

Electron–electron coalescence and interelectronic log-moments in atomic systems

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Abstract. A measure of the spatial electron–electron coalescence in atomic and molecular systems is given by the local quantity $\langle \delta(\mathbf{u}) \rangle$, $\mathbf{u} = \mathbf{r}_{12}$ being the interelectronic vector and δ the three-dimensional Dirac delta function. Here it is argued that there exists a function $H(s, t)$, $s > t > -3$, which depends on two interelectronic moments $\langle u^\alpha \rangle$ and plays an important role in the electron correlation problem. In particular it is rigorously fulfilled that for an arbitrary but fixed s ,

$$\lim_{t \rightarrow -3} H(s, t) = (1/4\pi) \lim_{t \rightarrow -3} [(t+3)\langle u^t \rangle] = \langle \delta(\mathbf{u}) \rangle.$$

Additionally, specific values of the function $H(s, t)$ are shown to be related to the log-moments $\langle u^t \ln u \rangle$; e.g., the interelectronic mean logarithmic radius $\langle \ln u \rangle$ is expressed in terms of $H(0, 0)$ in a simple manner. From a numerical point of view, the values of the quantities $\langle u^t \rangle$ and $\langle u^t \ln u \rangle$ as well as the values of the two-moment function $H(s, t)$ are calculated in the two-electron atoms with nuclear charge $Z = 1, 2, 3, 5$ and 10 by means of the optimum 20-term Hylleraas-type wave functions. Finally, further bounds to $\langle \delta(\mathbf{u}) \rangle$ valid for the aforementioned two-electron atoms are found by means of log-moments.

Keywords. Electron–electron coalescence; interelectronic log-moments; atomic systems.

1. Introduction

The electron-pair density $I(\mathbf{u})$ of a many-electron system represents the probability density for the interelectronic vector $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$. It is a very useful quantity to analyze electron-correlation effects (Coulson and Neilson 1961; Tatewaki and Tanaka 1974; Thakkar and Smith 1977a) of atomic and molecular systems. A nice review of those effects closely connected with electron-pair densities in position and momentum spaces is given by Thakkar (1987).

Last year we initiated (Dehesa *et al* 1992) a study of the properties associated with this interelectronic density by means of its moments

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

*For correspondence

where $h(u)$ is the spherical average of $I(\mathbf{u})$, i.e. $h(u) = (1/4\pi) \int I(\mathbf{u}) d\Omega_{\mathbf{u}}$. Now, we are specially interested in the local electron–electron quantity $\langle \delta(\mathbf{u}) \rangle$ which is equal (Thakkar and Smith 1976) to the value $h(0)$ of $h(u)$ at the origin. This quantity gives a measure of the electron–electron coalescence and it appears in the calculation of the relativistic (Bethe and Salpeter 1957) and radiative (Kabir and Salpeter 1957) corrections to the ground-state energy of atoms and ions as well as in the realization of the electron–electron or correlation cusp condition of many-electron systems (Thakkar and Smith 1976). Our attention will be centered around those systems with a unimodal $h(u)$; this situation occurs, e.g., in the two-electron atoms (Thakkar and Smith 1977a).

Recently we have found (Dehesa *et al* 1993) analytical lower and upper bounds to this electron–electron coalescence measure. These bounds involve the interelectronic moments $\langle u^s \rangle$ and the location u_{\max} of the maximum of $h(u)$. Besides, it is known (Dehesa *et al* 1992a) that the maximum intensity h_{\max} of $h(u)$ is bounded from below by the following two-moment function $H(s, t)$:

$$H(s, t) = \frac{1}{4\pi} \left\{ \frac{[(t+3)\langle u^t \rangle]^{s+3}}{[(s+3)\langle u^s \rangle]^{t+3}} \right\}^{1/(s-t)} \quad (1)$$

where s and t are real numbers, $s > t > -3$.

This paper is structured as follows. In section 2 the main theoretical results are described in a limiting form which depends on the interelectronic moments $\langle u^t \rangle$ and log-moments $\langle u^t \ln u \rangle$. The latter quantities as well as the fundamental function $H(s, t)$ are numerically analyzed in section 3 for several two-electron atoms by means of the optimum 20-term Hylleraas-type wave functions. In doing so, new and interesting lower bounds to the electron–electron coalescence measure $\langle \delta(\mathbf{u}) \rangle$ are encountered. Finally, in section 4, some concluding remarks are given.

