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An orbital localization criterion based on the topological analysis of the electron localization function at correlated level

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Abstract

This work describes a procedure for localizing orbitals based on the topological analysis of the electron localization function at correlated level. The decomposition of the overlap matrix according to the partitioning of the three dimensional physical space into basins provided by that function allows us to define a localization index to be maximized using isopycnic orbital transformations. The localization algorithm has been computationally implemented and its efficiency tested on selected molecular systems at equilibrium, stretched, and twisted geometries. We report results which allow to analyze the influence of the correlated and uncorrelated treatments on the orbital localization.

KEYWORDS
electron localization function, isopycnic transformation, orbital localization criterion

1 | INTRODUCTION

The Lewis–Linnett picture has satisfactorily explained most aspects of molecular electronic structure by means of intuitive and meaningful chemical concepts such as localized bonds, valences, lone electron pairs, and core orbitals.[1,2] However, these concepts are not observable quantities in the quantum-mechanical sense and, consequently, cannot be directly reproduced within the modern quantum theory framework. In fact, the orbitals arising from the standard Hartree–Fock theory reflect the symmetry of the irreducible representations of the molecular point group, but they are generally extended over the whole molecular system and unfortunately they do not reproduce the mentioned classical Lewis–Linnett picture concepts. One of the procedures to recover that approach is the orbital localization. This technique is based on the invariance of the *N*-electron wave functions under unitary transformations of the orbital basis sets, without requiring additional approximations.

Several schemes were proposed long time ago for localizing Hartree–Fock canonical molecular orbitals, which are based on maximization of a determined quantity by means of 2×2 rotations or second-order maximization procedures.[3–7] All of them present drawbacks, mainly in the description of planar molecules, where they predict τ or banana orbitals[5] rather than the σ and π ones as expected.[8,9] Other similar procedures (see e.g., Refs. [10,11]) have been used beyond the Hartree–Fock wave function level. Likewise, in a different approach, the partitioning of the three-dimensional (3D) physical space into atomic basins has proven to be useful for localizing Hartree–Fock and natural spin orbitals, enabling the study of the electron correlation effects.[8,9,12] These techniques, which use isopycnic orbital transformations, were initially formulated using two partitioning schemes to define the localization, the atoms-in-molecules (AIM) procedure[13] and the Fuzzy atom (FA) treatment.[14–16] A

TABLE 1 Orbital occupation numbers (n_i and v_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the HF($^1\Sigma^+$) molecule ($R_{HF} = 0.9168\,\text{Å}$)

	Canonical natural orbitals (L = 7.6628)					Localized natural orbitals (L = 7.9242)				
i	n_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(F,H)}$	$\Omega_{V(F)}$	i	v_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(F,H)}$	$\Omega_{V(F)}$
1	2.000	1.166	0.923	0.004	0.072	1	2.000	1.135	0.937	0.004	0.059
2	1.991	1.209	0.030	0.064	0.907	2	1.989	1.066	0.019	0.013	0.968
3	1.984	1.162	0.042	0.032	0.926	3	1.984	1.162	0.042	0.032	0.926
4	1.984	1.164	0.043	0.032	0.925	4	1.984	1.164	0.043	0.032	0.925
5	1.970	2.105	0.030	0.438	0.531	5	1.973	2.112	0.027	0.490	0.482
6	0.027	2.130	0.058	0.580	0.360	6	0.027	2.149	0.057	0.569	0.372
7	0.015	1.281	0.064	0.055	0.879	7	0.015	1.284	0.067	0.054	0.878
8	0.015	1.285	0.066	0.055	0.878	8	0.015	1.289	0.069	0.054	0.876
9	0.009	1.122	0.029	0.026	0.943	9	0.009	1.087	0.024	0.017	0.959
10	0.002	1.873	0.013	0.338	0.648	10	0.002	1.815	0.021	0.299	0.679
11	0.000	1.957	0.007	0.683	0.209	11	0.000	1.866	0.005	0.708	0.187
	Canonical molecular orbitals (L = 7.4532)					Localized molecular orbitals (L = 7.9957)				
i	n_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(F,H)}$	$\Omega_{V(F)}$	i	v_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(F,H)}$	$\Omega_{V(F)}$
1	2.000	1.154	0.929	0.004	0.068	1	2.000	1.129	0.940	0.004	0.057
2	2.000	1.621	0.026	0.221	0.753	2	2.000	1.069	0.020	0.013	0.967
3	2.000	1.172	0.043	0.035	0.922	3	2.000	1.172	0.043	0.035	0.922
4	2.000	1.175	0.044	0.035	0.921	4	2.000	1.175	0.044	0.035	0.921
5	2.000	1.852	0.033	0.294	0.673	5	2.000	2.112	0.028	0.502	0.470

Results correspond to the standard 6–31G basis set.

generalization of the Pipek–Mezey scheme,[11] which has more recently been reported, allows to perform orbital localizations using several partitioning schemes in the Hilbert and physical spaces.[17,18] The 3D physical space has also been partitioned according to the topological analysis of the electron localization function (ELF).[19–22] The abilities of this technique have been widely studied shedding new lights on this methodology.[23–26] Using that partitioning we have reported a new localization procedure[27,28] which only additionally requires the overlap integrals over the ELF basins. Our treatment preserves the σ/π-separability of planar systems and allows to evaluate the orbital localization in terms of basin occupancies and localization indices although the ELF analyses were performed from the self-consistent field method. However, many systems require highly correlated calculations to be properly described, mainly molecules at nonequilibrium (stretched and twisted) geometries and, consequently, a localization procedure for correlated wave functions is needed for a correct description of their electronic structure. Therefore, the aim of this work is to implement the extension of our ELF-based localization procedure at correlated level of theory, and to evaluate its performance in a series of selected molecules.

The organization of this article is as follows. In section 2, we describe the localization procedure associated with the definition of correlated ELF. In section 3, we report the computational details and the results obtained in selected systems. Finally, some remarks and conclusions are presented in the last section.

2 | LOCALIZATION CRITERION BASED ON THE TOPOLOGICAL ANALYSIS OF THE ELECTRON LOCALIZATION FUNCTION AT CORRELATED LEVEL

The first-order reduced density matrix $^1D(x|x')$ corresponding to an N-electron wave function, describing the state of a system, allows one to determine all expectation values of one-electron quantities for that state. As is well known, the simplest expression of this matrix is

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

in which n_i are the eigenvalues of the first-order reduced density matrix, $\psi_i(x)$ its eigenfunctions and x the spatial and spin coordinates. The one-electron functions $\psi_i(x)$, also called natural spin orbitals, satisfy the orthonormality condition $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ (where δ_{ij} stands for the Kronecker deltas).

