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Electron-pairing analysis from localization and delocalization indices in the framework of the atoms-in-molecules theory

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Abstract. This article presents an overview of recent advances in the study of electron pairing through the use of localization and delocalization indices obtained from double integration over atomic basins of the exchange–correlation density in the framework of the atoms-in-molecules theory. These localization and delocalization indices describe the intra- and interatomic distribution of the electron pairs in a molecule. The main results of the application of these second-order indices to the analysis of molecular structure and chemical reactivity are briefly reviewed. It is shown that localization and delocalization indices represent a powerful tool to describe the electron-pair structure of molecules, which, in turn, provides deeper insight into relevant chemical phenomena such as electron correlation effects and the formation of localized α, β electron pairs.

Key words: Localization and delocalization indices – Electron pairing – Two-electron density – Fermi hole – Exchange–correlation density

1 Introduction

Modern quantum chemistry offers highly powerful and reliable approaches to the detailed comprehension of many intricate aspects concerning the structure and reactivity of molecular systems. In the last 2 decades, parallel to the fast development of new accurate quantum-chemical methods, there have been important advances in the design of auxiliary methods for interpreting wave functions. A significant number of the interpretative tools currently available to quantum chemists are based on the analysis of the one-electron density, $\rho(\vec{r})$. Mulliken populations [1], atoms-in-molecules (AIM) topological analysis [2, 3, 4, 5, 6], bond orders [7, 8, 9], natural populations [10], quantum molecular similarity calculations [11, 12], and electron localization function (ELF) studies [13], are, among others, commonly used techniques for interpreting wave functions that make use of the one-electron density. This interest in the one-electron density for extracting chemical relevant information is not at all surprising considering that, according to density functional theory (DFT) [14, 15, 16, 17], the one-electron density contains all the information about the ground-state properties of a quantum-chemical system.

More scarce are the interpretative tools based on the two-electron density or pair density [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30], $\Gamma(1,2)$, in spite of the fact that this is the natural function to examine for understanding very relevant quantum-chemical phenomena such as electron-correlation effects [18, 19, 20, 21, 22, 23, 24, 25, 26, 27] or the formation of localized α,β pairs [31, 32]. The two-electron density can be interpreted as the probability of two electrons being simultaneously at positions $\vec{r_1}$ and $\vec{r_2}$ with spins σ_1 and σ_2, respectively. To stress that the spin of the two electrons at positions $\vec{r_1}$ and $\vec{r_2}$ is known, we will often use the notation $\Gamma^{\sigma_1\sigma_2}(\vec{r_1},\vec{r_2})$. After spin integration of $\Gamma(1,2)$, one gets the spinless pair density, which can be split into an uncorrelated pair density part and a part that gathers all exchange and correlation effects,

$$\Gamma(\vec{r_1},\vec{r_2}) = \rho(\vec{r_1})\rho(\vec{r_2}) + \Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2}). \quad (1)$$

The uncorrelated component of the pair density, given by the product $\rho(\vec{r_1})\rho(\vec{r_2})$, provides the probability of finding simultaneously two independent electrons at positions $\vec{r_1}$ and $\vec{r_2}$. The difference between $\Gamma(\vec{r_1},\vec{r_2})$ and $\rho(\vec{r_1})\rho(\vec{r_2})$ is the exchange–correlation density [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 33], $\Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})$, which is a measure of the degree to which density is excluded at $\vec{r_2}$ because of the presence of an electron at $\vec{r_1}$. Therefore, $\Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})$ contains all the information necessary for the study of electron correlation and electron-pair formation. Given the fact that the one-electron density and the pair density are normalized to N electrons and $N(N-1)$ nondistinct electron pairs, respectively, the double integration of the exchange–correlation density, as defined in Eq. (1), yields $-N$

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electrons. By dividing $\Gamma(\vec{r_1},\vec{r_2})$ by $\rho(\vec{r_1})$ one gets the so-called conditional pair density [18, 21, 27, 34, 35], $P(\vec{r_1},\vec{r_2})$, which gives the probability of finding an electron at position $\vec{r_2}$ when one electron is known to be at reference position $\vec{r_1}$

$$P(\vec{r_1},\vec{r_2}) = \frac{\Gamma(\vec{r_1},\vec{r_2})}{\rho(\vec{r_1})}. \tag{2}$$

Since $\Gamma(\vec{r_1},\vec{r_2})$ can be further partitioned in same-spin and unlike-spin electron contributions,

$$\Gamma(\vec{r_1},\vec{r_2}) = \Gamma^{\alpha\alpha}(\vec{r_1},\vec{r_2}) + \Gamma^{\alpha\beta}(\vec{r_1},\vec{r_2}) + \Gamma^{\beta\alpha}(\vec{r_1},\vec{r_2}) + \Gamma^{\beta\beta}(\vec{r_1},\vec{r_2}), \tag{3}$$

it is possible to write the $P^{\sigma\sigma}(\vec{r}_1,\vec{r_2})$ and $P^{\sigma\sigma'}(\vec{r_1},\vec{r_2})$ contributions to the conditional pair density as

$$\begin{aligned} P^{\sigma\sigma}(\vec{r_1},\vec{r_2}) &= \rho^{\sigma}(\vec{r_2}) + \rho^{\sigma\sigma}_{\mathrm{XC}}(\vec{r_1},\vec{r_2}),\\ P^{\sigma\sigma'}(\vec{r_1},\vec{r_2}) &= \rho^{\sigma'}(\vec{r_2}) + \rho^{\sigma\sigma'}_{\mathrm{XC}}(\vec{r_1},\vec{r_2}). \end{aligned} \tag{4}$$

In Eq. (4), the $\rho^{\sigma\sigma}_{\mathrm{XC}}(\vec{r_2},\vec{r_2})(\sigma=\alpha,\beta)$ term is the so-called Fermi hole [18, 19, 20, 21, 22, 23, 24, 25, 26, 27], which is a negative quantity determining the decrease in the probability of finding another electron with the same spin relative to a fixed position of the electron of reference located at $\vec{r_1}$. Its integral over $\vec{r_2}$ equals −1, corresponding to the removal of a same-spin electron from the σ-spin density, $\rho^{\sigma}(\vec{r_2})$. It is worth remarking that it is not the Coulomb repulsion between the electrons but the effect of antisymmetrization that is the main source of correlation between electrons of the same spin. Coulomb repulsion also plays a meaningful role, although the exchange correlation is by far dominant. For electrons of unlike spin, we have only Coulomb correlation that can be analyzed from the so-called Coulomb hole [18, 19, 20, 21, 22, 23, 24, 25, 26, 27], $\rho^{\sigma\sigma'}_{\mathrm{XC}}(\vec{r_1},\vec{r_2})$ $(\sigma,\sigma'=\alpha,\beta;\sigma\neq\sigma')$. At the Hartree–Fock (HF) level, the motions of unlike-spin electrons are not correlated and $\rho^{\sigma\sigma'}_{\mathrm{XC}}(\vec{r_1},\vec{r_2})=0$. This term also vanishes when the wave function is taken to be a single determinant of Kohn–Sham orbitals obtained from a DFT calculation.

