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Extracting Covalent and Ionic Structures from Usual Delocalized Wave Functions: The Electron-Expansion Methodology

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We present easily programmable expansions, allowing the calculation of the weights of local covalent and ionic structures of a chemical bond from usual delocalized wave functions; they are obtained in the framework of the electron-expansion methodology, in which the hole conditions (involved by definition in a covalent or ionic structure) are expanded in terms involving only electrons. From the derived relations, true for both HF and correlated levels, one can also express the covalency/ionicity and the localization of a usual two-electron two-center (2e/2c) bond in terms of electronic populations. The three-electron populations are crucial for bond localization. On the contrary, in 2e/2c bonding, and particularly in Charge−Shift bonds (which show enhanced covalent−ionic interactions) although the three-electron populations can be non-negligible, they are not important for the covalency/ionicity of these bonds. Numerical applications and discussion are given for correlated MO wave functions of butadiene, hexatriene, and pyrrole molecules on the basis of both natural atomic orbitals (NAOs) (orthogonal orbitals) and pre-NAOs (nonorthogonal orbitals).

1. Introduction

The covalent and ionic structures of a two-electron two-center (2e/2c) bond are involved in usual localized bonding schemes, which are directly issued from the traditional chemical formula and are widely used by experimental chemists. However, in the field of quantum chemistry, the usual molecular orbital (MO) calculations in both Hartree−Fock (HF) or configuration interaction (CI) levels, as well as calculations within density functional theory (DFT) provide delocalized pictures that are not appropriate for chemically meaningful interpretations. In this context, it is a challenge to retrieve fundamental chemical concepts, such as a covalent or an ionic structure from usual quantum chemical calculations. The way has been opened[1] by calculating the weights of valence-bond (VB) spin-eigenfunctions[1,2] from molecular orbital MO wave functions. Localized bonding schemes described by (spin-dependent) local Slater determinants have also been investigated in the basis of SCF-AOs,[3] as well as natural atomic orbitals[4] (NAOs), or the other types of natural orbitals[5] which have been introduced in the framework of the natural bond orbital (NBO) analysis[6,7] of chemical bonding. For polyelectron population analysis[8] (PEPA) investigations, we use the Moffitt's (or Cauchy's) theorem[9] to transform MO wave functions on the basis of local Slater determinants involving NAOs[10,11] or NBOs.[12] Localized bonding schemes can also be obtained by means of another methodology which is based on the population analysis of strongly localized MOs.[13] In a different framework, the natural resonance theory[14] (NRT), considers a weighted average of a set of Lewis-type structures, each of them defined by means of its own set of NBOs (and occupancies). The calculated resonance weights for these Lewis-type structures are such that the final weighted sum best describes the one-electron distributions in the considered molecule.

Although populations beyond the usual one and two electron types[15] (without conditions for electron−holes) provide very useful information for chemical bonding,[16] the investigation of covalent and ionic structures of a target bond necessitates that the employed population methodology can include conditions for electron−holes, because these structures refer to both electrons and electron−holes. For example, the ionic structure $[\mu(-)\nu(+)]$, between orbitals μ and ν, refers by definition to the simultaneous presence of two electrons in μ and two electron−holes in ν, respectively. The investigation of this structure can be achieved by means of PEPA, and the relations and developments for local structures[11,17] which were previously used always included conditions for electron− holes; however, most often these conditions make difficult the rationalization of the numerical results, because an "electron−hole" is a concept not obvious from common chemical intuition. In the present work we present an alternative methodology to approach these structures, in which the explicit calculation of the electron−hole conditions is circumvented. Our scope is (i) to give the possibility to various population analysis methodologies, going beyond usual one and two electron populations, to access to these structures, and (ii) to rationalize the behavior of these structures by means of populations which do not involve conditions for electron−holes. This article is organized as follows. In section 2 we obtain the weights of covalent and ionic structures as expansions of electronic populations by applying the electron-expansion methodology presented in the appendix; in subsections 2.1 and 2.2 we express the localization and the covalency/ionicity of a 2e/2c bond, respectively, as expansions of these populations. In section 3 we present numerical applications and discussion in the basis of both NAOs (orthogonal orbitals), and pre-NAOs (nonorthogonal orbitals).

2. Expanding Covalent and Ionic Structures in Terms of Electronic Populations

Any usual delocalized MO wave function, $\Psi(\mathrm{MO})$ (in both HF or CI levels), having the general form of a linear combina-

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tion of MO Slater determinants, can be transformed[9–12,17] into a totally local one, Ψ (TL):

$$|\Psi(\mathrm{TL})> = \sum_K T_K|K> \tag{1}$$

The local Slater determinants, *K*, can involve the SCF-AOs, or, in general, some linear combinations of these orbitals, but for chemically meaningful interpretations one can use (see section 3) natural orbitals, such as the (orthogonal) NAOs. In all cases the expansion coefficients, T_K, are calculated in the framework of Moffitt's theorem, which guarantees[9,10a,12a]

$$\Psi(\mathrm{MO}) = \Psi(\mathrm{TL}) \tag{2}$$

The weight of the local ionic structure, $\mathbf{W}[\mu(\uparrow\downarrow)\nu(+)]$, calculated in the basis of Ψ(TL), is the probability of finding simultaneously two electrons of opposite spin in μ, and two electron−holes (also of opposite spin) in ν, while the remaining electrons can reside anywhere else in the remaining orbitals. By $\nu(+)$ we symbolize an empty orbital ν, that is a spatial orbital occupied by two electron−holes of opposite spin (the sign (+) does not represent necessarily the formal global charge of the atom to which the orbital belongs); the spin−orbitals which correspond to spatial orbitals μ and ν, are represented by $\mu,\bar{\mu}$ and $\mathrm{v},\bar{\mathrm{v}}$, respectively. The electron expansion (see Appendix) of the two hole conditions, involved by definition in the ionic structure $[\mu(\uparrow\downarrow)\nu(+)]$, gives the weight of this local electronic structure as an expansion of usual electronic populations; substituting $i = \mu$, $j = \bar{\mu}$, $r = \mathrm{v}$, and $t = \bar{\mathrm{v}}$ in relation (A6) of Appendix we obtain

$$\mathbf{W}[\mu(\uparrow\downarrow)\nu(+)] = P_2(\mu,\bar{\mu}) - P_3(\mu,\bar{\mu},\nu) - P_3(\mu,\bar{\mu},\bar{\mathrm{v}}) + P_4(\mu,\bar{\mu},\mathrm{v},\bar{\mathrm{v}}) \tag{3a}$$

Similarly, the weight of the other local ionic structure, $\mathbf{W}\,[\nu(\uparrow\downarrow)\mu\,(+)]$, can be expanded as follows:

$$\mathbf{W}[\nu(\uparrow\downarrow)\mu(+)] = P_2(\mathrm{v},\bar{\mathrm{v}}) - P_3(\mathrm{v},\bar{\mathrm{v}},\mu) - P_3(\mathrm{v},\bar{\mathrm{v}},\bar{\mu}) + P_4(\mathrm{v},\bar{\mathrm{v}},\mu,\bar{\mu}) \tag{3b}$$

The weight of the local covalent structure, $\mathbf{W}[\mu(\uparrow)\ \nu(\downarrow)]$, is obtained by substituting $i = \mu$, $j = \bar{\mathrm{v}}$, $r = \bar{\mu}$ and $t = \mathrm{v}$ in relation (A6):

$$\mathbf{W}[\mu(\uparrow)\nu(\downarrow)] = P_2(\mu,\bar{\mathrm{v}}) - P_3(\mu,\bar{\mathrm{v}},\bar{\mu}) - P_3(\mu,\bar{\mathrm{v}},\mathrm{v}) + P_4(\mu,\bar{\mathrm{v}},\bar{\mu},\mathrm{v}) \tag{3c}$$

In relations 3, quantities P_2, P_3, and P_4 are the numbers of electron dyads (pairs), triads, and tetrads,[8a] respectively, occupying the corresponding orbitals or, alternatively (in the case of orthogonal orbitals) the probabilities of finding simultaneously two, three, and four electrons, respectively, in these orbitals. The weight of the spin-independent local covalent structure, $1/\sqrt{2}(\|\mu\ \bar{\mathrm{v}}...\| - \|\bar{\mu}\mathrm{v}...\|)$, can be obtained straightforwardly as $2\mathbf{W}[\mu(\uparrow)\nu(\downarrow)]$.

