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Entropy/information bond indices of molecular fragments

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The communication channels of the disconnected (mutually non-bonded, closed) parts of the molecule are investigated. The entropy/information indices of such subsystems are proposed as measures of the intra-fragment (*internal*) information bond-order and its covalent/ionic components. The molecular fragment bond-order conservation and a competition between its ionic and covalent contributions are examined. An approximate scheme in the spirit of the grouping theorem of the Information Theory (IT), for combining the subsystem entropy/information data into the corresponding global quantities describing the system as a whole, is derived and tested. It uses the independent subsystem approximation to estimate the entropy/information indices of the inter-fragment (*external*) chemical interactions in the molecule. The applications to simple orbital models, including the three-orbital model of the transition state complex and the π bond systems (butadiene and benzene) in the Hückel theory approximation, are used to illustrate the concepts proposed.

KEY WORDS: atoms-in-molecules, bond-orders, chemical bonds communication theory, entropy information, information theory, molecular fragments

1. Introduction

The *Information Theory* (IT) [1] has recently been applied to interpret the electronic structure of molecules in terms of their subsystems and the associated chemical bond multiplicities. It has been used to probe the promoted states of bonded atoms [2–7] and to diagnose the chemical bonds in molecules [8–12] or interactions between reactants [6b,13]. These applications have demonstrated the potential of the IT approach in extracting the *chemical* interpretation of the calculated molecular distributions of electrons. The theory allows one to treat various stages of the molecular reconstruction of the free (non-bonded) atoms in chemical processes, both intermediate and final. The Hirsheld [14] subsystems, e.g., *Atoms-in-Molecules* (AIM), have been shown to represent the unique, equilibrium pieces of the molecular one-electron density, which locally equalize their information-distance densities, relative to the free atoms of the isoelectronic promolecule, at the corresponding global value. The "*stockholder*" principle of Hirshfeld has been justified using the constrained variational principle for the information distance (entropy deficiency, missing information, cross-entropy) of Kullback and Leibler [1h,i], using the *global* (Shannon [1b,c] or *local* (Fisher [1a, g]) measure of the information content of the electron distribution. The densities of the missing-information and the Shannon entropy displacement have also been related to the molecular density difference function, which uses the same promolecular reference and is widely used by theoretical chemists to separate the charge redistribution due to the chemical bonds [6]. With this development the *surprisal* of the entropy deficiency of the molecular electron distribution has been related to the density difference function, thus providing the latter a novel missing information interpretation. The *Charge-Transfer Affinities*, representing the generalized forces driving changes in the electronic structure of the donor–acceptor reactive systems, have also been introduced [6b]. They combine the familiar *Fukui function* [15] response properties of molecular fragments (derivatives of the system energy) with the corresponding information-distance densities (derivatives of the system missing information), thus providing a more complete description of reactants.

This free-atom (promolecule) referenced information-theoretic approach to molecular systems demonstrates the importance of the entropy/information quantities of IT for extracting an understanding of the "*chemistry*" behind the calculated molecular electron distributions. Such information-theoretic concepts facilitate a more direct connection between the *ab initio* results of computational quantum chemistry and the intuitive *language* of chemistry, in which such concepts as bonded atoms, bond multiplicities, promotion energy, amount of charge transfer, electronegativity, and hardness/softness characteristics of the electron gas in a molecule, play a crucial role. The energy and entropy deficiency criteria for the equilibrium distribution of electrons in molecules and their fragments have been examined and the thermodynamic-like, local description of molecular subsystems have been proposed [7]. The effective external potential *representability* of the molecular fragment densities have also been discussed [2b,4b].