2 Definition of localization and delocalization indices

An important property of the Fermi hole density is that its on-top value (i.e., the Fermi hole density when $\vec{r_1}=\vec{r_2}$) equals $-\rho^{\sigma}(\vec{r_2})$, thus ensuring the complete removal of all like-spin electrons in the position of the reference electron [27, 28, 29]. If this total exclusion of same-spin density persists as $\vec{r_2}$ is displaced from $\vec{r_1}$, then the hole describes a region of space from which all other same-spin electrons are excluded. In this situation, the localization of the Fermi hole is maximized. Indeed, the Fermi hole is known to have approximately the shape of the localized orbital at reference positions where most of the total density can be ascribed to one particular localized orbital [18, 19, 20, 21, 22, 23, 24, 25]. In a closed-shell molecule, the spatial localization of a given electron in a certain region implies the same behavior for an electron of opposite spin, thus forming a localized α, β pair [32] in a confined region of space.

The two methodologies more commonly used in recent years to partition position space are the AIM theory due to Bader [2, 3, 4, 5, 6], and the topological analysis [13, 36, 37] of the ELF [38]. In both approaches, subsystems (basins) are defined in terms of the vector field of the gradient of the function involved, namely the electron density or the ELF, respectively. Other partitions, like the Mulliken-like partitioning in the Hilbert space spanned by the basis functions, are also possible. Because of some arbitrariness in the Mulliken-like partition and in the ELF definition [38], in our opinion the AIM partition of space is, in principle, the most realistic and physically meaningful [39, 40]. Thus, except otherwise stated, the calculations presented in this review were performed with the AIM partition defined by Bader [2, 3, 4, 5, 6].

In the AIM theory [2, 3, 4, 5, 6], the partition of space is done through the atomic basins that are defined as the regions in real space bound by zero-flux surfaces in $\rho(\vec{r})$ or by infinity [2, 3, 4, 5, 6]. Usually, each basin contains an atomic nucleus, which acts as a topological attractor for the basin; thus, each basin can be assigned to one of the atoms in a molecule. This partitioning scheme ensures that each atomic subsystem behaves as a proper open system [2, 3, 4, 5, 6]. Moreover, the atomic contributions to any molecular property can be calculated by integrating through the atomic basins. For instance, the average population of an atom A is defined as follows,

$$(N)_A = N(A) = \int_A \rho(\vec{r})\,\mathrm{d}\vec{r}, \tag{5}$$

where the subscript A indicates that the integration has to be carried out only through the space corresponding to the atomic basin of atom A. Summation of all the atomic populations in a molecule yields the total number of electrons, N.

Even though the AIM theory is mainly based on the topological analysis of the one-electron density, the second-order or pair density, $\Gamma(\vec{r_1},\vec{r_2})$, can also be used in the framework of the AIM theory to shed light on how electron pairs are distributed between the atoms in a molecule [41, 42, 43]. Since the localization or delocalization of an electron is determined by the corresponding localization or delocalization of its Fermi hole, the atomic localization indices (LIs) and delocalization indices (DIs) have been defined as [41, 43]

$$\lambda(A) = -\int_A \Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})\,\mathrm{d}\vec{r_1}\,\mathrm{d}\vec{r_2}, \tag{6}$$

$$\begin{aligned} \delta(A,B) &= -\iint_{AB} \Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})\,\mathrm{d}\vec{r_1}\,\mathrm{d}\vec{r_2} - \iint_{BA} \Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})\,\mathrm{d}\vec{r_1}\,\mathrm{d}\vec{r_2}\\ &= -2\iint_{AB} \Gamma_{\mathrm{XC}}(\vec{r_1},\vec{r_2})\,\mathrm{d}\vec{r_1}\,\mathrm{d}\vec{r_2}. \end{aligned} \tag{7}$$

The LIs and DIs in Eqs. (6) and (7) are obtained by the double integration of the Fermi hole density over the basins of atoms A or B, corresponding to every possible position of the reference electron in the basin of atom A, weighted by the density of the reference electron. Because of the requirement to average by the density of the reference electron, the exchange–correlation density $\Gamma_{\mathrm{XC}}\left(\vec{r_1},\vec{r_2}\right)$ is used in the definition of the LIs and DIs instead of the Fermi hole density. The LIs and DIs defined in Eqs. (6) and (7) are unaffected by a unitary transformation of the molecular orbital set.

It is worth noting that these indices are closely related to the fluctuation (or variance) in the average population of the basin of a given atom A, σ^2, defined by [44, 45]

$$\sigma^2[N(A)] = \left\langle N^2\right\rangle_A - \langle N\rangle_A^2, \tag{8}$$

where $\sigma^2[N(A)]$ represents the quantum mechanical uncertainty on $N(A)$ and it is related to the LIs and DIs through the following equations [36, 44, 45, 46]:

$$\sigma^2[N(A)] = N(A) - \lambda(A), \tag{9}$$

$$\sigma^2[N(A)] = \frac{1}{2}\sum_{B\neq A}\delta(A,B). \tag{10}$$

The LI, $\lambda(A)$, gives the number of electrons that are localized in atom A. For any atom, the LI is always smaller than or equal to the atomic population, $N(A)$. Actually, the ratio $100[\lambda(A)/N(A)]$ is the percentage of electron localization in atom A. It can reach 100% only for isolated atoms. In practice, values close to 100% are obtained for atoms that have only closed-shell interactions with their neighbors. The DI, $\delta(A,B)$, corresponds to the number of electrons delocalized or shared between atoms A and B. As indicated by Eq. (10), half of the sum of all DIs for a given atom is the fluctuation in the average population of atom A. Because of the normalization condition of the exchange–correlation density, the summation of all LIs and DIs (the latter divided by 2) in a molecule gives the total number of electrons in that molecule, N, that is,

$$\sum_A\left(\lambda(A) + \frac{1}{2}\sum_{B\neq A}\delta(A,B)\right) = N. \tag{11}$$

Equations (6) and (7) are completely general, and can be used at any level of theory, provided that the first- and second-order density functions are known. In particular, most of the current theoretical ab initio methods expand the molecular wave function in terms of molecular orbitals (MOs). Then, for a closed-shell molecule, $\lambda(A)$ and $\delta(A,B)$ can be expressed as

$$\lambda(A) = -\sum_{i,j,k,l} D_{ijkl}S_{ij}(A)S_{kl}(A) + N(A)^2 \tag{12}$$

and

$$\delta(A,B) = -2\sum_{i,j,k,l} D_{ijkl}S_{ij}(A)S_{kl}(B) + 2N(A)N(B), \tag{13}$$

respectively, where $\{D_{\mathrm{ijkl}}\}$ are density-matrix elements for the second-order density matrix in a MO base, and $\{S_{\mathrm{ij}}(A)\}$ are overlaps between MOs, integrated within the basin of atom A.[1] The four-index summations in Eqs. (12) and (13) run over all the occupied MOs in the molecule. These equations can also be expressed in terms of basis functions,

$$\lambda(A) = -\sum_{\mu,\upsilon,\lambda,\sigma} D_{\mu\upsilon\lambda\sigma}S_{\mu\upsilon}(A)S_{\lambda\sigma}(A) + N(A)^2, \tag{14}$$

$$\delta(A,B) = -2\sum_{\mu,\upsilon,\lambda,\sigma} D_{\mu\upsilon\lambda\sigma}S_{\mu\upsilon}(A)S_{\lambda\sigma}(B) + 2N(A)N(B), \tag{15}$$

where $\{\mathrm{D}_{\mu\upsilon\lambda\sigma}\}$ are density matrix elements for the second-order density matrix in the atomic orbital base, and $\{S_{\mu\upsilon}(A)\}$ are overlaps between basis functions, integrated within the basin of atom A.

