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Determination of Energies and Electronic Densities of Functional Groups According to Partitionings in the Physical Space

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This work formulates our previously reported partitionings of the first-order reduced density matrix and the molecular electronic energy using for both quantities an identical mathematical framework. The procedure provides a consistent and rigorous scheme for extending our algorithms to unions of atomic domains, in order to describe molecular fragments which can be identified as functional groups. Numerical determinations, performed in several series of organic compounds and clusters, support the reliability of our methodology to describe properties of atomic groups.

1. Introduction

The idea of expressing a molecular property as a sum of atomic contributions has aroused the interest of many chemists during decades. Partitionings of the number of molecular electrons N, the spin $\langle \hat{S}^2 \rangle$, the molecular electronic energy E and other properties have been extensively studied through various approaches and procedures.[1−18] The use of these techniques provides a fruitful chemical information, i.e., very useful and popular concepts in chemistry such as bond order, valence, charge density, local spin, etc. can be directly obtained and visualized from these treatments. The splitting of molecular electronic energy into one-center and two-center terms presents a double interest. The one-center terms provide information about the gain or loss of energy of the atoms within a molecule with respect to the free atoms, whereas the two-center ones evaluate the strength of the bondings within the system.

In previous works, we have performed partitionings of the first-order reduced density matrix[19,20] and the molecular energy,[17,21,22] corresponding to a determined state of an N-electron system, into first-order reduced density matrices and energies associated with the atomic domains defined in Bader's theory of atoms in molecules.[23] The matrix type methodology used in these decompositions is numerically more precise and computationally less expensive than other alternative direct integration treatments.[17] An appropriate management of these tools has allowed us to describe and to identify electronic populations, energies associated with each atomic domain and bonding energies between these domains,[17,19−21] achieving results in good agreement with the genuine chemical knowledge. Dealing with fragments arising from chemically meaningful partitionings, their corresponding associated reduced density matrices define electron densities which turns out to be near invariant in different molecular environments.[24] Consequently, these kinds of matrices constitute appropriate tools to describe the transferability of functional groups in the organic compound series.[25−28]

The main aim of this work is to extend our methodology[17,19,21] to the study of molecular partitionings in terms of groupings of Bader's domains. In previous works we have showed the appropriate behavior of our models concerning basis set dependence, influence of electronic correlation and trend of the theoretical results to the experimental ones. In the present work we focus attention in the study of the relationship between the energy and the electronic distribution. In this sense, we propose a complete study of molecular fragments involving both electron density and energy analyses that is performed consistently, i.e. sharing both analyses identical partitioning scheme and identical mathematical framework. Our treatment provides suitable determinations of atomic and group densities, group energies, bonding energies between two domains inside a determined functional group as well as bonding energies between a group and its molecular environment, which is of great chemical interest. This task has been performed by means of domain-restricted first-order reduced density matrices (reduced density matrices associated with Bader's domains and their unions), domain-restricted energies (their counterpart concepts in energy terms), and bonding energies between domains.

The organization of this article is as follows. The second section summarizes the decomposition of the first-order reduced density matrix into its domain-restricted matrix components and describes the splitting of the total electronic energy into one-center and two-center domain-restricted energies for any arbitrary wave function. A unified formulation for both decompositions is also presented in that section. The third section describes a procedure to determine functional group density matrices, energies of functional groups and bonding energies between a functional group and its environment. The fourth section reports the computational details, the results found in selected molecules and clusters as well as their corresponding discussion. Finally, the last section points out the conclusions of this work.

2. Partitionings of the First-Order Reduced Density Matrix and the Electronic Energy: A Unified Treatment

In ref 19, we have reported a topological partitioning of the spin-free first-order reduced matrix elements ${}^1D^i_j$, corresponding to an N-electron system described by a wave function Ψ as

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$$ {}^1D^i_j = \sum_{\Omega} {}^1D^i_j(\Omega) \tag{1} $$

with

$$ {}^1D^i_j(\Omega) = \sum_{\sigma}\sum_{k,l} \left({}^1D^{1/2}\right)^{i\sigma}_{k\sigma} S^k_l(\Omega) \left({}^1D^{1/2}\right)^{l\sigma}_{j\sigma} \tag{2} $$

where i, j, ... are a set of orthonormal orbitals, σ is the spin coordinate (α or β), and $({}^1D^{1/2})^{i\sigma}_{k\sigma}$ and $({}^1D^{1/2})^{l\sigma}_{j\sigma}$ mean the elements of the positive square root matrix arising from the first-order reduced density matrix. $S^k_l(\Omega) = \langle k|l\rangle_{\Omega}$ are the overlap integrals over Bader domains Ω.[23] According to Bader's theory, the whole real space $\cup\Omega$, is partitioned into the domains Ω holding $\Omega \cap \Omega' = \emptyset$.

