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REGULAR ARTICLE

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Reduced communication channels of molecular fragments and their entropy/information bond indices

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Abstract A *reduction* of the molecular "*communication channel*" in atomic resolution, which generates the entropy/information indices of the system chemical bonds, is performed by combining several atomic *inputs* and/or *outputs* into a single unit representing a collection of bonded atoms. The implications of such fragment-reduced communication channels for gaining both the *internal* (intra-subsystem) and *external* (inter-subsystem) bond-indices are examined. The entropy/information quantities of the reduced channels of molecular subsystems are proposed as descriptors of their information bond "order" and its covalent/ionic composition. These predictions are compared with the bond indices resulting from the molecular orbital (MO) theory. The rules for combining the subsystem entropy/information data into the corresponding global quantities describing the system as a whole are derived and tested. The so-called complementary reductions are used to formulate the exact *combination rules* for the molecular entropy/information bond indices. Applications to the three-orbital model and π-bond systems (butadiene and benzene) in the Hückel theory approximation are reported and used to illustrate the proposed concepts and techniques. The subsystem bond-order conservation and a competition between its ionic and covalent contributions are discussed. In contrast to the familiar MO bond indices, the entropic descriptors of molecular fragments are shown to exhibit a remarkable degree of equalization, thus emphasizing the information *equilibrium* of the ground-state distributions of electrons.

Keywords Chemical bond descriptors · Combination rules for entropic bond indices · Communication systems · Electronic structure theory · Entropy/information bond descriptors · Information theory · Molecular fragments · Reduced channels

This contribution is dedicated to Prof. Karl Jug on the occasion of his 65th birthday.

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1 Introduction

Information theory (IT) [1–5] has recently been applied to describe the electronic structure of molecules [6–15]. For example, it has been used to probe the promoted states of bonded atoms [6, 7, 9, 11, 12] as well as to diagnose the chemical bonds [7, 12–15] and interactions between reactants [7, 12b]. These applications have demonstrated the potential of the IT approach in extracting the *chemical* interpretation of the calculated molecular electron distributions. The theory allows one to treat various stages of the promolecular [16] density reconstruction in chemical processes, intermediate and final. The Hirshfeld [16] subsystems have been shown to represent the unique, *equilibrium* fragments of the molecule [6–9], which locally equalize their information-distance densities at the corresponding values for the system as a whole and give rise to the entropy deficiency additivity [6b–8, 12]. The unbiased, common sense "*stockholder*" principle has been justified using the locally constrained variational principles of both the global Shannon [2] and local Fisher [1] information-distance measures [6, 8c, 12a,b]. The missing-information [5] and the Shannon [2] entropy displacement densities of the stockholder *atoms-in-molecules* (AIM) have also been related [12] to the molecular density difference function, which uses the same promolecular reference as do stockholder atoms and is widely used by theoretical chemists in their interpretation of charge redistribution due to chemical bonds. With this development, the surprisal [5] function of the molecular electron density, which determines the density per electron of the entropy deficiency functional, has been related to the density difference function, thus providing the latter a novel missing-information interpretation [12a].

The *charge-transfer* (CT) affinities, representing the generalized forces driving changes in the electronic structure of the donor-acceptor reactive systems, have also been introduced [7c, 12b]. They combine the familiar Fukui function [17] response properties of molecular fragments (derivatives of the system energy) [18] with the corresponding information-distance densities (derivatives of the system missing information) [12b], thus providing a more complete descriptor of reactants. In the density-constrained ("*vertical*") processes, which play a vital role in the chemical interpretation of the computed results, the CT affinities have been shown to identically vanish for the unbiased fragments of the molecular one-electron distribution [12b]. A generalization of the stockholder principle to a division of the simultaneous many-electron probabilities has been given [7] and differences between the Hirshfeld AIM densities and effective one-electron distributions resulting from the stockholder partition of the molecular two-electron densities have been explored [12f].

The energy and entropy deficiency criteria for the equilibrium distribution of electrons in molecules and their fragments have been examined [6–8]. The effective external potential representability of the molecular fragment densities have also been discussed within the AIM resolved DFT [6b, 7c]. It has been argued, that the well-behaved densities of the embedded molecular fragments can be viewed as representing separate (free, non-interacting) subsystems defined by the effective external potential combining the nuclear potentials of the remaining fragments and the appropriately defined embedding electronic term, in the spirit of the Kohn-Sham theory [19]. Therefore, each manipulation performed on the Hirshfeld atomic density can in principle be interpreted as its ground-state response to the corresponding displacement in the subsystem effective external potential. Moreover, a given set of the intermediate (non-equilibrium) fragment densities can be attributed in this way an equilibrium-state interpretation, with the effective external potentials of subsystems providing the constraints responsible for the system displacement from its ground-state equilibrium, which also characterizes the molecule as a whole. This is vital for a thermodynamic-like interpretation of reconstructions of the electron distributions in typical molecular processes [6b, 7c, 8].

An important part of the chemical understanding of molecules is an adequate indexing of multiplicities ("orders") of the chemical bonds [10, 13–15, 20, 21]. These AIM *connectivities* define a *"transmission" network*, through which the information contained in the electron probability distributions can be transferred throughout the molecule [13]. The electron delocalization throughout this system of chemical bonds changes the promolecular, *input* "*signal*" of the atomic allocations of electrons. It has also been demonstrated [13–15] that the theory of communication systems [2–4] can be used to generate the entropy/information descriptors of the chemical bond multiplicity and its covalent/ionic composition.

Chemistry is the science about molecules and their fragments. Therefore, besides the global bond indices, characterizing the overall bond multiplicity and its total covalent/ionic components in the molecular system as a whole [13–15], of interest in chemistry are also the entropy/information characteristics of various molecular subsystems, i.e., groups of bonded atoms. It is the main purpose of this work to approach this classical problem of chemistry within the *communication theory* of the chemical bond [13–15]. It is based upon the molecular one- and two-electron probabilities in atomic resolution: the row vector $\boldsymbol{P} = \{P_m = \sum_n P_{m,n}\}$ grouping the atomic condensed one-electron probabilities, of finding an electron of the molecule M on the specified bonded atom m, and the square matrix $\mathbf{P} = \{P_{m,n}\}$ of the condensed joint two-electron probabilities, of simultaneously finding in M one electron on atom m, and another electron on atom n. The theory views the molecular system as the "communication" channel, in which "signals" of the electron allocations to constituent atoms are propagated from the molecular (or "promolecular") input ("source"), determined by the bonded atoms of the molecule (or the free atoms of the "promolecular" reference state), to the molecular output ("receiver"). The channel transmission network is determined by the system AIM-resolved conditional probabilities, which reflect the electron delocalization via the chemical bonds in M.

In what follows, we shall denote by $\mathbf{A}$ and $\mathbf{A}^0$ the atomic inputs of the molecule and its atomic "promolecule", respectively, while $\mathbf{B}$ will be used to denote the atomic outputs in the molecule. Therefore, the molecular input and output probabilities $\boldsymbol{P}(\mathbf{A}) = \boldsymbol{P}(\mathbf{B}) = \boldsymbol{P}$, while the promolecular input $\boldsymbol{P}(\mathbf{A}^0) = \boldsymbol{P}^0 = \{P_m^0\}$ groups the condensed one–electron probabilities in a collection of free constituent atoms shifted to their actual positions in M, which defines the (isoelectronic) *promolecule* M^0, a standard reference for calculating the density difference function and determining the "stockholder" AIM of Hirshfeld [16].

Thus, a propagation of the input signals throughout the molecule is in accordance with the molecular conditional two-electron probabilities $\mathbf{P}(\mathbf{B}|\mathbf{A}) = \{P(n|m) = P_{m,n}/P_m\} \equiv \mathbf{P}(\boldsymbol{n}|\boldsymbol{m})$, of finding an electron on atom n in the molecule, when it is already known beforehand that another (reference) electron has been located on atom m. The electron delocalization is responsible for the effective "noise" affecting the transmission of the atom-assignment signals and the flow of information through the molecular communication system. The average *conditional entropy* of the molecular output probabilities given the molecular input distribution of electrons,

$$S(\mathbf{B}|\mathbf{A}) = -\sum_{m\in M}\sum_{n\in M} P_{m,n}\log P(n|m) = -\sum_{m\in M}\sum_{n\in M} P_{m,n}\log[P_{m,n}/P_m] \equiv S(\boldsymbol{n}|\boldsymbol{m}), \quad (1)$$

and the average *mutual information* in the promolecular input and molecular output probability distributions,

$$I(\mathbf{A^0}|\mathbf{B}) = -\sum_{m\in M}\sum_{n\in M} P_{m,n}\log[P(m|n)/P_m^0] = \sum_{m\in M}\sum_{n\in M} P_{m,n}\log\{[P_{m,n}/P_m^0 P_0]\} \equiv I(\boldsymbol{m}^0:\boldsymbol{n}), \quad (2)$$

provide in IT the basic descriptors of the molecular communication system [13–15]. The former quantity represents the average amount of the uncertainty about the occurrence of the molecular output events, given that the molecular input events are known to have occurred, i.e., a degree of the communication noise. It has been argued recently [13–15] that it provides the entropic measure of the overall bond covalency in the molecule. The latter quantity measures the complementary aspect of the molecular communication network: the amount of information flowing through the channel. It has been identified [13–15] as the information measure of the overall bond ionicity in the molecule. The sum of these two bond components, $N(\mathbf{A};\mathbf{B}) = S(\mathbf{B}|\mathbf{A}) + I(\mathbf{A}^0 : \mathbf{B})$, provides the overall information index of all chemical bonds in M:

$$\begin{aligned} N(\mathbf{A};\mathbf{B}) &= S(\mathbf{B}|\mathbf{A}) + I(\mathbf{A^0} : \mathbf{B}) \\ &= \sum_{m\in M}\sum_{n\in M} P_{m,n}\log[P_m/(P_m^0 P_n)] \equiv N(\boldsymbol{m};\boldsymbol{n}), \\ &= \sum_{m\in M} P_m \log(P_m/P_m^0) - \sum_{n\in M} P_n \log P_n \\ &\equiv \Delta S(\boldsymbol{P}|\boldsymbol{P}^0) + S(\boldsymbol{P}) \equiv \Delta S(\mathbf{B}|\mathbf{A^0}) + S(\mathbf{B}), \end{aligned} \quad (3)$$

where $\Delta S(\boldsymbol{P}|\boldsymbol{P}^0)$ stands for the entropy deficiency (missing information, cross-entropy) [5] between the molecular and promolecular atomic probabilities and $S(\boldsymbol{P})$ denotes the Shannon entropy [2] of the molecular one-electron probabilities in AIM resolution [13–15].