At the HF level of theory, the pair density can be expressed in terms of the one-electron density matrix [47],

$$\Gamma\left(\vec{r_1},\vec{r_2}\right) = \begin{vmatrix} \rho\left(\vec{r_1},\vec{r_1}\right) & \rho\left(\vec{r_1},\vec{r_2}\right) \\ \rho\left(\vec{r_2},\vec{r_1}\right) & \rho\left(\vec{r_2},\vec{r_2}\right) \end{vmatrix}. \tag{16}$$

Then, the expressions for the LI and DI at the HF level can be written as [43]

$$\lambda(A) = \sum_{i,j}\left[S_{ij}(A)\right]^2, \tag{17}$$

$$\delta(A,B) = 2\sum_{i,j} S_{ij}(A)S_{ij}(B), \tag{18}$$

where the summations run over all the pairs of occupied molecular spin orbitals of the molecule. At the HF level, the LIs and DIs in Eqs. (17) and (18) reduce to Wiberg indices [48] if integrations over atomic basins are replaced by a Mulliken-like partitioning of the corresponding integrals. Using this approximation, Ponec and coworkers [31, 49, 50, 51, 52] have reported calculations of LIs and DIs at the semiempirical and HF levels of theory. Moreover, at the HF level, the definitions of bond order by Ángyán et al. [53] and Fulton and Mixon [54, 55] are equivalent to one another and to the DI given in Eq. (18). The formula of the bond order established by Fulton [54] using products of terms in the one-electron density to describe the sharing of electronic charge between two centers is

$$B_{AB} = 2\sum_{i,j} v_i^{1/2}v_j^{1/2}S_{ij}(A)S_{ij}(B), \tag{19}$$

where v_i is the occupation number of the ith natural spin orbital. It can be demonstrated that Eq. (19) can be generated from Eq. (7) using an approximation to the exact expression for the correlated pair density, although no reference to the second-order density was made by Fulton in the original work [54].

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[1] We consider here that the pair density is given by $\Gamma(\vec{r}_1,\vec{r}_2) = \sum_{i,j,k,l} D_{ijkl}\phi_i^*(\vec{r}_1)\phi_j(\vec{r}_1)\phi_k^*(\vec{r}_2)\phi_l(\vec{r}_2)$

In molecules having a plane of symmetry, the orbitals can be classified as σ or π, depending on their symmetric or antisymmetric behavior with respect to reflection in the plane. In this case, the overlap integrals $S_{ij}(A)$ vanish when i and j belong to different sets and, consequently, the contributions of σ or π electrons to the LIs and DIs can be separated. This separation, however, cannot be generalized to any set of orbitals belonging to different symmetry representations (e.g., A_1 and B_2 in $C_{2\mathrm{v}}$ molecules) since the partition into orbital contributions requires that all the overlap integrals between orbitals belonging to different sets be zero within each atomic basin [43].

As stated for the pair density (Eq. 3), the exchange–correlation density can also be separated into same-spin and unlike-spin electron contributions. Consequently, the LI and DI can also be partitioned into intraspin and interspin components [41]:

$$\lambda(A) = \lambda^{\alpha\alpha}(A) + \lambda^{\beta\beta}(A) + \lambda^{\alpha\beta}(A) + \lambda^{\beta\alpha}(A), \tag{20}$$

$$\delta(A,B) = \delta^{\alpha\alpha}(A,B) + \delta^{\beta\beta}(A,B) + \delta^{\alpha\beta}(A,B) + \delta^{\beta\alpha}(A,B). \tag{21}$$

At the HF level, only the $\alpha\alpha$ and $\beta\beta$ components are nonzero for both the LI and the DI.

Finally, it is worth noting that the definition of the DI can be generalized to study multicenter bonding [56, 57, 58, 59]. For instance, to analyze three-center bonding it is possible to define a DI between three centers that at the HF level has the form

$$\delta(A,B,C) = 2\sum_{i,j,k} S_{ij}(A)S_{jk}(B)S_{ki}(C). \tag{22}$$

Generalization of $\delta(A,B,C)$ beyond the HF approximation, although possible in principle, is quite difficult, since it would require knowledge of correlated higher-order densities.

Table 1. Atomic populations, N, localization indices, λ, and delocalization indices, δ, for a series of diatomic molecules computed at the Hartree–Fock (*HF*) level of theory with the 6-311+ +G(2d,2p) basis set

Molecule	Atom	N(A)	λ(A)	δ(A,B)
H_2	**H**	1.000	0.500	1.000
N_2	**N**	7.000	5.479	3.042
F_2	**F**	9.000	8.358	1.283
LiF	**Li**	2.060	1.971	0.178
	F	9.940	9.851	
CO	**C**	4.647	3.860	1.574
	O	9.354	8.567	
CN^-	**C**	5.227	4.121	2.210
	N	8.773	7.668	
NO^+	**N**	5.525	4.323	2.405
	O	8.475	7.273	

[a] From Ref. [43].

3 Examples and applications

This section is organized as follows. First, LIs and DIs for a series of simple diatomic molecules with molecular bonds of diverse degrees of ionicity and covalency are discussed. Second, we examine the application of LIs and DIs to two interesting polyatomic species. Third, the hydrogen bond (HB) is investigated from the point of view of these second-order indices. Finally, the use of LIs and DIs to analyze the changes in electron pairing along a chemical reaction is briefly reviewed.

3.1 Diatomic molecules

The HF/6-311+ +G(2d,2p) results of LIs and DIs for a series of diatomic molecules are listed in Table 1. H_2 is a representative example of a molecule with an equally shared pair of electrons. In this molecule, the two electrons occupy a bonding σ_g MO. The $D_{\infty\mathrm{h}}$ symmetry of the system imposes the restriction that the overlap between σ_g MOs over each atomic basin equals $^1/_2$, and thus the contribution to the LI is $2 \times {}^1/_2 \times {}^1/_2 = {}^1/_2$ for each atom and the delocalization contribution is $4 \times {}^1/_2 \times {}^1/_2 = 1$, which completely agrees with the prediction of the Lewis model [60] for the electronic structure of H_2. Let us now consider the Lewis structure for the N_2 molecule. According to the Lewis model [60], the LI should have a contribution of 2 from the $1s^2$ core electrons, 2 from the lone pair, and 1.5 from the three shared pairs, giving $\lambda(\mathrm{N}) = 5.5$. Moreover, these three equally shared pairs should give a DI of 3, achieving a total contribution of 14, the number of electrons. If we compare these values with the ones in Table 1, we realize that they are quite similar. The fact that $\delta(N,N') > 3$ means that there is a slight delocalization of the nonbonded pair of a N atom onto the basin of the other N atom.