The elements ${}^1D^i_j(\Omega)$ in eq 2 define a domain-restricted first-order reduced density matrix whose properties and foundations have been described in refs 19 and 29. For singlets and other spin symmetry states having $S_z = 0$ the elements of the spin-free first-order reduced density matrix associated with the region Ω can be calculated as[19]

$$ {}^1D^i_j(\Omega) = \sum_{k,l} \left({}^1D^{1/2}\right)^i_k S^k_l(\Omega) \left({}^1D^{1/2}\right)^l_j \tag{3} $$

so that the spin coordinate σ can be ignored.

On the other hand, the nonrelativistic electronic energy of an N-electron system with clamped nuclei corresponding to a determined state, Ψ, has been expressed by means of a sum of one-center and two-center terms as[17,21]

$$ E = \sum_{\Omega_A} E_{\Omega_A} + \sum_{\Omega_A < \Omega_B} E_{\Omega_A \Omega_B} \tag{4} $$

where

$$ E_{\Omega_A} = \sum_{i,j,k} T^{i\,1}_j D^j_k S^k_i(\Omega_A) - \sum_{i,j,k} {}^AV^{i\,1}_j D^j_k S^k_i(\Omega_A) + \sum_{i,j,k,l,m,n} C^{ik\,2}_{jl} F^{jl}_{mn} S^m_i(\Omega_A) S^n_k(\Omega_A) + \frac{1}{2} \sum_{i,j,k,l,m} C^{ik}_{jl} \Lambda^{jl}_{mk} S^m_i(\Omega_A) \tag{5} $$

and

$$ E_{\Omega_A\Omega_B} = -\sum_{i,j,k} {}^AV^{i\,1}_j D^j_k S^k_i(\Omega_B) - \sum_{i,j,k} {}^BV^{i\,1}_j D^j_k S^k_i(\Omega_A) + 2 \sum_{i,j,k,l,m,n} C^{ik\,2}_{jl} F^{jl}_{mn} S^m_i(\Omega_A) S^n_k(\Omega_B) + \frac{Z_A Z_B}{R_{AB}} \tag{6} $$

E_{Ω_A} and $E_{\Omega_A\Omega_B}$ have been denominated domain-restricted energies and bonding energies between domains, respectively. In eqs 5 and 6, A, B, ... are the nuclei of the system, R_{AB} the distance between those nuclei and Z_A, Z_B, ... are the corresponding nuclear charges. T and ${}^AV$ are the operators $(-{}^1\!/_2\nabla^2)$ and (Z_A/r_A) respectively. The quantity C is defined by its matrix elements $C^{ik}_{jl} = \langle ik|jl\rangle$ which are the standard two-electron integrals in the (12|12) convention. Λ^{ik}_{jl} stands for the spin-free density cumulant term of the second-order reduced density matrix, ${}^2D$, corresponding to the state Ψ and ${}^2F^{ik}_{jl} = {}^2D^{ik}_{jl} - {}^1\!/_2\Lambda^{ik}_{jl} = {}^1\!/_2\,{}^1D^i_j\,{}^1D^k_l - {}^1\!/_4\,{}^1D^i_l\,{}^1D^k_j$.[30] Equations 4−6 define a topological partitioning of the electronic energy E as a function of the nuclei A, B, ... and their corresponding atomic domains Ω_A, Ω_B, ..., so that eqs 5 and 6 can be interpreted as the energies of the atomic domains Ω_A and the bond energies between the atomic domains Ω_A and Ω_B, respectively (cf. refs 17 and 21) for closed shell systems. In the open shell case, the spin effects that appear in the density cumulant must be considered in the treatment of this term.[31]

