An Orbital Localization Criterion Based on the Theory of “Fuzzy” Atoms

DIEGO R. ALCOBA,[1] LUIS LAIN,[1] ALICIA TORRE,[1] ROBERTO C. BOCHICCHIO[2]
[1]*Departamento de Química Física, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain*
[2]*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina*

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Abstract: This work proposes a new procedure for localizing molecular and natural orbitals. The localization criterion presented here is based on the partitioning of the overlap matrix into atomic contributions within the theory of “fuzzy” atoms. Our approach has several advantages over other schemes: it is computationally inexpensive, preserves the σ/π-separability in planar systems and provides a straightforward interpretation of the resulting orbitals in terms of their localization indices and atomic occupancies. The corresponding algorithm has been implemented and its efficiency tested on selected molecular systems.

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Introduction

The procedures of orbital localization attempt to retrieve the classical Lewis–Linnett picture[1] of molecular systems from canonical molecular (natural) orbitals. Consequently, the localized orbitals arising from these procedures have become powerful tools for interpretation and description of molecular electronic structures providing the use of classical chemical concepts such as bonds, nonbonding electron pairs, core orbitals, valences, and so forth. Several methods of orbital localization are widely spread among chemists as those of Foster–Boys,[2] Edmiston–Ruedenberg,[3] von Niessen,[4] Magnasco–Perico,[5] Pipek–Mezey,[6] Weinhold et al.,[7] etc. (review articles of localization procedures can be found in refs. 8–11).

For a molecule with N electron, the Edmiston–Ruedenberg and von Niessen localization methods require approximately N^5 mathematical operations, while in the Foster–Boys localization the computational effort is proportional to N^3. An important drawback of these procedures is that in locally planar molecules, they lead to the so-called τ or banana orbitals rather than the σ and π ones[12] as expected. Another disadvantage of these methods is that they do not provide simple indices to quantify the extent of localization/delocalization and/or the atomic electron populations associated to the resulting orbitals. Other methods possessing the above-mentioned features like those of Weinhold (based on natural population analysis[13]) and Pipek–Mezey (arising from Mulliken population analysis[14]) turn out to be too much basis dependent, and have no well-defined basis sets limits. In the case of localization of Magnasco–Perico additional requirements like *a priori* definitions of bonds, lone pairs, and core orbitals have to be introduced, thus causing the resulting orbitals to be prescribed.

A different type of localization has been proposed by Cioslowski.[15,16] The procedure is based on partitioning the three-dimensional space into nonoverlapping atomic domains according to the theory of atoms in molecules (AIM).[17] This criterion, which uses isopycnic orbital transformations,[15] allows one to localize Hartree–Fock spin orbitals and natural spin orbitals, enabling the study of the electron correlation effects within a broad scope of the existing approximate methods of quantum chemistry. The localization method is computationally a N^3 procedure, preserves the σ/π-separability in planar systems and provides simple indices that allows one to quantify the localization/delocalization extent of the resulting orbitals as well as to calculate atomic electron populations for characterizing these orbitals. Despite these advantages, the procedure presents some difficulties related to both theoretical and practical aspects. On the one hand, it is computationally

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Correspondence to: D. R. Alcoba; e-mail: qfxaldad@lg.ehu.es

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very expensive because the partitioning of the three-dimensional space according to the AIM theory, which precedes localization of orbitals, requires the determination of Bader's atomic basins, which demands a high computational effort. On the other hand, there exist several molecular systems that present the so-called nonnuclear attractors,[18–20] that is, atomic domains that cannot be assigned to any nucleus composing the system, and therefore have not intutive chemical meaning. Thus, the interpretation of the localized orbitals resulting from the theory may run into difficulties.[16]

Recently, an alternative partitioning of the three-dimensional space based on the theory of "fuzzy" atoms[21–23] has been deeply studied.[24–28] This scheme, which renders a division of the three-dimensional space into atomic regions that have no sharp boundaries but show a continuous transition from one to another, has shown to be appropriate for describing atomic spatial regions with shared electrons, in agreement with the concept of chemical bonding.[24,26] Thus, the "fuzzy" atom procedure has successfully been applied to describe multicenter bond orders and other related quantities from population analysis,[24,26,28] including partitionings of molecular energy.[25,27] These results and the lower computational cost of the "fuzzy" atom approach in comparison with the AIM treatment indicate that this methodology could be used as a reliable and cost-competitive technique within the localization criteria. In this scenario the aim of this article is to propose and study the capabilities of a new localization algorithm based on this methodology. The procedure, whose algorithmic behavior is of N^3 type, preserves the σ/π-separability in planar systems and allows one a straightforward interpretation of the resulting orbitals in terms of their localization indices and atomic occupancies.

This article is organized as follows. In the second section the existing localization criteria are briefly summarized by repeating and extending somewhat the review given in ref. 15 to perform a suitable comparison with the proposed method. The localization functional of the new procedure and the associated indices and occupancies are described in the third section. In the fourth section we report the computational details and the results obtained in selected systems as well as a comparison with those arising from Cioslowski localization method. Finally, some remarks and conclusions are presented in the last section.

Review of Existing Localization Criteria

As has been reported,[15] localization of canonical molecular orbitals is equivalent to find a unitary transformation matrix $\underline{U}$ that maximizes the localization sum

$$L = \sum_{i} \sum_{klmn} U_{ik}^{*} U_{il} U_{im}^{*} U_{in} T_{klmn} . \tag{1}$$

This is usually achieved throughout 2 × 2 consecutive rotations[29] or by a second-order maximization procedure.[30] The tensor $\underline{T}$ defines the localization procedure. Let us briefly summarize the most widely used choices for $\underline{T}$. The Edmiston–Ruedenberg (ER) procedure chooses the tensor as

$$T_{klmn}^{ER} = \langle km | r_{12}^{-1} | ln \rangle, \tag{2}$$

where $\langle km | r_{12}^{-1} | ln \rangle$ stands for the two-electron repulsion integrals, which yields maximization of the self-repulsion energy. The Foster–Boys (FB) criterion is defined by the tensor

$$T_{klmn}^{FB} = -\langle k | \mathbf{r} | l \rangle \cdot \langle m | \mathbf{r} | n \rangle, \tag{3}$$

which yields maximization of the sum of the squares of distances of orbital centroids from the origin of the coordinate system. The von Niessen (VN) criterion, which seeks maximization of a self-charge density overlap functional, is defined by means of the tensor

$$T_{klmn}^{VN} = \langle km | \delta(\mathbf{r_1} - \mathbf{r_2}) | ln \rangle, \tag{4}$$

where $\delta(\mathbf{r_1} - \mathbf{r_2})$ is the Dirac delta function. The localization procedure of Pipek–Mezey (PM) is based on the tensor

$$T_{klmn}^{PM} = \sum_{A} \langle k | \mathbf{P}_A | l \rangle \langle m | \mathbf{P}_A | n \rangle \tag{5}$$

where $\mathbf{P}_A$ projects a given orbital onto the space of atomic orbitals centered at atom A, and seeks maximization of a gross atomic Mulliken based charge-density overlap functional.

In this work we are interested in the Cioslowski localization criterion. In this procedure the tensor $\underline{T}$ is defined through the AIM theory. As is well known, this theory carries out a partitioning of the physical space based on the topological properties of the electron density function. The whole three-dimensional space is divided into disjunct atomic basins Ω_A, which are defined by surfaces having zero flux in the gradient vector field of the electron density. These atomic basins let one express the Kronecker deltas as

$$\delta_{ij} = \langle i | j \rangle = \sum_{\Omega_A} \langle i | j \rangle_{\Omega_A} \tag{6}$$

in which $\langle i | j \rangle$ are the standard overlap integrals (where the integration is performed over the total space) and $\langle i | j \rangle_{\Omega_A}$ are the overlap integrals over the Bader atomic domains Ω_A (where the integration is limited to this kind of domains).