For molecular bonds with equally shared pairs, such as H_2 or N_2, a simple relationship between the DI and the number of Lewis bonded pairs (bond order) is generally found. However, with the exception of equally shared pairs, the DI cannot be identified with a bond order [43, 61, 62]. Indeed, in molecules such as LiF, where there is an important charge transfer, the electron pair is not equally shared but partly localized on the more electronegative atom, and as a consequence, $\lambda(A)$ increases at expenses of $\delta(A,B)$ and $\lambda(B)$ [43, 62, 63]. Thus, LiF presents a $\delta(\mathrm{Li,F})$ of 0.18 and a $\lambda(\mathrm{F})$ equal to 9.85 electrons. It is important to note that the DI of LiF does not imply a Lewis bond formed from 0.18 pairs of electrons; instead it means that in LiF there is a bonded pair that is very unequally shared. This can be further illustrated with the isoelectronic sequence involving N_2, NO^+, CN^-, and CO, all triply bonded molecules whose DI drops in the sequence 3.04, 2.41, 2.21, and 1.57 electrons, respectively. The DIs tend to decrease with the increased electronegativity difference (greater charge transfer) of the atoms involved in the bond.

Previous workers using indices that are equivalent at the HF level to the DI defined in Eq. (7), have identified the DI with a covalent bond order [59, 64, 65]. However, even the use of the DI as a covalent bond order can be criticized for several reasons. First, electrons are delocalized over every pair of atoms in a molecule and not just those linked by a bond path [40, 61, 66]. Second, atoms linked to *A* or *B* may have an important effect on $\delta(A,B)$ values. For instance, in acetylene, the delocalization of electrons from the C–C triple bond onto the H atoms decreases $\delta(\mathrm{C,C'})$ from 3 to 2.86 electrons [40]. Third, one can have significant DIs even for dissociative electronic states. For example, H_2 in the doubly excited singlet state σ_u^2 has a $\delta(\mathrm{H,H'})$ of 1 despite being a dissociative state [67]. This is also a clear indication that the DI by itself gives no indication of the energy associated with the bonding [54]. Finally, it is worth noting that for atoms sharing a unique electron pair in the Lewis model, it is possible to get DIs larger than 1, a result that must be usually attributed to the delocalization of lone-pair electrons.

Chesnut [68, 69, 70] has recently reported that DIs reflect the expected formal bond orders provided one compares the ratio of molecular quantities rather than their absolute values. Despite the relevance of these results, the use of ratios for the definition of the bond order is somewhat arbitrary since a particular bond of a given pair of atoms must be chosen as a reference to calculate bond orders. In our opinion, one has to consider the DI just as an index that provides a quantitative measure of the sharing of electrons between two atoms.

It has been demonstrated by different authors that, at the HF level, LIs and DIs usually have a small dependence on the basis set, converging smoothly to their appropriate limiting value with the extension of the basis set, even if a Mulliken-like partition of space is used [43, 53, 56, 59]. For instance, $\delta(\mathrm{N,N'})$ is 3.042, 3.037, 3.040, and 3.042 with the 6-31G, 6-31G*, 6-311G(2d), and 6-311 + G(2d) basis sets, respectively [43]. In general, LIs and DIs depend on the partition of electronic space because they are defined by integrations over basins. However, Chesnut and Bartolotti [71] have recently compared the DIs obtained from the AIM partition of space and ELF bond basin populations in some substituted cyclopentadienyl systems, reaching the conclusion that the two measures are essentially equal for the nonpolar C–C bond and somewhat different for bonds that are polar and/or have lone pairs in close proximity. As an example, the DI for the C–C double bond in the cyclopentadienyl cation is 1.65 and the ELF bond basin population is 1.64 electrons.

Table 2. *N*, λ, and δ for a series of diatomic molecules at the configuration interaction (*CI*) with singles and doubles excitations and approximate density functional theory (*DFT*) levels of theory using the 6-311 + + G(2d,2p) basis set

		N(A)		λ(A)		δ(A,B)	
Molecule	**Atom**	**DFT^a**	**CI^b**	**HF(DFT)^a**	**CI^b**	**HF(DFT)^a**	**CI^b**
H_2	**H**	1.000	1.000	0.500	0.575	1.000	0.849
N_2	**N**	7.000	7.000	5.477	5.891	3.046	2.219
F_2	**F**	9.000	9.000	8.361	8.498	1.279	1.005
LiF	**Li**	2.079	2.067	1.969	1.973	0.221	0.193
	F	9.921	9.932	9.810	9.838		
CO	**C**	4.853	4.794	3.946	4.072	1.814	1.443
	O	9.147	9.206	8.240	8.484		
CN^-	**C**	5.512	5.434	4.286	4.490	2.451	1.888
	N	8.488	8.566	7.262	7.621		
NO^+	**N**	5.857	5.803	4.529	4.837	2.656	1.934
	O	8.143	8.197	6.815	7.231		

[a] From Ref. [76].

[b] From Ref. [43].

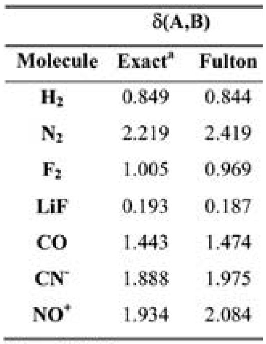
As mentioned in the Introduction, two α or β electrons already avoid each other at the HF level owing to the antisymmetry of the wave function. Since this is the main origin of the Fermi hole, changes in LIs and DIs owing to Coulomb correlation are predicted to be relatively small [34]. The LIs and DIs computed with the configuration interaction with singles and doubles excitations (CISD) and HF(DFT) (vide infra) methods of the same series of diatomic molecules reported in Table 1 are collected in Table 2. From the CISD results one can conclude that in equally shared systems (H_2, N_2, and F_2), Coulomb correlation causes electron density to be removed from the vicinity of the interatomic surface and to be concentrated in each atomic basin, with a decrease in the number of electron pairs shared between the two atoms and an increase in the pairing within each atomic basin [43]. Therefore, the HF values of DIs represent upper bounds to the number of electron pairs shared between atoms [43, 61]. On the other hand, in closed-shell or ionic systems (LiF), where the density is strongly localized within the basin of each atom, the net effect of Coulomb correlation on the pairing of electrons within each atomic basin is minimal. In shared polar interactions (CO, CN^-, and NO^+), the transfer of density from the interatomic region to the atomic basins is reduced with respect to the homonuclear molecules. Taking the HF calculation as a reference, Coulomb correlation causes an increase in the population of the less electronegative atom, consistent with a reduction in the bond ionicity. However, the decrease in the DI is smaller than that observed in the homonuclear species. It is important to mention that in some cases the introduction of Coulomb correlation is essential to get a correct picture of the chemical process. This is the case of the H_2 dissociation. As nuclei are pulled apart, the HF wave function retains its DI of 1 [67], thus reflecting through the DI the well-known deficiency of the HF method to deal with bond dissociation. However, the addition of correlation results in the expected value of zero for the DI at large internuclear separations.

