Theor Chem Account (2007) 118:827–835
DOI 10.1007/s00214-007-0332-4

REGULAR ARTICLE

Description of functional groups by means of domain-restricted reduced density matrices

**Diego R. Alcoba · Alicia Torre ·
Roberto C. Bochicchio · Luis Lain**

Received: 16 February 2007 / Accepted: 25 April 2007 / Published online: 6 June 2007

Abstract This report constitutes an application of our previous theoretical works on partitionings of the first-order reduced density matrix according to the atomic domains defined in the theory of atoms in molecules. The numerical determinations obtained reveal that the domain-restricted reduced density matrices, which are the tools resulting from the former treatments, are suitable devices to describe chemical features of molecular fragments. We have focused attention on a study of functional groups in several series of organic compounds confirming the usefulness of these tools.

Keywords Reduced density matrices · Electron population · Atoms in molecules

1 Introduction

In previous works [1–3] we have described partitionings of the first-order reduced density matrix corresponding to an N-electron system into first-order matrices which have been associated with Bader atomic domains [4]. Our treatments [2,3] have allowed us to study the mathematical features of these matrices, denominated hereafter *domain-restricted first-order reduced density matrices* [3] as well as to propose suitable procedures to extract the chemical information of interest contained in these devices. Contrary to the first-order matrices arising from the previous decomposition model [1], the domain-restricted first-order reduced density matrices fulfill all the necessary and sufficient conditions to be representative of a physical subsystem [5], such as a determined region within a molecule. Consequently, they turn out to be appropriate tools to perform local analyses of the electron population. Determinations of atomic charges, covalent bond indices, polarity of bondings, spatial localizations, etc. have been carried out in a natural way within this framework [3]. In addition to the domain-restricted first-order reduced density matrices associated with a certain Bader region which describes a single atom, it is also possible to construct this kind of matrices over more complex regions as those formed by a union of individual atomic regions which can be related with chemically meaningful molecular fragments.

On the other hand, the concept of transferability in chemistry attemps to be a suitable entity to describe the intrinsic properties of some atomic associations called *functional groups*. These atomic groups possess similar properties in different environments or molecular frameworks and thus we may talk about the transferability of functional groups [6–11]. However, the transferability is not itself a physical observable and thus it may not be described by an operator as quantum theory requires. The indirect determination of the transferability has been based on the invariance of the electron density in the domains defined by an atomic cluster or group within different environments [12]. In this paper, we attempt to give a detailed description of such invariance going beyond the electron density itself using the domain-restricted first-order reduced density matrices from which local descriptions of the density are obtained. As these matrices are diagonalizable, they may be completely described by means of their eigenvalues and eigenvectors and their invariance induces the invariance of these local descriptions which thus become nearly invariant for a determined functional group

---

D. R. Alcoba · R. C. Bochicchio
Departamento de Física, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, Ciudad Universitaria,
1428 Buenos Aires, Argentina

A. Torre · L. Lain (✉)
Departamento de Química Física, Facultad de Ciencias,
Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain
e-mail: qfplapel@lg.ehu.es

in different environments. Hence, this methodology ensures not only the invariance of the local descriptions of the electron density themselves but also of the contributions to them, i.e., the eigenvalues and eigenvectors of the domain-restricted first-order reduced density matrices. Consequently, the domain-restricted first-order reduced density matrices are appropriate entities to identify functional groups and to assess from a rigorous physical point of view the intuitive concept of transferability. The aim of this paper is therefore to study the abilities of the domain-restricted first-order reduced density matrices associated with unions of Bader regions to describe functional groups and the changes that they undergo by the influence of other groups.

The paper is organized as follows. The Sect. 2 summarizes the theoretical aspects of the partitioning of the N-electron first-order reduced density matrix in terms of domain-restricted reduced density matrices. The relationships between these tools and the sets of atoms which constitute the functional groups are also described in this section. In Sect. 3, we report the computational details, the results obtained in selected systems and the corresponding discussion. Finally, we have dedicated the last section to point out the remarks and conclusions of this work.

2 Theoretical background

We will express the N-electron first-order reduced density matrix, $\Gamma(x, x')$, in terms of its orthonormal natural spin-orbitals, $\psi_i(x)$, and their corresponding occupation numbers, n_i, [13]

$$\Gamma(x, x') = \sum_i n_i\ \psi_i^*(x)\psi_i(x'), \tag{1}$$

where x, x' stand for the space and spin coordinates.

