Entropic Measures of Bond Multiplicity from the Information Theory

Roman F. Nalewajski

Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland

Received: May 31, 2000; In Final Form: July 18, 2000

The entropic character of the bond multiplicity concept of chemistry is explored within the information theory. The probability schemes of finding a single and two electrons on specified atoms are used to formally interpret a molecule as the "*communication*" system, with the molecular or the separated atom *input* probabilities and the network of conditional two-electron probabilities in atomic resolution, which determine the molecular one-electron atomic probabilities, defining the system *output* probabilities. Several measures of uncertainties in such a molecular communication system are then introduced, including the *average entropies* of the two-electron joint and conditional probabilities, as well as the *average mutual information* between the input and output probability schemes. The average entropy of the conditional probabilities between molecular input and output probability schemes is then identified as the information theoretic measure of the *global covalent bond multiplicity* in a molecule. Similarly, the *global ionic bond order* is found to be well reflected by the mutual information between molecular output and the atomic equiprobability input schemes. These identifications are tested by comparing the entropy predictions for the two- and three-orbital models and the π bonds in butadiene and benzene (Hückel approximation) with the corresponding results from the earlier Wiberg-type and two-electron difference approaches. Finally, the *bond entropy* concept is introduced to provide a direct measure of the covalent bond component for each pair of atoms. It is demonstrated that this entropic bond order is in good agreement with both the chemical intuition and earlier predictions for all illustrative systems examined, thus providing a novel atrractive tool for chemical interpretation of calculated molecular electronic structures.

Introduction

The concept of a *bonded* (promoted) *atom* in a molecule, only slightly modified in its valence shell relative to the reference *isolated atom*/*ion* state due to the formation of chemical bonds, and that of a *bond multiplicity*, which gives rise to the *structural formula* of the molecular system, are crucial for providing a truly chemical interpretation of calculated electronic structures. Obviously, because they were originally introduced on intuitive grounds,[1] these quantities are not defined precisely. Nevertheless, a great deal of effort has been made in quantum chemistry to define these elusive quantities operationally,[2−22] in such a way that they reproduce the chemical intuition in standard molecules and processes, e.g., during a concerted bond-breaking−bond-forming atom exchange reaction. The bond multiplicity indices are usually defined[5,10−14,16−22] as functions of elements of the familiar charge-and-bond-order (CB0) matrix[5] of the standard Hartree−Fock[23] and Kohn−Sham[24] theories. These indices have been shown to follow many aspects of the "established" chemical intuition quite well.

Clearly, all such quantum-mechanical quantities, measuring the effective numbers of bonding electrons or electronic pairs in a molecule relative to the relevant states of the separated atoms or molecular fragments, are not of *energetical* character. Indeed, as we have observed in our earlier work formulating the two-electron difference approach,[17] the bond multiplicity and valence concepts are "*entropic*" in nature, i.e., they eventually follow from a separate, *entropic variational* principle.[26] Only together with the energetic variational principle of Schrödinger and Hohengerg−Kohn[24] do they provide the complete treatment of the electronic structure phenomena. This observation is in full analogy to the supplementary character of the entropic and energetical descriptions in thermodynamics.[25]

It has recently been demonstrated[26] that the information theory[27−30] can be successfully applied to define the "*atoms-in-molecules*" by generating the unique (Hirshfeld)[9] partitioning of the molecular density. The resulting "*stockholder*" *atoms* minimize the so-called *entropy deficiency* (*missing information*) of Kullback and Leibler[28] with respect to the molecularly placed isolated atom densities, which determine the *promolecule* density of the familiar density-difference diagrams. It has also been shown that similar entropic concepts can be used to solve the molecular similarity problems and to define the intermediate, *polarization* stage of the bonded atom reconstruction with respect to the corresponding isolated atomic states.[26]

However, to the best of author's knowledge, no explicit use of the entropy concepts of the information theory has been made to tackle the classical problem of bond multiplicities. The main purpose of the present work is to explore a possibility of formulating truly entropic measures of the global and localized "bond-orders" and their ionic and covalent components. In this search we shall adopt the obvious requirement that the formulated entropy functions follow, as closely as possible, the established chemical intuition in selected prototype and standard systems.

One of our guiding principles is to preserve the atomic description, which constitutes a natural reference frame for any chemical bonding concept. This principle implies that our efforts will be carried out within the framework of an appropriate network of the electron probability distributions in atomic resolution, i.e., the probabilities of finding a single electron on constituent bonded or isolated atoms, or the joint probabilities

10.1021/jp001999f CCC: $19.00

of simultaneously finding a pair of electrons on specified atoms in a molecule. A survey of such probabilities is given in the first section of the article.

The proper entropy functions of the molecular *input* and *output* probability schemes in such an atomic, coarse-grained description are defined in the second section. We begin this section by addressing the basic question for the present development: in what sense can we treat a molecule as a "*communication*" system? The average uncertainty measures of the standard information theory[29] are then used to define the proper entropic measures of the overall bond multiplicity and its partitioning into the covalent and ionic components. The suggested entropies are then tested within the *two-orbital model*[12,17,18,21] of a single chemical bond, the *three-orbital model*[18,20] of a symmetric transition-state complex in the collinear atom exchange reaction, and the systems of conjugate π bonds in the benzene ring and butadiene chain (Hückel theory).

Finally, a direct-information theoretic approach for determining the bond multiplicity between a specified pair of atoms in a molecule is proposed. In this development, the so-called *bond entropy* concept is introduced, which provides a direct measure of the bond order between any pair of atoms in a molecule. We shall demonstrate that for all the illustrative molecular systems mentioned above, a good agrement is obtained between the predicted bond entropies and both intuitive expectations and other, Wiberg[10]-type quantum-mechanical bond multiplicity indicators.

Electron Probabilities in Atomic Resolution

Atomic Probabilities in a Molecule. The chemical description of the electronic structure of molecular systems is usually formulated in terms of *atoms-in-molecules* (AIM) and bonds that connect them. The electron density at point $\boldsymbol{r}$ for the ground-state $\Psi(1, 2, ..., N)$ of a molecule $\mathrm{M}(\mathbf{R})$ consisting of m atoms (at fixed positions $\mathbf{R} = \{\mathbf{R}_a\}$) and N electrons (at positions $\{\mathbf{r}_k\}$) is given by the expectation value

$$\rho(\mathbf{r}) = \langle \Psi | \sum_{k=1}^{N} \delta(\mathbf{r}_k - \mathbf{r}) | \Psi \rangle = N \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}) | \Psi \rangle \equiv \sum_{a=1}^{m} \rho_a(\mathbf{r}) \geq 0 \quad (1)$$

where $\{\rho_a(\mathbf{r})\}$ groups the atomic densities obtained from the appropriate partitioning scheme of the molecular density. It defines the probability distribution of finding an electron at point $\mathbf{r}$, the so-called *shape function*

$$f(\mathbf{r}) = \rho(\mathbf{r})/N \geq 0, \qquad \int f(\mathbf{r})\,\mathrm{d}\mathbf{r} = 1 \quad (2)$$

In the one-determinant approximation, e.g., in the Hartree–Fock or Kohn–Sham theories, the electron density can be expressed as the sum of orbital contributions

$$\rho(\mathbf{r}) = \sum_{\alpha}^{\mathrm{SO}} |\psi_\alpha(\mathbf{r})|^2\, n_\alpha \qquad \psi_\alpha = \sum_{i}^{\mathrm{OAO}} \chi_i\, C_{i\alpha} \quad (3)$$

where the *molecular orbital* (MO) $\psi_\alpha(\mathbf{r})$ represents a spatial part of the *spin orbital* (SO) α, $\phi_\alpha(\mathbf{x}) \equiv \psi_\alpha(\mathbf{r})\, \xi_\alpha(\sigma)$, with $\xi_\alpha(\sigma)$ ($\sigma = \pm 1/2$) and $0 \leq n_\alpha \leq 1$ standing for the SO spin function and occupation number, respectively. The occupations satisfy the closure condition $\sum_\alpha n_\alpha = N$.

As also indicated in eq 1, the molecular electronic density $\rho(\mathbf{r})$ can be partitioned into atomic densities $\{\rho_a(\mathbf{r})\}$ using an appropriate division criterion. For example, this may involve the *physical space* partitioning into atomic basins $\{\Omega_a\}$, which define topological atoms of Bader et al. (B):[6,7] $\rho_a^{\mathrm{B}}(\mathbf{r}) = \rho(\mathbf{r})$ for $\mathbf{r} \in \Omega_a$ and $\rho_a^{\mathrm{B}}(\mathbf{r}) = 0$ for $\mathbf{r}$ outside Ω_a. In the *function space* division schemes[2] [*Populational Analysis* (PA)], which we adopt in the present work, one uses the known association of the basis functions $\{\chi_i(\mathbf{r})\}$ [*orthogonalized atomic orbitals* (OAO), $\langle \chi_i | \chi_j \rangle = \delta_{i,j}$], with the corresponding atoms:

$$\rho(\mathbf{r}) = \sum_{i}^{\mathrm{OAO}} \sum_{j}^{\mathrm{OAO}} \chi_i^*(\mathbf{r})\, P_{i,j}\, \chi_j(\mathbf{r}) = \sum_{a}^{\mathrm{atoms}} \{ \sum_{i \in a}^{\mathrm{OAO}} \sum_{j}^{\mathrm{OAO}} \chi_i^*(\mathbf{r})\, P_{i,j}\, \chi_j(\mathbf{r}) \} \equiv \sum_{a}^{\mathrm{atoms}} \rho_a^{\mathrm{PA}}(\mathbf{r}) \quad (4)$$

Here

$$\mathbf{P} \equiv \{ P_{i,j} \equiv \sum_{\alpha}^{\mathrm{SO}} = \langle \chi_i | \psi_\alpha \rangle\, n_\alpha\, \langle \psi_\alpha | \chi_j \rangle = \sum_{\alpha}^{\mathrm{SO}} C_{i\alpha}\, n_\alpha\, C_{j\alpha}^* \}$$

denotes the familiar CBO matrix in the OAO representation. Finally, in the so-called "*stockholder*" partitioning scheme of Hirshfeld[9]

$$\rho_a^{\mathrm{H}}(\mathbf{r}) = \rho(\mathbf{r})\, [\rho_a^{\mathrm{o}}(\mathbf{r} - \mathbf{R}_a)/\rho^{\mathrm{o}}(\mathbf{r})] \quad (5)$$

one locally divides the molecular density between all constituent atoms in proportion to the isolated atom share in the density $\rho^{\mathrm{o}}(\mathbf{r}) = \sum_a \rho_a^{\mathrm{o}}(\mathbf{r} - \mathbf{R}_a)$ of the *promolecule* $\mathrm{M}^{\mathrm{o}}(\mathbf{R})$, consisting of the atomic densities $\{\rho_a^{\mathrm{o}}(\mathbf{r} - \mathbf{R}_a)\}$ of a the *separated atoms limit* (SAL) shifted to the nuclear positions $\mathbf{R}$ in the molecule. Notice that the same reference is applied in the density difference diagrams: $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho^{\mathrm{o}}(\mathbf{r})$, extracting modifications of the AIM densities due to the formation of chemical bonds. As we have already remarked, the Hirshfeld scheme has recently been shown[26] to have a sound basis in the information theory, because the stockholder atoms directly follow from the minimum entropy deficiency[28] (minimum missing information) principle relative to the isolated atom densities of the promolecule, subject to the constraint of the exhaustive partitioning of the molecular density into atomic contributions at each point in space.