Several studies that report DFT calculations of LIs and DIs [59, 68, 69, 70, 71, 72, 73, 74, 75] have been published recently. In recent work [59, 76], the accuracy of LIs and DIs computed from the DFT density using the HF expressions (Eqs. 17, 18) in a scheme of calculation that we have denoted as HF(DFT) has been analyzed. In general, it has been found that DIs computed at the HF(DFT) level (with the B3LYP functional [77, 78, 79]) are larger than those obtained with the HF method, which in turn are greater than CISD DIs. Thus, despite the DFT one-electron density being clearly better than the HF one [80, 81, 82], the DFT two-electron density calculated using the HF formalism does not improve the HF one. This is not unexpected given the fact that the DFT two-electron density calculated using the HF formalism is formally derived from an approximate monodeterminantal wave function constructed with Kohn–Sham orbitals that is, at least from an energetic point of view, worse than the HF wave function.

Although at the HF level the definitions of bond order by Ángyán et al. [53] and Fulton and Mixon [54, 55] are equivalent to one another and to the DI defined in Eq. (7), differences emerge when correlated wave functions are used. The CISD/6-311++G(2d,2p) indices obtained from Eq. (15) using the exact correlated pair density and from Eq. (19) are compared in Table 3. The results in Table 3 show that in the two cases the DI decreases upon going from the HF to a CI wave function [43, 54]. One can also see that, in general, Fulton bond orders are good approximations to the exact DIs, with the advantage that the calculation of Fulton bond orders does not require the use of second-order densities. Moreover, unlike the bond order definition of Ángyán et al. [53], the sum of Fulton's bond indices equals N at all levels of theory. Cioslowski and Mixon [65] have also defined a bond order using products of overlap integrals defined over atomic basins, but their definition is not invariant to a unitary transformation of the MOs. Some comparisons between the indices of Fulton and Cioslowski and Mixon or Ángyán et al. have been reported [53, 55].

It is also enlightening to analyze a series of open-shell molecules from the point of view of LIs and DIs. Unpaired electrons have a significant effect on the interatomic DIs [67]. Indeed, for many radicals, the analysis of the spin components reveals that the interatomic delocalization is very different for α-and β-spin electrons [67]. An interesting working example is H_2^- in its doublet ground state. Using Eq. (18), one can easily derive that the DI for H_2^- at the ROHF level is $1.5–4[S_{ab}(A)]^2$, S_{ab} being the overlap integral between the σ_g and σ_u^* orbitals over an atomic basin [67]. Thus, the extra electron in H_2^- has two different effects on $\delta(\mathrm{H,H'})$. On one hand, an electron in the σ_u^* orbital, on its own, contributes 0.5 to $\delta(\mathrm{H,H'})$. On the other hand, the extra electron correlates with one same-spin electron in the σ_g orbital, leading to some localization and the consequent reduction by $-4[S_{ab}(A)]^2$ to $\delta(\mathrm{H,H'})$. Depending on the degree of overlap between the σ_g and σ_u^* orbitals, the net effect will be an increase or decrease in the DI, with respect to H_2. At the ROHF/STO-3G level, $S_{ab}(A)$ is ± 0.48, and $\delta(\mathrm{H,H'})$ is 0.59 electrons, sensibly lower than in H_2. In contrast, at the ROHF/6-311++G(2d,2p) level, $S_{ab}(A)$ is ± 0.14, and $\delta(\mathrm{H,H'})$ is 1.42 electrons, larger than in H_2. The result in this case is clearly basis-set dependent.

Table 3. δ obtained through Eqs. (11) and (18) for a series of diatomic molecules with the CI with singles and doubles excitations method using the 6-311++G(2d,2p) basis set



	δ(A,B)	
Molecule	**Exact**[a]	**Fulton**
H_2	0.849	0.844
N_2	2.219	2.419
F_2	1.005	0.969
LiF	0.193	0.187
CO	1.443	1.474
CN^-	1.888	1.975
NO^+	1.934	2.084

[a] From Ref. [43].

The results for O_2 collected in Table 4 provide further insight into the effect of unpaired electrons on LIs and DIs. Each of the two oxygen atoms has 4.5 α and 3.5 β electrons, respectively. The σ contribution to the DI is 1.04, corresponding to a perfectly delocalized electron pair plus some small contribution from electrons in nonbonding orbitals. The two β electrons with π symmetry are also perfectly shared between the two atoms, contributing exactly 1.00 to $\delta(\mathrm{O,O'})$. In contrast, the interatomic delocalization of the four α electrons with π symmetry is only 0.26 electrons in total. The orbital occupancies $[\sigma(2)\sigma^*(2)\sigma(2)\sigma^*(2)\sigma(2)\pi(2)\pi(2)\pi^*(1)\pi^*(1)]$ provide the explanation for the differences in the delocalization of the α and β electrons. For each of the π_x and π_y sets, there is an α electron in a bonding orbital and another one in an antibonding orbital, plus a β electron in a bonding orbital. There is no overlap between spin-orbitals of different symmetry (σ and π) or between orbitals of different spin. Accordingly, each of the β electrons in the π_x and π_y bonding orbitals does not interact directly with other electrons and is perfectly delocalized between the two oxygen atoms. In contrast, the mutual repulsion between the α electrons in the bonding and antibonding π_x and π_y orbitals leads to a high localization of these α electrons.

3.2 Polyatomic molecules

In general, the AIM analysis becomes more complex for polyatomic molecules because the number of interatomic interactions grows geometrically with the number of atoms. While electronic delocalization between distant atoms is generally small, in some cases, the DIs between nonbonded atoms can be significant, indicating through-space interactions between these atoms. Furthermore, the results obtained with the AIM theory for these molecules are often difficult to interpret with the Lewis model, even at the HF level of theory. In connection with this problem, molecules with the so-called three-center four electron (3c–4e) and three-center two electron (3c–2e) bonding interactions are interesting cases to analyze [83]. The results for CO_2 and B_2H_6 as examples of 3c–4e and 3c–2e bonding are gathered in Table 5 [43,

Table 4. The different contributions to the λ and δ indices of O_2 in its ground state computed at the ROHF/6-311++G(2d,2p) level

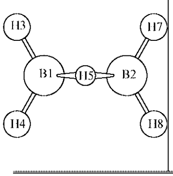
	λ(O)			δ(O,O')		
symmetry	**total**	α	β	**total**	α	β
total	6.853	4.113	2.740	2.294	0.775	1.519
σ	4.480	2.240	2.240	1.038	0.519	0.519
π	2.372	1.872	0.500	1.255	0.255	1.000

[a] From Ref. [67].

