An Orbital Localization Criterion Based on the Topological Analysis of the Electron Localization Function

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This work proposes a new molecular orbital localization procedure. The approach is based on the decomposition of the overlap matrix in accordance with the partitioning of the three-dimensional physical space into basins with clear chemical meaning arising from the topological analysis of the electron localization function. The procedure is computationally inexpensive, provides a straightforward interpretation of the resulting orbitals in terms of their localization indices and basin occupancies, and preserves the σ/π-separability in planar N-electron systems. The localization algorithm is tested on selected molecular systems. © 2012 Wiley Periodicals, Inc.

Introduction

Before the advent of quantum mechanical methods, the description of molecular electronic structures was performed by means of classical chemical concepts, such as bondings, lone pairs of electrons, core orbitals, valences, and so forth. However, most of the quantum mechanical methods do not reproduce these concepts, as is the case of the Hartree–Fock (HF) theory where the resulting molecular orbitals, that reflect the symmetry of the irreducible representations of the molecular point group, generally are extended over the whole molecular framework. In this scenario, the orbital localization procedures attempt to recover the classical Lewis–Linnett picture[1] from canonical molecular orbitals.[2–5] The localization procedures are based on the fact that the wave functions are invariant with respect to any unitary transformation among molecular orbitals. Several methods of orbital localization have been widely used as those of Foster–Boys,[2] Edmiston–Rueden-berg,[3] von Niessen,[4] Pipek–Mezey,[5] and so forth, although most of these methods present well-known drawbacks.[6,7] Some of them, in locally planar molecules, lead to the so-called τ or banana orbitals rather than the σ and π ones as expected.[7] Although there are not definite physical reasons for preferring the σ/π over the τ ones, one arrives to a much clearer picture of the bonding using the former ones. The Pipek–Mezey[5] method, which preserves σ/π representation, turns out to be too much basis dependent and has no well-defined basis set limits. Also, some of these methods do not provide simple indices to quantify the extent of localization/delocalization or the atomic electron population associated to the resulting orbitals, and usually the character of these orbitals has to be examined from their plots.[7]

A different approach of the localization problem which avoids most of the mentioned drawbacks aims to localize molecular orbitals according to criteria based on the partitioning of the three-dimensional (3D) physical space into atomic basins. Two partitioning schemes have been used so far to define these basins; the atoms-in-molecules (AIM) procedure[6] and the Fuzzy atom (FA)[8] treatment. Within the AIM procedure, the whole 3D space is divided into disjoint atomic basins, which are defined on the basis of the topological properties of the electron density. In this methodology, each basin is generally associated with a determined nucleus (or nuclear attractor). However, in certain cases non-nuclear attractors may appear that cannot be assigned to any nucleus composing the N-electron system.[9,10] This hampers to achieve a clear chemical interpretation of the resulting localized orbitals. Alternatively, within the FA treatment the physical space is divided into atomic regions which have not sharp boundaries, but exhibit a continuous transition from one to another. Although the resulting localization procedure within the FA framework is computationally very convenient, the atomic regions are not uniquely defined, as they depend on semiempirical parameters.[11]

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The aim of this work is to propose and study the capabilities of a new localization procedure, within the physical space partitioning approach, which is free of the drawbacks of the above mentioned treatments. The procedure is rooted in the concept of electron pair.[12,13] On this account, the partitioning of the 3D space is done on the topological analysis of the electron localization function (ELF) introduced by Becke and Edgecombe.[14] This partitioning provides basins of the 3D space with a clear chemical meaning corresponding to classical chemical concepts (core and valence shells, bonds and lone pairs)[12,15–17] in contrast with AIM and FA 3D space divisions. Hence, the new localization procedure has the advantage of providing a straightforward interpretation of the resulting orbitals in terms of their localization indices and basin occupancies. Similarly to the treatments based on AIM and FA partitionings, this procedure preserves the σ/π-separability in planar systems and has an algorithmic behavior of N^3 mathematical operations.

The organization of this article is as follows. In the 'Localization Criterion Based on the Topological Analysis of the ELF' section, we describe the new localization procedure along with the associated indices and occupancies. In the 'Computational Details, Results, and Discussion' section, we report the computational details and the results obtained in selected systems. Finally, some remarks and conclusions are presented in the last section.

Localization Criterion Based on the Topological Analysis of the ELF

As it has been mentioned in the Introduction, the ELF theory provides a partitioning of the physical space based on topological properties.[14] The whole 3D space is divided into disjoint basins Ω_A having a clear chemical meaning, which are classified basically into two types: core basins $\Omega_{C(X)}$ organized around nuclei, where X is the symbol of the central atom, and valence basins $\Omega_{V(X_1,X_2,...)}$ organized in the remaining space, which are characterized by their synaptic order (monosynaptic, disynaptic, etc.). In particular, monosynaptic valence basins $\Omega_{V(X)}$ correspond to lone pairs of the Lewis model, while disynaptic valence basins $\Omega_{V(X_1,X_2)}$ correspond to two-center bonds.[18,19]. The ELF basins let one express the overlap integrals corresponding to the orthonormal basis set $\{k,l,m,n,...\}$, constituted by the canonical molecular orbitals, as

$$<k|l> = \sum_{\Omega_A} <k|l>_{\Omega_A} = \delta_{kl} \tag{1}$$

in which $<k|l>$ are the standard overlap integrals (where the integration is performed over the total space), $<k|l>_{\Omega_A}$ are the overlap integrals over the ELF basins Ω_A (where the integration is limited to this kind of basins) and δ_{kl} are the Kronecker deltas. Taking into account that the quantity $<k|k>_{\Omega_A}$ may be identified as the population (occupancy) of the k orbital on the basin Ω_A, the quantity

$$L_k = \sum_{\Omega_A} <k|k>_{\Omega_A} <k|k>_{\Omega_A} \tag{2}$$

is the localization index of the k orbital and its inverse, L_k^{-1}, is the effective number of basins spanned by this orbital.[6]