Another physical meaning of relations 3 can be obtained by using the concept of "electronic event", introduced in the framework of Loge theory.[18] Let us suppose that the examined molecular system has *n* electrons and *M* orbitals; a given distribution of the *n* electrons of the system in the available 2 M spin−orbitals, represented by a local Slater determinant *K*, defines a *n*-electron event, characterized from its probability (weight), T_K^2. Placing a target bond of a given molecular system "under the microscope" one can distinguish various local electronic structures, such as a local covalent or ionic structure; each of them defines a local electronic event, characterized from a probability (weight), *W*, which is obtained from the sum (see relation A2 of Appendix) of the probabilities (weights) of all *n*-electron events having a fixed occupation by electrons and holes in the orbitals of the target bond. In this context, relations 3 provide the dependence of the considered local electronic events from usual electronic populations.

Although in the case of orthogonal orbitals the definition of populations P_2, P_3, and P_4 is unequivocal, in the case of nonorthogonal ones, the definition and calculation of the corresponding occupation numbers is not, in principle, unique, depending on the adopted partition. In the numerical applications of the present work we use the Mulliken partition, and we calculate these occupation numbers by means of the Coulson−Chirgwin weights,[19] *W*(*K*):

$$W(K) = T_K^2 + T_K \sum_{K' \neq K} T_{K'} <K|K'> \tag{4}$$

Generalizing the well-known relation showing that the sum of weights (4) of Slater determinants, K, involving one spin−orbital, μ, equals the Mulliken population, $P_1(\mu)$, on this spin−orbital,[20] we have shown[8a] that the sums of the weights of well selected *K* provide the polyelectron Mulliken populations.[8a,21] For example, the number of electron triads $P_3(\mu,\bar{\mu},\mathrm{v})$ is obtained from the sum of the weights of those *K*, which involve simultaneously μ, $\bar{\mu}$, and v:

$$P_3(\mu,\bar{\mu},\mathrm{v}) = \sum_K^{(\mu,\bar{\mu},\mathrm{v})} W(K) \tag{5}$$

The other occupation numbers can be calculated by means of expressions similar to (A5) of Appendix, by replacing the T_K^2 by *W*(*K*). Of course, at the HF or DFT levels, the same Mulliken populations can be obtained by means of more computationally efficient relations.[15,16]

2.1. Bond Localization As Expansion of Electronic Populations.

Let us consider the sum of the weights of the spin-independent covalent and the two ionic structures, describing a target 2e/2c bond between orbitals μ and ν:

$$L(\mu,\nu) = 2\mathbf{W}[\mu(\uparrow)\nu(\downarrow)] + \mathbf{W}[\mu(\uparrow\downarrow)\nu(+)] + \mathbf{W}[\nu(\uparrow\downarrow)\mu(+)] \tag{6}$$

Quantity $L(\mu,\nu)$ provides the sum of the weights of the four local electronic events occurring in μ and ν, which are related to a 2e/2c bond between these orbitals. If the target 2e/2c bond was totally localized, that is totally isolated from the remaining molecule, then this sum should be equal to one. Because the summation 6 includes all possible arrangements of an (α,β) electron pair in two orbitals, and in accord with the traditional thinking for bond (de)localization,[22] the above relation provides a measure of bond localization: the closer to unity $L(\mu,\nu)$ is, the more localized[23] is the considered 2e/2c bond. By means of expansions 3, this definition of localization of a 2e/2c bond can be expressed in terms of two and higher electron populations:

$$L(\mu,\nu) = S_2(\mu,\nu) - S_{\mathrm{h}}(\mu,\nu) \tag{7}$$

where S_2 is the sum of two electron populations and S_{h} is the sum of higher (i.e., three and four electron) ones contributing to $L(\mu,\nu)$; for a closed shell system these quantities are defined as follows:

$$S_2(\mu,\nu) = 2P_2(\mu,\bar{\mathrm{v}}) + P_2(\mu,\bar{\mu}) + P_2(\mathrm{v},\bar{\mathrm{v}}) \tag{8a}$$

$$S_{\mathrm{h}}(\mu,\nu) = S_3(\mu,\nu) - 4P_4(\mu,\bar{\mu},\mathrm{v},\bar{\mathrm{v}}) \tag{8b}$$

and

$$S_3(\mu,\nu)=4P_3(\mu,\bar{\mu},\mathrm{v})+4P_3(\mathrm{v},\bar{\mathrm{v}},\mu) \qquad (8c)$$

A general trend issued from expansions 3 (or 7 and 8) is that the greater the three electron populations are, the less important are both ionic and covalent structures, and thus the 2e/2c bonding (or the corresponding bond localization). This trend corroborates with results presented in other works. A weakening of a 2e/2c bond by three electron populations is found in the framework of a well-elaborated energetic analysis of interactions of VB structures, which is supported by experimental results:[24] the lone pair bond weakening effect (LPBWE) has the consequence of weakening[24–26] the heteronuclear 2e/2c bond between X (where X is halogen) and H in the transition state of a halogen transfer reaction, due to 3e/2c VB-resonance structures,[27] which, obviously, must increase the three-electron populations; this weakening of the 2e/2c bond explains why the energetic barriers are much larger than those of the hydrogen transfer reaction.[24,26b] The competition of 2e/2c and 3e/2c bonding can be also evidenced in the framework of increased valence theory,[28] in which the three electron resonance structures are described by means of the Linett's structures[29] (showing that a 3e/2c bond involves only one bonding electron, in contrast to the 2e/2c one involving two bonding electrons) instead of Pauling's ones.

2.2. Covalency/Ionicity as Expansion of Electronic Populations. The difference, ΔW, between the weight of the spin-independent covalent structure and the weights of the two ionic structures provides a global measure of the covalency/ionicity of a 2e/2c bond:

$$\Delta W(\mu,\nu)=2\mathbf{W}[\mu(\uparrow)\nu(\downarrow)]-\mathbf{W}[\mu(\uparrow\downarrow)\nu(+)]-\mathbf{W}[\nu(\uparrow\downarrow)\mu(+)] \qquad (9)$$

This quantity is defined in a VB-like framework, in which the various bonds are assumed to be composed from covalent and ionic resonance structures. This viewpoint is totally different from the NBO one, in which a bond is considered as one entity, described by a bonding NBO. Consequently, this measure of covalency/ionicity is basically different from the covalent and ionic bond orders[14a] provided by NRT (considering the weighted average of various NBO structures). The NRT ionic bond order depends essentially on the bond polarity, because it is proportional to the difference of the square of the expansion coefficients with which the NAOs contribute to a bonding NBO, and is referred also as "electrovalent"[14a] bond order. Similarly, there is a dependence on bond polarity of the covalent and ionic bond orders obtained in the framework of a topological partitioning of one-electron density, and investigated by means of the mathematical concepts of "similarity" and "metric spaces".[30] By using relations 3, one can obtain the above quantity, expressing the VB features of a 2e/2c bond which belongs to a closed shell system, as expansion of electronic populations:

$$\Delta W(\mu,\nu)=2P_2(\mu,\bar{\mathrm{v}})-P_2(\mu,\bar{\mu})-P_2(\mathrm{v},\bar{\mathrm{v}}) \qquad (10)$$

This relation shows that ΔW depends only on two electron populations (in both one and two centers), while higher populations (see subsection 2.1) cannot affect the global covalent/ionic features of the considered 2e/2c bond.

