Interelectronic moments of atomic systems

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The electron-pair density $I(\mathbf{u})$ of an atomic system, $\mathbf{u}$ being the interelectronic vector $\mathbf{r}_{12}$, may be completely characterized by means of the moments $\langle u^q\rangle$, $q>-3$, defined as $\langle u^q\rangle=\int u^q I(\mathbf{u})\mathbf{u}=4\pi\int_0^\infty u^{q+2}h(u)du$, where $h(u)$ is the spherical average of $I(\mathbf{u})$. These interelectronic quantities are basic elements in the study of the electron-electron correlation problem. Here it is analytically shown how a moment of a given order q is bounded from below in terms of moments with orders higher than or lower than q. To do that, the so-called extended-correlation cusp condition [i.e., $h(u)-h'(u)\geq 0$ for $u\geq 0$], recently found for various atomic systems in a variational Hylleraas-type framework, is used. The lower bounds turn out to be often very accurate.

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The electron-pair density $I(\mathbf{u})$, i.e, the probability density for the inter-electronic vector $\mathbf{u}=\mathbf{r}_{12}$, is a fundamental tool to investigate chemical and physical properties of the atomic and molecular systems [1,2]. This function may be completely characterized by means of the expectation values

$$\langle u^q\rangle=\int u^q I(\mathbf{u})d\mathbf{u}=4\pi\int_0^\infty u^{q+2}h(u)du\equiv 4\pi\mu_{q+2}\ , \qquad q>-3\ , \quad (1)$$

where $h(u)$ denotes the spherical average $I(\mathbf{u})$. These quantities are usually called interelectronic moments. They are not only the basic elements in the study of the electron-electron correlation problem but they also have a fundamental physical meaning, e.g., $\langle u^{-1}\rangle$ gives the total electron-electron repulsion energy E_{ee} of the N-electron system, and $\langle u^0\rangle=N(N-1)/2$.

Although numerical calculations of these moments have been performed, only recently has some rigorous information about them been found. In particular, they satisfy [3]

$$\langle u^n\rangle\geq\frac{\langle u^{n-1}\rangle^2}{\langle u^{n-2}\rangle}\ , \quad n>-1\ , \quad (2)$$

which is a consequence of the only known rigorous structural property of $h(u)$, namely, its non-negativity. The accuracy of this inequality gets improved by taking into account other monotonicity properties, if any, of the interelectronic density function $h(u)/u^\alpha$, $\alpha>0$, such as, e.g., monotonic decreasing from the origin, convexity, and log convexity [3–5].

Here we will show two sets of interelectronic moment inequalities which considerably generalize that given by Eq. (2). To find them we will make use of the so-called extended-correlation cusp condition [4], i.e.,

$$g_0(u)\equiv h(u)-h'(u)\geq 0\ . \quad (3)$$

This function can be completely characterized [6] by means of the quantities

$$\nu_p=\int_0^\infty u^p g_0(u)du=h(0)\delta_{p0}+\mu_p+p\mu_{p-1},\quad p\geq 0\ . \quad (4)$$

The application of the Stieltjes-moment-problem technique [6] to the non-negative function $g_m(u)\equiv u^m g_0(u)$ leads to the following Hadamard determinantal inequalities:

$$\Delta_k^{(m)}=\begin{vmatrix}\nu_m & \nu_{m+1} & \cdots & \nu_{m+k}\\ \nu_{m+1} & \nu_{m+2} & \cdots & \nu_{m+k+1}\\ \vdots & \vdots & \ddots & \vdots\\ \nu_{m+k} & \nu_{m+k+1} & \cdots & \nu_{m+2k}\end{vmatrix}\geq 0 \quad (5)$$

for any $m\geq 0$ and $k\geq 0$. The case $m=0$ was previously considered [7] and it allowed us to bound the electron-electron coalescence measure $h(0)$ by means of the interelectronic moments $\langle u^q\rangle$. The case $k=0$ gives a triviality. Here we will consider all the other cases in which $m>0$ and $k\geq 1$. The development of the $\Delta_k^{(m)}$ determinant (5) for the first row produces

$$\nu_m\geq-\frac{1}{A_m}\sum_{i=2}^{k+1}\nu_{i+m-1}A_{i+m-1}\ , \quad (6)$$

where A_j denotes the cofactor of the element ν_j, i.e., $(-1)^j$ times the determinant resulting from the elimination of the first row and $(j-m+1)$th column (i.e., the column with ν_j at the top) of $\Delta_k^{(m)}$. Then, taking into account Eqs. (1) and (4) one has an infinite set of lower bounds D_{km} to $\langle u^{m-3}\rangle$ given as

$$\langle u^{m-3}\rangle\geq D_{km},\quad k=1,2,3,\ldots;\ m>0\ , \quad (7)$$

with

$$D_{km}=-\frac{1}{m}\left\{\langle u^{m-2}\rangle+\frac{1}{A_m}\sum_{i=2}^{k+1}[\langle u^{i+m-3}\rangle+(i+m-1)\langle u^{i+m-4}\rangle]A_{i+m-1}\right\}\ . \quad (8)$$

It is worthwhile to remark that all the interelectronic moments $\langle u^q \rangle$ involved in these lower bounds are of order q higher than $m-3$, i.e., $q > m-3$. The value $k=1$ leads to the lower bounds D_{1m} given by

$$D_{1m} = \frac{1}{m}\left\{ \frac{[\langle u^{m-1}\rangle + (m+1)\langle u^{m-2}\rangle]^2}{\langle u^m\rangle + (m+2)\langle u^{m-1}\rangle} - \langle u^{m-2}\rangle \right\} . \tag{9}$$

Particular cases are the following.