To recover the classical Lewis–Linnett picture through procedures of orbital localization, a unitary transformation is performed from canonical molecular orbitals $\{k,l,m,n,...\}$ to localized ones $\{\mu,v,...\}$, by means of a matrix U so that the sum of the localization indices $L = \sum_{\mu} L_{\mu}$, in the transformed basis set, is maximized.[7]

The matrix U relates localized molecular orbitals (LMOs) with canonical ones

$$|\mu> = \sum_k U_{k\mu}|k> \tag{3}$$

and it is usually computed by a second-order maximization procedure[20] or throughout consecutive 2×2 rotations[21]

$$|\mu> = \cos(\alpha)|k> + \sin(\alpha)|l> \tag{4a}$$

$$|v> = -\sin(\alpha)|k> + \cos(\alpha)|l> \tag{4b}$$

The unitary transformation indicated by means of Eqs. (3) and (4) and maximization of the L_{μ} quantities lead to the determination of the rotation angles; a detailed description of this algorithm is reported in Ref. [5]. This allows one to express the sum L in the localized orbital basis set as

$$L = \sum_{\mu} \sum_{klmn} U_{\mu k}^* U_{\mu l} U_{\mu m}^* U_{\mu n} T_{klmn}^{ELF} \tag{5}$$

where

$$T_{klmn}^{ELF} = \sum_{\Omega_A} <k|l>_{\Omega_A} <m|n>_{\Omega_A} \tag{6}$$

Other procedures for orbital localization have an identical mathematical framework although the nature of the tensor T is different, for example, in the AIM and FA treatments the basins Ω_A are those provided by these theories.[6,8] In this work, we propose a new localization procedure in which the tensor T is formulated through the ELF theory. The above functional, which yields maximization of an ELF dependent charge-density overlap functional, retains the simplicity of AIM and FA localization schemes and does not invoke any reference to basis sets or external criteria.

The localization sum L, the values of L_k^{-1}, and the occupancies and classification of ELF basins for LMOs are important for the interpretation of results in the new procedure proposed in this work. The relevant occupancies on those basins that reflect the classical concepts of core, bond and/or lone electron pairs relative to the Lewis model, define the type of LMOs. Hence, localized orbitals of the core type have significant contributions of the core basin. Furthermore, lone pairs and bonding localized orbitals show high contribution associated with their respective lone pairs and bonding basins reminiscent of the Lewis model too.

In some cases, it is convenient to unify basins into a single domain, called superbasin. Usually, this occurs with multisynaptics basins of the same type, for example, in the ethylene molecule whose valence basins give support to the banana representation of the double bond.[15] If, we have n p-synaptic

basins ($\Omega_{Vv(X_1,X_2,...,X_p)}$ $v = 1... n$), sharing bounderies with the same core basin, it would be suitable to define a superbasin including all of them. Thus, the localization process will preserve the symmetry of the system in the orbitals localized. In these cases, we define the superbasin as

$$\Omega_{V(X_1,X_2,...,X_p)} = \bigcup_{v=1}^{n} \Omega_{V_v(X_1,X_2,...,X_p)} \qquad (7)$$

and the new elements of the overlap matrices will be

$$<k|l>_{\Omega_{V(X_1,X_2,...,X_p)}} = \sum_{v=1}^{n} <k|l>_{\Omega_{V_v(X_1,X_2,...,X_p)}} \qquad (8)$$

In the next section, the capabilities of this new localization algorithm are studied throughout numerical determinations.

Computational Details, Results, and Discussion

The performance of the new localization procedure has been tested on several simple molecules LiF, CO, H_2O, C_2H_4, C_6H_6, and Li_2. This set of systems has been chosen as prototype molecules with different bonding patterns in a chemical point of view. Some of them are ionic or with polarized bondings. Others are covalent with multiple bonds or with delocalized bondings. The localization of molecular orbitals within ELF approach was performed using the GAMESS program[22] and our own routines at the HF level with the basis sets 6-31G(d,p). All calculations have been accomplished with the largest Abelian subgroup of the point group describing the full symmetry of each system determined by GAMESS package. The overlap integrals over ELF regions, needed for these calculations, have been obtained from a modified version of the TopMod program.[23] We used the geometries optimized at the HF/6-31G(d,p) level. Tables 1–7 gather the results obtained in this new localization procedure.

Table 1. Results for the LiF molecule ($R_{Li\text{-}F} = 1.5543$ Å) within the ELF domain approach.