As has been pointed out in the Introduction, one of the purposes of this work is to describe a unique mathematical framework which allows us to deal with both quantities, domain-restricted first-order reduced density matrices and domain-restricted energies. Consequently, we rewrite eqs 5 and 6 in an equivalent symmetric way according to the procedure carried out in the partitioning of the first-order reduced density matrix expressed by formula (3), that is

$$ E_{\Omega_A} = \sum_{i,j,k} [(T\,{}^1D)^{1/2}]^i_j S^j_k(\Omega_A) [(T\,{}^1D)^{1/2}]^k_i - \sum_{i,j,k} [({}^AV\,{}^1D)^{1/2}]^i_j S^j_k(\Omega_A) [({}^AV\,{}^1D)^{1/2}]^k_i + \sum_{i,j,k,l,m,n} [(C\,{}^2F)^{1/2}]^{ik}_{jl} S^j_m(\Omega_A) S^l_n(\Omega_A) [(C\,{}^2F)^{1/2}]^{mn}_{ik} + \frac{1}{2} \sum_{i,j,k,l,m} [(C\Lambda)^{1/2}]^{ik}_{jl} S^j_m(\Omega_A) [(C\Lambda)^{1/2}]^{ml}_{ik} \tag{7} $$

and

$$ E_{\Omega_A\Omega_B} = -\sum_{i,j,k} [({}^AV\,{}^1D)^{1/2}]^i_j S^j_k(\Omega_B) [({}^AV\,{}^1D)^{1/2}]^k_i - \sum_{i,j,k} [({}^BV\,{}^1D)^{1/2}]^i_j S^j_k(\Omega_A) [({}^BV\,{}^1D)^{1/2}]^k_i + 2 \sum_{i,j,k,l,m,n} [(C\,{}^2F)^{1/2}]^{ik}_{jl} S^j_m(\Omega_A) S^l_n(\Omega_B) [(C\,{}^2F)^{1/2}]^{mn}_{ik} + \frac{Z_A Z_B}{R_{AB}} \tag{8} $$

In this way, energy and density expressions (eqs 7, 8, and 3) share identical mathematical structure, which provides a rigorous scheme for interpretation and comparative analysis of results concerning both quantities. This formulation can be extended to groupings of domains which correspond to molecular fragments of chemical interest. This extension is performed in the next section. Although the matrices defining the energy components in eqs 7 and 8 may become singular and consequently they might not be diagonalized to obtain the square root, this problem can be overcome using Jordan normal forms.[32]

3. Determination of Functional Group Energies

In order to apply our partitioning scheme to describe electronic densities of molecular fragments, in ref 19, we extended eq 3 to unions of Bader domains Ω_A through a simple manipulation of the overlap integrals, so that

$$ {}^1D^i_j(\cup_A\Omega_A) = \sum_{k,l} \left({}^1D^{1/2}\right)^i_k S^k_l(\cup_A\Omega_A) \left({}^1D^{1/2}\right)^l_j \tag{9} $$

where

$$ S^k_l(\cup_A\Omega_A) = \langle k|l\rangle_{\cup_A\Omega_A} = \sum_{\Omega_A}{}' S^k_l(\Omega_A) \tag{10} $$

and the sum $\sum_{\Omega_A}{}'$ is restricted to the Ω_A atomic domains that are included in the union set $\cup_A\Omega_A$. Obviously, if $\cup_A\Omega_A$ is the whole space ${}^1D^i_j(\cup_A\Omega_A) = {}^1D^i_j$.

According to that procedure, eq 7 can now be formulated in terms of unions of Bader domains leading to

$$E_{\cup_A\Omega_A} = \sum_{i,j,k} [(T^1D)^{1/2}]^i_j S^j_k(\cup_A\Omega_A)[(T^1D)^{1/2}]^k_i - \sum_B{}' \sum_{i,j,k} [({}^BV^1D)^{1/2}]^i_j S^j_k(\cup_A\Omega_A)[({}^BV^1D)^{1/2}]^k_i + \sum_{i,j,k,l,m,n} [(C^2F)^{1/2}]^{ik}_{jl} S^j_m(\cup_A\Omega_A) S^l_n(\cup_A\Omega_A)[(C^2F)^{1/2}]^{mn}_{ik} + \frac{1}{2}\sum_{i,j,k,l,m} [(C\Lambda)^{1/2}]^{ik}_{jl} S^j_m(\cup_A\Omega_A)[(C\Lambda)^{1/2}]^{ml}_{ik} + \frac{1}{2}\sum_{A\neq B}{}' \frac{Z_AZ_B}{R_{AB}} \quad (11)$$

in which the sum $\sum'_B$ refers to identical domains than $\cup_A\Omega_A$. The corresponding extension of eq 8 is

$$E_{\cup_A\Omega_A,\cup_B\Omega_B} = -\sum_A{}' \sum_{i,j,k} [({}^AV^1D)^{1/2}]^i_j S^j_k(\cup_B\Omega_B)[({}^AV^1D)^{1/2}]^k_i - \sum_B{}' \sum_{i,j,k} [({}^BV^1D)^{1/2}]^i_j S^j_k(\cup_A\Omega_A)[({}^BV^1D)^{1/2}]^k_i + \sum_{i,j,k,l,m,n} [(C^2F)^{1/2}]^{ik}_{jl} S^j_m(\cup_A\Omega_A) S^l_n(\cup_B\Omega_B)[(C^2F)^{1/2}]^{mn}_{ik} + \sum_A{}' \sum_B{}' \frac{Z_AZ_B}{R_{AB}} \quad (12)$$

where $\sum'_A$ and $\sum'_B$ contain identical domains than $\cup_A\Omega_A$ and $\cup_B\Omega_B$, respectively, and $(\cup_A\Omega_A)\cap(\cup_B\Omega_B) = \emptyset$.