The atomic discretization also defines the associated average (fractional) electron population of the bonded atom

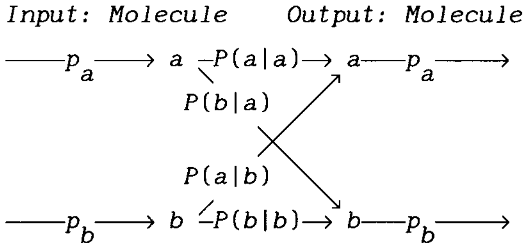
$$N_a = \int \rho_a(\mathbf{r})\, \mathrm{d}\mathbf{r}, \quad a = 1, 2, ..., m \quad (6)$$

and hence its effective net charge $Q_a = Z_a - N_a$, where Z_a denotes the atomic number of nucleus a. In this *coarse-grained* atomic representation of the *fine-grained*, local distribution $\rho(\mathbf{r})$, the probability vector $\mathbf{p} = \{p_a\}$, combining the probabilities of finding an electron on specified AIM, is defined by the ratios

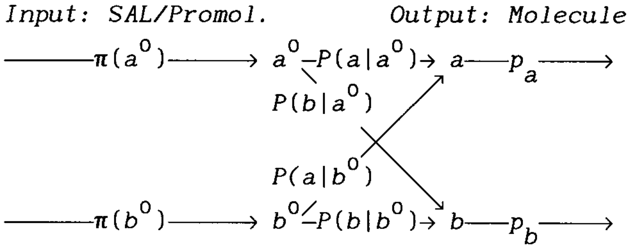
$$p_a = N_a/N, \quad a = 1, 2, ..., m; \quad \sum_a p_a = 1 \quad (7)$$

This molecular one-electron probability vector in atomic resolution, $\mathbf{p} = \{p_a\!: a \in \mathrm{M}(\mathbf{R})\}$, and the underlying AIM partitioning $\mathbf{a} = \{a = 1, 2, ..., m\}$ together define the so-called *molecular input* probability scheme: $I^{\mathrm{M}} = \{[a, p_a]\!: a \in \mathrm{M}(\mathbf{R})\}$. This is shown in Scheme 1, drawn for the simplest case of a diatomic a–b ($m = 2$). In this diagram, the same vector $\mathbf{p}$

SCHEME 1



SCHEME 2



also defines the *molecular output* one-electron probability scheme: $O^{\mathrm{M}} = \{[a, p_a]\colon\ a \in \mathrm{M}(\mathbf{R})\}$.

As also shown in Scheme 1, the initial allocation of electrons among atoms $\boldsymbol{a}$ may change as a result of the electron delocalization in a molecule. This is reflected in Scheme 1 by a network of the *conditional probabilities* $\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(b|a), a, b = 1, 2, ..., m\}$, with $P(b|a)$ denoting the probability of finding an electron initially associated with atom a on atom b in a molecule.

Atomic Probabilities in the SAL/Promolecule. Attributing an electron in M to specific atoms, i.e., assigning it the AIM label $a \in \mathbf{a}$, is therefore characterized by uncertainty. This is also true in the collections M^o and $\mathrm{M}^o(\mathbf{R})$; of the isolated constituent atoms/ions in the SAL, $\{a^o \in \mathrm{M}^o\}$, and in the promolecule, $\{a^o \in \mathrm{M}^o(\mathbf{R})\}$, respectively. The probabilities $\pi = \{\pi(a^o)\}$ of finding an electron of the N indistinguishable electrons of the promolecule/SAL on specific reference (isolated) atoms $\mathbf{a}^o = \{a^o\}$ provide the SAL/promolecule input (source) information of Scheme 2, which preserves the molecular output (*receiving end*) of Scheme 1.

We therefore conclude that both the atomic identifications a in M and a^o in M^o can be considered discrete random variables. The probability of finding one of the N indistinguishable electrons of M^o on $\mathbf{a}^o$ in $\mathrm{M}^o(\mathbf{R})$ is given by the ratios

$$\pi(a^o) = N_a{}^o/N, \quad a^o = 1, 2, ..., m; \quad \sum_{a^o} \pi(a^o) = 1 \qquad (8)$$

where $N_a{}^o = \int \rho_a{}^o(\mathbf{r})\, d\mathbf{r}$ denotes the integer number of electrons on atom a^o in the SAL/promolecule. These atomic electron populations also satisfy the overall molecular closure condition: $\sum_{a^o} N_a{}^o = N$.

The *SAL/promolecule input* probability vector $\pi = \{\pi(a^o)\colon\ a^o \in \mathrm{M}^o(\mathbf{R})\}$ and the associated isolated atom/ion partition $\mathbf{a}^o$ define the *SAL input* probability scheme: $I^{\mathrm{SAL}} = \{[a^o, \pi(a^o)]\colon\ a^o \in \mathrm{M}^o(\mathbf{R})\}$.

We would like to emphasize at this point that a choice of the most appropriate SAL/promolecule reference may in some cases create computational and conceptual difficulties. For example, a choice between a dissociation into atoms or ions, e.g., the *ionic* vs. *covalent* limits in the dissociation of the alkali metal halides,[31] introduces an element of arbitrariness, although only the atomic SAL reference may be considered as representing truly nonbonded molecular fragments at large separations. Therefore, in an eventual definition of the entropic (information) measures of the chemical bond multiplicity, one may prefer the molecular inputs of Scheme 1 over the SAL/promolecule inputs of Scheme 2.

Similar perspectives have been used in previous quantum mechanical approaches to the bond-order problem. For example, the Wiberg-type measure of the covalent bond,[10−12] given by the quadratic function of the corresponding CBO matrix elements, or the fluctuational definition[13] fall into the exclusively molecular category of Scheme 1. Similarly, the difference approach measuring the *molecularly* averaged displacents of the *molecular* CBO matrix elements relative to the corresponding SAL values combine the SAL and molecular electron configuration information, as shown in Scheme 2.

In the present development we shall adopt the molecular-only approach of Scheme 1, to define the entropy for the overall *covalent entropy*, and a separate *equiprobability* SAL input I^{EQ} of Scheme 2, to define the global *ionic entropy*. We would like to emphasize, however, that for distinguishing between the covalency of the *coordination bond*, in which the bonding electronic pair originates from a single atom, and that of a truly *covalent bond* formed by two atoms, each contributing a single valence electron, a reference to the SAL probabilities of Scheme 2 is required.[17,18,21]

Conditional and Joint Two-Electron Probabilities. There are two sources of uncertainty in making atomic allocations of electrons in a molecular system. As we have argued above, the first is associated with the "*input message*" specifying probabililties of "atomic" origins of an electron, either molecular (Scheme 1) or SAL/promolecule (Scheme 2) in character. In other words, it is not known with certainty which constituent "atomic" unit an electron originates from. This uncertainty is reflected by the two input probability schemes discussed in the preceding subsections.

The second source is linked to the *conditional probabilities*, $\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(b|a)\colon\ a, b \in \mathrm{M}(\mathbf{R})\}$ (Scheme 1) and $\mathbf{P}(\mathbf{b}|\mathbf{a}^o) = \{P(b|a^o)\colon\ b \in \mathrm{M}(\mathbf{R}), a^o \in \mathrm{M}^o(\mathbf{R})\}$ (Scheme 2), of the event that an electron originating from atom a or a^o is subsequently found on atom b in a molecule. They respectively define the corresponding *conditional probability schemes*: $C(\mathrm{M}|\mathrm{M}) = \{[(b|a), P(b|a)]\colon\ (a, b) \in \mathrm{M}(\mathbf{R})\}$ and $C(\mathrm{M}|\mathrm{SAL}) = \{[(b|a^o), P(b|a^o)]\colon\ b \in \mathrm{M}(\mathbf{R}), a^o \in \mathrm{M}^o(\mathbf{R})\}$, characterizing the electron "*transmission channels*" between AIM (Scheme 1) and between isolated and bonded atoms (Scheme 2), respectively.

The conditional probabilities $\mathbf{P}(\mathbf{b}|\mathbf{a})$ are linked to the corresponding *joint probabilities*, $P(\mathbf{ba}) = \{P(ba), a, b \in \mathrm{M}(\mathbf{R})\}$, of simultaneously finding one electron on a and another on b, or $P(\mathbf{ba}^o) = \{P(ba^o), b \in \mathrm{M}(\mathbf{R}), a^o \in \mathrm{M}^o(\mathbf{R})\}$

$$P(b|a) = P(ba)/p_a, \quad P(b|a^o) = P(ba^o)/\pi(a^o) \qquad (9)$$

The joint probabilities $P(\mathbf{ba})$ can be obtained from the relevant molecular spinless two-electron density (pair function) in the OAO representation:

$$\begin{aligned}\rho_2(\mathbf{r}, \mathbf{r}') &= \langle\Psi|\sum_{k=1}^{N}\sum_{l\neq k} \delta(\mathbf{r}_k - \mathbf{r})\, \delta(\mathbf{r}_l - \mathbf{r}')|\Psi\rangle \\ &= N(N-1)\, \langle\Psi|\delta(\mathbf{r}_1 - \mathbf{r})\, \delta(\mathbf{r}_2 - \mathbf{r}')|\Psi\rangle \\ &= \sum_{i,j}^{\mathrm{OAO}} \sum_{k,l}^{\mathrm{OAO}} \chi_i^*(\mathbf{r})\, \chi_j^*(\mathbf{r}')\, \bar{\Gamma}(i,j;k,l)\, \chi_k(\mathbf{r})\, \chi_l(\mathbf{r}') \end{aligned} \qquad (10)$$

