Unpaired Electrons, Spin Polarization, and Bond Orders in Radicals from the 2–RDM in Orbital Spaces. Basic Notions and Testing Calculations

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Unpaired Electrons at the Second-Order Reduced Density Matrix Level: Covalent Bonding, and Coulomb and Fermi Correlations in Closed Shell Systems

Padeleimon Karafiloglou* and Katerina Kyriakidou

The usual one-electron populations in atomic orbitals of closed shell systems are split into unpaired and paired at the (spin-dependent) second-order reduced density matrix level. The unpaired electron in an orbital is defined as the 'simultaneous occurrence of an electron and an electron hole of opposite spins in the same spatial orbital,' which for simplicity is called 'electropon.' The electropon population in a given orbital reveals whether and to what degree the Coulomb correlations, and hence, the chemical bonding between this orbital and the remaining orbitals of the system are globally favorable or unfavorable. The interaction of two electropons in two target orbitals reveals the quality (favorable or unfavorable) and the strength of the covalent bonding between these orbitals; this establish a bridge between the notion of "unpaired electrons" and the traditional covalent structure of valence-bond (VB) theory. Favorable/unfavorable bonding between two orbitals is characterized by the positive/negative (Coulomb) correlation of two electropons of opposite spins, or alternatively, by the negative/positive (Fermi) correlation of two parallel spin electropons. A spin-free index is defined, and the relationship between the electropon viewpoint for chemical bonding and the well-known two-electron Coulomb and Fermi correlations is established. Benchmark calculations are achieved for ethylene, hexatriene, benzene, pyrrole, methylamine, and ammonia molecules on the basis of physically meaningful natural orbitals. The results, obtained in the framework of both orthogonal and nonorthogonal population analysis methods, provide the same conceptual pictures, which are in very good agreement with elementary chemical knowledge and VB theory. © 2013 Wiley Periodicals, Inc.

Introduction

The "odd" electron density matrix[1,2] or the equivalent "effectively unpaired electron density matrix"[3–8] was introduced a long time ago as an appropriate tool to describe the spatial separation of α- and β-spin electrons. As shown, this matrix is connected to valence, free valence indices, and cumulant matrices[3,6,8-12,13-16]; in general, the unpaired electron density accounts also for the splitting of electron pairs that exists even in closed shell systems. Although the second-order reduced density matrix (2-RDM) is used to define unpaired electrons, the calculations are essentially based on the product of (spin-free) 1-RDMs, and the square of their elements (involving information for the behavior of electrons of the same spin). In this framework, various viewpoints for unpaired electron density have been presented.[17–21] The notion of unpaired electrons partitioned in different portions of space is used to describe and investigate the local spins,[22–27] and to explore the Heisenberg model Hamiltonians.[22–24] The effectively unpaired density has proved a versatile tool, as it can be used in various studies of population analysis,[7,8,28,29] or to elucidate the mechanisms of chemical reactions.[30–32] Recently, another type of analysis has been proposed, based on the assumption that local spins in closed shell systems must be minimum.[33–35]

The notion of "paired electron" refers to electron pairs and in general to two-electron interactions, which can be investigated rigorously at the 2-RDM level (mainly the α,β pairs,[36,37]

depending on the Coulomb correlations); hence, the opposite notion of "unpaired electron" could be defined and investigated at the same level. This scope is attempted in this work by means of the poly-electron population analysis[38–41] (PEPA), which calculates the diagonal elements of general E^{th}-order, E-RDM, in orbital spaces. In this population analysis methodology, besides the investigation of the simultaneous occurrence of E (in number) electrons in some target spin-orbitals, one can consider additional conditions for the simultaneous presence of H (in number) electron holes in other spin–orbitals. The expectation values, $P_{E;H}$, of generalized (E-electron and H-hole) density operators, $\hat{\rho}_{E;H}$, can be calculated efficiently (without introducing approximations) by means of the hole-expansion methodology[41] by employing usual molecular orbital (MO), Ψ (MO), wave functions:

$$\Psi(\mathrm{MO}) = \sum_{I}^{\mathrm{CI}} C_I |D_I| \qquad (1)$$

where $|D_I|$ are Slater determinants involving delocalized MOs, and CI is the configuration interaction space. In the basic theory of PEPA the initial wave function, $\Psi(MO)$, is transformed (more precisely, it is rewritten) to the totally local one, $\Psi(TL)$, by means of Moffitt's theorem.[42–45]

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$$\Psi(TL) = \sum_{K}^{\text{full basis}} T_K \; |\Phi_K| \tag{2a}$$

where

$$<\Psi(TL)|\Psi(TL)> = 1 \tag{2b}$$

and $|\Phi_K|$ are local Slater determinants involving atomic orbitals (AOs). The expansion coefficients, T_K, are expressed in terms of linear combination of atomic orbitals (LCAO) and CI coefficients,[43–45] so that:

$$\Psi(MO) = \Psi(TL) \tag{3}$$

Although PEPA holds for any type of usual AO basis set, in numerical applications we prefer to use natural orbital spaces, such as the natural atomic orbitals (NAOs),[46] developed in the framework of the natural bond orbital (NBO) methodology.[46–51] By adopting this type of orbitals, one can avoid serious conceptual problems (as for example, the distinction of valence and Rydberg orbitals) originating from the employment in the population analysis the usual AO basis sets involving multiple-zeta with polarization functions. A basic property of these orbitals (which are natural in the Löwdin sense) is the remarkable stability that they show with the extension of the AO basis set.

In the framework of PEPA, the second quantized[52] density operators are defined with respect to the vacuum state, $|0\rangle$, and not (as frequently) with respect to the Hartree–Fock (HF) one. For example, the electron pair density, $P_{2;0}(\lambda\bar{\lambda};)$, in a spatial NAO, ϕ_λ is obtained as follows (λ and $\bar{\lambda}$ are the α and β spin–orbitals, respectively, corresponding to ϕ_λ):

$$P_{2;0}(\lambda\bar{\lambda};) = \langle\Psi(TL)|a_\lambda^+ a_{\bar{\lambda}}^+ a_{\bar{\lambda}} a_\lambda|\Psi(TL)\rangle \tag{4}$$

In the same framework, the unpaired density in orbital ϕ_λ, is defined as the expectation value, $P_{1;1}(\lambda;\bar{\lambda})$, of the one-electron–one-hole density operator, $\hat{\rho}_{1;1} = a_\lambda^+ a_{\bar{\lambda}} a_{\bar{\lambda}}^+ a_\lambda$:

$$P_{1;1}(\lambda;\bar{\lambda}) = \langle\Psi(TL)|a_\lambda^+ a_{\bar{\lambda}} a_{\bar{\lambda}}^+ a_\lambda|\Psi(TL)\rangle \tag{5}$$

Quantity $P_{1;1}(\lambda;\bar{\lambda})$ provides the probability of finding an α spin electron and simultaneously a β spin electron hole in spatial orbital ϕ_λ.

The unpaired electron density (as well as the effectively unpaired density) refers to local properties of the N-electron assembly (where N is the total number of the electrons of the molecular system) in local positions, as for example in AO positions. On the other hand, in chemistry, a local description of the N electrons of a molecule can be obtained traditionally by means of valence-bond (VB) theory.[53,54] In this theory, the electrons are distributed in AO positions leading to local electronic structures, as for example the Pauling's "resonance structures." Unlike the delocalized description provided by MO theory, the VB one explores local electronic structures, and current methodological and conceptual VB developments provide new insights for chemical bonding[55] and chemical reactivity[56,57] on the basis of these local structures. VB-type local

structures can also be obtained from delocalized MO wavefunctions by means of appropriate methods such as the NBO-based natural resonance theory,[58] or another population analysis methodology, which uses localized bonds,[59–63] and other well-elaborated methods providing local descriptions.[64–70] Alternatively, quite compact local description is issued from appropriate VB treatments using both local and nonlocal (or semilocal) orbitals.[71,72] Local information for target bonds or in general for functional groups, belonging to a given molecule can also be obtained by means of PEPA. In this framework, one can place "under the microscope" the target fragment of the molecular system and investigate covalent, ionic and other VB-type structures.[73–79] In a VB framework, one can consider that the covalent structure of a bond between two orbitals arises from the interaction of two locally unpaired electrons of opposite spins in these orbitals; hence, the traditional VB covalent structures and unpaired electrons must be closely related.