We will perform a linear transformation

$$\phi_i(x) = \sum_j C_{ij}\psi_j(x), \tag{2}$$

so that the first-order reduced density matrix remains unchanged (an isopycnic transformation [14]) that is

$$\Gamma(x, x') = \sum_i \nu_i\ \phi_i^*(x)\phi_i(x'), \tag{3}$$

where ν_i are the occupation numbers of the functions ϕ_i fulfilling

$$\nu_i = \sum_j n_j\ U_{ij}^*\ U_{ij} \tag{4}$$

$$C_{ij} = U_{ij}\ (n_j/\nu_i)^{1/2} \tag{5}$$

with $0 \leq \nu_i \leq 1$ and where U_{ij} are the matrix elements of a unitary matrix.

Cioslowski has proposed to accomplish this isopycnic transformation finding a set of coefficients $\underline{C}$ which maximize the localization index [14,15]

$$L = \sum_i \sum_{klmn} \nu_i^2\ C_{ik}^* C_{il} C_{im}^* C_{in} \sum_\Omega \langle\psi_k|\psi_l\rangle_\Omega \langle\psi_m|\psi_n\rangle_\Omega \tag{6}$$

in which $\langle\psi_k|\psi_l\rangle_\Omega$ and $\langle\psi_m|\psi_n\rangle_\Omega$ are overlap integrals over the Bader atomic domains Ω. Although the resulting spin-orbitals, ϕ_i, obtained with this procedure are in general not orthonormal [16], they do indeed have many attributes usually associated with chemical concepts (appropriate localization in space, high transferability, etc.) [17,18] so that they can be regarded as the theoretical counterparts of the classical chemical pictures such as bonds, non-bonding electron pairs, core orbitals, valences and so forth, as has been shown in Ref. [19].

In Ref. [3], we have described the partitioning of the first-order reduced density matrix expressed by formula (3) into domain-restricted first-order reduced density matrices $\Gamma_\Omega(x, x')$ as

$$\Gamma(x, x') = \sum_\Omega \Gamma_\Omega(x, x') = \sum_\Omega \sum_i \nu_i(\Omega)\ \phi_i^*(x)\phi_i(x') \tag{7}$$

where $\nu_i(\Omega) = \nu_i\ \langle\phi_i|\phi_i\rangle_\Omega$ stands for occupation numbers for each Γ_Ω and the integrals $\langle\phi_i|\phi_i\rangle_\Omega$ are again defined over the Bader domains Ω, satisfying the relationships $0 \leq\ \langle\phi_i|\phi_i\rangle_\Omega\ \leq 1$ and $\sum_\Omega\ \langle\phi_i|\phi_i\rangle_\Omega = 1$.

We have shown [3,5] that the domain-restricted first-order reduced density matrices $\Gamma_\Omega(x, x')$ constitute first-order reduced density matrices associated with the domains Ω. All these matrices diagonalize in identical basis set $\{\phi_i\}$ and possess similar features to those of the ordinary reduced density matrix [20–23]: each matrix is Hermitian and its trace, given by $N_\Omega = \sum_i\ \nu_i(\Omega)$, is the Bader charge: the number of electrons within the domain Ω. Moreover, the occupation numbers $\nu_i(\Omega)$ of the nonorthogonal localized spin-orbitals ϕ_i fulfill $0 \leq \nu_i(\Omega) \leq 1$. All these properties allow us to identify the diagonal elements of each one of the $\Gamma_\Omega(x, x')$ matrices as electron densities associated with the domains Ω

$$\rho_\Omega(x) = \Gamma_\Omega(x, x) = \sum_i \nu_i(\Omega)\ \phi_i^*(x)\phi_i(x) \tag{8}$$

which, although being maximally localized within the associated domains and falling off quickly due to the localized character of the expansion functions, have infinite extents and non-vanishing overlaps. Moreover, these densities are non-negative, integrate to the total number of electrons within the domain Ω, and satisfy

$$\rho(x) = \sum_{\Omega} \rho_{\Omega}(x) \tag{9}$$

where $\rho(x)$ is the electron density of the system.

The domain-restricted first-order reduced density can be extented to unions between Bader regions $\cup_A \Omega_A$, that is,

$$\Gamma_{(\cup_A \Omega_A)}(x, x') = \sum_i \nu_i(\cup_A \Omega_A)\ \phi_i^*(x)\phi_i(x') \tag{10}$$

Table 1 Calculated eigenvalues $\nu_i(\Omega)$ (electronic populations), degeneracies and assigned eigenvectors of localized first-order reduced density matrices associated with methyl group region for several molecular systems in the CISD treatment using the 6-31G(d,p) basis set

