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A study of the partitioning of the first-order reduced density matrix according to the theory of atoms in molecules

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This work describes a simple spatial decomposition of the first-order reduced density matrix corresponding to an N -electron system into first-order density matrices, each of them associated to an atomic domain defined in the theory of atoms in molecules. A study of the representability of the density matrices arisen from this decomposition is reported and analyzed. An appropriate treatment of the eigenvectors of the matrices defined over atomic domains or over unions of these domains allows one to describe satisfactorily molecular properties and chemical bondings within a determined molecule and among its fragments. Numerical determinations, performed in selected molecules, confirm the reliability of our proposal. © 2005 American Institute of Physics.

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I. INTRODUCTION

The decomposition of a certain molecular quantity, usually described in terms of reduced density matrices, into contributions associated to atoms or groups of atoms in a molecule has proven to be a powerful technique to describe molecular properties and chemical bondings. Perhaps the most extensively studied case is the partitioning of the N molecular electrons, known as population analysis, that has been a subject of interest for a long time.^{1–3} As is well known, these types of studies, as well as the partitioning of the spin $\langle S^2 \rangle$,^{4,5} provide a wide chemical information avoiding the use of the N -electron wave functions. Similarly, the decomposition of the electronic energy into one- and two-center contributions^{6,7} enables one to describe quantitatively bonding strengths, providing a better insight of the interactions between the molecular components. Another case of paramount interest is the study of the partitioning of the electron density into meaningful chemical fragments^{8–10} as well as the inverse procedure, that is, the recombination of molecular fragments into new molecules.^{11–13}

Although the electron density is expressed by means of the first-order reduced density matrix elements, it has also been formulated in terms of the elements of the square root of the first-order reduced density matrix.^{14–16} This approach has allowed to describe point-point sharing indices as a measure of the degree to which an electron is delocalized between two space-spin points. A subsequent integration of these point-point sharing indices has led to satisfactory determinations of basin-basin sharing indices over distinct atomic domains defined in the theory of atoms in molecules of Bader.² This treatment requires, in fact, an implicit use of

first-order reduced density matrices associated to these types of domains although this aspect has not been studied yet. The main aim of this paper is to propose a direct partitioning of the elements of the first-order reduced density matrix, according to the disjoint atomic domains which appear in Bader's theory, that is based on the use of the square root of the first-order reduced density matrix and the overlap matrices calculated over Bader's regions. This spatial decomposition leads to a definition of first-order reduced density matrices associated to atomic domains. This concept may be extended to matrices associated to unions of this kind of domains, related to molecular fragments. A second purpose of this work is to perform a study of the representability¹⁷ of these matrices, and consequently, of their capacities to describe physical properties and chemical bondings within the domains to which these matrices have been associated.

The paper is organized as follows. Section II describes the decomposition of the usual first-order reduced density matrix into first-order matrices associated to atomic domains; it also presents the mathematical features of these tools in relation with the representability problem. Section III reports the computational aspects of this work and the treatment proposed to extract the information contained in these matrices. The results found in selected molecules, the corresponding discussion, and a comparison with the *domain-averaged correlated hole model* previously introduced by us¹⁸ are also included in this section. Finally, some remarks and conclusions are presented in Sec. IV.

II. THE PARTITIONING OF THE FIRST-ORDER REDUCED DENSITY MATRIX

Let us consider an N -electron system described by a determined wave function Ψ . As is well known, the matrix elements of the first-order reduced density matrix corresponding to that state are

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$${}^1D_{j\sigma}^{i\sigma} = \langle \Psi | c_{i\sigma}^\dagger c_{j\sigma} | \Psi \rangle, \quad (1)$$

where i, j, \dots constitute a set of orthonormal orbitals, $c_{i\sigma}^\dagger/c_{j\sigma}$ are the standard creation/annihilation fermion operators, and σ is the spin coordinate (α or β). This matrix is Hermitian; its trace is the number of electrons N and its eigenvalues lie between zero and 1.¹⁷

