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# Energy decompositions according to physical space partitioning schemes: Treatments of the density cumulant

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This article is a continuation of our previous paper on schemes of energy decompositions of molecular systems in the real space [D. R. Alcoba *et al.*, *J. Chem. Phys.* **122**, 074102 (2005)] now using correlated state functions. We study, according to physical arguments, the appropriate management of the density cumulant arising from the second-order reduced density matrix at correlated level, whose contributions can be assigned to one-center or to two-center terms in the energy partitioning. Our treatments are applied within two physical space partitioning schemes: the Bader partitioning into atomic basins and the fuzzy atom procedure. The results obtained in selected molecules are analyzed and discussed in detail. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772855]

## I. INTRODUCTION

The decomposition of the electronic energy of  $N$ -electron systems into contributions which can be associated with one, two, or more atom components has received significant attention from many authors recently.<sup>1–12</sup> This interest arises from the possibility of determining satisfactorily the strength of the chemical bondings between the atoms which compose a given molecule, atomic group, cluster, etc. The information provided by this type of studies is of paramount importance for chemists since it allows one to know the interactions within a system. As is well known, this kind of methodology has been tackled by different approaches. On the one hand, some methods perform the analyses of the one-center, two-center, etc., energy terms in the Hilbert space of basis functions, each of which is assigned to one of the atoms.<sup>1–5</sup> Alternatively, other methods use schemes based on the partitioning of the three-dimensional physical space into atomic domains.<sup>5–11</sup> This division of the physical space has usually been accomplished by means of Bader's atoms in molecules<sup>13</sup> (AIM) theory or by the fuzzy atom procedure.<sup>14–16</sup>

In Ref. 10, we have described a general algorithm to decompose the energy of a molecule into one- and two-center contributions, according to a partitioning of the real space. The procedure has been applied within the framework of the AIM theory and within the fuzzy atom approach. Moreover, our algorithm can be applied to any level of

theory, that is, at Hartree-Fock [self-consistent field (SCF)] level or at correlated one. However, we limited our calculations to the Hartree-Fock level, in order to establish an appropriate comparison with the results arising from procedures reported by other authors. The aim of this paper is to analyze the influence of many-body effects on the partitioning scheme itself and to explore all the capabilities of our method. For theoretical and practical reasons, the elements of the second-order reduced density matrix required for the energy expression are now formulated in terms of the elements of the first-order reduced density matrix and the elements of the density cumulant matrix.<sup>17–19</sup> Hence, the application of this formulation at correlated level rises the question of how to manage the matrix elements of the density cumulant within the partitioning of the energy into one-center and two-center terms.

The paper is organized as follows. Section II describes the energy partitioning into one-center and two-center terms by means of two different treatments of the matrix elements of the density cumulant. In a first procedure, these elements are assigned to the two-center terms while in another treatment, according to physical reasons,<sup>20</sup> they are managed as possessing one-center character. Both treatments are developed within the AIM theory and within the fuzzy atom approach. Section III reports the computational aspects and the numerical determinations performed in selected molecules, which provide the comparison with previous results at SCF level and the corresponding discussion. Finally, in Sec. IV we report the remarks and conclusions of this work.

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## II. TREATMENTS OF THE DENSITY CUMULANT

We will express the energy of an  $N$ -electron molecule with clamped nuclei as

$$E = \sum_{i,j} T_j^{i1} D_i^j + \sum_A \sum_{i,j} {}^A V_j^{i1} D_i^j + \sum_{i,j,k,l} B_{jl}^{ik2} D_{ik}^{jl} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}, \quad (1)$$

in which  $i, j, k, l, \dots$  are orbital functions of an orthonormal basis set,  $A, B, \dots$  are the nuclei of the molecule,  $R_{AB}$  the distance between those nuclei, and  $Z_A, Z_B, \dots$  the corresponding nuclear charges.  $T_j^i$  mean the matrix elements of the kinetic energy operator,  $(-\frac{1}{2}\nabla^2)$ .  ${}^A V_j^i$  are the matrix elements corresponding to the  $(-Z_A/r_A)$  operator and  $B_{jl}^{ik} = \langle ik | j l \rangle$  the standard two-electron integrals in the (12|12) convention.  ${}^1 D_j^i$  and  ${}^2 D_{jl}^{ik}$  denote the matrix elements of the spin-free first-order and second-order reduced density matrices,<sup>21</sup> respectively.