System	Fragment (Ω)	N_Ω	$\nu_i(\Omega)$	Degeneracy	Assignment
CH_4	CH_3	8.961	2.000	1	$1s_C$
(methane)			1.952	3	σ_{CH} (inner H)
			1.004	1	σ_{CH} (outer H)
CH_3F	CH_3	8.317	2.000	1	$1s_C$
(fluoromethane)			1.933	3	σ_{CH}
			0.353	1	σ_{CF}
CH_3OH	CH_3	8.424	2.000	1	$1s_C$
(methanol)			1.935	2	σ_{CH}
			1.930	1	σ_{CH}
			0.446	1	σ_{CO}
CH_3NH_2	CH_3	8.639	2.000	1	$1s_C$
(methylamine)			1.936	2	σ_{CH}
			1.942	1	σ_{CH}
			0.638	1	σ_{CN}
CH_3CH_3	CH_3	8.999	2.000	1	$1s_C$
(ethane)			1.946	3	σ_{CH}
			0.985	1	σ_{CC}
CH_3CH_2F	CH_3	8.947	2.000	1	$1s_C$
(fluoroethane)			1.944	2	σ_{CH}
			1.942	1	σ_{CH}
			0.959	1	σ_{CC}
CH_3CH_2OH	CH_3	8.956	2.000	1	$1s_C$
(ethanol)			1.944	2	σ_{CH}
			1.943	1	σ_{CH}
			0.962	1	σ_{CC}
$CH_3CH_2NH_2$	CH_3	9.034	2.000	1	$1s_C$
(ethylamine)			1.946	2	σ_{CH}
			1.947	1	σ_{CH}
			1.014	1	σ_{CC}
CH_3CHO	CH_3	8.927	2.000	1	$1s_C$
(acetaldehyde)			1.935	2	σ_{CH}
			1.944	1	σ_{CH}
			0.952	1	σ_{CC}
$CH_3CH_2CH_3$	CH_3	9.014	2.000	1	$1s_C$
(propane)			1.946	2	σ_{CH}
			1.948	1	σ_{CH}
			0.998	1	σ_{CC}
CH_3CH_2CHO	CH_3	8.941	2.000	1	$1s_C$
(propanal)			1.945	2	σ_{CH}
			1.947	1	σ_{CH}
			0.942	1	σ_{CC}

where

$$\nu_i(\cup_A \Omega_A) = \sum_{\Omega_A}{}^{\prime} \nu_i \; \langle \phi_i | \phi_i \rangle_{\Omega_A} \tag{11}$$

and the sum $\sum'_{\Omega_A}$ is restricted to the Ω_A regions that are included in the union set $\cup_A \Omega_A$. Obviously, if $\cup_A \Omega_A$ is the whole space $\Gamma_{(\cup_A \Omega_A)}(x, x') = \Gamma(x, x')$ and $N_{(\cup_A \Omega_A)} = N$. Similar considerations deserve the associated electron densities. These properties allow one to relate chemically meaningful molecular fragments, like atoms, functional groups, etc. with the tools $\Gamma_\Omega(x, x')$ and $\Gamma_{(\cup_A \Omega_A)}(x, x')$. As has been mentioned in Sect. 1, the aim of this paper is to study the abilities of the domain-restricted first-order reduced density matrices associated with unions of Bader regions, $\Gamma_{(\cup_A \Omega_A)}(x, x')$, to describe functional groups. In the following section, we report results arising from this treatment.

3 Results and dicussion

We have chosen several series of selected systems in the ground state in which the presence and significance of determined groups of atoms is well known. For practical reasons the calculations reported in the present work have been carried out in the spin-free formulation [2,3]. These calculations were performed at the level of configuration-interaction (CI) wave functions with single and double excitations (CISD), using a modified version of the GAUSSIAN03 package [24] which generated the spin-free first-order reduced density matrices while the Bader integrals, $\langle \psi_i | \psi_j \rangle_\Omega$, were obtained from both GAUSSIAN03 and PROAIM [25] programs. The localized orbitals ϕ_i, the integrals $\langle \phi_i | \phi_i \rangle_\Omega$ and the occupation numbers $\nu_i(\Omega)$, were calculated using our own codes, which are available upon request. The reported results have been obtained with the basis sets 6-31G(d,p). For all systems, the geometries were optimized for the corresponding basis sets at CISD level of approximation.

