J. Phys. Chem. A **2001,** *105,* 4524−4534

Looking at Chemical Bonding from Coulomb and Exchange Correlations in NAOs

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Received: November 7, 2000; In Final Form: January 31, 2001

Coulomb and exchange correlations, providing information for the interactions of antiparallel and parallel spin electrons, respectively, are investigated in orbitals appropriate for population analysis, such as the natural atomic orbitals (NAOs). In the proposed analysis, both correlations are treated on an equal footing in configuration interaction (CI) (or Hartree−Fock) levels, but an emphasis is given for coulomb correlations and their physical meaning. It is stressed that the two-center interactions of antiparallel spin electrons can be "repulsive" and "attractive" (as a direct consequence of chemical bonding), but the former are less important than the latter; their relative importance is determined by the magnitude of one-center interactions. These globally attractive two-center interactions are balanced by the repulsive one-center interactions. These conclusions are general and hold for any molecular system, under the only assumption that the one-center interactions are repulsive. Molecular orbital wave functions for the *cis*-butadiene molecule (in various approximations levels) are used to illustrate the relative role of coulomb and exchange interactions in chemical bonding. The magnitudes of exchange interactions are significantly larger (2−4 times) than those of the coulomb interactions; the signs of two-center coulomb and exchange correlations are opposite. Even though the CI is very crucial for coulomb interactions, the exchange interactions, in general, are not so sensitive. The provided description for chemical bonding is consistent with usual chemical pictures involving electron pairs.

1. Introduction

One-electron population analysis is widely used, and the majority of quantum chemical investigations contain or refer to results of such an analysis. Among the various ways to perform population analysis in orbital space, one can cite the natural population analysis (NPA),[1,2] which shows a very good stability with the extension of the SCF-AO basis set. NPA is based in natural atomic orbitals (NAOs), which are "natural" in the Lowdin sense (and orthogonal), and natural bond orbitals (NBOs), which are directly issued from NAOs. This kind of analysis is widely used in various types of current chemical topics.[3]

Beyond one-electron distributions, the theoretical grounds of second-order density matrices are well known,[4] and their role in the description of usual molecular systems is well established.[5] A second-order density matrix can be divided into coulomb and exchange parts; the former concerns the interaction of antiparallel spin electrons and the latter the interaction of parallel spins. Various schemes of pair populations are used,[6−11] giving new insights for chemical bonding in the framework mainly of noncorrelated (semiempirical or ab initio) wave functions. The using of exchange correlations in the examination of fluctuations of electronic populations in orbital space led to the reconciliation of quantum mechanical and classical pictures.[12] Bond orders directly proportional to exchange correlations are used[7−9] in the framework of generalized Wiberg indices.[13,14] Correlation analysis of bonds applied for Hartree−Fock wave functions allows the investigation of basic features of chemical reactivity.[15] The behavior of parallel spin electrons is also investigated by means of electron localization function (ELF).[16] The topological analysis of ELF leads to distinguish attractors and basins with a clear chemical meaning and investigate the exchange correlation, appearing as the variance of basin populations.[17,18] The topological examination in physical (coordinate) space of Fermi holes,[19,20] which are directly related to exchange correlations, leads to physically meaningful investigation of (de)localization of electrons. Apart from the above cited works concerning essentially the behavior of parallel spin electrons, systematic studies referring to population analysis and correlation of electron pairs of antiparallel spin (coulomb interactions) are scarce, mainly because this type of analysis necessitates correlated molecular wave functions. Recently, coulomb correlation is studied in the H_2 model system,[21] and its effect on the Lewis electron pair within the topological definition of atoms in coordinate space[22] is also investigated.

The purpose of the present work is to investigate both coulomb and exchange correlations in an orbital space appropriate for population analysis, as the space of NAOs. In the proposed analysis, coulomb and exchange parts of second-order density matrices are treated on an equal footing. However, an emphasis is given to the coulomb part (and its physical meaning), because the corresponding type of interactions have not been explored sufficiently. Exchange interactions are also considered and compared with the coulomb interactions. The *cis*-butadiene molecule is used as an example to illustrate the role of coulomb and exchange correlations within various levels of approximations.

The first part of our analysis necessitates the calculation of electron pair distributions from correlated wave functions. Unlike other pair population schemes, these calculations are based in Moffitt's theorem,[23] which allows the decomposition of MO Slater determinants[24] in local ones in both orthogonal[25,26] and nonorthogonal basis sets,[27] as well as the second quantized formulation[28] of generalized density matrices.[29] The use of Moffitt's decompositions can lead to a polyelectron population analysis[30] referring to both electrons and electron holes,[31] and allows the examination of the behavior of covalent and ionic

10.1021/jp004092q CCC: $20.00

resonance structures of bonds or, in general, the investigation of the probabilities of finding various types of electronic events.[31−33] In the present work, analyzing coulomb and exchange correlations we adopt implicitly two general assumptions, which, however, are also used in a direct or indirect way very frequently. (i) An atom is considered in Hilbert space and is assumed to be composed of nuclei-centered orbitals (with different populations from one molecule to another). To distinguish this point of view from the physical concept of an atom inside of a given molecular system, in this work we use the term “center” instead of “atom”. (ii) All pairs of centers (i.e., atoms) are considered to be bonded (more precisely, to interact) at least very weakly. This manner of visualizing chemical bonding is used in the investigation of various types of bond orders within one-electron population analysis and is closely related to usual valence bond (VB)[34] pictures of resonance structures, or to the NBO-based structures of natural resonance theory (NRT).[35,36]

2. Electron Pair Distributions as Two-Electron Events in the Framework of Moffitt’s Theorem

According to Moffitt’s theorem,[23,25] each (delocalized) MO Slater determinant of a MO wave function, $\Psi(\mathrm{MO})$, is decomposed into the complete (local) determinantal basis set {K}. Each K is a totally local (TL) Slater determinant involving the AOs, which are used in the MOs. The obtained wave function has the form

$$|\Psi(\mathrm{TL})\rangle = \sum_{\mathrm{K}} T_{\mathrm{K}}\,|\mathrm{K}\rangle \tag{1}$$

The expansion coefficients, T_{K}, are obtained from expressions involving LCAO and CI coefficients;[23,25] these expressions are the same for both orthogonal and nonorthogonal AOs. The calculation of $\Psi(\mathrm{TL})$ involves no approximations or additional assumptions, and the only approximations involved in eq 1 are those that are included in the initial wave function $\Psi(\mathrm{MO})$; thus Moffitt’s theorem guarantees the validity of the following relation:

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

In the framework of orthogonal orbitals, the expectation values of density operators $\mathrm{a}_{\mu}^{+}\mathrm{a}_{\bar{\lambda}}^{+}\mathrm{a}_{\bar{\lambda}}\mathrm{a}_{\mu}$ and $\mathrm{a}_{\mu}^{+}\mathrm{a}_{\lambda}^{+}\mathrm{a}_{\lambda}\mathrm{a}_{\mu}$ are the following:

$$P_2(\mu,\bar{\lambda}) = \langle\Psi(\mathrm{TL})|\mathrm{a}_{\mu}^{+}\mathrm{a}_{\bar{\lambda}}^{+}\mathrm{a}_{\bar{\lambda}}\mathrm{a}_{\mu}|\Psi(\mathrm{TL})\rangle = \sum_{\mathrm{K}}^{(\mu,\bar{\lambda})} W_{\mathrm{K}} \tag{3a}$$

$$P_2(\mu,\lambda) = \langle\Psi(\mathrm{TL})|\mathrm{a}_{\mu}^{+}\mathrm{a}_{\lambda}^{+}\mathrm{a}_{\lambda}\mathrm{a}_{\mu}|\Psi(\mathrm{TL})\rangle = \sum_{\mathrm{K}}^{(\mu,\lambda)} W_{\mathrm{K}} \tag{3b}$$

where $\sum_{\mathrm{K}}{}^{(\mu,\bar{\lambda})}$ is a summation over those Slater determinants in which the spin−AO μ is present conjointly with $\bar{\lambda}$; W_{K} is the weight of Slater determinants, K, which, in the case of orthogonal orbitals, is equal to $T_{\mathrm{K}}{}^2$. The expectation value calculated in eq 3a provides the *probability* of finding simultaneously two electrons of antiparallel spin in AOs μ and λ, while the remaining electrons can reside anywhere else. (No labels (1,2) are given for these two electrons; this means that we consider *any* of the available (α,β) pairs). Similar is the meaning of expectation value calculated in eq 3b, concerning electrons of parallel spin. Apart from these probability meanings, an alternative interpretation can be given, which refers to the *number* of electron pairs. Because the electron pair distributions are normalized to $N(N\text{-}1)/2$ (where N is the total number of electrons and $N = N^{\alpha} + N^{\beta}$), $P_2(\mu,\bar{\lambda})$ provides also the number of α,β electron pairs belonging to AOs μ and λ; it is a fraction of the number, $N^{\alpha}N^{\beta}$, of antiparallel spin electron pairs. Similarly, $P_2(\mu,\lambda)$ provides the number of α,α electron pairs belonging to the same AOs, and it is a fraction of the number, $N^{\alpha}(N^{\alpha}-1)/2$, of electron pairs with parallel (α,α) spin. In the above, we have adopted Lowdin’s normalization, i.e., the total number of electron pairs is equal to $N(N-1)/2$.