Equation 11 determines the energy of the molecular fragment $\cup_A \Omega_A$, whereas eq 12 describes bonding energies between the two molecular fragments corresponding to the unions of Bader regions $\cup_A\Omega_A$ and $\cup_B\Omega_B$, respectively. Obviously if $\cup_A\Omega_A = \Omega_A$ and $\cup_B\Omega_B = \Omega_B$, eqs 11 and 12 revert to eqs 7 and 8, respectively. Besides, if $\cup_A\Omega_A$ is the whole space, $\cup_B\Omega_B = \emptyset$, $E_{\cup_A}\ \Omega_A = E$ and eq 12 vanishes. It is worthy to note that both the energy and the first-order reduced density matrix decompositions in terms of molecular fragments preserve the structure of the decomposition in terms of atomic domains, showing that this methodology constitutes a suitable extension to incorporate more general domains to the energy decomposition treatment.

As has been pointed out above, the main aim of this paper is to study the quantities ${}^1D(\cup_A\Omega_A)$, $E_{\cup_A\Omega_A}$ and $E_{\cup_A\Omega_A,\cup_B\Omega_B}$ to check their capability to describe chemically meaningful molecular fragments, i.e, atoms, groups of atoms, functional groups, etc. The results are reported in the next section.

4. Results and Discussion

Several series of compounds (most of them organic), in their ground state, have been chosen to test the reliability of our methodology to describe properties of atomic groups and interfragment bonding energies. Tables 1−3 report the values of group energies (arising from eq 11) and interfragment bonding energies (arising from eq 12) for the functional groups methyl, methylene, hydroxyl, amine, and carbonyl, within different molecular environments. These tables also report the values of the electronic populations $N_{\cup_A\Omega_A}$ corresponding to each fragment $\cup_A\Omega_A$, known as Bader's charge, which are the traces of the matrices ${}^1D(\cup_A\Omega_A)$ (see eq 9). In Table 4, we present nonclassical systems whose structural study is of interest to materials scientists due to their importance in science and technology. We describe the isomers of the neutral clusters Si_6O_2, Si_6O_3, Si_6O_4 and Si_6O_5 corresponding to the structures (c), (c), (a), and (b), respectively, shown in Figure 1 of ref 33, all of them containing the characteristic unit Si_2O_2. Table 5 shows results of electronic population analyses arising from first-order reduced density matrices corresponding to the mentioned functional groups and the unit Si_2O_2. For the sake of brevity, we have included in this Table only two compounds for each functional group (those providing the largest and lowest group energy) and two clusters (those having the lowest and largest size). The results corresponding to the other reported compounds are available upon request. The Table describes the total electronic population of the fragment $N_{\cup_A\Omega_A}$, the orbital type, the orbital population $\nu_i(\cup_A\Omega_A)$, the degeneracy (in population) and, in the case of conventional groups, the ionicity (as a percentage)[19] for each significant molecular orbital i of the functional group in the localized isopynic picture.[19,34] These results allow us to relate the energies in Tables 1−4 with the reordering of the electron cloud provided by the group environment. The one-electron integrals T^i_j and ${}^AV^i_j$, and the two-electron ones C^{ik}_{jl} were computed with a modified version of GAMESS[35] program whereas the reduced density matrix elements were generated using Gaussian 03.[36] The overlap matrices $S(\Omega)$ were evaluated with Gaussian 03 and PROAIM[37] codes. In a subsequent step, these matrices were subjected to the proposed