TABLE 2 Orbital occupation numbers (n_i and v_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the HF($^1\Sigma^+$) molecule (R = 4R$_{HF}$)

	Canonical natural orbitals (L = 7.6322)					Localized natural orbitals (L = 8.2071)				
i	n_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(H)}$	$\Omega_{V(F)}$	i	v_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(H)}$	$\Omega_{V(F)}$
1	2.000	1.225	0.898	0.000	0.102	1	2.000	1.191	0.912	0.000	0.088
2	1.992	1.059	0.029	0.000	0.971	2	1.992	1.029	0.014	0.000	0.986
3	1.986	1.080	0.038	0.000	0.961	3	1.986	1.080	0.038	0.000	0.961
4	1.986	1.080	0.038	0.000	0.961	4	1.986	1.080	0.038	0.000	0.961
5	1.024	2.080	0.020	0.516	0.463	5	0.997	1.007	0.000	0.996	0.001
6	0.968	2.092	0.021	0.481	0.497	6	0.995	1.086	0.041	0.000	0.959
7	0.013	1.117	0.054	0.000	0.945	7	0.013	1.126	0.058	0.000	0.941
8	0.013	1.117	0.054	0.000	0.945	8	0.013	1.126	0.058	0.000	0.941
9	0.008	1.053	0.025	0.000	0.974	9	0.008	1.028	0.013	0.000	0.986
10	0.006	1.114	0.052	0.001	0.946	10	0.006	1.123	0.056	0.001	0.942
11	0.000	1.020	0.000	0.990	0.002	11	0.000	1.020	0.000	0.990	0.002
	Canonical molecular orbitals (L = 8.2828)					Localized molecular orbitals (L = 8.3955)				
i	n_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(H)}$	$\Omega_{V(F)}$	i	v_i	L_i^{-1}	$\Omega_{C(F)}$	$\Omega_{V(H)}$	$\Omega_{V(F)}$
1	2.000	1.229	0.896	0.000	0.104	1	2.000	1.191	0.912	0.000	0.088
2	2.000	1.062	0.030	0.000	0.970	2	2.000	1.028	0.014	0.000	0.986
3	2.000	1.077	0.037	0.000	0.963	3	2.000	1.077	0.037	0.000	0.963
4	2.000	1.077	0.037	0.000	0.963	4	2.000	1.077	0.037	0.000	0.963
5	1.997	1.879	0.022	0.322	0.654	5	1.997	1.879	0.022	0.322	0.654

Results correspond to the standard 6–31G basis set.

A linear transformation of the function set $\{\psi_i(x)\}$ to another one $\{\phi_i(x)\}$, leaving invariant the matrix $^1D(x|x')$, can be suitable to describe states of N-electron systems having properties localized in a determined spatial region. This type of transformations are known as isopycnic, so that[8,9,29–31]

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

where c_{ij} are the corresponding transformation coefficients, which are expressed as

$$c_{ij} = u_{ij}\sqrt{\frac{n_j}{v_i}} \tag{3}$$

in which u_{ij} are the coefficients of a unitary transformation matrix and

$$v_i = \sum_j u_{ij}^* u_{ij}\, n_j \tag{4}$$

The functions of the set $\{\phi_i(x)\}$ are normalized but they are not necessarily orthogonal. The first-order reduced density matrix, expressed in the new basis set $\{\phi_i\}$, turns out to be

$$^1D(x|x') = \sum_i v_i\, \phi_i^*(x)\, \phi_i(x') \tag{5}$$

which preserves the diagonal form in that basis set and the quantities v_i are the occupation numbers of the functions $\phi_i(x)$ similarly to the n_i ones in the orthonormal basis set $\{\psi_i(x)\}$. Obviously, in the case of the set $\{\psi_i(x)\}$ are the Hartree–Fock orbitals $n_j = 1$ for all occupied ones and, consequently, Equation 2 would express an ordinary unitary transformation.[8]

In this work we deal with the ELF theory[19] in which the ordinary physical space is divided into disjoint Ω_A basins so that the union of all of them yields the whole space. According to that theory the Ω_A basins, which possess a clear physical meaning, are classified into core basins $\Omega_{C(X)}$ (or atomic basins) and valence ones $\Omega_{V(X_1,X_2,...)}$ (the X symbol stands for a central atom). The basins $\Omega_{V(X)}$ stand for lone pairs, while the $\Omega_{V(X_1,X_2)}$ ones indicate two-center bonds.[32,33] In the framework of the ELF theory, the internal product of two functions ϕ_i and ϕ_j, $\langle\phi_i|\phi_j\rangle$, can be expressed as

TABLE 3 Orbital occupation numbers (n_i and v_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $H_2O(^1A_1)$ molecule ($R_{HO}=0.958\,\text{Å}$, $\widehat{HOH}=104^o\,28'\,47''$)

Canonical natural orbitals (L = 5.7200)							Localized natural orbitals (L = 6.8031)						
i	n_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(O,H_1)}$	$\Omega_{V(O,H_2)}$	$\Omega_{V(O)}^{sb}$	i	v_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(O,H_1)}$	$\Omega_{V(O,H_2)}$	$\Omega_{V(O)}^{sb}$
1	2.000	1.132	0.939	0.006	0.006	0.049	1	2.000	1.109	0.949	0.005	0.005	0.041
2	1.988	1.657	0.029	0.105	0.105	0.762	2	1.983	1.175	0.026	0.026	0.026	0.921
3	1.980	1.320	0.043	0.045	0.045	0.867	3	1.980	1.320	0.043	0.045	0.045	0.867
4	1.971	2.925	0.034	0.251	0.251	0.463	4	1.970	2.108	0.028	0.040	0.603	0.329
5	1.967	3.168	0.029	0.311	0.311	0.348	5	1.970	2.108	0.028	0.603	0.040	0.329
6	0.028	3.416	0.068	0.302	0.302	0.324	6	0.028	2.429	0.077	0.521	0.035	0.365
7	0.026	3.374	0.067	0.332	0.332	0.267	7	0.028	2.429	0.077	0.035	0.521	0.365
8	0.018	1.509	0.071	0.061	0.061	0.806	8	0.018	1.509	0.072	0.061	0.061	0.806
9	0.012	1.382	0.034	0.059	0.059	0.846	9	0.013	1.280	0.039	0.039	0.039	0.881
10	0.003	2.494	0.011	0.216	0.216	0.554	10	0.003	2.216	0.011	0.184	0.184	0.619
11	0.002	2.936	0.005	0.288	0.288	0.418	11	0.002	2.831	0.006	0.268	0.268	0.458
12	0.001	3.118	0.015	0.387	0.387	0.143	12	0.001	1.551	0.010	0.795	0.022	0.110
13	0.000	3.272	0.011	0.365	0.365	0.198	13	0.001	1.550	0.009	0.022	0.795	0.110
Canonical molecular orbitals (L = 5.7034)							Localized molecular orbitals (L = 6.8900)						
i	n_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(O,H_1)}$	$\Omega_{V(O,H_2)}$	$\Omega_{V(O)}^{sb}$	i	v_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(O,H_1)}$	$\Omega_{V(O,H_2)}$	$\Omega_{V(O)}^{sb}$
1	2.000	1.122	0.943	0.006	0.006	0.046	1	2.000	1.109	0.949	0.006	0.006	0.040
2	1.999	1.881	0.036	0.129	0.129	0.705	2	1.999	1.180	0.026	0.027	0.027	0.919
3	1.999	1.342	0.043	0.049	0.049	0.859	3	1.999	1.342	0.043	0.049	0.049	0.859
4	2.000	2.705	0.022	0.234	0.234	0.509	4	1.999	2.099	0.027	0.042	0.609	0.321
5	1.999	3.169	0.028	0.314	0.314	0.342	5	1.999	2.099	0.027	0.609	0.042	0.321