By calculating electron pair distributions in the framework of Moffitt’s theorem, one can easily rationalize the manner with which the quantities of eqs 3a and 3b are calculated in conjunction with their physical meaning. In a molecular system of M (spatial) AOs, there are $(M!/N^{\alpha}!(M-N^{\alpha})!)\,(M!/N^{\beta}!(M-N^{\beta})!)$ distinct ways to arrange the N^{α} and N^{β} electrons in the available AO positions. Each arrangement defines an N-electron event, which is represented from one Slater determinant K, and the whole molecular wave function (eq 1) is obtained from the superposition of all possible K. In this context, a weight, W_{K}, is the probability of finding simultaneously the N electrons in some (N in number) of the available AOs. Consequently, the probability of a *two-electron event* (as the simultaneous location of two electrons in two AOs) is obtained from the *summation of the probabilities* of well selected N electron events. The type of K that must be selected is determined by the type of chosen density operator: in eq 3a or eq3b, both the restriction in the location of two electrons in two AOs and the fact that the remaining electrons are allowed to reside anywhere else are satisfied from the summation of W_{K} of all possible N-electron events, which have as common feature the two-electron event in the target AOs.

When the AO basis set is non-orthogonal, the probabilistic interpretation is not possible because the quantities $P_2(\mu,\bar{\lambda})$ and $P_2(\mu,\lambda)$ are not expectation values of density operators, but just occupation numbers. In this case, the weights W_{K} can be calculated as $T_{\mathrm{K}}{}^2 + \sum_{\mathrm{K}'\neq\mathrm{K}} T_{\mathrm{K}}T_{\mathrm{K}'}\,\langle\mathrm{K}|\mathrm{K}'\rangle$, and thus the sums of the selected weights in equations 3a and 3b provide an occupation number meaning,[30] which is similar to that presented above in the case of orthogonal orbitals. The only difference between the two meanings is that in the nonorthogonal case, one must adopt a Mulliken partition[30,27] for the distribution of electron pairs in the nonorthogonal orbitals, in a manner quite similar to that frequently adopted for one-electron populations.

The Mulliken partition, even though it is quite convenient for numerical applications, has some important defects appearing primarily when very diffuse orbitals are used. To avoid these difficulties, the one-electron population analysis in orbital space is performed the most often with orthogonal natural orbitals such as NAOs (or NBOs).[1,2] The calculation of electron pair distributions in such a natural basis set by means of Moffitt’s theorem requires two more steps.[25,26] Here we summarize briefly the process that is used. First, the NAOs corresponding to the initially calculated (correlated) MO wave function, $\Psi(\mathrm{MO})$, are obtained by using the first-order density matrix. Then, $\Psi(\mathrm{MO})$ is rewritten in another MO wave function, $\Psi'(\mathrm{MO})$, in which the Slater determinants involve MOs that are a linear combination of NAOs. Because, by definition, NAOs span the complete SCF-AO basis set, this transformation can be performed without introducing approximations, and thus $\Psi'(\mathrm{MO}) = \Psi\,(\mathrm{MO})$. Finally, Moffitt’s theorem is applied to $\Psi'(\mathrm{MO})$; this wave function is decomposed into a $\Psi(\mathrm{TL})$ in which the Slater determinants K involve NAOs. Then, the electron pair distributions are calculated as above. Equation 2 remains valid even in this case, because, due to Moffitt's theorem, it follows that

$$\Psi(\mathrm{TL}) = \Psi'(\mathrm{MO}) \tag{4}$$

3. Coulomb and Exchange Interactions in Two NAOs from the Corresponding Correlations

Information for coulomb and exchange interactions, existing inside of a given molecular system, can be obtained quantitatively by using the corresponding correlations in AO space. In general, correlation of two events is the difference in the probability with which these events occur simultaneously minus the product of probabilities of the independent events. In this context, coulomb correlations (i.e., those describing the interactions of electrons of antiparallel spin), $F(\mu,\bar{\lambda})$, in a given pair of NAOs μ and λ, can be estimated by calculating the corresponding one- and two-electron distributions in the NAOs, as this is presented in previous section:

$$F(\mu,\bar{\lambda}) = P_2(\mu,\bar{\lambda}) - n_\mu^\alpha n_\lambda^\beta \tag{5}$$

where n_μ^α and n_λ^β are the one-electron probabilities, or occupation numbers, in NAOs μ and λ.

Because usual chemical bonds are composed essentially of (α,β) pairs, the physical meaning of $F(\mu,\bar{\lambda})$ is quite important because these quantities can provide direct information about the interaction of antiparallel spin electrons inside a molecular system. For these quantities, the following two interpretations can be given.

(i) Probabilistic Interpretation. Because $n_\mu^\alpha n_\lambda^\beta$ is the probability of finding simultaneously two electrons of antiparallel spin in NAOs μ and λ when these electrons are independent, coulomb correlation different from zero arises when the interaction is nonnegligible and is taken into account. Negative coulomb correlation means that the electrons inside the molecule behave in such a way that their repulsion appears to be greater than the repulsion of two independent charge densities n_μ^α and n_λ^β. This type of interaction of electrons in NAOs μ and $\bar{\lambda}$ will be referred to as "repulsive". In the opposite case, when the coulomb correlation is positive, the corresponding interaction will be referred as "attractive". By the term attractive we mean that between electrons in NAOs μ and λ there are *lesser repulsions* (as a direct consequence of the chemical bonding), than the repulsions which we expected between charge densities n_μ^α and n_λ^β.

(ii) Occupation Number Interpretation. Within the occupation number interpretation, n_μ^α and n_λ^β are one-electron populations, and thus the quantity $n_\mu^\alpha n_\lambda^\beta$ provides the number of electron pairs that can be formed between electrons occupying NAO μ with those of NAO λ; this number of electron pairs corresponds to the "statistical limit", which defines a reference state characterized from the absence of two-electron correlations. Because the real number of electron pairs formed inside the molecule is $P_2(\mu,\bar{\lambda})$, negative (or positive) values for $F(\mu,\bar{\lambda})$, which are issued when interactions of antiparallel spin electrons are nonnegligible, mean that the number of electron pairs obtained from the coupling of electrons in NAOs μ and λ is smaller (or greater) than that corresponding to the statistical limit.

Similarly, the exchange (or Fermi) correlations (i.e., those describing the interactions of electrons of parallel spin), $F(\mu,\lambda)$, in the same pair of NAOs μ and λ are

$$F(\mu,\lambda) = P_2(\mu,\lambda) - n_\mu^\alpha n_\lambda^\alpha \tag{6}$$

These quantities are, in general, nonzero at the Hartree–Fock (HF) level, and their physical meaning is well known and discussed in various contexts, providing new insights into chemical bonding.[6−9,11,12,15,17−20] Also, bond orders directly proportional to exchange correlations are used;[7−9] these quantities, as well as the effective pair populations,[10] are in fact equivalent to Wiberg[13] indices.

It is worth noticing that the statistical numbers (or probabilities) $n_\mu^\alpha n_\lambda^\beta$ and $n_\mu^\alpha n_\lambda^\alpha$ are fractions of the global statistical number, $n_\mu n_\lambda$

$$n_\mu n_\lambda = n_\mu^\alpha n_\lambda^\beta + n_\mu^\beta n_\lambda^\alpha + n_\mu^\alpha n_\lambda^\alpha + n_\mu^\beta n_\lambda^\beta \tag{7}$$

which gives the total number of electron pairs (or total probability) belonging to the pair of NAOs μ and λ, if any type of two-electron correlations (i.e., coulomb or exchange) were absent.