We will express the 1D matrix as a matrix factorization in terms of its Hermitian positive square-root matrix (${}^1D^{1/2}$), that is, ${}^1D = ({}^1D^{1/2})^\dagger ({}^1D^{1/2})$.^{14,19,20} Hence, its matrix elements can be written as

$${}^1D_{j\sigma}^{i\sigma} = \sum_{k,l} ({}^1D^{1/2})_{k\sigma}^{i\sigma} ({}^1D^{1/2})_{j\sigma}^{l\sigma} \delta_{k\sigma l\sigma}. \quad (2)$$

We will consider the partitioning of the whole real space, $\cup\Omega$, according to Bader's atomic regions Ω .² Taking into account that this partitioning holds $\Omega \cap \Omega' = \emptyset$, the Kronecker deltas can be written in the form

$$\delta_{i\sigma j\sigma} = \langle i|j \rangle = \sum_{\Omega} S_{\Omega}^i(\Omega), \quad (3)$$

in which $\langle i|j \rangle$ are the standard overlap integrals (where the integration is performed over the total space) and $S_{\Omega}^i(\Omega) = \langle i|j \rangle_{\Omega}$ are the overlap integrals over Bader domains Ω (where the integration is limited to this kind of domain).²

The substitution of the Kronecker deltas in Eq. (2) according to formula (3) leads to a topological partitioning of the elements of the first-order reduced density matrix

$${}^1D_{j\sigma}^{i\sigma} = \sum_{\Omega} {}^1D_{j\sigma}^{i\sigma}(\Omega), \quad (4)$$

where

$${}^1D_{j\sigma}^{i\sigma}(\Omega) = \sum_{k,l} ({}^1D^{1/2})_{k\sigma}^{i\sigma} S(\Omega)_l^k ({}^1D^{1/2})_{j\sigma}^{l\sigma}. \quad (5)$$

The elements ${}^1D_{j\sigma}^{i\sigma}(\Omega)$ constitute the *first-order reduced density matrix associated to the region Ω* . This matrix possesses similar features to those of the ordinary reduced density matrix: it is Hermitian and its trace is given by N_{Ω} , the number of electrons within the domain Ω , which is equivalent to Bader's atomic charge because of the cyclic property of the trace, i.e., $\text{Tr}({}^1D(\Omega)) = \text{Tr}({}^1D^{1/2} S(\Omega) {}^1D^{1/2}) = \text{Tr}({}^1D S(\Omega))$ [cf. Eq. (5)]. Moreover, since the matrix factorization $A = B^\dagger B$ implies that A is positive semidefinite,²¹ it follows that ${}^1D(\Omega) = ({}^1D^{1/2}) S^{1/2}(\Omega) S^{1/2}(\Omega) ({}^1D^{1/2})$ possesses this property, that is, its eigenvalues are non-negative

$${}^1D_{i\sigma}^{i\sigma}(\Omega) \geq 0, \quad \forall i, \Omega. \quad (6)$$

On the other hand, taking into account the N -representability condition of the 1D matrix¹⁷

$${}^1D_{i\sigma}^{i\sigma} = \sum_{\Omega} {}^1D_{i\sigma}^{i\sigma}(\Omega) \leq 1, \quad \forall i \quad (7)$$

and the positive semidefiniteness of ${}^1D(\Omega)$ matrix, it follows that

$${}^1D_{i\sigma}^{i\sigma}(\Omega) \leq 1, \quad \forall i, \Omega, \quad (8)$$

that is, its eigenvalues are lower than or equal to 1.