The pair-diagonal elements, $\Gamma(i,j) \equiv \bar{\Gamma}(i,j;i,j)$, satisfying McWeeny's normalization

$$\sum_{i,j}^{\mathrm{OAO}} \Gamma(i,j) = \mathrm{Tr}\,\bar{\Gamma} = N(N-1) \tag{11}$$

which multiply in eq 10 the orbital probability distributions $|\chi_i(\mathbf{r})|^2$ and $|\chi_j(\mathbf{r}')|^2$ of an electron "1" at $\mathbf{r}$ and another electron "2" at $\mathbf{r}'$, respectively, determine the joint probability that electron "1" is on the ith OAO while electron "2" simultaneously occupies the jth OAO:

$$\mathcal{P}\,(i,j) \equiv \Gamma(i,j)/[N(N-1)], \quad \sum_{i,j}^{\mathrm{OAO}} \mathcal{P}\,(i,j) = 1 \tag{12}$$

In the function-space AIM discretization of the populational analysis, the two-electron simultaneous probabilities are then obtained by the summation of these orbital probabilities over OAO centered on the specified pair of atoms:

$$\mathcal{P}\,(ab) = \mathcal{P}\,(ba) = \sum_{i\in a}^{\mathrm{OAO}} \sum_{j\in b}^{\mathrm{OAO}} \mathcal{P}\,(i,j), \quad \sum_{a,b}^{\mathrm{AIM}} \mathcal{P}(ab) = 1 \tag{13}$$

The joint partition $\mathbf{ba} = \{ba, (b, a) \in \mathrm{M}(\mathbf{R})\}$ [or $\mathbf{ba}^{\mathrm{o}} = \{ba^{\mathrm{o}}, b \in \mathrm{M}(\mathbf{R}), a^{\mathrm{o}} \in \mathrm{M}^{\mathrm{o}}(\mathbf{R})\}$] and the associated vector of the *joint probabilities* $\mathcal{P}\,(\mathbf{ba})$ [or $\mathcal{P}\,(\mathbf{ba}^{\mathrm{o}})$] together define the corresponding *joint* probability scheme: $\mathcal{J}\,(\mathcal{O}^{\mathrm{M}}\mathcal{I}^{\;\mathrm{M}}) = \{[ba, P(ba)]: (b, a) \in \mathrm{M}(\mathbf{R})\}$ [or $\mathcal{J}\,(\mathcal{O}^{\mathrm{M}}\mathcal{I}^{\;\mathrm{SAL}}) = \{[ba^{\mathrm{o}}, P(ba^{\mathrm{o}})]: b \in \mathrm{M}(\mathbf{R}), a^{\mathrm{o}} \in \mathrm{M}^{\mathrm{o}}(\mathbf{R})\}$.

Let us recall that the conditional probabilities must satisfy the following normalization over all output atomic events:

$$\sum_{b}^{\mathrm{outputs}} P(b|a) = 1 \quad \text{or} \quad \sum_{b}^{\mathrm{outputs}} P(b|a^{\mathrm{o}}) = 1 \tag{14}$$

It also follows from eq 9 and this normalization condition that the summation of the joint probabilities over all atomic outputs gives the input (molecular or SAL) one-electron probability:

$$\sum_{b}^{\mathrm{outputs}} \mathcal{P}\,(ba) = p_a \quad \text{or} \quad \sum_{b}^{\mathrm{outputs}} \mathcal{P}\,(ba^{\mathrm{o}}) = \pi(a^{\mathrm{o}}) \tag{15}$$

Finally, the summation of the joint probabilities over all atomic inputs must also give the corresponding one-electron AIM probability:

$$\sum_{a}^{\mathrm{inputs}} \mathcal{P}\,(ba) = \sum_{a^{\mathrm{o}}}^{\mathrm{inputs}} \mathcal{P}\,(ba^{\mathrm{o}}) = p_b \tag{16}$$

Entropy Functions

Molecule as a "Communication" System. One can regard a molecule $\mathrm{M}(\mathbf{R})$ as a "*communication*" system, in which the *signals* are being transmitted in terms of a finite set of m possible atomic allocations of N electrons in M. We call such a unit signal the *message*. When a signal conveying a message is received, it is known that one of the given set of possible messages has been sent. As in the real communication channel, the molecular system is characterized by disturbances of a random character (*noise*), which perturb the transmitted signal. This molecular uncertainty in ascribing electrons to atoms originates from the quantum-mechanical noise in the "*transmission channels*" of Schemes 1 and 2, linking the *input* and *output* atomic "events".

More specifically, as we have argued above, it is not known with certainty on which atom an electron will be found in the "*output*" of such a molecular communication system, even when its atomic origin in the *input* of Scheme 1 (2), i.e., in the molecule (SAL/promolecule), is known. This is a result of forming chemical bonds, i.e., of the electron delocalization. Similarly, it is not known with certainty from which constituent atom/ion in the molecular (SAL/promolecular) *input* an electron originates, i.e., which signal in the probability network of Scheme 1 (2) was transmitted, even when the received message in the *ouput*, i.e., finding an electron on a specific atom in a molecule, is known.

The set of *atomic identification signals* (atomic labels) is the same in the SAL/promolecule and in the molecule itself. The molecular system under consideration can thus be considered as the communication system. This system influences probabilities of such signals being sent (or received), thus introducing effects of a molecular *communication noise*, modifying the input one-electron probability distribution, $\{p_a$ (or $\pi_a)\}$, of the *input probability scheme* into the conditional molecular probability of b given the input a (or a^{o}), $\{P(b|a$ [or $a^{\mathrm{o}}])\}$. The input probability scheme defines the relevant *conditional probability scheme*, which gives rise to the molecular output probability scheme. Notice that the stationary character of the electron distribution requires that the output probability vector in Scheme 1 be identical to the input probability vector of eqs 7 and 16. This transformation of the input atomic probabilities into the output probabilities via the conditional probability network is the essence of the illustrative molecular communication systems shown in Schemes 1 and 2.

The formation of chemical bonds affects mainly the valence-shell electrons of constituent atoms in a molecule, with the inner, core electron distributions of isolated atoms (or ions) remaining practically unchanged. Therefore, in qualitative and semiquantitative bond-order considerations, one usually limits a discussion by explicitly taking into account only the valence electrons. We follow this valence-only approach in all illustrative examples reported in this work. In the butadiene and benzene cases, we similarly discuss the π bond-orders, separating the $2p_\pi$ valence electrons of carbon atoms from the remaining electrons of the molecular σ core.

Average Uncertainties of the Molecular Probability Schemes. Let us define the entropy of the molecular one-electron probabilities in the atomic resolution

$$H(\mathbf{p}) = -\sum_{i=1}^{m} p_i \log_2 p_i \equiv H(\mathcal{I}^{\;\mathrm{M}}) \equiv H(\mathcal{O}^{\;\mathrm{M}}) \tag{17}$$

which corresponds to both the molecular input and output probability distributions of Scheme 1. It measures the average uncertainty for both these probability schemes. Following the usual convention of the information theory, we have taken the logarithm in the entropy definition to the base 2, in which the unit of information is the *bit*.

The corresponding entropy for the joint two-electron probability scheme $\mathcal{J}\,(\mathcal{O}^{\;\mathrm{M}}\mathcal{I}^{\;\mathrm{M}})$ of the probabilities of simultaneous events in the molecular input and output is as follows:

$$H(\mathcal{J}\,) \equiv H(\mathcal{O}^{\;\mathrm{M}}\mathcal{I}^{\;\mathrm{M}}) = -\sum_{i=1}^{m}\sum_{j=1}^{m} \mathcal{P}\,(ij) \log_2 \mathcal{P}\,(ij) \equiv H(\mathcal{P}\,) \tag{18}$$

This entropy similarly measures the average uncertainty in the distribution of the two electron joint probabilities in atomic resolution.

Next we introduce the entropy difference[29]

$$H(O^{M} I^{M}) - H(I^{M}) = -\sum_{i=1}^{\text{inputs}} \sum_{j=1}^{\text{outputs}} P(ij) \log_2 [P(ij)/p_i]$$

$$= -\sum_{i=1}^{\text{inputs}} \sum_{j=1}^{\text{outputs}} P(ij) \log_2 P(j|i) \equiv H(O^{M}|I^{M}) \quad (19)$$

where we have used the sum rule of eq 16. It measures the average entropy of the output probability distribution, given the input probability scheme. If an input event occurs, it may or may not change the uncertainty about the output events. The entropy of eq 19 represents the residual average uncertainty about the output events when one has knowledge of the occurrence of the input events. Because conditioning, i.e., giving the information about the input probability scheme, cannot increase the average uncertainty about the output probability scheme, the following inequality holds:[29]

$$H(O^{M}|I^{M}) \leq H(O^{M}) \quad (20)$$

with equality if and only if the schemes O^{M} and I^{M} are independent.

The related molecular entropy function of potential importance for characterizing the electron configuration is the nonnegative *average mutual information* between the input and output schemes:[29]

$$H(O^{M}{:}\,I^{M}) = \sum_{i}^{\text{inputs}} \sum_{j}^{\text{outputs}} P(ij) \log_2 \frac{P(ij)}{p_i\, p_j}$$

$$= H(I^{M}) + H(O^{M}) - H(O^{M} I^{M})$$

$$= H(I^{M}) - H(I^{M}|O^{M}) =$$

$$H(O^{M}) - H(O^{M}|I^{M}) \geq 0 \quad (21)$$

where we have used the inequality of eq 20. It follows from eq 21 that the mutual information vanishes when the input and output probability schemes are independent, because then $H(O^{M} I^{M}) = H(I^{M}) + H(O^{M})$. This entropy function gives the average information about the output provided by the occurrence of events at the input.