An important part of the chemical understanding of molecules is an adequate indexing of multiplicities ("orders") of the chemical bonds [16–18]. It has been recently demonstrated, that this key issue can be also successfully approached using concepts and techniques of the IT [8–12]. It has been argued that the chemical bonds, representing the AIM "connectivities", define a "transmission" network, through which the information contained in the electron probability distributions can be transferred throughout the molecule. It has been shown that the theory of communication systems [1b–f] can be used to generate the global entropy/information descriptors of the chemical bonds and their covalent/ionic composition [8–10]. These overall entropy/information descriptors of the chemical bonds in several model bonding and non-bonding electron configurations were shown to generally agree with the chemical intuitive expectations.

Chemistry is the science about both molecules and their constituent fragments, e.g., a given pair of AIM or a larger collection of bonded atoms: functional groups, reactants, etc. Therefore, besides the *global* bond indices, characterizing the chemical bond multiplicity and its covalent/ionic composition of the system as a whole, of interest in chemistry also are the entropy/information bond characteristics of molecular subsystems, reflecting the overall multiplicities of both the *internal* chemical interactions, between the subsystem constituent AIM, and *external* chemical bonds linking the fragment in question and the rest of the molecule. In this work we shall approach this classical problem from the *Communication Theory* viewpoint [8–12], which naturally connects to the *two*-electron *Valence Bond* (VB) perspective of Heitler and London [19] thus representing a direct continuation of these classical ideas of quantum chemistry and providing them a complementary entropy/information extension. Since the details of this information-theoretic approach to the global chemical bond orders in molecular systems have already been presented elsewhere [8,10], we shall limit the present introduction only to its basic elements. In this theory the molecular system in atomic resolution $M = (i \mid j \mid k \mid l \mid \ldots)$, consisting of the mutually bonded (open) AIM (i, j, k, l, ...), is interpreted as the "communication" channel, in which the "signals" of the electron allocations to constituent atoms are propagated from the molecular (**A**) or promolecular ($\mathbf{A}^0$) *input* ("source") to the molecular *output* (**B**) ("receiver") via a transmission network defined by the AIM-resolved molecular two-electron conditional probabilities $\mathbf{P}(\mathbf{B}|\mathbf{A}) = \{P(j|i) = P_{i,j}/P_i\}$; here, the joint *two*-electron probabilities $\mathbf{P}=\{P_{i,j}\}$ correspond to the event of simultaneously finding two electrons on specified AIM and the molecularly normalized *one*-electron probabilities $\boldsymbol{P} = \{P_i = \Sigma_j P_{i,j}\}$ correspond to events of locating an electron on specified bonded atom: $\Sigma_i \Sigma_j P_{i,j} = \Sigma_i P_i = 1$. The corresponding set of the atomic probabilities $\boldsymbol{P}^0 = \{P_i^0\}$, where $\Sigma_i P_i^0 = 1$, for the isoelectronic *Atomic Promolecule* (AP) $\mathrm{M}^0 = (i^0|j^0|k^0|l^0|\ldots)$, defines the promolecular input scheme, corresponding to a collection of the promolecularly normalized one-electron probabilities of the free mutually non-bonded (closed) constituent atoms shifted to their actual positions in the molecule. The electron delocalization accompanying the bond formation is responsible for the communicational "noise" affecting the flow of information throughout the molecular channel.

The atomic *condensed* probabilities, which define the molecular communication network, are proportional to the corresponding electron and electron-pair populations in the bonded atom resolution, resulting from a division of the one- and two-electron densities of the constituent atoms, using, e.g., the *stockholder* partition scheme of the molecular electron density [6] and its generalization covering the exhaustive AIM-cluster division of the molecular many-electron distributions [7]. In the present illustrative applications to simple bond models using the *Orthogonal Atomic Orbital* (OAO) [1,3], in which each AIM contributes a single orbital to form the chemical bonds with remaining AIM, this division is uniquely determined by the structure of the *Molecular Orbitals* (MO) of the standard LCAO MO approximation. In the general case one can use for example the symmetrically (Löwdin) othogonalized OAO basis set to determine the AIM-resolved electron populations. It should be emphasized, that these AIM resolved probabilities can be alternatively extracted in the basis set independent way, e.g., by integrating the AIM-resolved stockholder pieces of the molecular one- and two-electron densities [3,14] from any sort of quantum mechanical calculations.

