.43	22.04	19.52	12.89
0.80	27.22	25.18	20.75	17.57	15.28	9.49
0.90	23.67	21.11	16.89	13.97	11.92	6.96
1.00	20.58	17.67	13.71	11.08	9.27	5.09

TABLE III. Accuracy of the upper bound $U_1^{(q)}$, given in percents, to the central electron-pair density $h(0)$.

q	$Z=1$	$Z=2$	$Z=3$	$Z=4$	$Z=5$	$Z=10$
0.000 01	100.0	100.0	100.0	100.0	100.0	100.0
0.000 1	99.99	100.0	100.0	100.0	99.99	99.99
0.001	99.91	99.96	99.96	99.95	99.95	99.93
0.01	99.07	99.53	99.52	99.47	99.42	99.22
0.10	91.72	93.61	92.29	90.92	89.68	85.22
0.20	85.05	84.33	80.27	76.80	73.93	64.78
0.30	79.32	73.68	67.10	62.16	58.34	47.29
0.40	74.16	62.94	54.82	49.26	45.20	34.25
0.50	69.34	52.94	44.23	38.70	34.81	24.84
0.60	64.72	44.08	35.49	30.33	26.79	18.08
0.70	60.23	36.47	28.42	23.76	20.64	13.18
0.80	55.82	30.06	22.74	18.63	15.92	9.62
0.90	51.48	24.72	18.19	14.61	12.28	7.02
1.00	47.21	20.31	14.56	11.46	9.48	5.11

TABLE IV. Accuracy of the upper bound $U_2^{(q)}$, given in percents, to the central electron-pair density $h(0)$.

q	$Z=1$	$Z=2$	$Z=3$	$Z=4$	$Z=5$	$Z=10$
0.000 01	100.0	100.0	100.0	100.0	100.0	100.0
0.000 1	99.99	100.0	100.0	100.0	100.0	100.0
0.001	99.93	99.98	99.98	99.98	99.98	99.97
0.01	99.31	99.75	99.77	99.76	99.73	99.61
0.10	93.84	95.43	94.22	92.92	91.75	87.40
0.20	88.92	87.09	82.80	79.17	76.18	66.58
0.30	84.72	76.62	69.41	64.09	60.01	48.32
0.40	80.92	65.60	56.59	50.60	46.27	34.77
0.50	77.30	55.13	45.49	39.56	35.45	25.09
0.60	73.73	45.78	36.34	30.85	27.16	18.19
0.70	70.13	37.74	28.97	24.08	20.85	13.24
0.80	66.42	30.99	23.10	18.82	16.03	9.65
0.90	62.59	25.39	18.42	14.72	12.35	7.03
1.00	58.63	20.78	14.70	11.53	9.51	5.12

the electron-pair function $h(u)/u^{\alpha}$ is monotonically decreasing and convex, respectively, and various interelectronic moments $\langle u^{\beta} \rangle$ of integer and half-integer orders β. Table I also includes, when available, the previous best values reported by Thakkar and Smith [13] for comparison.

In Tables II–IV, the quality of the upper bounds $U_k^{(q)}$, $k=0$, 1, and 2, to the electron-electron coalescence measure $h(0)$ is discussed for the aforementioned two-electron ions, respectively. It is observed that not only $U_0^{(q)}$, as rigorously shown in Eq. (5), but also $U_1^{(q)}$ and $U_2^{(q)}$ tend towards the exact value of $h(0)$ in the limiting case $q \to 0$. For a fixed Z, the accuracy of the upper bounds decreases when q increases, while for a fixed q, the higher the nuclear charge, the less accurate the upper bound.

A similar numerical analysis of bounds to $u_{\max}$ and $h_{\max}$ has also been done. We only note that, although rigorous, they are not as accurate. In particular, the accuracy of the inequality (18) is about 35% in all the ions here considered.

To summarize, the interelectronic moments $\langle u^{\beta} \rangle$ of a many-electron system have been used as basic elements to study in an inequality framework some local electron-electron properties, namely the central value $h(0)$ and the maximum characteristics $(u_{\max}, h_{\max})$ of the spherically averaged electron-pair density $h(u)$. The resulting inequalities are simple, compact, and transparent if, at most, two moments are included. In the case where we consider a higher number of moments, the corresponding bounds to $h(0)$ and $u_{\max}$ get much more involved but more accurate.

Looking at these inequalities in the opposite way, one finds how the interelectronic moments get bounded by means of the analytical properties of the electron-pair density $h(u)$ specified by $h(0)$, $u_{\max}$, and $h_{\max}$. In this sense, the upper and lower bounds, given by inequalities (8) and (17), to the total electron-electron repulsion energy E_{ee} of an N-electron system would be worth pointing out.

Finally, the worth of some of the present inequalities has been analyzed in several two-electron ions by means of the highly accurate 204-term Hylleraas-type wave functions recently constructed [12]. Generally speaking, the lower the order of the involved interelectronic moments and the nuclear charge, the more accurate the corresponding bound.

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