4. Distributions of Coulomb and Exchange Correlations in the Whole Molecule

In a molecular system having M AOs, one can consider 1/2 $M(M + 1)$ (in number) pairs of AOs (including the one-AO pairs). The N electrons of a molecular system can form $N_\pi = N(N - 1)/2$ (in number) electron pairs, distributed in the available pairs of AO positions; both the antiparallel ($N^\alpha\ N^\beta$ in number) and parallel (1/2 N^α $(N^\alpha - 1)$ and 1/2 N^β $(N^\beta - 1)$) spin electron pairs (where $N_\pi = N^\alpha N^\beta + 1/2\ N^\alpha (N^\alpha - 1) + 1/2\ N^\beta (N^\beta - 1)$) are distributed in the same pairs of AO positions. The comparison of the distributions of electron pairs (or probabilities), given by eqs 3a and 3b, with the pairs formed from the one-electron densities in the framework of the statistical limit, can provide useful information about the two-electron interactions and their distributions inside of the given molecular system. This will be done in this section by using the coulomb and exchange correlations in NAOs, presented in section 3, and examining their distributions in the available pairs of NAOs (including the one-NAO terms).

Let us consider the pairs that are formed from a given NAO μ with all NAOs of the system. The coulomb and exchange correlations in these pairs satisfy the following eqs 8a and 8b:

$$\sum_{\bar{\lambda}} F(\mu, \bar{\lambda}) = 0 \tag{8a}$$

$$\sum_{\lambda} F(\mu, \lambda) = -n_\mu^\alpha \tag{8b}$$

The above equations can be derived from analogous well-known expressions[4] (involving the so-called "correlation terms" and conditional probabilities) by replacing the integrations over electron coordinates by summations over all orbitals as NAOs, which span the complete space of the SCF AO basis set. Alternatively, eqs 8a and 8b can be derived in the framework of second quantized formalism by using basic anticommutation properties of creation and annihilation operators. Developing the summations of expectation values of second-order density operators,

$$\sum_{\bar{\lambda}} \langle \Psi(\mathrm{TL}) | a_\mu^+ a_{\bar{\lambda}}^+ \, a_{\bar{\lambda}} a_\mu | \Psi(\mathrm{TL}) \rangle = \langle \Psi(\mathrm{TL}) \, a_\mu^+ a_\mu \sum_{\bar{\lambda}} a_{\bar{\lambda}}^+ \, a_{\bar{\lambda}} | \Psi(\mathrm{TL}) \rangle$$

and

$$\sum_{\lambda\neq\mu}\langle\Psi(\mathrm{TL})|a_{\mu}^{+}a_{\lambda}^{+}\,a_{\lambda}a_{\mu}|\Psi(\mathrm{TL})\rangle = \langle\Psi(\mathrm{TL})|a_{\mu}^{+}a_{\mu}\,(\sum_{\lambda}a_{\lambda}^{+}a_{\lambda}-a_{\mu}^{+}a_{\mu})|\Psi(\mathrm{TL})\rangle$$

and by using relations of the type $\sum_{\mu} a_{\mu}^{+}a_{\mu}|\Psi(\mathrm{TL})\rangle = n_{\mu}^{\alpha}|\Psi(\mathrm{TL})\rangle$ or $(a_{\mu}^{+}a_{\mu})^2 = a_{\mu}^{+}a_{\mu}$ (idempotent operator), one can obtain straightforwardly eqs 8a and 8b. This second quantized way shows the complete consistency of expressions (8a) and (8b) with (3a) and (3b), respectively.

Equation 8b is a direct consequence of the Pauli principle and is the basis for the investigations of Fermi holes, or, in general, the behavior of parallel spin electrons. It is also used to obtain information about α,β pairing, despite the fact that it concerns parallel spins. Even though eq 8a is not sufficiently explored, we believe that this relation should be also of great importance because it concerns directly (α,β) electron pairs, which, in fundamental chemical intuition, are essential for chemical bonding. By considering all pairs of NAOs in the system, we obtain

$$\sum_{\mu}\sum_{\bar{\lambda}} F(\mu,\bar{\lambda}) = 0 \tag{9a}$$

$$\sum_{\mu}\sum_{\lambda} F(\mu,\lambda) = -N^{\alpha} \tag{9b}$$

It is worth noticing that the sums of coulomb correlations, eq 8a or eq 9a, are zero not because each element of these summations is zero, as this is usually assumed in the two-electron investigations (by adopting the HF level), but because chemical bonding implies the coexistence of negative and positive coulomb correlations. Equation 9a, for example, states that in any molecular system one must have necessarily repulsive and attractive α,β interactions, which are distributed in such a manner that the former are balanced by the latter.

As in a usual one-electron population analysis, a center V (e.g., an atomic center) is defined from all orbitals belonging to this center. For a systematic investigation of the distribution of electron pairs in a molecule and their role in chemical bonding, one must consider a partition of the total correlation into one- and two- center terms; each of those is further partitioned into terms referring to coulomb and exchange correlations. Apart from the Lowdin's normalization, which is adopted in the present work, one could use also the McWeeny's normalization; both are totally equivalent, differing only by a factor 2. McWeeny's normalization is more intuitive for one-center terms, whereas Lowdin's is more intuitive for two-center terms. We adopted the latter because in the present work we examine chemical bonding, which is essentially derived from the two-center terms.

The total number of pairs $\Pi(\mathrm{V})$ belonging to center V can be partitioned into pairs of antiparallel spin electrons (involving both one-NAO and two-NAO pairs) and parallel spin electrons (involving only two-NAO pairs, because the one-NAO terms are zero):

$$\Pi(\mathrm{V}) = \Pi(\mathrm{V}^{\alpha\beta}) + \Pi(\mathrm{V}^{\alpha\alpha}) + \Pi(\mathrm{V}^{\beta\beta}) \tag{10}$$

$$\Pi(\mathrm{V}^{\alpha\beta}) = \sum_{\mu}^{\mathrm{V}}\sum_{\overline{\mu'}}^{\mathrm{V}}\mathrm{P}_2(\mu,\overline{\mu'}) \tag{11}$$

$$\Pi(\mathrm{V}^{\alpha\alpha}) = \sum_{\mu}^{\mathrm{V}}\sum_{<\mu'}^{\mathrm{V}}P_2(\mu,\mu') \tag{12}$$

and similar definition for $\Pi(\mathrm{V}^{\beta\beta})$. Here μ,μ' are NAOs belonging to center V. $\Pi(\mathrm{V})$ is a fraction of N_{π}, whereas $\Pi(\mathrm{V}^{\alpha\beta})$ and $\Pi(\mathrm{V}^{\alpha\alpha})$ are fractions of $N^{\alpha}N^{\beta}$ and $N^{\alpha}(N^{\alpha}-1)/2$, respectively. In the framework of the probabilistic interpretation, $\Pi(\mathrm{V})$ provides the probability of finding simultaneously two electrons (regardless to their spin) on a center V, whereas $\Pi(\mathrm{V}^{\alpha\beta})$ and $\Pi(\mathrm{V}^{\alpha\alpha})$ are the probabilities of finding simultaneously on the same center two electrons of antiparallel and parallel spin, respectively.

Similarly, the total number of electron pairs, $\Pi(\mathrm{V,W})$, belonging to two centers V and W is partitioned into pairs of antiparallel and parallel spin:

$$\Pi(\mathrm{V,W}) = \Pi(\mathrm{V}^{\alpha}\,\mathrm{W}^{\beta}) + \Pi(\mathrm{V}^{\beta}\,\mathrm{W}^{\alpha}) + \Pi(\mathrm{V}^{\alpha}\,\mathrm{W}^{\alpha}) + \Pi(\mathrm{V}^{\beta}\,\mathrm{W}^{\beta}) \tag{13}$$

$$\Pi(\mathrm{V}^{\alpha}\,\mathrm{W}^{\beta}) = \sum_{\mu}^{\mathrm{V}}\sum_{\bar{\lambda}}^{\mathrm{W}}P_2(\mu,\bar{\lambda}) \tag{14}$$

$$\Pi(\mathrm{V}^{\alpha}\,\mathrm{W}^{\alpha}) = \sum_{\mu}^{\mathrm{V}}\sum_{\lambda}^{\mathrm{W}}P_2(\mu,\lambda) \tag{15}$$

and similar definitions for $\Pi(\mathrm{V}^{\beta}\,\mathrm{W}^{\alpha})$ and $\Pi(\mathrm{V}^{\beta}\,\mathrm{W}^{\beta})$. An analogous probabilistic interpretation can be given also for the above quantities.

The differences of the above probabilities (or numbers of electron pairs) of finding simultaneously two electrons minus the simple products of one-electron probabilities define the correlations of two electrons on center a V or between two centers V and W. By using the concept of fluctuations of the number of particles contained in a limited region of space,[37] one can obtain the fluctuations of electronic populations on a center V as the differences of the (real) number of electron pairs belonging to this center minus the corresponding statistical limit number. Correlations and fluctuations on a center V coincide numerically when they refer to electrons of antiparallel spin; however, they are different when they refer to parallel spin electrons on one center, because in this case the statistical number of electron pairs of the same type is different from the corresponding total probability of noncorrelated particles.