Although the quantity $\langle i | i \rangle_{\Omega_A}$ defines the atomic population (occupancy) of the ith spin orbital on the atomic region Ω_A, the quantity

$$L_i = \sum_{\Omega_A} \langle i | i \rangle_{\Omega_A} \langle i | i \rangle_{\Omega_A} \tag{7}$$

is the *localization index* of the ith spin orbital and its inverse, L_i^{-1}, is equal to the effective number of atoms spanned by the ith spin orbital.[16] Thus, within this procedure the tensor $\underline{T}$ is defined as

$$T_{klmn}^{AIM} = \sum_{\Omega_A} \langle k | l \rangle_{\Omega_A} \langle m | n \rangle_{\Omega_A}, \tag{8}$$

which yields maximization of the AIM charge-density overlap functional.

Localization of natural spin orbitals arising from arbitrary wave functions requires a different treatment than that of eq. (1). In this case the localization index may be reformulated as[15]

$$L = \sum_i \sum_{klmn} \nu_i^2 \; C_{ik}^* C_{il} C_{im}^* C_{in} T_{klmn} \tag{9}$$

or, equivalently,

$$L = \sum_i \sum_{klmn} (n_k n_l n_n n_m)^{1/2} \; U_{ik}^* U_{il} U_{im}^* U_{in} T_{klmn} \tag{10}$$

where the matrix $\underline{C}$, which is defined as

$$C_{ij} = U_{ij} \; (n_j/\nu_i)^{1/2}, \tag{11}$$

describes an isopycnic orbital linear transformation[15]

$$\phi_i(r) = \sum_j C_{ij} \psi_j(r) \tag{12}$$

relating the localized nonorthogonal spin orbitals $\phi_i(r)$ to the canonical ones $\psi_j(r)$ that leaves the first-order reduced density matrix ${}^1D$ invariant, rather than the wave function itself, that is,

$${}^1D(r|r') = \sum_i n_i \psi_i^*(r)\psi_i(r') = \sum_k \nu_k \phi_k^*(r)\phi_k(r') \tag{13}$$

where ν_i and n_i, which are related by

$$\nu_i = \sum_j n_j \; U_{ij}^* \; U_{ij}, \tag{14}$$

are the occupation numbers of the isopycnic-related and canonical natural spin orbitals of the first-order reduced density matrix corresponding to the system under study, respectively. As has been mentioned in the Introduction, this formulation allows one to study the electron correlation effects within a broad scope of the existing approximate methods of quantum chemistry.

Localization Criterion Based on the Theory of "Fuzzy" Atoms

In the AIM theory each basin Ω_A is generally associated with a determined nucleus (or nuclear attractor) A. Hence, the appearance of nonnuclear attractors implies that the atoms and the basins cannot be put into one-to-one correspondence with each other.[18] Consequently, in studies of orbital localization carried out within the framework of AIM theory the interpretation of the resulting orbitals does not result obvious and special treatments would be required to retrieve chemically useful quantities. Moreover, even in those molecular systems where the one-to-one correspondence is fulfilled, the partitioning according to the AIM theory is extremely expensive computationally because of the complex shape of the Bader's atomic domains Ω_A.

An alternative partitioning of the ordinary three-dimensional space may be carried out following a "fuzzy" atom approach.[21–28] According to the mathematical framework of this technique, a nonnegative continuous weight function $w_A(\mathbf{r})$ is introduced for each atom A. These weight functions, which are mutually overlapping, measure the degree in which a determined point of space, $\mathbf{r}$, is considered to belong to atom A and fulfill the conditions

$$w_A(\mathbf{r}) \geq 0 \tag{15}$$

and

$$\sum_A w_A(\mathbf{r}) = 1. \tag{16}$$

Consequently, there are not any sharp boundaries between the atomic regions $A, B, \ldots$ but a continuous transition from one to another. Obviously, the AIM formalism can be regarded as a particular case of the "fuzzy" atom approach in which all the $w_A(\mathbf{r})$ are zero or one. Using these tools, the Kronecker deltas can be expressed as

$$\delta_{ij} = \langle i|j\rangle = \sum_A \langle i|w_A(\mathbf{r})|j\rangle \tag{17}$$

which requires one to carry out a numerical integration for evaluating the $\langle i|w_A(\mathbf{r})|j\rangle$ integrals. This partitioning allows one to identify the quantity $\langle i|w_A(\mathbf{r})|i\rangle$ as the atomic population (occupancy) of the ith spin orbital on the atom A, the quantity

$$L_i = \sum_A \langle i|w_A(\mathbf{r})|i\rangle\langle i|w_A(\mathbf{r})|i\rangle \tag{18}$$

as the *localization index* of the ith spin orbital and its inverse, L_i^{-1}, as the effective number of atoms spanned by the ith spin orbital.

Taking the above observations into account, we put forward a new localization scheme with

$$L = \sum_i \sum_{klmn} \nu_i^2 \; C_{ik}^* C_{il} C_{im}^* C_{in} T_{klmn}^{FA} \tag{19}$$

and

$$T_{klmn}^{FA} = \sum_A \langle k|w_A(\mathbf{r})|l\rangle\langle m|w_A(\mathbf{r})|n\rangle \tag{20}$$

where *FA* stands for "fuzzy" atoms.

The above functional, which yields maximization of the "fuzzy" atom charge-density overlap functional, is invariant with respect to rotations and translations of the molecular coordinate system. Moreover, the tensor $\underline{T}$ retains the simplicity of Cioslowski localization scheme and does not invoke any reference to basis sets (unlike Pipek–Mezey and Weinhold localizations) or external criteria (unlike Magnasco–Perico localization). As the calculation of

Table 1. Results for the H_2O Molecule ($R_{O—H} = 0.9431$ Å, $\widehat{HOH} = 106° 2' 38''$) within "Fuzzy" Atom and AIM Approaches.

"Fuzzy" atom approach

	Canonical molecular orbitals ($L = 7.7892$)					Localized molecular orbitals ($L = 8.0513$)				
i	n_i	L_i^{-1}	$\langle i\|w_O\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$	ν_i	L_i^{-1}	$\langle i\|w_O\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$
1	2.0000	1.0000	1.0000	0.0000	0.0000	2.0000	1.0000	1.0000	0.0000	0.0000
2	2.0000	1.3740	0.8461	0.0769	0.0769	2.0000	1.0308	0.9849	0.0076	0.0076
3	2.0000	1.0856	0.9593	0.0203	0.0203	2.0000	1.0856	0.9593	0.0203	0.0203
4	2.0000	1.3317	0.8610	0.0695	0.0695	2.0000	1.7630	0.6918	0.2975	0.0107
5	2.0000	2.0213	0.6614	0.1693	0.1693	2.0000	1.7630	0.6918	0.0107	0.2975

AIM approach

	Canonical molecular orbitals ($L = 8.6503$)					Localized molecular orbitals ($L = 8.7422$)				
i	n_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_O}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_O}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$
1	2.0000	1.0000	1.0000	0.0000	0.0000	2.0000	1.0000	1.0000	0.0000	0.0000
2	2.0000	1.0846	0.9598	0.0201	0.0201	2.0000	1.0085	0.9958	0.0021	0.0021
3	2.0000	1.0227	0.9888	0.0056	0.0056	2.0000	1.0192	0.9905	0.0047	0.0047
4	2.0000	1.3199	0.8652	0.0674	0.0674	2.0000	1.4303	0.8166	0.1799	0.0036
5	2.0000	1.6031	0.7734	0.1133	0.1133	2.0000	1.4303	0.8166	0.0036	0.1799

Table 2. Results for the LiF Molecule ($R_{Li—F} = 1.5543$ Å) within "Fuzzy" Atom and AIM Approaches.