The purpose of this work is twofold: (i) to investigate the unpaired density that is responsible for chemical bonding at the 2-RDM level and (ii) to establish the bridge between the traditional covalent structure of VB theory and unpaired electrons (that exist even in a closed shell system), and quantify their relationship. It is worth noticing that in an open shell system, as for example a radical, the unpaired density can have originated from two sources. The first one comes from the spin density and the second from the fact that in any molecular system (closed or open shell) the electrons, distributed in AO positions, are locally unpaired. In this work, we give emphasis to the second source, because this is assumed to be responsible for covalent chemical bonding. The article is organized as follows. In 'Unpaired Electrons—Calculation, Boundary Values and the Role of Electronic Correlation' section, we examine the physical meaning and the boundary values of the proposed definition for unpaired electrons; then, we investigate the correlation content in terms of Coulomb electron–electron and electron–hole correlations. In 'Covalent Bonding and Correlation of Two Electropons' section, we show the connection that exists between two interacting unpaired electrons in two spatial orbitals and covalent VB structures. In 'Numerical Applications and Discussions' section, we achieve benchmark calculations to examine the applicability of the proposed definitions and the corresponding electronic correlations concerning unpaired density, covalent bonding, and their connection. These calculations are performed for closed shell systems, to check the theory by avoiding possible confusions that can arise from the 'contamination' of the defined unpaired density (assumed responsible for chemical bonding) from the spin density existing, for example, in a radical.

Unpaired Electrons—Calculation, Boundary Values, and the Role of Electronic Correlation

In the framework of PEPA, the unpaired electron density of relation (5) can be calculated as follows:

$$P_{1;1}(\lambda;\bar{\lambda}) = \sum_{K(\neq\bar{\lambda})}^{(\lambda)} W(\Phi_K) \tag{6}$$

The summation runs over Slater determinants involving spin–orbital λ, while simultaneously $\bar{\lambda}$ is absent, and $W(\Phi_K) = T_K^2$ (for orthogonal orbitals as, for example, the NAOs)[41]; the first order anticommutation relation, $a_\lambda^+ a_{\bar{\lambda}} + a_{\bar{\lambda}} a_\lambda^+ = 1$, leads directly to the following relation[41]:

$$P_{1;0}(\lambda;0) = P_{1;1}(\lambda;\bar{\lambda}) + P_{2;0}(\lambda\bar{\lambda};0) \tag{7}$$

In the above relation, $P_{1;0}(\lambda;0)$ is the usual number of α spin electrons (issued from the 1-RDM), and $P_{2;0}(\lambda\bar{\lambda};0)$ is the number of α,β pairs (within the Löwdin's normalization[36]) belonging to orbital ϕ_λ. Hence, in a coherent interpretation, quantity $P_{1;1}(\lambda;\bar{\lambda})$, which is complementary to $P_{1;0}(\lambda;0)$ and $P_{2;0}(\lambda\bar{\lambda};0)$, represents another occupation number, namely the number of α spin 'electropons'; the term electropon* is introduced for simplicity, to refer to the 'simultaneous occurrence of an electron and an electron hole of opposite spins in the same spatial orbital.' According to this definition and the well-known probabilistic interpretation for $P_{1;0}(\lambda;0)$ and $P_{2;0}(\lambda\bar{\lambda};0)$,[36] quantity $P_{1;1}(\lambda;\bar{\lambda})$ provides also the probability of finding an α spin electropon in ϕ_λ.

One must underline the fact that locally unpaired electrons do not lead necessarily to nonzero local spin-density. For example, in a closed-shell system, although the unpaired density is different from zero, the spin density, as it is well expected, is strictly zero (even locally); this can be demonstrated straightforwardly using relation (7) and the fact that in closed-shell systems holds $P_{1;1}(\lambda;\bar{\lambda}) = P_{1;1}(\bar{\lambda};\lambda)$

Boundary values

Defining 'unpaired electrons,' it is worthwhile to examine the implied boundary values.[17,20,21] To estimate the boundary values of quantity $P_{1;1}(\lambda;\bar{\lambda})$, we consider the limit case in which the electrons of a usual two-electron two-orbital bond of a conventional system are formally totally localized in orbitals ϕ_λ (with α spin) and ϕ_μ (with β spin); this limit (and hypothetical) situation is described by

$$\Psi'(TL) = \sum_{K(\neq\bar{\lambda},\mu)}^{(\lambda,\bar{\mu})} T'_K |\Phi_K|, \text{ where } \langle\Psi'(TL) \mid \Psi'(TL)\rangle = 1, \text{ and}$$

thus:

$$P_{1;1}(\lambda;\bar{\lambda}) = 1, \ P_{1;1}(\bar{\lambda};\lambda) = 0, \ P_{2;0}(\lambda\bar{\lambda};0) = 0; \ P_{1;1}(\mu;\bar{\mu})$$
$$= 0, \ P_{1;1}(\bar{\mu};\mu) = 1, \ P_{2;0}(\mu\bar{\mu};0) = 0 \tag{8a}$$

If the system formally involves two electrons (as for example a lone pair) totally localized in orbital ϕ_ν, then this limit (and hypothetical) situation is described by

$$\Psi''(TL) = \sum_K^{(\nu,\bar{\nu})} T''_K |\Phi_K|, \text{ where } \langle\Psi''(TL) \mid \Psi''(TL)\rangle = 1, \text{ and thus:}$$
$$P_{1;1}(\nu;\bar{\nu}) = P_{1;1}(\bar{\nu};\nu) = 0, \ P_{2;0}(\nu\bar{\nu};0) = 1 \tag{8b}$$

Coulomb correlations

(a) Correlations in one orbital: The Coulomb correlations in orbital spaces are meaningful for chemical bonding.[36] For a

given orbital ϕ_λ, this two-electron property is defined as the correlation, $C(e_\lambda e_{\bar{\lambda}})$, of an α and a β spin electron (e_λ and $e_{\bar{\lambda}}$), or more precisely as the correlation of the fluctuations of the α and β spin electronic populations from their average values n_λ^α and n_λ^β, respectively:

$$C(e_\lambda e_{\bar{\lambda}}) = P_{2;0}(\lambda\bar{\lambda};0) - n_\lambda^\alpha n_\lambda^\beta \tag{9}$$

where (for simplicity) $n_\lambda^\alpha \equiv P_{1;0}(\lambda;0)$ and $n_\lambda^\beta \equiv P_{1;0}(\bar{\lambda};0)$

In the same spirit, one can define the correlation, $C(e_\lambda h_{\bar{\lambda}})$, between an α spin electron (e_λ) and a β spin hole ($h_{\bar{\lambda}}$) in this orbital, or more precisely, the correlation of the fluctuations of the electron and hole populations from their average values n_λ^α and $(1 - n_\lambda^\beta)$, respectively:

$$C(e_\lambda h_{\bar{\lambda}}) = P_{1;1}(\lambda;\bar{\lambda}) - n_\lambda^\alpha(1 - n_\lambda^\beta) \tag{10}$$

Similarly, we define the correlation, $C(h_\lambda h_{\bar{\lambda}})$, between two holes ($h_\lambda$ and $h_{\bar{\lambda}}$), or more precisely, the correlation of the fluctuations of the two hole populations from their average values $(1 - n_\lambda^\alpha)$ and $(1 - n_\lambda^\beta)$, respectively:

$$C(h_\lambda h_{\bar{\lambda}}) = P_{0;2}(;\lambda\bar{\lambda}) - (1 - n_\lambda^\alpha)(1 - n_\lambda^\beta) \tag{11}$$

The electron–electron and hole–hole correlations are introduced to understand and describe the correlation content in local electronic structures formally exhibiting two or zero electrons, respectively, whereas the electron–hole correlations to describe those exhibiting unpaired electrons. Using relations (9)–(11), one can show straightforwardly that the electron–electron, electron–hole, and hole–hole correlations have the same absolute values:

$$C(e_\lambda e_{\bar{\lambda}}) = -C(e_\lambda h_{\bar{\lambda}}) = C(h_\lambda h_{\bar{\lambda}}) \tag{12}$$

These relations show also that the correlation content depends on the nature of the involved entities (i.e., electrons or holes): the sign is the same for electron–electron and hole–hole interactions, which is opposite for electron–hole ones. In other words, the electron–electron interactions typical for (formally) totally filled orbitals, are the same to the hole–hole ones typical for (formally) empty orbitals, but are opposite to the electron–hole ones characterizing unpaired electrons in orbital spaces. The positive/negative Coulomb correlations included in one orbital and the corresponding relations (12) can be read in the framework of the "attractive"/"repulsive" interpretation (these terms are in " ," because they do not refer to the energy, but to the deviation from the statistical limit corresponding to two mutually independent particles), presented in a previous work[36]: as the Coulomb electron–electron correlations included in a valence NAO are negative,[36] the two-electron interactions are 'repulsive', and hence, the electron–hole ones are "attractive".