(i) One-Center Correlations and Fluctuations. The interaction of two electrons of antiparallel spin, both occupying center V, is measured from coulomb correlation, $F(\mathrm{V}^{\alpha\beta})$. This term involves the correlations, $F(\mu,\overline{\mu'})$, concerning the interactions arising from all possible combinations between electrons in NAOs μ and μ' (both belonging to center V), including the one-NAO interactions. The coulomb part of fluctuations of the electronic population on center V, $\Lambda(\mathrm{V}^{\alpha\beta})$, is obtained by means of eq 11 and the corresponding statistical number of electron pairs; $\Lambda(\mathrm{V}^{\alpha\beta})$ coincides with the correlation $F(\mathrm{V}^{\alpha\beta})$:

$$F(\mathrm{V}^{\alpha\beta}) = \Lambda(\mathrm{V}^{\alpha\beta}) = \sum_{\mu}^{\mathrm{V}}\sum_{\overline{\mu'}}^{\mathrm{V}}[P_2(\mu,\overline{\mu'}) - n_{\mu}^{\alpha}n_{\mu'}^{\beta}] \tag{16}$$

Similarly, the exchange correlations issued from interactions of electrons of parallel (α-α) spin on center V, $F(\mathrm{V}^{\alpha\alpha})$, and the corresponding exchange part of fluctuations (obtained by using eq 11), $\Lambda(\mathrm{V}^{\alpha\alpha})$, are given from eqs 17 and 18, respectively:

$$F(\mathrm{V}^{\alpha\alpha}) = 1/2\sum_{\mu}^{\mathrm{V}}\sum_{\mu'}^{\mathrm{V}}[\mathrm{P}_2(\mu,\mu') - n_{\mu}^{\alpha}n_{\mu'}^{\alpha}] \tag{17}$$

$$\Lambda(\mathrm{V}^{\alpha\alpha}) = 1/2\,[\sum_{\mu}^{\mathrm{V}}\sum_{\mu'}^{\mathrm{V}}P_2(\mu,\mu') - \{\sum_{\mu}^{\mathrm{V}}\sum_{\mu'}^{\mathrm{V}}n_{\mu}^{\alpha}n_{\mu'}^{\alpha} - \sum_{\mu}^{\mathrm{V}}n_{\mu}^{\alpha}\}] \tag{18}$$

and similar expressions for β-β spins. The term in braces is the statistical number of α-α electron pairs that are formed from the one-electron population N_V^α ($N_V^\alpha = \sum_\mu^V n_\mu^\alpha$) on center V (taking into account the possibility of self-pairing of particles of the same type). In eqs 17 and 18, the factor 1/2 is due to the fact that the Lowdin's normalization is adopted (note also that $P_2\ (\mu, \mu) = 0$).

(ii) Two-Center Correlations. The interaction of two electrons of antiparallel spin, one occupying center V and the other W, is measured from the coulomb correlation, $F(V^\alpha\, W^\beta)$. This term involves the correlations, $F(\mu,\bar{\lambda})$, for the interactions arising from all possible combinations between electrons occupying NAOs (μ) of center V and those occupying NAOs (λ) of center W.

$$F(V^\alpha\, W^\beta) = \sum_\mu^V \sum_{\bar{\lambda}}^W [P_2(\mu,\bar{\lambda}) - n_\mu^\alpha n_\lambda^\beta] \qquad (19)$$

Similarly, the correlation, $F(V^\alpha\, W^\alpha)$, concerning electrons of the same spin on two centers are:

$$F(V^\alpha\, W^\alpha) = \sum_\mu^V \sum_\lambda^W [P_2(\mu,\lambda) - n_\mu^\alpha n_\lambda^\alpha] \qquad (20)$$

and similar expression for β-β spins.

The above presented grouping of coulomb correlations according to centers is consistent with eq 9a (by using definition (5)), because they satisfy eq 21:

$$\sum_V F(V^{\alpha\beta}) + \sum_{V<W}\sum [F(V^\alpha\, W^\beta) + F(V^\beta\, W^\alpha)] = 0 \quad (21)$$

This is the basic relation providing the distributions of coulomb correlations on one- and two-center component terms; it can be used to investigate the coulomb interactions (repulsive or attractive) and their distributions in the whole molecule.

Similarly, exchange correlations satisfy, as expected, eq 22:

$$\sum_V F(V^{\alpha\alpha}) + \sum_{V<W}\sum F(V^\alpha\, W^\alpha) = -N^\alpha/2 \qquad (22)$$

Because in the present work we are principally interested on two-center terms (responsible for chemical bonding), we do not give emphasis to fluctuations of the electronic populations, which concern essentially one-center terms. However, two-center fluctuations, $\Lambda(V^\alpha\, W^\beta)$ and $\Lambda(V^\alpha\, W^\alpha)$, could be defined also and calculated by considering the numbers of electron pairs (real and statistical) that are formed between two centers V and W. In this context, hold the equalities $F(V^\alpha\, W^\beta) = \Lambda(V^\alpha\, W^\beta)$ and $F(V^\alpha\, W^\alpha) = \Lambda(V^\alpha\, W^\alpha)$, and by using further expressions 16−20, one can derive that the total fluctuations issued from antiparallel spin electrons, as well as those issued from parallel spins, are equal to zero, in complete consistency with the above-defined quantities.

5. Example: Bonding in *cis*-Butadiene

In this section we present a numerical example concerning the chemical bonding in π-system of the *cis*-butadiene molecule to illustrate the physical meaning of the analysis presented in previous sections, and to show the relative role of coulomb and exchange correlations. In section 5.1, we explain the manner in which coulomb correlations are distributed and their role in chemical bonding; in section 5.2 we present the exchange correlations and their comparison with the coulomb correlations; in section 5.3 we explore bond orders defined from the sum of coulomb and exchange correlations; finally, in section 5.4 we investigate the role of CI and valence NAOs in two-electron properties.

The initial MO wave functions, which are treated within Moffitt's theorem, are obtained by means of two separate series of calculations. (a) Ab initio SCF + CI. For these calclulations, we adopted the chain of computer programs involving the PSHONDO algorithm[38] and the adapted multireference CI (CIPSI) process.[39] The basis set is a standard double-ζ with pseudopotentials implemented in these programs, increased by one d symmetry (five AOs per atom) orbital having exponent 0.5. To investigate the behavior of π-electrons, various types of density operators in the general form of eqs 3a and 3b are used. These operators involve all pairs of NAOs belonging to the π-system (e.g., valence−valence, valence−Rydberg, etc.), which are necessary for one- and two-center terms. (b) Parr-Pariser-Pople (PPP)+full CI. For the SCF part of these calculations, we adopted the parametrization of Soos and co-workers.[40] In this case, the density operators are obtained by using the model orthogonal AOs,[41] which are used in PPP as well as Hubbard methods (only one AO of π-symmetry per center). In each of the above series of calculations, we have considered and treated both the uncorrelated (HF) and correlated wave functions. The geometry used is standard: C−C bond lengths for the single and double bonds are 1.35Å and 1.45Å, respectively, and the bond angles are 120°.

The π-system of butadiene involves four π-centers (one for each carbon atom), and each of them is composed of 4 NAOs: one is the high occupancy valence P_z−NAO, whereas the other three are the low occupancy NAOs, which are issued from the double-ζ + polarization part of the SCF−AO basis set. To calculate the one- and two-center probabilities and the corresponding correlations, we have considered all of the possible combinations between electrons belonging to these NAOs (see section 4).

In Table 1 we present analytically the numbers of electron pairs and correlations in valence P_z−NAOs and the sums referring to all orbitals of the π-system belonging to one center V; Table 2 involves the analogous quantities corresponding to two-centers V and W; in Table 3 we regroup the parts of correlations and fluctuations belonging to each center, V. In the CI level of ab initio calculations, the number of π-electrons is slightly greater than 4 (4.0065). This is due to the fact that in this level there is a small electron transfer from the σ system to the π system. For simplicity in the presentation of the results, and coherency with the HF and PPP+full CI calculations, in this work we present only the results concerning the interactions inside the π-system (and not those of $\sigma-\pi$ interactions), even though the calculations of electron pair distributions are performed by considering the whole $\sigma + \pi$ system. In HF ab initio and PPP (both HF and full CI) levels, the total coulomb and exchange correlations, as expected, are 0.0 and −2.0, respectively; in the ab initio-CI level the small delocalization of the σ system to the π system has the consequence that the total coulomb correlation is 0.001 and the exchange correlation is −1.9915. The one-electron populations for centers 1 and 2 are found to be 1.0038 (0.9997) and 0.9995 (1.0003) in ab initio CI (the parenthesis correspond to the HF level), and 1.0243 (1.0306) and 0.9757 (0.9694) in PPP+full CI (HF level) wave functions.