A distinction between the electron-sharing and coordination (pair-sharing) bonds has also been explored and the illustrative applications to simple orbital models and π bonds in butadiene and benzene in the Hückel theory have been given [13–15]. The total bond-order conservation and a competition between its ionic and covalent components have been investigated, and the average entropies of the local "stockholder" communication channel [15], generated by the Hirshfeld partition of molecular electron densities, have been proposed as complementary information descriptors of the chemical bonds [12e]. These entropy/information bond indices from the communication theory complement the bond-order measures from the molecular orbital (MO) theory [20]. Clearly, the bonding patterns reflected by these two sets of bond descriptors, having different physical origins, may differ from each other. One of the goals of this work is to examine in more detail similarities and differences in bond-multiplicity measures emerging from the MO and entropy/information bond characteristics.

It is also of interest to examine how various levels of resolution of the electron distributions in the molecule, all derived from the canonical atomic resolution of all probability schemes describing the molecular channel, affect the information descriptors of the *internal* and *external* chemical bonds of molecular subsystems. The former characterize the intra-subsystem connections between atoms, while the latter measure the bonds between the subsystem in question and its molecular environment. It is the main purpose of this work to explore the implications of the molecular fragment *reductions*, performed by combining several atomic inputs and/or outputs into a single unit. The so-called complementary reductions will then be used to formulate the exact rules for combining the subsystem entropy/information bond indices into the corresponding global (molecular) entropy/information descriptors of the system as a whole. Illustrative results for the three-orbital model and the π-electron systems (butadiene and benzene) in the Hückel approximation [10, 13, 14, 21b, c, 22] will also be reported.

2 Input and output reductions of the molecular communication channel

By selecting a specific atomic partition of the molecular electron density $\rho(\boldsymbol{r}) = \sum_{m\in M}\rho_m(\boldsymbol{r}) = Np(\boldsymbol{r})$ or that of the associated probability distribution (*shape* factor) $p(\boldsymbol{r}) = \sum_{m\in M} p_m(\boldsymbol{r})$, one divides the molecular electron distribution into the corresponding "fine-grained" atomic components $\rho_m(\boldsymbol{r})$ or $\{p_m(\boldsymbol{r})\}$, which correspond the *local description* level of the atomic one-electron events. The associated *condensed description*, in terms of the AIM electron populations $\boldsymbol{N} = \{N_m = \int \rho_m(\boldsymbol{r})d\boldsymbol{r}\}$ or the atomic condensed one-electron probabilities $\boldsymbol{P} = \{P_m = \int p_m(\boldsymbol{r})d\boldsymbol{r} = N_m/N\}$, where $N = \sum_{m\in M} N_m$ stands for the overall number of electrons in M, amounts to the *reduction* of the local intra-atomic events into a single AIM event of finding an electron on a given atom m. Therefore, the "discrete" AIM description of the molecular electron distributions generates the entropy/information bond descriptors, which take into account only the communication links between AIM treated as whole units. This reduction can be pursued still further, e.g., into the molecular fragment resolution of *Subsystems-in-Molecules* containing specified groups $\boldsymbol{G} = \{L\}$ of AIM: $\boldsymbol{P}^G = \{P_L = \sum_{l\in L} P_l\}$. The ultimate *global* resolution level represents the trivial case of the *Molecule-in-Molecule* description, containing a single (sure) event of finding an electron of M in M, $P_M = \sum_{L\in M} P_L = 1$, which gives rise to the identically vanishing values of the entropy/information bond indices. Thus, the input and/or output reduction of the AIM *one*-electron probabilities involves a relevant summation over the intra-subsystem probabilities, which gives rise to the corresponding condensed probability for the specified group of AIM.

Consider now the reduction of the AIM-resolved *two*-electron probabilities $\mathbf{P} = \{P_{m,n}\}$. The molecular fragment reduction of these joint probabilities can be performed in the input and/or output of the molecular communication channel. A summation over the AIM events of the specific *input* fragment K of M, consisting of atoms $\boldsymbol{k} = \{k \in K\}$,

$$\boldsymbol{P}_K^G = \left\{ P_{K,n} = \sum_{k\in K} P_{k,n} \right\}, \quad (4)$$

produces the vector of the input-condensed probabilities of K. They in turn determine the corresponding conditional probabilities, relevant for this reduction scheme, of all AIM outputs given the condensed input of fragment K:

$$\boldsymbol{P}(\mathbf{B}|K) = \{P(n|K) = P_{K,n}/P_K\} \quad (5)$$

Here, $P(n|K)$ denotes the conditional probability of the occurrence of the atomic output n, given the occurrence of the reduced input event on fragment K.

The conditional probabilities for the reduced output fragment L of M, consisting of atoms $\boldsymbol{l} = \{l \in L\}$,

$$\boldsymbol{P}(L|\boldsymbol{A}) = \{P(L|m) = P_{m,L}/P_m = \textstyle\sum_{l\in L} P(l|m)\}, \quad (6)$$

of finding one electron on L in the output, when another electron has already been located on atom m in the input, involves a summation over columns $\boldsymbol{l}$ of the full molecular conditional probability matrix in atomic resolution, $\mathbf{P}(\mathbf{B}|\mathbf{A})$. Here, $P_{m,L} = \sum_{l \in L} P_{m,l}$ denotes the joint probability of finding one electron on atom m and another electron on fragment L.

Finally, a simultaneous *input-and-output* reduction of the joint two-electron probabilities in M, for the input fragments $\boldsymbol{K} = (K, K', \ldots)$ and the output fragments $\boldsymbol{L} = (L, L', \ldots)$, involves a double summation over the constituent atoms of the input and output fragments, respectively:

$$\mathbf{P}^G = \{P_{K,L} = \sum_{k \in K} \sum_{l \in L} P_{k,l}\} \equiv \mathbf{P}(\boldsymbol{KL}). \tag{7}$$

These subsystem-resolved simultaneous probabilities of finding two electrons on specified fragments of M define the associated conditional probabilities in this resolution,

$$\mathbf{P}(\boldsymbol{L}|\boldsymbol{K}) = \{P(L|K) = P_{K,L}/P_K\}, \tag{8}$$

where $P(L|K)$ is the probability of observing an electron on the (output) fragment L, when another electron has already been located on the (input) fragment K.

3 Internal and external entropy/information indices of molecular fragments

The constituent units of the *input* probability scheme $\mathbf{A}$ (or $\mathbf{A}^0$) in the molecular channel define the *origins* of the channel communications (bonds), while the molecular fragments of the *output* probability scheme $\mathbf{B}$ define the resolution level of the bonds being counted. For example, for the input reduction scheme $\mathbf{A} = \boldsymbol{G} \equiv (K, K', K'', \ldots)$, in which the constituent atoms of M are combined into the condensed groups $\boldsymbol{G}$ of AIM, and for the output scheme $\mathbf{B} = \boldsymbol{G}' = (L, L', L'', \ldots)$ of the molecular channel, the average conditional entropy $S(\boldsymbol{G}'|\boldsymbol{G})$ *approximately* indexes the effective inter-fragment (external) covalent component of bonds between the output groups, $(L - L', L - L'', \ldots)$, counting the contributions due to the communications originating from the *condensed* input groups $\boldsymbol{G}$. The *exact* overall covalent component of these bonds, $S(\boldsymbol{G}'|\boldsymbol{m})$, is thus obtained only when the AIM input scheme of the molecular communication system remains *unreduced*, $\mathbf{A} = \boldsymbol{m}$, when each constituent atom represents a separate building block of the molecule. Indeed, only in this case the complexity of the atomic origins of all communications into fragments $\boldsymbol{G}'$ is fully recognized and taken into account completely. One can also expect that this exact entropic measure of the sum of the external covalent bonds $(L - L', L - L'', \ldots)$ can be realistically approximated, when the input and output reductions are identical, $\mathbf{A} = \mathbf{B} = \boldsymbol{G}' : S(\boldsymbol{G}'|\boldsymbol{m}) \cong S(\boldsymbol{G}'|\boldsymbol{G}')$, since the overall covalency between molecular fragments $\boldsymbol{G}'$ should be weakly dependent on the details of their explicit atomic composition.

Thus, for the unreduced molecular input in AIM resolution $\mathbf{A} = \boldsymbol{m}$ and the reduced output $\mathbf{B} = \boldsymbol{G}'$ of the molecular communication channel, one takes into account all the inter-fragment (*external*) bond contributions, which result from the "communications" between the atomic inputs $\boldsymbol{m} = (m, m', \ldots)$ of $\boldsymbol{M}$, and the subsystems $\boldsymbol{G}' = (L, L', L'', \ldots)$ treated as condensed units. Therefore, the entropies generated by such an *output*-reduced channel include all but the *internal* contributions to the overall indices representing the sum of bonds $(L - L', L - L'')$:

$$\begin{aligned} &\boldsymbol{S}(\boldsymbol{G}'|\boldsymbol{m}) = \boldsymbol{S}^{\text{ext}}(\boldsymbol{G}'), \quad \boldsymbol{I}(\boldsymbol{m}^0 : \boldsymbol{G}') = \boldsymbol{I}^{\text{ext}}(\boldsymbol{G}'), \\ &\boldsymbol{N}(\boldsymbol{m}; \boldsymbol{G}') = \boldsymbol{N}^{\text{ext}}(\boldsymbol{G}'). \end{aligned} \tag{9}$$

One can thus extract the sums of all missing bond contributions, inside fragments G', by subtracting the above external fragment reduced entropy/information measures from the corresponding global indices of Eqs. (1)–(3) for the molecule as a whole:

$$\begin{aligned} &\boldsymbol{S}^{\text{int}}(\mathbf{G}') = \boldsymbol{S}(\boldsymbol{n}|\boldsymbol{m}) - \boldsymbol{S}^{\text{ext}}(\mathbf{G}'), \\ &\boldsymbol{I}^{\text{int}}(\mathbf{G}') = \boldsymbol{I}(\boldsymbol{m} : \boldsymbol{n}) - \boldsymbol{I}^{\text{ext}}(\mathbf{G}'), \\ &\boldsymbol{N}^{\text{int}}(\mathbf{G}') = \boldsymbol{N}(\boldsymbol{m}; \boldsymbol{n}) - \boldsymbol{I}^{\text{ext}}(\mathbf{G}'). \end{aligned} \tag{10}$$

As explicitly indicated above, the global quantities correspond to the *unreduced* molecular channel, in which both the input and output probability schemes are atomically resolved.