The global difference, ΔW, of relation 9 can be also partitioned in two component differences, δw, specific to each ionic local structure,

$$\Delta W(\mu,\nu)=\delta w[\mu(\uparrow)\nu(\downarrow)-\mu(\uparrow\downarrow)\nu(+)]+\delta \mathrm{w}[\mu(\uparrow)\nu(\downarrow)-\nu(\uparrow\downarrow)\mu(+)] \qquad (11)$$

where $\delta w[\mu(\uparrow)\nu(\downarrow)-\mu(\uparrow\downarrow)\nu(+)]=\mathbf{W}[\mu(\uparrow)\nu(\downarrow)]-\mathbf{W}[\mu(\uparrow\downarrow)\nu\,(+)]$ (and a similar definition for the second term of eq 11). In the above partition, the half of the weight, $2\mathbf{W}[\mu(\uparrow)\nu(\downarrow)]$, of the spin-independent covalent structure is compared with the weight of the first ionic structure, and the other half, with the second one. The component terms, δw, can be also expressed in terms of electronic populations:

$$\delta w[\mu(\uparrow)\nu(\downarrow)-\mu(\uparrow\downarrow)\nu(+)]=\delta_2(\mu)+\delta_3(\mu,\nu) \qquad (12a)$$

$$\delta w[\mu(\uparrow)\nu(\uparrow)-\nu(\uparrow\downarrow)\mu(+)]=\delta_2(\nu)-\delta_3(\mu,\nu) \qquad (12b)$$

where

$$\delta_2(\mu)=P_2(\mu,\bar{\mathrm{v}})-P_2(\mu,\bar{\mu});\ \delta_2(\mathrm{v})=P_2(\mu,\bar{\mathrm{v}})-P_2(\mathrm{v},\bar{\mathrm{v}});\ \delta_3(\mu,\nu)=P_3(\mu,\bar{\mu},\mathrm{v})-P_3(\mathrm{v},\bar{\mathrm{v}},\mu) \qquad (12c)$$

The covalency/ionicity of chemical bonds is revealed to be particularly important for 2e/2c bonding, by investigating the charge shift (CS) bonds.[24–26,31] Making a clear distinction between "polarity" and "ionicity", it is worthwhile to underline the fact that a 2e/2c bond with zero polarity can have non-negligible VB ionic components This holds, for example, in homonuclear symmetric bonds, such as the π-bonds of acetylene and ethylene, or the σ-bonds of F_2 and Cl_2 (in F_2, for example, the ionic components, $F^{(+)}F^{(-)}$ and $F^{(-)}F^{(+)}$, having the same weights, are non-negligible[25,26b]). Within CS-VB theory, a chemical bond is considered that it is formed by the interaction of the VB covalent and ionic resonance structures, in the framework of a nonorthogonal perturbational theory. The energy corresponding to this interaction (calculated, for example, as second order perturbational energy) is referred as resonance energy, and is controlled by the LPBWE. The CS bonds are characterized by an important CS-resonance energy, and are accounted when the LPBWE is important. A thorough investigation[25,26] of CS bonding shows that even though the interactions of the ionic structures with the covalent ones are important, and can differ widely for various bonds, the corresponding variations of the weights of covalent and ionic structures are much smaller and in general do not follow the LPBWE.[25,26] This trend can be explained straightforwardly by means of relation 10, providing the covalency/ionicity as expansion of electronic populations. Quantity ΔW is independent of three electron populations, which can be enhanced by the LPBWE. Consequently, even if the LPBWE is important, as this is true, for example, for various CS bonds,[24–26,31] this has no effect on the covalency/ionicity of the 2e/2c bond. In other terms, the LPBWE and the corresponding three electron populations shift by the same amount the weights of the spin-independent covalent structure and the sum of the weights of the two ionic structures. As far as a specific to an ionic structure difference, δw, is concerned, this depends formally on three electron populations, δ_3, as show relations 12. However, quantities δ_3 are very small or zero at least in the case of the most typical CS bonds, referring to homonuclear bonds. In these cases, for obvious symmetry reasons, δ_3 are zero or nearly zero, when the bonds are composed from equivalent or nearly equivalent atoms, respectively (this is illustrated by means of numerical examples in the next section).

3. Numerical Applications and Discussion

To compare numerically some typical 2e/2c bonds, we have considered cis-butadiene and all trans-hexatriene. To examine the influence of a lone pair to localization and covalency/ionicity of a vicinal 2e/2c bond, we have also considered the pyrrole molecule (composed formally from a cis-butadiene fragment and a >NH group). All these systems involve C=C bonds,

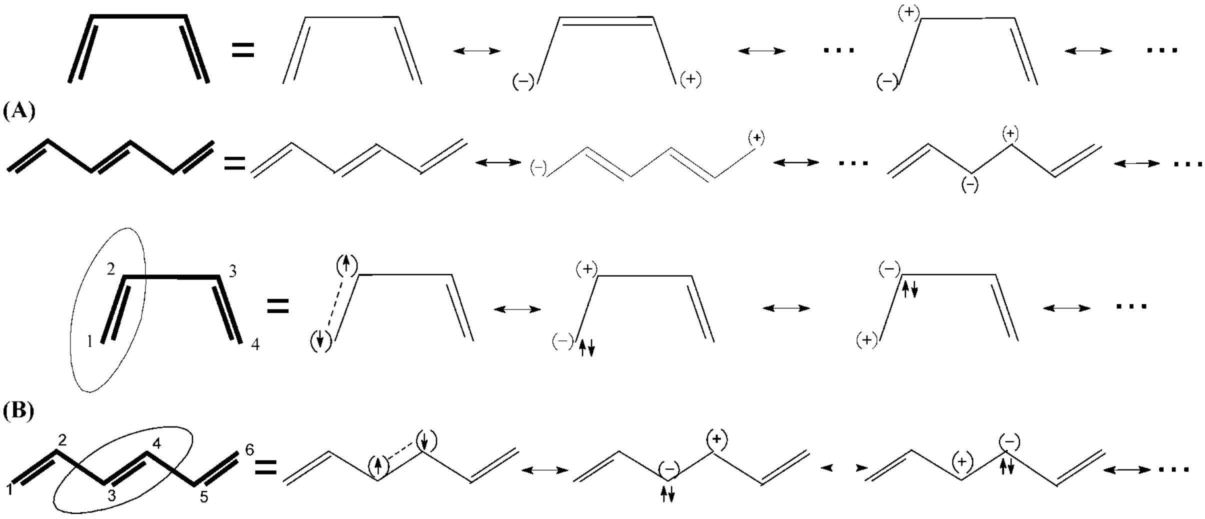

Figure 1. (A) Some VB structures appearing in the VB description of butadiene and hexatriene. (B) Placing "under the microscope" bond C_1C_2 of butadiene and C_3C_4 of hexatriene: the local (covalent and ionic) electronic structures describing these bonds as VB-like graphs.