The average molecular *conditional entropy*,

$$S(\mathbf{B}|\mathbf{A}) = -\Sigma_{i\in M}\Sigma_{j\in M}P_{i,j}\log[P_{i,j}/P_i] = -\Sigma_{i\in M}\Sigma_{j\in M}P_{i,j}\log P(j|i) \equiv S_M, \quad (1)$$

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

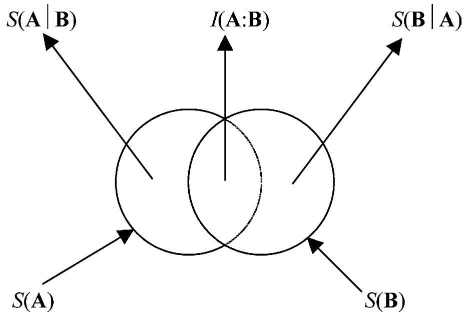
$$I(\mathbf{A}^0:\mathbf{B}) = I(\mathbf{B}:\mathbf{A}^0) = \Sigma_{i\in M}\Sigma_{j\in M}P_{i,j}\log[P_{i,j}/(P_i^0 P_j)]$$
$$= \Sigma_{i\in M}\Sigma_{j\in M}P_{i,j}\log[P(i|j)/P_i^0] \equiv I_M, \quad (2)$$

the standard descriptors of communication channels in the IT [1b-f], have been identified previously as adequate measures of the global *covalent* and *ionic* components of the system chemical bonds [8–12]. They define the associated overall entropy/information bond index:

$$N(\mathbf{A};\mathbf{B}) = S(\mathbf{B}|\mathbf{A}) + I(\mathbf{A}^0:\mathbf{B}) \equiv N_M. \quad (3)$$

The quantity of equation (1) 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. It thus provides a measure of the *communication noise* in the molecular channel. The quantity of equation (2) measures the complementary aspect of the molecular communication network, i.e., the *amount of information* flowing through the channel. These complementary entropy/information descriptors are illustrated in scheme 1.

The Communication Theory of the chemical bond views the molecular system as an information network exhibiting the quantum–mechanical *noise* in propagating the atom assignment signals of valence electrons, due to the chemical bonds connecting bonded atoms. Alternative entropy/information quantities, which can be used to characterize such molecular communication channels, have been examined. The information-theoretic measures of the system *global* entropic *covalency* and its information *ionicity* have been established [8–10] and the entropy/information descriptors of the chemical bonds of molecular fragments derived from the subsystem *partial* [12] and *reduced* [11] communication channels have been developed and tested. It is the main purpose of the present work to present alternative approach to the entropic bond indices of molecular subsystems, which is based upon the disconnected/independent fragment



Scheme 1. A qualitative diagram of the conditional entropy and mutual information quantities for two probability distributions: $\boldsymbol{P}(\boldsymbol{a}) = \boldsymbol{p}$ and $\boldsymbol{P}(\boldsymbol{b}) = \boldsymbol{q}$, where $\boldsymbol{a}$ and $\boldsymbol{b}$ denote the corresponding sets of events. They define the two *probability schemes*: $\mathbf{A} = \{\boldsymbol{a}; \boldsymbol{P}(\boldsymbol{a})\}$ and $\mathbf{B} = \{\boldsymbol{b}; \boldsymbol{P}(\boldsymbol{b})\}$. Two circles enclose the areas representing the Shannon entropies $S(\mathbf{A}) \equiv -\Sigma_i p_i \log p_i$ and $S(\mathbf{B}) \equiv -\Sigma_j q_j \log q_j$ of the two separate distributions. The common (overlap) area of the two circles corresponds to the mutual information $I(\mathbf{A} : \mathbf{B})$ in both distributions. The remaining parts of two circles represent the corresponding conditional entropies $S(\mathbf{A}|\mathbf{B})$ and $S(\mathbf{B}|\mathbf{A})$, measuring the residual uncertainty about events in a one set, when one has the full knowledge of the occurrence of the events in the other set of outcomes. The area enclosed by the envelope of the two overlapping circles then represents the entropy of the product (joint) distribution $\mathbf{P} = \mathbf{P}(\boldsymbol{a}, \boldsymbol{b})$: $S(\mathbf{AB}) = S(\mathbf{A}) + S(\mathbf{B}) - I(\mathbf{A} : \mathbf{B}) = S(\mathbf{A}) + S(\mathbf{B}|\mathbf{A}) = S(\mathbf{B}) + S(\mathbf{A}|\mathbf{B})$.