By appropriately selecting the molecular fragments in the communication channel, one can extract the bond indices required for diverse interpretations in chemistry of the known distribution of electrons in a molecule. In other words, one can "tailor" the reduction scheme to directly address the chemical problem in question.

Consider the illustrative example of the *complementary* output partition $\mathbf{B} = \mathbf{B}^r(L) \equiv (L, \boldsymbol{R}_L)$ of M into the condensed fragment L of interest and the reminder of the molecule $\boldsymbol{R}_L = \boldsymbol{l}' = \{l' \notin L\}$, which remains unreduced (atomically resolved). For the atomically resolved inputs $\mathbf{A} = \boldsymbol{m}$ or $\mathbf{A}^0 = \boldsymbol{m}^0$, this reduction scheme offers a possibility to extract the bonds inside L and to determine the *exact* overall indices of the external bonds $L - \boldsymbol{l}' = \{L - l'\}$, which couple L to all remaining atoms in M. The bond indices of such an output reduced channel,

$$\begin{aligned} S(\mathbf{B}^r(L)|\mathbf{A}) &= -\sum_{m \in M} \Big[P_{m,L} \log P(L|m) \\ &\qquad + \sum_{n \notin L} P_{m,n} \log P(n|m) \Big] \\ &= S(L, \boldsymbol{l}'|\boldsymbol{m}) \equiv S^{\text{ext}}(L), \end{aligned} \tag{11}$$

$$\begin{aligned} I(\mathbf{A}^0 : \mathbf{B}^r(L)) &= \sum_{m \in M} P_{m,L} \left\{ \log[P(m|L)/P_m^0] \right. \\ &\qquad \left. + \sum_{n \notin L} P_{m,n} \log[P(m|n)/P_m^0] \right\} = I(\boldsymbol{m}^0 : L, \boldsymbol{l}') \\ &\equiv I^{\text{ext}}(L), \end{aligned} \tag{12}$$

$$\begin{aligned} N(\mathbf{A}; \mathbf{B}^r(L)) &= S(\mathbf{B}^r(L)|\mathbf{A}) + I(\mathbf{A}^0 : \mathbf{B}^r(L)) \\ &= I(\boldsymbol{m}; L, \boldsymbol{l}') \equiv N_{\text{ext}}(L), \end{aligned} \tag{13}$$

contain all but the intra-L bond contributions, thus allowing a determination of the exact *internal* entropy/information bond descriptors for fragment L:

$$S^{\text{int}}(L) \equiv S(\boldsymbol{n}|\boldsymbol{m}) - S^{\text{ext}}(L),$$
$$I^{\text{int}}(L) \equiv I(\boldsymbol{m}^0 : \boldsymbol{n}) - I^{\text{ext}}(L),$$
$$N^{\text{int}}(L) \equiv N(\boldsymbol{m}; \boldsymbol{n}) - N^{\text{ext}}(L)\,, \tag{14}$$

Of interest also are the interactions between L and its *reduced* complementary environment $L' \equiv R_L$ in M. The exact indices for such interactions call for the unreduced atomic inputs (see also Sect. 6):

$$S(L, L'|\boldsymbol{m}) = S(L - L'), \quad I(\boldsymbol{m}^0 : L, L') = I(L - L)',$$
$$N(\boldsymbol{m}; L, L') = N(L - L'). \tag{15}$$

When the complementary fragment reduction is performed in both the input and output probability schemes of the molecular communication system, for $K = L$, i.e., $\mathbf{A}^r(L) \equiv (L, \boldsymbol{l}')$ or $\mathbf{A}^r(L)^0 \equiv (L^0, \boldsymbol{l}'^0)$ and $\mathbf{B}^r(L) \equiv (L, \boldsymbol{l}')$, only the "communications" between the events $\mathbf{A}^r(L)$ in the input and $\mathbf{B}^r(L)$ in the output of such a doubly reduced molecular channel contribute to the resulting entropy/information bond indices. In this network, the fragment L acts as a single unit in both the input and output probability schemes. Such a doubly reduced channel can thus be used to generate the approximate overall information-theoretic descriptors of the "*external*" bonds L-$\boldsymbol{l}'$:

$$\begin{aligned} S_{\text{ext}}(L) &\equiv S(L, \boldsymbol{l}'|L, \boldsymbol{l}') = S(\mathbf{B}^r(L)|\mathbf{A}^r(L)) \\ &= -P_{L,L} \log P(L|L) - \sum_{n \notin L} P_{L,n} \log P(n|L) \\ &\quad - \sum_{m \notin L} P_{m,L} \log P(L, m) \\ &\quad - \sum_{n \notin L} \sum_{m \notin L} P_{m,n} \log P(n|m) \cong S^{\text{ext}}(L)\,, \end{aligned} \tag{16}$$

$$\begin{aligned} I_{\text{ext}}(L) &\equiv I(L^0, \boldsymbol{l}'^0 : L, \boldsymbol{l}') = I(\mathbf{A}^r(L)^0 : \mathbf{B}^r(L)) \\ &= P_{L,L} \log[P(L|L)/P_L^0] \\ &\quad + \sum_{n \notin L} P_{L,n} \log[P(L|n)/P_L^0] \\ &\quad + \sum_{m \notin L} P_{m,L} \log[P(m|L)/P_m^0] \\ &\quad + \sum_{n \notin L} \sum_{m \notin L} P_{m,n} \log[P(m|n)/P_m^0] \cong I^{\text{ext}}(L)\,, \end{aligned} \tag{17}$$

$$\begin{aligned} N_{\text{ext}}(L) &\equiv N(L, \boldsymbol{l}'; L, \boldsymbol{l}') = N(\mathbf{A}^r(L); \mathbf{B}^r(L)) \\ &= S_{\text{ext}}(L) + I_{\text{ext}}(L) \cong N^{\text{ext}}(L)\,. \end{aligned} \tag{18}$$

These approximate external bond measures count the L-L' bond contributions, which result from communications between the input $\mathbf{A}^r(L) \equiv (L, \boldsymbol{R}_L)$ involving the condensed fragment L, while the exact quantities of Eqs. (11)–(13) fully recognize the atomic origins of the external bonds involving fragment L. One would expect that the exact internal indices of Eqs. (11)–(13) when supplemented by the approximate external indices of Eqs. (16)–(18) would roughly reproduce the corresponding global indices, as effectively accounting for *all* bonds in M in the resolution of molecular probabilities, which involves the reduced fragment L:

$$\begin{aligned} S(L) &\equiv S^{\text{int}}(L) + S_{\text{ext}}(L) = S(\mathbf{B}|\mathbf{A}) \\ &\quad + [S(\mathbf{B}^r(L)|\mathbf{A}^r(L)) - S(\mathbf{B}^r(L)|\mathbf{A})] \\ &\equiv S(\mathbf{B}|\mathbf{A}) + \Delta S(L) \cong S(\mathbf{B}|\mathbf{A}), \\ I(L) &\equiv I^{\text{int}}(L) + I_{\text{ext}}(L) = I(\mathbf{A}^{\mathbf{0}} : \mathbf{B}) \\ &\quad + [I(\mathbf{A}^{r,0}(L) : \mathbf{B}^r(L)) - I(\mathbf{A}^0 : \mathbf{B}^r(L))] \\ &\equiv I(\mathbf{A}^0 : \mathbf{B}) + \Delta I(L) \cong I(\mathbf{A}^0 : \mathbf{B}), \\ N(L) &\equiv N^{\text{int}}(L) + N_{\text{ext}}(L) = N(\mathbf{A}; \mathbf{B}) \\ &\quad + [N(\mathbf{A}^r(L) : \mathbf{B}^r(L)) - N(\mathbf{A}; \mathbf{B}^r(L))] \\ &\equiv N(\mathbf{A}; \mathbf{B}) + \Delta N(L) \cong N(\mathbf{A}; \mathbf{B})\,. \end{aligned} \tag{19}$$

Indeed, the internal and external communications for a given complementary division effectively exhaust all communications in the molecular system, be it in an approximate, condensed manner. The combination rules of Eq. (19) approximate the exact grouping theorems of Eqs. (10) and (14), which we shall also examine in Sect. 6.

For these approximate combination rules to work, the entropy/information differences in the square brackets of the preceding equation should be small compared to the global index. Let us examine the conditions under which this is the case. A straightforward transformation of these entropy/information displacements gives:

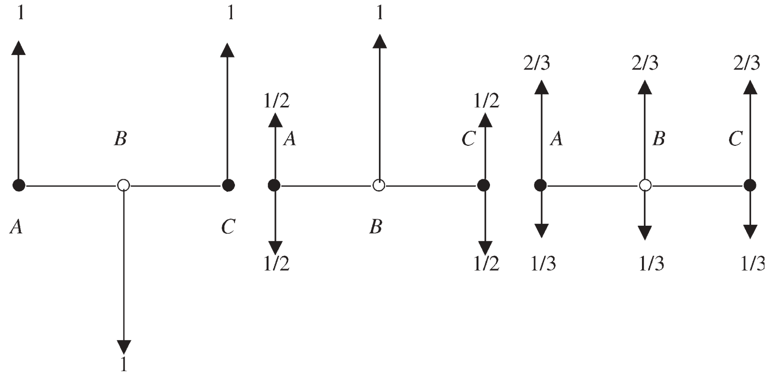
$$\begin{aligned} \Delta S(L) &= \sum_{m \in L} P_{m,L} \log[P(L|m)P(L|L)] \\ &\quad + \sum_{m \in L} \sum_{n \notin L} P_{m,n} \log[P(n|m)/P(n|L)], \end{aligned} \tag{20}$$

$$\begin{aligned} \Delta I(L) &= \sum_{m \in L} P_{m,L} \log[P_{L,L} P_m^0/(P_{m,L} P_L^0)] \\ &\quad + \sum_{m \in L} \sum_{n \notin L} P_{m,n} \log[P_{L,n} P_m^0/(P_{m,n} P_L^0)], \end{aligned} \tag{21}$$

$$\Delta N(L) = \sum_{m \in L} P_{m,M} \log(P_m/P_m^0) + P_{L,M} \log(P_L/P_L^0)\,. \tag{22}$$

The last term [Eq. (22)] indeed exactly vanishes for the identical molecular and promolecular input probabilities in the AIM resolution, $\boldsymbol{P} = \boldsymbol{P}^0$, which also imply the identical fragment probabilities $P_L = P_L^0$. Therefore, the approximate combination rule of Eq. (19) for the overall entropy/information index should be quite accurate, since the molecular AIM electron probabilities differ only slightly from their corresponding promolecular analogs.