5.1. Coulomb Interactions and Their Role in Chemical Bonding. Let us consider the sum, C_1, of one-center coulomb

TABLE 1: One-Center Two-Electron Probabilities (or numbers of electron pairs) and Correlations for Antiparallel (coulomb) and Parallel (exchange) Spin Electrons[a]

		coulomb				exchange			
		probabilities (or numbers of pairs)		correlations		probabilities (or numbers of pairs)		correlations	
center V	level of calc	valence $P_2(P_z,\bar{P}_z)$	all π orbitals of center V: $\Pi(V^{a\beta})$	valence $F(P_z, \bar{P}_z)$	all π orbitals of center V: $F(V^{a\beta})$	valence $P_2(P_z, P_z)$	all π orbitals of center V: $\Pi(V^{aa})$	valence $1/2F(P_z, P_z)$	all π orbitals of center V: $F(V^{aa})$
1 (or **4**)	I − CI	0.1848	0.1901	−0.0622	−0.0618	0.0	0.0006	−0.1235	−0.1253
	I − HF	0.2473	0.2498	0.0	0.0	0.0	0.0001	−0.1237	−0.1248
	II − CI	0.1771		−0.0852		0.0		−0.1311	
	II − HF	0.2655		0.0		0.0		−0.1328	
2 (or **3**)	I − CI	0.1913	0.1963	−0.0534	−0.0535	0.0	0.0010	−0.1224	−0.1239
	I − HF	0.2472	0.2502	0.0	0.0	0.0	0.0005	−0.1236	−0.1246
	II − CI	0.1678		−0.0702		0.0		−0.1190	
	II − HF	0.2349		0.0		0.0		−0.1175	

[a] The level of calculations concerns the initially considered wave function: I is ab initio (in HF and CI levels); II is PPP (in HF and full CI).

TABLE 2: Two-Center Two-Electron Probabilities (or numbers of electron pairs) and Correlations for Antiparallel (coulomb) and Parallel (exchange) Spin Electrons[a]

		coulomb				exchange			
		probabilities (or numbers of pairs)		correlations		probabilities (or numbers of pairs)		correlations	
centers V − W	calc level	valence $P_2[(P_z)_V,(\bar{P}_z)_W]$	all π orbitals of centers V,W: $\Pi(V^aW^\beta)$	valence $F[(P_z)_V,(\bar{P}_z)_W]$	all π orbitals of centers V,W: $F(V^aW^\beta)$	valence $P_2[(P_z)_V,(P_z)_W]$	all π orbitals of centers V,W: $\Pi(V^aW^a)$	valence $F[(P_z)_V,(P_z)_W]$	all π orbitals of centers V,W: $F(V^aW^a)$
1−2 (or **3−4**)	I − CI	0.3024	0.3072	0.0565	0.0563	0.0241	0.0259	−0.2218	−0.2250
	I − HF	0.2473	0.2500	0.0	0.0	0.0214	0.0219	−0.2259	−0.2281
	II − CI	0.3251		0.0752		0.0196		−0.2303	
	II − HF	0.2498		0.0		0.0187		−0.2310	
2−3	I − CI	0.2470	0.2519	0.0023	0.0021	0.2139	0.2180	−0.0308	−0.0317
	I − HF	0.2472	0.2502	0.0	0.0	0.2254	0.2279	−0.0218	−0.0223
	II − CI	0.2406		0.0026		0.2032		−0.0348	
	II − HF	0.2349		0.0		0.2162		−0.0187	
1−3 (or **2−4**)	I − CI	0.2410	0.2461	−0.0049	−0.0047	0.2541	0.2582	0.0082	0.0074
	I − HF	0.2473	0.2500	0.0	0.0	0.2473	0.2494	0.0000	−0.0006
	II − CI	0.2422		−0.0077		0.2651		0.0153	
	II − HF	0.2498		0.0		0.2497		0.0000	
1−4	I − CI	0.2576	0.2623	0.0105	0.0104	0.2173	0.2213	−0.0297	−0.0306
	I − HF	0.2473	0.2498	0.0	0.0	0.2264	0.2283	−0.0210	−0.0215
	II − CI	0.2800		0.0177		0.2275		−0.0348	
	II − HF	0.2655		0.0		0.2468		−0.0187	

[a] The level of calculations concerns the initially considered wave function: I is ab initio (in HF and CI); II is PPP (in HF and full CI).

TABLE 3: One-Center Coulomb, $F(V^{\alpha\beta})$, and Exchange, $F(V^{\alpha\alpha}) + F(V^{\beta\beta})$, Correlations and the Corresponding Fluctuations of Coulomb, $\Lambda(V^{\alpha\beta})$ (where $F(V^{\alpha\beta}) = \Lambda(V^{\alpha\beta})$), and Exchange, $\Lambda(V^{\alpha\alpha}) + \Lambda(V^{\beta\beta})$, Parts[a]

		correlations			fluctuations		
		parts			parts		
center **V**	calc level	coulomb	exchange	total	coulomb	exchange	total
1 (or **4**)	I − CI	−0.0618	−0.2507	−0.3124	−0.0618	0.2512	0.1895
	I − HF	0.0	−0.2496	−0.2496	0.0	0.2502	0.2502
	II − CI	−0.0852	−0.2623	−0.3475	−0.0852	0.2499	0.1646
	II − HF	0.0	−0.2655	−0.2655	0.0	0.2498	0.2498
2 (or **3**)	I − CI	−0.0535	−0.2477	−0.3012	−0.0535	0.2520	0.1985
	I − HF	0.0	−0.2491	−0.2491	0.0	0.2510	0.2510
	II − CI	−0.0702	−0.2380	−0.3082	−0.0702	0.2499	0.1797
	II − HF	0.0	−0.2349	−0.2349	0.0	0.2498	0.2498
SUM FOR ALL CENTERS	I − CI	−0.2305	−0.9968	−1.2272	−0.2305	1.0065	0.7760
	I − HF	0.0	−0.9975	−0.9975	0.0	1.0025	1.0025
	II − CI	−0.3107	−1.0006	−1.3113	−0.3107	0.9994	0.6887
	II − HF	0.0	−1.0009	−1.0009	0.0	0.9991	0.9991

[a] The sum for all centers, in the case of correlations, provides quantity C_1 of equation 23. The level of calculations concerns the initially considered wave function: I is ab initio (in HF and CI levels); II is PPP (in HF and full CI).

correlations (see Tables 1 and 3)

$$C_1 = \sum_{V} F(V^{\alpha\beta}) \qquad (23)$$

and the sum, C_2, of two-center coulomb correlations for all pairs V and W (see Table 2)

$$C_2 = \sum\sum_{V<W} [F(V^{\alpha}W^{\beta}) + F(V^{\beta}W^{\alpha})] \qquad (24)$$

According to eq 21, the sum of C_1 and C_2 is equal to zero for

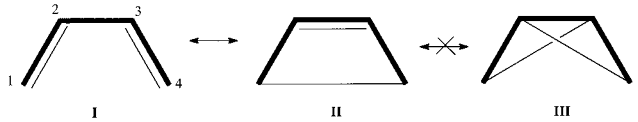

Figure 1. Numbering for butadiene molecule and various bonding schemes involved in mesomer (or resonance) structures I, II, and III.