Results correspond to the standard 6–31G basis set.

$$\langle\phi_i|\phi_j\rangle = \sum_{\Omega_A} \langle\phi_i|\phi_j\rangle_{\Omega_A} \tag{6}$$

where $\langle\phi_i|\phi_j\rangle_{\Omega_A} = \int_{\Omega_A}\phi_i^*\phi_j dx$. The quantity $\langle\phi_i|\phi_i\rangle_{\Omega_A}$ indicates the distribution of the spin orbital ϕ_i into the basins Ω_A (the population of the spin orbital ϕ_i in that basin) and consequently a localization index L_i of that spin orbital is formulated as[8,27]

$$L_i = \sum_{\Omega_A} \langle\phi_i|\phi_i\rangle_{\Omega_A}^2 \tag{7}$$

while its inverse L_i^{-1} is the effective number of basins spanned by the spin orbital ϕ_i.

The global localization index L is defined as

$$L = \sum_i v_i^2 L_i \tag{8}$$

That definition allows one to express the localization index L as

$$L = \sum_i \sum_{klmn} v_i^2\, c_{ik}^*\, c_{il}\, c_{im}^*\, c_{in}\, T_{ln}^{km} \tag{9}$$

in which T_{ln}^{km} are the components of a tensor defined as

$$T_{ln}^{km} = \sum_{\Omega_A} \langle\psi_k|\psi_l\rangle_{\Omega_A} \langle\psi_m|\psi_n\rangle_{\Omega_A} \tag{10}$$

The coefficients c_{ij} in Equation 2 are determined so that the localization index L in Equation 9 reaches a maximum value, yielding a set of spin orbitals which attempts to describe properties of chemical interest in a more localized manner. Other transformations of molecular or natural

TABLE 4 Orbital occupation numbers (n_i and v_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $H_2O(^1A_1)$ molecule (R= 2.4R_{HO}, $\widehat{HOH}$=104° 28′ 47″)

	Canonical natural orbitals (L = 6.1675)						Localized natural orbitals (L = 7.1406)				
i	n_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(H_1)}$	$\Omega_{V(H_2)}$	$\Omega_{V(O)}^{sb}$	i	v_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(H_1)}$	$\Omega_{V(H_2)}$	$\Omega_{V(O)}^{sb}$
1	2.000	1.123	0.942	0.000	0.000	0.058	1	2.000	1.103	0.951	0.000	0.000	0.049
2	1.989	1.077	0.029	0.006	0.002	0.963	2	1.988	1.057	0.021	0.005	0.002	0.972
3	1.982	1.124	0.047	0.009	0.001	0.942	3	1.982	1.124	0.047	0.009	0.001	0.942
4	1.370	2.719	0.025	0.232	0.232	0.509	4	1.015	1.206	0.051	0.002	0.038	0.908
5	1.313	2.740	0.025	0.235	0.235	0.504	5	1.015	1.206	0.051	0.039	0.002	0.908
6	0.680	2.934	0.029	0.257	0.256	0.456	6	0.978	1.117	0.001	0.945	0.000	0.052
7	0.623	2.977	0.030	0.262	0.262	0.445	7	0.978	1.117	0.001	0.000	0.945	0.052
8	0.017	1.183	0.067	0.008	0.007	0.917	8	0.017	1.195	0.073	0.008	0.006	0.912
9	0.010	1.117	0.027	0.014	0.013	0.946	9	0.010	1.082	0.019	0.010	0.009	0.961
10	0.006	1.300	0.064	0.031	0.031	0.874	10	0.006	1.318	0.070	0.008	0.055	0.866
11	0.006	1.365	0.065	0.042	0.042	0.851	11	0.006	1.319	0.070	0.055	0.008	0.866
12	0.000	2.162	0.001	0.480	0.480	0.031	12	0.000	1.072	0.000	0.001	0.965	0.026
13	0.000	2.154	0.001	0.481	0.481	0.030	13	0.000	1.072	0.000	0.965	0.001	0.026
	Canonical molecular orbitals (L = 7.5621)						Localized molecular orbitals (L = 7.6494)				
i	n_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(H_1)}$	$\Omega_{V(H_2)}$	$\Omega_{V(O)}^{sb}$	i	v_i	L_i^{-1}	$\Omega_{C(O)}$	$\Omega_{V(H_1)}$	$\Omega_{V(H_2)}$	$\Omega_{V(O)}^{sb}$
1	2.000	1.130	0.939	0.000	0.000	0.061	1	2.000	1.105	0.950	0.000	0.000	0.050
2	2.000	1.101	0.031	0.009	0.007	0.952	2	2.000	1.061	0.022	0.005	0.003	0.970
3	2.000	1.125	0.048	0.008	0.002	0.942	3	2.000	1.125	0.048	0.008	0.002	0.942
4	1.999	1.329	0.041	0.048	0.047	0.864	4	1.999	1.348	0.040	0.052	0.051	0.857
5	1.996	2.864	0.007	0.392	0.389	0.211	5	1.996	2.864	0.007	0.392	0.389	0.211

Results correspond to the standard 6–31G basis set.

orbitals, based on maximizing a determined index depending on a tensorial quantity, have been widely used;[3,5,6,8–12,27,34–38] in fact the nature of the tensorial quantity defines the type of localization criterion.

In some situations, it turns out useful to define superbasins Ω^{sb} which are basins resulting from the union of simpler basins[27,39]

$$\Omega_{V(X_1,X_2,\ldots)}^{sb} = \cup_{i=1}^p \Omega_{V_i(X_1,X_2,\ldots)} \tag{11}$$

in which $\Omega_{V_i(X_1,X_2,\ldots)}$ is one of the p valence basins of the atoms $X_1, X_2, \ldots$, satisfying

$$\langle \phi_k | \phi_l \rangle_{\Omega_{V(X_1,X_2,\ldots)}^{sb}} = \sum_{i=1}^p \langle \phi_k | \phi_l \rangle_{\Omega_{V_i(X_1,X_2,\ldots)}} \tag{12}$$

These tools allow to construct localization processes which preserve the symmetry of the orbitals.