For practical purposes this equation will be rewritten as

$$E = \sum_{i,j,k} T_j^{i1} D_k^j \delta_{ki} + \sum_A \sum_{i,j,k} {}^A V_j^{i1} D_k^j \delta_{ki} + \sum_{i,j,k,l,m,n} B_{jl}^{ik2} D_{mn}^{il} \delta_{mi} \delta_{nk} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}, \quad (2)$$

and the Kronecker deltas will be formulated in a general way as

$$\delta_{ij} = \langle i | j \rangle = \sum_A S_j^i(A), \quad (3)$$

in which  $\langle i | j \rangle$  are the standard overlap integrals (where the integration is performed over the total space). These integrals are partitioned according to the  $S_j^i(A)$  quantities related with the atomic domains of the centers  $A$ .

Within the AIM scheme, we will formulate the quantities  $S_j^i(A)$  as

$$S_j^i(A) = \langle i | j \rangle_A, \quad (4)$$

where  $\langle i | j \rangle_A$  are the overlap integrals over the Bader atomic domain associated with the nucleus  $A$ .<sup>13</sup>

Alternatively, in the fuzzy atom approach<sup>14-16</sup> the quantities  $S_j^i(A)$  will be formulated as

$$S_j^i(A) = \langle i | w_A(\mathbf{r}) | j \rangle, \quad (5)$$

in which a non-negative continuous weight function  $w_A(\mathbf{r})$  is introduced for each nucleus  $A$ . These weight functions measure the degree in which a given point of space  $\mathbf{r}$  is considered to belong to atom  $A$ , fulfilling the conditions

$$w_A(\mathbf{r}) \geq 0 \quad (6)$$

and

$$\sum_A w_A(\mathbf{r}) \equiv 1. \quad (7)$$

The introduction of the Kronecker deltas in Eq. (2) according to Eq. (3) allows us to express the energy as a sum of one-center and two-center terms

$$E = \sum_A E_A + \sum_{A<B} E_{AB}, \quad (8)$$

in which

$$E_A = \sum_{i,j,k} T_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k,l,m,n} B_{jl}^{ik2} D_{mn}^{il} S_i^m(A) S_k^n(A) \quad (9)$$

and

$$E_{AB} = \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(B) + \sum_{i,j,k} {}^B V_j^{i1} D_k^j S_i^k(A) + 2 \sum_{i,j,k,l,m,n} B_{jl}^{ik2} D_{mn}^{il} S_i^m(A) S_k^n(B) + \frac{Z_A Z_B}{R_{AB}}. \quad (10)$$

Equations (8)–(10) constitute a compact formulation for the partitioning of the electronic energy of an  $N$ -electron molecule in the three-dimensional physical space, which is expressed by means of one- and two-center terms ( $E_A$  and  $E_{AB}$ , respectively). From a mathematical point of view, both approaches, Bader and fuzzy atom ones, only differ in the formulation of the quantities  $S_j^i(A)$ . Further manipulations of Eq. (2) can lead to three- and four-center energy components which have no clear chemical significance.<sup>2,3</sup> Hence, we propose the partitioning scheme into one- and two-center contributions of Eq. (8).

The elements of the spin-free second-order reduced density matrix are formulated as<sup>4,18,19,22,23</sup>

$${}^2 D_{jl}^{ik} = \frac{1}{2} {}^1 D_j^{i1} D_l^k - \frac{1}{4} D_l^{i1} D_j^k + \frac{1}{2} \Lambda_{jl}^{ik}, \quad (11)$$

where  $\Lambda_{jl}^{ik}$  are the elements of the spin-free density cumulant matrix. All these matrix elements are zero at the SCF level (for singlet states). Consequently, the use of correlated functions implies the appearance of new contributions in the formulation of the partitioning of the molecular energy whose treatment requires to be studied.

The substitution of Eq. (11) into Eqs. (9) and (10) leads one to

$$E_A = \sum_{i,j,k} T_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k,l,m,n} B_{jl}^{ik} \left( \frac{1}{2} D_m^j D_n^l - \frac{1}{4} D_n^j D_m^l \right) S_i^m(A) S_k^n(A) + \frac{1}{2} \sum_{i,j,k,l,m,n} B_{jl}^{ik} \Lambda_{mn}^{il} S_i^m(A) S_k^n(A) \quad (12)$$

and

$$E_{AB} = \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(B) + \sum_{i,j,k} {}^B V_j^{i1} D_k^j S_i^k(A) + 2 \sum_{i,j,k,l,m,n} B_{jl}^{ik} \left( \frac{1}{2} D_m^j D_n^l - \frac{1}{4} D_n^j D_m^l \right) S_i^m(A) S_k^n(B) + \sum_{i,j,k,l,m,n} B_{jl}^{ik} \Lambda_{mn}^{il} S_i^m(A) S_k^n(B) + \frac{Z_A Z_B}{R_{AB}}. \quad (13)$$