However, a reference to Eqs. (20) and (21) indicates that the combination rules of Eq. (19) for the conditional entropy (bond covalency) and the mutual information (bond ionicity) should be less accurate. It also directly follows from these expressions that for $\boldsymbol{P} = \boldsymbol{P}^0$ one indeed obtains $\Delta I(L) = -\Delta S(L)$, and thus the vanishing deviation of the global entropy/information bond index. One also predicts that the deviations of the global ionic and covalent components vanish identically when $P(L|m) = P(L|L), m \in L$, and



Scheme 1 The atomic populations of the spin-up (↑) and spin-down (↓) electrons in the 3-AO model of the symmetric TS for $q = 1$ and $\Sigma = -1$ (Panel *a*), $\Sigma = 1$ (Panel *b*), and $\Sigma = 1/3$ [*maximum global covalency* (MGC), Panel *c*]. The *broken* vertical lines separating the mutually *open* AIM in M signify the presence of the inter-atomic communications (*bonds*), while the *solid* vertical lines in M^0 separate the mutually *closed* free atoms of AP, exhibiting the vanishing inter-atomic communications (*bonds*)

$P(n|m) = P(n|L)$, $m \in L$, $n \notin L$. These equalities can indeed be approximately satisfied by the molecular conditional probabilities, when there are small differences between the AIM probabilities in L, e.g., between the carbon atoms in the benzene ring or in butadiene chain, which we shall consider in the applicative part of this work. This is because the reduction of probabilities in a given subsystem amounts to *averaging* (equalizing) the atomic probabilities in this molecular fragment.

4 Illustrative application to the three-orbital model

The 3-AO model [10, 14, 21b,c, 22] describes three electrons contributed by three atoms $\boldsymbol{X} = (A, B, C)$ of the symmetric *Transition-State* (TS) complex $[A—B—C]^{\ddagger} = [A_1—B—A_2]^{\ddagger}$ in the atom-exchange reaction $A_1 - B + A_2 \rightarrow A_1 + B - A_2$, e.g., in the H_2 + H reactive system, which occupy the two lowest MO obtained by combining three (orthonormal) AO $\boldsymbol{x}(\boldsymbol{r}) = \{a(\boldsymbol{r}), b(\boldsymbol{r}), c(\boldsymbol{r})\}$ centered on the respective constituent atoms. The relevant *Atomic Promolecule* (AP) reference assumes one electron on each atom/orbital with the alternant spin orientations, $A_1^0(\uparrow)+B^0(\downarrow)+A_2^0(\uparrow)$, in $M^0 = (A_1^0|B^0|A_2^0) \equiv (A^1|B^1|C^1)$, which exhibits the highest degree of the spin-pairing between the neighboring free atoms and thus the highest spin distribution similarity to that of the molecular ground-state of the TS complex.

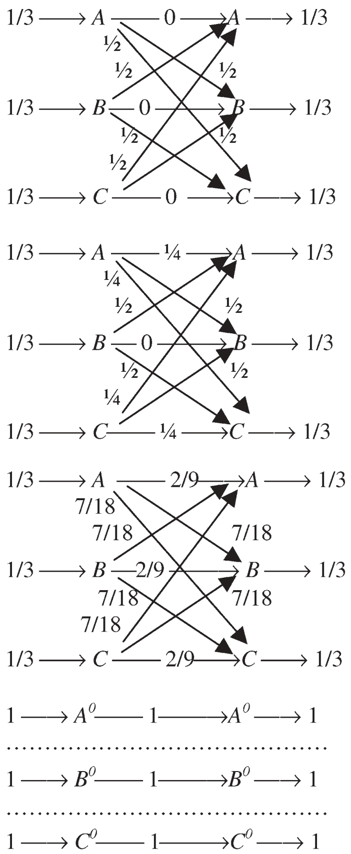
The molecular electron configuration of the 3-AO model is controlled by the charge of the middle atom B, $q = q_B$, and its spin polarization $\Sigma = q_{B\alpha} - q_{B\beta}$. For a given value of Σ, the allowed values of q are in the range $|\Sigma| \leq q \leq 2 - |\Sigma|$ and the overall AP spin polarization $N^{\alpha,0} - N^{\beta,0} = 1$ is assumed to be preserved during the bond-breaking−bond-forming process. It follows from the extended basis set UHF calculations for H_3 [21c] that the optimum TS configuration exhibits an almost uniform distribution of electrons among the constituent AIM, $q = 1.086$, and a positive, fractional spin polarization on the middle atom: $\Sigma = 0.135$. In this TS complex, all pairs of AIM exhibit fractional bond multiplicities.

Let us examine selected distributions of electronic spins in the model, for the three crucial values of the spin polarization parameter $\Sigma = (-1, 1, 1/3)$, and the uniform distribution of electrons among three constituent atoms, for $q = 1$, i.e., $\mathbf{A} = \mathbf{A}^0$, which also marks the maximum entropic covalency for any fixed value of Σ [10,14]. They are reported in Scheme 1.

Let us examine the global entropy/information indices of the model chemical bonds for the crucial *molecular* electron configurations of Scheme 1. The communication channels of these molecular systems, all of them exhibiting the identical input and output Shannon entropies, due to the identical molecular and promolecular probability distributions,

$$S(\mathbf{A}^0) = S(\mathbf{A}) = S(\mathbf{B}) \equiv S(\mathbf{P}) = -\sum_{m \in M} P_m \log P_m = \log_2 3 = 1.585 \text{ bits}, \qquad (23)$$

are shown in Scheme 2a–c; Panel *d* of the figure shows the communication channel corresponding to the truly non-bonded constituent atoms in the promolecule M^0, representing a collection of the mutually closed free atoms, for which the inter-atomic communications vanish identically. The corresponding values (in bits) of the two-electron entropy, $S(\mathbf{AB}) = S(\mathbf{P})$ [or $S(\mathbf{A}^0\mathbf{B}^0)$ in Panel *d*], the conditional entropy $S(\mathbf{B}|\mathbf{A})$ [or $S(\mathbf{B}^0|\mathbf{A}^0) = 0$ in Panel *d*] (the global entropic bond covalency), and the mutual information $I(\mathbf{A}^0 : \mathbf{B})$ [or $I(\mathbf{A}^0 : \mathbf{B}^0) = 0$ in Panel *d*] (the global information bond ionicity) are also reported in Scheme 2.



a) $\Sigma = -1$, $M = (A \vdots B \vdots C)$;

$S(\mathbf{AB}) = 2.585$, $S(\mathbf{B}\,|\,\mathbf{A}) = 1$, $I(\mathbf{A}^0{:}\mathbf{B}) = 0.585$

b) $\Sigma = 1$, $M = (A \vdots B \vdots C)$;

$S(\mathbf{AB}) = 2.918$, $S(\mathbf{B}\,|\,\mathbf{A}) = 1.333$, $I(\mathbf{A}^0{:}\mathbf{B}) = 0.252$

c) $\Sigma = 1/3$, $M = (A \vdots B \vdots C)$ (MGC);

$S(\mathbf{AB}) = 3.127$, $S(\mathbf{B}\,|\,\mathbf{A}) = 1.542$, $I(\mathbf{A}^0{:}\mathbf{B}) = 0.043$

d) $\Sigma = -1$, $M^0 = (A^0|B^0|C^0)$ (AP);

$S(\mathbf{A}^0\mathbf{B}^0) = 0$, $S(\mathbf{B}^0\,|\,\mathbf{A}^0) = 0$, $I(\mathbf{A}^0{:}\mathbf{B}^0) = 0$

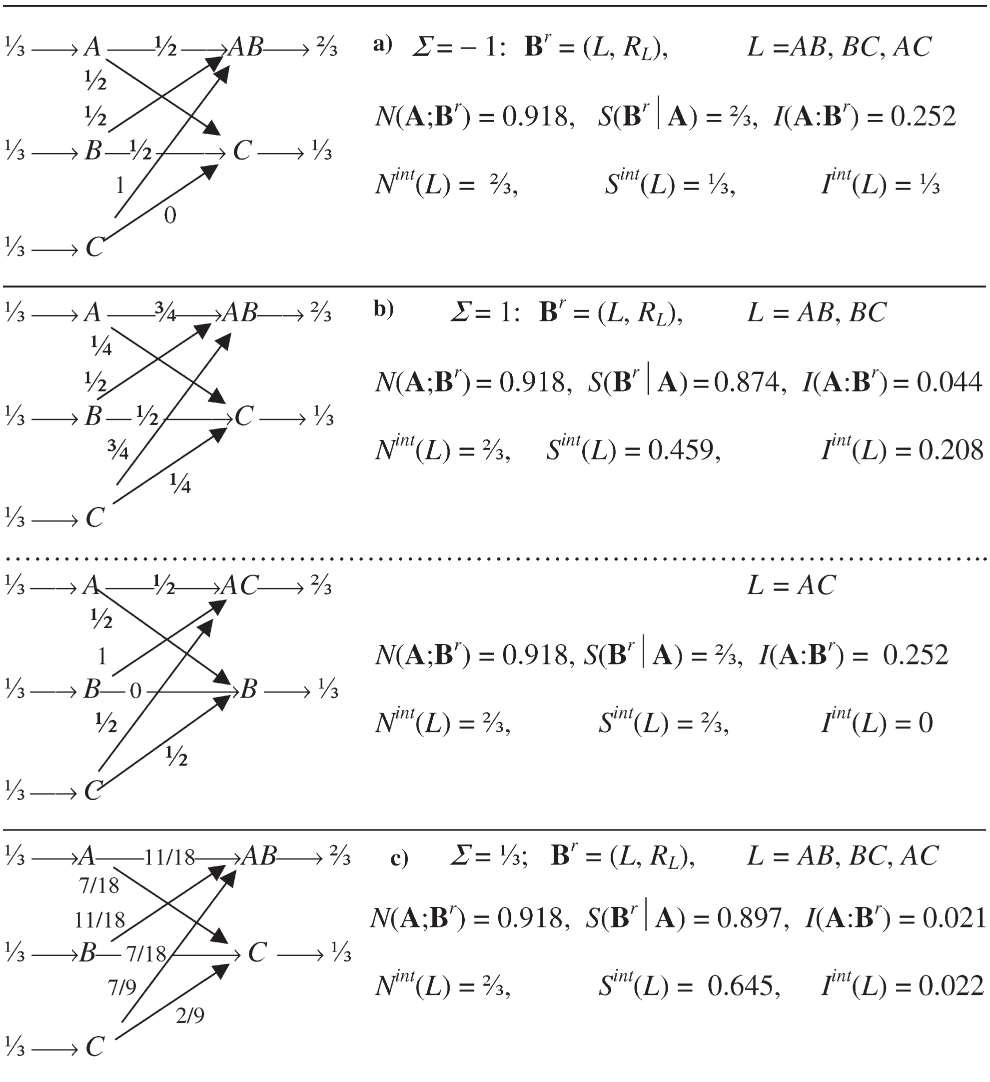
Scheme 2 The molecular communication channels for the mutually bonded (*open*) AIM for $q = 1$ and $\Sigma = -1(a)$, $1(b)$, and $1/3(c)$, in the 3-AO model of the symmetric TS complex. In panel d, the corresponding AP channel is shown, representing the mutually non-bonded (*closed*) free atoms giving rise to the three (disconnected, deterministic, noiseless) atomic channels. The inter-atomic probabilities are the conditional probabilities $\mathbf{P}(\mathbf{B}|\mathbf{A})$ in atomic resolution. The same convention is used in the remaining schemes of communication channels. For each channel, the two-electron and conditional entropies, as well as the mutual information descriptors (*in bits*) are also reported