All these properties ensure the (ensemble) representability^{22,23} of the ${}^1D(\Omega)$ matrices and therefore their physical grounds and usefulness to describe first-order properties within the Ω regions. These aspects are shown in Sec. III. We must emphasize that the partitioning described in Eq. (4), based on the direct use of first-order reduced density matrices, leads to true first-order reduced density matrices associated to regions Ω . In a previous study of the domain-averaged correlated holes,¹⁸ we described a partitioning of the first-order reduced density matrix from the second-order reduced density matrix contraction mapping. Both partitionings are distinct and obviously lead to different results except at the closed-shell Hartree-Fock level where the two treatments are coincident. These studies show that the partitioning of reduced density matrices allows different approaches which deserve to be considered in the description of atomic or functional groups.

III. COMPUTATIONAL ASPECTS, RESULTS, AND DISCUSSION

Although in Sec. II the elements of the first-order reduced density matrices have been expressed in terms of spin orbitals, the numerical determinations reported in this paper have been performed through a spin-free formulation, which is more suitable for computational purposes. As is well known, the elements of the spin-free first-order reduced density matrix are given by

$${}^1D_j^i = \langle \Psi | \sum_{\sigma} c_{i\sigma}^\dagger c_{j\sigma} | \Psi \rangle = \sum_{\sigma} {}^1D_{j\sigma}^{i\sigma}. \quad (9)$$

Analogously, the spin-free matrix elements of the ${}^1D(\Omega)$ quantity will be defined as

$${}^1D_j^i(\Omega) = \sum_{\sigma} {}^1D_{j\sigma}^{i\sigma}(\Omega). \quad (10)$$

For singlet states and others having $S_z=0$ the elements of the spin-free first-order reduced density matrix associated to the region Ω can be calculated straightforwardly as

$${}^1D_j^i(\Omega) = \sum_{k,l} ({}^1D^{1/2})_k^i S(\Omega)_l^k ({}^1D^{1/2})_j^l, \quad (11)$$

where $({}^1D^{1/2})_j^l$ mean the elements of the positive square-root matrix arising from the spin-free matrix 1D [Eq. (9)]. This procedure allows one to handle matrices of lesser size, requiring lower computational expenses than those demanded when using spin orbitals. The treatment of spin symmetries with $S_z \neq 0$ requires the independent evaluation of the ${}^1D_{j\alpha}^{i\alpha}(\Omega)$ and ${}^1D_{j\beta}^{i\beta}(\Omega)$ matrix elements, because ${}^1D_{j\alpha}^{i\alpha}(\Omega) \neq {}^1D_{j\beta}^{i\beta}(\Omega)$,^{24,25} and then to perform the sum of both blocks according to Eq. (10).

The physical nature of the ${}^1D(\Omega)$ matrices provides a wide and important information of the Ω regions. These devices can be extended to unions between domains $\cup_A \Omega_A$, that is, ${}^1D(\cup_A \Omega_A) = ({}^1D^{1/2}) S(\cup_A \Omega_A) ({}^1D^{1/2})$, where $S(\cup_A \Omega_A) = \sum_A S(\Omega_A)$ and, obviously, if $\cup_A \Omega_A$ is the whole space ${}^1D(\cup_A \Omega_A) = {}^1D$ and $N(\cup_A \Omega_A) = N$. These properties allow to relate chemically meaningful molecular fragments, such as atoms, functional groups, etc., with the tools ${}^1D(\Omega)$.

The diagonalization of these quantities leads to determine their eigenvectors $I(\Omega)$, which are interpreted as natural orbitals associated to the regions Ω . It also determines their corresponding eigenvalues or occupation numbers $n_I(\Omega)$, fulfilling $N_\Omega = \sum_I n_I(\Omega)$, as well as their degeneracies. In practice, most of the eigenvalues $n_I(\Omega)$ are zero so that only a few eigenvectors are really populated and need to be studied. The eigenvectors are subjected to isopycnic orbital transformations,²⁶ that is, linear orbital transformations that leave the first-order density matrices ${}^1D(\Omega)$ invariant, in order to get localized orbitals. In this way, it is possible to analyze the resulting orbitals, their populations and their degeneracies in terms of inner shells, lone pairs, inner bondings within the region Ω , broken bondings (bondings of a region Ω with the rest of the system), etc.