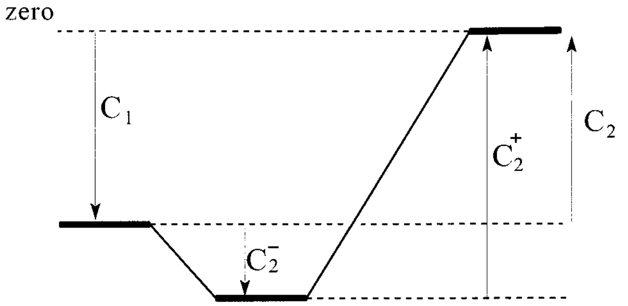

Figure 2. Schematic representation of the interaction of antiparallel spin electrons in a molecular system. The two-center, C_2, globally attractive interactions (responsible for chemical bonding) are balanced by the one-center, C_1, repulsive ones so that their sum is equal to zero. C_2 is issued from the sum of attractive, C_2^+, and repulsive, C_2^-, two-center interactions.

any molecular system:

$$C_1 + C_2 = 0 \tag{25}$$

The quantity C_1 (given in Table 3) is negative, because each term, $F(V^{\alpha\beta})$, of the sum (eq 23) is negative. This means that the interactions of two electrons of antiparallel spin belonging to one center are repulsive, and can be easily rationalized from the fact that the two electrons are restricted to being located in the same (limited) space of one center. One must note that this holds not only for the expected case of a valence orbital but also for the summation of all possible interactions in all orbitals of one center, including the diffuse orbitals (see Table 1). On the contrary, examining the component terms of quantity C_2 (see Table 2) we are led to distinguish two kinds of interactions, depending on the pairs of AO-positions, that are considered the attractive and the repulsive interactions. Let C_2^+ be the sum of the former and C_2^- the sum of the latter:

$$C_2 = C_2^+ + C_2^- \tag{26}$$

By using eqs 25 and 26, and taking into account that C_1 is a negative quantity, one can conclude (i) that the two-center coulomb interactions are globally attractive, that is the repulsive interactions are less important than the attractive ones:

$$C_2^+ > |C_2^-|$$

and (ii) that the extent by which the attractive interactions overcome the repulsive ones is determined by the magnitude of one-center interactions: larger is the absolute value of C_1, more important are the attractive two-center interactions with respect to the repulsive interactions. These conclusions are quite general and must hold for a large range of usual molecular systems, because they are based only on the assumption that the one-center interactions are globally repulsive (which must hold in most of the usual systems). In Figure 2 we give a schematic representation of one-center (repulsive) and two-center (globally attractive) interactions, and the spitting of the latter in two components (attractive and repulsive). In the case of butadiene, C_2^+ and C_2^- are found to have the following values in ab initio-CI/PPP+full CI levels: $C_2^+ = 0.2502/0.3416$ and $C_2^- = -0.0188$ / -0.0308.

The analysis of the distribution of C_2^+ and C_2^- in various NAOs reveals in which pairs of centers the interactions are attractive or repulsive. In the case of butadiene, one can find (see Table 2) four attractive and two repulsive interactions: the former concern centers (1,2), (2,3), (3,4), and (1,4), whereas the latter concerns centers (1,3) and (2,4). These results are completely consistent with usual pictures for chemical bonding, involving α,*β* pairs which are disposed into alternating α,*β* schemes.

According to VB theory, the bonding of butadiene is described from the resonance of the first two structures (I ↔ II) of Figure 1. Mesomer (or resonance) structure III is forbidden, because the corresponding VB spin eigenfunction describing this structure is linearly dependent on those of structures I and II. This VB description is in agreement with the finding of repulsive coulomb interactions for centers (1,3) or (2,4), which are included in structure III, and attractive interactions for (1,4), which are included in structure II. On the contrary, if we were limited to one-electron population analysis, the positive bond order in (1,3) and the negative one in (1,4) should lead to the conclusion that there is a bonding character between 1 and 3 and an antibonding character between 1 and 4 (for more details see section 5.3).

For a given pair of centers (V,W) the quantity $R_C(V,W) = [F(V^\alpha\ W^\beta) + F(V^\beta\ W^\alpha)]100/C_2^+$ provides the percentage of the attractive coulomb interactions that belongs to the pair (V,W). In the framework of Mesomeric or Resonance theory (see also refs 35, 36), the electron pairs of butadiene can be arranged into pairs of centers according to bonding schemes of either mesomer structures I or II of Figure 1. Because structure I is composed of bonding schemes between pairs (1,2) and (3,4), one can conclude that the quantity $W_C\ (I) = R_C(1,2) + R_C(3,4)$ provides the total amount of the attractive coulomb interactions belonging to this structure. Similarly, the quantity $W_C(II) = R_C(2,3) + R_C(1,4)$ provides the analogous amount corresponding to mesomer structure II. These quantities are found to have the following values: $W_C(I)/W_C(II) = 89.98\%/10.02\%$ from the ab initio CI wave function, and $W_C(I)/W_C(II) = 88.12\%/11.88\%$ from the PPP + full CI wave function.

Coulomb Holes In NAOs. In general, in an electronic assembly (not necessarily forming bonds), a coulomb hole measures the extent to which an electron in a target position V (frequently called reference electron or reference position) excludes (within a negative value of the hole) an electron of opposite spin in various positions X. The ratio $\Pi(X^\beta V^\alpha)/N_V^\alpha$ is a conditional probability describing the probability of finding an electron of *β* spin on center X, under the condition that an electron of α spin is located on center V. Following the definition of coulomb hole in coordinate space,[4] one can introduce the quantity $h_C(X^\beta/V^\alpha)$,

$$h_C(X^\beta/V^\alpha) = \Pi(X^\beta V^\alpha)/N_V^\alpha - N_X^\beta$$

which defines the coulomb hole on various centers X with respect the reference electron located on a center V (where both X and V are assumed to be composed of NAOs). In this context, a coulomb hole indicates how the conditional one-electron density on X deviates from the usual one-electron density (i.e., the unconditional probability) on the same center. By using expressions from section 4, one can show that the above-defined holes on centers have the following property, in good agreement with an analogous property in coordinate space:[4]

$$\sum_{X} h_C(X^{\beta}/V^{\alpha}) = 0$$

Coulomb holes, $h_C(X^{\beta}/1^{\alpha})$, on the four π centers of butadiene ($X = 1...4$) with respect to an electron on the first center ($V = 1$) are found to have the following values in ab initio/PPP (both in CI) levels: $-0.1231/-0.1664$, $0.1123/0.1469$, $-0.0095/-0.0150$, and $0.0208/0.0345$. For $X = V$, the negative value of $h_C(1^{\beta}/1^{\alpha})$ is a consequence of the usual one-center self-repulsion of two electrons (see coulomb correlations); for $X \neq V$, coulomb holes are also of a great importance for chemical bonding: the negative value for $X = 3$ and the positive values for $X = 2$ or $X = 4$ mean that the presence of an α spin on center $V = 1$ excludes the presence of opposite spin in $X = 3$, and at the same time favors the presence of opposite spins on centers $X = 2$ or $X = 4$. The absolute values of these holes give a measure of the extent of (unfavorable) exclusion or (favorable) simultaneous presence of the opposite spin electron. Both quantitative and qualitative pictures are in complete agreement with fundamental chemical intuition: for example, comparing the magnitudes of the above holes, one can conclude that the presence of an α-spin electron in $V = 1$ favors more the presence of a β-spin in $X = 2$ than in $X = 4$.

Grouping Centers into Bonds. The equations in section 4 show how two-electron populations and correlations in NAOs can be grouped according to centers. Let us consider now that centers V and W are further grouped into bonds, Ω. By using equations that are isomorphic to those of section 4, one can obtain the intrabond correlation of antiparallel spin electrons, $F(\Omega^{\alpha\beta})$, which are equal to the coulomb part of electronic fluctuation, $\Lambda(\Omega^{\alpha\beta})$

$$F(\Omega^{\alpha\beta}) = \Lambda(\Omega^{\alpha\beta}) = F(V^{\alpha\beta}) + F(W^{\alpha\beta}) + F(V^{\alpha}W^{\beta}) + F(W^{\alpha}V^{\beta})$$

where bond Ω is assumed to be composed of two centers V and W.

In mesomer structure I of butadiene (Figure 1) the first bond is composed of centers 1 and 2; the intrabond correlation is found from both ab initio and PPP (both in CI) levels to be quite small: -0.0026 and -0.0049, respectively. Because this quantity is negative, the interbond correlation

$$\sum\sum_{\Omega<\Omega'} [F(\Omega^{\alpha}\Omega'^{\beta}) + F(\Omega'^{\alpha}\Omega^{\beta})]$$

is necessarily positive, so that the global correlation of the system is equal to zero. (In butadiene, this summation involves only one interbond term.)

In mesomer structure II, one bond, Ω_1, is composed of centers 1 and 4, and the other, Ω_2, from 2 and 3. The intrabond correlations in ab initio/PPP (both in CI) calculations are found to be $-0.1027/-0.1351$ for bond Ω_1, and $-0.1028/-0.1351$ for Ω_2. Consequently, the (totally negative) coulomb correlations in bonds of mesomer structure II are much larger than those of structure I. These results will be used below in conjunction with the exchange part of fluctuations in order to obtain information about the degree of (de)localization of chemical bonds in mesomer structures I and II.