Table 1 The external and internal bond indices (in bits) in the 3-AO model for the three molecular electron configurations of Scheme 1 (from the reduced channels of Schemes 3 and 4, respectively). The last two columns test the performance of the approximate combination rules of Eq. (19)

Σ	Diatomic fragment	Bond component	Internal indices: Scheme 3 [Eq. (14)]	External indices: Scheme 4 [Eqs. (16)–(18)]	Overall indices: [Eqs. (19)]	Global indices: Scheme 2 [Eqs.(1)–(3)]
−1	AB, BC, AC	S	0.333	0.667	1.000	1.000
		I	0.333	0.252	0.585	0.585
		N	0.667	0.918	1.585	1.585
+1	AB, BC	S	0.459	0.907	1.366	1.333
		I	0.208	0.011	0.219	0.252
		N	0.667	0.918	1.585	1.585
	AC	S	0.667	0.667	1.333	1.333
		I	0.000	0.252	0.252	0.252
		N	0.667	0.918	1.585	1.585
+ 1/3	AB, BC, AC	S	0.645	0.897	1.542	1.542
		I	0.022	0.021	0.043	0.043
		N	0.667	0.918	1.585	1.585

The symbols S, I, and $N = S + I$ denote the relevant conditional entropy, mutual information, and the total bond-order measures, respectively. The overall entry is the sum of its internal and approximate external contributions. The same notation is used in Tables 2 and 4

The non-diagonal conditional probabilities of the *molecular* configuration of Scheme 2a describe the mutually open AIM in M, allowed to delocalize electrons onto the remaining bonded atoms. In a collection of the mutually closed free atoms in the AP reference of Scheme 2d, the inter-atomic flows of electrons are forbidden, so that only the diagonal, intra-atomic electron density displacements are allowed. In Schemes 1 and 2, this is symbolically represented by the broken and solid vertical lines, respectively.



Scheme 3 The *output*-reduced channels for alternative diatomics $L = AB, BC, AC$ in the 3-AO model for the three molecular electron configurations of Scheme 1. The reduced channel entropy/information descriptors and the resulting *internal* bond indices for L (*in bits*) are also reported

The resultant molecular spin distribution for the ($q = 1$, $\Sigma = -1$) configuration in $M = (A\!\mid\! B\!\mid\! C)$, consisting of the mutually *open* (bonded) AIM, is shown in Scheme 1 a. It is identical to the atomic electron spin populations corresponding to the AP reference configuration, consisting of the mutually *closed* (non-bonded) free atoms in $M^0 = (A^0|B^0|C^0)$ (Scheme 2d). It should be emphasized, however, that these two species exhibit dramatically different networks of conditional probabilities. The other extreme configuration, ($q = 1$, $\Sigma = 1$), has been previously linked to the *atom-diatom limit* (ADL): $B^0 + A_1 - A_2$[14]. However, this dissociation limit would require quite a different communication network, than that shown in Scheme 2b, in which the middle atom is *closed* relative to the pair of the mutually open peripheral atoms: $M^*(\text{ADL}) = (A\!\mid\! C|B^0)$. It also follows from Scheme 2d that the overall entropic bond-order of the promolecule $N^0(q = 1, \Sigma = -1) = 0$ contains the vanishing entropy covalency and information ionicity, while the *Maximum Global Covelency* (MGC) molecular configuration, for $q = 1$ and $\Sigma = 1/3$, for which the spin populations of all AIM equalize (Scheme 1c), exhibits almost purely covalent bonds. The ($q = 1$, $\Sigma = 1$) case of Scheme 2 b is seen to exhibit 4/3 bits of bond covalency and around 1/4 bit of bond ionicity. This prediction explicitly shows that in fact this communication channel does not describe the $B + AC$ dissociation limit, for which the overall entropy/information index of the diatomic dissociation product should amount to roughly 1 bit of information. This difference is due to the observed communications (partial bonds) in Scheme 2 b between atom B and the AC subsystem.

Table 2 A comparison of the approximate external [Eqs. (16)–(18)] and internal [Eq. (14)] π-bond indices for alternative diatomics $K = L$ in the butadiene carbon chain. The last two columns test the performance of the combination rules of Eq. (19) for transforming the fragment internal and approximate external entropy/information descriptors into the corresponding global measures characterizing the system as a whole

Diatomic fragment	Bond component	Internal indices	External indices [Eqs. (16)–(18)]	Overall indices [Eqs. (19)]	Global indices Scheme 5
(1,2), (3,4)	S	0.498	1.447	1.945	1.944
	I	0.002	0.053	0.055	0.056
	N	0.500	1.500	2.000	2.000
(1,3), (2,4)	S	0.472	1.480	1.952	1.944
	I	0.028	0.020	0.048	0.056
	N	0.500	1.500	2.000	2.000
(2,3), (1,4)	S	0.473	1.483	1.956	1.944
	I	0.027	0.017	0.044	0.056
	N	0.500	1.500	2.000	2.000

A reference to the molecular Schemes 2a–c indicates that the overall entropy/information bond-order measure, $N(\mathbf{A};\mathbf{B}) = S(\mathbf{B}|\mathbf{A}) + I(\mathbf{A}^0 : \mathbf{B}) = N(q, \Sigma)$, is preserved for all three molecular configurations examined: $N(q = 1, \Sigma) = S(\boldsymbol{P}) = 1.585$, $\Sigma = -1, 1, 1/3$. Therefore, as also observed in the 2-AO model of the $A - B$ chemical bond [13–15], the overall entropic bond index remains conserved when the spin polarization parameter changes for the identical overall electron distributions on AIM, $q_A = q_B = q_C = 1$. Only the covalent/ionic bond composition changes in such molecular configurations. Additional degrees of freedom for the spin delocalization detected in the molecular MGC structure of Scheme 2 *c*, relative to Scheme 2 *a* exhibiting vanishing diagonal conditional probabilities, are seen to give rise to more covalency (less ionicity) in the MGC structure. A reference to Scheme 2 *b* also shows that in the $\Sigma = 1$ communication channel, which exhibits only one vanishing diagonal conditional probability, the probability "scattering" (communication noise) is only partially restricted relative to the unconstrained MGC network, thus also generating less entropic covalency (more information ionicity). Accordingly, since the $\Sigma = 1$ channel is less restrictive in comparison to the $\Sigma = -1$ molecular channel, it is seen to generate relatively more covalent (less ionic) chemical bonds.

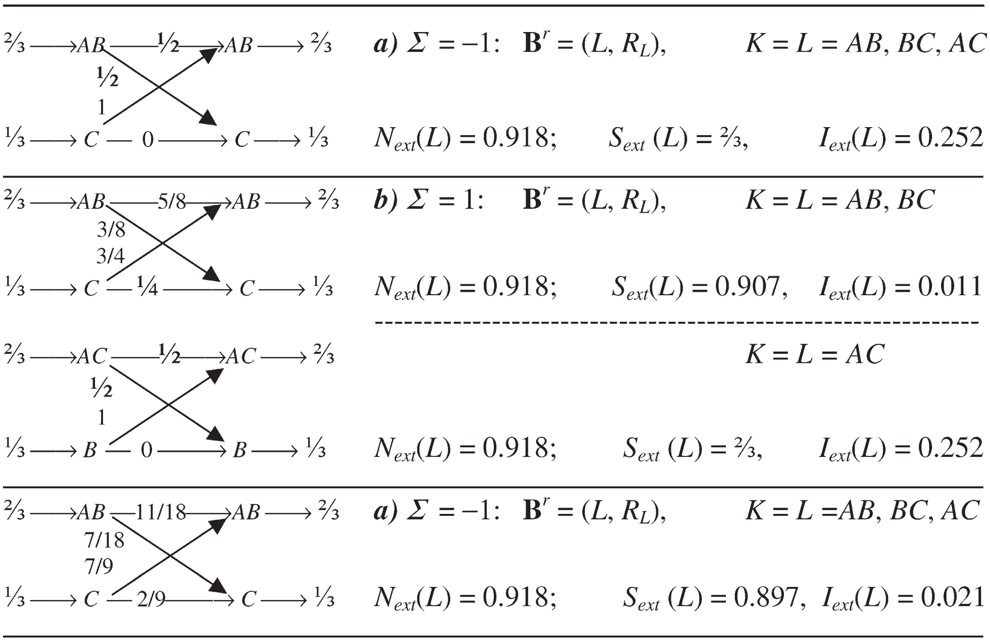
The *output*-reduced channels of the 3-AO model for alternative selections of the condensed diatomic fragment $L = AB, BC, AC$ are shown in Scheme 3, where the corresponding *internal* bond descriptors from the communication theory [Eq. (14)] have also been reported. The relevant *input-and-output*-reduced channels and the approximate external bond indices [Eqs. (16)–(18)] they generate are reported in Scheme 4.