	Canonical molecular orbitals ($L = 6.6272$; $1.180 \leq L_k^{-1} \leq 3.058$)			
k	C(Li)	C(F)	V(F)	V(Li,F)
1	0.344	0.020	0.372	0.264
2	0.000	0.918	0.059	0.023
3	0.027	0.043	0.579	0.348
4	0.632	0.011	0.261	0.096
5	0.004	0.035	0.748	0.211
6	0.004	0.035	0.748	0.211
	Localized molecular orbitals ($L = 9.0121$; $1.027 \leq L_\mu^{-1} \leq 1.826$)			
μ	C(Li)	C(F)	V(F)	V(Li,F)
1	0.987	0.000	0.009	0.004
2	0.000	0.933	0.048	0.018
3	0.014	0.032	0.260	0.692
4	0.002	0.027	0.952	0.017
5	0.004	0.035	0.747	0.211
6	0.004	0.035	0.747	0.211
ELF domain occupancies are shown for all the basins Ω_A.				

Table 2. Results for the CO molecule ($R_{C\text{-}O} = 1.1138$ l Å) within the ELF domain approach.

	Canonical molecular orbitals ($L = 9.2578$; $1.112 \leq L_k^{-1} \leq 2.682$)				
k	C(C)	C(O)	V(C)	V(O)	V(C,O)
1	0.000	0.935	0.000	0.042	0.023
2	0.947	0.000	0.029	0.000	0.023
3	0.008	0.035	0.017	0.831	0.109
4	0.035	0.002	0.899	0.012	0.052
5	0.019	0.029	0.026	0.177	0.748
6	0.011	0.032	0.113	0.465	0.378
7	0.011	0.032	0.113	0.465	0.378
	Localized molecular orbitals ($L = 9.9515$; $1.088 \leq L_\mu^{-1} \leq 2.682$)				
μ	C(C)	C(O)	V(C)	V(O)	V(C,O)
1	0.000	0.946	0.000	0.035	0.017
2	0.958	0.000	0.023	0.000	0.018
3	0.001	0.026	0.002	0.935	0.035
4	0.028	0.001	0.913	0.004	0.052
5	0.021	0.028	0.032	0.087	0.832
6	0.011	0.032	0.113	0.465	0.378
7	0.011	0.032	0.113	0.465	0.378
ELF domain occupancies are shown for all the basins Ω_A.					

In the LiF molecule, the ELF partitioning yields four basins: two core basins each associated to one atom, one monosynaptic lone pair V(F) basin associated to the F atom, and one disynaptic V(Li,F) basin associated with the Li—F bond, which bifurcates from the Li core basin at very small values of ELF,[24] and hence, it may be classified as a lone pair basin at the F atom. Table 1 shows a large increase in the localization sum L when going from the canonical molecular orbitals to the LMOs. The interpretation of the LMOs can be performed entirely by considering the relevant ELF basins occupancies and the classification according to their chemical characteristics. Hence, the set of LMOs describes two core orbitals, each one localized on a nucleus, together with one s-type and three p-type lone-pair orbitals localized on the F atom, which are

Table 3. Results for the H_2O molecule ($R_{O\text{-}H} = 0.9431$ Å, $\widehat{HOH} = 106°2'38''$) within the ELF domain approach.

	Canonical molecular orbitals ($L = 3.9398$; $1.137 \leq L_k^{-1} \leq 4.158$)				
k	C(O)	V_1(O)	V_2(O)	V(H_1,O)	V(H_2,O)
1	0.937	0.023	0.023	0.008	0.008
2	0.027	0.270	0.270	0.216	0.216
3	0.043	0.399	0.399	0.080	0.080
4	0.034	0.285	0.285	0.198	0.198
5	0.028	0.143	0.143	0.343	0.343
	Localized molecular orbitals ($L = 5.8971$; $1.114 \leq L_\mu^{-1} \leq 2.108$				
μ	C(O)	V_1(O)	V_2(O)	V(H_1,O)	V(H_2,O)
1	0.947	0.019	0.019	0.007	0.007
2	0.034	0.118	0.728	0.060	0.060
3	0.034	0.728	0.118	0.060	0.060
4	0.027	0.127	0.127	0.056	0.662
5	0.027	0.127	0.127	0.662	0.056
ELF domain occupancies are shown for all the basins Ω_A.					

Table 4. Results for the H_2O molecule (R_{O-H} = 0.9431 Å, $\widehat{HOH}$ = 106°2′38″) within the ELF domain approach.

	Canonical molecular orbitals (L = 5.2751; $1.136 \leq L_k^{-1} \leq 3.152$)			
k	C(O)	V(O)	V(H$_1$,O)	V(H$_2$,O)
1	0.937	0.046	0.008	0.008
2	0.042	0.798	0.080	0.080
3	0.034	0.569	0.198	0.198
4	0.028	0.285	0.343	0.343
5	0.027	0.541	0.216	0.216
	Localized molecular orbitals (L = 6.7592; $1.113 \leq L_\mu^{-1} \leq 1.950$)			
μ	C(O)	V(O)	V(H$_1$,O)	V(H$_2$,O)
1	0.947	0.039	0.007	0.007
2	0.042	0.798	0.080	0.080
3	0.027	0.896	0.038	0.038
4	0.026	0.254	0.667	0.052
5	0.026	0.254	0.052	0.667

ELF domain occupancies are shown for all the basins Ω_A.

Table 5. Results for the C_2H_4 molecule (R_{C-C} = 1.3165 Å, R_{C-H} = 1.0763 Å, $\widehat{HCH}$ = 116°32′42″) within the ELF domain approach.