approximation. The latter supplements the *internal* bond descriptors, resulting from the disconnected communication channels of molecular parts, with the approximate *external* bond contributions of the independent molecular fragments treated as whole units.

The key issue in the molecular fragment development is an extraction of the relevant subsystem communication channel from the known molecular channel. Previously, the bonding patterns of the constituent subsystems have been generated from the *partial* channels [12] of the mutually *bonded* (connected, open, and embedded) molecular fragments, which appear in the additive decomposition of the global entropic bond-order measures. Alternatively, one can apply the molecular channel *reduction* [11], by combining several AIM into a single input/or output unit, to extract both the internal and external bond multiplicities of molecular subsystems. The key issue to be addressed in such an approach is a judicious targeting of the reduction scheme to address specific chemical problems. The subsystem reductions of the molecular channel were shown to offer a flexible way to *turn-on* or *turn-out* specific bonds in the molecule, and thus to extract measures of the internal and external bonds of the bonded molecular fragment. Both the partial and reduced channel approaches effectively take into account all "communications" between the subsystem in question and the rest of the molecule. These treatments give rise to the subsystem entropy/information indices of both the *internal* (intra-fragment) and *external* (between the subsystem and its molecular environment) chemical bonds which emphasize the *equilibrium* (equalized) character of the molecular ground-state. More specifically, the predictions for the localized bonds between alternative pairs of AIM, exhibit only a minor variations, contrary to the Molecular Orbital description [16–18], which predicts larger variations between bond indices.

In the present work we shall approach this problem through the communication channels of the mutually *non-bonded* (disconnected, closed, separated) fragments of the molecule. The communication channels describing the *separated* (closed, disconnected) parts of the molecule, which generate the fragment *internal* bond indices, can be subsequently coupled in the molecule in accordance with the conditional probabilities of the *independent* molecular fragments, to generate the approximate *external* bond descriptors of the Communication Theory. We shall evaluate the accuracy of such an approximation by applying it to several simple orbital models which have previously been used to test the entropy/information indices of the chemical bond [8–12]. These internal and external information bond indices of molecular subsystems will then be combined into the corresponding global descriptors. The resulting approximate combination rules will be related to the *Grouping Axiom* of the Shannon IT [1b]. This simple scheme will be shown to reproduce the global indices of simple model systems to a remarkably high accuracy.