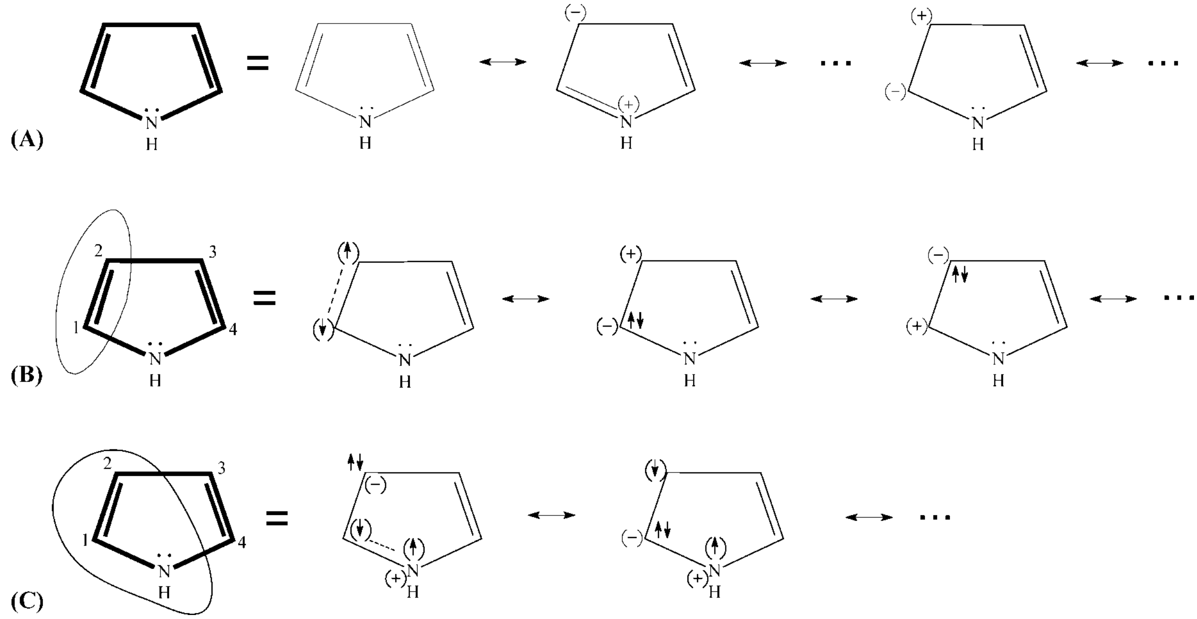

Figure 2. (A) Some VB structures appearing in the VB description of pyrrole. (B) Placing "under the microscope" two valence orbitals: local (covalent and ionic) electronic structures of bond C_1C_2. (C): Placing "under the microscope" three valence orbitals: local electronic structures describing the delocalization of the lone pair of N to bond C_1C_2.

which show significant covalent−ionic interactions, measured by means of the CS-delocalization energy.[26a]

In Figure 1 and Figure 2 the bold graphs represent the traditional chemical formulas of the considered molecules. In Figures 1A and 2A we give some VB resonance structures appearing in the VB description of the π system of these molecules, where the π bond lines represent the covalent components of the corresponding π bonds. One must underline the fact that this VB description is completely different from the NRT description, in which a bond line is assumed to incorporate both covalent and ionic components (which are included intrinsically in a bonding NBO). In Figures 1B and 2B we place "under the microscope" a chosen bond, and we examine various local electronic structures as local electronic events occurring in the orbitals defining the target bond. In general, looking at the electrons of a given molecule from a perspective referring to the coexistence of various types of electronic events, we necessarily generate VB-like graphs, as those presented in Figures 1B and 2B. However, the descriptions provided by VB methods and our analysis are basically different. A VB wave function provides information concerning the whole electronic assembly, while in our analysis the provided information concerns a target bond, or, in general, a limited number of AO-positions, and a limited number of electrons and holes.

In common chemical thinking and reasoning, the covalent or ionic electronic structures are developed on the basis of valence orbitals; consequently, the same valence orbitals must also be used for the electronic populations involved in expansions 3. However, very important conceptual difficulties may arise in distinguishing this type of orbitals when a nonminimal basis set is used for MO or DFT calculations. For example, examining a covalent or an ionic structure in the π system of the molecules considered in this work by means of a double-ζ (or higher) basis set (with or without polarization orbitals), one cannot know, in principle, which orbitals represent the valence ($2p_z$) orbitals responsible for the π bonding and which the Rydberg ($3p_z$) ones. This is true for almost all the available SCF-AO basis sets, and presents a serious dilemma of using an

TABLE 1: The Weights of Covalent (Spin-Dependent) and Ionic Structures and Electronic Populations Appearing in Expansions 3, on the Basis of NAOs.

bond position										
μ	ν	**W** $[\mu\ (\uparrow)\nu(\downarrow)]$	**W** $[\mu(\uparrow\downarrow)\nu\ (+)]$	**W** $[\nu(\uparrow\downarrow)\mu\ (+)]$	$P_2(\mu, \bar{\mathrm{v}})$	$P_2(\mu, \bar{\mu})$	$P_2(\mathrm{v}, \bar{\mathrm{v}})$	$P_3(\mu, \bar{\mu}, \mathrm{v})$	$P_3(\mathrm{v}, \bar{\mathrm{v}}, \mu)$	$P_4(\mu, \bar{\mu}, \mathrm{v}, \bar{\mathrm{v}})$
					Butadiene					
C_1	C_2	0.2810	0.1673	0.1661	0.3024	0.1849	0.1913	0.0091	0.0129	0.0006
C_2	C_3	0.1115	0.0558	0.0558	0.2470	0.1913	0.1913	0.0807	0.0807	0.0259
C_1	C_3	0.0892	0.0364	0.0362	0.2410	0.1849	0.1913	0.0932	0.0965	0.0379
					Hexatriene					
C_1	C_2	0.2730	0.1651	0.1544	0.3024	0.1889	0.1894	0.0122	0.0178	0.0006
C_2	C_3	0.1169	0.0578	0.0587	0.2492	0.1894	0.1917	0.0777	0.0784	0.0238
C_3	C_4	0.2464	0.1453	0.1453	0.2928	0.1917	0.1917	0.0243	0.0243	0.0022
C_1	C_3	0.0868	0.0401	0.0363	0.2389	0.1889	0.1917	0.0922	0.0955	0.0356
C_2	C_4	0.0847	0.0393	0.0406	0.2353	0.1894	0.1917	0.0930	0.0935	0.0359
					Pyrrole					
C_1	C_2	0.1612	0.1219	0.1418	0.3017	0.2491	0.2956	0.0697	0.0830	0.0123
C_2	C_3	0.1035	0.0880	0.0880	0.3112	0.2956	0.2956	0.1285	0.1285	0.0493
C_1	C_3	0.0803	0.0555	0.0676	0.2911	0.2491	0.2956	0.1297	0.1469	0.0658

appropriate basis set to explore local structures and electronic populations. All these conceptual problems can be avoided by using natural orbitals such as the (orthogonal) NAOs or the (nonorthogonal) pre-NAOs, which can be clearly distinguished as valence or Rydberg orbitals, providing the necessary chemical basis to develop chemically meaningful electronic structures.

We recall briefly some elementary features[6,7] of the used natural orbitals. The NAOs are mutually orthogonal, as mathematically required for eigenfunctions of any physical Hermitian operator. Although NAOs are both intraatomically and interatomically orthogonal, in pre-NAOs the interatomic orthogonality is removed. For a given atom, the pre-NAOs preserve the necessary angular and radial nodal features to remain orthogonal within each atom, but they overlap with the pre-NAOs of other atoms.[6] The pre-NAOs exhibit the idealized spherical symmetries of isolated atoms, while NAOs present small delocalization tails in vicinal atoms. In the present work two separate series of calculations are performed in the basis of both NAOs and pre-NAOs. The presented results concern the valence NAOs or pre-NAOs of π symmetry, which are responsible for the π bonding.