	Canonical molecular orbitals (L = 5.2907; $1.905 \leq L_k^{-1} \leq 5.237$)						
k	C(C$_1$)	C(C$_2$)	V(H$_1$,C$_1$)	V(H$_2$,C$_1$)	V(H$_3$,C$_2$)	V(H$_4$,C$_2$)	V(C$_1$,C$_2$)
1	0.477	0.477	0.007	0.007	0.007	0.007	0.020
2	0.475	0.475	0.007	0.007	0.007	0.007	0.022
3	0.022	0.022	0.060	0.060	0.060	0.060	0.714
4	0.012	0.012	0.229	0.229	0.229	0.229	0.060
5	0.013	0.013	0.206	0.206	0.206	0.206	0.148
6	0.019	0.019	0.089	0.089	0.089	0.089	0.605
7	0.017	0.017	0.207	0.207	0.207	0.207	0.137
8	0.011	0.011	0.233	0.233	0.233	0.233	0.044
	Localized molecular orbitals (L = 11.6279; $1.086 \leq L_\mu^{-1} \leq 2.509$)						
μ	C(C$_1$)	C(C$_2$)	V(H$_1$,C$_1$)	V(H$_2$,C$_1$)	V(H$_3$,C$_2$)	V(H$_4$,C$_2$)	V(C$_1$,C$_2$)
1	0.959	0.000	0.012	0.012	0.000	0.000	0.017
2	0.000	0.959	0.000	0.000	0.012	0.012	0.017
3	0.023	0.000	0.050	0.847	0.003	0.003	0.074
4	0.000	0.023	0.003	0.003	0.050	0.847	0.074
5	0.000	0.023	0.003	0.003	0.847	0.050	0.074
6	0.023	0.000	0.847	0.050	0.003	0.003	0.074
7	0.019	0.019	0.089	0.089	0.089	0.089	0.605
8	0.023	0.023	0.035	0.035	0.035	0.035	0.816

ELF domain occupancies are shown for all the basins Ω_A.

shown in Figure 1. This is in accordance with the classical Li^+F^- picture.

Results for the CO molecule, shown in Table 2, are also clear-cut. Because of its heteronuclear and covalent character, the localization increases the sum L only very slightly from the canonical molecular orbitals to the LMOs. Similarly to the above example, monosynaptic basins V(C) and V(O) contribute dominantly to the σ lone pair orbitals on the C and O atoms, respectively. However, π bonding orbitals (labeled 6 and 7 in Table 2) show high contribution from both V(O) and V(C,O) basins. These resulting LMOs are less localized than the rest. In Figure 2, we can see a triple bond and two lone pairs around the nuclei.

The H_2O molecule represent an interesting example of a systems for which the partitioning of the 3D space in the topological analysis of the ELF requires an additional definition of the domains. Among the basins that arise from that topological analysis, there are two monosynaptic basins associated to lone pair at the O atom. The lone pair orbitals, with relevant contributions from these monosynaptic basins, are highly symmetric and coming out from the molecular plane, as can be seen in Table 3 and Figure 3. In contrast with previous systems, in this molecule these two monosynaptic basins require the definition of a superbasin including both of them for the

localization process to overcome these drawbacks. If, we define a new basin taking into account the expressions (7) and (8) with both lone pair basins (V$_1$(O) $\cup$ V$_2$(O)), we will recover the σ/π-separability in the orbitals localized. These results are shown in Figure 4; we can see the LMOs π and σ lone pair orbitals at the O atom with high contributions associated with their respective lone pair basin. Table 4 presents the LMOs resulting from this partitioning, where the localization increases the sum L a little from the canonical molecular orbitals. Furthermore, in the new ELF partitioning the canonical molecular orbitals and the LMOs show values of the L_k^{-1}/L_μ^{-1} quantities with smaller upper limits than those resulting from the previous partitioning.

A similar case, which requires to define a superbasin, occurs in the C_2H_4 molecule. Its ELF partitioning produces two equivalent disynaptic basins associated to the double bond C—C. These disynaptic basins contribute significantly to the equivalent τ or banana orbitals, proportional to the linear combinations $\sigma + \pi$ and $\sigma - \pi$ orbitals, for double bonds. As in the

Table 6. Results for the C_6H_6 molecule (R_{C-C} = 1.3859 Å, R_{C-H} = 1.0758 Å, $\widehat{CCC}$ = 120° $\widehat{HCC}$ = 120°) within the ELF domain approach.

	Canonical molecular orbitals (L = 8.2747; $2.280 \leq L_k^{-1} \leq 9.959$) Localized molecular orbitals (L = 28.4704; $1.089 \leq L_\mu^{-1} \leq 4.976$)																	
μ	C(C$_1$)	C(C$_2$)	C(C$_3$)	C(C$_4$)	C(C$_5$)	C(C$_6$)	V(H$_1$,C$_1$)	V(H$_2$,C$_2$)	V(H$_3$,C$_3$)	V(H$_4$,C$_4$)	V(H$_5$,C$_5$)	V(H$_6$,C$_6$)	V(C$_1$,C$_2$)	V(C$_1$,C$_6$)	V(C$_2$,C$_3$)	V(C$_3$,C$_4$)	V(C$_4$,C$_5$)	V(C$_5$,C$_6$)
1	0.000	0.000	0.000	0.000	0.000	0.958	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.014	0.000	0.000	0.000	0.015
2	0.000	0.000	0.000	0.000	0.022	0.022	0.002	0.000	0.000	0.002	0.041	0.041	0.001	0.043	0.000	0.001	0.043	0.781
3	0.000	0.000	0.000	0.000	0.000	0.022	0.003	0.000	0.000	0.000	0.003	0.855	0.002	0.055	0.000	0.000	0.002	0.056
4	0.002	0.001	0.001	0.002	0.016	0.016	0.010	0.008	0.008	0.010	0.079	0.079	0.015	0.175	0.032	0.015	0.174	0.354
5	0.015	0.016	0.002	0.001	0.001	0.002	0.079	0.079	0.010	0.008	0.008	0.010	0.352	0.175	0.177	0.015	0.032	0.015
6	0.001	0.002	0.016	0.015	0.002	0.001	0.008	0.010	0.079	0.079	0.001	0.008	0.015	0.032	0.176	0.352	0.176	0.016