76]. The δ(C,O) value found for CO_2 is close to unity, despite the electronic structure being consistent with the presence of four bonded Lewis pairs. Each bonding π_u orbital contributes with 0.26 electrons to δ(C,O), while the contribution from the σ_g and σ_u orbitals is 0.51 electrons. The large δ(O,O′) between nonbonded oxygen atoms of 0.3 electrons mainly arises from the π_g orbital in CO_2 (Fig. 1) [43]. It seems that a large DI between nonbonded atoms may be a clear indication of the existence of 3c–4e bonding. This is confirmed by a large δ(F,F′) between nonbonded fluorine atoms in FHF^- and FFF^- [83, 84]. For B_2H_6, it is found that *d*(B,H) is larger for the terminal hydrogens than for the bridge hydrogens. Interestingly, the electron delocalization between the two bridge hydrogen atoms is significantly larger (0.24) than between the two boron atoms (0.05). This small δ(B,B′) has been attributed to the low electron density around each boron atom [43]. However, one cannot rule out the possibility that 3c–2e bonding is distinguished, in general, by low DIs between terminal atoms, as opposed to 3c–4e bonding. Finally, it is worth noting that Ponec and coworkers [56, 57, 58] have recently characterized the three-center bonding by means of the three-center bond index given by Eq. (22). The authors found that this index allows easy differentiation between 3c–2e and 3c–4e bonding, the three-center bond index being positive for 3c–2e bonding and negative for 3c–4e bonding.

The nonbonded DIs are of particular interest in benzene [42, 43, 55], where the delocalization of the density is greater between para-related carbons, $\delta(C,C') = 0.10$, than between meta-related atoms, $\delta(C,C') = 0.07$. It looks like the DIs of aromatic molecules can be used as an index of aromaticity. Indeed, Chesnut and Bartolotti [71] found a good correlation for the DI of the formally single C–C bond in substituted cyclopentadienyl systems and the corresponding homomolecular–homodesmotic resonance energy. More research must still be undertaken to confirm the validity of the DIs to quantify aromaticity.

Table 5. *N*, λ and δ for CO_2 and B_2H_6 at the HF and CI with singles and doubles excitations levels of theory using the 6-31G** basis set

		N(A)		λ(A)		δ(A,B)		
molecule	**atom**	**HF**	**CI**	**HF**	**CI**	**pair**	**HF**	**CI**
CO_2	**C**	3.243	3.518	2.187	2.443	**C,O**	1.056	1.075
	O	9.378	9.241	8.660	8.547	**O,O**	0.380	0.313
B_2H_6	**B**	2.881	2.993	2.103	2.207	**B_1,B_2**	0.047	0.033
	H_3	1.699	1.660	1.257	1.235	**B_1,H_3**	0.473	0.477
	H_5	1.719	1.685	1.103	1.100	**B_1,H_5**	0.264	0.282
						B_1,H_7	0.017	0.009
						**H_3,H_4**	0.134	0.120
						H_5,H_6	0.237	0.194
						H_3,H_5	0.116	0.103
						H_3,H_7(c)	0.011	0.021
						H_3,H_8(t)	0.015	0.017

[a] From Ref. [43]

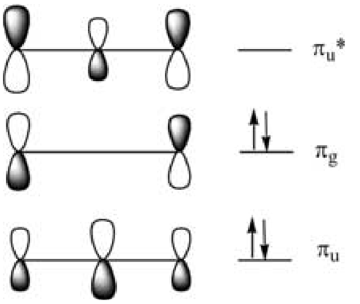


Fig. 1. A schematic picture of the π orbitals in CO_2

The changes in the electron-pair structure of molecules due to solvent effects have also been analyzed through these second-order indices [85]. The analysis showed that solute–solvent interactions modify the electron-pair distribution of the solute by increasing the polarization of the molecular bonds. This polarization is reflected in a larger degree of charge transfer between electronegative and electropositive atoms, an increase of the electron localization for electronegative atoms, and a decrease of the electron delocalization between bonded atoms. Moreover, these effects are also more important for charged species, especially anions, than for neutral molecules.

Other systems that have been analyzed by means of LIs and DIs include hypervalent molecules [73], four-coordinated titanium complexes [75], gallium compounds [40], ylides of phosphorus [86], and the 6-tricyclo $[3.2.1.0^{2,4}]$ octyl cation [87].

3.3 Hydrogen bond

The characterization of hydrogen bonding from the point of view of the AIM theory has recently received some interest. In particular, Koch and Popelier [88] have put forward a set of topological criteria that a bond must fulfill in order to be considered a HB. Furthermore, Espinosa and coworkers [89, 90] have attempted a classification of HBs using the topological and energetic properties of intermolecular bond critical points (BCP) derived from experimental electron densities. Also, Fulton and Perhacs [91] have investigated the nature of the HBs in some representative complexes by using the index defined by Eq. (22). Fuster and Silvi [92] have analyzed the ELF in several HB complexes and have established topological criteria to distinguish between weak, medium, and strong HBs. Finally, Muñoz et al. [93] have investigated through LIs and DIs the improper, blueshifting HBs.

We have carried out a preliminary study on the relationship between the interatomic delocalization and the interaction energy (E_{int}) for different kinds of HBs with the B3LYP/6-31++G** method using the HF(DFT) scheme to calculate DIs (vide supra). The interaction energy of the HB complex is defined as the energy released when the two monomers, at the geometry that they have in the complex and separated by an infinite distance, are brought to the position they have in the complex. $\delta(X,\mathrm{H})/r_{X\text{–H}}$ is plotted in Fig. 2 versus the interaction energy (δ/r versus E_{int}) for a set of representative hydrogen-bonded complexes, where X and H are the atoms most involved in the intermolecular HB. Note that the complexes are grouped into four series, according to the hydrogen-donor molecule: HF, HCl, H_2O, and H_2S. Even though the number of complexes in each group is very small, some interesting trends appear in Fig. 2. For each series, the relationship between δ/r and E_{int} appears to be approximately linear. $\delta(X,\mathrm{H})/r_{X\text{–H}}$ has been used instead of $\delta(X,\mathrm{H})$ to allow a direct comparison between complexes with second- and third-row atoms in the acceptor molecule. As for the comparison between the four series, it is worth remarking that the slope of the plot increases (in absolute value) as the polarity of the donor molecule decreases (HF > H_2O > HCl > H_2S). Indeed, one could consider the ratio $(\delta/r)/|E_{\mathrm{int}}|$ as a rough measure of the polarity of the HB. Consider, for instance, the $\mathrm{ClH}\cdots\mathrm{NH_3}$ complex, with an E_{int} of -11.3 kcal mol^{-1}. The delocalization between the nitrogen and hydrogen atoms involved in the HB is relatively large (0.21), while the charges on the nitrogen and hydrogen atoms are -1.10 and 0.36, respectively. In contrast, the $\mathrm{FH}\cdots\mathrm{H_2CO}$ complex, which has an E_{int} of -8.6 kcal mol^{-1}, has a lower delocalization between the hydrogen and oxygen atoms connected through the HB (0.10), and charges of -1.12 and 0.72 on the oxygen and hydrogen atoms, respectively. Altogether, these values reveal that the HB in $\mathrm{FH}\cdots\mathrm{H_2CO}$ is more polar that in $\mathrm{ClH}\cdots\mathrm{NH_3}$, in agreement with the values of $(\delta/r)/|E_{\mathrm{int}}|$ for these molecules. A similar reasoning can be carried out for the other complexes in Fig. 2. It is worth remarking that, for these complexes, the relationship between the values of $\rho_{\mathrm{BCP}}(\mathbf{r})$ or its Laplacian and E_{int} is approximately linear, with similar slopes for all the series. All in all, these results suggest that the properties of the intermolecular BCP in HB complexes are mainly related to the strength of the HB, in agreement with the results of Espinosa and coworkers [89, 90]. In contrast, electron delocalization between the atoms in the HB may be rather related to the polarity of the bond.

