

Charge-density concentration and electron-electron coalescence density in atoms and molecules

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Values for the average electron density $\langle\rho\rangle$ and the electron-electron coalescence density or intracule density at the origin $I(0)$ have been calculated for a number of atoms and molecules using several *ab initio* methodologies. $\langle\rho\rangle$ can be taken as a measure of local one-electron density concentration, and shows little dependence on the theoretical level employed. In contrast, $I(0)$ has found to be highly dependent on the level of calculation. In particular, for a given *ab initio* method, the difference $\langle\rho\rangle/4 - I(0)$ can be related to the degree of Coulomb electron correlation introduced by that method in an atomic or molecular system.

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I. INTRODUCTION

Relationships between one- and two-electron properties have been receiving considerable attention in recent years, and are of special interest in density-functional theory, for they could be important for the construction of improved exchange-correlation functionals [1]. The electron-electron coalescence density or intracule density at the origin $I(0)$ has been the subject of many studies [2,3], and a number of upper and lower bounds have been found for $I(0)$ [4]. In particular, Ugalde and Sarasola [5] showed that at the Hartree-Fock (HF) level of theory, the intracule density at the origin can be expressed as a functional of the α and β one-electron densities,

$$I(0) = \int \rho^\alpha(\mathbf{r})\rho^\beta(\mathbf{r})d\mathbf{r}. \quad (1)$$

Thus, for the restricted case where $\rho^\alpha(\mathbf{r}) = \rho^\beta(\mathbf{r}) = \rho(\mathbf{r})$, Eq. (1) can be written as

$$I(0) = \frac{\langle\rho\rangle}{4}. \quad (2)$$

$\langle\rho\rangle$ stands for the average electron density [6],

$$\langle\rho\rangle = \int \rho^2(\mathbf{r})d\mathbf{r} \quad (3)$$

and $\rho = \rho^\alpha + \rho^\beta$ is the total charge density of the system.

Nevertheless, it is worth mentioning that for the restricted case, at correlated levels of theory, it has been hypothesized [5] that the equality of Eq. (2) converts into the following inequality:

$$I(0) < \frac{\langle\rho\rangle}{4}. \quad (4)$$

Although, as far as we know, this equation has not been given a formal proof, it has been checked by computation in a number of cases for both atoms [5,7] and molecules [8].

Recall that for any atom or molecule, the difference between $I(0)$ and $\langle\rho\rangle/4$ can be related to the degree of correlation between the antiparallel electrons of the system. To

understand this one could take into account that, because of the antisymmetry principle, the density of probability for the coalescence of two electrons of the same spin is zero. Hence, $I(0)$ turns out to be the density of probability for the coalescence of two electrons of different spin at all points of space. Namely,

$$I(0) = 2I^{\alpha\beta}(0) = 2 \int \Gamma^{\alpha\beta}(\mathbf{r},\mathbf{r})d\mathbf{r}, \quad (5)$$

where $\Gamma^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$ is the $\alpha\beta$ component of the electron-pair density. $\Gamma^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$ can be expressed as the sum of two different contributions, namely, an *uncorrelated* contribution, arising from the product of two one-electron density functions, and a *correlated* contribution, $f^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$, which accounts for all kind of correlations between α and β electrons [9], therefore,

$$\Gamma^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}[\rho^\alpha(\mathbf{r}_1)\rho^\beta(\mathbf{r}_2) + f^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)]. \quad (6)$$

Consequently, $I(0)$ can finally be expressed as

$$I(0) = \frac{\langle\rho\rangle}{4} + \int f^{\alpha\beta}(\mathbf{r},\mathbf{r})d\mathbf{r}. \quad (7)$$

Within the Hartree-Fock approximation, there is no correlation between electrons of different spin, so Eq. (7) reduces to the equality reported by Ugalde and Sarasola [see Eq. (2)]. For correlated wave functions, the second term on the right-hand side of Eq. (7) can be reasonably expected to be negative since it reflects the Coulomb *hole* at short inter-electronic distances [10], thus leading to the inequality conjectured in Eq. (4).