2. Theoretical results

Here we discuss the function $H(s, t)$ defined by (1) to gain physical insight in the correlation problem of a multielectronic system, with emphasis in the electron–electron coalescence. From an analytical point of view let us point out that the limit $s \rightarrow t$ in (1) produces

$$H(t, t) = \frac{1}{4\pi} (t+3) \langle u^t \rangle \exp \left[-1 - (t+3) \frac{\langle u^t \ln u \rangle}{\langle u^t \rangle} \right], \quad t > -3, \quad (2)$$

where we have used the rigorous relation

$$d\langle u^t \rangle / dt = \langle u^t \ln u \rangle.$$

Equation (2) may be used for various purposes, in particular to estimate the ratio $\langle u^t \ln u \rangle / \langle u^t \rangle$ and to evaluate the interelectronic mean logarithmic radius $\langle \ln u \rangle$ as

$$\langle \ln u \rangle = \frac{\langle u^0 \rangle}{3} \left[-1 - \ln \frac{4\pi H(0, 0)}{3\langle u^0 \rangle} \right],$$

where $\langle u^0 \rangle = \frac{1}{2}N(N-1)$ for an N -electron system.

On the other hand, the limit $t \rightarrow -3$ in (1) allows us to express the quantity $\langle \delta(\mathbf{u}) \rangle$ as

$$\langle \delta(\mathbf{u}) \rangle = \lim_{t \rightarrow -3} H(s, t) \quad (3)$$

for any constant value of s . In doing so, we have made use of the following simple, but not known up to now, expression of the same quantity,

$$\langle \delta(\mathbf{u}) \rangle = (1/4\pi) \lim_{t \rightarrow -3} [(t+3)\langle u^t \rangle],$$

which may be obtained in a straightforward manner following some indications contained in Gálvez *et al* (1988).

3. Numerical study

From a numerical point of view, we study the interelectronic moments $\langle u^t \rangle$ and log-moments $\langle u^t \ln u \rangle$ as well as the fundamental function $H(s, t)$ in the two-electron atoms with $Z = 1, 2, 3, 5$ and 10 . To do that we use the optimum 20-term Hylleraas-type wave functions recently described in Koga and Matsui (1993). They are very appropriate for this purpose as it is shown in table 1 where the values of various ground-state properties obtained with these wave functions are compared, where it is possible, with the near-exact ones (Thakkar and Smith 1977b). The properties listed are the total energy E , the central electron-pair density or electron-electron coalescence measure $\langle \delta(\mathbf{u}) \rangle = h(0)$, the values α_1 and α_2 (i.e. the α values which make the electron-pair function $h(u)/u^\alpha$ monotonically decreasing from the origin and convex, respectively), interelectronic moments $\langle u^t \rangle$ and log-moments $\langle u^t \ln u \rangle$ for selected values of t , as well as the maximum characteristics (h_{\max} , u_{\max}) of the electron-pair density. This table shows that the optimum 20-term Hylleraas-type wave functions are of sufficiently high accuracy, except possibly in the $Z = 1$ (H^-) case where better wave functions would be desirable.

The interelectronic moments $\langle u^t \rangle$, $-5/2 \leq t \leq 4$, summarized in table 1, are much more accurate than the corresponding values given in table 7 of Dehesa *et al* (1992b), which were obtained by means of the optimum six-term Hylleraas-type wave functions, although the general dependence on t is the same as that shown in table 7 and figure 2 of that reference. The improvement is specially remarkable in the H^- ion case and for the moments of negative orders in the other cases. The reader should consult Dehesa *et al* (1992b) for further discussion and comments.

The calculated values of the interelectronic log-moments $\langle u^t \ln u \rangle$ are also shown in table 1 and drawn as a function of t in figure 1. This function has a monotonic increasing behavior with increasing t . Its rate decreases with increasing Z . For a given Z there exists a critical value below which the log-moments take on negative values. This critical value increases with Z , being approximately -2.3 , -0.7 and 1.1 in the H^- , He and Li^+ cases, respectively, and higher than 4.0 in the remaining two cases.