It is known that the one-orbital Coulomb correlation, $C(e_\lambda e_{\bar{\lambda}})$, included in an orbital ϕ_λ depends directly on the (de)localization of the electrons in this orbital[36]; for example, when two electrons of opposite spins are well localized in ϕ_λ, then this one-orbital correlation[74] is small (it is zero in the

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*The term "electropon" arises from the contraction of two Greek words: "electron" and "opy" (meaning "hole").

limit case of strictly localized electrons). Consequently, the electropon probability in orbital ϕ_λ depends directly on the (de)localization of the electrons in this orbital.

(b) Correlations in two orbitals: Positive/negative two-orbital Coulomb correlations, $C(e_\lambda e_{\bar{\chi}})$, characterize respectively favorable/unfavorable chemical bonding between orbitals ϕ_λ and ϕ_χ.[36] As for a given orbital ϕ_λ, the sum of all Coulomb correlations is zero,[36] $\sum_{\bar{\chi}} C(e_\lambda e_{\bar{\chi}}) = 0$, quantity $P_{1;1}(\lambda;\bar{\lambda})$ can be expressed in function of two-orbital correlations:

$$P_{1;1}(\lambda;\bar{\lambda}) = n_\lambda^\alpha(1 - n_\lambda^\beta) + \sum_{\bar{\chi} \neq \bar{\lambda}} C(e_\lambda e_{\bar{\chi}}) \tag{13}$$

The summation in the r.h.s. of the above relation provides a global picture for the favorable/unfavorable two-orbital Coulomb interactions. Therefore, the electropon probability in ϕ_λ depends on whether and to what degree the chemical bonding between ϕ_λ and the remaining, ϕ_χ, orbitals of the system is globally favorable or unfavorable. Beyond this global picture, more detailed information concerning the interactions of electrons in two target orbitals can be obtained by the treatment of "Covalent Bonding and Correlation of Two Electropons" section.

Classification of electropons

From the above analysis, it follows that the electropon probability depends on two component factors: (i) a correlation-free factor, $n_\lambda^\alpha(1 - n_\lambda^\beta)$ and (ii) the one-orbital Coulomb correlation, $C(e_\lambda e_{\bar{\lambda}})$ (according to relations (9), (10) and (12)), or alternatively, the two-orbital ones, $C(e_\lambda e_{\bar{\chi}})$ (according to relation (13)). The behavior of the correlation-free component for a closed-shell system ($n_\lambda^\alpha = n_\lambda^\beta$) is given in Figure 1. It is worth noticing that at the HF level the correlation factor is trivially zero; however, even at this level the unpaired density is nonzero regardless of the
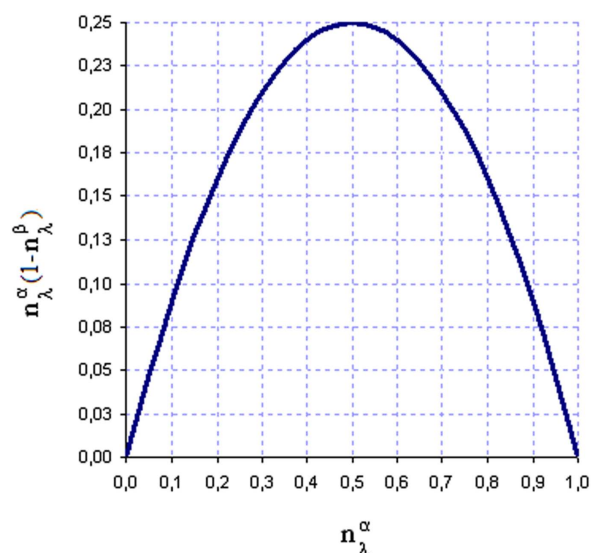
Figure 1. The behavior of the correlation-free component of the electropon population for a closed-shell system $(n_\lambda^\alpha = n_\lambda^\beta)$; n_λ^α around 0.5 corresponds to the 1e/1AO model, while n_λ^α approaching to one (or to zero) corresponds to the 2e/1AO (or to the zero) model occupation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

closed- or open-shell nature of the molecular system. The electropons can be classified into two model classes, depending on the formal occupation of a given orbital in the conventional chemical formula of the molecular system to which it belongs:

(i) Orbital ϕ_λ is formally occupied by one electron ($n_\lambda^\alpha = n_\lambda^\beta \approx 0.5$). In this case, the correlation-free component is around its maximum value ($\sim$0.25), and all Coulomb correlations are significant for the electropon probability.

(ii) Orbital ϕ_λ is formally occupied by two electrons ($n_\lambda^\alpha = n_\lambda^\beta \rightarrow 1$) or is formally totally empty (i.e., is occupied by two holes of opposite spins ($n_\lambda^\alpha = n_\lambda^\beta \rightarrow 0$). In both cases, the correlation-free component is small. As, by assumption, two electrons or two holes are well localized in ϕ_λ, the one-orbital electron–electron or hole–hole correlation, respectively, is small; hence, due to relations (9)–(12) or relation (13), the same also holds for the second component factor of the electropon probability (i.e., the one-orbital Coulomb correlation, or alternatively, the two-orbital electron–electron ones).

Covalent Bonding and Correlation of two Electropons

Using the concept of "electronic event" introduced by Loge Theory,[80] a covalent structure between orbitals ϕ_λ and ϕ_μ can be viewed as a local electronic event[36,40,41] occurring in these orbitals, namely, a two-electron–two-hole event, characterized by a $P_{2;2}$ ($E = 2$, $H = 2$) probability. For example, the probability $P_{2;2}(\lambda\bar{\mu};\bar{\lambda}\mu)$, obtained from the expectation value of a two-electron–two-hole density operator $a_\lambda^+ a_{\bar{\mu}}^+ a_{\bar{\lambda}} a_\mu a_\mu^+ a_{\bar{\lambda}}^+ a_{\bar{\mu}} a_\lambda$,[38–40] describes the covalent structure involving α and β spin electrons in ϕ_λ and ϕ_μ, respectively. Adopting the electropon viewpoint, the above two-electron–two-hole density operator can be considered as the product of two electropon operators $(a_\lambda^+ a_{\bar{\lambda}} a_{\bar{\lambda}}^+ a_\lambda)(a_{\bar{\mu}}^+ a_\mu a_\mu^+ a_{\bar{\mu}})$; hence, the covalent probability can be expressed in terms of the Coulomb correlation, $C_{EP}(\lambda,\bar{\mu})$, between two electropons of opposite spins, or more precisely, the correlation of fluctuations of the two electropon populations from their average values $P_{1;1}(\lambda;\bar{\lambda})$ and $P_{1;1}(\bar{\mu};\mu)$. This correlation,

$$C_{EP}(\lambda,\bar{\mu}) = P_{2;2}(\lambda\bar{\mu};\bar{\lambda}\mu) - P_{1;1}(\lambda;\bar{\lambda})P_{1;1}(\bar{\mu};\mu) \tag{14}$$

controls the interaction of two electropons of opposite spins in the target orbitals ϕ_λ and ϕ_μ, and characterizes the covalent (α,β) bonding[39,79] between these orbitals in the framework of the electropon definition. In relation (14), the probability $P_{2;2}(\lambda\bar{\mu};\bar{\lambda}\mu)$ is calculated by means of the following expression:

$$P_{2;2}(\lambda\bar{\mu};\bar{\lambda}\mu) = \sum_{K(\neq\bar{\lambda},\mu)}^{(\lambda,\bar{\mu})} W(\Phi_K) \tag{15}$$

The summation runs over Slater determinants involving spin–orbitals λ and $\bar{\mu}$, while simultaneously $\bar{\lambda}$ and μ are absent. In Appendix A, Supporting Information, it is shown that $C_{EP}(\lambda,\bar{\mu})$ can be expressed in terms of the well-known electron–electron Coulomb correlation, $C(e_\lambda e_{\bar{\mu}})$, and higher-order populations:

$$C_{EP}(\lambda,\overline{\mu}) = C(e_\lambda e_{\overline{\mu}}) - [P_{3;0}(\lambda\overline{\lambda}\mu;) - P_{2;0}(\lambda\overline{\lambda};)\,n_\mu^\beta] - [P_{3;0}(\lambda\mu\overline{\mu};)$$
$$- P_{2;0}(\mu\overline{\mu};)n_\lambda^\alpha] + [P_{4;0}(\lambda\overline{\lambda}\mu\overline{\mu};) - P_{2;0}(\lambda\overline{\lambda};)P_{2;0}(\mu\overline{\mu};)]$$

(16)

In the r.h.s. of the above relation, the second or third terms (in brackets) represent the correlations of an electron pair in one orbital (ϕ_λ or ϕ_μ) with the one-electron population in the other orbital (ϕ_μ or ϕ_λ, respectively), whereas the last term represents the correlation between two electron pairs.