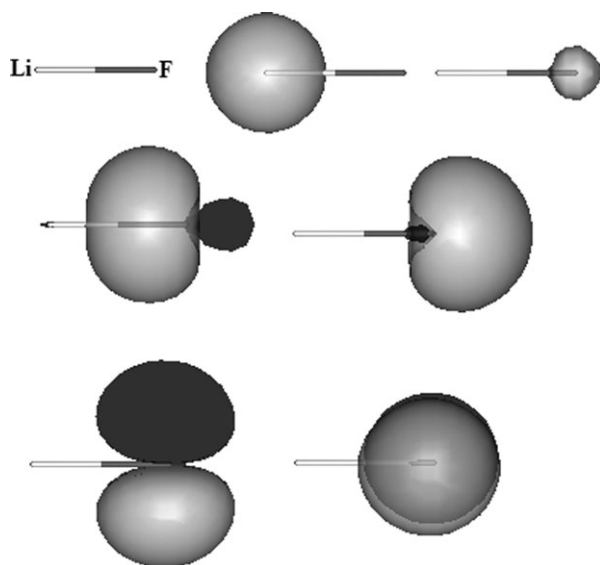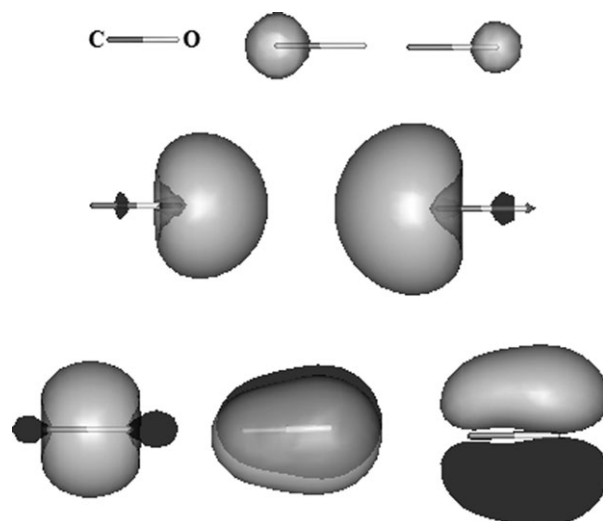ELF domain occupancies are shown for all the basins Ω_A.

Table 7. Results for the Li_2 molecule ($R_{Li\text{-}Li}$ = 2.8070 Å) within the ELF domain approach.

	Canonical molecular orbitals (L = 3.6569; $1.133 \leq L_k^{-1} \leq 2.057$)		
k	C(Li_a)	C(Li_b)	V(Li_a,Li_b)
1	0.493	0.493	0.014
2	0.493	0.493	0.013
3	0.023	0.023	0.939
	Localized molecular orbitals (L = 5.6274; $1.025 \leq L_\mu^{-1} \leq 1.125$)		
μ	C(Li_a)	C(Li_b)	V(Li_a,Li_b)
1	0.000	0.988	0.012
2	0.988	0.000	0.012
3	0.021	0.021	0.942

ELF domain occupancies are shown for all the basins Ω_A.

Figure 2. Isosurfaces of the localized orbitals for the CO molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The geometry of the molecule is specified in Table 2. The ELF domains are $\Omega_{C(C)}$, $\Omega_{C(O)}$, $\Omega_{V(C)}$, $\Omega_{V(O)}$, and $\Omega_{V(C,O)}$.

water molecule, these basins have been gathered together in a superbasin, thus the localization process preserves the σ/π-separability of this planar system. In Table 5, the canonical molecular orbitals show a high delocalization due to the molecular symmetry requirements. Therefore, this transformation leads to a huge increase in the localization sum L from the canonical molecular orbitals. In Figure 5, the last two localized orbitals π and σ present high contribution of the new superbasin associated to the double bond C—C.

Another interesting example to study is the benzene molecule, which is the prototype of aromatic compounds. Its high symmetry complicates the determination of localized orbitals.[2,5] The ELF partitioning presents 18 basins: six C(C) core, six V(C,H) protonated disynaptic, and six V(C,C) disynaptic. The localization transformation yields six core orbitals, six σ bonding orbitals corresponding to the C—H bonds, six σ bonding orbitals corresponding to the C—C bonds, and other three bonding orbitals with high contributions of several V(C,C)