"Fuzzy" atom approach

	Canonical molecular orbitals ($L = 11.5469$)				Localized molecular orbitals ($L = 11.5792$)			
i	n_i	L_i^{-1}	$\langle i\|w_{Li}\|i\rangle$	$\langle i\|w_F\|i\rangle$	ν_i	L_i^{-1}	$\langle i\|w_{Li}\|i\rangle$	$\langle i\|w_F\|i\rangle$
1	2.0000	1.0000	0.0000	1.0000	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0380	0.9814	0.0186	2.0000	1.0302	0.9851	0.0148
3	2.0000	1.0264	0.0130	0.9870	2.0000	1.0015	0.0007	0.9993
4	2.0000	1.0877	0.0421	0.9579	2.0000	1.1063	0.0506	0.9494
5	2.0000	1.0436	0.0214	0.9786	2.0000	1.0436	0.0214	0.9786
6	2.0000	1.0436	0.0214	0.9786	2.0000	1.0436	0.0214	0.9786

AIM approach

	Canonical molecular orbitals ($L = 11.7586$)				Localized molecular orbitals ($L = 11.7917$)			
i	n_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_{Li}}$	$\langle i\|i\rangle_{\Omega_F}$	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_{Li}}$	$\langle i\|i\rangle_{\Omega_F}$
1	2.0000	1.0000	0.0000	1.0000	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0246	0.9879	0.0121	2.0000	1.0161	0.9920	0.0080
3	2.0000	1.0125	0.0062	0.9938	2.0000	1.0004	0.0002	0.9998
4	2.0000	1.0493	0.0241	0.9759	2.0000	1.0531	0.0259	0.9741
5	2.0000	1.0191	0.0095	0.9905	2.0000	1.0191	0.0095	0.9905
6	2.0000	1.0191	0.0095	0.9905	2.0000	1.0191	0.0095	0.9905

Table 3. Results for the N_2 Molecule ($R_{N—N} = 1.0784$ Å) within "Fuzzy" Atom and AIM Approaches.

"Fuzzy" atom approach

	Canonical molecular orbitals ($L = 7.0000$)				Localized molecular orbitals ($L = 10.8975$)			
i	n_i	L_i^{-1}	$\langle i \vert w_{N_1} \vert i\rangle$	$\langle i \vert w_{N_2} \vert i\rangle$	ν_i	L_i^{-1}	$\langle i \vert w_{N_1} \vert i\rangle$	$\langle i \vert w_{N_2} \vert i\rangle$
1	2.0000	2.0000	0.5000	0.5000	2.00000	1.0006	0.9997	0.0003
2	2.0000	2.0000	0.5000	0.5000	2.00000	1.0006	0.0003	0.9997
3	2.0000	2.0000	0.5000	0.5000	2.00000	2.0000	0.5000	0.5000
4	2.0000	2.0000	0.5000	0.5000	2.00000	1.0258	0.0127	0.9873
5	2.0000	2.0000	0.5000	0.5000	2.00000	1.0258	0.9873	0.0127
6	2.0000	2.0000	0.5000	0.5000	2.00000	2.0000	0.5000	0.5000
7	2.0000	2.0000	0.5000	0.5000	2.00000	2.0000	0.5000	0.5000

AIM approach

	Canonical molecular orbitals ($L = 7.0000$)				Localized molecular orbitals ($L = 10.9627$)			
i	n_i	L_i^{-1}	$\langle i \vert i\rangle_{\Omega_{N_1}}$	$\langle i \vert i\rangle_{\Omega_{N_2}}$	ν_i	L_i^{-1}	$\langle i \vert i\rangle_{\Omega_{N_1}}$	$\langle i \vert i\rangle_{\Omega_{N_2}}$
1	2.0000	2.0000	0.5000	0.5000	2.0000	1.0000	1.0000	0.0000
2	2.0000	2.0000	0.5000	0.5000	2.0000	1.0000	0.0000	1.0000
3	2.0000	2.0000	0.5000	0.5000	2.0000	2.0000	0.5000	0.5000
4	2.0000	2.0000	0.5000	0.5000	2.0000	1.0094	0.0047	0.9953
5	2.0000	2.0000	0.5000	0.5000	2.0000	1.0094	0.9953	0.0047
6	2.0000	2.0000	0.5000	0.5000	2.0000	2.0000	0.5000	0.5000
7	2.0000	2.0000	0.5000	0.5000	2.0000	2.0000	0.5000	0.5000

Table 4. Results for the CO molecule ($R_{C—O} = 1.1138$ Å) within "Fuzzy" Atom and AIM Approaches.

"Fuzzy" atom approach

	Canonical molecular orbitals ($L = 11.5365$)				Localized molecular orbitals ($L = 12.1315$)			
i	n_i	L_i^{-1}	$\langle i \vert w_C \vert i\rangle$	$\langle i \vert w_O \vert i\rangle$	ν_i	L_i^{-1}	$\langle i \vert w_C \vert i\rangle$	$\langle i \vert w_O \vert i\rangle$
1	2.0000	1.0000	0.0000	1.0000	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0139	0.9931	0.0069	2.0000	1.0124	0.9938	0.0062
3	2.0000	1.2453	0.1107	0.8892	2.0000	1.0016	0.0008	0.9992
4	2.0000	1.3174	0.1401	0.8599	2.0000	1.3735	0.1623	0.8377
5	2.0000	1.3372	0.1480	0.8520	2.0000	1.1684	0.9218	0.0781
6	2.0000	1.3372	0.1480	0.8520	2.0000	1.3372	0.1480	0.8520
7	2.0000	1.3809	0.8348	0.1651	2.0000	1.3372	0.1480	0.8520

AIM approach

	Canonical molecular orbitals ($L = 11.8915$)				Localized molecular orbitals ($L = 12.4914$)			
i	n_i	L_i^{-1}	$\langle i \vert i\rangle_{\Omega_C}$	$\langle i \vert i\rangle_{\Omega_O}$	ν_i	L_i^{-1}	$\langle i \vert i\rangle_{\Omega_C}$	$\langle i \vert i\rangle_{\Omega_O}$
1	2.0000	1.0000	0.0000	1.0000	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0063	0.9969	0.0031	2.0000	1.0047	0.9977	0.0023
3	2.0000	1.1524	0.0712	0.9288	2.0000	1.0003	0.0001	0.9999
4	2.0000	1.2718	0.1216	0.8784	2.0000	1.2289	0.1040	0.8961
5	2.0000	1.2893	0.1288	0.8712	2.0000	1.1291	0.9391	0.0609
6	2.0000	1.2893	0.1288	0.8712	2.0000	1.2893	0.1288	0.8712
7	2.0000	1.3393	0.8512	0.1488	2.0000	1.2893	0.1288	0.8712

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 “Fuzzy” Atom and AIM Approaches.

“Fuzzy” atom approach

Canonical molecular orbitals ($L = 5.1207$)

i	n_i	L_i^{-1}	$\langle i\|w_{C_1}\|i\rangle$	$\langle i\|w_{C_2}\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$	$\langle i\|w_{H_3}\|i\rangle$	$\langle i\|w_{H_4}\|i\rangle$
1	2.0000	2.0005	0.4999	0.4999	0.0000	0.0000	0.0000	0.0000
2	2.0000	2.0005	0.4999	0.4999	0.0000	0.0000	0.0000	0.0000
3	2.0000	2.8981	0.4105	0.4105	0.0447	0.0447	0.0447	0.0447
4	2.0000	5.0342	0.2699	0.2699	0.1150	0.1150	0.1150	0.1150
5	2.0000	5.2869	0.2533	0.2533	0.1233	0.1233	0.1233	0.1233
6	2.0000	4.0468	0.3304	0.3304	0.0848	0.0848	0.0848	0.0848
7	2.0000	5.9750	0.1821	0.1821	0.1589	0.1589	0.1589	0.1589
8	2.0000	2.4195	0.4534	0.4534	0.0233	0.0233	0.0233	0.0233