(a) For $m=1$,

$$\langle u^{-2}\rangle \geq D_{11} = \frac{[\langle u^0\rangle + 2\langle u^{-1}\rangle]^2}{\langle u\rangle + 3\langle u^0\rangle} - \langle u^{-1}\rangle . \tag{10}$$

(b) For $m=2$,

$$E_{ee} = \langle u^{-1}\rangle \geq D_{12} \equiv \frac{1}{2}\left\{ \frac{[\langle u\rangle + 3\langle u^0\rangle]^2}{\langle u^2\rangle + 4\langle u\rangle} - \langle u^0\rangle \right\} . \tag{11}$$

(c) For $m=3$,

$$\langle u^0\rangle \geq D_{13} \equiv \frac{1}{3}\left\{ \frac{[\langle u^2\rangle + 4\langle u\rangle]^2}{\langle u^3\rangle + 5\langle u^2\rangle} - \langle u\rangle \right\} . \tag{12}$$

The consideration of higher k values in Eqs. (7) and (8) leads naturally to more accurate but intricate lower bounds since they involve a larger number of interelectronic moments.

The case $m=2$ and arbitrary k gives

$$E_{ee} \geq D_{k2} , \tag{13}$$

with

$$D_{k2} = -\frac{1}{2}\left\{ \langle u^0\rangle + \frac{1}{A_2}\sum_{i=2}^{k+1}[\langle u^{i-1}\rangle + (i+1)\langle u^{i-2}\rangle] \times A_{i+1} \right\} ,$$

which allows us to bound from below the total repulsion energy E_{ee} of the system by means of the interelectronic moments $\langle u^t\rangle$, $t \geq 0$, to any degree of accuracy.

On the other hand, the development of the Δ determinant (5) for the last row produces in a parallel manner the following set of inequalities:

$$\langle u^{m+2k-2}\rangle \geq E_{km}, \quad m>0; \ k=1,2,3,\ldots , \tag{14}$$

with

$$E_{km} = -\left\{ (m+2k)\langle u^{m+2k-3}\rangle + \frac{1}{\Delta_{k-1}^{(m)}}\sum_{i=1}^{k}[\langle u^{i+m+k-3}\rangle + (i+m+k-1)\langle u^{i+m+k-4}\rangle]A_{i+m+k-1} \right\} .$$

They allow us to bound from below an interelectronic moment with a given order, say $m+2k-2$, by means of moments of lower orders. The case in which $k=1$ produces the lower bounds E_{1m} to the moment $\langle u^m\rangle$ as

$$\langle u^m\rangle \geq E_{1m}, \quad m>0 , \tag{15}$$

with

TABLE I. Accuracy in percent of the lower bounds D_{km}, $k=1$, 2, and 3, to the interelectronic moment $\langle u^{m-3}\rangle$ in the He-like ions with nuclear charges $Z=1$, 2, 3, 5, and 10. The accuracy is given by the ratio $100D_{km}/\langle u^{m-3}\rangle$. The optimum 20-term Hylleraas-type atomic wave functions have been used.

Z \ m	1	2	3	4	5	6	7	8	9	10
					$k=1$					
1	28.45	45.82	53.61	58.60	62.96	67.42	71.99	76.35	80.17	83.32
2	64.50	73.13	78.02	81.27	83.60	85.37	86.77	87.90	88.85	89.67
3	70.05	76.82	80.87	83.64	85.66	87.22	88.45	89.46	90.30	91.02
5	73.68	79.25	82.74	85.17	86.98	88.38	89.51	90.44	91.22	91.89
10	76.03	80.85	83.96	86.17	87.83	89.12	90.16	91.01	91.73	92.34
					$k=2$					
1	71.15	81.18	85.99	89.09	91.42	93.31	94.87	96.12	97.09	97.81
2	87.26	91.90	94.25	95.66	96.59	97.24	97.71	98.07	98.36	98.58
3	89.25	93.03	95.03	96.24	97.05	97.62	98.03	98.35	98.59	98.78
5	90.53	93.75	95.52	96.61	97.34	97.85	98.23	98.52	98.74	98.92
10	91.35	94.22	95.83	96.83	97.51	97.98	98.33	98.60	98.81	98.97
					$k=3$					
1	85.80	92.05	94.81	96.40	97.46	98.21	98.76	99.15	99.42	99.60
2	94.13	96.79	98.00	98.65	99.04	99.29	99.46	99.58	99.67	99.73
3	95.06	97.25	98.28	98.84	99.17	99.39	99.54	99.64	99.71	99.77
5	95.65	97.54	98.45	98.96	99.26	99.46	99.59	99.68	99.75	99.80
10	96.01	97.72	98.56	99.02	99.30	99.49	99.61	99.70	99.76	99.80