In Table 1, we have compared the internal, external, and overall bond descriptors to check how these complementary bond measures combine into the approximate global indices. It follows from the table that these complementary quantities, respectively characterizing the internal chemical bond of a diatomic and its coupling to the third atom, do indeed combine semi-quantitatively into the corresponding global bond-order measures. In all cases, the global bond composition is also exactly reproduced. This is because the atomic electron probabilities have already been equalized before the diatomic fragment reduction of electron probabilities.

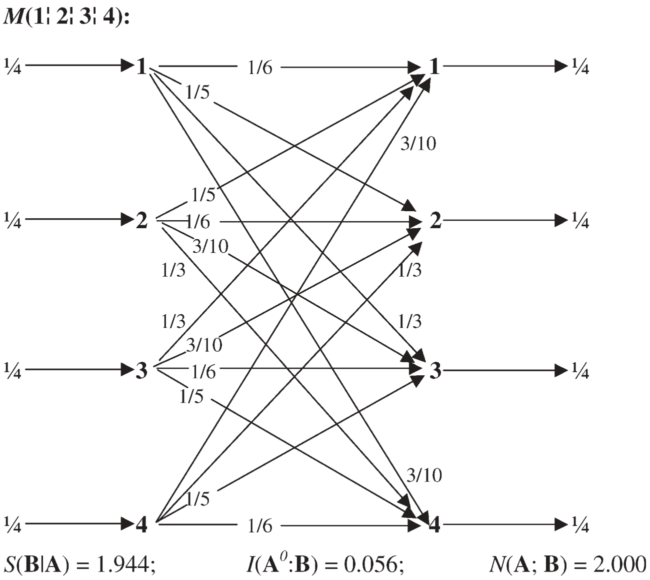
5 Reduced channel entropies in butadiene

The results of a similar analysis for the π-bond interactions of alternative diatomic fragments in butadiene (the Hückel approximation), for the consecutive numbering of atoms in the carbon chain, are reported in Scheme 5 and Table 2. The internal bond descriptors predict equal 1/2 bit bond index for all pairs of carbons in the π chain, and about 1.5 bits for the chemical interactions of each diatomic fragment with the remaining carbon atoms in the molecule, giving rise to the conserved "double" (two-bit) overall π-bond in the system as a whole. The highest covalent component for the terminal (1,2)-pair is only qualitatively consistent with the corresponding MO result. All internal and external bond descriptors of diatomic fragments in butadiene predict almost pure covalent interactions. The strongest *internal* ionic component is detected for the middle bond, while the terminal bonds exhibit the highest *external* ionic contribution.

Although the peripheral bond covalency is predicted to be slightly higher than that for the pair of middle AIM, the bond components for all diatomics are almost equalized in the communication theory description. This is in contrast to the MO theory description, which predicts large variations of bond indices for different choices of a diatomic fragment. Therefore, the communication theory description is quite different from that generated by the bond-multiplicity measures developed in the MO theory, which closely follow the chemical intuition and the structural formulas of chemical species. In general, the information-theoretic quantities emphasize the information *equilibrium* of the bonded subsystems. This indeed should be expected of the mutually open molecular fragments. This feature is also exhibited by the unbiased, stockholder fragments of the molecular electron distribution [6b, 7, 12a]. The same general conclusion also follows from the alternative fragment developments [22] within the communication theory of the chemical bond. All these approaches thus identify within the information *entropy*-representation a novel class of molecular *invariants*, which describe the bonded parts of the molecule. The equalization of these entropic "*intensities*" is reminiscent of the *electronegativity/chemical potential* equalization [17, 18, 23, 24] exhibited by the mutually open (bonded) subsystems, which marks the equilibrium distribution of electrons in the *energy* representation.



Scheme 4 The *input-and-output*-reduced channels for alternative diatomics $K = L = AB, BC, AC$ in the 3-AO model, for the three electron configurations of Scheme 1. The approximate *external* bond descriptors (in bits) resulting from these reduced channels are also reported



Scheme 5 The AIM-resolved molecular communication channel and entropy/information descriptors of π electrons in butadiene. The reported probabilities are from the Hückel theory

Of similar character also is the *local hardness* equalization principle [18].

In Table 2, the approximate combination rules for the reduced fragments are seen to reproduce exactly the overall bond-order indices reported in Scheme 5, while the conditional entropy and mutual information components agree only semi-quantitatively with the corresponding exact global values.

6 Exact combination rule for molecular fragments

The additive character of the entropic bond indices gives rise to the flexibility of the information-theoretic description of the chemical bonds by offering several alternative ways to generate the information bond-order measures for the whole system [22]. Consider now the *exact* rule for combining the entropy/information data of molecular fragments into the corresponding global quantities. In butadiene, which we select as an appropriate illustrative example, combining the molecular *output* into the two reduced complementary subsystems, e.g., $\mathbf{B}^r\ (L, L') \equiv (1,2), (3,4)$, where the brackets enclose the carbon atoms to be condensed in this double reduction scheme of the molecular output probabilities, and preserving the full (unreduced) atomic *input* $\mathbf{A} = \mathbf{A}^0$ in the reduced channel of Scheme 6 *a* gives the following (*exact*) external bond descriptors of the effective inter-fragment (L-L') chemical interactions:

$$\begin{aligned} &S(\mathbf{B}^r(L, L')|\mathbf{A}) \equiv S(L, L'|\mathbf{A}) \equiv S^{\text{ext}}(L, L') \\ &\quad = -\sum_{i\in M}\sum_{G\in(L,L')} P_{i,G}\log(P_{i,G}/P_i) = 0.948, \\ &I(\mathbf{A}^0 : \mathbf{B}^r(L, L')) \equiv I(\mathbf{A}^0 : L, L') \equiv I^{\text{ext}}(L, L') \\ &\quad = \sum_{i\in M}\sum_{G\in(L,L')} P_{i,G}\log[(P_{i,G}/P_i^0 P_G)] = 0.052, \\ &N(\mathbf{A}; \mathbf{B}^r(L, L')) \equiv N(\mathbf{A} : L, L') \\ &\quad \equiv S^{\text{ext}}(L, L') + I^{\text{ext}}(L, L') \equiv N^{\text{ext}}(L, L') = 1.000, \quad (24) \end{aligned}$$

where $P_{i,G} = \sum_{g\in G} P_{i,g}$ is the joint probability of simultaneously detecting one electron on atom i and another electron on fragment G, and the condensed one-electron probability $P_G = \sum_{g\in G} P_g$. The preceding equation defines the external complements of the internal subsystem quantities [see Eq. (14) and Table 2]:

$$S^{\text{int}}(L) = S(\mathbf{B}|\mathbf{A}) - S(L, \boldsymbol{L}'|\mathbf{A})$$
$$= -\sum_{i\in M}\sum_{j\in M} P_{i,j}\log(P_{i,j}/P_i)$$
$$+\sum_{i\in M} P_{i,L}\log(P_{i,L}/P_i)$$
$$+\sum_{i\in M}\sum_{l\in L'} P_{i,l}\log(P_{i,l}/P_i)$$
$$\equiv S(\mathbf{B}|\mathbf{A}) - S(L|\mathbf{A}) - S(\boldsymbol{L}'|\mathbf{A}), \quad (25)$$

$$I^{\text{int}}(L) = I(\mathbf{A}^0:\mathbf{B}) - I(\mathbf{A}^0:L,\boldsymbol{L}')$$
$$= \sum_{i\in M}\sum_{j\in M} P_{i,j}\log[P_{i,j}/(P_i^0 P_j)]$$
$$-\sum_{i\in M} P_{i,L}\log[P_{i,L}/(P_i^0 P_L)]$$
$$+\sum_{i\in M}\sum_{l\in L'} P_{i,l}\log[P_{i,l}/(P_i^0 P_l)]$$
$$\equiv I(\mathbf{A}^0:\mathbf{B}) - I(\mathbf{A}^0:L) - I(\mathbf{A}^0:\boldsymbol{L}'), \quad (26)$$

$$N^{\text{int}}(L) = S^{\text{int}}(L) + I^{\text{int}}(L) = N(\mathbf{A};\mathbf{B}) - N(\mathbf{A};L,\boldsymbol{L}')$$
$$= N(\mathbf{A};\mathbf{B}) - N(\mathbf{A};L) - N(\mathbf{A};\boldsymbol{L}'), \quad (27)$$

where $\boldsymbol{L}'$ stands for the constituent AIM of fragment L'. The preceding equation expresses the internal bond index of fragment L as the difference between the global index and the sum of indices measuring the chemical interactions in L and bonds between AIM in $\boldsymbol{L}'$. Indeed, the sum of the associated internal and external terms reproduces exactly the corresponding global quantity. For example,

$$S^{\text{int}}(L) + S^{\text{int}}(L') + S^{\text{ext}}(L, L')$$
$$= 2S(\mathbf{B}|\mathbf{A}) - [S(\boldsymbol{L}'|\mathbf{A}) + S(\boldsymbol{L}|\mathbf{A})]$$
$$+S(L, L'|\mathbf{A}) - [S(L|\mathbf{A}) + S(L'|A)] = S(\mathbf{B}|\mathbf{A}) \quad (28)$$

since

$$S(\mathbf{B}|\mathbf{A}) = S(\boldsymbol{L}'|\mathbf{A}) + S(\boldsymbol{L}|\mathbf{A}) \quad \text{and}$$
$$S(L, L'|\mathbf{A}) = S(L|\mathbf{A}) + S(L'|\mathbf{A}) \quad (29)$$

The same exhaustive character can be demonstrated for the mutual information quantities:

$$I^{\text{int}}(L) + I^{\text{int}}(L') + I^{\text{ext}}(L, L')$$
$$= 2I(\mathbf{A}^0:\mathbf{B}) - [I(\mathbf{A}^0:\boldsymbol{L}) + I(\mathbf{A}^0:\boldsymbol{L}')]$$
$$+I(\mathbf{A}^0:L, L') - [I(\mathbf{A}^0:L) + I(\mathbf{A}^0:L')]$$
$$= I(\mathbf{A}^0:\mathbf{B}), \quad (30)$$

since also

$$I(\mathbf{A}^0:\mathbf{B}) = I(\mathbf{A}^0:\boldsymbol{L}) + I(\mathbf{A}^0:\boldsymbol{L}') \quad \text{and}$$
$$I(\mathbf{A}^0:L, L') = I(\mathbf{A}^0:L) + I(\mathbf{A}^0:L'). \quad (31)$$

Therefore, Eqs. (28)–(31) also imply the same property of the overall fragment indices:

$$N^{\text{int}}(L) + N^{\text{int}}(L') + N^{\text{ext}}(L, L')$$
$$= 2N(\mathbf{A};\mathbf{B}) - [N(\mathbf{A};\boldsymbol{L}) + I(\mathbf{A};\boldsymbol{L}')]$$
$$+N(\mathbf{A};L, L') - [N(\mathbf{A};L) + N(\mathbf{A};L')] = N(\mathbf{A};\mathbf{B}), \quad (32)$$

where we have used the overall additivity relations:

$$N(\mathbf{A};\mathbf{B}) = N(\mathbf{A};\boldsymbol{L}) + N(\mathbf{A};\boldsymbol{L}') \quad \text{and} \quad N(\mathbf{A};L, L')$$
$$= N(\mathbf{A};L) + N(\mathbf{A};L'). \quad (33)$$

Supplementing the exact external bond indices of Eq. (19), reported in Scheme 6 a, with the internal contributions for both fragments (equal by symmetry), from Table 2, then reproduces exactly all global indices listed in the last column of this table: 0.948 + 2×0.498 = 1.944, 0.052 + 2×0.002 = 0.056, and 1.000 + 2×0.500 = 2.000.