Finally, the values of the fundamental function $H(s, t)$, $-2.99999 \leq t \leq +2.00000$ and $s = -2.0, -1.0, 0.0, +1.0$ and $+2.0$, are collected in table 2 for $Z = 1, 2, 3, 5$ and 10 . The values of the electron-electron coalescence measure given by the quantity

Table 1. Comparison (where 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} , h_{\max}' and $\langle u^s \ln u \rangle$ denote the total energy, the electron-pair density at the origin, the intensity and the location of the maximum of the electron-pair density $h(u)$ and the interelectronic moment and log-moment of u^s order, respectively. The α values α_1 and α_2 are those which make the electron-pair function $h(u)/u^s$ monotonically decrease from the origin and convex, respectively. Atomic units are used throughout.

	Z = 1		Z = 2		Z = 3		Z = 5		Z = 10	
	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact
$-E$	0.527742	0.527751	2.903722	2.903724	7.279910	7.279913	22.030966	22.030970	93.906798	93.906802
$h(0)$	0.00282245	0.002740	0.106852	0.106352	0.535251	0.533808	3.31617	3.31478	32.6619	32.6432
h_{\max}	0.00403015		0.116518		0.556017		3.36256		32.7686	
h_{\max}'	0.926347		0.191818		0.0819881		0.0290989		0.00702138	
α_1	0.165766		0.0422427		0.0187900		0.00690733		0.00162868	
α_2	0.387817		0.208200		0.160958		0.128500		0.106181	
$\langle u^{-5/2} \rangle$	0.159814		2.78610		10.2233		45.3992		299.350	
$\langle u^{-2} \rangle$	0.155344	0.155108	1.46510	1.46477	4.08291	4.08225	13.3080	13.3075	59.6975	59.6946
$\langle u^{-3/2} \rangle$	0.203191		1.08024		2.31488		5.58758		17.1603	
$\langle u^{-1} \rangle$	0.311136	0.311022	0.945819	0.945818	1.56772	1.56772	2.81471	2.81470	5.93725	5.93724
$\langle u^{-1/2} \rangle$	0.533101		0.930219		1.19646		1.60189		2.32514	
$\langle u^0 \rangle$	1	1	1	1	1	1	1	1	1	1
$\langle u^{1/2} \rangle$	2.02757		1.15614		0.899952		0.672893		0.463964	
$\langle u \rangle$	4.40654	4.41269	1.42208	1.42207	0.862320	0.862315	0.482435	0.482436	0.229492	0.229492
$\langle u^{3/2} \rangle$	10.2039		1.84658		0.872666		0.365498		0.120002	
$\langle u^2 \rangle$	25.0595	25.2020	2.51649	2.51644	0.927083	0.927064	0.290790	0.290791	0.0659173	0.0659174
$\langle u^{5/2} \rangle$	65.0207		3.58263		1.02899		0.241769		0.0378482	
$\langle u^3 \rangle$	177.627	180.601	5.30840	5.30800	1.18864	1.18856	0.209239	0.209243	0.0226253	0.0226254
$\langle u^{7/2} \rangle$	509.244		8.16095		1.42449		0.187886		0.0140352	
$\langle u^4 \rangle$	1527.21	1590.0	12.9839	12.9812	1.76633	0.7660	0.174568	0.17458	0.00900984	0.0090100

(Continued)

Table 1. (Continued)