Localized molecular orbitals ($L = 9.5192$)

i	ν_i	L_i^{-1}	$\langle i\|w_{C_1}\|i\rangle$	$\langle i\|w_{C_2}\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$	$\langle i\|w_{H_3}\|i\rangle$	$\langle i\|w_{H_4}\|i\rangle$
1	2.0000	1.0006	0.9997	0.0002	0.0001	0.0001	0.0000	0.0000
2	2.0000	1.0006	0.0002	0.9997	0.0000	0.0000	0.0001	0.0001
3	2.0000	2.1232	0.4852	0.4852	0.0074	0.0074	0.0074	0.0074
4	2.0000	2.1316	0.4639	0.0166	0.5034	0.0125	0.0018	0.0018
5	2.0000	2.1316	0.4639	0.0166	0.0125	0.5034	0.0018	0.0017
6	2.0000	2.1316	0.0166	0.4639	0.0017	0.0018	0.5034	0.0125
7	2.0000	2.1316	0.0166	0.4639	0.0018	0.0017	0.0125	0.5034
8	2.0000	2.4195	0.4534	0.4534	0.0233	0.0233	0.0233	0.0233

AIM approach

Canonical molecular orbitals ($L = 5.2562$)

i	n_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_{C_1}}$	$\langle i\|i\rangle_{\Omega_{C_2}}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$	$\langle i\|i\rangle_{\Omega_{H_3}}$	$\langle i\|i\rangle_{\Omega_{H_4}}$
1	2.0000	2.0001	0.5000	0.5000	0.0000	0.0000	0.0000	0.0000
2	2.0000	2.0001	0.5000	0.5000	0.0000	0.0000	0.0000	0.0000
3	2.0000	2.7853	0.4199	0.4199	0.0401	0.0401	0.0401	0.0401
4	2.0000	3.8850	0.3406	0.3406	0.0797	0.0797	0.0797	0.0797
5	2.0000	4.7971	0.2847	0.2847	0.1077	0.1077	0.1077	0.1077
6	2.0000	5.1807	0.2604	0.2604	0.1198	0.1198	0.1198	0.1198
7	2.0000	5.9677	0.1840	0.1840	0.1580	0.1580	0.1580	0.1580
8	2.0000	2.2592	0.4700	0.4700	0.0150	0.0150	0.0150	0.0150

Localized molecular orbitals ($L = 9.6678$)

i	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_{C_1}}$	$\langle i\|i\rangle_{\Omega_{C_2}}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$	$\langle i\|i\rangle_{\Omega_{H_3}}$	$\langle i\|i\rangle_{\Omega_{H_4}}$
1	2.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	2.0000	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
3	2.0000	2.0929	0.4887	0.4887	0.0056	0.0056	0.0056	0.0056
4	2.0000	2.0904	0.4894	0.0110	0.4885	0.0083	0.0012	0.0016
5	2.0000	2.0904	0.4894	0.0110	0.0083	0.4885	0.0016	0.0012
6	2.0000	2.0904	0.0110	0.4894	0.0012	0.0016	0.4885	0.0083
7	2.0000	2.0904	0.0110	0.4894	0.0016	0.0012	0.0083	0.4885
8	2.0000	2.2592	0.4700	0.4700	0.0150	0.0150	0.0150	0.0150

Table 6. Results for the Li_2 Molecule ($R_{Li—Li} = 2.8070$ Å) within "Fuzzy" Atom and AIM Approaches.

"Fuzzy" atom approach

	Canonical molecular orbitals ($L = 2.9999$)				Localized molecular orbitals ($L = 4.9980$)			
i	n_i	L_i^{-1}	$\langle i\vert w_{Li_1}\vert i\rangle$	$\langle i\vert w_{Li_2}\vert i\rangle$	ν_i	L_i^{-1}	$\langle i\vert w_{Li_1}\vert i\rangle$	$\langle i\vert w_{Li_2}\vert i\rangle$
1	2.0000	2.0000	0.5000	0.5000	2.0000	1.0005	0.9998	0.0002
2	2.0000	2.0000	0.5000	0.5000	2.0000	1.0005	0.0002	0.9998
3	2.0000	2.0000	0.5000	0.5000	2.0000	2.0002	0.5000	0.5000

AIM approach

	Canonical molecular orbitals ($L = 2.8532$)					Localized molecular orbitals ($L = 4.8512$)				
i	n_i	L_i^{-1}	$\langle i\vert i\rangle_{\Omega_{Li_1}}$	$\langle i\vert i\rangle_{\Omega_{Li_2}}$	$\langle i\vert i\rangle_{\Omega}$	ν_i	L_i^{-1}	$\langle i\vert i\rangle_{\Omega_{Li_1}}$	$\langle i\vert i\rangle_{\Omega_{Li_2}}$	$\langle i\vert i\rangle_{\Omega}$
1	2.0000	2.0036	0.4996	0.4996	0.0009	2.0000	1.0014	0.9993	0.0000	0.0007
2	2.0000	2.0029	0.4996	0.4996	0.0007	2.0000	1.0014	0.0000	0.9993	0.0007
3	2.0000	2.3354	0.2076	0.2076	0.5848	2.0000	2.3342	0.2075	0.2075	0.5851

Ω, stands for the nonnuclear attractor region.

Table 7. Results for the H_2O Molecule ($R_{O—H} = 0.9431$ Å, $\widehat{HOH} = 106° 2' 38''$) within the "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 7.6607$)					Localized natural orbitals ($L = 7.9017$)				
i	n_i	L_i^{-1}	$\langle i\vert w_O\vert i\rangle$	$\langle i\vert w_{H_1}\vert i\rangle$	$\langle i\vert w_{H_2}\vert i\rangle$	ν_i	L_i^{-1}	$\langle i\vert w_O\vert i\rangle$	$\langle i\vert w_{H_1}\vert i\rangle$	$\langle i\vert w_{H_2}\vert i\rangle$
1	2.0000	1.0000	1.0000	0.0000	0.0000	2.0000	1.0000	1.0000	0.0000	0.0000
2	1.9866	1.1884	0.9154	0.0423	0.0423	1.9824	1.0317	0.9845	0.0078	0.0078
3	1.9755	1.0870	0.9587	0.0206	0.0206	1.9754	1.0869	0.9588	0.0206	0.0206
4	1.9712	1.5550	0.7878	0.1061	0.1061	1.9712	1.7651	0.6908	0.2987	0.0105
5	1.9696	2.0305	0.6591	0.1705	0.1705	1.9712	1.7651	0.6908	0.0105	0.2987
6	0.0221	2.4176	0.5647	0.2177	0.2177	0.0223	1.9436	0.3966	0.0056	0.5977
7	0.0203	2.4182	0.5646	0.2177	0.2177	0.0223	1.9436	0.3966	0.5977	0.0058
8	0.0147	1.2336	0.8974	0.0513	0.0513	0.0147	1.2427	0.8939	0.0530	0.0530
9	0.0101	1.2460	0.8926	0.0536	0.0536	0.0104	1.1368	0.9369	0.0315	0.0315
10	0.0055	1.4896	0.8080	0.0960	0.0960	0.0053	1.4504	0.8206	0.0897	0.0897
11	0.0053	1.3638	0.8497	0.0751	0.0751	0.0050	1.2618	0.8851	0.0217	0.0933
12	0.0051	1.3072	0.8698	0.0651	0.0651	0.0050	1.2577	0.8866	0.0925	0.0209
13	0.0046	1.1202	0.9440	0.0280	0.0280	0.0048	1.2007	0.9089	0.0094	0.0818
14	0.0046	1.1486	0.9318	0.0341	0.0341	0.0048	1.2007	0.9089	0.0818	0.0094
15	0.0010	2.3310	0.5862	0.2066	0.2066	0.0009	1.9283	0.6568	0.0523	0.2907
16	0.0009	2.5815	0.5232	0.2383	0.2383	0.0009	1.9281	0.6567	0.2911	0.0520
17	0.0008	2.8926	0.4238	0.2882	0.2882	0.0008	1.8099	0.3088	0.0151	0.6760
18	0.0006	2.9715	0.3798	0.3101	0.3101	0.0008	1.8094	0.3087	0.6761	0.0151
19	0.0005	2.9997	0.3307	0.3347	0.3347	0.0004	1.5315	0.2190	0.0036	0.7778
20	0.0005	2.9836	0.3011	0.3497	0.3497	0.0004	1.5315	0.2190	0.7778	0.0036
21	0.0004	2.9933	0.3156	0.3424	0.3424	0.0004	1.5803	0.2191	0.0161	0.7646
22	0.0003	2.9951	0.3149	0.3426	0.3426	0.0004	1.5768	0.2189	0.7655	0.0154
23	0.0002	1.4536	0.8196	0.0902	0.0902	0.0002	1.3148	0.8670	0.0664	0.0666
24	0.0001	2.8943	0.2428	0.3785	0.3785	0.0001	1.5122	0.2020	0.7876	0.0106
25	0.0001	2.8137	0.2133	0.3936	0.3936	0.0001	1.5092	0.2008	0.0107	0.7888