The partitioning of the energy expressed by Eqs. (12) and (13) will be denominated *two-center model* because the

elements of the density cumulant  $\Lambda$  are distributed between the one-center and two-center energy components. Alternatively, as a consequence of the physical meaning of the cumulant describing effectively unpaired electrons, which do not contribute to bondings,<sup>20</sup> its matrix elements  $\Lambda_{ij}^{ik}$  should be assigned to the one-center components. From this point of view, the elements  $\Lambda_{ij}^{ik}$  will only contribute to one-center energies; this treatment of the density cumulant will be called *one-center model*. In this case, the energy partitioning leads one to the formulas

$$E_A = \sum_{i,j,k} T_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(A) + \sum_{i,j,k,l,m,n} B_{jl}^{ik} \left( \frac{1}{2} D_m^j {}^1 D_n^l - \frac{1}{4} {}^1 D_n^j {}^1 D_m^l \right) S_i^m(A) S_k^n(A) + \frac{1}{2} \sum_{i,j,k,l,m} B_{jl}^{ik} \Lambda_{mk}^{jl} S_i^m(A) \quad (14)$$

and

$$E_{AB} = \sum_{i,j,k} {}^A V_j^{i1} D_k^j S_i^k(B) + \sum_{i,j,k} {}^B V_j^{i1} D_k^j S_i^k(A) + 2 \sum_{i,j,k,l,m,n} B_{jl}^{ik} \left( \frac{1}{2} D_m^j {}^1 D_n^l - \frac{1}{4} {}^1 D_n^j {}^1 D_m^l \right) S_i^m(A) S_k^n(B) + \frac{Z_A Z_B}{R_{AB}} \quad (15)$$

As has been mentioned in the Introduction, the aim of this paper is to study both treatments of the density cumulant. In Sec. III, we report results arising from both models.

### III. COMPUTATIONAL ASPECTS AND RESULTS

The numerical determinations performed in this work have required the calculation of the one-electron integrals  $T_j^i$  and  ${}^A V_j^i$  as well as that of the two-electron integrals  $B_{ij}^{ik}$ . All of them were computed with the basis sets 6-31G using a modified version of GAMESS program.<sup>24</sup> The overlap integrals  $\langle i|j \rangle_A$  (calculated over the Bader domains) were evaluated with the PROAIM code,<sup>25</sup> while the integrals  $\langle i|w_A(\mathbf{r})|j \rangle$  were obtained with the modified code cited in Ref. 26 which follows a Becke integration scheme<sup>27</sup> based on the weight functions  $w_A(\mathbf{r})$  originally proposed by this author. The atomic radii used for determining the  $w_A(\mathbf{r})$  weights were identical to those employed in our previous work.<sup>10</sup> The PSI3 program package<sup>28</sup> provided the first-order and second-order reduced density matrices derived from  $N$ -electron state functions calculated at the level of configuration interaction (CI) with single and double excitations (CISD). All the calculations were implemented with the experimental geometries in order to compare more directly the resulting energies with the experimental ones arising from dissociation measures.<sup>29</sup>

To test the behavior of the above described models we have performed energy partitionings in simple systems ( $H_2$ ) and hydrocarbons with nonpolar bonds ( $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ ) as well as in hydrides with growing polarity