Tables 1, 2, 3, 4 and 5 collect the values calculated for the non-negligible ($> 10^{-2}$) electronic populations $\nu_i(\Omega)$ and the Bader charge N_Ω (where all populations have been taken into account) for the groups –CH_3, –CH_2–, –OH, –NH_2 and –CO–, respectively. These tables also report the degeneracy of the values $\nu_i(\Omega)$ and the assignments of the corresponding eigenvectors which turn out to be in complete accordance with the genuine chemical knowledge of these groups. Additionally to the information contained in the tables, we also present the density plots for these groups within different

Table 2 Calculated eigenvalues $\nu_i(\Omega)$ (electronic populations), degeneracies and assigned eigenvectors of localized first-order reduced density matrices associated with methylene group region for several molecular systems in the CISD treatment using the 6-31G(d,p) basis set

System	Fragment (Ω)	N_Ω	$\nu_i(\Omega)$	Degeneracy	Assignment
CH_4	CH_2	7.922	2.000	1	$1s_C$
(methane)			1.933	2	σ_{CH} (inner H)
			0.985	2	σ_{CH} (outer H)
CH_3CH_2F	CH_2	7.359	2.000	1	$1s_C$
(fluoroethane)			1.910	2	σ_{CH}
			0.980	1	σ_{CC}
			0.336	1	σ_{CF}
CH_3CH_2OH	CH_2	7.448	2.000	1	$1s_C$
(ethanol)			1.911	2	σ_{CH}
			0.973	1	σ_{CC}
			0.424	1	σ_{CO}
$CH_3CH_2NH_2$	CH_2	7.581	2.000	1	$1s_C$
(ethylamine)			1.909	2	σ_{CH}
			0.933	1	σ_{CC}
			0.601	1	σ_{CN}
$CH_3CH_2CH_3$	CH_2	7.966	2.000	1	$1s_C$
(propane)			1.920	2	σ_{CH}
			0.953	2	σ_{CC}
$CH_3CH_2C'HO$	CH_2	7.963	2.000	1	$1s_C$
(propanal)			1.909	2	σ_{CH}
			0.920	1	$\sigma_{CC'}$
			1.009	1	σ_{CC}

Table 3 Calculated eigenvalues $\nu_i(\Omega)$ (electronic populations), degeneracies and assigned eigenvectors of localized first-order reduced density matrices associated with hydroxyl group region for several molecular systems in the CISD treatment using the 6-31G(d,p) basis set

System	Fragment (Ω)	N_Ω	$\nu_i(\Omega)$	Degeneracy	Assignment
H_2O	OH	9.574	2.000	1	$1s_O$
(water)			1.963	2	σ-lone pair; σ_{OH} (inner H)
			1.979	1	π-lone pair
			1.581	1	σ_{OH} (outer H)
CH_3OH	OH	9.576	2.000	1	$1s_O$
(methanol)			1.972	1	σ-lone pair
			1.949	1	σ_{OH}
			1.928	1	π-lone pair
			1.521	1	σ_{CO}
CH_3CH_2OH	OH	9.592	2.000	1	$1s_O$
(ethanol)			1.970	1	σ-lone pair
			1.949	1	σ_{OH}
			1.928	1	π-lone pair
			1.535	1	σ_{CO}
C_6H_5OH	OH	9.621	2.000	1	$1s_O$
(phenol)			1.974	1	σ-lone pair
			1.952	1	σ_{OH}
			1.894	1	π-lone pair
			1.587	1	σ_{CO}

Table 4 Calculated eigenvalues $\nu_i(\Omega)$ (electronic populations), degeneracies and assigned eigenvectors of localized first-order reduced density matrices associated with amine group region for several molecular systems in the CISD treatment using the 6-31G(d,p) basis set

System	Fragment (Ω)	N_Ω	$\nu_i(\Omega)$	Degeneracy	Assignment
NH_3	NH_2	9.337	2.000	1	$1s_N$
(ammonia)			1.960	1	lone pair
			1.958	2	σ_{NH} (inner H)
			1.364	1	σ_{NH} (outer H)
NH_2NH_2	NH_2	9.000	2.000	1	$1s_N$
(hydrazine)			1.932	1	lone pair
			1.947	2	σ_{NH}
			0.983	1	σ_{NN}
CH_3NH_2	NH_2	9.360	2.000	1	$1s_N$
(methylamine)			1.937	1	lone pair
			1.948	2	σ_{NH}
			1.329	1	σ_{NC}
$CH_3CH_2NH_2$	NH_2	9.380	2.000	1	$1s_N$
(ethylamine)			1.935	1	lone pair
			1.947	2	σ_{NH}
			1.349	1	σ_{NC}
$C_6H_5NH_2$	NH_2	9.492	2.000	1	$1s_N$
(aniline)			1.846	1	lone pair
			1.958	2	σ_{NH}
			1.511	1	σ_{NC}

compounds, in order to graphically show slight deformations of the electron clouds associated with them. Although the tables only show non-negligible eigenvalues, all the eigenvalues, even the negligible ones (whose cardinality is high), have been taken into account for the determination of the maps.