TABLE 1: Calculated Energies of the Methyl Group and Its Bonding Energies (a.u.) with Different Molecular Environments in the 6-31G(d,p) Basis Set at SCF Level

system	group	N_{CH_3}[a]	group energy	bonding	group-fragment bonding energy
CH_3F	CH_3	8.257	−39.2479	CH_3-F	−0.5930
CH_3OH	CH_3	8.351	−39.3176	CH_3-OH	−0.5565
CH_3NH_2	CH_3	8.553	−39.4370	CH_3-NH_2	−0.3441
CH_4	CH_3	8.937	−39.5495	CH_3-H	−0.1198
CH_3CH_3	CH_3	8.997	−39.5484	CH_3-CH_3	−0.1384
CH_3CH_2F	CH_3	8.941	−39.5283	CH_3-CH_2	−0.1075
				CH_3-F	−0.0505
CH_3CH_2OH	CH_3	8.953	−39.5345	CH_3-CH_2	−0.1109
				CH_3-OH	−0.0414
$CH_3CH_2NH_2$	CH_3	9.039	−39.5433	CH_3-CH_2	−0.1406
				CH_3-NH_2	−0.0127
$CH_3CH_2CH_3$	CH_3	9.017	−39.5520	CH_3-CH_2	−0.1485
				CH_3-CH_3	0.0050
CH_3CH_2CHO	CH_3	8.931	−39.5396	CH_3-CH_2	−0.1440
				CH_3-CO	0.0024
				CH_3-H	0.0000
CH_3CHO	CH_3	8.915	−39.5249	CH_3-CO	−0.1564
				CH_3-H	0.0003
CH_3COCH_3	CH_3	8.933	−39.5239	CH_3-CO	−0.1637
				CH_3-CH_3	0.0066

[a] Bader's charge corresponding to the methyl group.

TABLE 2: Calculated Energies of the Methylene Group and its Bonding Energies (a.u.) with Different Molecular Environments in the 6-31G(d,p) Basis Set at the SCF Level

system	group	N_{CH_2}[a]	group energy	bonding	group-fragment bonding energy
CH_4	CH_2	7.875	−38.8942	CH_2-H_2	−0.2469
CH_3CH_2F	CH_2	7.309	−38.6355	CH_2-CH_3	−0.1075
				CH_2-F	−0.5582
CH_3CH_2OH	CH_2	7.387	−38.6886	CH_2-CH_3	−0.1109
				CH_2-OH	−0.5379
$CH_3CH_2NH_2$	CH_2	7.493	−38.7700	CH_2-CH_3	−0.1406
				CH_2-NH_2	−0.3618
CH_3CH_2CHO	CH_2	7.957	−38.8663	CH_2-CH_3	−0.1440
				CH_2-CO	−0.1662
				CH_2-H	0.0006
$CH_3CH_2CH_3$	CH_2	7.959	−38.8787	CH_2-CH_3	−0.1485

[a] Bader's charge corresponding to the methylene group.

TABLE 3: Calculated Energies of the Groups Hydroxyl, Amine and Carbonyl, and Their Bonding Energies (a.u.) with Different Molecular Environments in the 6-31G(d,p) Basis Set at the SCF Level

system	group	N_X[a]	group energy	bonding	group-fragment bonding energy
H_2O	OH	9.620	−75.2816	OH−H	−0.4302
CH_3OH	OH	9.648	−75.1721	$OH-CH_3$	−0.5565
CH_3CH_2OH	OH	9.656	−75.1744	$OH-CH_2$	−0.5379
				$OH-CH_3$	−0.0414
C_6H_5OH	OH	9.670	−75.1123	$OH-C_6H_5$	−0.6981
NH_3	NH_2	9.373	−55.5100	NH_2-H	−0.2049
CH_3NH_2	NH_2	9.446	−55.4407	NH_2-CH_3	−0.3441
$CH_3CH_2NH_2$	NH_2	9.462	−55.4317	NH_2-CH_2	−0.3618
				NH_2-CH_3	−0.0127
$C_6H_5NH_2$	NH_2	9.513	−55.3434	$NH_2-C_6H_5$	−0.5579
CH_2O	CO	13.934	−112.5802	$CO-H_2$	−0.2736
CH_3CHO	CO	14.035	−112.5942	$CO-CH_3$	−0.1564
				CO−H	−0.1441
CH_3CH_2CHO	CO	14.056	−112.5979	$CO-CH_2$	−0.1662
				CO−H	−0.1455
				$CO-CH_3$	0.0024
CH_3COCH_3	CO	14.131	−112.6034	$CO-CH_3$	−0.1637

[a] Bader's charge corresponding to the groups X (X = OH, NH_2, CO).