basins. It is worthy to point out that we have found only one maximum of the L quantity for each molecule described in this work, with the obvious exception of the benzene molecule. According to the number and the character of the Kekulé structures, for this molecule, we have obtained two identical maxima with the pattern of localized orbital exhibiting
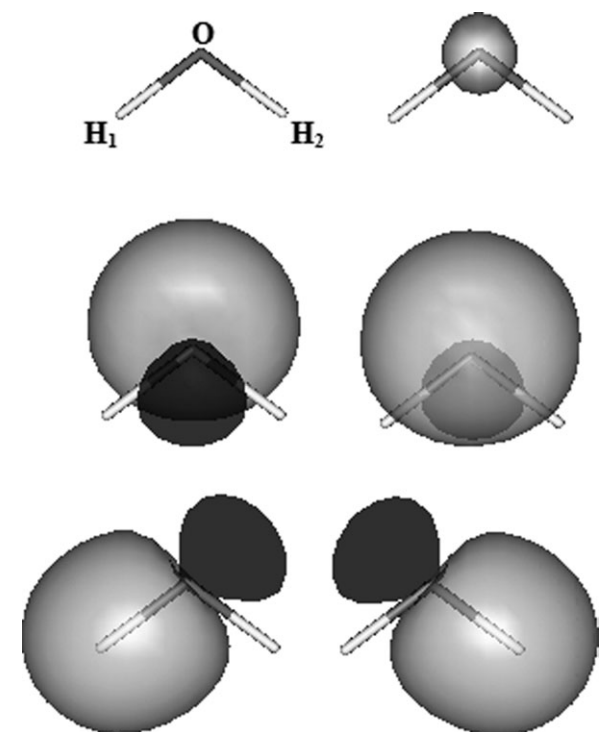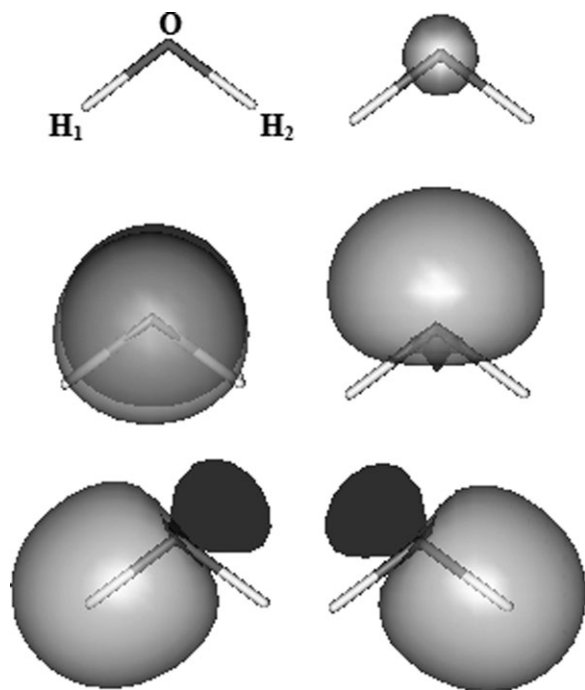

Figure 3. Isosurfaces of the localized orbitals for the H_2O molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The localized oxygen lone pair orbitals can be found on the second row, coming out from the molecular plane. The geometry of the molecule is specified in Table 3. The ELF domains are $\Omega_{C(O)}$, $\Omega_{V1(O)}$, $\Omega_{V2(O)}$, $\Omega_{V(H1,O)}$, and $\Omega_{V(H2,O)}$.

Figure 1. Isosurfaces of the localized orbitals for the LiF molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The geometry of the molecule is specified in Table 1. The ELF domains are $\Omega_{C(Li)}$, $\Omega_{C(F)}$, $\Omega_{V(F)}$, and $\Omega_{V(Li,F)}$.
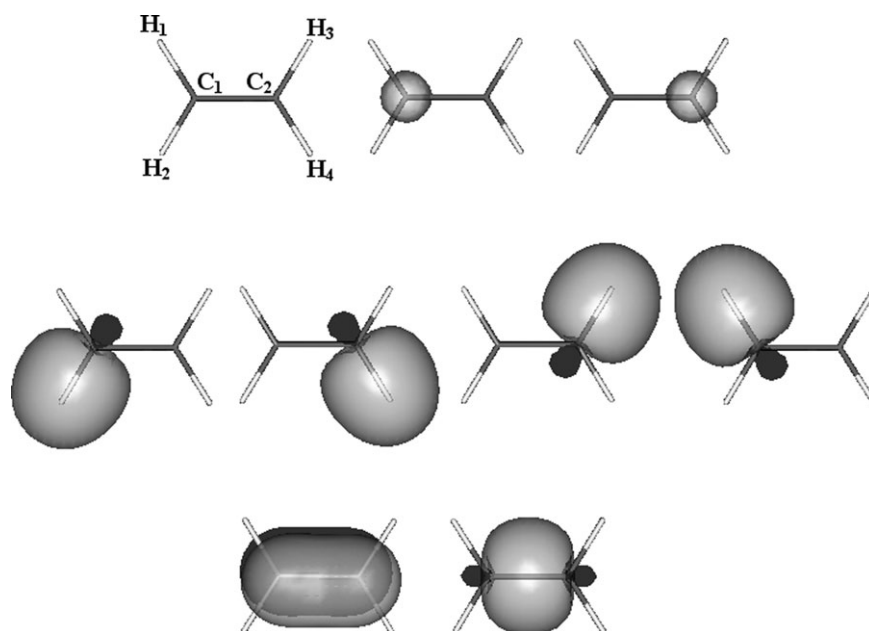
Figure 4. Isosurfaces of the localized orbitals for the H_2O molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The localized oxygen lone pair orbitals, π and σ, are shown on the second row. The geometry of the molecule is specified in Table 4. The ELF domains are $\Omega_{C(O)}$, $\Omega_{V(O)}$, $\Omega_{V(H1,O)}$, and $\Omega_{V(H2,O)}$. The V(O) ELF domain is a combination from basins associated to the lone pairs on the oxygen atom.