Similar is the definition of the Fermi correlation, $C_{EP}(\lambda,\mu)$, referring to the correlation of two electropons of the same spin:

$$C_{EP}(\lambda,\mu) = P_{2;2}(\lambda\mu;\overline{\lambda\mu}) - P_{1;1}(\lambda;\overline{\lambda})P_{1;1}(\mu;\overline{\mu}) \qquad (17)$$

where

$$P_{2;2}(\lambda\mu;\overline{\lambda\mu}) = \sum_{K \neq (\overline{\lambda},\overline{\mu})}^{(\lambda,\mu)} W(\Phi_K) \qquad (18)$$

The electropon–electropon correlation, $C_{EP}(\lambda,\mu)$, can be expressed in terms of electron–electron Exchange or Fermi correlations,[36,81] $C(e_\lambda e_\mu)$, and higher-order populations:

$$C_{EP}(\lambda,\mu) = C(e_\lambda e_\mu) - \left[P_{3;0}(\lambda\overline{\lambda}\mu;) - P_{2;0}(\lambda\overline{\lambda};)n_\mu^\alpha\right]$$
$$- \left[P_{3;0}(\lambda\mu\overline{\mu};) - P_{2;0}(\mu\overline{\mu};)n_\lambda^\alpha\right]$$
$$+ \left[P_{4;0}(\lambda\overline{\lambda}\mu\overline{\mu};) - P_{2;0}(\lambda\overline{\lambda};)P_{2;0}(\mu\overline{\mu};)\right] \qquad (19)$$

where $C(e_\lambda e_\mu) = P_{2;0}(\lambda\mu;) - n_\lambda^\alpha n_\mu^\alpha$

In both relations (16) and (19), the terms in brackets depend (besides the two-electron Coulomb and Fermi correlations) on higher-order correlations. For example, in Appendix B, Supporting Information, it is shown that the second term in the r.h.s. of (16) involves the three-electron correlation,[82–83] $C(e_\lambda e_{\overline{\lambda}} e_{\overline{\mu}})$:

$$P_{3;0}(\lambda\overline{\lambda}\mu;)n_\mu^\beta - P_{2;0}(\lambda\overline{\lambda};)n_\mu^\beta = C(e_\lambda e_{\overline{\lambda}} e_{\overline{\mu}}) + n_\lambda^\alpha C(e_{\overline{\lambda}} e_{\overline{\mu}}) + n_\lambda^\beta C(e_\lambda e_{\overline{\mu}})$$

(20)

In this Appendix, Supporting Information, we present also the relations concerning the analogous terms of (16) and (19).

Correlation $C(e_\lambda e_\mu)$, appearing in Eq. (19), is related to the Wiberg–Mayer index[84–87] (calculated by means of the 1-RDM, and used frequently at the HF or density functional theory (DFT) levels) in the sense that both concern the behavior of electrons of the same spin. However, it is worth noticing that using quantities $C(e_\lambda e_\mu)$ one can detect the favorable or unfavorable bonding between two orbitals as negative or positive Fermi correlations, respectively (even at the HF level), unlikely to the Wiberg–Mayer index, which depends on the square of the 1-RDM elements. In general, the electron–electron Coulomb, $C(e_\lambda e_{\overline{\mu}})$, and Fermi, $C(e_\lambda e_\mu)$, correlations have opposite signs[36]: a favorable chemical bonding between valence orbitals ϕ_λ and ϕ_μ can be characterized from either the positive Coulomb correlation (which is a consequence of the favorable α,β spin interaction within a covalent structure) or the negative Fermi one (which is a consequence of the Pauli principle).

The numerical results presented in "Numerical Applications and Discussions" section show that the signs of the electropon–electropon Coulomb, $C_{EP}(\lambda,\overline{\mu})$ (or Fermi, $C_{EP}(\lambda,\mu)$), correlations are in general the same as those of the corresponding electron–electron Coulomb, $C(e_\lambda e_{\overline{\mu}})$ (or Fermi, $C(e_\lambda e_\mu)$), ones. This can lead to a definition of an electropon based index, $I_{EP}(\phi_\lambda,\phi_\mu)$, between spatial orbitals ϕ_λ and ϕ_μ, in which the Coulomb and Fermi correlations have opposite signs:

$$I_{EP}(\phi_\lambda,\phi_\mu) = C_{EP}(\lambda,\overline{\mu}) + C_{EP}(\overline{\lambda},\mu) - C_{EP}(\lambda,\mu) - C_{EP}(\overline{\lambda},\overline{\mu})$$

(21a)

This index is a spin-free quantity, which in closed-shell systems depends only on the two-electron correlations (this can be derived straightforwardly by means of relations of the type (16) and (19)):

$$I_{EP}(\phi_\lambda,\phi_\mu) = 2C(e_\lambda e_{\overline{\mu}}) - 2C(e_\lambda e_\mu) \qquad (21b)$$

It is worth noticing that in HF or DFT levels in which $C(e_\lambda e_{\overline{\mu}})$ is trivially zero, this index, based on the electropon definition (5) and the corresponding correlations (of relations (14) and (17)), is reduced to Fermi correlations. Hence, this index shows the connection of the electropon viewpoint to various molecular descriptors that are used in investigations based mainly on the behavior of parallel spin electrons.[7–9,12,27,36,88–89]

Numerical Applications and Discussions

To check the applicability of the presented theory, we achieved benchmark numerical applications. We considered ethylene, hexatriene, and benzene molecules as typical π systems within the one electron per one orbital (1e/1AO) model, in which the chemical bonding arises formally from the interaction of electrons in valence Pz AOs of π symmetry, as well as ammonia, methylamine, and pyrrole molecules as typical systems formally involving a lone pair in the N atom (Fig. 2).

For the planar π molecules (ethylene, hexatriene, benzene, and pyrrole), the basic calculations are achieved by using the NAOs, which are orthogonal orbitals as mathematically required for eigenfunctions of any physical Hermitian operator. As the interatomic nonorthogonality underlies basic VB concepts and in general the VB perspective for chemical bonding, analogous calculations have been repeated on the basis of pre-natural atomic orbitals (PNAOs), which are interatomically nonorthogonal. In the case of PNAOs, the probabilistic interpretation is not valid (as this holds for orthogonal ones), and one must refer to the "occupation number" interpretation[36,40,41] (or, alternatively, to the "weight" in the VB sense). By adopting the traditional Coulson–Chirgwin definition for the weights[100] of determinantal wave functions,

$$W(\Phi_K) = T_K^2 \langle \Phi_K \mid \Phi_K \rangle + T_K \sum_{K' \neq K}^{\text{full basis}} T_{K'} \langle \Phi_K \mid \Phi_{K'} \rangle \qquad (22)$$

we obtain Mulliken occupation numbers; this holds for one[101] or higher ($E \geq 2$) order populations,[102,103] as well as for structures involving both electrons and holes,[104–106] as for
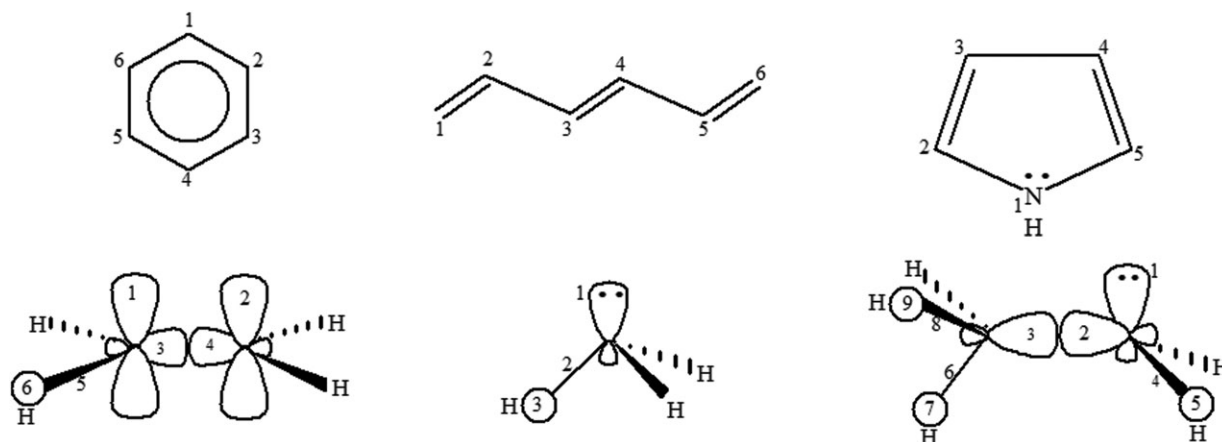
Figure 2. Numbering of valence Pz orbitals (NAOs or PNAOs) belonging to the π-systems of benzene, hexatriene, pyrrole, ethylene, and valence σ-hybrids (PNHOs) belonging to the σ-systems of ethylene, ammonia, and methylamine.