Performing additionally the same double reduction in the input of the molecular channel (Scheme 6 b), for $K = L$ and $K' = L'$, offers alternative (approximate) estimates of the fragment-fragment indices,

$$S(L, L'|L, L') \equiv S_{\text{ext}}(L, L') = N(L, L'; L, L')$$
$$\equiv N_{\text{ext}}(L, L') = 1.000,$$
$$I(L, L':L, L') = I_{\text{ext}}(L, L') = 0.000, \quad (34)$$

representing a single (1 bit), purely covalent $L - L'$ bond.

Of interest in chemistry also are the overall indices, which characterize an effective bond between a given atom i and its reduced molecular remainder $R(i)$. The descriptors of the external interactions of a specified atom of the π-electron system in butadiene with its complementary molecular environment are identical in the Hückel approximation for all AIM positions in the carbon chain,

$$S(i, R(i)|i, R(i)) = 0.802, \quad I(i, R(i):i, R(i)) = 0.009,$$
$$N(i, R(i); i, R(i)) = 0.811, \quad i = 1-4, \quad (35)$$

thus marking the information equilibrium in the molecule.

7 Illustrative results for benzene

The AIM-resolved communication channel for benzene (Hückel theory) is shown in Scheme 7, where the global entropy/information indices are reported. It gives rise to a qualitatively similar result as that reported in the preceding equation for butadiene: for all carbon atoms in the ring, i = 1–6,

$$S(i, R(i)|i, R(i)) = 0.645, \quad I(i, R(i):i, R(i)) = 0.005,$$
$$N(i, R(i); i, R(i)) = 0.650. \quad (36)$$

Therefore, a reference to Eq. (35) indicates that the effective entropy/information bond index, reflecting an overall participation of the bonded carbon atom in the delocalized system of π-bonds, is distinctly higher in butadiene than that in benzene.

Next, let us summarize the entropy/information data for the output-reduced complementary fragments of the benzene ring, involving a pair of carbon atoms defining the condensed (output) diatomic L and four remaining atoms of the ring

Table 3 The entropy/information characteristics of the reduced channels for alternative diatomic and complementary tetraatomic fragments in the benzene π-electron ring (the Hückel approximation)

Entropy/Information	L: $(i, i+1)$	$(i, i+2)$	$(i, i+3)$
$S(L, \boldsymbol{L}' \mid \mathbf{A}) = S^{\text{ext}}(L)$	2.221	2.226	2.226
$S(\boldsymbol{L}, L' \mid \mathbf{A}) = S^{\text{ext}}(L')$	1.237	1.239	1.239
$S(L, L' \mid \mathbf{A}) = S(L - L')$	0.908	0.914	0.915
$S(L, L' \mid L, L') = S_{\text{ext}}(L, L')$	0.908	0.916	0.915
$I(\mathbf{A}^0 : L, \boldsymbol{L}') = I^{\text{ext}}(L)$	0.030	0.026	0.025
$I(\mathbf{A}^0 : \boldsymbol{L}, L') = I^{\text{ext}}(L')$	0.015	0.013	0.013
$I(\mathbf{A}^0 : L, L') = I(L - L')$	0.011	0.004	0.003
$I(L^0, L'^0 : L, L') = I_{\text{ext}}(L, L')$	0.010	0.002	0.003
$N(\mathbf{A} ; L, \boldsymbol{L}') = N^{\text{ext}}(L)$	2.252	2.252	2.252
$N(\mathbf{A}; \boldsymbol{L}, L') = N^{\text{ext}}(L')$	1.252	1.252	1.252
$N(\mathbf{A}; L, L') = N(L - L')$	0.918	0.918	0.918
$N(L, L'; L, L') = N_{\text{ext}}(L, L')$	0.918	0.918	0.918

defining the condensed, complementary four-atom system L'. When the AIM-resolved fragments define the communication channel, we shall again use the bold symbol notation: $\boldsymbol{L}$ and/or $\boldsymbol{L}'$. Table 3 collects the relevant entropy/information data (in bits) for the reduced channels of interest, while the resulting internal and external bond indices (in bits), reflecting the intra-L and $L - L'$ bonds, respectively, are listed in Table 4.

The calculated entropy/information quantities for the output reductions $(L, \boldsymbol{L}')$ and $(\boldsymbol{L}, L')$, and the full AIM resolved input $\mathbf{A}$ (or $\mathbf{A}^0$), which are the subject of the first two rows of each group of entries in Table 3, contain all entropy/information bond contributions but the internal components of the reduced fragment. Therefore, subtracting them from the corresponding global index of Scheme 7, describing the benzene π-electron system as a whole, generates the fragment *internal* descriptors, which are listed in columns a and b of Table 4. Again, the complementary (L, L') reduction in the output of the molecular channel (third rows of each group in Table 3), for the inputs $\mathbf{A}$ (or $\mathbf{A}^0$), gives rise to the exact external $L - L'$ bond contributions of Eq. (15), listed in Column c of Table 4. Finally, a double complementary reduction, in the input and output of the molecular communication network (fourth row of each group in Table 3), generates the approximate inter-subsystem bond entropy/information indices of Eq. (34), which have been collected in column d of Table 4.

A reference to Table 4 reveals that combining (in column e) the internal and the external bond indices of Columns a–c reproduces exactly the corresponding global descriptors of column f for the system as a whole. The external terms of column d are also seen to approximate quite accurately the exact external contributions of column c. For alternative atomic pairs L, the total entropy/information indices are the same for any choice of the diatomic fragment, with only their covalent/ionic components exhibiting minor variations, when the identity of L changes in the (*ortho*, *meta*, *para*) mutual position of two carbons. This picture of the equalized information descriptors is dramatically different from that emerging from the corresponding bond-order measures in the MO description [20, 21], e.g., the Wiberg index [20a], which predicts for these three carbon pairs (0.44, 0.00, 0.11), respectively.

In fact, the present information indices of molecular fragments represent the *entropic "intensities"* of the mutually open (bonded) subsystems, and their equalization identifies the equilibrium distribution of electrons in the system as a whole. Indeed, in all model systems considered in this work the sum of the internal and external (*embedding*) bond descriptors of any part of the molecule is equal to the corresponding global index, which characterizes the whole system. This *entropy* representation principle parallels the familiar equalization of the subsystem chemical potentials (negative electronegativities), which constitutes the equilibrium criterion in the complementary *energy* representation of the molecular electronic structure.

8 Conclusion

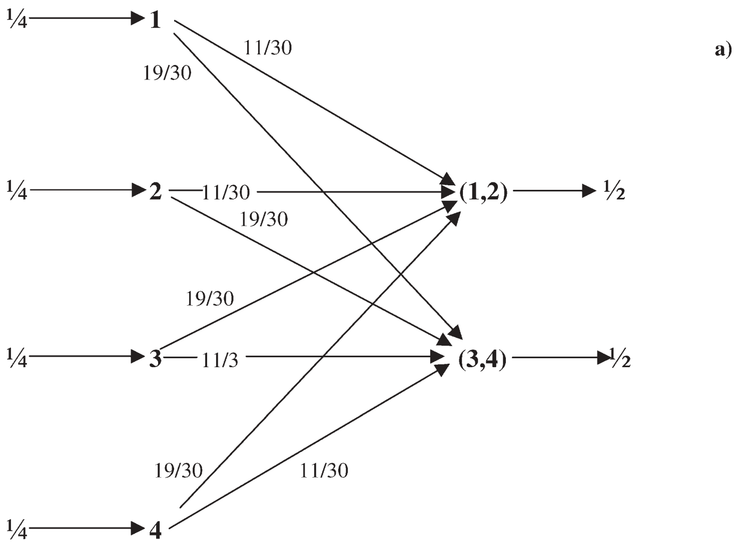
We have explored a variety of the entropy/information descriptors of the internal and external chemical bonds in molecular fragments, resulting from the subsystem reduced molecular communication channels in atomic resolution. The quantitative rules for combining the fragment entropy/information data into the corresponding global quantities, which characterize the system as a whole, have been derived and tested on model molecular systems. The equalization of the *resultant* (internal + external) bond indices of molecular subsystems has been observed in all model systems examined in this study. Alternative reductions of the molecular channel in the atomic resolution, by combining the fragment constituent AIM into a single unit, have been explored. The *output* reduction scheme determines the molecular parts, between which the effective external communications (bonds) are counted, while the *input* reduction defines the communication origins (sources). For a given output reduction, a relatively weak dependence of the external bond indices on the assumed input reduction has been observed.

It has been argued that the molecular channel reductions offer a versatile framework for extracting the subsystem internal and external information-theoretic indices, which reflect the intra-fragment and the fragment environmental chemical interactions in the molecule, respectively. The reduction scheme can be targeted to answer specific chemical problems. In particular, the so-called fragment *complementary* reductions, into the fragment of interest and the rest of the molecule, which represents the fragment embedding molecular environment, have been shown to provide the right framework for extracting the internal bond indices and for formulating the exact combination rules for the entropy/information bond descriptors of molecular subsystems.