A Search for the Entropic Measures of the Global Bond Multiplicity

Two-Orbital Model of a Single Bond. *Probabilities*. Consider the simplest case of a two-orbital model[12,17,18,21] of the A−B bond, consisting of a single bonding molecular orbital (MO) ψ given as a combination of the two OAOs, $\chi_A \equiv a$ and $\chi_B \equiv b$, centered on nuclei of atoms A and B, respectively

$$\psi(\mathbf{r}) = \alpha\, a(\mathbf{r}) + \beta\, b(\mathbf{r}), \quad \langle i|j\rangle = \delta_{ij}, \quad i, j \in \{a, b\} \quad (22)$$

and occupied by $n_\psi = 2$ electrons with opposite spins (singlet state). In this case the four elements of the CBO matrix of eq 4 can be expressed as functions of a single element, e.g., the electron population on atom A, $q_a \equiv P_{a,a} \equiv q$:

$$q_b(q) \equiv P_{b,b}(q) = 2 - q, \quad P_{a,b}(q) = P_{b,a}(q) = [q(2-q)]^{1/2} \quad (23)$$

These CBO functions of the independent variable q determine the corresponding expressions for the elements of the pair-diagonal, two-particle density matrix in the OAO representation (eqs 10−12):

$$\Gamma(a,a) = q^2/2; \quad \Gamma(b,b) = (2-q)^2/2;$$

$$\Gamma(a,b) = \Gamma(b,a) = q(2-q)/2 \quad (24)$$

By the quantum-mechanical superposition principle, the one-electron probabilities $\{p_i = = |\langle i|\psi\rangle|^2\}$ of the events that an electron in state ψ occupies the ith OAO, $\{i = a, b\}$, are:

$$p_a = |\alpha|^2 = q/2 \equiv \mathrm{P}; \quad p_b = |\beta|^2 = (2-q)/2 \equiv \mathrm{Q};$$

$$\mathrm{P} + \mathrm{Q} = 1 \quad (25)$$

In this single MO model, the spatial part of the singlet two-electron function is given by the product of the common MO part of the two occupied spin orbitals:

$$\Psi(1,2) = \psi(1)\psi(2) = \alpha^2 a(1)a(2) +$$

$$\alpha\beta[a(1)b(2) + b(1)a(2)] + \beta^2 b(1)b(2) \quad (26)$$

where the spatial coordinates of electrons are abbreviated as $\{\mathbf{r}_k \equiv k,\ k = 1, 2\}$. Hence, the joint two-electron probabilities $P(i,j) = |\langle i(1)j(2)|\Psi\rangle|^2 = \Gamma(i,j)/2$ of the events that for the two electrons in state Ψ, electron "1" is on $i = a, b$ and simultaneously electron "2" is on $j = a, b$, are:

$$P(aa) = P(a,a) = p_a^{\,2} = q^2/4 = \mathrm{P}^2;$$

$$P(bb) = P(b,b) = p_b^{\,2} = (2-q)^2/4 = \mathrm{Q}^2;$$

$$P(ab) = P(a,b) = P(ba) = P(b,a) = p_a p_b =$$

$$q(2-q)/4 = \mathrm{PQ} \quad (27)$$

These joint probabilities satisfy the normalization conditions of eqs 15 and 16

$$\textstyle\sum_i P(i,j) = \sum_i P(j,i) = p_j \quad \sum_i \sum_j P(j,i) = \sum_i p_i = 1 \quad (28)$$

and determine the corresponding conditional two-electron probabilities $\mathbf{P}(\mathbf{b}|\mathbf{a})$ of eq 9:

$$P(a|a) = P(aa)/p_a = \mathrm{P}; \quad P(b|a) = P(ba)/p_a = \mathrm{Q};$$

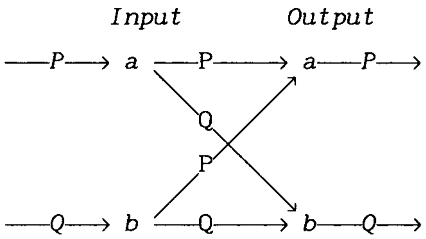
$$P(a|b) = P(ab)/p_b = \mathrm{P}; \quad P(b|b) = P(bb)/p_b = \mathrm{Q} \quad (29)$$

satisfying the sum rule of eq 14:

$$P(a|a) + P(b|a) = P(a|b) + P(b|b) = 1 \quad (30)$$

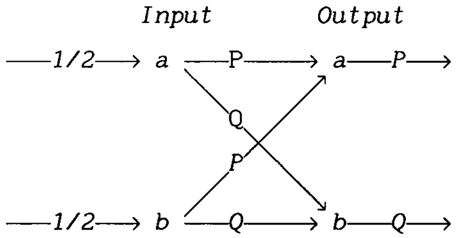
These probabilities determine the probability network of the *binary nonsymmetric channel* shown in Scheme 3(see also Scheme 1):

SCHEME 3

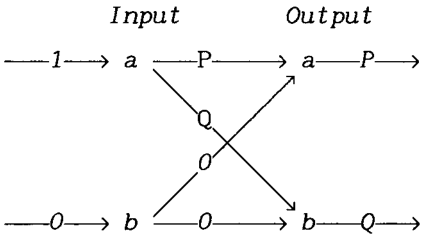


In the related Schemes 4 and 5, representing Scheme 2 for the two-orbital model and alternative SAL choices, one replaces the molecular one-electron input probabilities $\mathbf{p}$ with the corresponding SAL probabilities π: $\pi(i^{o}) = N_i^{o}/2$, $i = a, b$. In this model, the integer atomic occupations sum up to two

SCHEME 4



SCHEME 5



electrons: $N_a^{\mathrm{o}} + N_b^{\mathrm{o}} = 2$. For example, in the *covalent dissociation* case of Scheme 4, $(\mathrm{A}{\uparrow}) + ({\downarrow}\mathrm{B})$ (SAL1), when both separated atoms contribute a single electron with opposite spins, $\pi(a^{\mathrm{o}}) = \pi(b^{\mathrm{o}}) = 1/2$.

Setting the identical input probabilities equal to $1/N$ (as in SAL1) so that either input atomic allocation is equally likely defines the *equiprobability* (EP) *SAL* input scheme, $I^{\mathrm{EP}} = \{(a^{\mathrm{o}}, 1/N)\colon\ a^{\mathrm{o}} \in \mathrm{M}^{\mathrm{o}}(\mathbf{R})\}$. For this input, the entropy function reaches the maximum value

$$H(I^{\mathrm{EP}}) = -N\left(\frac{1}{N}\right)\log_2\left(\frac{1}{N}\right) = \log_2 N \tag{31}$$

This SAL input can be used to probe the ways in which the entropies of the actual molecular probabilities deviate from the reference entropy $H(I^{\mathrm{EP}})$. Such deviations from the perfectly equalized probabilities should contribute to the *bond ionicity.* In the two-orbital model, $I^{\mathrm{EP}} = I^{\mathrm{SAL1}}$ and

$$H(I^{\mathrm{EP}}) = H(I^{\mathrm{SAL1}}) = \log_2 2 = 1 \tag{32}$$

Similarly, in the *ionic dissociation* limit (Scheme 5), when the valence electron pair is, say, on A, $(\mathrm{A}{\uparrow\downarrow})^- + \mathrm{B}^+$ (SAL2), $\pi(a^{\mathrm{o}}) = 1$, and $\pi(b^{\mathrm{o}}) = 0$. In this case $P(a|a^{\mathrm{o}}) = \mathrm{P}$, $P(b|a^{\mathrm{o}}) = \mathrm{Q}$, and $P(a|b^{\mathrm{o}}) = P(b|b^{\mathrm{o}}) = 0$:

Entropy Functions for the Covalent and Ionic Bond Components. From eqs 27 and 29 (see also Scheme 3), one obtains the conditional entropy function (eq 19) for the two-orbital model given by the *binary entropy function*[29]

$$H(O^{\mathrm{M}}|I^{\mathrm{M}}) = H(\mathrm{P}) = -\mathrm{P}\log_2\mathrm{P} - \mathrm{Q}\log_2\mathrm{Q} = H(1-\mathrm{P}) = H(\mathrm{Q}) \tag{31}$$

shown in Figure 1. As is also shown in the figure, this function runs very close to the *quadratic valence index* (QVI) of the previous Wiberg-type[10,12] and two-electron difference approaches:[17,18,20−22]

$$V_{\mathrm{cov}}(\mathrm{P}) = [P_{a,b}(\mathrm{P})]^2 = q_a(\mathrm{P})\,q_b(\mathrm{P}) = 4\mathrm{P}(1-P) = q(\mathrm{P})\,[2-q(\mathrm{P})] \tag{32}$$

Indeed, this function exhibits correct limiting value, $H(1) = H(0) = 0$, for $q = 2, 0$, i.e., for the configuration of the lone, nonbonding electronic pair on a and b, respectively. Moreover, the maximum for the exact electron-sharing configuration $q = 1$, $H(1/2) = 1$, signifies a single covalent bond in the model under consideration.

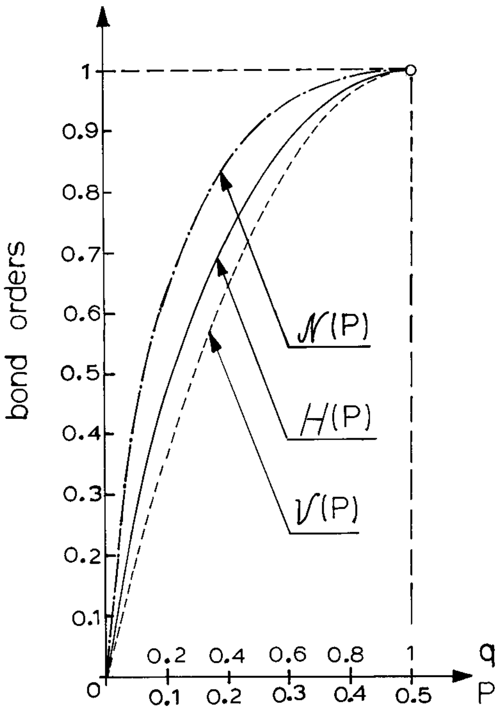


Figure 1. The bond entropy, $N(\mathrm{P}) = N(1-\mathrm{P}) \equiv N(\mathrm{Q})$, and binary entropy, $H(\mathrm{P}) = H(1-\mathrm{P}) \equiv H(\mathrm{Q})$, functions for the two-orbital model compared with the corresponding quadratic valence index: $V_{\mathrm{cov}}(\mathrm{P}) = [P_{a,b}(\mathrm{P})]^2 = 4\mathrm{P}(1-P) = 4\mathrm{Q}(1-\mathrm{Q}) \equiv V_{\mathrm{cov}}(\mathrm{Q})$.