As has been mentioned in the Introduction, in this work we study the influence of the electronic correlation on the ELF-based orbital localization. The recently reported results arising from the ELF theory[27,40] were obtained from the self-consistent field method, but the suitable description of the electronic features of a considerable number of systems demand correlated treatments. In recent past,[41] an alternative ELF definition in terms of the Fermi hole curvature has allowed to formulate a correlated version of this function, which was proposed by Becke and Edgecombe at uncorrelated level.[19] This framework requires the use of the second-order reduced density matrix $^2D(x_1, x_2|x_1', x_2')$ which, in its diagonal form ($x_1'=x_1$ and $x_2'=x_2$), is formulated as

$$^2D(x_1, x_2) = {}^1D(x_1)\,{}^1D(x_2) - {}^1D(x_1|x_2)\,{}^1D(x_2|x_1) + \Gamma(x_1, x_2) \tag{13}$$

In this equation, the first and second terms are usually denominated Coulomb- and exchange-type interactions, respectively,[41,42] while the term $\Gamma(x_1, x_2)$ represents the cumulant density.[42–46] The expressions for the Coulomb and exchange interaction terms, in the natural spin-orbital basis sets, involve sums over only two indices, whereas the cumulant contribution is much more complicated, requiring the use of approximations to

TABLE 5 Orbital occupation numbers (n_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $C_2H_4(^1A_g)$ molecule at equilibrium (D_{2h}) experimental geometry ($R_{CC} = 1.339$ Å, $R_{CH} = 1.086$ Å, $\widehat{HCH} = 117°\,36'$, $\widehat{HCC} = 121°\,12'$)

i	n_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega^{sb}_{V(C_1,C_2)}$
Canonical natural orbitals (L = 4.8574)									
1	2.000	2.254	0.470	0.470	0.008	0.008	0.008	0.008	0.029
2	2.000	2.252	0.471	0.471	0.008	0.008	0.008	0.008	0.028
3	1.984	2.847	0.014	0.014	0.104	0.104	0.104	0.104	0.554
4	1.978	4.850	0.010	0.010	0.222	0.222	0.222	0.222	0.089
5	1.977	5.128	0.009	0.009	0.207	0.207	0.207	0.207	0.156
6	1.974	4.783	0.014	0.014	0.163	0.163	0.163	0.163	0.321
7	1.973	4.574	0.008	0.008	0.232	0.232	0.232	0.232	0.055
8	1.882	2.297	0.018	0.018	0.081	0.081	0.081	0.081	0.639
9	0.118	3.144	0.027	0.027	0.106	0.106	0.106	0.106	0.521
10	0.025	4.949	0.018	0.018	0.164	0.164	0.164	0.164	0.306
11	0.024	4.972	0.017	0.017	0.220	0.220	0.220	0.220	0.083
12	0.024	5.377	0.019	0.019	0.187	0.187	0.187	0.187	0.213
13	0.019	4.781	0.047	0.047	0.136	0.136	0.136	0.136	0.361
14	0.018	5.639	0.032	0.032	0.193	0.193	0.193	0.193	0.160
Canonical molecular orbitals (L = 5.5685)									
1	2.000	2.237	0.472	0.472	0.008	0.008	0.008	0.008	0.025
2	2.000	2.258	0.470	0.470	0.008	0.008	0.008	0.008	0.028
3	2.000	1.555	0.017	0.017	0.042	0.042	0.042	0.042	0.797
4	1.999	5.128	0.009	0.009	0.207	0.207	0.207	0.207	0.155
5	1.999	4.828	0.011	0.011	0.224	0.224	0.224	0.224	0.083
6	1.999	4.576	0.008	0.008	0.232	0.232	0.232	0.232	0.054
7	1.999	4.779	0.011	0.011	0.225	0.225	0.225	0.225	0.076
8	2.000	2.365	0.018	0.018	0.084	0.084	0.084	0.084	0.628

Results correspond to the standard STO-3G basis set.

tackle its computational cost. Several approximate formulations based on the natural orbitals and their occupancies have been proposed for the last term.[41,47–49] In this work we use the Hartree–Fock-like approximation (HF-XC), implemented in the ToPMoD package,[50] consisting in formulating $\Gamma(x_1, x_2) = 0$ so that the basin calculations are affected by the HF-XC approximation. This approximation provides the calculation of the second-order reduced density matrix elements in terms of the correlated first-order ones, and it is used for the calculation of the ELF basins itself. The performance of this approximation has turned out to be extremely good[41,51] and, therefore, as shown below, it also allows one to localize natural or molecular spin orbitals originated by correlated or uncorrelated wave functions, respectively.

3 | COMPUTATIONAL ASPECTS, NUMERICAL RESULTS, AND DISCUSSION

The performance of the above proposed ELF procedure for correlated wave functions has been assessed on a series of molecules with different bonding patterns or with no conventional electronic structures. We have chosen compounds involving some second-row elements and hydrogen atoms such as HF, H_2O, $C_2H_4(D_{2h})$, and $C_2H_4(C_{2v})$, at experimental equilibrium,[52] stretched and twisted geometries, in their singlet ground states. This set of systems has been selected as prototype of molecules possessing one and two covalent bonds, a double covalent bond, and a twisted bond, respectively. The localization of natural and molecular orbitals within ELF approach was performed using the Gamess program[53] as well as our own routines, with the basis sets 6–31G for all systems except for the ethylene molecules, in which the STO-3G basis set was used. The

TABLE 6 Orbital occupation numbers (v_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $C_2H_4(^1A_g)$ molecule at equilibrium (D_{2h}) experimental geometry (R_{CC} = 1.339 Å, R_{CH} = 1.086 Å, $\widehat{HCH}$ = 117° 36′, $\widehat{HCC}$ = 121° 12′)

i	v_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega_{V(C_1,C_2)}^{sb}$
	Localized natural orbitals (L = 11.2553)								
1	2.000	1.108	0.949	0.000	0.013	0.013	0.000	0.000	0.024
2	2.000	1.108	0.000	0.949	0.000	0.000	0.013	0.013	0.024
3	1.980	1.495	0.015	0.015	0.039	0.039	0.039	0.039	0.814
4	1.975	1.403	0.016	0.000	0.049	0.838	0.003	0.002	0.092
5	1.975	1.403	0.016	0.000	0.838	0.049	0.002	0.003	0.092
6	1.975	1.403	0.000	0.016	0.003	0.002	0.049	0.838	0.092
7	1.975	1.403	0.000	0.016	0.002	0.003	0.838	0.049	0.092
8	1.882	2.297	0.018	0.018	0.081	0.081	0.081	0.081	0.639
9	0.118	3.144	0.027	0.027	0.106	0.106	0.106	0.106	0.521
10	0.023	2.060	0.000	0.046	0.001	0.003	0.663	0.105	0.179
11	0.023	2.060	0.046	0.000	0.105	0.663	0.003	0.001	0.179
12	0.023	2.060	0.000	0.046	0.003	0.001	0.105	0.663	0.179
13	0.021	2.384	0.041	0.041	0.072	0.072	0.072	0.072	0.629
14	0.023	2.060	0.046	0.000	0.663	0.105	0.001	0.003	0.179
	Localized molecular orbitals (L = 11.5009)								
1	2.000	1.107	0.950	0.000	0.013	0.013	0.000	0.000	0.023
2	2.000	1.107	0.000	0.950	0.000	0.000	0.013	0.013	0.023
3	2.000	1.496	0.016	0.016	0.039	0.039	0.039	0.039	0.814
4	1.999	1.401	0.016	0.000	0.050	0.839	0.003	0.002	0.089
5	1.999	1.401	0.016	0.000	0.839	0.050	0.002	0.003	0.089
6	1.999	1.401	0.000	0.016	0.003	0.002	0.050	0.839	0.089
7	1.999	1.401	0.000	0.016	0.002	0.003	0.839	0.050	0.089
8	2.000	2.365	0.018	0.018	0.084	0.084	0.084	0.084	0.628