2. Renormalized channels of the separated diatomics-in-molecules

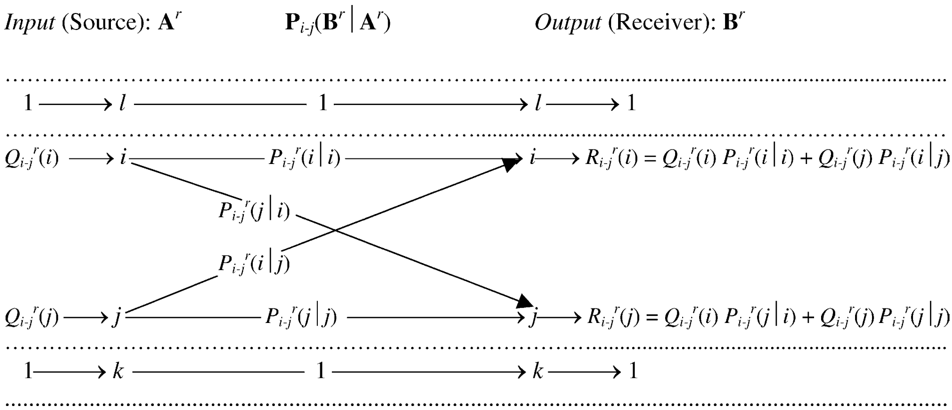
By *closing* a group of the externally non-bonded atoms in the molecular communication channel one can limit the range of the electron delocalization to any set of AIM, e.g., a pair or a larger subset of constituent atoms. The renormalized (r) communication channel for the diatomic (i, j) in the constrained system $M^*(i, j) = (\ldots|l|i\,\vdots\, j|k|\ldots)$, in which only atoms i and j are mutually bonded (open), is shown in scheme 2; here the vertical solid line separates the mutually closed subsystems, while the vertical broken line signifies the freedom of the two subsystems to exchange electrons, i.e., to form chemical bonds.

The renormalized conditional probabilities of such a communication channel have to satisfy the closure relations: $Q^r_{i-j}(i) + Q^r_{i-j}(j)=1$ and $\Sigma_{m=(i,j)} P^r_{i-j}(m|n)=1$, for $n\in(i, j)$. They are obtained from the (i, j)-block, $\mathbf{P}_{i-j}$, of the molecular condensed two-electron probabilities $\mathbf{P}$, which determines the subsystem sums:

$$\Sigma_{k=(i,j)}\Sigma_{l=(i,j)}P_{k,l} = \wp_{i-j}, \quad \Sigma_{k=(i,j)}P_{k,l} = \wp_{i-j}(l), \quad \Sigma_{l=(i,j)}P_{k,l} = \wp_{i-j}(k)$$
$$\text{for } (k,l) \in (i, j), \tag{4}$$

and the renormalized probabilities:

$$\begin{aligned}&\{Q^r_{i-j}(n) = \wp_{i-j}(n)/\wp_{i-j}\} = \boldsymbol{P}_{i-j}(\mathbf{A}^r) = \boldsymbol{P}_{i-j}(\mathbf{B}^r),\\ &\{P^r_{i-j}(m,n) = P_{m,n}/\wp(i,j)\} = \mathbf{P}_{i-j}(\mathbf{A}^r\mathbf{B}^r),\\ &\{P^r_{i-j}(m|n) = P^r_{i-j}(m,n)/Q^r_{i-j}(n)\} = \mathbf{P}_{i-j}(\mathbf{B}^r|\mathbf{A}^r);\ (n,m)\in(i,j).\end{aligned} \tag{5}$$

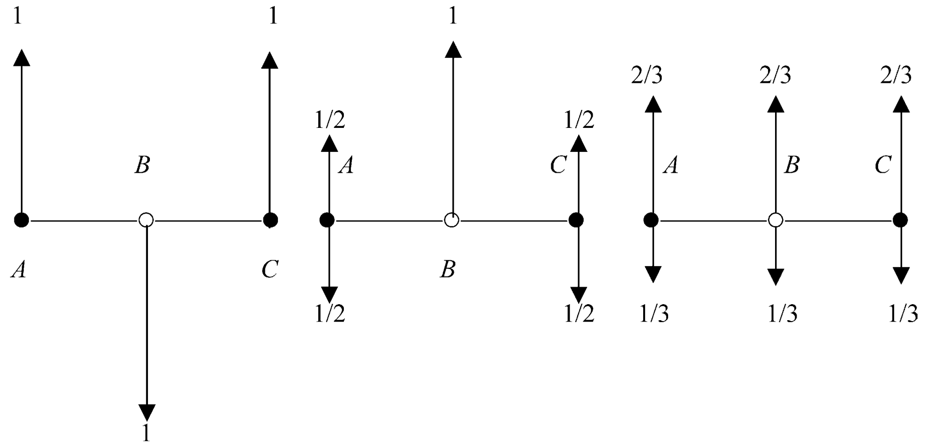


Scheme 2. Schematic diagram of the communication channel for the separated diatomic in molecule, consisting of mutually open AIM i and j in $M^*(i, j) = (\ldots |l|i|j|k| \ldots)$. The inter-atomic probabilities are the AIM-resolved conditional probabilities. The same convention is used in the remaining schemes of communication channels.