We are therefore adopting the entropy function of eq 31 as a measure of the *covalent bond* multiplicity:

$$N_{\mathrm{cov}}(\mathrm{P}) \equiv H(O^{\mathrm{M}}|I^{\mathrm{M}}) = H(\mathrm{P}) \tag{33}$$

By the same argument, the entropy function

$$N_{\mathrm{ion}}(\mathrm{P}) = H(I^{\mathrm{EP}}) - H(O^{\mathrm{M}}|I^{\mathrm{M}}) = H(I^{\mathrm{EP}}) + H(I^{\mathrm{M}}) - H(O^{\mathrm{M}}I^{\mathrm{M}}) = 1 - H(\mathrm{P}) \tag{34}$$

which combines the reference entropy $H(I^{\mathrm{EP}}) = H(I^{\mathrm{SAL1}}) = 1$ of Scheme 4 with the current entropies $H(I^{\mathrm{M}}) = H(\mathrm{P})$ and $H(O^{\mathrm{M}}I^{\mathrm{M}}) = 2H(\mathrm{P})$ of Scheme 3, exhibits a qualitatively correct behavior expected of the *ionic bond* multiplicity. Namely, it reaches the maximum value $N_{\mathrm{ion}}(0) = N_{\mathrm{ion}}(1) = 1$ for the lone-pair configurations, corresponding to the single ionic pair, $\mathrm{A}^+\mathrm{B}^-$ ($\mathrm{P} = 0$) or $\mathrm{A}^-\mathrm{B}^+$ ($\mathrm{P} = 1$), and the minimum value $N_{\mathrm{ion}}(1/2) = 0$ for the covalent, electron-sharing configuration. Notice that for the equal distribution of valence electrons among the AIM, $I^{\mathrm{M}} = I^{\mathrm{EP}}$, e.g., in the case of π electrons in butadiene or benzene in the Hückel theory, $N_{\mathrm{ion}} = H(O^{\mathrm{M}}\colon I^{\mathrm{M}})$ (see eq 21).

The two components therefore complement each other, preserving the total single bond order

$$N(\mathrm{P}) = N_{\mathrm{cov}}(\mathrm{P}) + N_{\mathrm{ion}}(\mathrm{P}) = \log_2 2 = 1 \tag{35}$$

in the whole range of argument $\mathrm{P} \in \langle 0, 1\rangle$. The covalent bond-order measure

$$N_{\mathrm{cov}}(\mathrm{P}) \cong V(\mathrm{P}) = q_a(\mathrm{P})\,q_b(\mathrm{P}) = 4\mathrm{P}(1-\mathrm{P}) = 4\mathrm{PQ} \tag{36}$$

roughly reflects the number of shared electronic pairs between atoms, or, equivalently, as explicitly shown in Figure 1 and eq 36, the product of the valence electron populations of AIM.

Similarly, a reference to Figure 1 and eq 36 shows that in the neutral molecule, $Q_A + Q_B = 0$, the complementary ionic bond-order generally resembles the negative product of the net atomic charges $Q_i = 1 - V_i$, i = A_1B,

$$N_{\text{ion}}(\text{P}) \cong 1 - V_{\text{cov}}(\text{P}) = (Q_A + Q_B) - Q_A Q_B = - Q_A Q_B \quad (37)$$

The question that naturally arises is how to distinguish between the truly *covalent* (electron-sharing) and the *coordination* (donor–acceptor) bond orders in a molecule. The same molecular electron configuration may correspond to either of these types of chemical bond, since only the SAL reference, i.e., a "history" of the bond formation, differs in both these cases. More specifically, the former "compares" the molecular output electron probabilities with those for the $I^{\text{SAL1}} = I^{\text{M}}(1/2)$ input, whereas the latter combines the molecular probabilities with the reference SAL2-input ones. Indeed, the model electron configuration for P = 1/2 represents both the single covalent bond with respect to the atomic I^{SAL1}, and a single coordination bond with respect to the ionic I^{SAL2} references. Similarly, for the P = 1 (SAL2 configuration), one identifies a vanishing coordination component with respect to I^{SAL2} and a single ionic bond with respect to I^{SAL1}.

Therefore, the A→B *coordination bond* is the *covalent bond* component (eqs 19, 31, and 33) with respect to the ionic ($A^- + B^+$) SAL2 input reference:

$$N_{\text{coord}}(\text{P; SAL2}) = H(O^{\text{M}}|I^{\text{SAL2}}) = H(O^{A}I^{\text{SAL2}}) - H(I^{\text{SAL2}}) = H(O^{\text{M}}I^{\text{SAL2}}) = H(P) \quad (38)$$

This entropy function roughly measures the amount $N_{\text{CT}} = N_B - N_B{}^o = N_A{}^o - N_A$ of the $A^- \xrightarrow{\text{CT}} B^+$ *charge transfer* (CT).

Finally, we observe that, because of the independent character of the molecular output and alternative input probability schemes in the two-orbital model, the mutual information between the input and output distributions exactly vanishes (see eq 21):

$$H(O^{\text{M}}:I^{\text{M}}) = H(P) + H(P) - 2H(P) = 0, \quad \text{Scheme 3;}$$
$$H(O^{\text{M}}:I^{\text{SAL1}}) = 1 + H(P) - [1 + H(P)] = 0, \quad \text{Scheme 4;}$$
$$H(O^{\text{M}}:I^{\text{SAL2}}) = 0 + H(P) - H(P) = 0, \quad \text{Scheme 5.} \quad (39)$$

Application to a Model Transition State. Next we consider the three-OAO model of the symmetric transition state [A_1- - -B- - -A_2] (see Appendix), with atoms A_1, B, and A_2 contributing the *a*(↑), *b*(↓), and c(↑) OAOs, respectively, each occupied by a single electron in the SAL with the indicated spins.

Two independent variables control the model electron configuration. For example, one can select the electron population of the middle atom B, $q = q{\uparrow}_b + q{\downarrow}_b$, and its spin polarization, $\sigma = q{\uparrow}_b - q{\downarrow}_b$. In the Appendix we have listed the relevant expressions (eq A5) for the two-electron joint probabilities in the atomic (OAO) resolution, $\{P(ij) = P(i,j) = P(i,j;\, q,\sigma)\}$, which determine the joint distribution entropy $H(O^{\text{M}}I^{\text{M}}) = H(O^{\text{M}}I^{\text{M}};\, q,\sigma)$ of the model.

The UHF minimum basis set values of the controlling parameters in the collinear transition-state complex [H- - -H- - -H] ($R_{AB} = R_{BC}$ = 0.93 Å) are q = 0.972 au and σ = −0.203 au.[20] From the joint probabilities of eq A5, one then obtains $H(O^{\text{M}}I^{\text{M}}) = 3.07$ and $H(I^{\text{M}}) = 1.58$. Hence $N_{\text{cov}} = 1.49$ and $N_{\text{ion}} = 0.10$, giving rise to the total bond order

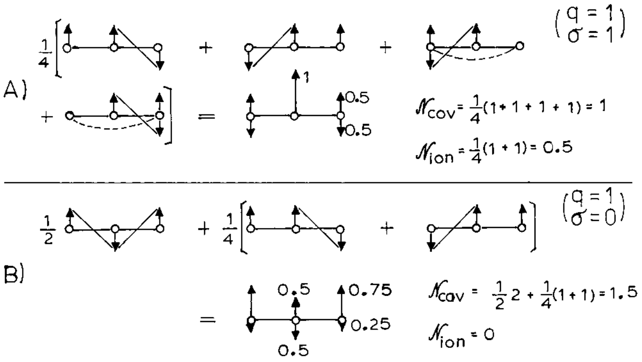


Figure 2. Electron configurations in the three-orbital model of a symmetric transition state (see Table 1) for the extreme spin polarizations of the middle atom, σ = 1, 0, and equal distribution of electrons among atoms, q = 1, and their resolutions into ensembles of the integer spin-population diagrams. This analysis shows that the overall covalent and ionic entropic bond multiplicities reflect the ensemble averages of the diagram elementary "bonds": covalent (spin paired electrons on neighboring atoms, solid lines) and ionic (ion pairs, broken lines).

TABLE 1: Information–Theoretic Predictions of the Overall Bond Multiplicities in the Three-Orbital Model *a*--*b*--*c* of the Symmetric Transition State [A_1- -B- -A_2] for the Fixed Populations $q_a = q_b = q_c = 1$ (au)

electronic configuration					bond orders	
σ	$q_b^{\uparrow}$	$q_b^{\downarrow}$	$q_a^{\uparrow} = q_c^{\uparrow}$	$q_a^{\downarrow} = q_c^{\downarrow}$	N_{cov}	N_{ion}
+1	1	0	0.5	0.5	1.04	0.55
+0.5	0.75	0.25	0.625	0.375	1.54	0.05
0	0.5	0.5	0.75	0.25	1.53	0.06
−0.5	0.25	0.75	0.875	0.125	1.18	0.41
−1	0	1	1	0	1	0.59

$$N = N_{\text{cov}} + N_{\text{ion}} = 1.59 \quad (40a)$$

The nonvanishing mutual information in the collinear H_3, $H(O^{\text{M}}:I^{\text{M}}) = 0.10$ (practically equal to the ionic conponent because $I^{\text{M}} \approx I^{\text{EP}}$), reflects the exchange correlation between the two spin-up electrons.

Let us now consider a few selected extreme configurations of the model. To simplify the problem, we fix an equal distribution of electrons among the three atoms, q = 1, for which

$$H(I^{\text{M}}) = H(I^{\text{EP}}) = \log_2 3 = N = N_{\text{cov}} + N_{\text{ion}} = 1.59 \quad (40b)$$

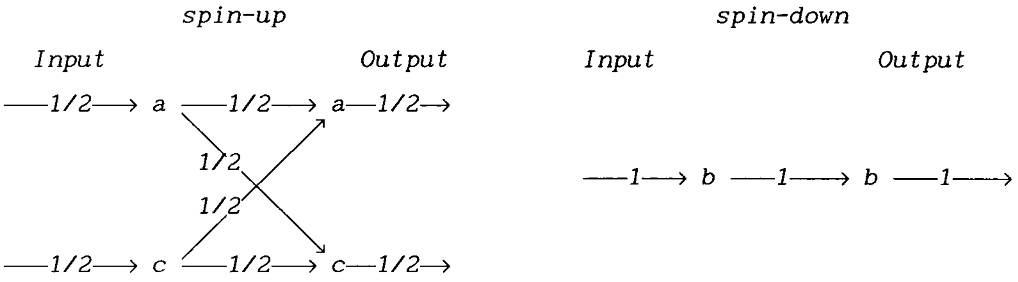
and examine how the changing spin polarization σ affects the proposed overall information-theoretic bond orders. We are particularly interested in the partitioning of the total bond order into the covalent and ionic components when the electronic structure changes as a function of this remaining degree of freedom for q = 1. The predictions are summarized in Table 1 and Figure 2.