	Z = 1		Z = 2		Z = 3		Z = 5		Z = 10	
	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact	Hylleraas	Near-exact
$\langle u^{-3/2} \ln u \rangle$	-0.100046		-5.39809		-25.6572		-142.705		-1174.74	
$\langle u^{-2} \ln u \rangle$	0.0498722		-1.24863		-5.66176		-26.5369		-164.559	
$\langle u^{-3/2} \ln u \rangle$	0.145590		-0.443773		-2.15082		-8.51867		-39.0996	
$\langle u^{-1} \ln u \rangle$	0.303103		-0.130112		-1.01505		-3.48016		-11.7889	
$\langle u^{-1/2} \ln u \rangle$	0.625236		0.0580388		-0.529583		-1.64615		-4.12446	
$\langle \ln u \rangle$	1.33922		0.221705		-0.280312		-0.862749		-1.60703	
$\langle u^{1/2} \ln u \rangle$	3.01174		0.410557		-0.130510		-0.488326		-0.681390	
$\langle u \ln u \rangle$	7.12821		0.669042		-0.0245673		-0.293304		-0.309790	
$\langle u^{3/2} \ln u \rangle$	17.7500		1.05710		0.0647448		-0.184368		-0.149477	
$\langle u^2 \ln u \rangle$	46.4386		1.67128		0.154075		-0.119756		-0.0759670	
$\langle u^{5/2} \ln u \rangle$	127.411		2.67818		0.256918		-0.0792856		-0.0404269	
$\langle u^3 \ln u \rangle$	365.788		4.37520		0.387738		-0.0525532		-0.0224221	
$\langle u^{7/2} \ln u \rangle$	1096.19		7.30581		0.565397		-0.0338802		-0.0129111	
$\langle u^6 \ln u \rangle$	3420.07		12.4831		0.817262		-0.0199916		-0.00769338	

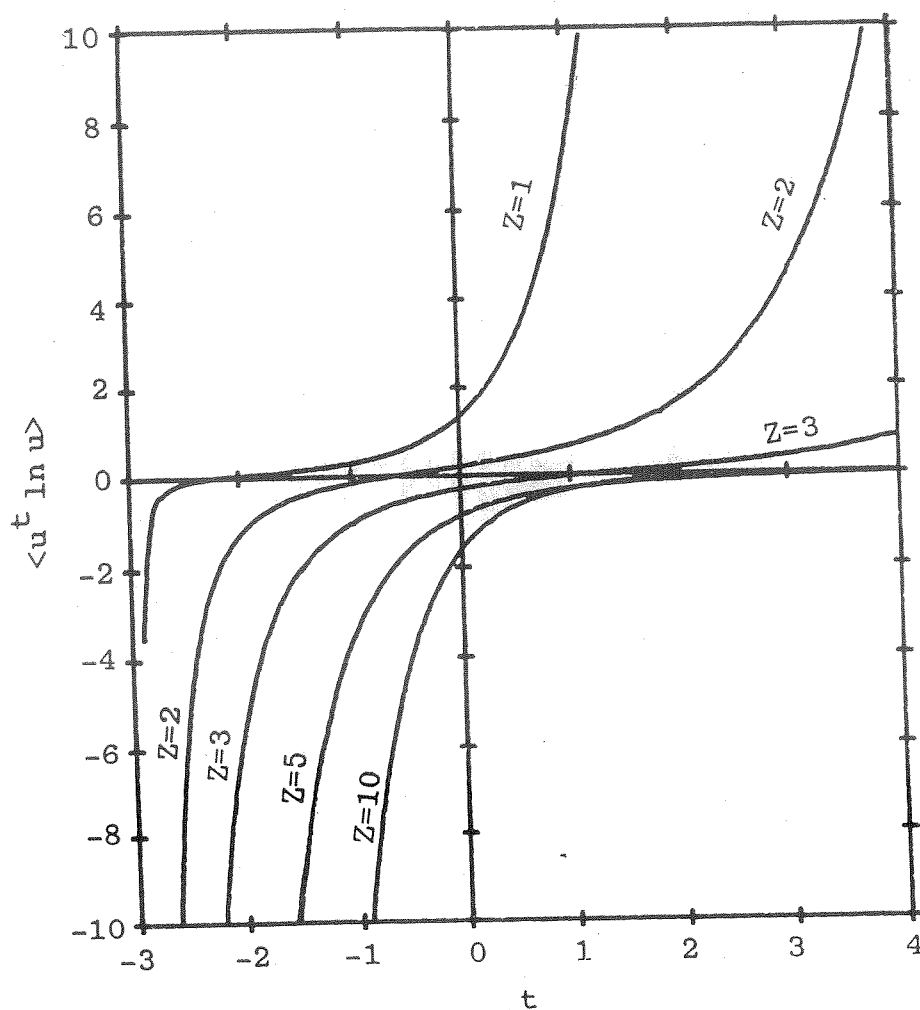


Figure 1. Graphical representation of the interelectronic log-moments $\langle u^t \ln u \rangle$ as a function of t in the region $-3 < t \leq 4$. Atomic units are used throughout.