The series of hydrides of the second-row elements, some diatomic molecules, and simple hydrocarbons, all of them in the singlet ground states, have been chosen to test the usefulness of the proposed topological partitioning of the first-order reduced density matrix. In this sense, the results arisen from this methodology have been compared with the genuine chemical knowledge of the corresponding systems. The calculations were carried out using GAUSSIAN03 (Ref. 27) program, which generated the first-order reduced density matrix elements and the overlap matrices $S(\Omega)$. In a subsequent step, these matrices were subjected to the proposed formalism using our own codes. The reported results have been obtained with the basis sets 6-31G(*d,p*) except for the acetylene molecule which has been calculated with the 6-31G basis set to avoid the occurrence of the non-nuclear attractor which appears with the former set.²⁸ For all systems, the geometries were optimized for these basis sets within configuration-interaction (CI) wave functions with single and double excitation configuration interaction (SDCI) arising from Hartree-Fock reference states.

Table I describes the values N_Ω found in the monoatomic and diatomic fragments of the series of hydrides of the second-row elements. This table also reports the partitioning $N_\Omega = \sum_I n_I(\Omega)$ in terms of the non-negligible $n_I(\Omega)$ eigenvalues arising from the isopycnic transformation, as well as the degeneracy of the corresponding eigenvectors. These quantities allow us to perform a suitable assignment of the eigenvectors in good agreement with the genuine chemical knowledge, as is shown in column six. As can be observed, the n_I values point out the polarity of the corresponding bonding. Hence, for the A–H fragments ($A = \text{Be, B, C, N, O, F}$), $n_I(\text{H}) > n_I(\text{A})$ in the systems BeH_2 ($1.804 > 0.141$) and BH_3 ($1.576 > 0.313$), showing the negative character of the H domains but $n_I(\text{H}) < n_I(\text{A})$, as expected, in the compounds NH_3 ($0.622 < 1.339$), H_2O ($0.402 < 1.573$), and HF ($0.275 < 1.705$). Column seven of this table gathers the ionicity (as a percentage) of the bondings A–H, that is reported as an example of additional chemical information that can be obtained with this methodology. Because the framework of our theory provides electronic populations associated to bondings between atomic domains, we propose that the ionicity of a bond may be evaluated in terms of the values $n_I(\text{A})$ and $n_I(\text{H})$ corresponding to the eigenvectors $I(\text{A})$ and $I(\text{H})$ which describe the bonding A–H, as

$$\left| \frac{n_I(\text{A}) - n_I(\text{H})}{n_I(\text{A}) + n_I(\text{H})} \right|. \quad (12)$$

For the sake of comparison with this proposal, we have collected in the last column of Table I the values of the ionicity of the bondings A–H arising from the more conventional method reported by Cioslowski and Mixon.²⁹ As is well known this last procedure, used in the GAUSSIAN03 code, evaluates the ionicity of a bond by a formula similar to Eq. (12) in which the electronic populations n_I are replaced by the overlap integrals $S_i^i(\Omega)$ defined by Eq. (3). The results show that both procedures lead to quite close values, confirming the suitability of our proposal.

Table II reports the identical quantities to those mentioned in Table I, describing fragments of chemical interest in diatomic (homonuclear and heteronuclear) molecules and in the simplest hydrocarbons possessing single, double, and triple bond orders. As can be observed, the degeneracies and assignments found are in excellent agreement with the expected features for these systems. The polarity of the bond in homonuclear molecules (N_2 and F_2) is zero while the CO molecule presents reasonable values for both σ_{CO} and π_{CO} bonds. In relation with the bonds C–H in the studied hydrocarbons, our method predicts very low polarity values for the C_2H_6 and C_2H_4 molecules and a higher value for the C_2H_2 one in which the H fragment has a positive charge in good agreement with the well-known experimental properties of this system.