As an illustration let us consider the 3-OAO model of the symmetric TS complex [17b, c]. It describes three electrons contributed by the three constituent atoms in a symmetric Transition-State (TS) complex $[A_1—B—A_2]^{\ddagger}$ of 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 the three OAO $\boldsymbol{X}(\boldsymbol{r}) = \{A(\boldsymbol{r}), B(\boldsymbol{r}), C(\boldsymbol{r})\}$, centered on the respective AIM. The relevant 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 $M^0 = (A_1^0|B^0|A_2^0) = (A^1|B^1|C^1)$, which exhibits the highest degree of spin-pairing between the neighboring free atoms and thus – the highest spin distribution similarity to that of the molecular ground-state of TS complex.

The model molecular electron configuration is controlled by the charge of the middle atom B, $q{=}q_B = q_B^{\alpha} + q_B^{\beta}$, 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 $|\Sigma| \leqslant q \leqslant 2 - |\Sigma|$ and the overall spin polarization of the AP, $N^{\alpha,0} - N^{\beta,0} = 1$, is preserved in the bond-breaking–bond-forming process. It follows from the extended basis set UHF calculations for H_3 [17b,c] that the optimum TS configuration exhibits almost uniform distribution of electrons among 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.

In scheme 3 selected distributions of electronic spins of the model are reported 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 marks the maximum covalency (average electron uncertainty) for any fixed value of Σ [9, 10c], with the *Maximum Global*



(a) $\Sigma = -1$ **(b)** $\Sigma = 1$ **(c)** $\Sigma = 1/3$ (MGC)

$M = (\mathrm{A}\,¦\,\mathrm{B}\,¦\,\mathrm{C})$, $M = (\mathrm{A}\,¦\,\mathrm{B}\,¦\,\mathrm{C})$ $M = (\mathrm{A}\,¦\,\mathrm{B}\,¦\,\mathrm{C})$

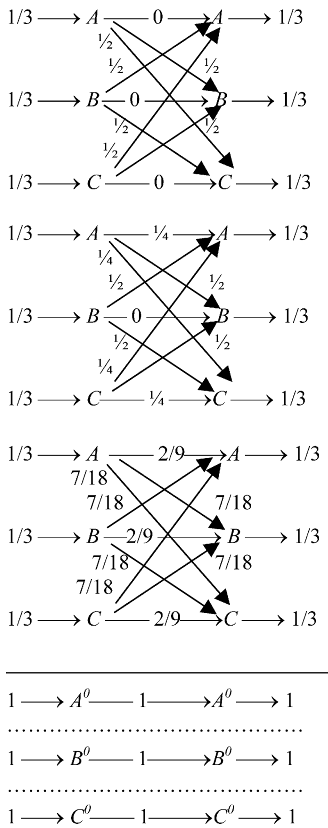
$M^0 = (\mathrm{A}^0|\mathrm{B}^0|\mathrm{C}^0)$ (AP)

Scheme 3. The atomic populations of the spin-up (↑) and spin-down (↓) electrons in the 3-OAO model of the symmetric TS for the uniform distribution of electrons among AIM ($q = 1$) and $\Sigma = \{-1$ (Panel *a*), 1 (Panel *b*), 1/3 (Panel *c*)$\}$. As also indicated in Panel *a* the ($\Sigma = -1$, $q = 1$) spin populations also characterize the assumed AP reference.