Results correspond to the standard STO-3G basis set.

calculations were performed at Hartree–Fock and full configuration interaction (FCI) levels, although the frozen core approximation, in which the two lowest-lying molecular orbitals are constrained to remain doubly-occupied in all configurations, was used for the C_2H_4 systems. The overlap integrals over ELF regions, required for this type of calculations, have been obtained from a modified version of the ToPMoD program.[50] The results have been gathered in Tables 1–8, in which the reported occupation numbers n_i and v_i are the sums of their corresponding spin orbitals, $n_i = n_{i\alpha} + n_{i\beta}$ and $v_i = v_{i\alpha} + v_{i\beta}$ respectively, to highlight the double, single or unoccupied character of the corresponding orbital. However, the orbital populations of the basins $\Omega_{C(X)}$, $\Omega_{V(X_1,X_2)}$, and $\Omega_{V(X)}$ are referred to a spin orbital α or β. These Tables allow one to compare suitably the results arising from the correlated and uncorrelated treatments as well as the localization effects produced by the isopycnic transformations.

For the HF molecule the partitioning of the 3D space, according to the ELF analysis, provides one monosynaptic core basin $\Omega_{C(F)}$ and one monosynaptic lone pair basin $\Omega_{V(F)}$, both associated with the F atom, as well as one disynaptic basin $\Omega_{V(F,H)}$ standing for the F−H bond, which becomes a monosynaptic valence basin $\Omega_{V(H)}$ at the stretched geometry. The interpretation of the localized molecular and natural orbitals can be performed by considering their relevant populations in the ELF basins which, as mentioned above, have a clear chemical meaning. At the equilibrium geometry, the sets of localized molecular orbitals and the five most occupied localized natural orbitals describe one core orbital and three lone-pair orbitals, all of them localized on the F atom, and one σ-bonding orbital, which are shown in Figure 1. As can be observed in Table 1, the orbital populations in the core $\Omega_{C(F)}$ basin are very similar in both correlated and uncorrelated treatments. In the case of the orbital $i = 1$, which has the highest population in the $\Omega_{C(F)}$ basin, the low values of the L_1^{-1} quantity point out a narrow distribution of this orbital into the ELF basins. However, in the

TABLE 7 Orbital occupation numbers (n_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $C_2H_4(^1A_1)$ molecule at twisted geometry (C_{2v} at 90°) from experimental one

i	n_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega_{V(C_1,C_2)}$	$\Omega^{sb}_{V(C_1)}$	$\Omega^{sb}_{V(C_2)}$
	Canonical natural orbitals (L = 4.0603)										
1	2.000	2.255	0.469	0.473	0.007	0.007	0.007	0.007	0.016	0.008	0.008
2	2.000	2.257	0.472	0.468	0.007	0.007	0.007	0.007	0.016	0.008	0.008
3	1.981	2.832	0.017	0.017	0.051	0.051	0.051	0.051	0.569	0.097	0.097
4	1.975	5.224	0.010	0.010	0.215	0.215	0.215	0.215	0.010	0.055	0.055
5	1.974	5.484	0.011	0.011	0.208	0.208	0.208	0.208	0.084	0.030	0.030
6	1.972	5.486	0.009	0.009	0.203	0.203	0.213	0.213	0.084	0.033	0.033
7	1.972	5.486	0.009	0.009	0.213	0.213	0.203	0.203	0.084	0.033	0.033
8	1.000	6.385	0.020	0.020	0.094	0.094	0.094	0.094	0.126	0.229	0.229
9	1.000	6.385	0.020	0.020	0.094	0.094	0.094	0.094	0.126	0.229	0.229
10	0.029	6.769	0.015	0.015	0.176	0.176	0.176	0.176	0.078	0.092	0.092
11	0.027	5.395	0.018	0.018	0.211	0.212	0.212	0.212	0.009	0.054	0.054
12	0.023	6.409	0.030	0.025	0.199	0.199	0.168	0.168	0.122	0.045	0.042
13	0.023	6.409	0.025	0.030	0.168	0.168	0.199	0.199	0.122	0.042	0.045
14	0.018	5.879	0.049	0.049	0.112	0.112	0.112	0.112	0.327	0.064	0.064

i	n_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega^{sb}_{V(C_1,C_2)}$
	Canonical molecular orbitals (L = 4.9812)								
1	2.000	2.268	0.470	0.468	0.011	0.011	0.010	0.010	0.020
2	2.000	2.248	0.470	0.472	0.010	0.010	0.010	0.010	0.017
3	2.000	1.949	0.017	0.017	0.066	0.066	0.066	0.066	0.704
4	1.999	4.882	0.009	0.009	0.221	0.221	0.221	0.221	0.098
5	1.999	4.531	0.009	0.009	0.234	0.234	0.234	0.234	0.048
6	1.999	4.514	0.011	0.011	0.234	0.234	0.234	0.234	0.041
7	1.999	4.409	0.011	0.011	0.238	0.238	0.238	0.238	0.027
8	2.000	4.564	0.020	0.020	0.151	0.151	0.151	0.151	0.357

Results correspond to the standard STO-3G basis set.

case of the canonical orbital $i = 2$ the correlated treatment predicts a 0.907 value for the $\Omega_{V(F)}$ basin population, which states a markedly higher localization than in the uncorrelated case in which the population of this orbital is distributed into the $\Omega_{V(F,H)}$ and $\Omega_{V(F)}$ basins with values 0.221 and 0.753, respectively. The isopycnic transformation further increases the localization of this orbital yielding values 0.968 and 0.967 for the $\Omega_{V(F)}$ basin within the correlated and uncorrelated approaches, respectively. The orbital $i = 5$ also undergoes important changes in the L_5^{-1} value; the electronic correlation effect itself as well as the isopycnic localization procedure produce a wider distribution of this orbital between the basins $\Omega_{V(F,H)}$ and $\Omega_{V(F)}$. The remainders of the most occupied orbitals do not present significant population changes within these treatments. We have also studied this molecule in a stretched geometry in which a higher static electron correlation[54] is expected. The uncorrelated treatments are not able to describe the bond breaking; the σ-bonding orbital is also present at this stretched geometry, as shown in Figure 2. However, in the correlated treatment, the σ-bonding doubly occupied orbital of the HF molecule is transformed into one s-like and one p-like singly occupied orbitals which, after the localization procedure, turn out to be centered on the H atom and on the F atom, respectively. As can be seen in Table 2, the uncorrelated treatments yield population values 0.322 and 0.654 for the canonical molecular orbital $i = 5$ in the $\Omega_{V(H)}$ and $\Omega_{V(F)}$ basins, respectively, while in the correlated one the canonical orbital $i = 6$ possesses a considerable occupation number and both orbitals ($i = 5$ and $i = 6$) are distributed between the basins $\Omega_{V(H)}$ and $\Omega_{V(F)}$. In the correlated treatment, the orbital population is highly localized after the isopycnic localization procedure, with values of 0.996 for the orbital $i = 5$ and 0.959 for the $i = 6$ one in the basins $\Omega_{V(H)}$ and $\Omega_{V(F)}$, respectively. Obviously, these situations require the use of more than one Slater determinant to formulate the N-electron wave function, which is characteristic of systems possessing high static electron correlation.