example, the two-electron–two-hole covalent structures. In this framework, the weights of local electronic structures, considered in this work, are computed by means of the same relations that are used for the orthogonal case (namely relations (6), (15), and (18)) but the involved weights $W(\Phi_k)$ are calculated by using definition (22). It is worth noticing that this definition, concerning the weights of determinantal wave functions, is also widely used in VB methods to obtain the weights of the local VB spin-eigenfunctions. Hence, in our treatment, the Mulliken partition provides weights that are coherent with those of VB theories; the main difference is that VB weights concern structures involving the whole electronic assembly, whereas our weights concern local electronic structures (or, alternatively, local electronic events) in some target AO positions.

For the nonplanar σ molecules, we used hybrid orbitals, because according to genuine knowledge both the N lone pair and the other orbitals forming the two-electron σ bonds are hybrid orbitals. For this purpose, and to avoid various conceptual problems, arising from hybrid orbitals obtained within basis sets involving multiple-zeta + polarization AO functions, we adopted the natural and unequivocally calculated pre-natural hybrid orbitals (PNHOs),[46–51] which are intratomically orthogonal and interatomically nonorthogonal. For all molecules, the initial correlated (and normalized) wave function, $\Psi(MO)$, is obtained by means of the PSHONDO program and the adapted multireference CI process (CIPSI).[107] The used self consistent field (SCF)-AO basis sets are the standard ones included in this chain of programs (double-zeta increased by polarization functions of d symmetry). The $\Psi(MO)$ wave functions are transformed in the basis of natural orbitals obtained in the framework of NBO methodology.[46–51] As these natural orbitals span the complete self consistent field (SCF)-AO basis set, the initial correlated $\Psi(MO)$, having the form of linear combinations of MO Slater determinants, is transformed (more precisely, is rewritten) in the natural basis without affecting its approximation level.[44] Subsequently, the probabilities (or, in general, the weights) of local VB-type resonance structures are calculated in the framework of PEPA using the hole-expansion methodology. All these operations (transformations and expansions) are achieved by means of the appropriately developed Natural PEPA (NPEPA) computer program.[†]

Unpaired electrons and one-orbital correlations

The results are presented in Tables 1–3; the numbering of orbitals is given in Figure 2. The order of magnitude and the

Table 1. Unpaired electrons, $P_{1;1}(\lambda;\bar{\lambda})$, in Pz valence NAOs, ϕ_λ, of π-systems, and Coulomb correlations included in ϕ_λ (in the CI level).

	AO-position ϕ_λ	n_λ^α	$P_{1;1}(\lambda;\bar{\lambda})$	Coulomb correlation $C(e_\lambda h_\lambda) = -C(e_\lambda e_\lambda)$
Ethylene	1	0.4947	0.3219	0.0720
Benzene	1	0.4963	0.2854	0.0354
Hexatriene	1	0.5038	0.3211	0.0711
	2	0.4914	0.3071	0.0572
	3	0.4942	0.3080	0.0580
Pyrrole	1	0.8082	0.1568	0.0018
	2	0.5235	0.2743	0.0249
	3	0.5541	0.2584	0.0113

Table 2. Unpaired electrons, $P_{1;1}(\lambda;\bar{\lambda})$, in Pz valence PNAOs, ϕ_λ, of π-systems, and Coulomb correlations included in ϕ_λ (in the CI level).

	AO-position ϕ_λ	n_λ^α	$P_{1;1}(\lambda;\bar{\lambda})$	Coulomb correlation $C(e_\lambda h_\lambda) = -C(e_\lambda e_\lambda)$
Ethylene	1	0.4949	0.3430	0.0930
Benzene	1	0.4901	0.2959	0.0460
Hexatriene	1	0.5109	0.3321	0.0822
	2	0.4758	0.3220	0.0726
	3	0.4872	0.3235	0.0737
Pyrrole	1	0.7732	0.1888	0.0134
	2	0.5289	0.2888	0.0398
	3	0.5419	0.2920	0.0433

[†]A. user-friendly computer program, NPEPA, in which all operations (transformations, expansions, etc.) are performed without the user intervention, is available from an author (PK) upon request.

Table 3. Unpaired electrons, $P_{1;1}(\lambda;\bar{\lambda})$, in hybrid orbitals, PNHOs, ϕ_λ, of σ-systems, and Coulomb correlations included in ϕ_λ (in the CI level).

	AO-position ϕ_λ	n_λ^α	$P_{1;1}(\lambda;\bar{\lambda})$	Coulomb correlation $C(e_\lambda h_\lambda) = -C(e_\lambda e_\lambda)$
Ethylene	3	0.4812	0.3797	0.1300
	5	0.5519	0.3722	0.1249
	6	0.4219	0.3564	0.1125
Ammonia	1	0.9954	0.0011	−0.0035
	2	0.6148	0.3424	0.1056
	3	0.3811	0.3421	0.1063
Methylamine	1	0.9737	0.0271	0.0015
	2	0.5936	0.3758	0.1345
	3	0.6030	0.3115	0.0721
	4	0.3782	0.2985	0.0633
	5	0.3909	0.3761	0.1380
	6	0.5368	0.3591	0.1105
	7	0.4506	0.3404	0.0929
	8	0.5495	0.3574	0.1098
	9	0.4317	0.3361	0.0908

general trends for electropons and the one-orbital Coulomb correlations, obtained from the series of calculations in the basis of the interatomically orthogonal NAOs (Table 1), are very close to those obtained in the basis of the nonorthogonal PNAOs (Table 2). Both basis sets lead to the same conceptual pictures.

Comparing the electropon populations, $P_{1;1}(\lambda;\bar{\lambda})$, in nitrogen orbitals, bearing formally a lone pair, to those in Pz orbitals of a π system, it turns out that in the former orbitals these populations as well as the one-orbital correlations, $C(e_\lambda h_{\bar\lambda})$, are smaller. Comparing the same quantities within the three compounds which involve the NH$_2$ group, one can find that both diminish in the series pyrrole > methylamine > ammonia. The intermediate value of $P_{1;1}(\lambda;\bar{\lambda})$ for the nitrogen lone pair orbital in methylamine is in good agreement with the fact that the hyperconjugation of this orbital with the CH bonds of CH3 group‡ is clearly weaker than the π conjugation in pyrrole and do not exist in ammonia. The same trend also exists for the electron–hole correlations, which become even negative in ammonia; in this case, the highly localized lone pair corroborates the very small absolute value of the (negative) electron–hole (or, alternatively, positive one-orbital electron–electron) correlation included in a lone pair orbital, which do not participate in an even weak chemical bond. The above trends are in agreement with fundamental chemical knowledge. Furthermore, our numerical results show that the smaller the electron–hole correlation is, the smaller the unpaired electrons are.

The one-orbital correlation, $C(e_\lambda h_{\bar\lambda})$, and thus $P_{1;1}(\lambda;\bar{\lambda})$, can provide a global picture for the favorable/unfavorable two-orbital interactions. Tables 1–3 show that the Coulomb correlation, included in a hybrid σ orbital (formally a sp^x hybrid) forming a σ bond within the 1e/1AO model, is in general greater than that included in a Pz orbital forming π bonds: The average value in σ orbitals of C in ethylene and methylamine is

‡This hyperconjugative effect is exhaustively analyzed in the tutorial examples involved in Ref. [51].

clearly greater than that in Pz orbitals. This conclusion, concerning the global behavior of two-electron Coulomb correlations, and hence the electropon population, is in good agreement with the general trend stating that σ bonds are stronger than π ones. Beyond this global picture, more detailed information, especially for π bonding, can be obtained by investigating the interaction of two electropons in two target Pz orbitals, presented in "Favorable/Unfavorable Bonding and Correlations of Two Electropons in Two Orbitals" subsection.