Table 8. Results for the LiF Molecule ($R_{\text{Li—F}} = 1.5543$ Å) within the "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 11.3749$)				Localized natural orbitals ($L = 11.3868$)			
i	n_i	L_i^{-1}	$\langle i \vert w_{\text{Li}} \vert i \rangle$	$\langle i \vert w_{\text{F}} \vert i \rangle$	ν_i	L_i^{-1}	$\langle i \vert w_{\text{Li}} \vert i \rangle$	$\langle i \vert w_{\text{F}} \vert i \rangle$
1	2.0000	1.0001	0.0001	0.9999	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0325	0.9840	0.0160	2.0000	1.0301	0.9852	0.0148
3	1.9899	1.0174	0.0086	0.9914	1.9884	1.0018	0.0009	0.9991
4	1.9770	1.0957	0.0457	0.9543	1.9784	1.1100	0.0523	0.9477
5	1.9747	1.0517	0.0252	0.9748	1.9746	1.0515	0.0251	0.9749
6	1.9747	1.0517	0.0252	0.9748	1.9746	1.0515	0.0251	0.9749
7	0.0184	1.2547	0.1146	0.8854	0.0185	1.2593	0.1165	0.8835
8	0.0184	1.2547	0.1146	0.8854	0.0185	1.2593	0.1165	0.8835
9	0.0162	1.3538	0.1545	0.8455	0.0163	1.3723	0.1618	0.8382
10	0.0090	1.0367	0.0180	0.9820	0.0090	1.0480	0.0234	0.9766
11	0.0039	1.0407	0.0199	0.9801	0.0039	1.0447	0.0219	0.9781
12	0.0039	1.0407	0.0199	0.9801	0.0039	1.0447	0.0219	0.9781
13	0.0038	1.0795	0.0383	0.9617	0.0039	1.0966	0.0462	0.9538
14	0.0038	1.0146	0.0073	0.9927	0.0038	1.0145	0.0072	0.9928
15	0.0038	1.0146	0.0073	0.9927	0.0038	1.0145	0.0071	0.9928
16	0.0007	1.9112	0.3911	0.6085	0.0008	1.9932	0.4670	0.5326
17	0.0007	1.9112	0.3911	0.6085	0.0008	1.9932	0.4670	0.5326
18	0.0004	1.8293	0.3466	0.6531	0.0004	1.9113	0.3913	0.6084
19	0.0002	1.1984	0.0909	0.9089	0.0002	1.1676	0.0777	0.9222
20	0.0001	1.6689	0.7223	0.2784	0.0001	1.6609	0.7255	0.2752
21	0.0001	1.6699	0.7223	0.2777	0.0001	1.6620	0.7255	0.2752
22	0.0000	1.7261	0.7003	0.2981	0.0000	1.7035	0.7097	0.2888
23	0.0000	1.4400	0.1889	0.8116	0.0000	1.4524	0.1938	0.8068
24	0.0000	1.6875	0.7155	0.2841	0.0000	1.6742	0.7209	0.2787
25	0.0000	1.6875	0.7155	0.2841	0.0000	1.6742	0.7209	0.2787
26	0.0000	1.4537	0.8069	0.1920	0.0000	1.3964	0.8290	0.1700
27	0.0000	1.7495	0.6900	0.3090	0.0000	1.7295	0.6985	0.3005
28	0.0000	1.7495	0.6900	0.3090	0.0000	1.7295	0.6985	0.3005
29	0.0000	1.6028	0.7493	0.2498	0.0000	1.5860	0.7559	0.2433
30	0.0000	1.1650	0.9233	0.0766	0.0000	1.1650	0.9233	0.0766

the quantity L requires the evaluation of the matrix elements of the weight function $w_A(\mathbf{r})$, $\langle i|w_A(\mathbf{r})|j\rangle$, the computational effort increases with the number of electrons like N^3. Moreover, because in (locally) planar molecules $\langle \sigma|w_A(\mathbf{r})|\pi\rangle = 0$ for all atoms A, the orbitals can be block-localized without affecting the localization sum L. This means that there is no σ/π mixing and no possible formation of banana bonds (unlike Edmiston–Ruedenberg, Foster–Boys, and von Niessen localizations). In the next section the capabilities of this new localization algorithm are studied throughout numerical determinations.

Computational Details, Results and Discussion

The localization of molecular/natural orbitals within the "fuzzy" atom approach has been carried out with programs that localize canonical molecular/natural orbitals with only a slight modification. In fact, the localized orbitals were obtained using a modified version of the Gaussian03 package.[31] The values of weight functions, w_A, and the numerical integration of the expressions $\langle i|w_A|j\rangle$ have been determined with our own computer codes following a Becke integration scheme[32] based on the weight functions originally proposed by this author. These weight functions, which satisfy eqs. (15) and (16), depend on both atomic radii of the atoms composing the system under study and a parameter k, which defines the cutoff profiles of the functions. According to ref. 26, we have chosen the value $k = 3$ and used the position of the extremum of the electron density (usually a minimum, but maximum in the cases for which there is a nonnuclear attractor) located along the straight line connecting the atoms which are chemically bonded to determine the ratio of the atomic radii entering Becke's formula instead of using the empirical Slater–Bragg atomic radii, as suggested by this author. The canonical and localized orbitals were computed for the H_2O, LiF, N_2, CO, C_2H_4, and Li_2 molecules within the Hartree–Fock and CISD levels of theory with the basis set 6-31G(d,p). For all systems, the geometries were optimized for these basis sets within Hartree–Fock wave functions. Although Tables 1–6 gather the results obtained in the Hartree–Fock approximation, Tables 7–12 report the results obtained in the CISD level of theory. For the sake of comparison, the results arising from the Cioslowski procedure at the Hartree–Fock level of theory are also included in the first six tables. The overlap integrals over Bader's regions, needed for these calculations, have also been obtained from a modified version of the Gaussian03 package. Values of L_i^{-1} close to 1 indicate core or lone-pair orbitals.