Computational Details. The considered (orthogonal) NAOs as well as (nonorthogonal) pre-NAOs span the complete SCF-AO basis set, and thus, a correlated wave function, $\Psi(\mathrm{MO})$, can be transformed in the basis of these natural orbitals without affecting the approximation level of the inital $\Psi(\mathrm{MO})$; this transformation can be performed, for example, by solving a system of linear equations[10a,12a] by using the NAOs or pre-NAOs in the basis of SCF-AOs, provided by the NBO program.[6b]

Moffitt's theorem holds in both orthogonal and nonorthogonal basis sets (because the involved decomposition processes of MO-Slater determinants are independent of the orthogonality conditions), while the principal differences between these two types of basis sets concern the weights. For computational facility in the case of nonorthogonal orbitals, the Mulliken populations of the type (5) are calculated by means of the following formula:

$$P_3(\mu,\bar{\mu},\mathrm{v}) = \sum_{\mathrm{K}}^{(\mu,\bar{\mu},\mathrm{v})} T_K \sum_{I} C_{\mathrm{I}} < I|K> \qquad (13)$$

This formula is completely equivalent to 5, and can be derived straightforwardly by using relation 2; $<I|K>$ are the overlaps between the MO Slater determinants, I, and the local ones, K, and C_{I} are the usual CI expansion coefficients. In this context, the mixed local/nonlocal formalism of Slater determinants[32] can be also used to improve the computational efficiency. This efficient computational process is built in a user-friendly computer program,[8c] available from one of the authors (P.K.).

The initial correlated wave functions, $\Psi(\mathrm{MO})$, having the form of a linear combination of Slater determinants involving MOs in the basis of a double-ζ + polarization SCF-AO basis set, are obtained by means of the PSHONDO and the adapted multireference CI process;[33] the used SCF-AO basis sets are the standard ones included in this chain of programs.

The results of calculations performed in the basis of NAOs, concerning the weights and populations of various quantities appearing in expansions 3, are presented in Table 1, and those in the basis of pre-NAOs in Table 2. The weights given in these tables are in very good agreement with fundamental chemical knowledge and intuition: For example, in butadiene, comparing the formal bond C_1C_2 with a bond between C_2C_3, and the clearly unfavorable bond between C_1C_3, both the covalent and ionic components (and, thus, the 2e/2c bonding) diminish. Also, the weight of covalent structures is at a maximum for bond C_1C_2. These conclusions hold both in NAOs and pre-NAOs and are also valid comparing the same bonds of hexatriene and pyrrole.

In general, the results obtained in the basis of valence NAOs and pre-NAOs of a π system are similar and completely coherent. Since pre-NAOs preserve the interatomic orbital overlap that underlies classical VB concepts for chemical bonding, the provided description of chemical bonds by means of covalent and ionic structures in the basis of these orbitals is closer to a traditional VB description. The variations of weights and electronic populations on going from one bond to another (for a given molecule) are quite similar in these two types of natural orbitals, providing the same conceptual pictures. The main difference is that a local covalent structure has a systematically smaller weight in the basis of NAOs than in pre-NAOs; the opposite holds for ionic local structures. A very detailed comparison of these natural basis sets is out of the purposes of the present work. The principal conclusion which is issued comparing Tables 1 and 2 is that the delocalization tails (which are a direct consequence of interatomic orthogonality) of NAOs, are not crucial for polyelectron populations of the valence NAOs of a π system, and the corresponding local electronic structures. This is in agreement with the comparison of results obtained by means of NAOs and pre-NAOs for other type of π bonding,[34] showing that both descriptions are equivalent, leading to the same conclusions. In other work,[4b] it

TABLE 2: The Weights of Covalent (Spin-Dependent) and Ionic Structures and Electronic Populations Appearing in Expansions 3, on the Basis of pre-NAOs

bond position										
μ	ν	W $[\mu\,(\uparrow)\nu(\downarrow)]$	W $[\mu(\uparrow\downarrow)\nu\,(+)]$	W $[\nu(\uparrow\downarrow)\mu\,(+)]$	$P_2(\mu, \bar{v})$	$P_2(\mu, \bar{\mu})$	$P_2(v, \bar{v})$	$P_3(\mu, \bar{\mu}, v)$	$P_3(v, \bar{v}, \mu)$	$P_4(\mu, \bar{\mu}, v, \bar{v})$
					Butadiene					
C_1	C_2	0.2898	0.1628	0.1486	0.3087	0.1794	0.1698	0.0085	0.0108	0.0004
C_2	C_3	0.1219	0.0534	0.0534	0.2383	0.1698	0.1698	0.0667	0.0667	0.0170
C_1	C_3	0.0947	0.0322	0.0272	0.2396	0.1794	0.1698	0.0917	0.0894	0.0362
					Hexatriene					
C_1	C_2	0.2828	0.1608	0.1300	0.3104	0.1852	0.1608	0.0124	0.0156	0.0004
C_2	C_3	0.1325	0.0519	0.0557	0.2454	0.1608	0.1726	0.0639	0.0679	0.0189
C_3	C_4	0.2570	0.1330	0.1330	0.2966	0.1726	0.1726	0.0206	0.0206	0.0016
C_1	C_3	0.0948	0.0422	0.0332	0.2360	0.1852	0.1726	0.0881	0.0863	0.0332
C_2	C_4	0.0948	0.0378	0.0416	0.2218	0.1608	0.1726	0.0763	0.0803	0.0296
					Pyrrole					
C_1	C_2	0.1933	0.1193	0.1235	0.3149	0.2427	0.2434	0.0674	0.0656	0.0113
C_2	C_3	0.1458	0.0887	0.0887	0.3005	0.2434	0.2434	0.0881	0.0881	0.0214
C_1	C_3	0.0806	0.0424	0.0415	0.2817	0.2427	0.2434	0.1320	0.1328	0.0637

TABLE 3: Bond Localization, L, Given by Expansion (7), and the Sums of Two (S_2), Three (S_3), and High Populations (S_h), on the Basis of NAOs[a]

bond position						
μ	ν	$L(\mu,\nu)$	$S_2(\mu,\nu) = 2P_2(\mu, \bar{v}) + P_2(\mu, \bar{\mu}) + P_2(v, \bar{v})$	$S_3(\mu,\nu) = 4P_3(\mu, \bar{\mu}, v) + 4P_3(v, \bar{v}, \mu)$	$S_h(\mu,\nu) = S_3(\mu,\nu) - 4P_4(\mu, \bar{\mu}, v, \bar{v})$	$-d_h$ (%)
				Butadiene		
C_1	C_2	0.8954	0.9810	0.0880	0.0856	−8.73%
C_2	C_3	0.3346	0.8766	0.6456	0.5420	−61.83%
C_1	C_3	0.2510	0.8582	0.7588	0.6072	−70.75%
				Hexatriene		
C_1	C_2	0.8655	0.9831	0.1200	0.1176	−11.96%
C_2	C_3	0.3503	0.8795	0.6244	0.5292	−60.17%
C_3	C_4	0.7834	0.9690	0.1944	0.1856	−19.15%
C_1	C_3	0.2500	0.8584	0.7508	0.6084	−70.88%
C_2	C_4	0.2493	0.8517	0.7460	0.6024	−70.73%
				Pyrrole		
C_1	C_2	0.5865	1.1481	0.6108	0.5616	−48.92%
C_2	C_3	0.3828	1.2136	1.0280	0.8308	−68.46%
C_1	C_3	0.2837	1.1269	1.1064	0.8432	−74.82%

[a] $d_h = (S_h/S_2)100$, providing the diminution of S_2 (due to S_h) to give L (i.e., $L(\mu,\nu) = S_2(\mu,\nu)(1 - d_h(\mu,\nu)/100)$).

is found that the use of NAOs to expand CASSCF wave functions provides a sequence for the weights of various bonding schemes, which is similar to the sequence of VB nonorthogonal functions. The use of orthogonal and nonorthogonal orbitals is also explored within a CASVB methodology,[35] and it is found that these two types of orbitals provide similar conceptual pictures for π systems.