We report in Table III the results corresponding to the domain-averaged correlated hole model, recently defined by us in Ref. 18, in order to compare it with the partitioning reported in this paper. That model performs a topological partitioning of the first-order reduced density matrix in terms of domain-averaged holes, $\Theta(\Omega)$, which are defined as

$$\Theta_j^i(\Omega) = \sum_{k,l} \left(\frac{1}{2} {}^1D_l^{i1} D_j^k - \Lambda_{jl}^{ik} \right) S_l^k(\Omega), \quad (13)$$

where Λ_{jl}^{ik} stands for the matrix elements of the second-order reduced density matrix cumulant.^{30–32} These correlated holes are obtained by domain-restricted contractions of the second-order reduced density matrix and explicitly deal with the cumulant contributions to that matrix. However, as reported above, the treatment of regional matrices ${}^1D(\Omega)$ is based on a symmetrical expansion of the first-order reduced density matrix that preserves the essential properties of that matrix. Hence, it only uses first-order tools which require much lower computational effort and the interpretation of results is simpler. The results in Table III have been obtained using the GAMESS package³³ which provides the second-order reduced density matrix necessary for the correlated hole model. The molecules described in that table have been chosen among the systems reported in Tables I and II, selecting those that stress similarities and differences between both models. The comparison of the eigenvalues (the occupation numbers of the orbitals) reported in Table III with those of Tables I and II shows a spread of electron population in the case of correlated hole model that is due to the explicit use of cumulants (and thus of the effectively unpaired electron density³⁴). The orbitals which are not related with bondings (i.e., inner shells

TABLE I. Calculated eigenvalues $n_i(\Omega)$ (electronic populations) and assigned eigenvectors of first-order reduced density matrices associated to Bader's regions, and ionicities of bonds (as a percentage) for second-row hydrides in the SDCI treatment using the 6-31G(*d,p*) basis set.

System	Fragment (Ω)	N_Ω	$n_i(\Omega)$	Degeneracy	Assignment	Ionicity	Ionicity Ref. 29
BeH ₂	Be	2.277	1.991	1	1s _{Be}		
			0.141	2	σ_{BeH}	85.5	85.8
	H	1.862	1.804	1	σ_{BeH}	85.5	85.8
	BeH	4.138	1.995	1	1s _{Be}		
			1.941	1	σ_{BeH} (inner H)		
			0.167	1	σ_{BeH} (outer H)		
BH ₃	B	2.946	1.997	1	1s _B		
			0.313	3	σ_{BH}	66.9	67.4
	H	1.685	1.576	1	σ_{BH}	66.9	67.4
	BH	4.631	1.998	1	1s _B		
			1.884	1	σ_{BH} (inner H)		
			0.357	2	σ_{BH} (outer H)		
CH ₄	C	5.845	2.000	1	1s _C		
			0.953	4	σ_{CH}	1.1	1.1
	H	1.039	0.975	1	σ_{CH}	1.1	1.1
	CH	6.884	2.000	1	1s _C		
			1.918	1	σ_{CH} (inner H)		
			0.971	3	σ_{CH} (outer H)		
NH ₃	N	8.010	2.000	1	1s _N		
			1.929	1	lone pair		
			1.339	3	σ_{NH}	36.6	37.7
	H	0.663	0.622	1	σ_{NH}	36.6	37.7
	NH	8.674	2.000	1	1s _N		
			1.949	1	lone pair		
			1.944	1	σ_{NH} (inner H)		
			1.350	2	σ_{NH} (outer H)		
H ₂ O	O	9.148	2.000	1	1s _O		
			1.974	1	σ -lone pair		
			1.953	1	π -lone pair		
			1.573	2	σ_{OH}	59.3	60.4
	H	0.426	0.402	1	σ_{OH}	59.3	60.4
	OH	9.574	2.000	1	1s _O		
			1.964	2	σ -lone pair; σ_{OH} (inner H)		
			1.979	1	π -lone pair		
1.579			1	σ_{OH} (outer H)			
HF	F	9.711	2.000	1	1s _F		
			1.988	1	σ -lone pair		
			1.975	2	π -lone pair		
			1.705	1	σ_{FH}	74.1	73.0
	H	0.289	0.275	1	σ_{FH}	74.1	73.0