Another difference between σ and Pz orbitals arises from the fact that the former orbitals interact mainly with only one vicinal σ orbital (with which it forms the σ bond), whereas the latter interact with more than one orbital of the same symmetry. For example, in benzene, the interaction of electrons in *meta* positions (i.e., 1-3 interactions) are significant, leading to non-negligible negative two-electron Coulomb correlations (presented in "Favorable/Unfavorable Bonding and Correlations of Two Electropons in Two Orbitals" subsection). These correlations appear twice (as $C(e_1 e_{\bar3})$ and $C(e_1 e_{\bar5})$) and as a consequence they diminish the one-orbital correlation $C(e_1 h_{\bar1})$ (or, alternatively, the absolute value of $C(e_1 e_{\bar1})$) and, thus, the unpaired electrons. This is also the key reason for the fact that $P_{1;1}(\lambda;\bar{\lambda})$ has the smaller value in benzene among the considered systems within the 1e/1AO model.

The numerical results show that when n_λ^α is close to 0.5 ($0.45 < n_\lambda^\alpha < 0.55$), the electropon populations, $P_{1;1}(\lambda;\bar{\lambda})$, grow with Coulomb correlation, $C(e_\lambda h_{\bar\lambda})$, and in most cases this correlation component factor (see "Unpaired Electrons—Calculation, Boundary Values and the Role of Electronic Correlation" section) varies in the same direction as the correlation-free factor (shown in Fig. 1). However, when these two factors are in opposite direction, then $P_{1;1}(\lambda;\bar{\lambda})$ is controlled by the correlation; this occurs examining their relative role when σ and π bonds are compared.

Favorable/unfavorable bonding and Correlations of two Electropons in two orbitals

The results concerning the interactions of two electropons in two different orbitals are presented in Tables 4–6. The general trends and the conceptual pictures obtained from various types of correlations of two electropons, and the electropon indices, are the same from both NAOs (Table 4) and PNAOs (Table 5).

The Coulomb, $C_{EP}(\lambda;\bar\mu)$ and Fermi, $C_{EP}(\lambda,\mu)$, correlations of two electropons, are of an opposite sign; the absolute values of Fermi correlations are in general larger than the Coulomb ones; also, the larger absolute values of Fermi correlations correspond to the larger absolute values of Coulomb ones. From the results presented in Tables 4–6, one can conclude that the correlations of two electropons are in general of the same sign to the corresponding Coulomb and Fermi correlations of two electrons.

All numerical results clearly show that positive/negative Coulomb (or, alternatively negative/positive Fermi) correlations of two electropons characterize chemical bonding, which according to genuine chemical knowledge and elementary VB

Table 4. Weights (probabilities) of covalent structures, Coulomb and Fermi (or Exchange) correlations, and electropon indices in valence Pz NAOs, ϕ_λ,ϕ_μ; where $|\varepsilon| < 5 \times 10^{-4}$ (the Coulomb correlations of two electrons are trivially zero at the HF level).

| | AO Positions $\phi_\lambda - \phi_\mu$ | Antiparallel spins | | | | | Parallel spins | | | | | | Index $I_{EP}(\phi_\lambda,\phi_\mu)$ | |
| | | $P_{2;2}$ $(\lambda\overline{\mu};\overline{\lambda}\mu)$ | | Two Electropons $C_{EP}(\lambda,\overline{\mu})$ | | Two Electrons $C(e_\lambda e_\mu)$ | $P_{2;2}$ $(\lambda\mu;\overline{\lambda}\overline{\mu})$ | | Two Electropons $C_{EP}(\lambda,\mu)$ | | Two Electrons $C(e_\lambda e_\mu)$ | | | |
		HF	CI	HF	CI	CI	HF	CI	HF	CI	HF	CI	HF	CI
Ethylene	1-2	0.247	0.314	0.184	0.211	0.072	ε	0.002	−0.062	−0.102	−0.247	−0.241	0.494	0.625
Benzene	1-2	0.130	0.163	0.067	0.082	0.019	0.019	0.028	−0.043	−0.053	−0.110	−0.116	0.221	0.269
	1-3	0.062	0.074	ε	−0.007	−0.006	0.062	0.090	ε	0.008	ε	0.009	ε	−0.031
	1-4	0.077	0.104	0.014	0.022	0.011	0.050	0.062	−0.013	−0.020	−0.027	−0.031	0.055	0.084
Hexatriene	1-2	0.220	0.279	0.157	0.180	0.061	0.001	0.005	−0.061	−0.094	−0.219	−0.213	0.437	0.548
	1-3	0.062	0.091	ε	−0.008	−0.010	0.062	0.108	ε	0.009	ε	0.008	ε	−0.035
	1-4	0.074	0.122	0.012	0.023	0.015	0.052	0.077	−0.011	−0.022	−0.022	−0.029	0.045	0.090
	2-3	0.078	0.120	0.015	0.026	0.006	0.049	0.075	−0.013	−0.020	−0.029	−0.039	0.057	0.091
	2-4	0.062	0.088	ε	−0.006	−0.007	0.062	0.101	ε	0.006	ε	0.006	ε	−0.025
	1-5	0.062	0.095	ε	−0.004	−0.004	0.062	0.103	ε	0.004	ε	0.004	ε	−0.016
	3-4	0.199	0.251	0.137	0.156	0.053	0.003	0.008	−0.060	−0.087	−0.196	−0.190	0.392	0.487
	1-6	0.065	0.114	0.003	0.011	0.008	0.060	0.092	−0.003	−0.011	−0.006	−0.014	0.011	0.044
Pyrrole	1-2	0.069	0.076	0.031	0.033	0.007	0.010	0.013	−0.027	−0.030	−0.058	−0.056	0.117	0.126
	2-3	0.158	0.161	0.097	0.090	0.012	0.009	0.011	−0.053	−0.059	−0.150	−0.138	0.299	0.300
	2-5	0.080	0.105	0.018	0.019	0.007	0.046	0.057	−0.016	−0.019	−0.034	−0.031	0.068	0.075
	3-4	0.105	0.103	0.043	0.037	0.004	0.028	0.033	−0.033	−0.034	−0.076	−0.067	0.152	0.142

Table 5. Weights of covalent structures, Coulomb and Fermi (or Exchange) correlations, and electropon indices in valence Pz PNAOs, ϕ_λ,ϕ_μ; where $|\varepsilon| < 5 \times 10^{-4}$ (the Coulomb correlations of two electrons are trivially zero at the HF level).

| | AO Positions $\phi_\lambda - \phi_\mu$ | Antiparallel spins | | | | | Parallel spins | | | | | | Index $I_{EP}(\phi_\lambda,\phi_\mu)$ | |
| | | $P_{2;2}$ $(\lambda\overline{\mu};\overline{\lambda}\mu)$ | | Two Electropons $C_{EP}(\lambda,\overline{\mu})$ | | Two Electrons $C(e_\lambda e_\mu)$ | $P_{2;2}$ $(\lambda\mu;\overline{\lambda}\overline{\mu})$ | | Two Electropons $C_{EP}(\lambda,\mu)$ | | Two Electrons $C(e_\lambda e_\mu)$ | | | |
		HF	CI	HF	CI	CI	HF	CI	HF	CI	HF	CI	HF	CI
Ethylene	1-2	0.252	0.336	0.190	0.219	0.093	ε	0.001	−0.062	−0.116	−0.252	−0.242	0.504	0.670
Benzene	1-2	0.131	0.174	0.068	0.087	0.025	0.019	0.031	−0.043	−0.056	−0.112	−0.118	0.224	0.286
	1-3	0.063	0.082	ε	−0.005	−0.008	0.062	0.102	ε	0.014	ε	0.012	ε	−0.039
	1-4	0.074	0.111	0.011	0.024	0.011	0.052	0.072	−0.010	−0.015	−0.021	−0.028	0.043	0.078
Hexatriene	1-2	0.219	0.288	0.157	0.182	0.073	0.001	0.006	−0.061	−0.101	−0.218	−0.210	0.436	0.566
	1-3	0.062	0.101	ε	−0.007	−0.013	0.063	0.122	ε	0.015	ε	0.009	−0.001	−0.043
	1-4	0.072	0.131	0.009	0.024	0.015	0.054	0.090	−0.009	−0.017	−0.018	−0.026	0.036	0.083
	2-3	0.079	0.139	0.017	0.035	0.014	0.047	0.081	−0.015	−0.023	−0.032	−0.044	0.064	0.116
	2-4	0.062	0.101	ε	−0.003	−0.011	0.062	0.117	ε	0.013	ε	0.005	ε	−0.033
	1-5	0.062	0.107	ε	ε	−0.003	0.062	0.112	ε	0.005	ε	0.002	ε	−0.009
	3-4	0.197	0.263	0.135	0.158	0.068	0.003	0.010	−0.059	−0.095	−0.194	−0.185	0.389	0.506
	1-6	0.065	0.122	0.002	0.012	0.007	0.060	0.103	−0.002	−0.006	−0.005	−0.012	0.010	0.037
Pyrrole	1-2	0.074	0.090	0.033	0.036	0.006	0.013	0.018	−0.028	−0.036	−0.061	−0.066	0.122	0.144
	2-3	0.159	0.193	0.097	0.109	0.030	0.009	0.016	−0.053	−0.068	−0.150	−0.147	0.301	0.354
	2-5	0.075	0.102	0.013	0.018	0.006	0.050	0.069	−0.012	−0.015	−0.026	−0.027	0.051	0.066
	3-4	0.108	0.146	0.046	0.060	0.014	0.028	0.041	−0.034	−0.043	−0.080	−0.090	0.160	0.208