5.2. Exchange Interactions and their Comparison with Coulomb Interactions. Due to the Pauli principle, the correlation of two electrons of parallel spin in one orbital, as the valence P_Z-NAO, is strongly negative. The same holds also for the entire one-center exchange interactions involved in $F(V^{\alpha\alpha})$, even though this term includes correlations on two different orbitals (on the same center). On the contrary, the two-center correlations can be both positive or negative. The signs of exchange correlations are *opposite* to those of coulomb correlations: they are negative for pairs of centers (1,2), (2,3), (3,4), and (1,4) and positive for (1,3) and (2,4). Consequently, in regions (i.e., in pairs of centers as (1,2)...(1,4)) where antiparallel spin electrons are attractive, the parallel spin electrons are repulsive; the exact opposite holds for other regions (such as (1,3) and (2,4)). In this context, exchange interactions are *complementary* to coulomb interactions and confirm the conclusions that are obtained in section 5.1. The general trends are that attractive coulomb as well as repulsive exchange interactions specify regions considered to have bonding character, whereas opposite interactions hold for regions of antibonding character. One must note also that coulomb or exchange correlations considered separately lead to the same pictures for chemical bonding.

An important difference between the two correlations is that the absolute values of exchange are larger (about 2−4 times) than the coulomb values. Therefore, it is interesting to compare quantitatively the overall picture for chemical bonding, which is obtained in the framework of investigation of exchange correlations, with the picture obtained previously from the coulomb correlations. For this purpose, for a given pair of centers (V,W), one can consider the ratio $R_E(V,W) = [F(V^{\alpha}W^{\alpha}) + F(V^{\beta}W^{\beta})]100/E_2^{-}$ (where E_2^{-} is the sum the negative two-center exchange correlations), which provides the percentage of the repulsive exchange interactions belonging to the pair (V,W). Therefore, the quantities $W_E(I) = R_E(1,2) + R_E(3,4)$ and $W_E(II) = R_E(2,3) + R_E(1,4)$, provide the total amount of repulsive exchange interactions belonging in mesomer structures I and II, respectively. These quantities can be calculated in both HF and CI levels, and are found to be $W_E(I)/W_E(II) = 87.84\%/12.16\%$ ($91.24\%/8.76\%$) from ab initio-CI wave function, and $W_E(I)/W_E(II) = 86.86\%/13.14\%$ ($92.52\%/7.48\%$) from the PPP + full CI wave function (the value in parentheses corresponds to the HF level).

One must note that the results obtained from the HF and CI levels are quite comparable; this is due essentially to the fact that parallel spin electrons (as a result of the Pauli principle) are partially correlated in the single Slater determinant of the HF level. Quantities $W_E(I)$ and $W_E(II)$ are of the same magnitude with $W_C(I)$ and $W_C(II)$ (calculated from coulomb correlations in section 5.1), respectively. Therefore, one can conclude that the overall picture for chemical bonding obtained from the investigation of coulomb or exchange interactions is quite similar. This holds despite the fact that both of the signs and magnitudes of coulomb and exchange correlations are quite different.

The exchange part of fluctuations on one-center is given from eq 18 (see also Table 3), and according to usual interpretations[6−9,11,12,17,19,20] it provides a measure of the degree of delocalization. The coulomb part of one-center fluctuations is the same as the one-center correlations. From the sum of the two parts, which is presented in the last column of Table 3, one can conclude that the degree of delocalization of electrons from each center is important. From this table it follows that the coulomb part contributes to lower the fluctuations, and thus the delocalization (despite the fact the total delocalization remains important). The nonnegligible differences between the fluctuations in CI and HF levels are due essentially to the coulomb part.

Fermi Holes in NAOs. As for coulomb holes, Fermi holes are defined with respect to a reference electron (or position). Following the definition of a Fermi hole in coordinate space,[4] and by using the conditional probability, $\Pi(X^{\alpha}V^{\alpha})/N_V^{\alpha}$, in orbital space, one can define the Fermi hole, $h_F(X^{\alpha}/V^{\alpha})$, on various centers X with respect to the reference electron located on center V

$$h_F(X^{\alpha}/V^{\alpha}) = \Pi(X^{\alpha}V^{\alpha})/N_V^{\alpha} - N_X^{\alpha}$$

where centers are assumed to be composed of NAOs) and where $\sum_X h_F(X^{\alpha}/V^{\alpha}) = -1$, in agreement with the equivalent relation in coordinate space.[4]

Fermi hole measures the degree to which an electron in V excludes (due to the Pauli principle) electrons of the same spin in various positions of space (the sum for all positions is equal to -1). If there was not chemical bonding, then Fermi hole should be negative for all positions. Fermi holes, $h_F(X^{\alpha}/1^{\alpha})$, on the four π centers of butadiene ($X = 1...4$) with respect to an electron on the first center ($V = 1$) are found to have the following values in ab initio/PPP (both in CI) levels: $-0.4995/-0.5122$, $-0.4482/-0.4497$, 0.0148/0.0299, and $-0.0610/-0.0681$. These results mean that the presence of an α spin electron in $V = 1$ excludes the presence of the same spin in $X = 2$ and $X = 4$ (negative values), but not in $X = 3$ (positive values); for $X = 3$, the favorable presence of parallel spin electrons (due to chemical bonding) overcomes the Pauli exclusion.

The above results, concerning Fermi holes, are complementary to analogous results for antiparallel spins from coulomb holes presented previously. Both are in agreement with usual mesomer structures (as this holds also for coulomb and exchange correlations) and chemical intuition, in which chemical bonding is formed from alternating α,β spins.

Grouping Centers into Bonds. By grouping centers into bonds, Ω, as this is presented previously for coulomb interactions, one can obtain the part of correlation (i.e., intrabond exchange correlation),

$$F(\Omega^{\alpha\alpha}) = F(V^{\alpha\alpha}) + F(W^{\alpha\alpha}) + F(V^{\alpha}W^{\alpha})$$

and fluctuation,

$$\Lambda(\Omega^{\alpha\alpha}) = F(V^{\alpha\alpha}) + F(W^{\alpha\alpha}) + F(V^{\alpha}W^{\alpha}) + 1/2\,(N_V^{\alpha} + N_W^{\alpha})$$

corresponding to parallel spin electrons of a bond Ω.

Our calculations for a bond of mesomer structure I of butadiene, in ab initio/PPP (both in CI) levels give $-0.4741/-0.4804$ for correlations, and 0.0267/0.0196 for fluctuations. For bond Ω_1 of mesomer structure II we obtained $-0.2812/-0.2971$ for correlations and 0.2206/0.2150 for fluctuations; for bond Ω_2 of the same structure, the correlations are found to be $-0.2794/-0.2728$ and the fluctuations 0.2203/0.2150.

The fluctuation, $\Lambda(\Omega)$, of the electronic population in a bond, Ω, provides a measure of the (de)localization of electrons in this bond: closer to zero is $\Lambda(\Omega)$, more localized is this bond. This quantity is obtained from the sum of the part of coulomb fluctuations (which are equal to coulomb correlations presented in section 5.1) and this of exchange ones:

$$\Lambda(\Omega) = \Lambda(\Omega^{\alpha\beta}) + \Lambda(\Omega^{\alpha\alpha}) + \Lambda(\Omega^{\beta\beta})$$

In butadiene, for the bond of mesomer structure I the electron population fluctuation is 0.0508/0.0342, whereas for bonds of structure II it is found to be 0.3387/0.2950 for Ω_1, and 0.3379/0.2950 for Ω_2. These results are in agreement with fundamental chemical intuition, according to which of the two bonds in mesomer structure II are more delocalized than those of structure I. It is worth noticing also that the coulomb correlations (being negative) contribute to lower the fluctuations of the electronic population in these chemical bonds, and thus increase their localization; this holds for bonds of both mesomer structure I and II.

TABLE 4: Bond Orders, *B*(V,W), from the Spin-Free Correlation[a]

calc level	centers V−W **1−2** (or **3−4**)	**2−3**	**1−3** (or **2−4**)	**1−4**
I − CI	0.3372	0.0592	−0.0054	0.0403
I − HF	0.4562	0.0446	0.0013	0.0431
II − CI	0.3101	0.0644	−0.0152	0.0343
II − HF	0.4625	0.0374	0.0000	0.0374

[a] The level of calculations concerns the initially considered wave function: I is ab initio (in HF and CI levels); II is PPP (in HF and full CI).