$\langle \delta(\mathbf{u}) \rangle = h(0)$ are also shown for comparison. One observes that for a fixed s the values of $H(s, t)$ tend towards $h(0)$ when $t \rightarrow -3$ as predicted by (3). Furthermore, it is remarkable to note that

$$\langle \delta(\mathbf{u}) \rangle \geq H(s, t), \quad s > t > -3, \quad (4)$$

provided that (i) $s + t \geq -2$ in all cases, (ii) $s + t \geq -\frac{9}{2}$ and $Z = 3, 5$ and 10 , or (iii) $Z = 5$ and 10 . This numerical observation together with (2) gives rise to many interesting characteristics about the quantity $\langle \delta(\mathbf{u}) \rangle$, such as, e.g.,

$$\langle \delta(\mathbf{u}) \rangle \geq (3/4\pi) \exp(-1 - 3 \langle \ln u \rangle) = H(0, 0). \quad (5)$$

This inequality correlates the electron-electron coalescence and the interelectronic

mean logarithmic radius $\langle \ln u \rangle$. Its accuracy goes from 99.67% in the H^- case down to 64.88% in the Ne^{8+} case.

In an analogous manner, if $s = t = -1$ one has

$$\langle \delta(\mathbf{u}) \rangle \geq (E_{ee}/4\pi) \exp(-1 - 2\langle u^{-1} \ln u \rangle / E_{ee}). \quad (6)$$

This expression, which involves the log-moment $\langle u^{-1} \ln u \rangle$, allows correlation of the

Table 2. Values of the interelectronic two-moment function $H(s, t)$, $-2.99999 \leq t \leq +2.0$ and $s = -2, -1, 0, +1$ and $+2$, evaluated by means of the optimum 20-term Hylleraas-type wave functions in the ions H^- , He, Li^+ , B^{3+} and Ne^{8+} .

The value of the electron-electron coalescence measure $\langle \delta(\mathbf{u}) \rangle = h(0)$ is shown for comparison. Atomic units are used throughout.

$t/$	$s = -2.0$	-1.0	0.0	$+1.0$	$+2.0$
Z = 1	$h(0) = 0.00282245$				
-2.99999	0.00282247	0.00282247	0.00282247	0.00282247	0.00282247
-2.99900	0.00282440	0.00282452	0.00282439	0.00282418	0.00282395
-2.90000	0.00298559	0.00299080	0.00297336	0.00294990	0.00292471
-2.50000	0.00327090	0.00320807	0.00307942	0.00294157	0.00280761
-2.00000	0.00329884	0.00308601	0.00281300	0.00255346	0.00231965
-1.00000	0.00308601	0.00259605	0.00213054	0.00174821	0.00144144
0.00000	0.00281300	0.00213054	0.00158039	0.00117707	0.00088446
1.00000	0.00255346	0.00174821	0.00117707	0.00079895	0.00054930
2.00000	0.00231965	0.00144144	0.00088446	0.00054930	0.00034706
Z = 2	$h(0) = 0.10685224$				
-2.99999	0.10685230	0.10685221	0.10685211	0.10685201	0.10685192
-2.99900	0.10685863	0.10684963	0.10683930	0.10682937	0.10682012
-2.90000	0.10721301	0.10624858	0.10520238	0.10421798	0.10331431
-2.50000	0.10540405	0.10010752	0.09508812	0.09067114	0.08680749
-2.00000	0.10057527	0.09029952	0.08147599	0.07417964	0.06810548
-1.00000	0.09029952	0.07291578	0.05984975	0.05005914	0.04256080
0.00000	0.08147599	0.05984975	0.04516076	0.03502075	0.02779356
1.00000	0.07417964	0.05005914	0.03502075	0.02536254	0.01890785
2.00000	0.06810548	0.04256080	0.02779356	0.01890785	0.01330816
Z = 3	$h(0) = 0.53525148$				
-2.99999	0.53525115	0.53525052	0.53524992	0.53524938	0.53524888
-2.99900	0.53521927	0.53515633	0.53509613	0.53504146	0.53499197
-2.90000	0.53139965	0.52506277	0.51916031	0.51388244	0.50916045
-2.50000	0.50926162	0.47874489	0.45252056	0.43028388	0.41121559
-2.00000	0.47829950	0.42308785	0.37903941	0.34369555	0.31476058
-1.00000	0.42308785	0.33510298	0.27254976	0.22680917	0.19226341
0.00000	0.37903941	0.27254976	0.20362464	0.15706890	0.12429686
1.00000	0.34369555	0.22680917	0.15706890	0.11316598	0.08415439
2.00000	0.31476058	0.19226341	0.12429686	0.08415439	0.05911535
Z = 5	$h(0) = 3.316167$				
-2.99999	3.316163	3.316158	3.316154	3.316151	3.316147
-2.99900	3.315720	3.315254	3.314843	3.314482	3.314160
-2.90000	3.270276	3.224613	3.185103	3.150791	3.120572
-2.50000	3.081154	2.875150	2.707622	2.568857	2.451412