3.4 Chemical reactivity

Pair population and bond order analysis have been applied to the study of electron reorganization in the course of chemical reactions [51, 63, 94, 95, 96, 97]. As an example, we discuss the results obtained for the Diels–Alder (DA) reaction between butadiene and ethylene to yield hexadiene [98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111], which is often taken as the prototype of a pericyclic concerted reaction (see Fig. 3 for a description of the reactants, transition state, TS, and product involved in this reaction).

The atomic populations and LIs for all nonequivalent atoms of the reactants, TS, and product for the concerted and synchronous DA reaction, calculated at the HF level of theory, are gathered in Table 6. The DIs are reported only for relevant nonequivalent pairs of atoms. The $\delta(\mathrm{C,H})$ indices have values between 0.9 and 1.0 electrons, corresponding to a rather apolar sharing of the electrons between the carbon and hydrogen at-

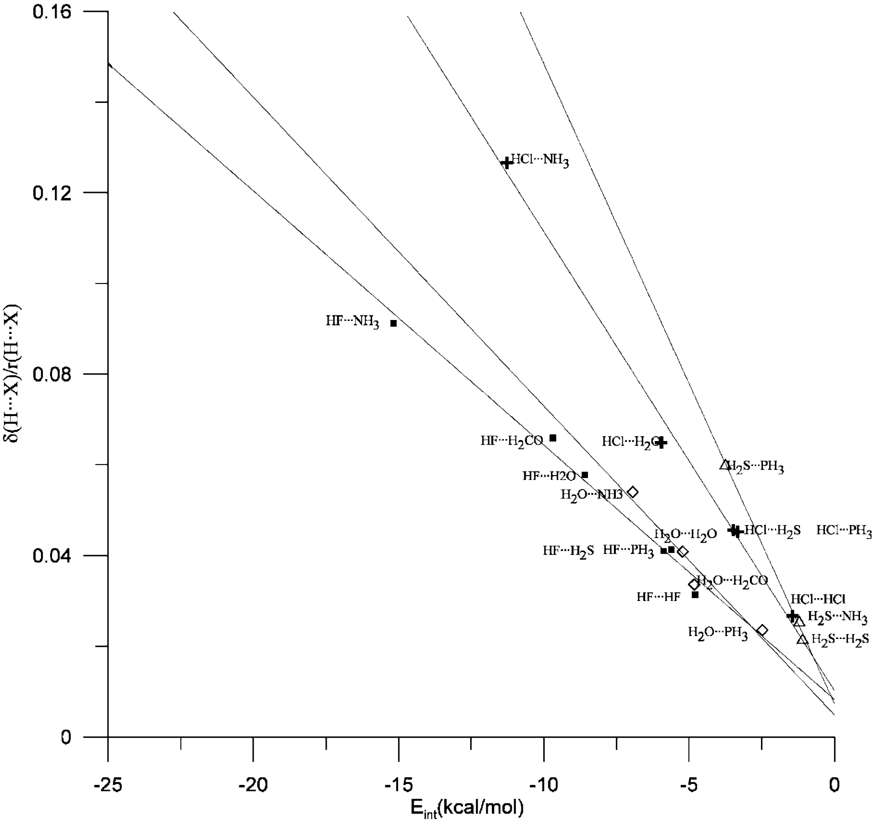


Fig. 2. $\frac{\delta(X,\mathrm{H})}{r_{X\text{–H}}}$ versus the interaction energy of hydrogen-bonded complexes computed at the B3LYP/6-31++G** level of theory. The *squares* are for HF as a donor, the *diamonds* are for H_2O as a donor, the *crosses* are for HCl as a donor, and the *triangles* are for H_2S as a donor

$C_2H_4 + C_4H_6 / C_6H_{10}$

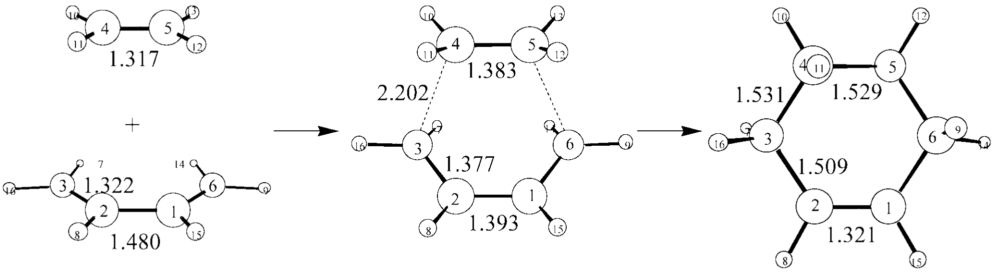


Fig. 3. HF/6-31G* optimized geometries for reactants, transition state, and product for the Diels–Alder reaction between butadiene and ethylene. Bond lengths are given in angstroms and angles in degrees

oms, and also remain nearly constant throughout the reaction. Indeed, the most significant changes during the DA reaction are found in the $\delta(C,C)$ indices. For the three structures, pairs of carbon atoms that are formally single-bonded have $\delta(C,C)$ values between 1.0 and 1.1 electrons, while formally double-bonded carbon atoms correspond to $\delta(C,C)$ values between 1.8 and 1.9 electrons. For the reactants, it is worth noting that the $\delta(C,C)$ values between double-bonded atoms are lower for butadiene (1.83) than for ethene (1.92), while the $\delta(C,C)$ values between formally single-bonded atoms in butadiene are slightly larger than 1 (1.07), revealing, as expected, that the C–C bonds in butadiene have intermediate character between a single and a typical double bond. Moreover, the DIs between the nonbonded carbons in butadiene reveal that 1,4 delocalization [$\delta(C_3,C_6) = 0.072$] is slightly more important than 1,3 delocalization [$\delta(C_3,C_6) = 0.067$]. The $\delta(C,C)$ values for reactants and products are consistent with the formation of a new bond between the C_5 and C_6 atoms (and the equivalent C_4 and C_3 atoms). At the same time, the C_1–C_2 single bond of the butadiene molecule evolves to a double bond in the hexadiene molecule, while the C_4–C_5 double bond in ethene and the C_1–C_6 and C_2–C_3 double bonds in butadiene are transformed to formal single bonds in hexadiene. The evolution of the C_1–C_2, C_1–C_6, C_4–C_5, and C_5–C_6 DIs along the intrinsic reaction path (IRP) is depicted in Fig. 4. Although the entire electron DIs change gradually along the IRP, the largest changes in electron-pair reorganization take place mainly in a small region around the TS.