Table 5 Calculated eigenvalues $\nu_i(\Omega)$ (electronic populations), degeneracies and assigned eigenvectors of localized first-order reduced density matrices associated with carbonyl group region for several molecular systems in the CISD treatment using the 6-31G(d,p) basis set

System	Fragment (Ω)	N_Ω	$\nu_i(\Omega)$	Degeneracy	Assignment
CH_2O	CO	13.963	2.000	2	$1s_C$; $1s_O$
(formaldehyde)			1.984	1	σ_O-lone pair
			1.007	2	σ_{CH}
			1.944	1	π_O-lone pair
			1.959	1	σ_{CO}
			1.912	1	π_{CO}
CH_3CHO	CO	14.039	2.000	2	$1s_C$; $1s_O$
(acetaldehyde)			1.985	1	σ_O-lone pair
			0.986	1	σ_{CH}
			1.006	1	σ_{CC}
			1.942	1	π_O-lone pair
			1.960	1	σ_{CO}
			1.916	1	π_{CO}
CH_3CH_2CHO	CO	14.055	2.000	2	$1s_C$; $1s_O$
(propanal)			1.986	1	σ_O-lone pair
			0.983	1	σ_{CH}
			1.021	1	σ_{CC}
			1.936	1	π_O-lone pair
			1.962	1	σ_{CO}
			1.921	1	π_{CO}
CH_3COCH_3	CO	14.108	2.000	2	$1s_C$; $1s_O$
(acetone)			1.986	1	σ_O-lone pair
			0.992	2	σ_{CC}
			1.941	1	π_O-lone pair
			1.961	1	σ_{CO}
			1.915	1	π_{CO}

Table 1 shows the features of methyl group which is described by three σ_{C-H} bonds with similar electronic populations which lie among 1.952, in the CH_4 molecule, and 1.930 or 1.933, in the CH_3OH and CH_3F ones, respectively. All these bonds can be regarded as threefold degenerate ones since the small differences of population between them are negligible. In relation to the bond σ_{CH_3-X} (X = H, F, OH, NH_2 ...) the found populations describe appropriately the polarity of that bond; as can be observed the lowest population values are 0.353, 0.446 and 0.638, in the CH_3F, CH_3OH and CH_3NH_2 molecules, increasing in the remainder systems which are constituted by bonds σ_{C-C} or σ_{C-H} (in the CH_4 case). These predictions agree with the classical knowledge of these molecules. These results are graphically confirmed in the density maps of CH_3 group shown in Fig. 1a–d. Note that, irrespective of the environment in which the methyl group is immersed, its electron cloud is only sligthly distorted as expected for a functional group. It must be noted that, due to the nearly invariance of the electronic populations $\nu_i(\Omega)$ and the corresponding eigenvectors, these quantities can be used as local quantum descriptors of funtional groups [12]. Therefore, our treatment of domain-restricted first-order reduced density matrices allows one to know which atoms constitute a functional group. Table 2 describes the features of the methylene group which is present in some of the compounds reported in the previous table. As can be observed, the double degeneracy predicted for the σ_{C-H} bonds turns out to be perfect in all the systems, and the decreasing of polarity of the bonds σ_{CH_2-X} (X = F, OH, NH_2, CH_3) produces an increasing of the corresponding electronic populations $\nu_i(CH_2)$. A comparison between the populations of the bonds σ_{C-H} in the compounds $CH_3CH_2C'HO$ and $CH_3CH_2CH_3$ shows a lower value of population in the bond $\sigma_{C-C'}$ (0.920) than in the bond σ_{C-H} (1.009 and 0.953) which can be explained in terms of the polarity of the carbonyl group. Figure 2a–c show the density maps of the electron cloud for that group in CH_4, CH_3CH_2F and $CH_3CH_2CH_3$ systems respectively. As in the previous case the invariance of the electron cloud may clearly be observed.

In Table 3, we report the results corresponding to the hydroxyl group present in several systems of different chemical nature. We must highlight the similar numerical values