and lone pairs) transfer electron population to those counterpart ones centered at a nucleus corresponding to another domain Ω . However, this behavior is not observed in orbitals associated to bondings, except in some systems containing hydrogen atoms, where the lack of inner shells and lone pairs may lead to a charge transference between bonding orbitals. In fact, in the correlated hole model the unpaired electrons associated to a Ω domain tend to be delocalized out of the domain considered, but this effect does not appear in the model reported in this paper. These results need to be explained in terms of the cumulant contribution that governs the electronic charge transference because the bondings are described by the paired part of the density.^{35,36} Another rea-

son supporting this interpretation is that the correlated hole model differs from the present model in the way of dealing with the unpaired electron contribution. It is also interesting to relate this behavior with the ionicity index of a bond introduced here. It may be noted that this index turns out to be almost identical in both models since the orbitals describing bondings do not transfer population.

IV. CONCLUDING REMARKS

In conclusion, in this work we have proposed a partitioning of the first-order reduced density matrix of an N -electron system according to the three-dimensional domains defined

TABLE II. Calculated eigenvalues $n_l(\Omega)$ (electronic populations) and assigned eigenvectors of first-order reduced density matrices associated to Bader's regions, and ionicities of bonds (as a percentage) for diatomic molecules and hydrocarbons in the SDCI treatment using the 6-31G(d,p) basis set.

System	Fragment (Ω)	N_Ω	$n_l(\Omega)$	Degeneracy	Assignment	Ionicity	Ionicity Ref. 29			
N ₂	N	7.000	2.000	1	1s _N					
			1.966	1	σ -lone pair					
			0.996	1	$\sigma_{NN'}$					
			0.994	2	$\pi_{NN'}$					
CO	C	4.738	1.996	1	1s _C					
			1.856	1	σ -lone pair					
			0.231	1	σ_{CO}	76.7	77.4			
			0.318	2	π_{CO}	67.9	70.5			
	O	9.262	2.000	1	1s _O					
			1.983	1	σ -lone pair					
			1.754	1	σ_{CO}	76.7	77.4			
			1.665	2	π_{CO}	67.9	70.5			
F ₂	F	9.000	2.000	1	1s _F					
			1.977	1	σ -lone pair					
			1.956	2	π -lone pair					
			0.996	1	$\sigma_{FF'}$					
C ₂ H ₆ (<i>D</i> _{3h}) (H ₃ C-C'H ₃)	C	5.838	2.000	1	1s _C					
			0.949	1	$\sigma_{CC'}$					
			0.937	3	σ_{CH}	2.7	2.6			
			1.054	0.988	1	σ_{CH}	2.7	2.6		
			CC'	11.675	2.000	2	1s _C , 1s _{C'}			
					1.882	1	$\sigma_{CC'}$			
	CH ₃	9.000	2.000	1	1s _C					
			1.950	3	σ_{CH}					
			0.993	1	$\sigma_{CC'}$					
			C ₂ H ₄ (H ₂ C-C'H ₂)	C	5.953	2.000	1	1s _C		
						0.990	2	σ_{CH}	1.3	1.6
						0.974	1	$\sigma_{CC'}$		
0.935	1	$\pi_{CC'}$								
H	11.905	0.965	1	σ_{CH}	1.3	1.6				
		2.000	2	1s _C ; 1s _{C'}						
		1.938	1	$\sigma_{CC'}$						
		1.835	1	$\pi_{CC'}$						
		1.005	4	$\sigma_{CH}; \sigma_{C'H'}$						
		0.990	1	$\pi_{CC'}$						
C ₂ H ₂ ^a (HC-C'H')	C	6.137	2.000	1	1s _C					
			1.226	1	σ_{CH}	19.6	19.2			
			0.976	2	$\pi_{CC'}$					
			0.934	1	$\sigma_{CC'}$					
			0.863	0.825	1	σ_{CH}	19.6	19.2		
			H	12.274	2.000	2	1s _C ; 1s _{C'}			
	1.960	1			$\sigma_{CC'}$					
	1.910	2			$\pi_{CC'}$					
	1.117	2			$\sigma_{CH}; \sigma_{C'H'}$					
	CH	7.000			2.000	1	1s _C			
					1.976	1	σ_{CH}			
			0.997	1	$\sigma_{CC'}$					
0.993			2	$\pi_{CC'}$						