(Continued)

Table 2. (Continued)

-2.00000	2.861647	2.503540	2.230489	2.015775	1.842023
-1.00000	2.503540	1.953892	1.577380	1.306824	1.104576
0.00000	2.230489	1.577380	1.168635	0.896972	0.707571
1.00000	2.015775	1.306824	0.896972	0.642894	0.476528
2.00000	1.842023	1.104576	0.707571	0.476528	0.333673
Z = 10	h(0) = 32.661909				
-2.99999	32.661849	32.661798	32.661755	32.661717	32.661685
-2.99900	32.655888	32.650778	32.646473	32.642757	32.639484
-2.90000	32.066826	31.573360	31.163745	30.814380	30.509747
-2.50000	29.862980	27.719450	26.034275	24.659591	23.506178
-2.00000	27.517370	23.882927	21.191612	19.103935	17.427823
-1.00000	23.882927	18.440174	14.804487	12.223440	10.307874
0.00000	21.191612	14.804487	10.899008	8.332851	6.555998
1.00000	19.103935	12.223440	8.332851	5.947442	4.395897
2.00000	17.427823	10.307874	6.555998	4.395897	3.068992

electron-electron coalescence and the total electron-electron repulsion energy $E_{ee} = \langle u^{-1} \rangle$ of the system. Its accuracy goes from 91.98% in the H^- case down to 56.46% in the Ne^{8+} case.

It is worth remarking that the combination of the empirical bound (4) and the rigorous expression (2) leads not only to the bounds given by the inequalities (5) and (6) but also to other numerous bounds to the electron-electron coalescence $\langle \delta(\mathbf{u}) \rangle$. These bounds may be, at times, of great quality as one can easily check by looking at table 2, so that they might be used as a gross measure of electron-electron correlation. One should remember that the spatial and spin coincidence will lead, to a vanishing probability density via the antisymmetry of the atomic wave function, and hence, a two-electron coalescence will, in effect, grossly measure the (antiparallel spin-) correlation. We conjecture that these bounds or similar ones are of universal validity (i.e. they are valid not only for two-electron atoms) although we have not yet been able to prove them in a fully rigorous way. To this respect, some reduced diagonal two-electron density matrix considerations would be pertinent.

4. Concluding remarks

In summary, it is argued that the two-moment function $H(s, t)$ plays a relevant role in the electron-correlation problem. For all atomic and molecular systems having a unimodal electron-pair density $h(u)$, it is analytically shown that the electron-electron coalescence measure $\langle \delta(\mathbf{u}) \rangle$ can be obtained in a limiting form from both the one-moment function $(4\pi)^{-1}(t+3)\langle u^t \rangle$ and the two-moment function $H(s, t)$.

Further the interelectronic moments $\langle u^t \rangle$ and log-moments $\langle u^t \ln u \rangle$ as well as the function $H(s, t)$ have been numerically studied for the two-electron atoms with nuclear charge $Z = 1, 2, 3, 5$ and 10 in a numerical Hylleraas framework. From this numerical study one observes that the electron-electron coalescence measure $\langle \delta(\mathbf{u}) \rangle$ is bounded from below by $H(s, t)$ for certain values of the parameters s and t . Finally, it is

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