symmetry reduced from D_{6h} to D_{3h}. Figure 6 only shows one core orbital, one σ bonding orbital associated to the bond C—H, one σ bonding orbital associated to the bond C—C and

the three bonding orbitals associated with one Kekulé structure. Table 6 shows these LMOs and the lower and upper limits of the quantities L_k^{-1} (for the canonical orbitals) and L_μ^{-1} (for the localized orbitals). The canonical molecular orbitals are completely delocalized due to the molecular symmetry requirements and their L_k^{-1} limit value is twice those derived from LMOs. The localization process recovers one of the Kekulé structures[25] through the last three bonding orbitals, since these orbitals are mainly localized in three alternate V(C,C) basins.

The last system studied in this work to test the performance of this new localization procedure is the Li_2 molecule. In this system, the AIM topological space partitioning leads to a non-nuclear attractor, which is an empty basin defined by surfaces having zero flux in the gradient vector field of the electron density.[6] Consequently, there is no one-to-one correspondence between atoms and Bader domains. Nevertheless, the ELF partitioning provides indeed three domains: two core basins, $C(Li_a)$ and $C(Li_b)$, and one disynaptic $V(Li_a,Li_b)$ basin associated with the Li–Li bond. Results for this system can be observed in Table 7. The localization has a large increase in the sum L and the upper limit of L_μ^{-1} of the LMOs is only 1.125. It is a clear indicator of the high localization achieved. The set of LMOs describes two core orbitals and one σ bond orbital, which are shown in Figure 7. In this procedure, the description is in agreement with the genuine chemical picture of this molecular system.

To check the basis set dependence of this methodology, we report some additional results for the molecules H_2O (Table 8) and Li_2 (Table 9), using the basis sets aug-cc-pVDZ and 6-311+G(2d,2p). In these calculations, the molecular geometries have also been optimized for the corresponding basis sets
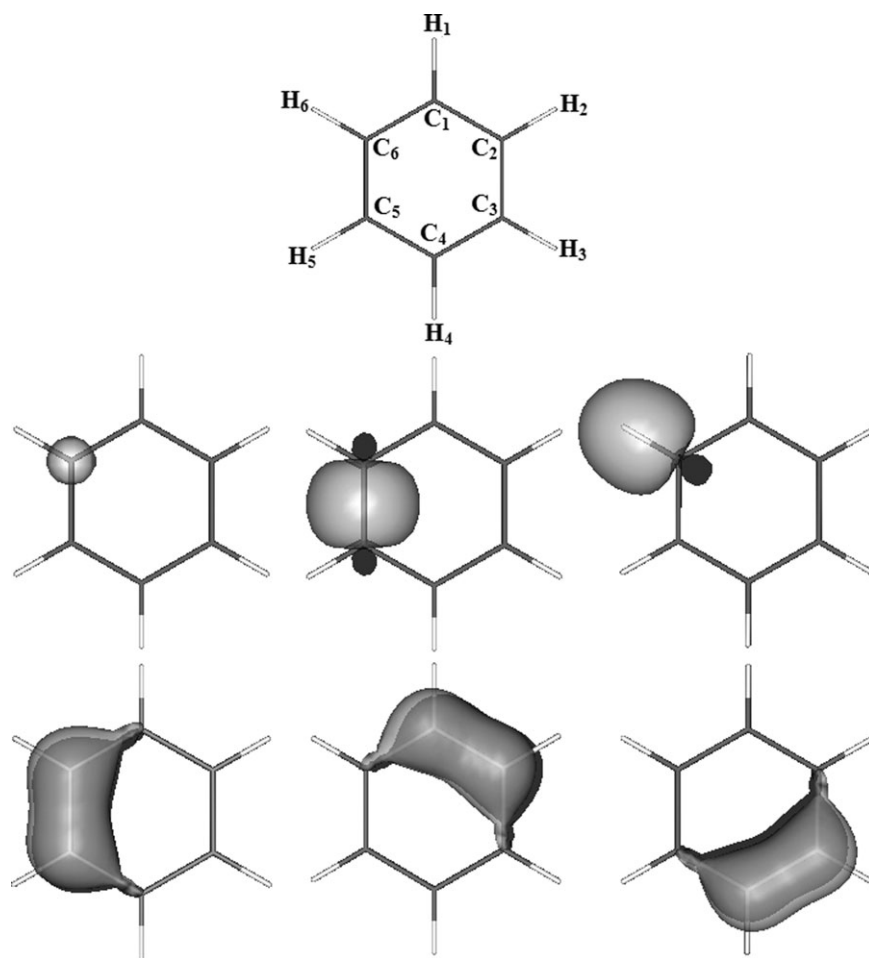

Figure 5. Isosurfaces of the localized orbitals for the C_2H_4 molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The geometry of the molecule is specified in Table 5. The ELF domains are $\Omega_{C(C1)}$, $\Omega_{C(C2)}$, $\Omega_{V(H_1,C1)}$, $\Omega_{V(H2,C1)}$, $\Omega_{V(H3,C2)}$, $\Omega_{V(H4,C2)}$, and $\Omega_{V(C1,C2)}$. The last ELF domain is a combination from bonding basins corresponding to the C—C bond.