3.1. Bond Localization and the Crucial Role of Three Electron Populations. The results for the 2e/2c bond localization and the related quantities, involved in relations 7 and 8, are presented in Tables 3 and 4 for NAOs and pre-NAOs, respectively.

According to relation 7, the localization, L, is obtained from the two electron populations, S_2, diminished by the higher populations, S_h. From Tables 3 and 4 it follows that the ratio S_h/S_3 is about 0.8−0.97, and, thus, one can conclude that S_h values are controlled by the three electron populations. On the other hand, for a given molecular system, S_2 values do not vary importantly for various bonds. For example, in butadiene, S_2 varies from 0.98 (in NAOs) for a C_1C_2 bond, to 0.86 for the hypothetical and strongly unfavorable C_1C_3 bond. On the contrary, the variations of S_h (more precisely those of three electron populations) are clearly more important, and the larger values of S_h concern the more unfavorable bonds. In Tables 3 and 4 quantity d_h (%) provides the percentage by which S_2 is diminished (due to S_h, in the framework of relation 7) in order to obtain the bond localization, L. In the above cited bonds of butadiene, S_2 of C_1C_2 is diminished by 8.7%, while the same type of diminution for C_1C_3 is 71%, that is, significantly larger, to give bond localizations $L(C_1C_2) = 0.90$ and $L(C_1C_3) = 0.25$, respectively. Similar important differences are also found comparing favorable and unfavorable bonds of hexatriene or pyrrole. All results presented in Tables 3 and 4 show that the role of three electron populations is crucial for the bond localization.

In pyrrole, the localization of the formal bond C_1C_2 is clearly smaller than the same bond of butadiene. This result can be rationalized from the delocalization of the nitrogen electron pair to the C atoms, described by means of usual structures exhibiting a (−) formal charge in C atoms of the ring and a (+) in N, as, for example, those showed in the graphs of Figure 2C (see also section 3.3). Alternatively, in the framework of NBO viewpoint, the nitrogen electron pair delocalization can be described by means of the electron transfer from this pair to the antibonding NBO of C_1C_2 bond (n → π_{12}*). This transfer enhances the presence of three electrons between C_1 and C_2 and, thus, weakens the target 2e/2c bond.[36] This NBO picture has a sense of déjà vu, and is reminiscent to the LPBWE (which is due to

TABLE 4: Bond Localization, L, Given by Expansion (7), and the Sums of Two (S_2), Three (S_3), and High Populations (S_h), on the Basis of pre-NAOs[a]

bond position						
μ	ν	$L(\mu,\nu)$	$S_2(\mu,\nu) = 2P_2(\mu, \bar{\mathrm{v}}) + P_2(\mu, \bar{\mu}) + P_2(\mathrm{v}, \bar{\mathrm{v}})$	$S_3(\mu,\nu) = 4P_3(\mu, \bar{\mu}, \mathrm{v}) + 4P_3(\mathrm{v}, \bar{\mathrm{v}}, \mu)$	$S_h(\mu,\nu) = S_3(\mu,\nu) - 4P_4(\mu, \bar{\mu}, \mathrm{v}, \bar{\mathrm{v}})$	$-d_h$ (%)
			Butadiene			
C_1	C_2	0.8910	0.9666	0.0772	0.0756	−7.82%
C_2	C_3	0.3506	0.8162	0.5336	0.4656	−57.04%
C_1	C_3	0.2488	0.8284	0.7244	0.5796	−69.97%
			Hexatriene			
C_1	C_2	0.8564	0.9668	0.1120	0.1104	−11.42%
C_2	C_3	0.3726	0.8242	0.5272	0.4516	−54.79%
C_3	C_4	0.7800	0.9384	0.1648	0.1584	−16.88%
C_1	C_3	0.2650	0.8298	0.6976	0.5648	−68.06%
C_2	C_4	0.2690	0.7770	0.6264	0.5080	−65.38%
			Pyrrole			
C_1	C_2	0.6291	1.1159	0.5320	0.4868	−43.62%
C_2	C_3	0.4686	1.0878	0.7048	0.6192	−56.92%
C_1	C_3	0.2451	1.0495	1.0592	0.8044	−72.09%

[a] $d_h = (S_h/S_2)100$, providing the diminution of S_2 (due to S_h) to give L (i.e., $L(\mu,\nu) = S_2(\mu,\nu)(1 - d_h(\mu,\nu)/100)$).

TABLE 5: The Global Covalency/Ionicity, ΔW, Given by Expansion 10, the Specific to an Ionic Structure Differences, δw, and Other Terms Defined in Relations 11 and 12, on the Basis of NAOs.

bond position							
μ	ν	$\Delta W(\mu,\nu)$	$\delta_2(\mu) = P_2(\mu, \bar{\mathrm{v}}) - P_2(\mu, \bar{\mu})$	$\delta_2(\nu) = P_2(\mu, \bar{\mathrm{v}}) - P_2(\mathrm{v}, \bar{\mathrm{v}})$	$\delta_3(\mu,\nu) = P_3(\mu, \bar{\mu}, \mathrm{v}) - P_3(\mathrm{v}, \bar{\mathrm{v}}, \mu)$	$\delta w[\mu(\uparrow)\nu(\downarrow) - \mu(\uparrow\downarrow)\nu(+)]$	$\delta w[\mu(\uparrow)\nu(\downarrow) - \nu(\uparrow\downarrow)\mu(+)]$
				Butadiene			
C_1	C_2	0.2286	0.1175	0.1111	−0.0038	0.1137	0.1149
C_2	C_3	0.1114	0.0557	0.0557	0.0000	0.0557	0.0557
C_1	C_3	0.1058	0.0561	0.0497	−0.0033	0.0528	0.0530
				Hexatriene			
C_1	C_2	0.2265	0.1135	0.1130	−0.0056	0.1079	0.1186
C_2	C_3	0.1173	0.0598	0.0575	−0.0007	0.0592	0.0581
C_3	C_4	0.2022	0.1011	0.1011	0.0000	0.1011	0.1011
C_1	C_3	0.0972	0.0500	0.0472	−0.0033	0.0467	0.0505
C_2	C_4	0.0895	0.0459	0.0436	−0.0005	0.0454	0.0441
				Pyrrole			
C_1	C_2	0.0587	0.0526	0.0061	−0.0133	0.0393	0.0194
C_2	C_3	0.0312	0.0156	0.0156	0.0000	0.0156	0.0156
C_1	C_3	0.0375	0.0420	−0.0045	−0.0172	0.0248	0.0127

3e/2c structures) of VB-CS theory. From both NBO and VB pictures one must expect an increasing of three electron populations and, thus, according to expansions 3, a decreasing of both covalent and ionic structures. Consequently, the bond localization must decrease, as this is confirmed from our numerical results: for example, on the basis of NAOs the $S_3(C_1C_2)$ increases from 0.09 in butadiene to 0.61 in pyrrole, and the bond localization, $L(C_1C_2)$ decreases from 0.90 to 0.59, respectively.

In hexatriene, the three electron populations $S_3(C_3C_4)$ are greater than $S_3(C_1C_2)$, and the localization of the first formal bond C_1C_2 is smaller than that of the second one, C_3C_4. This result is in agreement with chemical intuition, according to which we expect, that the central C_3C_4 bond, communicating with two other vicinal bonds (i.e., C_1C_2 and C_5C_6), must have a greater delocalization than the extreme C_1C_2 bond.