theory is commonly referred to as favorable/unfavorable. In Figures 3 and 4, we show some typical VB resonance structures of benzene and hexatriene, respectively, involving both favorable and unfavorable chemical bonding. In benzene, for example, the unfavorable bonding in *meta* (i.e., 1-3) positions is characterized by negative Coulomb or positive Fermi correlations of two electropons. In *ortho* (1-2) and *para* (1-4) positions, these correlations have an opposite sign (positive Coulomb and negative Fermi), and the greater absolute values are for *ortho* positions. These results are in very good agreement with the fact that the Kekulé structures of benzene (first structure of Fig. 3) are more favorable than the Dewar ones (second structure of Fig. 3), and both are more favorable than the clearly unfavorable third structure of Figure 3. In hexatriene, the two-electropon Coulomb correlations are positive (and Fermi negative) for positions (1-2) > (1-4) > (1-6), and

Table 6. Weights of covalent structures, Coulomb and Fermi (or Exchange) correlations, and electropon indices in valence hybrids, PNHOs, ϕ_λ, ϕ_μ; where $|\varepsilon| < 5 \times 10^{-4}$ (the Coulomb correlations of two electrons are trivially zero at the HF level).

		Antiparallel spins						Parallel spins						
		P2;2 ($\lambda\bar{\mu};\bar{\lambda}\mu$)		Coulomb Correlations			P2;2 ($\lambda\mu;\bar{\lambda}\bar{\mu}$)		Fermi correlations				Index $I_{EP}(\phi_\lambda,\phi_\mu)$	
				Two Electropons $C_{EP}(\lambda,\bar{\mu})$		Two Electrons $C(e_\lambda e_\mu)$			Two Electropons $C_{EP}(\lambda,\mu)$		Two Electrons $C(e_\lambda e_\mu)$			
	AO Positions $\phi_\lambda - \phi_\mu$	HF	CI	HF	CI	CI	HF	CI	HF	CI	HF	CI	HF	CI
Ethylene	3-4	0.250	0.369	0.187	0.225	0.123	ε	0.001	−0.063	−0.143	−0.250	−0.245	0.500	0.736
	5-6	0.238	0.350	0.178	0.218	0.116	ε	ε	−0.060	−0.132	−0.238	−0.234	0.477	0.700
Ammonia	1-2	ε	0.003	ε	0.003	0.005	ε	0.001	ε	ε	ε	0.002	ε	0.005
	2-3	0.246	0.351	0.191	0.234	0.106	ε	0.001	−0.054	−0.117	−0.245	−0.244	0.491	0.700
Methylamine	1-2	0.004	0.009	ε	−0.001	−0.004	0.004	0.010	ε	−0.001	−0.001	−0.004	0.001	ε
	2-3	0.246	0.378	0.189	0.237	0.132	ε	0.001	−0.056	−0.140	−0.246	−0.244	0.492	0.753
	1-4	0.004	0.008	ε	ε	ε	0.004	0.009	0.001	0.001	0.001	0.001	−0.002	−0.001
	1-6	0.006	0.011	0.002	0.002	0.002	0.001	0.008	−0.003	−0.002	−0.005	−0.002	0.010	0.007
	1-8	0.004	0.010	ε	ε	0.003	0.004	0.008	ε	−0.001	−0.001	0.002	0.001	0.003
	1-7	0.005	0.009	0.001	ε	−0.002	0.003	0.006	−0.001	−0.003	−0.002	−0.005	0.005	0.006
	1-9	0.004	0.008	ε	−0.001	−0.002	0.004	0.008	ε	−0.001	ε	−0.002	ε	ε
	4-5	0.238	0.299	0.182	0.206	0.065	ε	ε	−0.056	−0.093	−0.238	−0.235	0.476	0.599
	6-7	0.244	0.337	0.182	0.215	0.096	ε	0.001	−0.061	−0.121	−0.244	−0.241	0.488	0.673
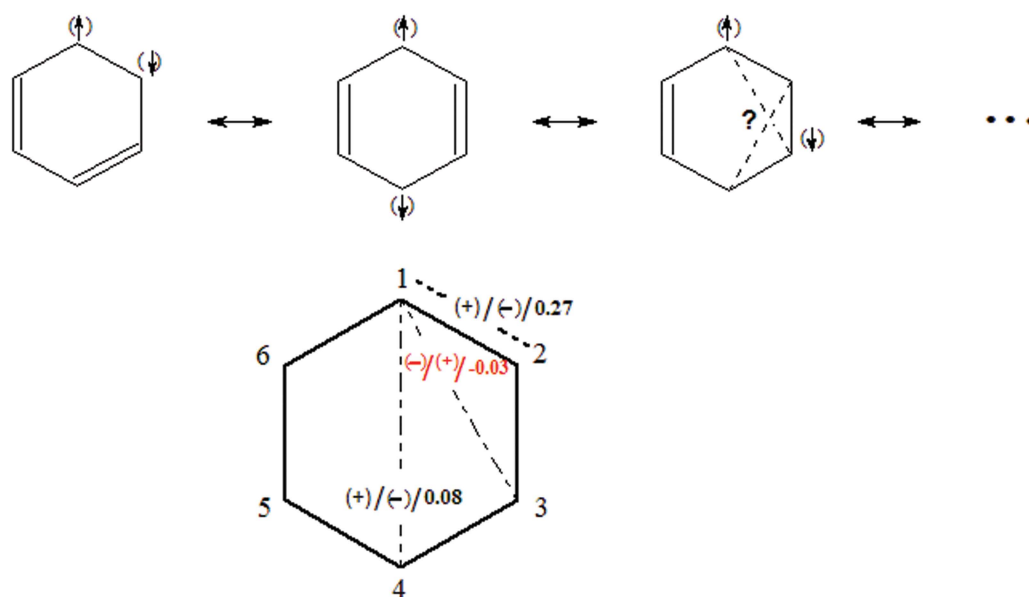
Figure 3. Upper panel: Interacting electropons of opposite spins (represented by (↑) and (↓)) appearing in some VB structures of benzene. Lower panel: Summary of the signs of the two-electron Coulomb and Fermi correlations and the electropon index, I_{EP} at the CI level (within the NAO basis set): sign of Coulomb/sign of Fermi/Index I_{EP} [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

state. On the contrary, the two electron Coulomb correlations at the HF level cannot provide any information for favorable/unfavorable bonding.

From Tables 4–6, one can conclude that the pairs of orbitals forming π bonds show in general smaller (in absolute values) Coulomb electropon correlations than those forming σ bonds; the same trend holds also for the Fermi correlations. Also, the negative Coulomb (or alternatively, positive Fermi) correlations in two orbitals are non-negligible and more frequent in π than in σ systems. Both conclusions agree to the fact that π bonds are weaker than the σ ones.

The index based on the electropon definition, I_{EP}, is in good agreement with genuine chemical knowledge for favorable/unfavorable bonding. Apart the correct description of both π and σ bonds, one can also note that in methylamine the long range secondary correlations of two electropons, having small absolute values, are larger (as expected) between orbitals (1-6) than (1-8).§

negative (and Fermi positive) for positions (1-3) > (1-5); the inequality symbols refer to the absolute values of both Coulomb and Fermi correlations. In general, the results presented in Tables 4–6 are in very good agreement with genuine chemical knowledge, elementary VB theory and the structures presented in Figures 3 and 4.