TABLE 8 Orbital occupation numbers (ν_i), effective number of basins (L_i^{-1}), and orbital populations of core (C) and valence (V) regions arising from ELF approach for the $C_2H_4(^1A_1)$ molecule at twisted geometry (C_{2v} at 90°) from experimental one

						Localized natural orbitals (L = 10.0879)					
i	ν_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega_{V(C_1,C_2)}$	$\Omega_{V(C_1)}^{sb}$	$\Omega_{V(C_2)}^{sb}$
1	2.000	1.1090	0.0000	0.9493	0.0001	0.0001	0.0120	0.0120	0.0134	0.0002	0.0129
2	2.000	1.1090	0.9493	0.0000	0.0120	0.0120	0.0001	0.0001	0.0134	0.0129	0.0002
3	1.980	2.2613	0.0156	0.0156	0.0394	0.0394	0.0394	0.0394	0.6500	0.0806	0.0806
4	1.951	1.4379	0.0155	0.0001	0.0430	0.8289	0.0005	0.0005	0.0364	0.0706	0.0038
5	1.951	1.4380	0.0001	0.0155	0.0005	0.0005	0.0430	0.8288	0.0364	0.0038	0.0706
6	1.951	1.4380	0.0001	0.0155	0.0005	0.0005	0.8288	0.0430	0.0364	0.0038	0.0706
7	1.951	1.4380	0.0155	0.0001	0.8288	0.0430	0.0005	0.0005	0.0364	0.0706	0.0038
8	1.042	3.3742	0.0009	0.0402	0.0124	0.0124	0.1470	0.1470	0.1590	0.0056	0.4753
9	1.042	3.3745	0.0402	0.0009	0.1470	0.1470	0.0124	0.0124	0.1590	0.4752	0.0056
10	0.027	2.2450	0.0008	0.0457	0.0017	0.0017	0.6410	0.0826	0.0855	0.0043	0.1353
11	0.027	2.2450	0.0457	0.0008	0.6410	0.0826	0.0017	0.0017	0.0855	0.1353	0.0043
12	0.027	2.2449	0.0457	0.0008	0.0826	0.6410	0.0017	0.0017	0.0855	0.1353	0.0043
13	0.027	2.2450	0.0008	0.0457	0.0017	0.0017	0.0826	0.6410	0.0855	0.0043	0.1353
14	0.019	4.6504	0.0446	0.0446	0.0753	0.0753	0.0753	0.0753	0.4106	0.0994	0.0994

					Localized molecular orbitals (L = 11.2268)				
i	ν_i	L_i^{-1}	$\Omega_{C(C_1)}$	$\Omega_{C(C_2)}$	$\Omega_{V(H_1,C_1)}$	$\Omega_{V(H_2,C_1)}$	$\Omega_{V(H_3,C_2)}$	$\Omega_{V(H_4,C_2)}$	$\Omega_{V(C_1,C_2)}^{sb}$
1	2.000	1.111	0.000	0.948	0.000	0.000	0.017	0.017	0.017
2	2.000	1.111	0.948	0.000	0.017	0.017	0.000	0.000	0.017
3	2.000	1.851	0.016	0.016	0.061	0.061	0.061	0.061	0.724
4	1.999	1.310	0.016	0.000	0.060	0.870	0.003	0.002	0.047
5	1.999	1.310	0.000	0.016	0.003	0.002	0.060	0.870	0.047
6	1.999	1.310	0.000	0.016	0.002	0.003	0.870	0.060	0.047
7	1.999	1.310	0.016	0.000	0.870	0.060	0.002	0.003	0.047
8	2.000	4.481	0.019	0.019	0.149	0.149	0.149	0.149	0.365

Results correspond to the standard STO-3G basis set.

In Tables 3 and 4, we report results arising from this methodology for the H_2O molecule at equilibrium and symmetrically stretched geometries, respectively. As can be observed in these tables, among the basins provided by the ELF partitioning appear one core basin $\Omega_{C(O)}$ associated with the O atom and two valence basins $\Omega_{V(O,H_1)}$ and $\Omega_{V(O,H_2)}$ associated with the two O−H bonds at the equilibrium geometry, which are transformed into two monosynaptic valence basins $\Omega_{V(H_1)}$ and $\Omega_{V(H_2)}$ at the stretched geometry. Finally, we build one superbasin $\Omega_{V(O)}^{sb}$ resulting from the union of two lone pair basins centered on the O atom, to recover the σ/π separability of the orbitals resulting from the localization process. At the equilibrium geometry, the sets of localized molecular orbitals and the five most occupied localized natural orbitals correspond to one core orbital, one σ-type and one π-type lone-pair orbitals, all of them localized on the O atom, and two σ-bonding orbitals (O–H), which are shown in Figure 3. At this geometry, the population of the orbital $i = 1$ is almost totally contained in the basin $\Omega_{C(O)}$ for all the methods reported in Table 3, which also provide similar values of the L_1^{-1} quantity. However, the population of the orbital $i = 2$ undergoes important changes depending on the procedure used; the correlated treatment and the isopycnic transformations increase the values of its population on the superbasin $\Omega_{V(O)}^{sb}$. The orbital $i = 3$ shows identical L_3^{-1} value for all the methods described, and its orbital population is also concentrated on that superbasin. The correlated treatment produces a slightly wider distribution of the canonical orbital $i = 4$ between the basins $\Omega_{V(O,H_1)}$, $\Omega_{V(O,H_2)}$, and $\Omega_{V(O)}^{sb}$ than the uncorrelated one. For the canonical orbital $i = 5$ the populations in these basins are nearly identical for both treatments. However, the isopycnic transformation at correlated and uncorrelated levels shows that the orbitals $i = 4$ and $i = 5$ turn out to be equivalent, in agreement with the genuine structure of the H_2O molecule. For the stretched H_2O molecule, the set of the seven most occupied localized natural orbitals describe one core orbital, one s-like and three p-like orbitals, all of them localized on the O atom, and two s-like orbitals localized on the H atoms, which are shown in Figure 4. A survey of
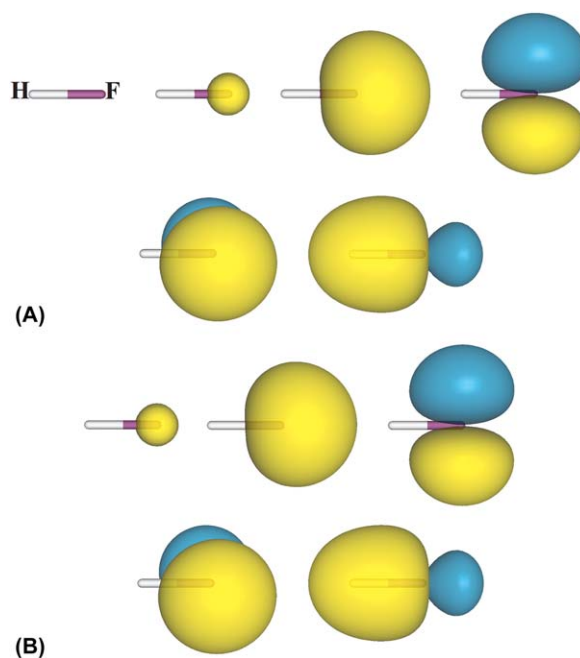
FIGURE 1 Isosurfaces of the localized molecular and five most occupied natural orbitals for the HF molecule at equilibrium geometry. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ± 0.1 a.u. The geometry of the molecule is specified in Table 1. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(F)}$, $\Omega_{V(F,H)}$, and $\Omega_{V(F)}$

