Upper bounds to the electron-electron coalescence density in terms of the one-electron density function

Jesus M. Ugalde and Cecilia Sarasola
Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072, 20080 Donostia, Euskadi, Spain
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An expression that allows one to evaluate the electron-electron coalescence density in terms of the one-electron density function at the Hartree-Fock level is derived. Then it is shown, by calculation with highly accurate wave functions of He-like ions, that this expression represents a simple and accurate upper bound to the electron-electron coalescence density for nearly exact wave functions.

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Electron-pair properties are important in modern electronic structure theory because of the electron correlation energy. Also, relationships between electron-pair properties and one-electron properties are of considerable interest in density-functional theory for they may give the clue for better exchange-correlation functionals [1–4]. In particular the electron-electron coalescence or intracule (relative motion) density at the origin $\langle\delta(\mathbf{u})\rangle$, with $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$, has recently received considerable attention [5,6]. Thus, Dehesa *et al.* [5], starting from the unimodal character of the spherically averaged electron-pair density function $h(u)$, and the inequality $h(u)\geq h'(u)$, have derived analytically, with the aid of Stieltje's theorem, upper and lower bounds of increasing accuracy to the electron-electron coalescence density which involve moments of the interelectronic vector $\mathbf{u}$. Further, the lower bounds have been improved by Koga *et al.* [6], who found after extensive calculations that

$$\langle\delta(\mathbf{u})\rangle\geq\frac{3}{4\pi}e^{-1-3\langle\ln u\rangle} \tag{1}$$

and

$$\langle\delta(\mathbf{u})\rangle\geq\frac{E_{ee}}{4\pi}e^{-1-2\langle u^{-1}\ln u\rangle/E_{ee}}\ , \tag{2}$$

which correlate various expectation values of the interelectronic vector $\mathbf{u}$, like the total electron-electron repulsion $E_{ee}=\langle u^{-1}\rangle$, with the electron-electron coalescence density. The accuracy of these bounds, for He-like ions, is found to decrease with increasing nuclear charge Z. Thus Eq. (1) has an accuracy of 99.67% for H^- and only 54.46% for Ne^{+8}. Nevertheless, it is worth noting that both bounds involve electron-pair properties.

In this paper a simpler and accurate upper bound to the electron-electron coalescence density, which for the Hartree-Fock-like wave functions turns out to be exact, is presented. Let us start out from a Hartree-Fock wave function Ψ for N^α α-spin and N^β β-spin electrons, and let $N=N^\alpha+N^\beta$. Then, the intracular density

$$I_{\mathrm{HF}}(\mathbf{u})=\sum_{i<j}\langle\Psi|\delta(\mathbf{u}-\mathbf{r}_i+\mathbf{r}_j)|\Psi\rangle \tag{3}$$

can be written as [7]

$$I_{\mathrm{HF}}(\mathbf{u})=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}[(\psi_i^{\sigma_i}\psi_i^{\sigma_i}|\delta|\psi_j^{\sigma_j}\psi_j^{\sigma_j})-(\psi_i^{\sigma_i}\psi_j^{\sigma_j}|\delta|\psi_j^{\sigma_j}\psi_i^{\sigma_i})\delta_{\sigma_i,\sigma_j}]\ , \tag{4}$$

where $\psi_i^{\sigma_i}$ stands for the orbital part of the spin orbital $\chi_i=\psi_i^{\sigma_i}\sigma_i$ with spin σ_i, $\delta_{\sigma_i,\sigma_j}$ is the Kronecker delta, and $\delta=\delta(\mathbf{u}-\mathbf{r}_1+\mathbf{r}_2)$ is the Dirac delta function. Hence the electron-electron coalescence density is

$$I_{\mathrm{HF}}(\mathbf{0})=\frac{1}{2}\left[\sum_{i=1}^{N^\alpha}\sum_{j=N^\alpha+1}^{N}\int d\mathbf{r}\,\psi_i^{*,\alpha}\psi_i^{\alpha}\psi_j^{*,\beta}\psi_j^{\beta}+\sum_{i=N^\alpha+1}^{N}\sum_{j=1}^{N^\alpha}\int d\mathbf{r}\,\psi_i^{*,\beta}\psi_i^{\beta}\psi_j^{*,\alpha}\psi_j^{\alpha}\right]\ , \tag{5}$$

or

$$I_{\mathrm{HF}}(\mathbf{0})=\sum_{i=1}^{N^\alpha}\sum_{j=N^\alpha+1}^{N}\int d\mathbf{r}\,\psi_i^{*,\alpha}\psi_i^{\alpha}\psi_j^{*,\beta}\psi_j^{\beta}\ . \tag{6}$$