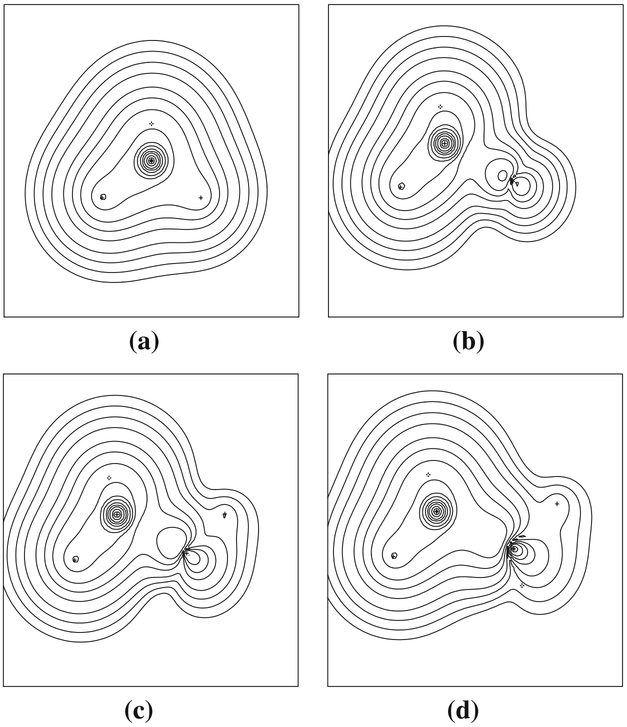


Fig. 1 Contour maps of the electron density for the CH_3 domain in different environments: **a** CH_4, **b** CH_3F, **c** CH_3OH and **d** C_2H_6. The outer contour value is 0.001 a.u. and the remaining contours increase in value in the order 2×10^n, 4×10^n, 8×10^n a.u., with n beginning at -3 and increasing in steps of unity. The same contours are used in all density maps

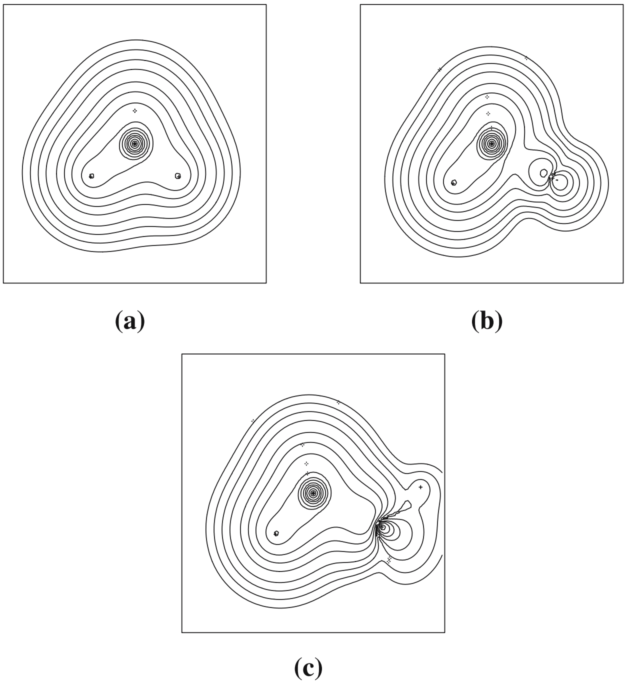


Fig. 2 Contour maps of the electron density for the CH_2 domain in different environments: **a** CH_4, **b** CH_3CH_2F and **c** $CH_3CH_2CH_3$

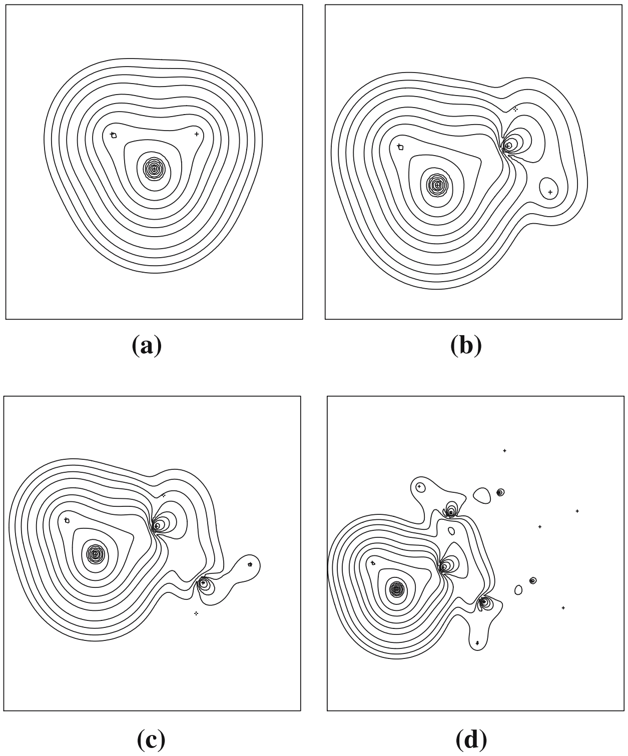
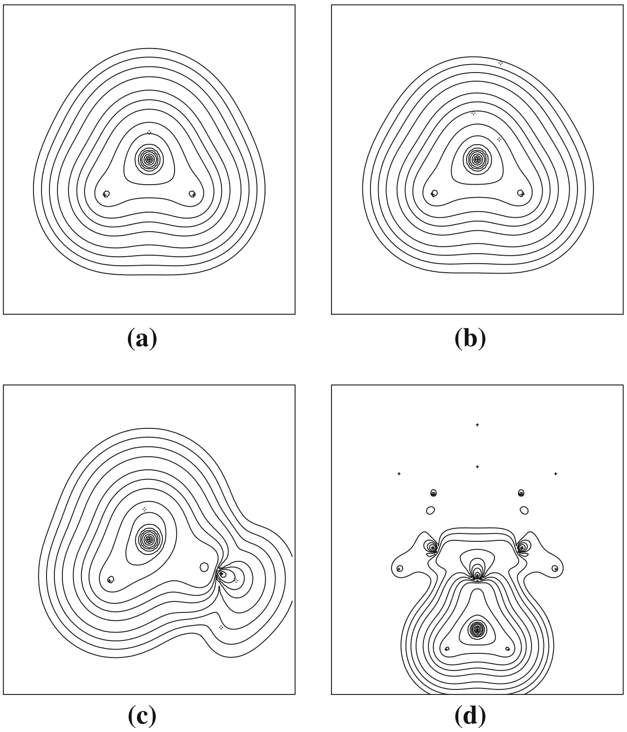