Table 9. Results for the N_2 Molecule ($R_{N—N}$ = 1.0784 Å) within the "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 6.8325$)				Localized natural orbitals ($L = 10.6793$)			
i	n_i	L_i^{-1}	$\langle i \vert w_{N_1} \vert i \rangle$	$\langle i \vert w_{N_2} \vert i \rangle$	ν_i	L_i^{-1}	$\langle i \vert w_{N_1} \vert i \rangle$	$\langle i \vert w_{N_2} \vert i \rangle$
1	2.0000	2.0000	0.5000	0.5000	2.0000	1.0006	0.9997	0.0003
2	2.0000	2.0000	0.5000	0.5000	2.0000	1.0006	0.0003	0.9997
3	1.9862	2.0000	0.5000	0.5000	1.9803	2.0000	0.5000	0.5000
4	1.9732	2.0000	0.5000	0.5000	1.9752	1.0268	0.0132	0.9868
5	1.9713	2.0000	0.5000	0.5000	1.9752	1.0268	0.9868	0.0132
6	1.9494	2.0000	0.5000	0.5000	1.9494	1.9999	0.5000	0.5000
7	1.9494	2.0000	0.5000	0.5000	1.9494	1.9999	0.5000	0.5000
8	0.0474	2.0000	0.5000	0.5000	0.0474	1.9999	0.5000	0.5000
9	0.0474	2.0000	0.5000	0.5000	0.0474	1.9999	0.5000	0.5000
10	0.0158	2.0000	0.5000	0.5000	0.0158	2.0000	0.5000	0.5000
11	0.0089	2.0000	0.5000	0.5000	0.0079	1.0444	0.9783	0.0217
12	0.0069	2.0000	0.5000	0.5000	0.0079	1.0443	0.0217	0.9783
13	0.0056	2.0000	0.5000	0.5000	0.0040	2.0003	0.4999	0.5001
14	0.0056	2.0000	0.5000	0.5000	0.0040	2.0003	0.4999	0.5001
15	0.0055	2.0000	0.5000	0.5000	0.0035	1.4257	0.1828	0.8173
16	0.0046	1.9991	0.5001	0.5001	0.0035	1.4245	0.8178	0.1823
17	0.0046	2.0003	0.5000	0.5000	0.0036	1.3718	0.8383	0.1617
18	0.0039	2.0003	0.5000	0.5000	0.0036	1.3718	0.8383	0.1617
19	0.0039	2.0003	0.5000	0.5000	0.0036	1.3718	0.1617	0.8383
20	0.0017	1.9988	0.5002	0.5002	0.0036	1.3718	0.1617	0.8383
21	0.0017	2.0003	0.5000	0.5000	0.0032	1.2521	0.8864	0.1139
22	0.0017	1.9996	0.5000	0.5000	0.0032	1.2522	0.1135	0.8864
23	0.0017	1.9996	0.5000	0.5000	0.0032	1.2522	0.8864	0.1135
24	0.0014	1.9994	0.5001	0.5001	0.0032	1.2521	0.1139	0.8864
25	0.0008	2.0003	0.5000	0.5000	0.0008	2.0003	0.5004	0.4995
26	0.0005	2.0003	0.5000	0.5000	0.0005	2.0003	0.5010	0.4990
27	0.0005	2.0003	0.5000	0.5000	0.0005	2.0003	0.5010	0.4990
28	0.0002	1.9982	0.5002	0.5002	0.0002	1.3649	0.1594	0.8410
29	0.0002	1.9990	0.5001	0.5001	0.0002	1.3684	0.8396	0.1608
30	0.0001	2.0004	0.4999	0.4999	0.0001	2.0007	0.4981	0.5018

Those lying between 1 and 2 are characteristic for localized orbitals describing localized bonds and those larger than two correspond to delocalized bonds.

Table 1 reports the results for the H_2O molecule. The canonical molecular orbitals are already fairly localized in the sense that the localization sum L undergoes minor change when going from the canonical molecular orbitals to the localized molecular orbitals. The interpretation of localized orbitals can be performed by regarding their localization indices and the relevant atomic occupancies, which lead to identify the first molecular orbital as a core orbital of the oxigen atom; the second and third localized molecular orbitals are the σ and π lone pairs on the oxigen atom, while the last two localized molecular orbitals describe two equivalent O—H bond orbitals. Results for the LiF molecule are also clearcut, as can be appreciated from Table 2. In this system, the localization also increases the sum L only very slightly. The set of localized molecular orbitals comprises two core orbitals ($i = 1, 2$), each one localized on each nucleus together with one s-type ($i = 3$) and three p-type ($i = 4, 5, 6$) lone-pair orbitals on the fluorine atom. This is in accordance with the ionic Li^+F^- bond. Table 3 describes the results for the N_2 molecule. Due to the molecular symmetry requirements, all canonical molecular orbitals are completely delocalized. It can be seen that the localization is accompanied by a significant increase of the sum L. The localization transformation yields two core orbitals ($i = 1, 2$) on the atoms, a σ orbital ($i = 3$), two lone-pair orbitals ($i = 4, 5$) and two equivalent π orbitals ($i = 6, 7$). The situation in the isoelectronic CO molecule is quite similar as shown in Table 4. However, due to its heteronuclear character, the resulting localized molecular orbitals are less delocalized, as reflected by smaller values of the corresponding localization indices. The localization scheme yields two core orbitals ($i = 1, 2$) on the atoms, a σ orbital ($i = 4$), two equivalent π orbitals ($i = 6, 7$) and two lone-pair orbitals, one on the oxigen ($i = 3$) and the other on the carbon ($i = 5$), the last one being slightly delocalized. It may be noted that bonding orbitals reveal the strong ionic character of CO bonding. This ionic character in "fuzzy" atom approach is due to the choice of the atomic radii as the distance between the nucleus and the bond critical point. In fact, as Slater–Bragg atomic radii are used the ionic character decreases to chemical expected values as reflected by the resulting atomic populations (0.4383, 0.2991, and 0.2991 and 0.5617, 0.7008, and 0.7008 for the 4, 6, and 7th localized orbitals of the carbon and oxigen atoms, respectively) and charges (−0.0692 and 0.0692 for the oxygen and the carbon atoms, respectively). Canonical molecular orbitals of the C_2H_4 molecule are highly delocalized (Table 5).

Table 10. Results for the CO Molecule ($R_{C—O} = 1.1138$ Å) within the "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 11.4681$)				Localized natural orbitals ($L = 11.8098$)			
i	n_i	L_i^{-1}	$\langle i \vert w_C \vert i \rangle$	$\langle i \vert w_O \vert i \rangle$	ν_i	L_i^{-1}	$\langle i \vert w_C \vert i \rangle$	$\langle i \vert w_O \vert i \rangle$
1	2.0000	1.0379	0.9814	0.0186	2.0000	1.0000	0.0000	1.0000
2	2.0000	1.0247	0.0122	0.9878	2.0000	1.0122	0.9939	0.0061
3	1.9879	1.1847	0.0852	0.9148	1.9833	1.0017	0.0008	0.9992
4	1.9759	1.2380	0.1077	0.8923	1.9788	1.3731	0.1622	0.8378
5	1.9627	1.2457	0.8891	0.1108	1.9632	1.1768	0.9182	0.0817
6	1.9579	1.3703	0.1611	0.8389	1.9549	1.3621	0.1579	0.8422
7	1.9579	1.3703	0.1611	0.8389	1.9549	1.3621	0.1579	0.8422
8	0.0414	1.9960	0.5208	0.4794	0.0439	1.8005	0.6662	0.3339
9	0.0414	1.9960	0.5208	0.4794	0.0439	1.8005	0.6662	0.3339
10	0.0166	1.9143	0.3942	0.6058	0.0176	1.9830	0.4535	0.5464
11	0.0090	1.4229	0.1817	0.8185	0.0086	1.0298	0.0147	0.9853
12	0.0063	1.8102	0.6612	0.3394	0.0066	1.2059	0.9057	0.0951
13	0.0054	1.3453	0.1512	0.8488	0.0056	1.1299	0.0613	0.9387
14	0.0054	1.3453	0.1512	0.8488	0.0056	1.1299	0.0613	0.9387
15	0.0051	1.6123	0.2546	0.7453	0.0052	1.5524	0.2315	0.7685
16	0.0050	1.8868	0.3774	0.6225	0.0052	1.5524	0.2315	0.7685
17	0.0050	1.8868	0.3774	0.6225	0.0051	1.2451	0.1107	0.8893
18	0.0044	1.2656	0.1191	0.8809	0.0042	1.1411	0.0662	0.9338
19	0.0044	1.2675	0.1191	0.8802	0.0042	1.1411	0.0662	0.9338
20	0.0016	1.9935	0.5369	0.4619	0.0018	1.7580	0.6867	0.3119
21	0.0012	1.8378	0.6483	0.3519	0.0014	1.8996	0.6147	0.3854
22	0.0012	1.8495	0.6483	0.3470	0.0014	1.8996	0.6147	0.3854
23	0.0012	1.9757	0.4451	0.5550	0.0014	1.5701	0.7615	0.2387
24	0.0012	1.9757	0.4451	0.5550	0.0014	1.5701	0.7615	0.2387
25	0.0007	1.7106	0.2952	0.7053	0.0007	1.7350	0.3055	0.6950
26	0.0004	1.9259	0.5968	0.4038	0.0003	1.1667	0.0767	0.9226
27	0.0004	1.9259	0.5968	0.4038	0.0004	1.8219	0.6556	0.3451
28	0.0002	1.3518	0.1524	0.8465	0.0004	1.8219	0.6556	0.3451
29	0.0001	1.7425	0.6963	0.2985	0.0001	1.3914	0.8315	0.1655
30	0.0000	1.9994	0.4859	0.5139	0.0001	1.9976	0.4594	0.5381