We emphasize again that for such an equal distribution of electrons between atoms $I^{\text{M}} = I^{\text{EP}}$ the ionic bond multiplicity must be exactly equal to the mutual information between the molecular output and input probability schemes:

$$H(O^{\text{M}}:I^{\text{M}};\, q = 1, \sigma) = 2\,H(I^{\text{EP}}) - H(O^{\text{M}}I^{\text{M}};\, q = 1, \sigma) = N_{\text{ion}}(q = 1, \sigma)$$

The predicted bond orders of Table 1 show that the delocalization of electronic spins in such a triatomic model may

SCHEME 6



increase the overall bond-order measure in the transition-state complex in comparison to the (diatom + atom) bond order $N = 1$ of the two-orbital model. This effect has indeed been independently confirmed by our earlier prediction of the increased bond order in H_3, from the two-electron difference approach.[20]

In an attempt to rationalize these results, we have resolved in Figure 2 the effective (fractional) spin populations reported in Table 1, for the two illustrative [$q = 1$; $\sigma = 1, 0$] electron configurations. The effective spin populations are broken down into the corresponding ensembles of the integer spin-population diagrams, which reproduce the average atomic populations of the spin-up and spin-down electrons, reported in Table 1 and Figure 2. To conform to the spin assumption of the model, each diagram represents a possible distribution of the two spin-up electrons and a single spin-down electron (see the Appendix), with the diagram ensemble probability chosen in such a way that the required σ and q values, and thus the spin populations of Table 1, are exactly reproduced. In these diagrams we have used a solid line to connect the paired spins of electrons on the neighboring atoms, signifying elementary covalent bonds. The broken lines in the figure similarly connect ionic pairs, thus identifying elementary "ionic" interactions.

A reference to Figure 2 and Table 1 shows that the overall covalent and ionic bond orders N_{cov} and N_{ion} of Table 1 do indeed reflect the ensemble averages of such elementary spin-paired electrons and ionic interactions, respectively. This demonstration explains the increased ionicity of the first ($q = 1$, $\sigma = 1$) configuration (*A*), caused by the two ionic diagrams required to reproduce the average spin distribution in a molecule. Such ionic diagrams are missing in the second ($q = 1$, $\sigma = 0$)− configuration (*B*); this explains the relatively high value of the covalent bond order obtained in this case. The (*B*) configuration results roughly correspond to the H_3 transition state, which we discussed at the begining of this section. The entropic measures thus predict an increase in the global bond multiplicity relative to the (H_2 + H) value of $N(H_2) = 1$ by about a half-bond.

One should realize that the "covalent" and "ionic" diagrams of Figure 2 are related to the corresponding valence structures of the classical *valence-bond* (VB) theory. Indeed, as is explicitly shown in Figure 2, the present entropic approach based on the simultaneous two-electron probabilities in the atomic resolution measures a degree of an effective spin-pairing in a molecule. This is also the guiding principle of the VB aproach, where the paired spins are associated with chemical bonds.

The last ($q = 1$, $\sigma = -1$) example of Table 1 calls for an additional comment. This example generates the same average spin distribution as in SAL: $a(\uparrow) + b(\downarrow) + c(\uparrow)$. This does not imply, however, that this electron configuration has no extra electron delocalization in the system, because in the transition-state complex the two spin-up electrons are perfectly delocalized between peripheral orbitals *a* and *c*. The predicted covalent bond measure $N_{\mathrm{cov}} = 1$ reflects this very delocalization effect in the *a*−*b*−*c* molecular system.

At first sight the values of the ionic bond component reported in Table 1 are surprising in view of the assumed equal distribution of electrons among the three orbitals (atoms). One should realize, however, that there are differences in the separate distributions of the spin-up and spin-down electrons, as is indeed reflected by variations in the spin populations of the three orbitals in Table 1 and Figure 2. In fact, one could define separate, spin-resolved measures of the covalent and ionic entropy differences for the two spin orientations:

$$\bar{N}^{\sigma}_{\mathrm{cov}} = H(O_{\sigma}^{\mathrm{M}} I_{\sigma}^{\mathrm{M}}) - H(I_{\sigma}^{\mathrm{M}}),$$

$$\bar{N}^{\sigma}_{\mathrm{ion}} \equiv H(I_{\sigma}^{\mathrm{EP}}) - N^{\sigma}_{\mathrm{cov}} = H(I_{\sigma}^{\mathrm{EP}}) + H(I_{\sigma}^{\mathrm{M}}) - H(O_{\sigma}^{\mathrm{M}} I_{\sigma}^{\mathrm{M}}), \quad \sigma = \uparrow, \downarrow \tag{41}$$

Let us consider the last configuration in Table 1 as an illustrative example. In this case the separate probability networks for the two spin orientations are as shown in Scheme 6. These probabilities give the following entropies: $H(O_{\uparrow}^{\mathrm{M}} I_{\uparrow}^{\mathrm{M}}) = 2$; $H(I_{\uparrow}^{\mathrm{M}}) = 1$; $H(O_{\downarrow}^{\mathrm{M}} I_{\downarrow}^{\mathrm{M}}) = H(I_{\downarrow}^{\mathrm{M}}) = 0$; $H(I_{\uparrow}^{\mathrm{EP}}) = H(I_{\downarrow}^{\mathrm{EP}}) = -3(1/3)\log_2(1/3) = \log_2 3 = 1.59$, hence $\bar{N}^{\uparrow}_{\mathrm{cov}} = 1$ (delocalization of the spin-up electrons); $\bar{N}^{\downarrow}_{\mathrm{cov}} = 0$ (zero delocalization of β electron); $\bar{N}^{\uparrow}_{\mathrm{ion}} = 0.59$ (smaller asymmetry in the distribution of the spin-up electrons); $\bar{N}^{\downarrow}_{\mathrm{ion}} = 1.59$ (maximum asymmetry in the distribution of the spin-down electron), and hence $\bar{N}^{\sigma} = \bar{N}^{\sigma}_{\mathrm{ion}} + \bar{N}^{\sigma}_{\mathrm{cov}} = 1.\ 59$, $\sigma = \pm 1/2$. Indeed, weighting these spin-resolved bond orders in accordance with the probabilities of the spin-up and spin-down electrons in the system, $P\uparrow = 2/3$ and $P\downarrow = 1/3$, reproduces the overall bond order reported in the last row of Table 1:

$$\begin{aligned} N &= P\uparrow \bar{N}^{\uparrow} + P\downarrow \bar{N}^{\downarrow} = 1.59 \\ &= P\uparrow (\bar{N}^{\uparrow}_{\mathrm{cov}} + \bar{N}^{\uparrow}_{\mathrm{ion}}) + P\downarrow (\bar{N}^{\downarrow}_{\mathrm{cov}} + \bar{N}^{\downarrow}_{\mathrm{ion}}) \equiv \\ &\qquad N\uparrow + N\downarrow = 1.06 + 0.53 \\ &= (P\uparrow \bar{N}^{\uparrow}_{\mathrm{cov}} + P\downarrow \bar{N}^{\downarrow}_{\mathrm{cov}}) + (P\uparrow \bar{N}^{\uparrow}_{\mathrm{ion}} + P\downarrow \bar{N}^{\downarrow}_{\mathrm{ion}}) \equiv \\ &\qquad \bar{N}_{\mathrm{cov}} + \bar{N}_{\mathrm{ion}} = 0.67 + 0.92 \end{aligned}$$

***π* Bonds in Benzene and Butadiene.** Let us examine the overall π bond order in benzene, originating from pairing the six $2p_{\pi}$ electrons contributed by the carbon atoms $\{C_i, i = 1, 2, ..., 6\}$ ordered consecutively in the ring. In the present qualitative analysis we use the three occupied π orbitals from the simple Hückel MO theory, which generate the following CBO matrix elements of π electrons:

$$q_i = P_{i,i} = 1; \quad P_{i,i+1} = 2/3; \quad P_{i,i+2} = 0; \quad P_{i,i+3} = -1/3 \tag{42}$$

These give rise to the following RHF Γ-matrix elements, $\{\Gamma(i,j) = q_i q_j - P_{i,j}^2/2\}$

$$\Gamma(i,i) = 1/2; \quad \Gamma(i,i+1) = 7/9; \quad \Gamma(i,i+2) = 1; \quad \Gamma(i,i+3) = 17/18 \tag{43}$$

and the corresponding two-electron joint probabilities $\{\mathcal{P}(ij) = \Gamma(i,j)/30\}$:

$$\mathcal{P}(ii) = 1/60; \quad \mathcal{P}[i(i+1)] = 7/270; \quad \mathcal{P}[i(i+2)] = 1/30; \quad \mathcal{P}[i(i+3)] = 17/540 \tag{44}$$

The relevant entropies of the atomic probabilities are

$$\mathcal{N} = \mathcal{N}_{\text{cov}} + \mathcal{N}_{\text{ion}} = H(\mathcal{I}^{\text{M}}) = H(\mathcal{I}^{\text{EP}}) = \log_2 6 = 2.59, \quad H(\mathcal{O}^{\text{M}}\mathcal{I}^{\text{M}}) = 5.14 \tag{45a}$$

They generate the following predictions of the overall π-bond multiplicities in the benzene carbon ring:

$$\mathcal{N}_{\text{cov}} = 5.14 - 2.59 = 2.55; \; \mathcal{N}_{\text{ion}} = 2.59 - 2.55 = 0.04 \tag{45b}$$

The entropic measure of the π bond order thus predicts, on average, 2.59/6 = 0.43 bond multiplicity per each of the six bonds between nearest neighbors in the carbon ring. This value should be compared with the intuitive chemical value of a half π bond in the benzene ring, the Wiberg[10] result $P_{i,i+1}^2 = 0.44$, and the prediction of the finite difference approach $\mathcal{V}_{i,i+1} = 0.45$.[21]

The nonvanishing, residual ionic component for the equal distributions of electrons between atoms should not come as a surprise (see also Table 1 and Figure 2), because it also includes a contribution due to spin pairings of two electrons located on the same atom.