TABLE 4: Calculated Energies of the Si_2O_2 Unit and Its Bonding Energies (a.u.) with the Remainder of the Corresponding Cluster in the 6-31G Basis Set at the SCF Level

cluster	group	$N_{Si_2O_2}$[a]	group energy	bonding	group-fragment bonding energy
Si_6O_2	Si_2O_2	44.209	−727.4230	$Si_2O_2-Si_4$	−0.0785
Si_6O_3	Si_2O_2	43.193	−727.1143	$Si_2O_2-Si_4O$	−0.6544
Si_6O_4	Si_2O_2	42.403	−726.5897	$Si_2O_2-Si_4O_2$	−1.5814
Si_6O_5	Si_2O_2	42.354	−726.5504	$Si_2O_2-Si_4O_3$	−1.6956

[a] Bader's charge corresponding to the Si_2O_2 unit.

TABLE 5: Bader's Charge $N_{\cup_A\Omega_A}$, Eigenvalues $\nu_i(\cup_A\Omega_A)$ (Orbital Populations), Degeneracies, Assigned Localized Eigenvectors, and Orbital Ionicity from the First-Order Reduced Density Matrices for Functional Groups in Several Molecular Environments in the SCF Treatment[a]

system	fragment $(\cup_A\Omega_A)$	$N_{\cup_A\Omega_A}$	ν_i $(\cup_A\Omega_A)$	degeneracy	assignment	ionicity
CH_3F	CH_3	8.257	1.999	1	$1s_C$	
			1.954	3	σ_{CH}	
			0.328	1	σ_{CF}	67.2
$CH_3CH_2CH_3$	CH_3	9.017	2.000	1	$1s_C$	
			1.970	2	σ_{CH}	
			1.972	1	σ_{CH}	
			1.016	1	σ_{CC}	2.5
CH_3CH_2F	CH_2	7.309	2.000	1	$1s_C$	
			1.931	2	σ_{CH}	
			0.997	1	σ_{CC}	1.2
			0.321	1	σ_{CF}	67.9
$CH_3CH_2CH_3$	CH_2	7.959	2.000	1	$1s_C$	
			1.946	2	σ_{CH}	
			0.967	2	σ_{CC}	2.5
system	fragment $(\cup_A\Omega_A)$	$N_{\cup_A\Omega_A}$	ν_i $(\cup_A\Omega_A)$	degeneracy	assignment	ionicity
H_2O	OH	9.620	2.000	1	$1s_O$	
			1.996	2	σ-lone pair; σ_{OH} (inner H)	
			1.991	1	π-lone pair	
			1.638	1	σ_{OH} (outer H)	62.3
C_6H_5OH	OH	9.670	2.000	1	$1s_O$	
			1.986	1	σ-lone pair	
			1.973	1	σ_{OH}	
			1.922	1	π-lone pair	
			1.626	1	σ_{CO}	62.5
NH_3	NH_2	9.373	2.000	1	$1s_N$	
			1.985	1	lone pair	
			1.990	2	σ_{NH} (inner H)	
			1.408	1	σ_{NH} (outer H)	40.7
$C_6H_5NH_2$	NH_2	9.513	2.000	1	$1s_N$	
			1.919	1	lone pair	
			1.974	2	σ_{NH}	
			1.495	1	σ_{NC}	51.4
system	fragment $(\cup_A\Omega_A)$	$N_{\cup_A\Omega_A}$	ν_i $(\cup_A\Omega_A)$	degeneracy	assignment	ionicity
CH_2O	CO	13.934	2.000	3	$1s_C$; $1s_O$ σ_O-lone pair	
			0.998	2	σ_{CH}	0.5
			1.979	1	π_O-lone pair	
			1.989	1	σ_{CO}	
			1.970	1	π_{CO}	
CH_3COCH_3	CO	14.131	2.000	2	$1s_C$; $1s_O$	
			1.999	1	σ_O-lone pair	
			1.013	2	σ_{CC}	1.6
			1.971	1	π_O-lone pair	
			1.987	1	σ_{CO}	
			1.959	1	π_{CO}	
system	fragment $(\cup_A\Omega_A)$	$N_{\cup_A\Omega_A}$	ν_i $(\cup_A\Omega_A)$	degeneracy	assignment	ionicity
Si_6O_2	Si_2O_2	44.209	1.998	1	σ_{Si^2}-lone pair	
			1.996	2	σ_{Si^2O}	
			1.999	2	σ_O-lone pair	
			1.994	2	π_O-lone pair	
			1.987	2	σ_{Si^1O}	
			1.222	1	$\sigma_{Si^3Si^1Si^3}$	
			0.749	1	$\pi_{Si^3Si^1Si^3}$	
Si_6O_5	Si_2O_2	42.354	1.998	1	σ_{Si^2}-lone pair	
			1.992	2	σ_{Si^2O}	
			1.998	2	σ_O-lone pair	
			1.982	2	π_O-lone pair	
			1.966	2	σ_{Si^1O}	
			0.191	1	σ_{Si^1O}	
			0.183	1	σ_{Si^1O}	

[a] Superscripts are as follows: 1, silicon atom directly bonded to the remaining fragment; 2, Silicon atom nondirectly bonded to the remaining fragment; 3, Silicon atom in the remaining fragment.

formulas using our own codes. Our treatments can be applied at any level of theory. However, in this work we have limited ourselves to the Hartree−Fock level [self-consistent field (SCF)]. The results reported for the classical functional groups have been obtained with the basis sets 6-31G(d,p), and those corresponding to the clusters have been calculated with the basis sets 6-31G.