Fig. 3 Contour maps of the electron density for the OH domain in different environments: **a** H_2O, **b** CH_3OH, **c** CH_3CH_2OH and **d** C_6H_5OH

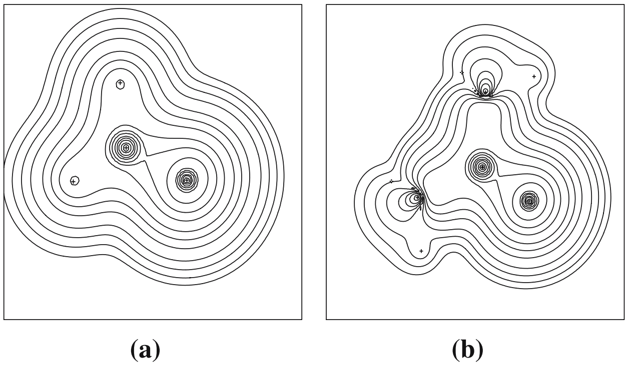
obtained for the two described alcohols which only show a slight difference in the population of the bond σ_{CO} (1.521 in the methanol and 1.535 in the ethanol) which agrees with the similar chemical environment supported by the OH group in these compounds. This population only increases up to 1.587 in the phenol although the chemical behaviour of this molecule is markedly different. The values found for the water molecule, as expected, are more different. Figure 3a–d show the density maps of these domains. As can be seen, the different nature of the compounds studied points out a small distortion of the electron cloud remaining the same shape of group. The results obtained for the $-NH_2$ group are reported in Table 4 which shows quite similar values of $\nu(NH_2)$ for the bonds σ_{N-H} in the hydrazine (1.947), methylamine (1.948) and ethylamine (1.947) while this quantity is slightly higher in the ammonia (1.958) and aniline (1.958). These results confirm that this methodology also describes the NH_2 group as an own entity. In relation with the bond σ_{NH_2--X} ($X = H, NH_2, CH_3, C_6H_5$) the main differences are found in the aniline (1.511) and hydrazine (0.983); in this last case this theory predicts a single nonpolar N–N bond as expected. Similar comments to those reported in previous cases may be done for the density maps of this group which are shown in Fig. 4a–d. The results in Table 5 describe the features of the carbonyl group in a satisfactory way. The values of $\nu(CO)$ quantity are very close for the bonds



(a) **(b)**

(c) **(d)**

Fig. 4 Contour maps of the electron density for the NH_2 domain in different environments: **a** NH_3, **b** NH_2NH_2 in the plane of the domain, **c** NH_2NH_2 in the plane NNH and **d** $C_6H_5NH_2$



(a) **(b)**

Fig. 5 Contour maps of the electron density for the CO domain in different environments: **a** CH_2O and **b** CH_3COCH_3

σ_{CO} and π_{CO} as well as for the σ_O-lone pair and π_O-lone pair in all aldehydes and the ketone studied. The electronic populations for the bonds C–C or C–H (in the case of the aldehydes) show that the carbonyl group, as expected, is bonded with the molecular remainder through single bonds. Figure 5a–b show the strong localizability of the electrons of this group.