One must underline the fact that the Coulomb correlations of two electropons are different from zero even at the HF level, although the Coulomb correlations of two electrons are trivially zero. Furthermore, the electropon correlations at the HF level have in general the same sign as those obtained at CI level, providing a reasonable (although less accurate) description of these closed shell molecules in their ground electronic

§This trend is in agreement to the well known more favorable "antiperiplanar" interactions with respect to the *gauche* ones.[51]
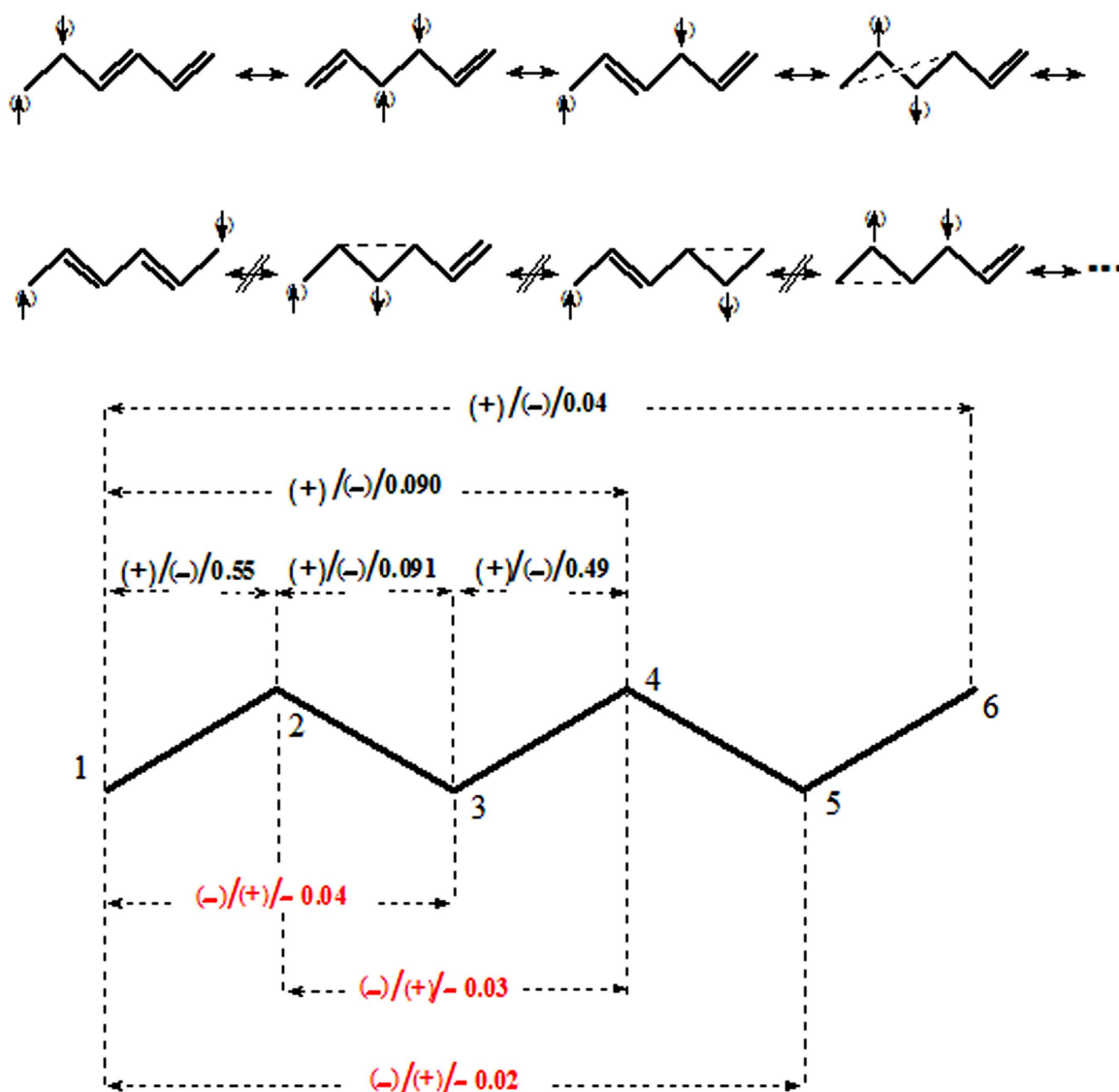
Figure 4. Upper panel: Interacting electropons of opposite spins (represented by ($\uparrow$) and ($\downarrow$)) appearing in some VB structures of hexatriene. Lower panel: Summary of the signs of the two-electropon Coulomb and Fermi correlations and the electropon index, I_{EP} at the CI level (within the NAO basis set): sign of Coulomb/sign of Fermi/Index I_{EP} [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

The electropon population represents the fraction of the conventional one-electron population that is responsible for covalent bonding. The investigation of this quantity in one orbital reveals whether and to what degree the Coulomb correlations, and hence, the chemical bonding between this orbital and the remaining orbitals of the system are globally favorable or unfavorable. The investigation of the interaction of two electropons in two target orbitals reveals the quality (favorable or unfavorable) and the strength of the bonding between these orbitals. The electropon viewpoint is checked by means of benchmark calculations on well-known closed-shell molecules and all results are in good agreement with genuine chemical knowledge and elementary VB theory.

The electropon population in an orbital ϕ_λ depends on a correlation-free, $n_\lambda^\alpha(1 - n_\lambda^\alpha)$, and a correlation, $C(e_\lambda h_{\bar\lambda}) =$

$-C(e_\lambda e_{\bar\lambda})$, component factor. Therefore, the unpaired density is nonzero even for closed shell molecules at the HF level, in which only the correlation factor vanishes. When the usual (spin-free) one-electron population is around to one ($n_\lambda^\alpha + n_\lambda^\beta \approx 1$), then the correlation-free component is close to its maximum value (0.25), and the Coulomb correlations (namely, the one-orbital, $C(e_\lambda e_{\bar\lambda})$, or alternatively, the sum of two-orbital, $C(e_\lambda e_{\bar\chi})$ (where $\bar\chi \neq \bar\lambda$), correlations) are significant. When the one-electron population approaches to two ($n_\lambda^\alpha + n_\lambda^\beta \to 2$), both component factors are small.

The connection between the traditional covalent structure of VB theory and the notion of "unpaired electrons" is established by means of the correlation of two electropons of opposite spins, namely the Coulomb electropon, $C_{EP}(\lambda,\bar\mu)$, correlation. Positive or negative correlation characterizes favorable or unfavorable VB-type covalent bonding. In the same spirit, we have defined the Fermi (or Exchange) electropon, $C_{EP}(\lambda,\mu)$,

correlation, showing an opposite behavior to the Coulomb one (i.e., the favorable or unfavorable bonding is characterized by negative or positive electropon correlations, respectively).

The index, $I_{EP}(\phi_\lambda, \phi_\mu)$, based on the electropon definition, is a spin-free quantity providing a valuable (global spin-free) description of favorable or unfavorable bonding between spatial orbitals ϕ_λ and ϕ_μ. It also shows (quantitatively) the relationship that exists between the electropon viewpoint and the two-electron Coulomb and Fermi correlations. Especially in the case of HF or DFT levels, this index can reveal the connection that exists between the electropon viewpoint and other molecular descriptions based on the behavior of parallel spin electrons.

In this work, no restrictions for the unpaired electron density of closed shell systems have been imposed. The definition of the "unpaired electron" (i.e., the electropon) arises merely from the fact that this notion must be the opposite of the "paired electron" notion. Given an orbital occupied by one electron (within the full determinantal basis set, $\{\Phi_K\}$), there are two possibilities for a second electron of opposite spin: this can be present, creating an electron pair, or absent, creating an electropon. These two mutually exclusive possibilities are described by the expectation values (see relations (4), (5), and (7)) of two-electron and one-electron–one-hole density operators, which express in the framework of the first-order anticommutation relation the opposite nature of the notions of "paired" and "unpaired" electrons. Strictly zero unpaired electronic density can be found only in the classical (formal) Lewis structures in which the electron pairing is assumed to be perfect. In real quantum (molecular) systems locally unpaired electrons and covalent (and, thus, chemical) bonding are closely related. Placing "under the microscope" local AO positions we have shown that the unpaired electrons in these positions are basic ingredients for chemical bonding.

Keywords: unpaired electrons · electron holes · Coulomb correlation · Fermi (exchange) correlation · reduced density matrices · valence bond

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