Figure 6. Isosurfaces of the localized orbitals for the C_6H_6 molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.08 a.u. The localization process recovers the Kekulé structure through the last three bonding orbitals. The geometry of the molecule is specified in Table 6. The ELF domains are $\Omega_{C(C1)}$, $\Omega_{C(C2)}$, $\Omega_{C(C3)}$, $\Omega_{C(C4)}$, $\Omega_{C(C5)}$, $\Omega_{C(C6)}$, $\Omega_{V(H1,C1)}$, $\Omega_{V(H2,C2)}$, $\Omega_{V(H3,C3)}$, $\Omega_{V(H4,C4)}$, $\Omega_{V(H5,C5)}$, $\Omega_{V(H6,C6)}$, $\Omega_{V(C1,C2)}$, $\Omega_{V(C1,C6)}$, $\Omega_{V(C2,C3)}$, $\Omega_{V(C3,C4)}$, $\Omega_{V(C4,C5)}$, and $\Omega_{V(C5,C6)}$.

within the HF approximation. The comparison of the results in Tables 4 and 8 for the H_2O molecule, and in Tables 7 and 9 for the Li_2 one shows that no significant changes appear for the values of L and orbital populations among the different basis sets.
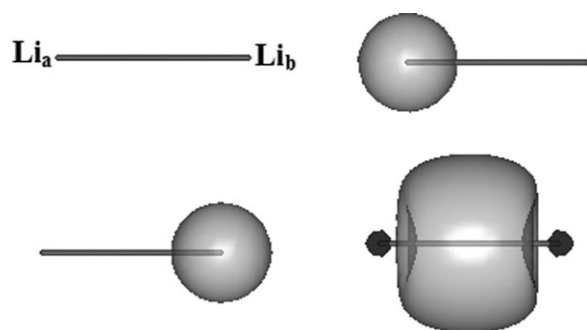

Figure 7. Isosurfaces of the localized orbitals for the Li_2 molecule. Positive values are indicated in gray and negative values in black. The isovalues are ± 0.05 a.u. The geometry of the molecule is specified in Table 7. The ELF domains are $\Omega_{C(Lia)}$, $\Omega_{C(Lib)}$, and $\Omega_{V(Lia,Lib)}$.

Table 8. Localized orbitals for the H_2O molecule within the ELF domain approach, with geometries optimized for the basis sets aug-cc-pVDZ ($R_{O-H} = 0.9436$ Å $\widehat{HOH} = 105°56'31''$) and 6–311+G(2d,2p) ($R_{O-H} = 0.9400$ Å $\widehat{HOH} = 106°19'12''$).

| | Basis set aug-cc-pVDZ ($L = 6.6946$; $1.110 \le L_\mu^{-1} \le 1.932$) | | | |
μ	C(O)	V(O)	V(H$_1$,O)	V(H$_2$,O)
1	0.949	0.036	0.008	0.008
2	0.042	0.778	0.089	0.089
3	0.029	0.888	0.041	0.041
4	0.027	0.243	0.674	0.055
5	0.027	0.243	0.055	0.674
	Basis set 6–311+G(2d,2p) ($L = 6.7137$; $1.115 \le L_\mu^{-1} \le 1.941$)			
μ	C(O)	V(O)	V(H$_1$,O)	V(H$_2$,O)
1	0.946	0.038	0.008	0.008
2	0.042	0.785	0.086	0.086
3	0.027	0.893	0.040	0.040
4	0.026	0.249	0.671	0.054
5	0.026	0.249	0.054	0.671

ELF domain occupancies are shown for all the basins Ω_A.

Table 9. Localized orbitals for the Li_2 molecule within the ELF domain approach, with geometries optimized for the basis sets aug-cc-pVDZ (R_{Li-Li} = 2.8025 Å) and 6–311+G(2d,2p) (R_{Li-Li} = 2.7848 Å).

	Basis set aug-cc-pVDZ (L = 5.6121; $1.024 \leq L_\mu^{-1} \leq 1.127$)		
μ	$C(Li_a)$	$C(Li_b)$	$V(Li_a, Li_b)$
1	0.000	0.988	0.012
2	0.988	0.000	0.012
3	0.020	0.020	0.941
	Basis set 6–311+G(2d,2p) (L = 5.6208; $1.023 \leq L_\mu^{-1} \leq 1.126$)		
μ	$C(Li_a)$	$C(Li_b)$	$V(Li_a, Li_b)$
1	0.000	0.989	0.011
2	0.989	0.000	0.011
3	0.020	0.020	0.942

ELF domain occupancies are shown for all the basins Ω_A.

Concluding Remarks

In this work, we have proposed and implemented a new localization procedure based on the partitioning of the 3D physical space into basins resulting from the topological analysis of ELF. This procedure, whose algorithmic behavior is N^3, does not require any additional quantities to be calculated beyond the overlap integrals over ELF basins, preserves the σ/π-separability of planar systems and provides simple indices to quantify the extent of the localization and population of the resulting orbitals. Moreover, this localization procedure has the advantage of taking into account partitionings of the molecular space into disjoint domains with a clear chemical meaning, which is not pointed out by other schemes. In this framework, the interpretation of localized orbitals can straightforwardly be carried out by considering their ELF basins occupancies and the classification of these basins according to their chemical features, avoiding further analyses.

Acknowledgments

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