bonds ( $NH_3$ ,  $H_2O$ , and  $HF$ ). Tables I and II report the results within the schemes AIM and fuzzy atoms, respectively. Both tables collect results arising from the SCF approximation and from the two-center and one-center models of treatment of the density cumulant (calculated within the CISD approximation). In the SCF case,<sup>10</sup> all the elements of the density cumulant matrix are zero and consequently, no distinction between both models can be made. However, we have included the SCF results (obtained with the experimental geometries) for the sake of comparison with the results at correlated level. As is well known, the two-center energy components ( $E_{AB}$ ) characterize the strengths of the bonds between the individual atoms within the molecule but they cannot be related immediately to the dissociation energies.<sup>2,5</sup> Hence, although it is not obvious to compare the numerical values obtained with this methodology with the experimental values,<sup>8-10</sup> we have included in the tables the experimental dissociation energies, in order to check the tendency of our results. A common feature of the results reported in both tables is that all of them are in the chemical scale, showing negative values for the energy related with classical chemical bonds and negligible values otherwise (e.g., in the hypothetical bondings H...H for the hydrocarbons). A survey of the results in Table I (partitioning of the physical space according to the AIM picture) shows that the bonding energy numerical values obtained with the one-center model for the density cumulant are closer to the experimental ones than those obtained with the two-center model. This behavior is observed in all the values related with classical chemical bonds. Moreover, these one-center model results are also closer to the SCF ones than their two-center counterparts and the differences  $|E_{AB}^{SCF} - E_{AB}^{one-center}|$  lies in the interval ( $10^{-4}$ ,  $3 \times 10^{-2}$ ) a.u. The lower limit corresponds to the CC bond in  $C_2H_6$  molecule, while the higher one corresponds to the bonds OH and HF in the systems  $H_2O$  and  $HF$ , respectively. These results seem to indicate that the differences between both bonding energy values grow up from pure covalent bonds to polar ones passing through multiple bonds in the  $C_2H_4$  and  $C_2H_2$  molecules. Consequently, such differences, although small, tend to increase in systems in which the effectively unpaired electron density concentrates in atomic sites.<sup>30,31</sup> The results reported in Table II (partitioning of the physical space according to the fuzzy atom picture) show a similar trend, although the values  $E_{CC}$  (in the  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$  systems) turn out to be higher (in all the cases) than in the AIM picture. As in the previous table, the results derived from the one-center model are also closer to the SCF ones than those arising from the two-center model although the behavior of the differences  $|E_{AB}^{SCF} - E_{AB}^{one-center}|$  is less clear. This may be interpreted as a consequence of the bias of the surfaces defining the atoms due to the semiempirical character of the fuzzy atom methodology choosing the same atomic radii for the elements in different compounds.

The physical meaning of the density cumulant and the results described in this paper confirm our previous suggestions on the role played by the density cumulant. In fact, in Ref. 20 we pointed out the nonpairing character of the density cumulant in the description of bond orders. Similar arguments can be exhibited from the fact that a tensorial con-

TABLE I. Energy (a.u.) partitioning in the AIM picture for selected molecules at the SCF level and by means of the two- and one-center models for the density cumulant at CISD level (6-31G basis set).

System	Fragment	Bonding	$E_{\text{SCF}}$	$E_{\text{two-center}}$	$E_{\text{one-center}}$	$E_{\text{expt.}}^a$
H <sub>2</sub>	H		-0.4770	-0.5058	-0.4929	
		HH	-0.1727	-0.1401	-0.1659	-0.1661
CH <sub>4</sub>	C		-37.5087	-37.6493	-37.5971	
		H	-0.5320	-0.5566	-0.5464	
	H	CH	-0.1430	-0.1097	-0.1358	-0.1657
		HH	0.0047	0.0033	0.0052	
C <sub>2</sub> H <sub>6</sub> (D <sub>3d</sub> )	C		-37.5365	-37.6740	-37.6222	
		H	-0.5407	-0.5637	-0.5544	
	H	CC	-0.1098	-0.0811	-0.1092	-0.1402
		CH	-0.1454	-0.1124	-0.1376	-0.1562
	H	C...H	0.0102	0.0101	0.0102	
		HH (CH <sub>3</sub> )	0.0059	0.0042	0.0061	
		H...H <sup>b</sup>	0.0008	-0.0006	0.0007	
H...H <sup>c</sup>	0.0003	0.0003	0.0003			
C <sub>2</sub> H <sub>4</sub>	C		-37.5728	-37.7205	-37.6635	
		H	-0.5280	-0.5499	-0.5409	
	H	CC	-0.2235	-0.1421	-0.2124	-0.2741
		CH	-0.1370	-0.1087	-0.1306	-0.1721
	H	C...H	0.0048	0.0050	0.0051	
		HH (CH <sub>2</sub> )	0.0035	0.0018	0.0038	
		H...H <sup>b</sup>	0.0005	-0.0011	0.0005	
H...H <sup>c</sup>	-0.0008	-0.0009	-0.0007			
C <sub>2</sub> H <sub>2</sub>	C		-37.5943	-37.7636	-37.6914	
		H	-0.5074	-0.5262	-0.5174	
	H	CC	-0.3202	-0.1734	-0.2996	-0.3665
		CH	-0.1255	-0.1036	-0.1220	-0.1992
	H	C...H	-0.0121	-0.0115	-0.0113	
		HH	0.0066	0.0049	0.0054	
NH <sub>3</sub>	N		-54.0499	-54.2147	-54.1799	
		H	-0.5828	-0.6010	-0.5914	
	H	NH	-0.1719	-0.1352	-0.1585	-0.1753
		HH	0.0510	0.0460	0.0481	
H <sub>2</sub> O	O		-74.5624	-74.7302	-74.7158	
		H	-0.5445	-0.5673	-0.5611	
	H	OH	-0.2253	-0.1779	-0.1922	-0.1896
		HH	0.1181	0.1065	0.1083	
HF	F		-99.3543	-99.4945	-99.4912	
		H	-0.4437	-0.4752	-0.4719	
	H	HF	-0.1858	-0.1405	-0.1471	-0.2166

<sup>a</sup>Experimental energy.<sup>b</sup>Closer H atoms in different groups.<sup>c</sup>More distant H atoms in different groups.

taction of the  $\Lambda$  matrix<sup>19</sup> leads to the effectively unpaired electron matrix<sup>32,33</sup> which as is well known describes unpaired electrons assigned to determined domains.