The fourth, fifth, sixth, and seventh orbitals are spread across the entire molecular system. The localization transformation brings about a substantial increase in the localization sum L. The set of localized molecular orbitals comprises two core orbitals on the carbon atoms ($i = 1, 2$), together with one σ orbital of the C—C bond ($i = 3$), four equivalent σ orbitals of the C—H bonds ($i = 4, 5, 6, 7$) and one π orbital of the C—C bond ($i = 8$). As can be appreciated, the σ/π-separability is preserved in this planar molecule. As can be observed on these tables, the description of all the above-reported systems turn out to be quite similar in both "fuzzy" atom and AIM approaches. Table 6 shows the results for the Li_2 molecule. In this sytem, all canonical molecular orbitals are completely delocalized. The localization procedure within "fuzzy" atom approach yields two core orbitals ($i = 1, 2$) and a bonding orbital ($i = 3$). All these results perfectly agree with the genuine chemical picture of this molecular system. However, the AIM localization procedure does not provide a similar picture for this molecule as in the previous systems. This molecule is an example of a system in which atoms and Bader domains cannot be put into one-to-one correspondence, and consequently, the interpretation of the localized orbitals resulting from the AIM theory runs into difficulties. In this case, the AIM-based localization transformation yields two core orbitals ($i = 1, 2$) and one delocalized orbital over two Li atoms and an empty basin ($i = 3$).

The localized orbitals obtained from post-Hartree–Fock calculations present a little bit more complex interpretation. This level of description involves a larger number of nonzero occupation numbers and isopycnic-related natural orbitals of the spin-free first-order reduced density matrix than in the Hartree–Fock case. However, this larger number of orbitals does not complicate too much the final chemical picture of the systems in terms of the localized natural orbitals as may be noted from the results in Tables 7–12. Therefore, electron distribution pictures of all molecular systems described by localized orbitals in "fuzzy" atoms model at correlated level are similar than those of Hartree–Fock one, as confirmed by the values in the tables. In general, the natural orbitals are both less localized and less localizable than the Hartree–Fock ones. This is in agreement with the well-known observation that ionicity (and thus also localizability of orbitals) is overestimated at the Hartree–Fock level.

The above results make worthwhile to emphasize two important features. On the one hand, canonical orbitals are less localized and less localizables in the "fuzzy" atom than in the AIM model; this remark may be noted from the localization sum and indices of the

Table 11. 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 "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 5.0242$)							
i	n_i	L_i^{-1}	$\langle i\|w_{C_1}\|i\rangle$	$\langle i\|w_{C_2}\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$	$\langle i\|w_{H_3}\|i\rangle$	$\langle i\|w_{H_4}\|i\rangle$
1	2.0000	2.0005	0.4999	0.4999	0.0000	0.0000	0.0000	0.0000
2	2.0000	2.0006	0.4999	0.4999	0.0000	0.0000	0.0000	0.0000
3	1.9822	3.3340	0.3774	0.3774	0.0613	0.0613	0.0613	0.0613
4	1.9758	4.9830	0.2732	0.2732	0.1134	0.1134	0.1134	0.1134
5	1.9738	5.2295	0.2572	0.2572	0.1213	0.1213	0.1213	0.1213
6	1.9708	5.9685	0.1839	0.1839	0.1581	0.1581	0.1581	0.1581
7	1.9695	3.4979	0.3660	0.3660	0.0670	0.0670	0.0670	0.0670
8	1.9439	2.3887	0.4565	0.4565	0.0218	0.0218	0.0218	0.0218
9	0.0453	2.4081	0.4545	0.4545	0.0227	0.0227	0.0227	0.0227
10	0.0169	5.1195	0.2644	0.2644	0.1178	0.1178	0.1178	0.1178
11	0.0165	2.9723	0.4046	0.4046	0.0477	0.0477	0.0477	0.0477
12	0.0152	5.4696	0.2401	0.2401	0.1299	0.1299	0.1299	0.1299
13	0.0139	4.9900	0.2727	0.2727	0.1136	0.1136	0.1136	0.1136
14	0.0136	4.7746	0.2860	0.2860	0.1070	0.1070	0.1070	0.1070

	Localized natural orbitals ($L = 9.3649$)							
i	ν_i	L_i^{-1}	$\langle i\|w_{C_1}\|i\rangle$	$\langle i\|w_{C_2}\|i\rangle$	$\langle i\|w_{H_1}\|i\rangle$	$\langle i\|w_{H_2}\|i\rangle$	$\langle i\|w_{H_3}\|i\rangle$	$\langle i\|w_{H_4}\|i\rangle$
1	2.0000	1.0006	0.9997	0.0002	0.0001	0.0001	0.0000	0.0000
2	2.0000	1.0006	0.0002	0.9997	0.0000	0.0000	0.0001	0.0001
3	1.9747	2.1208	0.4854	0.4854	0.0073	0.0073	0.0073	0.0073
4	1.9742	2.1319	0.0169	0.4691	0.0018	0.0016	0.0120	0.4986
5	1.9742	2.1319	0.0169	0.4691	0.0016	0.0018	0.4986	0.0119
6	1.9742	2.1319	0.4691	0.0169	0.4986	0.0119	0.0016	0.0018
7	1.9742	2.1319	0.4691	0.0169	0.0119	0.4986	0.0018	0.0016
8	1.9438	2.3882	0.4565	0.4565	0.0217	0.0217	0.0217	0.0217
9	0.0452	2.3946	0.4559	0.4559	0.0221	0.0221	0.0221	0.0221
10	0.0159	2.2887	0.4668	0.4668	0.0166	0.0166	0.0166	0.0166
11	0.0149	2.1306	0.0215	0.5151	0.0012	0.0015	0.4511	0.0096
12	0.0149	2.1306	0.0215	0.5151	0.0015	0.0012	0.0096	0.4511
13	0.0149	2.1306	0.5151	0.0215	0.4511	0.0096	0.0012	0.0015
14	0.0149	2.1306	0.5151	0.0215	0.0096	0.4511	0.0015	0.0012

Only the canonical and localized natural orbitals with occupation numbers greater than 0.01 are listed.

canonical and localized orbitals satisfying

$$L^{FA} \leq L^{AIM} \tag{21}$$

and

$$(L_i^{FA})^{-1} \geq (L_i^{AIM})^{-1} \tag{22}$$

where the last inequality is valid for orbitals corresponding to each other. This is due to the nature and overlapping character of the atomic regions within the "fuzzy" atom theory. In fact, when the parameter k of the Becke's funtion[32] is increased (and thus the sharpness of the atomic boundaries) the diferences between "fuzzy" atom and AIM derived localization sum and indices diminish. This behavior is illustrated in Table 13 for the H_2O molecule at the Hartree–Fock level. On the other hand, there are some small differences between the total atomic occupancies of the canonical orbitals and those of the localized orbitals as well as in the localization indices and atomic occupancies for the equivalent localized orbitals. This feature is due to the limited numerical accuracy of the discrete integration procedure used in both the "fuzzy" atom and Bader partitionings.