^aCalculated in the 6-31G basis set.

TABLE III. Calculated eigenvalues $n_I(\Omega)$ (electronic populations) and assigned eigenvectors of domain-averaged correlated holes, and ionicities of bonds (as a percentage) for selected systems in the SDCl treatment using the 6-31G(*d,p*) basis set.

System	Fragment (Ω)	N_Ω	$n_I(\Omega)$	Degeneracy	Assignment	Ionicity
BeH ₂	Be	2.275	1.988	1	1s _{Be}	
			0.143	2	σ_{BeH}	80.8
	H	1.862	1.349	1	σ_{BeH}	80.8
			0.475	1	$\sigma_{\text{BeH}'}$	
	BeH	4.138	1.993	1	1s _{Be}	
			1.491	1	σ_{BeH} (inner H)	
			0.618	1	σ_{BeH} (outer H)	
N ₂	N	7.000	1.500	1	1s _N	
			1.466	1	σ -lone pair	
			0.989	1	$\sigma_{\text{NN}'}$	
			0.974	2	$\pi_{\text{NN}'}$	
			0.509	1	$\sigma_{\text{N}'}$ -lone pair	
			0.500	1	1s _{N'}	
			CO	C	4.735	1.995
1.697	1	σ -lone pair				
0.295	1	σ_{CO}				70.3
0.305	1	π_{CO}				68.8
0.315	1	π_{CO}				67.8
0.117	1	σ_{O} -lone pair				
O	9.265	2.000		1	1s _O	
		1.858		1	σ -lone pair	
		1.691		1	σ_{CO}	70.3
		1.652		1	π_{CO}	68.8
		1.642		1	π_{CO}	67.8
F ₂	F	9.000	1.500	1	1s _F	
			1.475	1	σ -lone pair	
			1.472	2	π -lone pair	
			0.974	1	$\sigma_{\text{FF}'}$	
			0.513	1	$\sigma_{\text{F}'}$ -lone pair	
			0.508	2	$\pi_{\text{F}'}$ -lone pair	
			0.500	1	1s _{F'}	

in the theory of atoms in molecules. We have carried out a study of the fulfillment of the representability conditions for the resulting regional matrices. This fulfillment guarantees the physical grounds and the usefulness of the information contained in these tools. Similarly, we have described first-order reduced density matrices associated to unions of Bader domains, whose treatment provides an important chemical information related with groups of atoms. The obtained results have allowed us to describe molecular fragments and their bondings. We have proposed a treatment to evaluate the polarity of the bonds from the information contained in the regional matrices. The excellent agreement between our results and those arising from the genuine chemical knowledge indicates that this methodology is a reliable technique within the chemical bonding theory. We are currently studying in our laboratories the deviation of the idempotency of the regional density matrices and the application of this methodology to describe the valences of the fragments which constitute the molecules. Likewise, we are working on the application of this partitioning scheme to higher-order density matrices and to other partitionings of the real space.

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¹R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).

²R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, UK, 1990), and references therein.

³A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* (Washington, D.C.) **88**, 899 (1988), and references therein.