The results obtained in the basis of NAOs and pre-NAOs are similar and all the above conclusions hold in both types of natural orbitals, providing the same conceptual pictures. Furthermore, because of the systematic increasing of the weights of covalent and decreasing those of ionic structures on going from NAOs to pre-NAOs, and taking into account the fact that quantity $L(\mu,\nu)$ is obtained from the sum of these weights, one can expect that the differences in the results between these two types of orbitals are, in general, small.

3.2. Covalency/Ionicity and the Negligible Role of Three Electron Populations. The results for covalency/ionicity and the related quantities involved in relations 9−12 are presented in Table 5 and 6 for NAOs and pre-NAOs, respectively. In butadiene and hexatriene, the covalency/ionicity between C−C atoms, measured by the difference ΔW, is clearly larger for pairs of atoms involved in formal double bonds (almost twice in most cases) than in formal single bonds. The general trend is that the ionicity decreases and the covalency increases, as the bond localization increases.

In pyrrole, the differences ΔW for the bond C_1C_2 or for C_2C_3 are clearly smaller than those for the same bonds of butadiene (or hexatriene), showing that the pyrrole molecule has an enhanced ionicity. This result can be also rationalized by means of the delocalization of the N lone pair to the C atoms of pyrrole (see Figure 2C) and relation 10. According to this relation, ΔW depends on the two electron populations involved in one ($P_2(\mu, \bar{\mu})$) and two orbitals ($P_2(\mu,\bar{\mathrm{v}})$). Comparing these quantities (Tables 1 and 2 for NAOs and pre-NAOs, respectively), for C_1C_2 bond of butadiene (or hexatriene) with the same bond of pyrrole, one can see that $P_2(C_1,\bar{C}_2)$ are of the same magnitude

TABLE 6: The Global Covalency/Ionicity, ΔW, Given by Expansion 10, the Specific to an Ionic Structure Differences, δw, and Other Terms Defined on Relations 11 and 12, on the Basis of pre-NAOs

bond position							
μ	ν	$\Delta W(\mu,\nu)$	$\delta_2(\mu) = P_2(\mu, \bar{\nu}) - P_2(\mu, \bar{\mu})$	$\delta_2(\nu) = P_2(\mu, \bar{\nu}) - P_2(\nu, \bar{\nu})$	$\delta_3(\mu,\nu) = P_3(\mu, \bar{\mu}, \nu) - P_3(\nu, \bar{\nu}, \mu)$	$\delta w[\mu(\uparrow)\nu(\downarrow) - \mu(\uparrow\downarrow)\nu(+)]$	$\delta w[\mu(\uparrow)\nu(\downarrow) - \nu(\uparrow\downarrow)\mu(+)]$
				Butadiene			
C_1	C_2	0.2682	0.1293	0.1389	−0.0023	0.1270	0.1412
C_2	C_3	0.1370	0.0685	0.0685	0.0000	0.0685	0.0685
C_1	C_3	0.1300	0.0602	0.0698	0.0023	0.0625	0.0675
				Hexatriene			
C_1	C_2	0.2748	0.1252	0.1496	−0.0032	0.1220	0.1528
C_2	C_3	0.1574	0.0846	0.0728	−0.0040	0.0806	0.0768
C_3	C_4	0.2480	0.1240	0.1240	0.0000	0.1240	0.1240
C_1	C_3	0.1142	0.0508	0.0634	0.0018	0.0526	0.0616
C_2	C_4	0.1102	0.0610	0.0492	−0.0040	0.0570	0.0532
				Pyrrole			
C_1	C_2	0.1437	0.0722	0.0715	0.0018	0.0740	0.0697
C_2	C_3	0.1142	0.0571	0.0571	0.0000	0.0571	0.0571
C_1	C_3	0.0773	0.0390	0.0383	−0.0008	0.0382	0.0391

in these molecules: 0.30−0.31 in butadiene and 0.30−0.32 in pyrrole. On the contrary, the one-orbital, that is, ionic, electron pairs, $P_2(C_1,\bar{C}_1)$ and $P_2(C_2,\bar{C}_2)$, increase significantly in pyrrole: these populations are 0.17−0.19 in butadiene, and 0.24−0.30 in pyrrole. Consequently, the effect of the N lone pair on the C atoms of pyrrole is to increase the ionic electron pairs (see also Figure 2C and section 3.3), and this (according to relation 10) has the consequence of diminishing the covalency of the C−C bonds of this molecule.

Although the three electron populations are significant, particularly in pyrrole, and control the bond (de)localization, their role is negligible for the covalency/ionicity of a 2e/2c bond. These populations not only do not have any impact on ΔW (see relation 10), but their role is minor even for the ionic structure difference, δw (relations 12). As shown in Tables 5 and 6, quantities δ_3 (on which the δw depend) are small or zero, despite the fact that the three electron populations, P_3 (given in Tables 1 and 2), are significant. Consequently, the differences δw are controlled by the two electron populations, δ_2. Comparing the small absolute values of δ_3 for various bonds, we found that they depend on the equivalence of the atoms defining the considered bond: the more equivalent the atoms are, the closer to zero is δ_3. For example, for bond C_1C_2 of butadiene and hexatriene we obtained for P_3 and δ_3 in the basis of NAOs (see Tables 1 and 5): $P_3(C_1, \bar{C}_1,C_2) = 0.009-0.012$, $P_3(C_2,\bar{C}_2,C_1) = 0.013-0.018$, and $|\delta_3(C_1,C_2)| = 0.004-0.006$. This is in remarkable contrast with bond C_3C_4 of hexatriene, in which, although the three electron populations are larger, $P_3(C_3,\bar{C}_3,C_4) = P_3(C_4,\bar{C}_4,C_3) = 0.024$, they do not have effect on the differences δw (because $\delta_3(C_3,C_4) = 0.0$). The same contrasting picture holds for pyrrole, in which δ_3 for C_2C_3 bond is zero, and δw are also controlled by δ_2.

Although covalency is systematically larger on the basis of pre-NAOs than on NAOs, and in general the differences between these two types of natural orbitals are larger for covalency/ionicity than for localization, all the above presented conclusions are valid in both natural basis sets. This is true mainly for the principal conclusion concerning the negligible role that have the three electron populations for the covalency/ionicity of a 2e/2c bond, despite the fact that these populations are significant on the basis of both NAOs and pre-NAOs.

3.3. Electronic Structures for N Electron Pair Delocalization in Pyrrole. The electron-expansion methodology, on which the present work is based, is quite general, allowing the investigation of other types of electronic structures. Let us consider, for example, the N electron pair delocalization in C_1C_2 bond of pyrrole, which enhances (see above) the three electron populations of this bond. Placing now "under the microscope" the valence $2p_z$ orbitals of N,C_1 and C_2 atoms involved in this delocalization effect, one can distinguish various local electronic structures, as those presented in Figure 2C. Among the two principal local electronic structures, $[N^+(\uparrow)\ C_1(\downarrow)\ C_2^-(\uparrow\downarrow)]$ and $[N^+(\uparrow)\ C_1^-(\uparrow\downarrow)\ C_2(\downarrow)]$, we want to examine which represents better the N electron pair delocalization. Following an expansion process similar to this which is presented in the Appendix, the weight of the first local structure, $\mathbf{W}\ [N^+(\uparrow)\ C_1(\downarrow)\ C_2^-(\uparrow\downarrow)]$, is expanded as follows:

$$\mathbf{W}[N^+(\uparrow)C_1(\downarrow)C_2^-(\uparrow\downarrow)] = P_4(N,\ \bar{C}_1, C_2, \bar{C}_2) - P_5(N, C_1,\ \bar{C}_1, C_2, \bar{C}_2) - P_5(N, \bar{N},\ \bar{C}_1, C_2, \bar{C}_2) + P_6(N, \bar{N}, C_1, \bar{C}_1, C_2, \bar{C}_2) \quad (14)$$