the numerical values in Table 4 shows a considerable decrease of the occupation numbers of the p-like orbitals $i = 4$ and $i = 5$ (centered on the O atom), along with the increase of those of the s-like orbitals $i = 6$ and $i = 7$ (centered on the H atoms) in the localized correlated treatment, with respect to its counterpart values at the equilibrium geometry. This effect has already been observed in the results of the HF molecule, but it is more marked in the current system. Again, the isopycnic transformation treatment shows that the $i = 6$ and $i = 7$ orbitals become equivalent in accordance with the molecular symmetry. Obviously, the Hartree–Fock treatments present shortcomings to describe suitably this stretched molecule, while the localization treatment at correlated level provides the most chemically meaningful description for both geometries.

Tables 5 and 6 show results for the ethylene molecule in its equilibrium experimental geometry $C_2H_4(^1A_g)$, arising from the canonical (natural and molecular) and localized (natural and molecular) orbitals, respectively. Our treatment provides one core basin $\Omega_{C(C)}$ associated with each C atom (C_1 and C_2), four disynaptic valence basins of type $\Omega_{V(H,C)}$ which describe the bonds of each C atom with two H atoms, and one superbasin $\Omega_{V(C_1,C_2)}^{sb}$ obtained from the union of two equivalent disynaptic basins corresponding to the bond C_1-C_2 to preserve the σ/π separability in the localization process. The results presented in Table 5 exhibit much higher values of the L_i^{-1} indices than those found in the previous systems. These values point out a wide distribution of the canonical orbital populations into the ELF basins, at both correlated and uncorrelated treatments. In contrast with these results, the isopycnic transformation causes a high increase of the L quantities, as well as a drastic decrease of the L_i^{-1} ones, as is shown in Table 6, providing a clear chemical interpretation of the localized orbitals whose shapes have been represented in Figure 5. According to the results reported in Table 6, the orbitals $i = 1$ and $i = 2$ are of doubly occupied core type, each corresponding to one C atom, the orbital $i = 3$ describes a
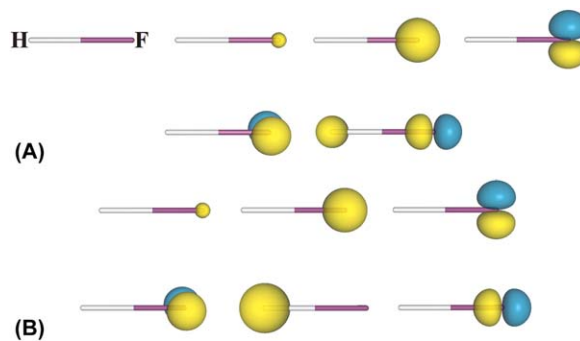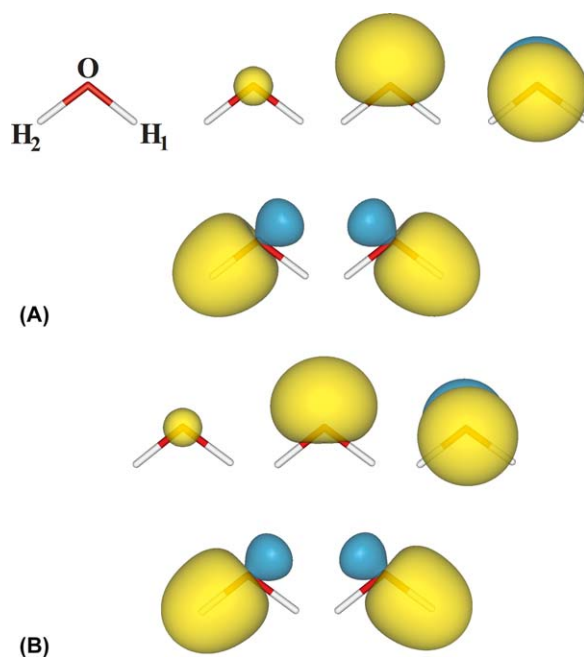

FIGURE 2 Isosurfaces of the localized molecular and six most occupied natural orbitals for the HF molecule at stretched geometry. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ± 0.1 a.u. The geometry of the molecule is specified in Table 2. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(F)}$, $\Omega_{V(H)}$, and $\Omega_{V(F)}$

FIGURE 3 Isosurfaces of the localized molecular and five most occupied natural orbitals for the H_2O molecule at equilibrium geometry. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ± 0.1 a.u. The geometry of the molecule is specified in Table 3. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(O)}$, $\Omega_{V(O,H_1)}$, $\Omega_{V(O,H_2)}$, and $\Omega_{V(O)}^{sb}$

σ-type bond between both C atoms, the orbitals $i = 4$, $i = 5$, $i = 6$, and $i = 7$ stand for the four σ-type C$-$H bonds, and the orbital $i = 8$ describes the π-type bond C_1-C_2.