As a final illustrative example, we examine the four π electrons in butadiene, occupying the two lowest Hückel molecular orbitals obtained from the four carbon 2p$_\pi$ orbitals, again numbered consecutively in the chain. This simple LCAO MO theory predicts the following CBO matrix elements

$$q_i = P_{i,i} = 1, P_{1,2} = P_{3,4} = 0.89, P_{2,3} = 0.45 = -P_{1,4}, \quad P_{1,3} = P_{2,4} = 0$$

and hence the following probabilities in atomic resolution:

$$p_i = 1/4, \mathcal{P}(ii) = 1/24, \quad i = 1, 2, 3, 4;$$

$$\mathcal{P}(12) = 1/20 = \mathcal{P}(34), \quad \mathcal{P}(23) = 3/40 = \mathcal{P}(14), \quad \mathcal{P}(13) = 1/12 = \mathcal{P}(24)$$

They give rise to the overall π bond order $\mathcal{N} = \log_2 4 = 2$, which includes the dominating covalent component, $\mathcal{N}_{\text{cov}} = 3.94$, and a small ionic contribution, $\mathcal{N}_{\text{ion}} = 0.06$. The above global π bond multiplicity index reproduces both the intuitive chemical expectation and the overall bond order obtained from the summation of the diatomic Wiberg indices:

$$\mathcal{N} = \mathcal{N}^{\text{w}} \equiv \sum\sum_{i<j} P_{i,j}^2 = 2 \tag{46}$$

Bond Entropies

Direct Bond Measure. To obtain a specific diatomic bond multiplicity, $\mathcal{N}_{\text{AB}}$, from the overall entropic bond order $\mathcal{N}$ of the preceding sections, one would have to introduce some extra assumptions about how to partition the atomic contributions among diatomic multiplicities. This weakness of the above overall approach in comparison with, e.g., the Coulson (C)[5] and Wiberg (W)[10] approaches, which associate the (A−B) bond multiplicity with the coresponding sums over the OAO of the two atoms

$$\mathcal{N}_{\text{A,B}}^{\text{C}} = \sum_{i\in\text{A}}^{\text{OAO}} \sum_{j\in\text{B}}^{\text{OAO}} P_{i,j}, \quad \mathcal{N}^{\text{w}} = \sum_{i\in\text{A}}^{\text{OAO}} \sum_{j\in\text{B}}^{\text{OAO}} P_{i,j}^{\;2} \tag{47}$$

respectively, can be remedied only by linking the entropic orbital contribution $\mathcal{N}_{i,j}$ of the overall diatomic index

$$\mathcal{N}_{\text{A,B}} = \sum_{i\in\text{A}}^{\text{OAO}} \sum_{j\in\text{B}}^{\text{OAO}} \mathcal{N}_{i,j} \tag{48}$$

directly to the entropy contribution from the corresponding matrix element $\Gamma(i,j)$ or the related orbital joint probability $\mathcal{P}(i,j)$: $\mathcal{N}_{i,j} = \mathcal{N}_{i,j}[\Gamma(i,j)]$.

When designing such a direct, information−theoretic measure of the bond multiplicity, one would also aim at improving the predicted bond orders for some configurations in the three-orbital model. Consider for example the configuration $(A) = (q = 1, \sigma = 1)$ in Figure 2, in which the terminal atoms have the perfectly paired spin-up and spin-down electron populations, while the localized spin-up electron of the middle atom does not participate in any delocalization, i.e., covalency. This observation suggests that a realistic multiplicity index of the localized covalent bond should indicate in this case a single $a-c$ bond and the zero $(a-b)$ and $(b-c)$ bonds. Similarly, for the last configuration $(q = 1, \sigma = -1)$ of Table 1, we have detected that the resulting spin distribution is identical to that of the SAL. Thus, to have the bond indices, which reflect changes in distribution of electrons relative to the SAL, one would intuitively expect in this case no bonds for all pairs of orbitals.

Bond Entropy Function in the Two-Orbital Model. In our search for an appropriate candidate for the bond entropy function, we first consider the simplest case of the interactions between two OAOs. Clearly, the new entropy function should retain the general features of the H(P) and $\mathcal{V}$(P) plots of Figure 1, which qualitatively agree with chemical expectations.

Consider the following *bond entropy function*

$$\mathcal{N}_{a,b}[\Gamma(a,b)] = -\Gamma(a,b)\log_2\Gamma(a,b) - \Gamma(b,a)\log_2\Gamma(b,a) = -2\,\Gamma(a,b)\log_2\Gamma(a,b) \equiv \mathcal{N}(\text{P}) \tag{49}$$

of the model off-diagonal element of the Γ matrix in the atomic resolution:

$$\Gamma(a,b) = \Gamma(b,a) = q(2-q)/2 = 2\text{P}(1-\text{P}) \equiv \Gamma_{a,b}(\text{P}) \tag{50}$$

As shown in Figure 1, the bond entropy function $\mathcal{N}$(P) retains the correct qualitative features of the $H(P)$ and $\mathcal{V}(P)$ plots, predicting zero covalent bonds for the lone-pair configurations $q = (0, 2)$, for which $P_{a,b} = 0$, and a single covalent bond for $q = 1$, when $P_{a,b} = 1$. This function deviates more substantially from the Wiberg quadratic estimate $\mathcal{V}$(P) than does the binary entropy function H(P), predicting much faster growth of the entropic covalent bond order with increasing delocalization of the lone-pair electrons toward the orbital of the bonding partner.

Performance of the Bond Entropy in the Three-Orbital Model. As we have argued above, this model, exhibiting the spin polarization degree of freedom, provides a crucial test of the applicability of the bond-entropy function. Using the explicit

TABLE 2: Bond-Multiplicity Predictions from the Bond Entropies in the [*a*--*b*--*c*] Model for the Electronic Configurations of Table 1

σ	$\Gamma_{a,b}$	$\Gamma_{a,c}$	$\mathcal{N}_{a,b}$	$\mathcal{N}_{a,c}$	$\mathcal{N} = 2\mathcal{N}_{a,b} + \mathcal{N}_{a,c}$	$\mathcal{N}_{cov}$[a]
+1	1	0.5	0	1	1	1.03
+0.5	0.81	0.72	0.49	0.68	1.66	1.54
0	0.75	0.87	0.62	0.34	1.58	1.52
−0.5	0.81	0.97	0.49	0.09	1.06	1.18
−1	1	1	0	0	0	1

[a] Overall covalent bond multiplicities from Table 1 (for comparison).

expressions for the off-diagonal elements of the Γ matrix (eq A4 in Appendix) gives the following expressions for the $q = 1$ constrained electronic configurations:

$$\Gamma_{a,b}(1, \sigma) = (3 + \sigma^2)/4; \quad \Gamma_{a,c}(1, \sigma) = [7 - \sigma(\sigma + 2)]/8 \tag{51}$$

In Table 2 we report the corresponding bond entropies

$$\mathcal{N}_{i,j}(1, \sigma) = -2\Gamma_{i,j}(1, \sigma) \log_2 \Gamma_{i,j}(1, \sigma), \quad (i, j) = (a, b), (b, c) \tag{52}$$

These results clearly show that the bond entropy measure has indeed remedied the previously identified problems with the global entropy measure for the first and last configurations, while generally reproducing the $\mathcal{N}_{cov}$ values for the remaining configurations. With the purely molecular bond-entropy concept, we have thus achieved a full conformity with the intuitive chemical expectations. Moreover, from the bond-entropy function we have a direct multiplicity measure associated with each bond, without an arbitrary partitioning of the global bond order into effective diatomic contributions.

We conclude this section with the bond multiplicities for the earlier-reported ab initio electronic structure parameters of H_3. Using eqs A4 and 52 gives

$$\Gamma_{a,b}(0.972, -0.203) = 0.75; \quad \Gamma_{a,c}(0.972, -0.203) = 0.95;$$
$$\mathcal{N}_{a,b}(0.972, -0.203) = 0.63; \quad \mathcal{N}_{a,c}(0.972, -0.203) = 0.14 \tag{53}$$

These bond orders amount to $\mathcal{N} = 2\mathcal{N}_{a,b} + \mathcal{N}_{a,c} = 1.41$, a value close to the previous result $\mathcal{N}_{cov} = 1.52$.

This increase in bond multiplicity of the transition-state complex relative to the (H_2 + H) limit, $\mathcal{N}(H_2) = 1$, has also been predicted by our earlier multiconfigurational SCF calculations, using a basis set that includes the polarization functions MC + POL.[20] The corresponding QVI values for the two SAL reference states, identified by the two spin orientations of electrons on *a*, *b*, and *c* orbitals, respectively, are as follows:[20]

$$\mathcal{V} = 1.21; \quad \text{SAL: up + down + up;}$$
$$\mathcal{V} = 1.31; \text{SAL: up + up + up}$$

Therefore, the above information−theoretic predictions for the model of the H_3 collinear transition state provide additional validation of the bond-entropy concept as an adequate measure of the covalent bond order in the bond-forming−bond-breaking process.

***π* Bonds in Benzene and Butadiene.** Next we calculate the diatomic π bond orders in the benzene ring, using the Hückel Γ matrix elements of eq 43. They predict the following bond entropies:

$$\mathcal{N}_{i,i+1} = 0.56; \quad \mathcal{N}_{i,i+2} = 0; \quad \mathcal{N}_{i,i+3} = 0.16 \tag{54}$$

This result agrees well with the chemical value of a half-bond between the neighboring carbons in the ring. It also correctly predicts a much lower order between two carbons in the mutual para positions, and a vanishing π bond between two carbons in the mutual meta positions. This finding is in full conformity with the Wiberg[10] results (see eq 42)

$$P^2_{i,i+1} = 4/9 = 0.44; \quad P^2_{i,i+1} = 0; \quad P^2_{i,i+3} = 1/9 = 0.11 \tag{55}$$

and with our earlier predictions from the two-electron difference approach (QVI):[21]

$$\mathcal{V}_{i,i+1} = 0.45; \quad \mathcal{V}_{i,i+2} = 0.00; \quad \mathcal{V}_{i,i+3} = 0.12 \tag{56}$$

As we have observed previously,[21] this result can be physically justified within the VB theory. Namely, the meta−meta bond can be achieved only through the diradical valence structure, in which the π electrons of the two carbons are localized, as in the Wheland intermediate. No such localization is required for the para−para bond. The diradical configuration is thus expected to participate much less in the ground-state wave function.

The bond entropies obtained for the π bond system in butadiene (Hückel theory) are as follows:

$$\mathcal{N}_{1,2} = 0.88; \quad \mathcal{N}_{1,3} = 0; \quad \mathcal{N}_{2,3} = \mathcal{N}_{1,4} = 0.27 \tag{57}$$

They should be compared with the corresponding Wiberg indices:

$$P_{1,2}{}^2 = 0.80; \quad P_{1,3}{}^2 = 0; \quad P_{2,3}{}^2 = P_{1,4}{}^2 = 0.20 \tag{58}$$

Thus, in both approaches the peripheral π bonds are predicted to be much stronger than the central bond of the carbon chain, in accordance with the familiar chemical interpretation.