The results gathered in Table 1 allow us to relate the values of N_{CH_3} with the energies E_{CH_3} and the interfragment bonding energies E_{CH_3-X} in different molecular environments. Let us start with the sequence CH_3-X (X = F, OH, NH_2, H, CH_3). As can be observed, these group energies E_{CH_3} and their electronic populations N_{CH_3} vary in good agreement with the polarity of the corresponding bond C−X. The highest values of the energy of group (in absolute value) correspond to the highest values of the Bader's charge as expected (the difference $E_{CH_3}^{\text{methane}}-E_{CH_3}^{\text{ethane}} = 0.0011$ a.u. is not significant). The tendency of the interfragment bonding energies E_{CH_3-X} in that series is also reasonable according to the chemical nature of the environment *X*. In the set of chemical compounds CH_3CH_2F, CH_3CH_2OH, $CH_3CH_2NH_2$, $CH_3CH_2CH_3$, and CH_3CH_2CHO, the methyl group is situated further from the polar group X than in the former series, which is reflected in the energies E_{CH_3} found; all of them are quite similar. Near-invariant character of the E_{CH_3} quantity can also be observed in the compounds CH_3CHO and CH_3COCH_3; in these systems the close values found can be explained by the fact that the methyl group neighbors the carbonyl group in both compounds and consequently, the interactions group-environment are again very similar in both.

We must highlight that our procedure predicts very low or negligible values of E_{CH_3-X} in all situations in which the methyl and X groups are not directly bonded such as CH_3-F in the CH_3CH_2F molecule, CH_3-OH in the CH_3CH_2OH alcohol, CH_3-NH_2 in the ethylamine, CH_3-H in both aldheydes, and CH_3-CH_3 in the propane and in the acetone. The compounds $CH_3CH_2CH_3$ and CH_3F present the largest difference in the E_{CH_3} values (−0.3 a.u.). Table 5 shows that the electron rearrangement in the CH_3 group in these compounds is only significant at the single bond that connect that group with the environment X. The molecules $CH_3CH_2CH_3$ and CH_3F exhibit a pure covalent CC bond (2.5% ionicity) and a highly polarized CF bond (67.2% ionicity), respectively. The difference between the total electron population of the group N_{CH_3} in both systems indicates a flux of charge from the localized molecular orbital assigned to the single CF bond of the corresponding CH_3 fragment to the environment F.

The results concerning the fragment CH_2 (the methylene group) are shown in Table 2. Regarding the sequence CH_3-CH_2-X (X = F, OH, NH_2, CO, CH_3) the differences between the values of the E_{CH_2} can be interpreted in terms of the polarity of the bond CH_2-X. The value $E_{CH_2} = -38.8942$ a.u. in the methane molecule, which does not belong to that series, is slightly lower but close to that in propane (−38.8787 a.u.) in which the methylene group has a similar environment. As in the previous Table, the energy E_{CH_2-H} in the propanaldheyde is negligible since it refers to nonbonded groups. The results for this group in the CH_3CH_2F and $CH_3CH_2CH_3$ molecules reported in Table 5 suggest similar comments to those discussed for the CH_3 fragment. The results collected in Table 3 correspond to the functional groups hydroxyl, amine, and carbonyl. They deserve very similar comments to those mentioned for the methyl and methylene groups. The main difference found for the OH group energy is $E_{OH}^{water} - E_{OH}^{phenol} = 0.1693$ a.u. which corresponds to markedly different chemical compounds. Similarly, the counterpart compounds for the NH_2 group present the highest difference $E_{NH_2}^{ammonia} - E_{NH_2}^{aniline} = 0.1666$ a.u. Both the OH group and the NH_2 one are bonded in these cases to very different groups H and C_6H_5. Despite the energy differences, Table 5 shows similar inner structures for OH group in phenol and H_2O as well as for the group NH_2 in aniline and ammonia and the ionicity values point out the electronegative character of oxygen and nitrogen atoms. In the compound sequence reported for the carbonyl group, the differences are even lower as correspond to identical functional group, being $E_{CO}^{acetone} - E_{CO}^{formaldheyde} = 0.0232$ a.u. the highest one. Table 5 reveals the similar structure of the CO group in both systems according to their chemically similar environments. According to the above-reported observations, this methodology is able to provide a right picture of the fragments and the fragment-environment interactions, in total agreement with the genuine chemical knowledge.