Having in mind that $\rho^\alpha=\sum_{i=1}^{N^\alpha}|\psi_i^\alpha|^2$ and $\rho^\beta=\sum_{i=N^\alpha+1}^{N}|\psi_i^\beta|^2$, we obtain

$$I_{\mathrm{HF}}(\mathbf{0})=\int d\mathbf{r}\,\rho_{\mathrm{HF}}^{\alpha}(\mathbf{r})\rho_{\mathrm{HF}}^{\beta}(\mathbf{r})\ . \tag{7}$$

Equations (5)–(7) are due to the particular form of the second-order density matrix within the Hartree-Fock approximation, as pointed out earlier by Löwdin [8]. Recall that for the diamagnetic case $\rho_{\mathrm{HF}}^{\alpha}=\rho_{\mathrm{HF}}^{\beta}=\frac{1}{2}\rho_{\mathrm{HF}}$; then

$$I_{\mathrm{HF}}(\mathbf{0})=\tfrac{1}{4}\int d\mathbf{r}\,\rho_{\mathrm{HF}}^{2}(\mathbf{r})\ . \tag{8}$$

Equations (7) and (8) are important since they tell us how to calculate the intracular density at the origin through a functional of the one-electron density function, namely, a quantity referred earlier to as the "average electron density" and denoted as $\langle\rho\rangle$. However, these equations have been derived for Hartree-Fock-like wave functions, and therefore, they will not, in principle, apply for exact wave functions. In fact, this has been found to be the case for the He-like isoelectronic sequence. We have calculated both $I_{\mathrm{ex}}(0)$ and $\frac{1}{4}\langle\rho_{\mathrm{ex}}\rangle$ for the explicitly correlated nearly exact wave functions of Hart and Herzberg [9] for the

He-like ions with $Z=1$, 2, 3, 4, 8, 10, and 12. Results are shown in Table I. For completeness we have also included values of electron-electron coalescence density evaluated from a Hartree-Fock near-limit wave function. It is immediately observed that the Hartree-Fock and the exact values for $\frac{1}{4}\langle\rho\rangle$ compare very well, which reinforces the well-known fact [10] that Hartree-Fock one-electron densities are reasonably accurate. On the other hand, the table shows that the equality of Eqs. (7)–(8) does not hold for the "exact" wave functions. However, it does show the following inequality,

$$I(0)\leq\tfrac{1}{4}\langle\rho\rangle\ , \tag{9}$$

namely, the average electron density divided by 4 is an upper bound to the electron-electron coalescence density. In order to ascertain the quality of this bound, Table I lists previously reported [5] upper bounds (U_3). Inspection of these data clearly reveals that for $Z<5$ our bounds are poorer, but for $Z\geq 5$ our bounds are appreciably tighter. Indeed, the quality of our bounds increases with Z from 17% for H^- to 91% for Mg^{10+}, unlike U_3, which decreases with increasing Z from 78% for H^- to 63% for O^{+6}. It is worth noting that Eq. (9) represents an accurate upper bound to the electron-electron coalescence density and is easier to calculate than the $U_k(k=0,1,\ldots)$ upper bounds, previously reported by Dehesa *et al.* [5], for the latter involve the electron-pair density while our equation (7) only involves the more familiar one-electron density through the average electron density. It should be mentioned that upper [11] and lower [12] bounds to the latter quantity $\langle\rho\rangle$, which has been shown to be experimentally accessible via x-ray scattering intensities [11], have been reported.

TABLE I. Electron-electron coalescence density and its bounds in atomic units for He-like ions.

	Exact		Hartree-Fock[a]	
Z	$I(0)$	$\langle\rho\rangle/4$	U_3[b]	$I(0)=\langle\rho\rangle/4$
1	0.002 854	0.016 589	0.003 643	0.016 286
2	0.107 495	0.191 900	0.121 600	0.190 460
3	0.536 025	0.783 991	0.625 200	0.769 882
5	3.322 380	4.133 372	4.236 000	4.089 110
8	15.897 330	18.095 541		18.044 612
10	32.664 735	36.322 103	52.860 000	36.122 153
12	58.364 877	64.073 826		63.347 454

[a]Obtained with the 6-311G** basis set [13].
[b]Taken from Ref. [5].

In summary, we have shown an expression that allows us to evaluate at the Hartree-Fock level, the electron-electron coalescence density as a functional of the one-electron density function. For exact wave functions of He-like ions with $Z\geq 5$, it appears to be an upper bound to the electron-electron coalescence density of appreciably greater accuracy than those previously reported. This accuracy is found to increase with increasing nuclear charge. Finally, we would like to point out that for the general case we have not proven Eq. (9); however, in view of the evidence given for the He-like ions, it looks like a plausible conjecture. More research to further clarify this point is in progress.

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