These results suggest that comparisons of $I(0)$ and $\langle\rho\rangle/4$ values for atomic and molecular systems could provide valuable insight on the effects of Coulomb electron correlation on one-electron and electron-pair distributions, especially taking into account that both $I(0)$ and $\langle\rho\rangle$ are amenable to experimental determination by means of x-ray diffraction experiments [6]. Moreover, by comparing $I(0)$ and $\langle\rho\rangle/4$ values calculated at the same level of theory, a reference methodology, like the Hartree-Fock method, is no longer required for the assessment of electron correlation effects.

TABLE I. Electron-electron coalescence density $I(0)$ and average electron density $\langle\rho\rangle$ at the HF, CISD, and MP2 levels of theory with the 6-311++G(2d,2p) basis set.

	HF	CISD			MP2		
	$I(0)=\frac{\langle\rho\rangle}{4}$	$I(0)$	$\frac{\langle\rho\rangle}{4}$	$\frac{\langle\rho\rangle}{4}-I(0)$	$I(0)$	$\frac{\langle\rho\rangle}{4}$	$\frac{\langle\rho\rangle}{4}-I(0)$
				(10 e.)			
CH ₄	7.9667	7.5884	7.9665	0.3780	7.5743	7.9644	0.3901
NH ₃	13.1376	12.6222	13.1419	0.5197	12.5994	13.1390	0.5397
OH ₂	20.3348	19.6428	20.3420	0.6992	19.6130	20.3400	0.7271
FH	30.0348	29.1109	30.0392	0.9283	29.0778	30.0378	0.9601
Ne	42.5288	41.3305	42.5284	1.1979	41.3069	42.5287	1.2218
				(14 e.)			
N ₂	26.3425	25.3919	26.3377	0.9459	25.3032	26.3188	1.0156
CO	28.3244	27.3385	28.3232	0.9847	27.2615	28.3152	1.0536
CN ⁻	21.0608	20.2653	21.0590	0.7937	20.1932	21.0477	0.8545
NO ⁺	33.5958	32.4649	33.5935	1.1286	32.3591	33.5751	1.2160
				(18 e.)			
SiH ₄	131.9351	129.7826	131.9430	2.1604	129.6622	131.9414	2.2792
PH ₃	165.7774	163.6090	165.7236	2.1146	163.4946	165.7324	2.2378
SH ₂	204.9240	202.4448	204.8571	2.4123	202.3085	204.8657	2.5571
CIH	250.2995	247.4635	250.2182	2.7547	247.3362	250.2251	2.8888
Ar	302.3402	299.0827	302.2392	3.1566	298.9627	302.2444	3.2817

II. COMPUTATIONAL METHODS

Ab initio geometry-optimized HF, configuration interaction (CISD), and Möller-Plesset (MP2) wave functions were generated for all the atoms and molecules reported in Table I, using the 6-311++G(2d,2p) basis set [11,12]. For the H₂ molecule, geometry optimized HF and full-configuration interaction (CI) wave functions were generated using the same basis set. Additionally, HF and full-CI wave functions were also calculated for a number of selected values of the H-H distance (see Table II). In all cases, the GAMESS package [13], was used to generate the first- and second-order density matrices necessary for the calculation of $\langle\rho\rangle/4$ and $I(0)$. $I(0)$ values were calculated following the algorithm described by Cioslowski and Liu [14]. No integrals were neglected for the calculation of the $I(0)$ values. Thus, the $I(0)$

TABLE II. Electron-electron coalescence density $I(0)$ and average electron density $\langle\rho\rangle$ at the HF and full-CI levels of theory with the 6-311++G(2d,2p) basis set for selected values of the internuclear distance, R .