5.3. Bond Orders from the Sum of Exchange and Coulomb Correlations. Exchange correlations are used to define bond order indices[7−9] at the HF level. In view of the analysis presented in sections 5.1 and 5.2, the two-center coulomb and exchange correlations, separately considered, could be used as two different types of bond order indices (depending on the spin of pairs). Alternatively, the correlation of electrons *regardless of their spin* can be considered as another bond order index. This type of correlation can be obtained as follows: The number of electron pairs, regardless of their spin, that are formed between two centers, is obtained from the sum of the corresponding antiparallel and parallel spin pairs; this holds for both the real number and the number of the statistical limit. In these numbers of pairs, the electrons are considered as particles in general without reference to their spin. For a given pair of centers, V and W, the correlation of electrons, regardless of their spin, is obtained from the comparison (i.e., the difference) of the above real and the statistical limit numbers of electron pairs; this correlation can be used to define a bond order index, *B*(V,W), and is obtained from the sum of coulomb and exchange correlations:

$$B(V,W) = -\left(F(V^{\alpha}W^{\alpha}) + F(V^{\beta}W^{\beta}) + F(V^{\alpha}W^{\beta}) + F(V^{\beta}W^{\alpha})\right)$$

The negative sign is adopted to be consistent with the sign convention of other indices[7−9] based in exchange correlations (in the framework of generalized Wiberg indices), as well as the effective pair populations.[10] Indices *B*(V,W) are positive (in the range from 0 to 0.5) when there is a bonding character between centers V and W, and negative when there is an antibonding character. These quantities can be reduced to the well-known indices[7−9] if multiplied by 2 and the coulomb correlations are neglected; they differ from effective pair populations[10] by only the coulomb correlations. Within *B*(V,W) we examine the behavior of electron pairs without being able to refer to their spins.

Table 4 presents the values of *B*(V,W) for the π-centers of *cis*-butadiene; from this table, apart from the strong bonding character for (1,2) (or (3,4)) centers, one can conclude that between centers (1,3) there is an antibonding character; this holds in the CI level (in both ab initio and PPP), where coulomb correlations are taken into account (but not in the HF level where these quantities are neglected). Also, between centers (1,4) there is a clear bonding character; this holds in all approximation levels. These conclusions are in good agreement with the results presented in previous sections, where coulomb and exchange correlations are considered separately as two distinct (spin-dependent) quantities.

In the framework of one-electron population analysis, the off-diagonal elements of the first-order density matrix (from all types of wave functions as the simple Hückel or ab initio-CI) are negative for centers (1,4) (from the wave functions of the present work are found from -0.2736 to -0.2360 depending on the approximation level), whereas they are positive for (1,2) (from 0.9613 to 0.8951) and (1,3) centers (from 0.010 to 0.0017). This suggests that the (1,4) bond has a character that is necessarily the opposite of the bond (1,2), i.e., an antibonding character; also, between centers 1 and 3 one should expect that there is a (weak) bond. This point of view, arising from one-electron analysis, does not agree with either of the usual pictures provided by VB theory (see Figure 1) or with the presented analysis. Furthermore, one must notice that in the framework of usual thinking and reasoning of a chemist, one can evoke a weak bond between (1,4) (which increases in the exited states), even though a bond between (1,3) is usually excluded. This shows the limits of some aspects of an analysis of chemical bonding when this is restricted exclusively to one-electron densities, when in fact a chemical bond is essentially a matter of electron pairs. NRT, which arranges electron pairs in NBOs in order to construct NBO-based resonance structures, also does not find structure III. This theory instead of structure II, finds a small weight for a resonance structure exhibiting a covalent bond between (2,3) and an ionic (+,−) bond between (1,4).

5.4. The Role of CI and Valence NAOs in Two-Electron Properties. The effects of CI are quite important for the probabilities (or numbers of electron pairs) concerning antiparallel spins in two cases: (i) for one-center (or one-NAO) terms, and (ii) for *vicinal* two centers (or two NAOs) defining formal bonds (as 1,2 or 3,4). In the first case, the CI diminishes the two-electron probabilities, whereas in the latter CI increases the corresponding probabilities. On the contrary, the probabilities for parallel spin electrons are not so sensitive in CI; in both of the above cited cases, the CI preserves the magnitudes of probabilities that are found at the HF level. Regarding the sign of the variations imposed by CI, it is the *opposite* for antiparallel and parallel spin electrons. Apart from the above two cases, the effects of CI for electron pairs of antiparallel spin are smaller (or negligible), for example, for vicinal centers not defining formal bonds or for distant centers (or NAOs). The same holds for parallel spins, and the trend of opposite sign in the variations imposed by CI is also confirmed. These effects of CI are found in NAOs or groups of NAOs or the model orthogonal orbitals of PPP methods, and are in complete agreement with other results of population analysis in nonorthogonal orbitals[27] that are found in other systems.

The role of CI in correlations is crucial for coulomb but not for exchange correlations, especially for vicinal centers (or NAOs) defining formal bonds, as shown in Table 2.

To examine the role of valence NAOs in two-electron effects, one can examine the differences between the results obtained by considering all orbitals belonging to each center with those obtained in valence NAOs (see Tables 1 and 2). For example, in one-center terms, the mean difference in correlations is only ~0.6% for antiparallel and ~1.3% for parallel spin electrons; the corresponding differences in two-center terms are ~0.6% and ~ 4%, respectively. A more profound analysis of the results presented in Tables 1 and 2 leads to the conclusion that all effects in electron pair probabilities and correlations in both one- or two-center terms are remarkably well described by considering only the valence NAOs. This is essentially due to the very definition of NAOs, which are “natural” in the Lowdin sense. However, if we were limited to, for example, the inner part of a well chosen double-ζ SCF-AO basis set, then the results would not be as good, because only valence NAOs involving the optimum weights of the inner and outer SCF-AO functions can represent satisfactorily the two-electron effects occurring between valence orbitals.

The results obtained from PPP wave functions overestimate the one-center correlations. This is due to the fact that in this level of calculations only one orbital is available for each center (in contrast to the valence + Rydberg NAOs, which are involved in each center in the ab initio level of calculations). Otherwise, the results from PPP levels lead to the conclusion that both coulomb and exchange correlations follow the principal trends presented previously, and mainly the sign of correlations on two centers, which control the chemical bonding. Another general conclusion, that can be drawn (from Tables 1 and 2) is that the σ-electrons are not important for two-electron effects occurring in the π-system, as for example the two-center coulomb and exchange interactions. The magnitudes of correlations obtained from PPP wave functions converge better to the ab initio ones for exchange interactions rather than for coulomb; this holds despite the fact that in ab initio CI calculations there is an electron transfer from the σ to the π system.

6. Conclusion

In this work the chemical bonding has been examined by referring to the traditional thinking of a chemist that bonds are mainly a matter of electron pairs. The calculation of electron pair distributions, considered as two-electron events within Moffitt’s theorem, leads to investigations of coulomb and exchange correlations, which provide useful information about the interactions of two electrons of antiparallel and parallel spin.

The correlations of electrons in NAOs (coulomb and exchange) are grouped according to centers, and the sums of intra- and intercenter correlations obey eqs 21 and 22. An emphasis is given for the two-center coulomb correlations, because, according to fundamental chemical intuition, chemical bonds are composed essentially of antiparallel spin electron pairs. The investigation of eq 21 leads to the conclusion that in the two-center terms, the attractive interactions are more important than the repulsive ones. These globally attractive two-center interactions are balanced by the repulsive one-center ones. The extent by which the attractive interactions are larger than the repulsive interactions is determined by the magnitude of one-center interactions. All of these conclusions are quite general because they are based only on the assumption that one-center interactions are repulsive, which must hold for most molecules.

The general trend is that the two-center coulomb and exchange correlations are complementary: the corresponding interactions show a remarkably opposite behavior, even though both lead to same conclusions concerning chemical bonding. In regions, i.e., in pairs of centers as (1,2), (2,3), (3,4), and (1,4), where the interactions of antiparallel spin electrons are attractive, those of parallel spin electrons are repulsive; exactly the opposite holds for pairs of centers (1,3) and (2,4). These conclusions are completely consistent with usual pictures for chemical bonding, involving α,β pairs that are disposed into alternating α,β schemes, as well as the bonding schemes of mesomer structures provided by VB theory (see Figure 1).

The effects of CI are very crucial in some cases concerning the probabilities of finding electron pairs of antiparallel spin and in all cases of coulomb correlations; however, the probabilities for parallel spins and exchange correlations, in general, are not so sensitive.

The defined coulomb or Fermi holes on centers (i.e., in groups of NAOs) have suitable properties (that is their sums is equal to 0 or -1, respectively) and provide useful information for the corresponding conditional probabilities. The further grouping of centers (and the corresponding correlations) into bonds allows the calculation of the fluctuations of the electronic populations in one bond, and thus to the quantitative estimation of delocalization. In the case of butadiene, it is found that the inclusion of coulomb correlation increases the localization of one bond.

From topological methods[17] dealing with exchange correlations, it is found that the probability for parallel spin electrons is high at the boundaries between regions in which electrons form pairs of antiparallel spin. This agrees with the finding in this work (see Table 2) that the probabilities for $\alpha-\alpha$ pairs in regions defined by centers (2,3) and (1,4) are higher (both are about 10 times larger) than the same quantities concerning regions (1,2) and (3,4), i.e., bonded regions involving mainly antiparallel spins. As expected, the opposite holds for the absolute values of the (negative) exchange correlations.

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