TABLE II. Accuracy in percent of the lower bounds E_{1m}, E_{2m}, and E_{3m} (globally E_{km}, $k=1,2,3$) to the interelectronic moments $\langle u^m \rangle$, $\langle u^{m+2} \rangle$, and $\langle u^{m+4} \rangle$, respectively, in the He-like ions with nuclear charges $Z=1$, 2, 3, 5, and 10. The accuracy is given by the ratios $100E_{1m}/\langle u^m \rangle$, $100E_{2m}/\langle u^{m+2} \rangle$, and $100E_{3m}/\langle u^{m+4} \rangle$, respectively. The optimum 20-term Hylleraas-type atomic wave functions have been used.

Z \ m	1	2	3	4	5	6	7	8	9	10
					$k=1$					
1	59.95	64.60	67.96	70.98	74.13	77.46	80.78	83.79	86.34	88.37
2	32.92	42.69	49.75	55.16	59.45	62.94	65.85	68.34	70.49	72.41
3	3.08	17.04	27.21	35.03	41.27	46.37	50.63	54.25	57.37	60.11
5	−56.81	−34.53	−18.19	−5.56	4.55	12.86	19.82	25.77	30.93	35.45
10	−206.81	−163.64	−131.89	−107.29	−87.57	−71.37	−57.79	−46.23	−36.28	−27.59
					$k=2$					
1	87.08	89.92	92.19	94.06	95.55	96.67	97.50	98.09	98.52	98.84
2	81.97	86.47	89.39	91.42	92.89	94.01	94.89	95.60	96.18	96.67
3	73.87	80.45	84.73	87.69	89.85	91.47	92.73	93.74	94.55	95.22
5	57.49	68.22	75.20	80.06	83.60	86.27	88.35	90.00	91.33	92.42
10	16.36	37.46	51.20	60.74	67.67	72.89	76.92	80.10	82.66	84.76
					$k=3$					
1	96.16	97.49	98.35	98.90	99.26	99.49	99.64	99.74	99.81	99.86
2	95.11	96.60	97.52	98.13	98.56	98.87	99.10	99.27	99.41	99.51
3	92.98	95.15	96.48	97.36	97.97	98.40	98.72	98.96	99.15	99.29
5	88.60	92.15	94.34	95.77	96.76	97.47	97.98	98.37	98.66	98.88
10	77.51	84.50	88.80	91.62	93.56	94.93	95.94	96.69	97.26	97.71

$$E_{1m}=\frac{[\langle u^{m-1}\rangle+(m+1)\langle u^{m-2}\rangle]^2}{\langle u^{m-2}\rangle+m\langle u^{m-3}\rangle}-(m+2)\langle u^{m-1}\rangle \ .$$

Notice that these lower bounds depend on the three moments $\langle u^q \rangle$ with $q=m-1$, $m-2$, and $m-3$.

Finally, for completeness and illustration we have studied the accuracy of the aforementioned lower bounds D_{km} and E_{km} in the cases $k=1$, 2, and 3, and $m=1-10$ for various He-like ions with nuclear charges $Z=1$, 2, 3, 5, 10. In doing so, we have used the optimum 20-term Hylleraas-type atomic wave functions recently found by [8], which have been shown to describe with sufficiently high accuracy several interelectronic global [3–5] and local [7,9] properties. The resulting accuracy in percent of the lower bounds D_{km} and E_{km} is given in Tables I and II, respectively. Several observations are in order.

(1) The accuracy of the bounds D_{1m}, D_{2m}, and D_{3m} increases with increasing m and increasing Z. The bounds D_{2m} are much more accurate than D_{1m} for a specific m value and/or a given atom. Notice that the accuracy of the bounds D_{2m} is never less than 71%, being usually bigger than 90%.

(2) The bounds D_{22} to the total electron-electron repulsion energy E_{ee} are good in all the components of the atomic samples considered in this work. Indeed, its accuracy oscillates between 81.18% and 94.22%. Moreover, the bounds D_{32} to E_{ee} are really tight; its accuracy is always larger than 96% except in the H^- case where it is *only* 92.05%.

(3) The accuracy of the bounds E_{km}, $k=1$, 2, and 3, increases with increasing m but, contrary to the D bounds, decreases with increasing Z. The bounds E_{1m} to $\langle u^m \rangle$ are reasonably accurate only in the H^- and He cases. The bounds E_{2m} and, especially E_{3m}, are of much greater quality in the whole atomic sample.

In summary, two infinite sets of lower bounds to interelectronic moments of a specific order have been shown. The bounds of one of the sets depend only on the moments of lower orders and those of the other set depend only on the moments of higher order. They are valid for all the atomic and molecular systems where the extended-correlation cusp condition is fulfilled. The latter has been numerically shown to occur in the two-electron ions with $Z=1$, 2, 3, 5, and 10. Here it has been observed also that the aforementioned bounds to a specific moment can approach it to almost any degree of accuracy.

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