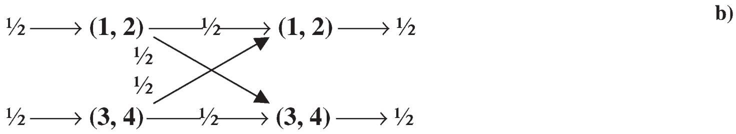
It has been demonstrated that the bonding patterns emerging from the communication theory descriptors of both AIM and diatomic fragments in the molecule are quite different from those generated by the bond multiplicity measures from

Table 4 Same as in Table 2 for benzene

Diatomic fragment	Information/entropy	Internal in L	Internal in L'	External $L - L'$: Exact	Approx.	Overall	Global
		a	b	c	d	$e = a + b + c$	f
$(i, i+1)$	S	0.330	1.314	0.908	0.908	2.551	2.551
	I	0.004	0.019	0.011	0.010	0.034	0.034
	N	0.333	1.333	0.918	0.918	2.585	2.585
$(i, i+2)$	S	0.325	1.312	0.914	0.916	2.551	2.551
	I	0.008	0.021	0.004	0.002	0.034	0.034
	N	0.333	1.333	0.918	0.918	2.585	2.585
$(i, i+3)$	S	0.325	1.312	0.915	0.915	2.551	2.551
	I	0.009	0.021	0.003	0.003	0.034	0.034
	N	0.333	1.333	0.918	0.918	2.585	2.585



$S^{ext}(L, L') = 0.948$, $I^{ext}(L, L') = 0.052$, $N^{ext}(L, L') = 1.000$

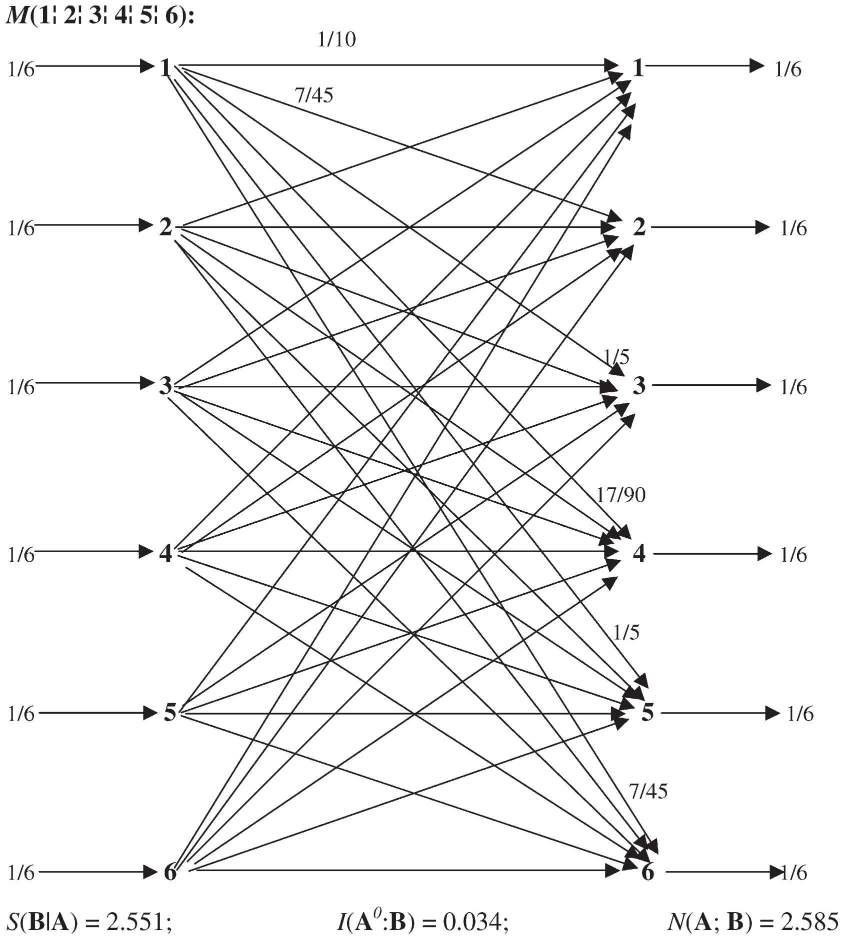


$S_{ext}(L, L') = 1.000$, $I_{ext}(L, L') = 0.000$, $N_{ext}(L, L') = 1.000$

Scheme 6 A double reduction of the molecular channel of the butadiene carbon chain (Scheme XI.6 *a*) into two complementary diatomics $\boldsymbol{G} = (1, 2), (3, 4) \equiv (L, L')$: *output* reduction (Panel *a*) and *input-and-output*-reduction (Panel b). The corresponding external entropy/information indices (in bits), exact (Panel *a*) and approximate (Panel *b*), are also reported

the MO theory. In general, the information-theoretic indices, derived from the one-electron and two-electron electron probabilities in atomic resolution, strongly emphasize the information *equilibrium* of the molecular electronic structure, which is manifested by a remarkable *equalization* of various atomic and diatomic indices, irrespectively of the fragment position in the molecule. This is in contrast to the related MO description of bond multiplicities, which gives rise to a strong differentiation between alternative sites and bonds, which reflects the chemical intuition of the familiar structural formulas. Often, as in the case of the π -bonds C_1–C_3 in butadiene and C_i–C_{i+2} bond in benzene, the MO approach unrealistically predicts exactly vanishing bond indices, which can be regarded only as the artifacts of the adopted bond-order measure.

The present analysis of the implications of the reduced molecular channels complements a related analysis of the *partial* channels for molecular fragments [22], representing both the separated (mutually disconnected, closed) subsystems [22a] and those exhibiting the inter-subsystem "communications" (mutually connected, open fragments) [22b]. These alternative approaches also generate additive combination rules and provide an independent confirmation of the fundamental difference between the MO and entropy/



Scheme 7 The AIM-resolved molecular communication channel for π electrons in benzene. Probabilities are from the Hückel theory. Only the first column $\boldsymbol{P}(\mathbf{B}|1)$ of the conditional probability matrix $\boldsymbol{P}(\mathbf{B}|\mathbf{A})$ is shown in the diagram; the remaining columns are uniquely determined by symmetry and represent the permutations of the elements in the first column

information descriptions of the bonding patterns in molecular systems. It follows from all these entropy/information measures of the internal and external chemical bonds of molecular subsystems that they are practically equalized for the ground-state molecular distributions of the electron probabilities in the atomic resolution. Thus, within the communication system approach these stationary quantum mechanical distributions of electrons correspond to the equilibrium entropic *intensities* of chemical bonds in the molecule.

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References

1. Fisher RA (1925) Proc Cambridge Philos Soc 22:700; Frieden BR (2000) Physics from the Fisher information – a unification. Cambridge University Press, Cambridge
2. Shannon CF (1948) Bell System Tech J 27: 379, 623; Shannon CE, Weaver W (1949) A mathematical theory of communication. University of Illinois, Urbana
3. Abramson N (1963) Information theory and coding. McGraw-Hill, New York
4. Pfeifer PE (1978) Concepts of probability theory. Dover, New York
5. Kullback S, Leibler RA (1951) Ann Math Stat 22:79; Kullback S (1959) Information theory and statistics. Wiley, New York
6. (a) Nalewajski RF, Parr RG (2000) Proc Natl Acad Sci USA 97:8879; (b) (2001) J Phys Chem A 105:7391
7. (a) Nalewajski RF (2002) Phys Chem Chem Phys 4:1710; (b) (2002) Int J Mol Sci 3:237; (c) (2003) Adv Quant Chem 43:119
8. (a) Nalewajski RF (2003) J Phys Chem A 107:3792; (b) (2002) Acta Chim Phys Debr 34–35: 131; (c) (2004) Ann Phys (Leipzig) 13:201
9. Nalewajski RF (2003) Chem Phys Lett 372:28; (2003) Chem Phys Lett 375:196
10. Nalewajski RF (2004) Chem Phys Lett 386:265
11. Nalewajski RF, Loska R (2001) Theoret Chem Acc 105:374
12. (a) Nalewajski RF, Świtka E, Michalak A (2002) Int J Quantum Chem 87:198; (b) Nalewajski RF, Świtka E (2002) Phys Chem Chem Phys 4:4952; (c) Nalewajski RF, Broniatowska E (2003) J Phys Chem A 107:6270; (d) (2003) Chem Phys Lett 376:33; (e) (2005) Int J Quantum Chem 101:349; (f) (2005) Mol Phys, (submitted)
13. Nalewajski RF (2000) J Phys Chem A 104:11940
14. Nalewajski RF, Jug K (2002) In: Sen KD (ed) Reviews of modern quantum chemistry: a cellebration of the contributions of Robert G. Parr, vol. 1. World Scientific, Singapore, p 148

15. Nalewajski RF (2004) Mol Phys 102:531, 547; (2004) Struct Chem 15:395
16. Hirshfeld FL (1977) Theoret Chim Acta (Berlin) 44:129
17. Parr RG, Yang W (1984) J Am Chem Soc 106:4049
18. Nalewajski RF, Korchowiec J (1997) Charge sensitivity approach to electronic structure and chemical reactivity. World Scientific, Singapore; Nalewajski RF, Korchowiec J, Michalak A (1996) In: Nalewajski RF (ed) Density functional theory IV: theory of chemical reactivity. Top Curr Chem 183:25
19. Kohn W, Sham LJ (1965) Phys Rev 140A:1133
20. (a) Wiberg KA (1968) Tetrahedron 24:1083; (b) Gopinathan MS, Jug K (1983) Theoret Chim Acta (Berl) 63:497, 511; (c) Jug K, Gopinathan MS (1990) In: Maksić ZB (ed) Theoretical models of chemical bonding, vol. II. Springer, Berlin Heidelberg New York, 77, and references therein
21. (a) Nalewajski RF, Köster AM, Jug K (1993) Theoret Chim Acta (Berl) 85:463; (b) Nalewajski RF, Mrozek J (1994) Int J Quantum Chem 51:187; (c) Nalewajski RF, Formosinho, SJ, Varandas AJC, Mrozek J (1994) Int J Quantum Chem 52:1153; (d) Nalewajski RF, Mrozek J, Mazur G (1996) Can J Chem 74:1121; (e) Nalewajski RF, Mrozek J, Michalak A (1997) Int J Quantum Chem 61:589; (f) Mrozek J, Nalewajski RF, Michalak A (1998) Polish J Chem 72:1779
22. (a) Nalewajski RF (2005) J Math Chem 38:43; (b) (2005) Mol Phys 103:451
23. Sanderson, RT (1976) Chemical bonds and bond energy, 2nd edn. Academic, New York
24. Parr RG, Donnelly RA, Levy M, Palke WE (1978) J Phys Chem 69:4431