In view of the results found we may remark that the regions associated with atoms forming a functional group and with their environments can clearly be detected throughout the domain-restricted density maps. The group electron density remains nearly invariant in the domain in which it is defined, as expected in the classical concept of transferability. As can be observed on the maps, the shape of each group is similar in the different environments and only shows distortions in the spatial zones corresponding to the bonds that link the group with its environment. These results are in excellent agreement to the numerical values of the quantities chosen (electronic populations and degeneracies) to describe the groups with chemical meaning and their transferability (see tables). The numerical determinations of the populations and degeneracies and the assignment of orbitals can be interpreted in terms of the invariance of the character of the inner structure of each group; the only differences are found for the population of the broken bonds between the group and the environment. These considerations indicate the strong physical localization of the electron density in the domain defining the group.

4 Concluding remarks

In conclusion, in this work we have applied the domain-restricted first-order reduced density matrices associated with unions of Bader's regions, to describe molecular fragments with chemical meaning. As these matrices fulfill all the conditions to be representative of physical subsystems, they are appropriate tools to perform this task. The results obtained in several series of compounds show their suitability to describe the main characteristics of functional groups. The numerical determinations provide nearly invariant features for these atomic groups within different compounds, although this methodology also allows one to detect the influence of the chemical environment around a determined functional group. These results and properties indicate that the domain-restricted reduced density matrices are adequate devices to represent functional groups and to formulate their transferability.

Finally, we must highlight that this methodology is independent of the quality of the wave function used to derive the first-order reduced density matrix, i.e., it is valid for both independent and interacting particle systems and for variational (Hartree-Fock, configuration-interaction or multiconfigurational) and diagrammatic (coupled cluster) wave functions. Moreover, any general partitioning of the three-dimensional space into overlaping domains (as those of "fuzzy atoms" type) or non-overlaping domains (as those of Bader or electron localization function type) may be used for its implementation. We are currently working in our laboratories in reverse way, that is, describing molecular properties by addition of individual atoms and functional groups described by this kind of quantities.

Acknowledgements D.R.A and R.C.B. acknowledge grants in aid from the University of Buenos Aires (Project No. X-024), the Consejo

Nacional de Investigaciones Científicas y Técnicas, República Argentina (PIP No 5098/05), and the Department of Physics, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, for facilities provided during the course of this work. A.T. and L.L. acknowledge partial support by the Spanish Ministry of Education (Grant No. CTQ2006-01849/BQU) and the Universidad del Pais Vasco (Grant No. GIU06/03). We thank the Universidad del Pais Vasco for allocation of computational resources.

References

1. Bochicchio RC, Torre A, Lain L (2005) J Chem Phys 122:084117
2. Alcoba DR, Lain L, Torre A, Bochicchio RC (2005) J Chem Phys 123:144113
3. Alcoba DR, Bochicchio RC, Torre A, Lain L (2006) J Phys Chem A 110:9254
4. Bader RFW (1994) Atoms in molecules: a quantum theory. Clarendon Press, Oxford, see also references therein
5. Alcoba DR, Bochicchio RC, Massacessi GE, Lain L, Torre A (2007) Phys Rev A 75:012509
6. Ayers PW (2000) J Chem Phys 113:10886
7. Bader RFW, Bayles D (2000) J Phys Chem A 104:5579
8. Popelier PLA, Aicken FM (2003) J Am Chem Soc 125:1284
9. Popelier PLA, Aicken FM (2003) Chem Eur J 9:1207
10. Popelier PLA, Aicken FM (2003) Chem Phys Chem 4:824
11. Gidofalvi G, Mazziotti DA (2005) J Chem Phys 122:094107
12. Monev V (2004) MATCH Commun Math Comput Chem 51:7
13. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, New York
14. Cioslowski J (1990) Int J Quantum Chem S24:15
15. Cioslowski J (1991) J Math Chem 8:169
16. Surjan PR (1989) Second quantized approach to quantum chemistry. Springer, Berlin
17. Cioslowski J, Mixon S (1991) J Am Chem Soc 113:4142
18. Cioslowski J, Mixon S (1993) Inorg Chem 32:3209
19. Alcoba DR, Lain L, Torre A, Bochicchio RC (2006) J Comput Chem 27:596
20. Coleman AJ (1963) Rev Mod Phys 35:668
21. Erdahl RM (1978) Int J Quantum Chem 13:697
22. Mazziotti DA (2002) Phys Rev E 65:026704
23. Alcoba DR (2007) Purification of correlated reduced density matrices: review and applications.In: Mazziotti DA (ed) Advances in chemical physics vol 134. Wiley, New York
24. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, revision C.02. Gaussian Inc., Wallingford CT
25. Biegler-König FW, Bader RFW, Tang TH (1982) J Comput Chem 3:317