We have also studied the ethylene molecule in a 90° twisted geometry from the equilibrium one, to know the ability of this methodology to describe the breaking of the π-type bond between the two C atoms. The results are reported in Table 7 for canonical (molecular and natural) orbitals and in Table 8 for localized (molecular and natural) orbitals. As can be observed in Table 7 the Hartree–Fock treatment predicts similar basins for this twisted geometry than for the equilibrium one. However, in the correlated treatment the superbasin $\Omega_{V(C_1,C_2)}^{sb}$ is substituted by one valence basin $\Omega_{V(C_1,C_2)}$ and two monosynaptic valence superbasins $\Omega_{V(C_1)}^{sb}$ and $\Omega_{V(C_2)}^{sb}$ which represent the fragments of the π-type bond broken by the torsion of 90°. These results show that the breaking of the π-type bond can only be explained within the correlated framework. The decrease of one unit in the n_8 value and the increase of one unit in the n_9 one in the correlated results with respect to the uncorrelated ones confirm this interpretation. The results from the localized treatment reported in Table 8 present an identical performance in relation to the breaking of π-type bond, although their L_i^{-1} values are lower, which is a consequence of their higher localization. In Figure 6, we show the shape of the resulting localized orbitals which provide a well-known chemical description of this system.
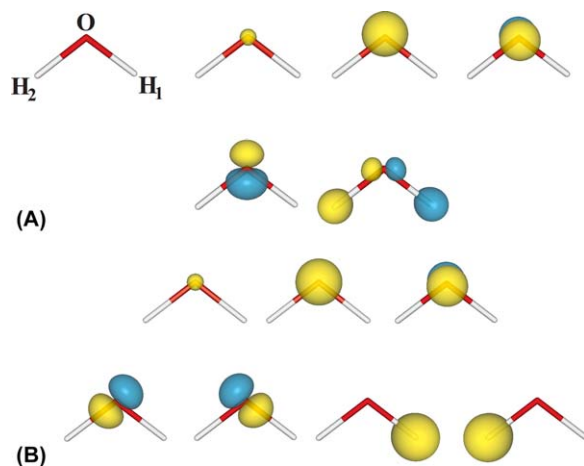

FIGURE 4 Isosurfaces of the localized molecular and seven most occupied natural orbitals for the H_2O molecule at stretched geometry. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ± 0.1 a.u. The geometry of the molecule is specified in Table 4. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(O)}$, $\Omega_{V(H_1)}$, $\Omega_{V(H_2)}$, and $\Omega_{V(O)}^{sb}$
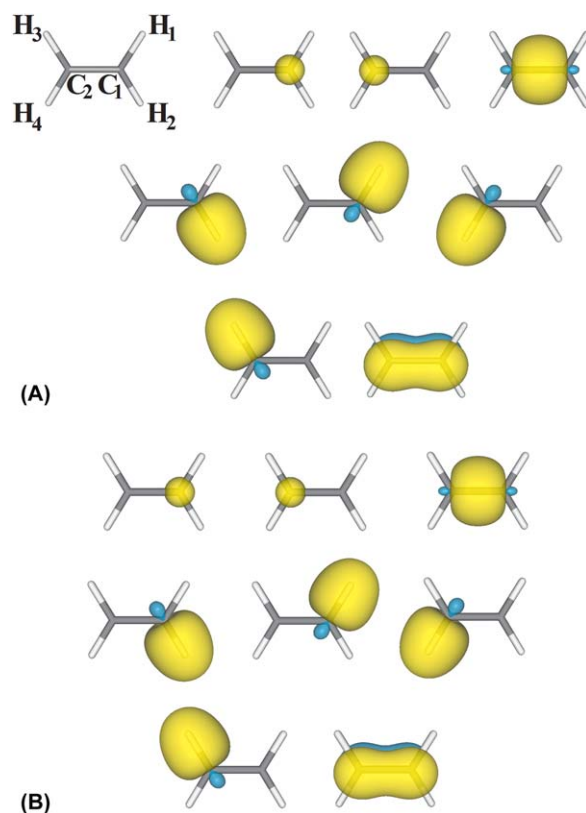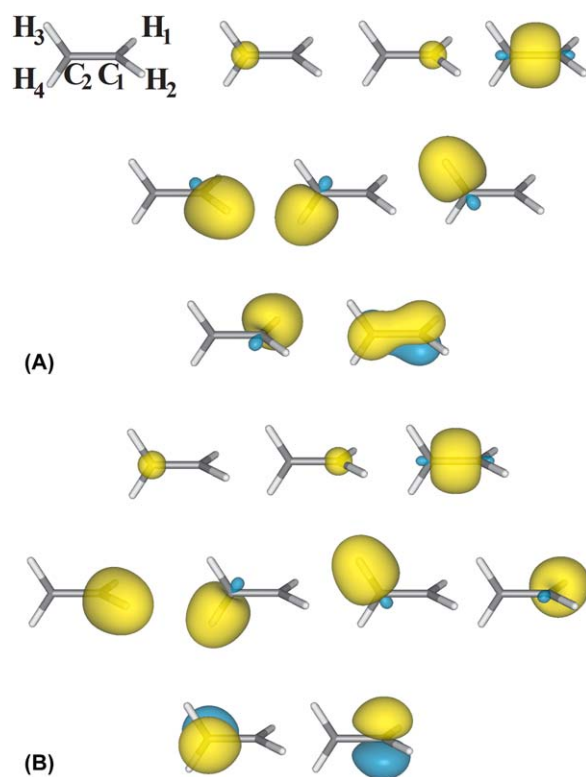
FIGURE 5   Isosurfaces of the localized molecular and eight most occupied natural orbitals for the $C_2H_4(^1A_g)$ molecule at equilibrium experimental geometry. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ±0.1 a.u. The geometry of the molecule is specified in Tables 5 and 6. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(C_1)}$, $\Omega_{C(C_2)}$, $\Omega_{V(H_1,C_1)}$, $\Omega_{V(H_2,C_1)}$, $\Omega_{V(H_3,C_2)}$, $\Omega_{V(H_4,C_2)}$, and $\Omega^{sb}_{V(C_1,C_2)}$

FIGURE 6   Isosurfaces of the localized molecular and nine most occupied natural orbitals for the $C_2H_4(^1A_1)$ molecule at twisted geometry (C_{2v} at 90º) from experimental one. Positive values are indicated in yellow and negative values in pastel blue. The isovalues are ±0.1 a.u. The geometry of the molecule is specified in Table 8. A, Hartree–Fock, B, FCI results. The ELF domains are $\Omega_{C(C_1)}$, $\Omega_{C(C_2)}$, $\Omega_{V(H_1,C_1)}$, $\Omega_{V(H_2,C_1)}$, $\Omega_{V(H_3,C_2)}$, $\Omega_{V(H_4,C_2)}$, and: A, $\Omega^{sb}_{V(C_1,C_2)}$, B, $\Omega_{V(C_1,C_2)}$, $\Omega^{sb}_{V(C_1)}$, $\Omega^{sb}_{V(C_2)}$

4 | CONCLUDING REMARKS

In this work, we have extended, at electronic correlation level, the procedure for localizing orbitals based on the partitioning of the physical space into basins arising from the ELF topological analysis. Within this correlated treatment, the basins have been obtained by approximating the second-order reduced density matrix elements in terms of the elements of the correlated first-order reduced density matrix, neglecting the contribution of the cumulant matrix. Numerical determinations have been performed in prototype systems, in equilibrium, stretched, and twisted geometries by means of the correlated and uncorrelated treatments. The results from both treatments are significantly different, mainly for system at nonequilibrium geometries, pointing out that our procedure constitutes a suitable method to localize orbitals in systems possessing strong correlation.

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