The TS in this reaction corresponds to a nonplanar structure with the six carbon atoms forming a ring. This structure is usually considered to be aromatic, and theoretical calculations of magnetic susceptibilities and ^1H chemical shifts support this point of view [107, 108]. Indeed, according to the LIs and DIs reported in Table 6, the TS is clearly aromatic. First of all, one must take into account that there are three nonequivalent carbon atoms (e.g., C_1, C_5, and C_6); therefore, the following pairs of nonequivalent carbon pairs exist: four ortho pairs, three meta pairs, and two para pairs (Fig. 3). For the ortho pairs, the associated $\delta(C,C)$ indices are about 1.4, except for $\delta(C_5,C_6)$, and the equivalent $\delta(C_3,C_4)$, which are about 0.4. Therefore, from an electronic point of view, this structure is nearly equivalent to that of the benzene molecule, with the difference that there is no σ bonding associated with the C_3–C_4 and C_5–C_6 pairs. Moreover, the values of the $\delta(C,C)$ indices associated to pairs of carbon atoms in the meta position are rather small (ranging from 0.04 to 0.07), while the atoms in the para position have slightly larger $\delta(C,C)$ values (0.09 and 0.10). As already mentioned, the fact that there is more delocalization between the atoms in para position than between the atoms in meta position, in spite of the larger interatomic distance between the atoms in para position, is characteristic of aromatic systems. Thus, according to the $\delta(C,C)$ values just discussed, one can consider that the TS has a set of six π electrons delocalized between the six carbon atoms, although the nonplanar character of this structure prevents it from separating strictly the electrons into σ and

Table 6. N, λ, and δ for the reactants, transition state, and product of the $C_2H_4 + C_4H_6 \rightarrow C_6H_{10}$ Diels–Alder cycloaddition reaction, calculated at the HF/6-31G* level of theory. *o*, *m*, and *p* are used to denote pairs of atoms that are in ortho, meta, and para positions, respectively, in the transition state

	Reactants		**TS**	**Product**
	butadiene	**ethylene**		
$N(C_1)$	6.010		5.992	6.056
$N(C_5)$		6.035	6.030	5.911
$N(C_6)$	6.033		6.039	5.909
$N(H_9)$	0.979		0.988	1.027
$N(H_{12})$		0.983	0.981	1.036
$N(H_{13})$		0.983	0.990	1.035
$N(H_{14})$	0.985		0.981	1.027
$N(H_{15})$	0.994		1.000	1.001
$\lambda(C_1)$	3.960		3.928	3.998
$\lambda(C_5)$		4.042	3.976	3.846
$\lambda(C_6)$	4.037		3.990	3.846
$\lambda(H_9)$	0.437		0.442	0.475
$\lambda(H_{12})$		0.441	0.431	0.481
$\lambda(H_{13})$		0.441	0.439	0.483
$\lambda(H_{14})$	0.438		0.424	0.473
$\lambda(H_{15})$	0.450		0.454	0.455
$\delta(C_1,C_2)$ **o**	1.068		1.347	1.828
$\delta(C_1,C_6)$ **o**	1.839		1.438	1.008
$\delta(C_4,C_5)$ **o**		1.924	1.455	0.978
$\delta(C_5,C_6)$ **o**			0.397	0.976
$\delta(C_1,H_{15})$	0.959		0.961	0.963
$\delta(C_5,H_{12})$		0.972	0.960	0.945
$\delta(C_5,H_{13})$		0.972	0.959	0.951
$\delta(C_6,H_9)$	0.972		0.967	0.946
$\delta(C_6,H_{14})$	0.965		0.942	0.941
$\delta(C_1,C_3)$ **m**	0.067		0.073	0.043
$\delta(C_1,C_4)$ **p**			0.086	0.009
$\delta(C_1,C_5)$ **m**			0.050	0.059
$\delta(C_3,C_6)$ **p**	0.072		0.103	0.014
$\delta(C_4,C_6)$ **m**			0.042	0.059

[a] From Ref. [97].

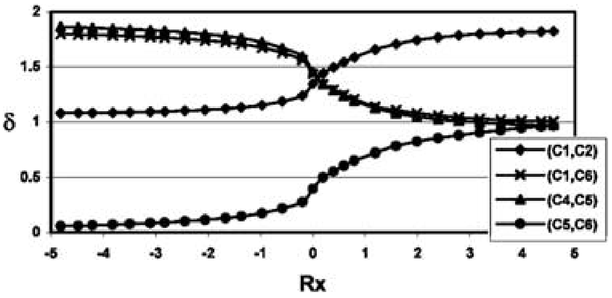


Fig. 4. Evolution of the values of selected delocalization indices along the Diels-Alder cycloaddition reaction, calculated at the HF/6-31G* level of theory. Negative and positive values of the reaction coordinate, R_x, correspond to reactants (C_2H_4 + C_4H_6) and product (C_6H_{10}), respectively. The transition state is located at $R_x = 0$

π sets. Furthermore, the fact that different C–C distances exist (about 1.4 Å for the σ-bonded atom pairs, and about 2.2 Å for the C_3–C_4 and C_5–C_6 pairs) leads to slightly different delocalizations for the different ortho, meta, and para pairs. Indeed, it is remarkable that the main electron delocalization patterns associated with aromaticity take place in spite of the large C_3–C_4 and C_5–C_6 distances.

4 Conclusions

In the framework of the theory of AIM, the electron-pair density provides important information, which has proven to be very useful for a quantitative description of the electron-pairing phenomena that take place between the atoms in a molecule. An important feature of the analysis reviewed here is that it is model-independent, with LIs and DIs being obtained only from first- and second-order densities, which are physical observables. In principle, there is no need to resort to any particular model, such as MO theory, for these calculations. Therefore, provided that first- and second-order densities are available, this analysis could be performed at any level of theory. At present, practice provides exact second-order densities only for the HF and CISD methodologies. At the DFT level, second-order densities based on the single determinant of Kohn–Sham orbitals can be used even though they are an approximation to the unknown exact DFT second-order density.

We have shown that LIs and DIs, together with AIM atomic populations, are very useful interpretative tools for describing accurately the chemical bond and changes in electron pairing that take place along the reaction path for reactions in the gas phase and in solution. In general, the results reviewed in here confirm that a proper account of electron correlation is important for the correct description of atomic interactions from the point of view of electron LIs and DIs. The HF method consistently overestimates the interatomic delocalization between bonded atoms with open-shell interactions, compared to the CI method. In contrast, qualitatively good results are obtained at the HF level for closed-shell or nonbonded interactions, for which the interatomic correlation is small.

All in all, this is a very promising field that has just provided some successful applications and that shows itself as an interesting area of research work for the future.

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