R	HF	Full-CI		
	$I(0)=\frac{\langle\rho\rangle}{4}$	$I(0)$	$\frac{\langle\rho\rangle}{4}$	$\frac{\langle\rho\rangle}{4}-I(0)$
Opt. ^a	0.0437	0.0238	0.0435	0.0197
1.600	0.0365	0.0190	0.0371	0.0180
3.000	0.0165	0.0041	0.0195	0.0154
10.00	0.0117	0.0000	0.0199	0.0199

^aOptimized H-H distances (in a.u.) are 1.388 (HF) and 1.402 (full-CI).

values reported are exact within each of the levels of theory employed. $\langle\rho\rangle/4$ values were also computed exactly using the definition given in Eq. (3). Atomic units will be used throughout the paper.

III. RESULTS AND DISCUSSION

Table I gathers $I(0)$ and $\langle\rho\rangle$ values for a number of atoms and molecules within three isoelectronic series, and Table II for the H₂ molecule at several H-H distances, obtained by means of the Hartree-Fock, CISD and MP2 methodologies.

Solà *et al.* [15] found a good correlation between $\langle\rho\rangle$ and the local concentration of electronic charge density for a number of isoelectronic atomic and molecular series. Our results are consistent with this view. Thus, within each of the isoelectronic series, and for all the levels of theory investigated, the average density depends on the actual degree of electronic charge concentration, in agreement with the results reported earlier by Solà *et al.* [15]. For instance, for the 10- and 18-electron series, $\langle\rho\rangle$ increases with increasing nuclear charge in the heavy atom and decreasing number of H atoms. For the 14-electron series, the anionic (CN⁻) and cationic (NO⁺) systems have the smallest and largest values of $\langle\rho\rangle$, respectively, while the neutral molecules, N₂ and CO, exhibit $\langle\rho\rangle$ values between those of CN⁻ and NO⁺. The fact that CO has its charge density more locally concentrated on the oxygen than on the carbon leads to a larger averaged density for this molecule, in comparison to N₂. At the MP2 and CISD levels of theory, $\langle\rho\rangle$ and $I(0)$ exhibit the same trends found at the Hartree-Fock level.

The comparison between $\langle\rho\rangle$ and $I(0)$ values obtained at different levels of calculation yields interesting insights on

the effect of electron correlation. First of all, for all molecules, the Hartree-Fock, CISD and MP2 $\langle\rho\rangle$ values are very similar as should be expected, for the one-electron density has no first-order corrections and consequently the Hartree-Fock one-electron density should give accurate values for one-electron expectation values like the average electron density. Data such as that shown on Table I for $\langle\rho\rangle$ are compatible with this claim. Moreover, the effect of electron correlation on local charge concentration is not the same in all the molecules. Thus, for most systems studied, $\langle\rho\rangle$ decreases upon inclusion of Coulomb correlation. However, it increases for some systems like NH_3 , CH_4 , OH_2 , FH , and SiH_4 . In all cases, the changes in one-electron charge concentration are very slight (always less than 0.1%), in accordance with our previous statement.

In contrast, the effects of Coulomb correlation on $I(0)$ are significantly larger, with differences up to 5% between Hartree-Fock and post-HF results. Additionally, there is still the problem of the convergence of the electron-electron coalescence density. This point was elegantly illustrated by Davidson and Jones [16], who calculated $I(0)$ for the hydrogen molecule for various truncations of the CI expansion. The calculated *exact* value at the equilibrium distance was 0.0170, which should be compared with our CISD value of 0.0238. Nevertheless, it should be mentioned that our value compares well with Davidson's best truncated CI value of 0.0234. This is indicative that within our finite one-electron basis set we have got the same CI expansion as Davidson and Jones. This shows how slowly the electron-electron coalescence density converges.