Table 4 reports preliminary results on the rhombic unit Si_2O_2 in the above-mentioned clusters. One of the silicon atoms of this unit is directly bonded to two silicon atoms of the remaining fragment in the cluster Si_6O_2, to a silicon atom and an oxygen atom in the Si_6O_3 one and to two oxygen atoms in the Si_6O_4 and Si_6O_5 compounds. The obtained numerical values show that the electronic population $N_{Si_2O_2}$, the energy $E_{Si_2O_2}$ and the Si_2O_2 unit-remaining cluster fragment bonding energy $E_{Si_2O_2-X}$ also vary according to the polarity of the Si_2O_2-X bondings in these compounds. In this sense, it can be observed a low charge transference from the Si_4 fragment to the Si_2O_2 unit in the Si_6O_2 cluster which exhibits the highest $N_{Si_2O_2}$ value. However, when the unit Si_2O_2 is directly bonded to oxygen atoms of the remaining fragment the charge is transferred in opposite sense. Consequently, the $N_{Si_2O_2}$ values found in the clusters Si_6O_4 and Si_6O_5 are similar but lower than in the Si_6O_2 one; in the Si_6O_3 cluster that quantity takes an intermediate value. The highest values for the energy of Si_2O_2 unit and the lowest values for the unit-remaining fragment bonding energy (both in absolute value), correspond to the highest Bader's charge $N_{Si_2O_2}$. These results agree with those reported in ref 33 which have been obtained through a quite different procedure. At the end of Table 5, we show the results arising from the electronic population analyses, limited to the valence shells, for the Si_2O_2 unit in the clusters Si_6O_2 and Si_6O_5 (according to the obtained values, the core shells turn out to be completely occupied). Our analysis detects the presence of three-center delocalized bonding orbitals involving three silicon atoms, one of them belonging to the Si_2O_2 unit and the other two to the remaining fragment in the Si_6O_2 cluster. The nature of these multicenter bondings prevents the calculation of ionization indices. More classical patterns have been found in the Si_6O_5 cluster. The low electronic population values of the orbitals σ_{SiO} in the Si_6O_5 cluster can be interpreted as high accumulation of electronic charge on the oxygen atoms of the fragment Si_4O_3.

5. Concluding Remarks

In this work, we have performed a reformulation of our previously reported partitioning of the electronic energy of an *N*-electron system in terms of domain-restricted energies and bonding energies between domains. The used procedure, which has been developed in the framework of the theory of atoms in molecules, is similar to that described in the formulation of domain-restricted reduced density matrices previously proposed by some of us. This provides a consistent and rigorous scheme to treat jointly both density and energy quantities. The extension of this procedure to describe molecular fragments has allowed us to evaluate consistently energies and densities corresponding to groups of atoms with chemical meaning as well as bonding energies between these groups. The results show reasonable values for the group energies, that vary according to the nature of the molecule in which the group is immersed. Likewise, the calculated bonding energies between two determined groups show similar values for chemically bonded groups within not too different environments, and very small or negligible values for not directly bonded fragments. The density analyses indicate that the inner structure of the groups remain unchanged; the only found changes refer to the bonds that connect the groups with the rest of the molecule in agreement with the energy results. All these results indicate that the domain-restricted tools (energies and reduced density matrices) are suitable devices to describe functional groups and to formulate their transferability. We point out that these treatments are able to describe as conventional molecules as more complex systems like clusters or aggregates.

We must also highlight that this methodology is independent of the quality of the wave function used to obtain the first- and second-order reduced density matrices; that is, it is valid for both variational (Hartree−Fock, configuration-interaction or multiconfigurational) and diagrammatic (coupled cluster) wave functions as well as for the methods in which the reduced density matrices are directly computed without using wave functions.[38] The proposed treatment can be implemented for any general partitioning of the three-dimensional space into overlaping domains (as those of "fuzzy" atoms type[3]) or nonoverlaping domains (as those of Bader and electron localization function type.[7] Moreover, the fragment properties determined by our treatment could be used to predict total properties of larger systems, by addition of molecular fragments. Work in this direction is currently being carried out in our laboratories.

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