Covalency (MGC) structure corresponding to $\Sigma = 1/3$ (scheme 3*c*), for which the AIM spin populations are equalized. The communication channels for these three electron configurations of the model are shown in scheme 4, where the global entropy/information indices $N(\mathbf{A};\mathbf{B})$, $S(\mathbf{B}|\mathbf{A})$, and $I(\mathbf{A}:\mathbf{B})$ have also been reported. Throughout the paper the entropic bond descriptors are measured in bits. The renormalized channels of the separated (A, B) fragment for the uniform AIM electron populations ($q = 1$) are shown in scheme 5, while the corresponding channels for the (A, C) fragment are the subject of scheme 6. The overall (internal) entropy/information bond indices of the separated diatomic $(X, Y) \equiv X - Y$,

$$N^r_{X-Y} = S_{X-Y}(\mathbf{B}^r|\mathbf{A}^r) + I_{X-Y}(\mathbf{A}^r : \mathbf{B}^r), \tag{6}$$

are also reported in schemes 5 and 6, together with their components: the bond covalency, measured by the diatomic conditional entropy $S_{X-Y}(\mathbf{B}^r|\mathbf{A}^r)$, and its ionicity, measured by the mutual information $I_{X-Y}(\mathbf{A}^r : \mathbf{B}^r)$, for the renormalized diatomic input and output probabilities of equation (5). A reference to schemes 5 shows that the predicted diatomic bond multiplicities N^r_{A-B} (or – by symmetry – N^r_{B-C}) and N^r_{A-C} remain roughly preserved at about 1 bit level. Their composition reflects the relative importance of the ionic and covalent bond contributions.



$\Sigma = -1$, $M = (A{\mid}B{\mid}C)$; **(a)**

$N(\mathbf{A};\mathbf{B}) = 1.585$, $S(\mathbf{B}\mid\mathbf{A}) = 1$, $I(\mathbf{A}:\mathbf{B}) = 0.585$

$\Sigma = 1$, $M = (A{\mid}B{\mid}C)$; **(b)**

$N(\mathbf{A};\mathbf{B}) = 1.585$, $S(\mathbf{B}\mid\mathbf{A}) = 1.333$, $I(\mathbf{A}:\mathbf{B}) = 0.252$

$\Sigma = 1/3$, $M = (A{\mid}B{\mid}C)$ (MGC); **(c)**

$N(\mathbf{A};\mathbf{B}) = 1.585$, $S(\mathbf{B}\mid\mathbf{A}) = 1.542$, $I(\mathbf{A}:\mathbf{B}) = 0.043$

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

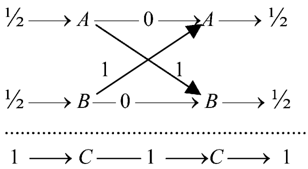
$N(\mathbf{A};\mathbf{B}) = 0$, $S(\mathbf{B}^0\mid\mathbf{A}^0) = 0$, $I(\mathbf{A}^0:\mathbf{B}^0) = 0$

Scheme 4. The molecular communication channels for the mutually bonded (open) AIM in the 3-OAO model of the molecular symmetric TS complex for $q = 1$ and $\Sigma = -1$ (a), 1(b), and 1/3(c). In panel d the corresponding AP channel is shown, representing the mutually non-bonded (closed) free atoms giving rise to three (disconnected, deterministic, noiseless) atomic channels and vanishing bond indices. For each channel the two-electron and conditional entropies, as well as the mutual information descriptors (in bits) are also reported.

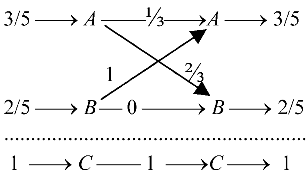
It is seen to change with both the molecular spin polarization and the choice of a diatomic. The A–B and A–C bonds are seen to be identical and almost purely covalent in the MGC structure, for $\Sigma = 1/3$ (panels c). For the $\Sigma = 1$ configuration (panels b) the A–B bond is predicted to be approximately half covalent and half ionic, while the A–C bond remains purely covalent. Finally, for the $\Sigma = -1$ (panels a) both the $A - B$ and $A - C$ bonds are diagnosed as purely ionic, as indeed reflected by the spin separation shown in scheme 3.