An important feature such as the basis set dependence of the present procedure may be considered to complete our study. We choose H_2O molecule in the Hartree–Fock approximation as an illustrative example for this goal. Table 14 shows the values of the localization parameters L and L_i and the populations of the localized molecular orbitals of this system in minimal STO-3G, intermediate 3-21G, and double ζ 6-31G(d,p) basis sets. The molecular geometry was optimized for each basis set within the

Table 12. Results for the Li_2 Molecule ($R_{Li—Li} = 2.8070$ Å) within the "Fuzzy" Atom Approach.

	Canonical natural orbitals ($L = 2.8291$)				Localized natural orbitals ($L = 4.8273$)			
i	n_i	L_i^{-1}	$\langle i\|w_{Li_1}\|i\rangle$	$\langle i\|w_{Li_2}\|i\rangle$	ν_i	L_i^{-1}	$\langle i\|w_{Li_1}\|i\rangle$	$\langle i\|w_{Li_2}\|i\rangle$
1	2.0000	2.0000	0.5000	0.5000	2.0000	1.0005	0.9998	0.0002
2	2.0000	2.0000	0.5000	0.5000	2.0000	1.0005	0.0002	0.9998
3	1.8189	2.0002	0.5000	0.5000	1.8189	2.0001	0.5000	0.5000
4	0.0449	2.0000	0.5000	0.5000	0.0545	2.0000	0.5000	0.5000
5	0.0545	2.0000	0.5000	0.5000	0.0545	2.0000	0.5000	0.5000
6	0.0545	2.0000	0.5000	0.5000	0.0357	1.7556	0.3134	0.6866
7	0.0266	2.0006	0.4999	0.4999	0.0357	1.7556	0.6866	0.3136
8	0.0001	1.9978	0.5003	0.5003	0.0001	2.0000	0.5002	0.5004
9	0.0001	2.0014	0.4998	0.4998	0.0001	1.9484	0.4177	0.5821
10	0.0001	2.0014	0.4998	0.4998	0.0001	1.9484	0.5821	0.4177
11	0.0001	2.0008	0.4999	0.4999	0.0001	1.9484	0.5821	0.4177
12	0.0001	2.0008	0.4999	0.4999	0.0001	1.9484	0.4177	0.5821
13	0.0001	2.0007	0.4999	0.4999	0.0001	2.0009	0.4999	0.4999
14	0.0000	2.0013	0.4998	0.4998	0.0000	2.0014	0.5000	0.4997
15	0.0000	1.9994	0.5001	0.5001	0.0000	1.2323	0.1055	0.8946
16	0.0000	2.0026	0.4997	0.4997	0.0000	1.2323	0.8946	0.1055
17	0.0000	1.9993	0.5001	0.5001	0.0000	1.2327	0.1048	0.8946
18	0.0000	2.0030	0.4996	0.4996	0.0000	1.2327	0.8946	0.1048
19	0.0000	1.9980	0.5002	0.5002	0.0000	1.9980	0.5004	0.5001
20	0.0000	2.0082	0.4990	0.4990	0.0000	2.0082	0.4990	0.4989
21	0.0000	2.0011	0.4999	0.4999	0.0000	2.0011	0.4999	0.4999
22	0.0000	2.0011	0.4999	0.4999	0.0000	2.0011	0.4999	0.4999
23	0.0000	2.0059	0.4993	0.4993	0.0000	2.0059	0.4993	0.4993
24	0.0000	2.0059	0.4993	0.4993	0.0000	2.0059	0.4993	0.4993
25	0.0000	2.0049	0.4994	0.4994	0.0000	2.0050	0.5002	0.4986
26	0.0000	1.9950	0.5006	0.5006	0.0000	1.9950	0.5006	0.5006
27	0.0000	2.0034	0.4996	0.4996	0.0000	2.0034	0.4996	0.4996
28	0.0000	2.0034	0.4996	0.4996	0.0000	2.0034	0.4996	0.4996
29	0.0000	2.0044	0.4995	0.4995	0.0000	2.0044	0.4995	0.4995
30	0.0000	2.0018	0.4998	0.4998	0.0000	2.0019	0.4998	0.4998

Hartree–Fock approximation. As may be seen, the values for L and all orbital populations show a minor change between the different basis sets. All other systems in both approaches, Hartree–Fock and CISD, show the same behavior under different basis set description.

Table 13. Dependence of the Localization Sum and Indices on the Parameter k of Becke'S Function for the H_2O Molecule ($R_{O—H} = 0.9431$ Å, $\widehat{HOH} = 106° 2' 38''$).

	L_i^{-1}			
	"Fuzzy" atom approach			
i	$k = 3$	$k = 5$	$k = 7$	**AIM approach**
1	1.0000	1.0000	1.0000	1.0000
2	1.0308	1.0241	1.0232	1.0085
3	1.0856	1.0686	1.0649	1.0192
4	1.7630	1.7465	1.7440	1.4303
5	1.7630	1.7465	1.7440	1.4303
	$L = 8.0513$	$L = 8.1148$	$L = 8.1264$	$L = 8.7422$

Concluding Remarks

In conclusion, in this work we have proposed and implemented a localization method based on the minimization of an appropriately defined mean localization measure of the occupied molecular or natural orbitals. The present scheme extends the applicability of the theory of "fuzzy" atoms to orbital localization. The technique, whose algorithmic complexity is N^3, does not require any additional quantities to be calculated beyond the atomic overlap integrals. The treatment turns out to be suitable for separating core and valence orbitals and supports σ/π separation. The resulting orbitals are almost identical to the Cioslowski localized orbitals. Both the atomic populations and localization indices defined here have been shown to be useful tools for interpretation of the results because the character of the localized orbitals can be inferred from them without plotting the orbitals. All these results and the lower computational cost of the "fuzzy" atom approach in comparison with the AIM treatment indicate that this methodology can be used as a reliable and cost-competitive technique within the localization criteria. Extension of this methodology to determine atomic orbitals in molecules and its application to the description of the theory of regional reduced density matrices

Table 14. Basis Set Dependence of the Localized Orbitals for the H_2O Molecule within the "Fuzzy" Atom Approach.

STO-3G
Localized molecular orbitals ($L = 8.0770$)

i	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_O}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$
1	2.0000	1.0000	1.0000	0.0000	0.0000
2	2.0000	1.0162	0.9920	0.0040	0.0040
3	2.0000	1.0294	0.9856	0.0072	0.0072
4	2.0000	1.8468	0.6525	0.3401	0.0074
5	2.0000	1.8468	0.6525	0.0074	0.3401

3-21G
Localized molecular orbitals ($L = 8.0909$)

i	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_O}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$
1	2.0000	1.0001	1.0000	0.0000	0.0000
2	2.0000	1.0243	0.9881	0.0060	0.0060
3	2.0000	1.0544	0.9737	0.0132	0.0132
4	2.0000	1.7845	0.6821	0.3084	0.0096
5	2.0000	1.7845	0.6821	0.0096	0.3084

6-31G(d,p)
Localized molecular orbitals ($L = 8.0513$)

i	ν_i	L_i^{-1}	$\langle i\|i\rangle_{\Omega_O}$	$\langle i\|i\rangle_{\Omega_{H_1}}$	$\langle i\|i\rangle_{\Omega_{H_2}}$
1	2.0000	1.0000	1.0000	0.0000	0.0000
2	2.0000	1.0308	0.9849	0.0076	0.0076
3	2.0000	1.0856	0.9593	0.0203	0.0203
4	2.0000	1.7630	0.6918	0.2975	0.0107
5	2.0000	1.7630	0.6918	0.0107	0.2975

recently introduced by us[33] is currently being considered in our laboratories.

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