Conclusion

In interpreting the electronic structure of molecular systems in *chemical* terms, the intuitive concepts of both *atoms in molecules* and *chemical bonds*, which connect AIM in a generalized structural formula of the system under consideration, are essential. In the present and previous[26] studies, we have demonstrated that both these concepts can be established within the *information theory* using appropriate entropy functions of both the molecular (or isolated atom) electron densities and the associated probabilities in the atomic discretization. These concepts are not defined uniquely, as is the case with many chemical ideas. Nevertheless, in this work we have achieved, particularly in the case of the bond-entropy function, a high degree of agreement between the information−theoretic bond orders, the chemical intuitive values, and the previous quantum mechanical measures for all models considered in this study.

Clearly, a more extensive numerical testing of these novel entropic concepts is required, for both typical molecules and "controversial" systems for which no apparent chemical intuition is available. However, a degree of success in a semiquantitative reproduction of the "established" chemical bond multiplicities, which we have already achieved in the present exploratory analysis, strongly suggests the relevance and importance of the proposed information−theoretic bond orders as new tools for a supplementary analysis in the familiar chemical terms of numerical results from the standard quantum-chemical computations.

The present analysis can be extended in several directions. For example, in the future one could examine the role of the exchange-only contribution to the joint two-electron probabilities, in an attempt to relate the present entropic bond orders more directly to the Lewis classical picture of bonding and to the pair-population analysis involving the domain-averaged Fermi holes.[33] Also, the multicenter bonding indices[16,18b,33] could be tackled within the information theory. More specifically, the three-center bonds would require the joint three-electron probabilities and the related conditional probabilities, e.g., the AIM-resolved joint two-electron probabilities, given the atomic location of a third electron. The average entropies for such three-atom events are also directly available within the information theory.[29]

The present analysis supports our earlier conjecture,[17] that the bond multiplicity and valence concepts are "entropic" in character, i.e., they are defined in the perspective complementary to the familiar energetical description of the Schrödinger equation. The latter follows from the energy variational principle for constant entropy defined by the fixed, say single occupations of the molecular SO: $n_\alpha = 1$, $\alpha = 1, 2, ..., N$. Obviously, this uniform SO occupation pattern of the Pauli principle, and the associated value of electron occupational entropy, follows directly from the maximum SO occupational entropy principle in the selected set of the occupied orbitals.

Therefore, in the electronic structure theory we indeed encounter an interplay between the supplementary entropic and energetical descriptions. This is particularly true in the density functional theory,[24] where, e.g., the Levy constrained search construction[34] of the universal part of the density functional for energy[24] can be classified as entropic because the search is carried out for the fixed electron density ρ, i.e., the constant energy. We believe that we have explicitly demonstrated, in the present development, that the chemical concept of the bond multiplicity does belong to the entropic "world" of the information theory.

Acknowledgment. This work was supported by a grant from the State Committee for Scientific Research in Poland (Grant No. 3TO9A 14119).

Appendix: Summary of the Three-Orbital Model

Consider the model *a*- - -*b*- - -*c*, consisting of the three (real) OAOs, $\chi_{A_1} = a$, $\chi_B = b$, and $\chi_{A_2} = c$, of a symmetrical (collinear) transition state (TS) of the bond-breaking–bond-forming atom exchange reaction:

$$A_1 + B{-}A_2 \rightarrow [A_1\text{- - -}B\text{- - -}A_2] \rightarrow A_1{-}B + A_2; \quad a \in A_1;\ b \in B;\ c \in A_2 \qquad (A1)$$

The three UHF MOs, which are occupied in the symmetrical TS complex, are:

$$\psi_1^{\uparrow}(\mathbf{r}) = \alpha\, a(\mathbf{r}) + \beta\, b(\mathbf{r}) + \alpha\, c(\mathbf{r}); \quad \psi_2^{\uparrow}(\mathbf{r}) = \mu[a(\mathbf{r}) - c(\mathbf{r})];$$
$$\psi_1^{\downarrow}(\mathbf{r}) = \gamma\, a(\mathbf{r}) + \delta\, b(\mathbf{r}) + \gamma\, c(\mathbf{r}) \qquad (A2)$$

These molecular orbitals define the corresponding UHF Slater determinant $\Psi(1, 2, 3) = |\overset{+}{\psi}{}_1^{\uparrow}\ \overset{-}{\psi}{}_1^{\downarrow}\ \overset{+}{\psi}{}_2^{\uparrow}|$

Expressing the MO coefficients in terms of the two independent parameters controlling the electron configuration in this system, the middle atom electron population q and its spin polarization σ

$$q = q_b = P_{b,b} = P_{b,b}^{\uparrow} + P_{b,b}^{\downarrow}, \quad \sigma = \sigma_b = P_{b,b}^{\uparrow} - P_{b,b}^{\downarrow} \qquad (A3)$$

gives the following expressions for the elements of the UHF Γ-matrix in McWeeny's normalization
$\Gamma(i,j) = P_{i,i}P_{j,j} - (P_{i,j}^{\uparrow})^2 - (P_{i,j}^{\downarrow})^2 = \Gamma_{i,j}(q,\sigma)$:

$$\Gamma_{a,a}(q,\sigma) = [(q-2)(q-4) - \sigma(\sigma-2)]/8 = \Gamma_{c,c}(q,\sigma),$$
$$\Gamma_{b,b}(q,\sigma) = (q^2 - \sigma^2)/2;$$
$$\Gamma_{a,b}(q,\sigma) = q - (q^2 - \sigma^2)/4 = \Gamma_{b,c}(q,\sigma);$$
$$\Gamma_{a,c}(q,\sigma) = [(8-q)(2-q) - \sigma(\sigma+2)]/8 \qquad (A4)$$

Multiplying these expressions by the renormalization factor $[3(3 - 1) = 6]^{-1}$ finally gives the corresponding expressions for the four independent elements of the symmetric matrix grouping the simultaneous two-electron probabilities $P(i,j)$ in the atomic resolution (eq 12):

$$P\,(a,a) = [(q-2)(q-4) - \sigma(\sigma-2)]/48;$$
$$P\,(a,b) = [q(4-q) + \sigma^2]/24;$$
$$P\,(a,c) = [(q-8)(q-2) - \sigma(\sigma+2)]/48;$$
$$P\,(b,b) = (q^2 - \sigma^2)/12 \qquad (A5)$$

References and Notes

(1) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(2) Mulliken, R. S. *J. Chem. Phys.* **1935**, *3*, 573; **1955**, *23*, 1833.

(3) Moffitt, W. *Proc. R. Soc. London* **1951**, *210A*, 245.

(4) Pauling, L. *The Nature of the Chemical Bond*; Cornell: Ithaca, 1960.

(5) Coulson, C. A. *Valence*, 2nd ed.; Oxford: New York, 1961; see also: McWeeny, R. *Coulson's Valence*, 3rd ed.; Oxford: New York, 1979.

(6) Bader, R. F. W. *An Introduction to the Electronic Structure of Atoms and Molecules*; Clarke: Toronto, 1970. *Atoms in Molecules*; Oxford: New York, 1994. *Chem. Rev.* **1991**, *91*, 893.

(7) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

(8) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

(9) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

(10) Wiberg, K. *Tetrahedron* **1968**, *24*, 1093.

(11) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, *838*, 2273.

(12) Gopinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *63*, 497, 511. Jug, K.; Gopinathan, M. S. In *Theoretical Models of Chemical Bonding*, Vol. 2; Maksić, Z. B., Ed.; Springer-Verlag: Berlin, 1990; p 77. Sannigrachi, A. B. *Adv. Quantum Chem.* **1992**, *52*, 307.

(13) Giambiagi, M.; Giambiagi, M. S.; Grempel, D. R.; Heynman, C. D. *J. Chim. Phys.* **1974**, *72*, 15.

(14) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270; **1984**, *110*, 440.

(15) Ciosłowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(16) Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1990**, *173*, 569. Kar, T.; Marcos, E. S. *Chem. Phys. Lett.* **1992**, *192*, 14. Sannigrachi, A. B.; Kar, T. *J. Mol. Struct.* (THEOCHEM) **2000**, *496*, 1.

(17) Nalewajski, R. F.; Köster, A. M.; Jug, K. *Theor. Chim. Acta* **1993**, *85*, 463.

(18) Nalewajski, R. F.; Mrozek, J. (a) *Int. J. Quantum Chem.* **1994**, *51*, 187. (b) **1996**, *57*, 377.

(19) Ángyán, J. G.; Loos, M.; Mayer, I. *J. Phys. Chem.* **1994**, *98*, 5244.

(20) Nalewajski, R. F.; Formosinho, S. J.; Varandas, A. J. C.; Mrozek, J. *Int. J. Quantum Chem.* **1994**, *52*, 1153.

(21) Nalewajski, R. F.; Mrozek, J.; Mazur, G. *Can. J. Chem.* **1996**, *74*, 1121.

(22) Nalewajski, R. F.; Mrozek, J.; Michalak, A. *Int. J. Quantum Chem.* **1997**, *61*, 589. Nalewajski, R. F.; Michalak, A. *J. Phys. Chem.* **1996**, *100*, 20076. Mrozek, J.; Nalewajski, R. F.; Michalak, A. *Pol. J. Chem.* **1998**, *72*, 1779.

(23) Hartree, D. R. *Proc. Cambridge Philos. Soc.* **1928**, *24*, 328. Fock, V. A. *Z. Phys.* **1930**, *15*, 126.

(24) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140A*, 1133. Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136B*, 864.

(25) Callen, H. B. *Thermodynamics: An Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics*; Wiley: New York, 1960.

(26) Nalewajski, R. F.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 8879; *J. Phys. Chem. A*, submitted.

(27) Shannon, C. F. *Bell System Technol. J.* **1948**, *27*, 379, 623. Kullback, S. *Information Theory and Statistics*; Wiley: New York, 1959. Mathai, A. M.; Tathie, P. N. *Basic Concepts in Information Theory and Statistics*; Wiley: New York, 1975.

(28) Kullback, S.; Leibler, R. A. *Ann. Math. Stat.* **1951**, *22*, 79.

(29) Pfeiffer, P. E. *Concepts of Probability Theory*; Dover: New York, 1978.

(30) Sears, S. B.; Parr, R. G.; Dinur, U. *Isr. J. Chem.* **1980**, *19*, 165.

(31) Nalewajski, R. F.; Loska, R. *Theor. Chem. Acc.*, in press.

(32) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 328. McWeeny, R. *Methods of Molecular Quantum Mechanics*; Academic: London, 1989.

(33) Ponec, R.; Strnad, M. *Int. J. Quantum Chem.* **1994**, *50*, 43. Ponec, R.; Uhlik, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *391*, 159. Bochicchio, R.; Ponec, R.; Lain, L.; Torre, A. *J. Phys. Chem. A* **1998**, *102*, 7176.

(34) Levy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6062.