#### IV. CONCLUDING REMARKS

In this work, we have proposed and examined two possible treatments for the density cumulant in the studies of energy decompositions according to partitionings of the physical space at correlated level. In the two-center model

the elements of the density cumulant matrix are assigned to one-center and to two-center energy components, while in the one-center model those elements are assigned only to one-center components. The numerical determinations, performed within the AIM and fuzzy atom schemes of partitioning of the physical space, point out our one-center model as the most appropriate treatment, mainly in the AIM scheme. These results agree with the physical meaning of the density cumulant and confirm our previous predictions on the management of this device. We are currently studying the treatment of the correlation effects within energy partitionings

TABLE II. Energy (a.u.) partitioning in the fuzzy atom picture for selected molecules at SCF level and by means of the two- and one-center models for the density cumulant at CISD level (6-31G basis set).

System	Fragment	Bonding	$E_{\text{SCF}}$	$E_{\text{two-center}}$	$E_{\text{one-center}}$	$E_{\text{expt.}}^a$
H <sub>2</sub>	H		-0.4633	-0.4890	-0.4789	
		HH	-0.2002	-0.1736	-0.1939	-0.1661
CH <sub>4</sub>	C		-37.3771	-37.5089	-37.4677	
		H	-0.5213	-0.5389	-0.5313	
	H	CH	-0.1892	-0.1647	-0.1853	-0.1657
		HH	0.0065	0.0047	0.0065	
C <sub>2</sub> H <sub>6</sub> (D <sub>3d</sub> )	C		-37.3442	-37.4656	-37.4301	
		H	-0.5247	-0.5411	-0.5343	
	H	CC	-0.3511	-0.3366	-0.3490	-0.1402
		CH	-0.1829	-0.1596	-0.1790	-0.1562
	H	C...H	0.0037	0.0035	0.0034	
		HH (CH <sub>3</sub> )	0.0088	0.0070	0.0088	
		H...H <sup>b</sup>	0.0016	0.0005	0.0016	
H...H <sup>c</sup>	0.0015	0.0015	0.0015			
C <sub>2</sub> H <sub>4</sub>	C		-37.3727	-37.5027	-37.4638	
		H	-0.5098	-0.5262	-0.5198	
	H	CC	-0.5202	-0.4655	-0.5101	-0.2741
		CH	-0.1789	-0.1587	-0.1747	-0.1721
	H	C...H	-0.0001	0.0008	0.0003	
		HH (CH <sub>2</sub> )	0.0057	0.0037	0.0057	
		H...H <sup>b</sup>	0.0022	0.0007	0.0020	
H...H <sup>c</sup>	0.0007	0.0002	0.0006			
C <sub>2</sub> H <sub>2</sub>	C		-37.3959	-37.5433	-37.4924	
		H	-0.4888	-0.5046	-0.4985	
	H	CC	-0.6421	-0.5355	-0.6246	-0.3665
		CH	-0.1724	-0.1563	-0.1686	-0.1992
	H	C...H	-0.0204	-0.0187	-0.0191	
		HH	0.0052	0.0042	0.0047	
NH <sub>3</sub>	N		-53.9857	-54.1410	-54.1042	
		H	-0.5564	-0.5711	-0.5620	
	H	NH	-0.1806	-0.1518	-0.1763	-0.1753
		HH	0.0113	0.0081	0.0112	
H <sub>2</sub> O	O		-74.4945	-74.6543	-74.6283	
		H	-0.5992	-0.6102	-0.5997	
	H	OH	-0.1517	-0.1231	-0.1491	-0.1896
		HH	0.0124	0.0071	0.0120	
HF	F		-99.1597	-99.3018	-99.2902	
		H	-0.6176	-0.6245	-0.6129	
	H	HF	-0.2062	-0.1841	-0.2073	-0.2166

<sup>a</sup>Experimental energy.<sup>b</sup>Closer H atoms in different groups.<sup>c</sup>More distant H atoms in different groups.

carried out in the Hilbert space of atomic orbitals and the results will be discussed in a forthcoming paper.<sup>34</sup>

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