(Alternatively, the above relation could be obtained by multiplying both sides of relation A4 by the two electron operator $a_{\bar{2}}^+ a_2^+ a_2 a_{\bar{2}}$, where 2 represents the valence $2p_z$ orbital of C_2 atom). Similarly, for the second local electronic structure we obtain the following expansion:

$$\mathbf{W}[N^+(\uparrow)C_1^-(\uparrow\downarrow)C_2(\downarrow)] = P_4(N, C_1, \bar{C}_1, \bar{C}_2) - P_5(N, C_1,\ \bar{C}_1, C_2, \bar{C}_2) - P_5(N, \bar{N}, C_1, \bar{C}_1, \bar{C}_2) + P_6(N, \bar{N}, C_1, \bar{C}_1, C_2, \bar{C}_2) \quad (15)$$

Since in expansions 14 and 15 the second and fourth terms are the same, the differences between the two structures originated from the other two terms; a deeper analysis shows that the weights 14 and 15 are controlled by P_4, and the weights of the spin-independent structures are found $2\mathbf{W}[N^+(\uparrow)C_1(\downarrow)C_2^-(\uparrow\downarrow)] = 0.0726/0.0652$ and $2\mathbf{W}[N^+(\uparrow)C_1^-(\uparrow\downarrow)C_2(\downarrow)] = 0.0546/0.0634$ in NAOs/pre-NAOs basis sets. Consequently, the local electronic structure $[N^+(\uparrow)\ C_1(\downarrow)\ C_2^-(\uparrow\downarrow)]$ (involved in the first graph of Figure 2C) is the dominant one, representing better the electron transfer from N electron pair to C_1C_2 bond.

4. Conclusion

By using the electron-expansion methodology, that is by expanding the hole conditions involved (by definition) in covalent and ionic structures in terms involving only electrons, one can obtain the weights of covalent and ionic structures as expansions of electronic populations.

Expansions of the type 3, 14, or 15 allow the calculation of the weights of local electronic structures, involving both electrons and holes, without needing to calculate explicitly probabilities for holes, and can be also used to understand of various aspects of chemical bonding. For example, expansions 3 can be used to understand and rationalize various aspects of a 2e/2c bond. By means of relations 7−12 one can express the 2e/2c bond localization and its covalency/ionicity in terms of electronic populations; the investigation of these relations show the versatile role that the three electron populations have.

The three electron populations are crucial for the localization of a 2e/2c bond. The greater these populations are, the smaller the localization is. This result corroborates with both NBO and VB perspectives. In the framework of NBO theory, the increasing of one-electron population of an antibonding NBO of a 2e/2c bond has the consequence of increasing the three electron populations, and, thus, to weaken this bond. In VB theory of CS bonding, a similar weakening effect of a 2e/2c bond (confirmed by both theoretical and experimental arguments) is the LPBWE (which is due to 3e/2c structures), which is responsible for specific features of CS bonding.

Unlike localization, the role of three electron populations is negligible in covalency/ionicity, because a variation of these populations has the consequence of shifting equivalently the weights of both covalent and ionic structures in the same direction. Specially, in typical CS bonding referring to homonuclear (symmetric) bonds, the difference of the weights of covalent and ionic structures is not influenced by three electron populations, and thus, even if the LPBWE (and the CS-resonance energy) is important, this does not control the covalency/ionicity of 2e/2c bonds.

Appendix

The Electron-Expansion Methodology

Let i, j, r, and t represent orthonormal spin−orbitals, and let us consider a local electronic structure involving two electrons in i and j, and two holes in r and t. The corresponding two-electron-two-hole density operator, $\hat{\rho}_{2;2}$, is

$$\hat{\rho}_{2;2} = a_t a_r a_j^+ a_i^+ a_i a_j a_r^+ a_t^+ \qquad \text{(A1)}$$

The expectation value of this operator is the weight, **W**[i,j; r,t], of the corresponding local electronic structure inside the given molecule, because it provides the probability of finding simultaneously two electrons in i and j and two holes in r and t, while the remaining electrons can reside anywhere else in the remaining spin- orbitals.

$$\mathbf{W}[\mathrm{i,j;\ r,t}] = <\Psi(\mathrm{TL})|\hat{\rho}_{2;2}|\Psi(\mathrm{TL})> = \sum_{\mathrm{K}(\neq \mathrm{r,t})}^{(\mathrm{i,j})} T_K^2 \qquad \text{(A2)}$$

where $\sum_{\mathbf{K}(\neq\ \mathrm{r,t})}^{(\mathrm{i,j})}$ represents a summation of the weights of those Slater determinants, *K*, which involve spin−orbitals i, j and simultaneously spin−orbitals r, t are absent. The electron expansion of the hole condition in spin−orbital r by means of the first order anticommutation relation ($a_r^+ a_r + a_r a_r^+ = 1$), gives (after some appropriate commutations)

$$a_t a_r a_j^+ a_i^+ a_i a_j a_r^+ a_t^+ = a_t a_j^+ a_i^+ a_i a_j a_t^+ - a_t a_r^+ a_j^+ a_i^+ a_i a_j a_r a_t^+ \qquad \text{(A3)}$$

Similarly, the electron expansion of the hole condition in spin−orbital t (by means of relation $a_t^+ a_t + a_t a_t^+ = 1$), in both terms of the right-hand side of (A3) gives

$$a_t a_r a_j^+ a_i^+ a_i a_j a_r^+ a_t^+ = a_j^+ a_i^+ a_i a_j - a_t^+ a_j^+ a_i^+ a_i a_j a_t - a_r^+ a_j^+ a_i^+ a_i a_j a_r + a_t^+ a_r^+ a_j^+ a_i^+ a_i a_j a_r a_t \qquad \text{(A4)}$$

The expectations values of right-hand side density operators provide the two, P_2, three, P_3, and four, P_4, electron populations:

$$P_2(\mathrm{i,\ j}) = \sum_K^{(\mathrm{i,j})} T_K^2; P_3(\mathrm{i,\ j,\ t}) = \sum_K^{(\mathrm{i,j,t})} T_K^2;$$
$$P_3(\mathrm{i,\ j,\ r}) = \sum_K^{(\mathrm{i,j,r})} T_K^2; P_4(\mathrm{i,\ j,\ r,\ t}) = \sum_K^{(\mathrm{i,j,r,}t)} T_K^2 \qquad \text{(A5)}$$

where a symbol such as $\sum_{\mathrm{K}}^{(\mathrm{i,j})}$ (or $\sum_{\mathrm{K}}^{(\mathrm{i,j,r})}$, etc) represents a summation over Slater determinants, *K*, which involve simultaneously spin−orbitals i,j (or i,j,r, etc), regardless of the occupation of the remaining orbitals; similar is the meaning of the other symbols. Consequently, relation (A4) leads to the expansion of the two-electron-two-hole structure, in terms of electronic populations without hole conditions:

$$\mathbf{W}[\mathrm{i,j;\ r,t}] = P_2(\mathrm{i,j}) - P_3(\mathrm{i,j,r}) - P_3(\mathrm{i,j,t}) + P_4(\mathrm{i,j,r,t}) \qquad \text{(A6)}$$

The above used electron-expansion technique can be easily extended for any other structure involving conditions for electron−holes, such as the structures characterizing radical cations or radical anions, etc.

References and Notes

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