Another remarkable point observed from the inspection of Table I, concerns CISD and MP2 $I(0)$ values, which are always smaller than the Hartree-Fock ones, i.e., Coulomb electron correlation reduces the density of probability for the coalescence of two electrons of different spin as a consequence of the electron-electron cusp [2]. This was earlier pointed out by Cioslowski who calculated the radius of the sphere surrounding $\mathbf{r}=0$ on whose surface the intracule density attains a local maximum value for some two-electron systems [17]. Consequently $\langle\rho\rangle/4 - I(0)$, which is equal to $-\int f^{\alpha\beta}(\mathbf{r},\mathbf{r})d\mathbf{r}$, can be taken as a reference-independent measure of antiparallel electron correlation. Interestingly, this difference appears to be slightly larger at the MP2 than at the CISD level of calculation, even though CISD energies are sometimes lower than MP2 ones.

The H_2 molecule is used to illustrate the fact that $I(0)$ and $\langle\rho\rangle$ do not always follow similar trends. Values of $\langle\rho\rangle/4$ and $I(0)$ calculated at the full-CI level of theory with the 6-311++G(2d,2p) basis set for several values of the H-H interatomic distance R are shown in Table II. For H_2 at the full-CI level of theory, the value of $\langle\rho\rangle/4$ (0.0435) is about twice that of $I(0)$ (0.0238). This is very supportive of the importance of the electron correlation as a natural phenomenon that must be taken into account for a reliable description of this singular two-electron system. As the H-H distance is progressively increased, the electron-electron

coalescence density decreases steadily and tends to zero in the dissociation limit. In contrast, the average charge density decreases also as the internuclear distance increases until a minimum value is reached at $R=3.5$ a.u. From this point up, $\langle\rho\rangle/4$ approaches steadily to the value of $\langle\rho\rangle/4=1/16\pi$ for $R\rightarrow\infty$. This value agrees with the picture of two dissociated H atoms at a noninteracting distance, for which there is no probability for the coalescence of the two electrons. The value of $1/4\pi$ of the average electron density $\langle\rho\rangle$, simply reflects the concentration of each of the electrons around its corresponding nucleus and, can be easily obtained from the exact dissociated wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)=\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)+\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)$, being ψ the ground state wave function of the hydrogen atom.

For the dissociated atoms, the $\langle\rho\rangle/4 - I(0)$ difference amounts, therefore, to $1/16\pi$. However, this does not mean that the motions of the two electrons are actually correlated. Rather, the role of the correlation function $\int f^{\alpha\beta}(\mathbf{r},\mathbf{r})d\mathbf{r}$, is to prevent the electron pair from the possibility of being on the same H atom. Recall that at the Hartree-Fock level when the two nuclei are far apart, $I(0)$ has a value of 0.0132, which corresponds to the $I(0)$ value for H^- [5]. This is a well-known consequence of neglecting electron correlation in the description of the dissociation of the hydrogen molecule.

IV. SUMMARY

In summary, we have shown that the electron-electron coalescence density can be expressed as a functional of the one-electron density $\langle\rho\rangle/4$ plus a term depending on the correlation density between electrons of different spin, $\int f^{\alpha\beta}(\mathbf{r},\mathbf{r})d\mathbf{r}$. Within the Hartree-Fock approximation, this expression reduces to that previously reported by Ugalde and Sarasola [5]. We have examined the $\langle\rho\rangle/4$ and $I(0)$ values of several atoms and molecules within three isoelectronic series, at the Hartree-Fock, CISD, and MP2 levels of theory. Within each series, both $\langle\rho\rangle/4$ and $I(0)$ depend on the charge-density concentration of each molecule. However, $I(0)$ appears to be more sensitive on the level of calculation than $\langle\rho\rangle/4$.

Comparisons between the results obtained at the Hartree-Fock and CISD or MP2 levels show that electron correlation has a very subtle effect on charge-density concentration, but reduces strongly the probability of coalescence of electrons of different spin. These results confirm that electron-pair properties are much more sensitive to the level of calculation, and are better suited to evaluate the quality of molecular wave functions.

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