⁴A. E. Clark and E. R. Davidson, *J. Chem. Phys.* **115**, 7382 (2001).

⁵E. R. Davidson and A. E. Clark, *Mol. Phys.* **100**, 373 (2002).

- ⁶P. Salvador, M. Duran, and I. Mayer, *J. Chem. Phys.* **115**, 1153 (2001).
- ⁷D. R. Alcoba, A. Torre, L. Lain, and R. C. Bochicchio, *J. Chem. Phys.* **122**, 074102 (2005).
- ⁸V. H. Smith, in *Electron Distribution and the Chemical Bond*, edited by P. Coppens and M. B. Hall (Plenum, New York, 1982), and references therein.
- ⁹J. Fernandez Rico, R. Lopez, and G. Ramirez, *J. Chem. Phys.* **110**, 4213 (1999).
- ¹⁰J. Fernandez Rico, R. Lopez, G. Ramirez, I. Ema, and E. V. Ludeña, *J. Comput. Chem.* **25**, 1355 (2004).
- ¹¹P. D. Walker and P. G. Mezey, *J. Am. Chem. Soc.* **115**, 12423 (1993).
- ¹²P. D. Walker and P. G. Mezey, *J. Am. Chem. Soc.* **116**, 12022 (1994).
- ¹³T. E. Exner and P. G. Mezey, *J. Phys. Chem. A* **106**, 11791 (2002).
- ¹⁴R. L. Fulton, *J. Phys. Chem.* **97**, 7516 (1993).
- ¹⁵R. L. Fulton and S. T. Mixon, *J. Phys. Chem.* **99**, 9768 (1995).
- ¹⁶R. L. Fulton, *J. Phys. Chem. A* **108**, 11691 (2004).
- ¹⁷A. J. Coleman, *Rev. Mod. Phys.* **35**, 668 (1963).
- ¹⁸R. C. Bochicchio, A. Torre, and L. Lain, *J. Chem. Phys.* **122**, 084117 (2005).
- ¹⁹J. E. Harriman, *Phys. Rev. A* **17**, 1249 (1978).
- ²⁰D. A. Mazziotti, *Phys. Rev. Lett.* **93**, 213001 (2004).
- ²¹G. Strang, *Linear Algebra and Its Applications*, 4th ed. (Brooks/Cole, Belmont, CA 2005).
- ²²E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic, New York, 1976).
- ²³R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ²⁴R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960).
- ²⁵D. R. Alcoba and C. Valdemoro, *Int. J. Quantum Chem.* **102**, 629 (2005).
- ²⁶J. Cioslowski, *Int. J. Quantum Chem.* **S24**, 15 (1990).
- ²⁷M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN03, Revision C.02 (Gaussian Inc., Wallingford, CT, 2004).
- ²⁸D. R. Alcoba, L. Lain, A. Torre, and R. C. Bochicchio, *Chem. Phys. Lett.* **407**, 379 (2005).
- ²⁹J. Cioslowski and S. T. Mixon, *Inorg. Chem.* **32**, 3209 (1993).
- ³⁰D. A. Mazziotti, *Chem. Phys. Lett.* **289**, 419 (1998).
- ³¹W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.* **116**, 4787 (2002).
- ³²L. Lain, A. Torre, and R. Bochicchio, *J. Chem. Phys.* **117**, 5497 (2002).
- ³³M. W. Schmidt, K. K. Baldrige, J. A. Boatz *et al.*, *J. Comput. Chem.* **14**, 1347 (1993).
- ³⁴A. Torre, L. Lain and R. Bochicchio, *J. Phys. Chem. A* **107**, 127 (2003).
- ³⁵R. C. Bochicchio, L. Lain, and A. Torre, *Chem. Phys. Lett.* **374**, 567 (2003).
- ³⁶R. M. Lobayan, R. C. Bochicchio, L. Lain, and A. Torre, *J. Chem. Phys.* (to be published).