Next, let us examine the separated π-bonds in the hypothetical *biradical* butadiene, $M^*(A, B) = (A{\mid}B|C|D)$, with the π electrons of the remaining two (closed) carbon atoms C and D being excluded from the bond formation. We are interested in the entropy/information descriptors of the covalent/ionic

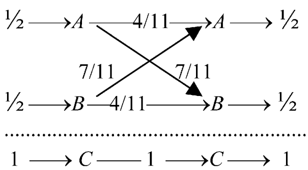
$M^*(A, B) = (A \mid B \mid C)$



(a) $\Sigma = -1$: $S_{A\text{-}B}(\mathbf{B}^r \mid \mathbf{A}^r) = 0$, $I_{A\text{-}B}(\mathbf{A}^r{:}\mathbf{B}^r) = 1$, $N_{A\text{-}B}{}^r = 1$;



(b) $\Sigma = 1$: $S_{A\text{-}B}(\mathbf{B}^r \mid \mathbf{A}^r) = 0.551$, $I_{A\text{-}B}(\mathbf{A}^r{:}\mathbf{B}^r) = 0.420$, $N_{A\text{-}B}{}^r = 0.971$;



(c) $\Sigma = ⅓$: $S_{A\text{-}B}(\mathbf{B}^r \mid \mathbf{A}^r) = 0.946$, $I_{A\text{-}B}(\mathbf{A}^r{:}\mathbf{B}^r) = 0.054$, $N_{A\text{-}B}{}^r = 1$.

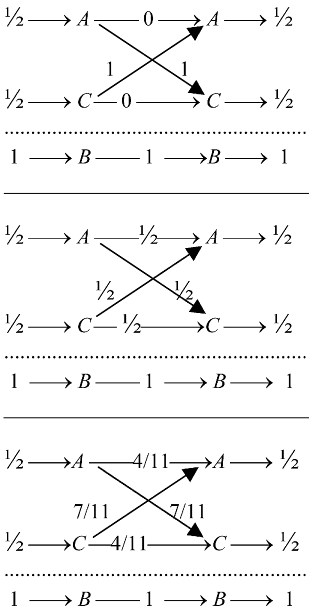
Scheme 5. Renormalized communication systems of the $A - B$ fragment in $M^*(A, B) = (A|B|C)$, for $q = 1$ and $\Sigma = -1$ (a), 1(b), and 1/3(c), in the 3-OAO model of the symmetric TS.

composition of the three sets of equivalent bonds in the Hückel approximation, {1–2, 3–4}, {2–2, 1–4}, and {1–3, 2–4}, for the consecutive numbering of atoms in the carbon chain. The corresponding renormalized communication channels, with the closed atoms removed to simplify the diagram, are shown in scheme 7, where the relevant entropy/information bond indices are also reported. The molecular channel and its entropic quantities are reported in scheme 9Ba.

As in the 3-OAO model, the resulting overall information index of 1 bit is preserved. It follows from the entropy/information data reported in scheme 7 that the terminal (1–2) and (3–4) bonds in the carbon chain practically exhibit the purely covalent character (panel a), while the (2–3) and (1–4) bonds, between the middle and terminal carbons, respectively, have distinctly higher ionic content (about 12%) (panel b). A comparable level of ionicity (around 8%) is predicted for the (1–3) and (2–4) bonds (panel c).

Of interest also are the corresponding diatomic channels for alternative pairs of carbon atoms in the benzene ring, shown in scheme 8. The corresponding molecular channel and its entropy/information indices are reported in scheme 10Ba. It should be stressed, that these hypothetical separated channels are defined by a single pair of bonded (open) ring atoms, thus corresponding to

$\boldsymbol{M^* = (A\,¦\,C|B)}$



(a) $\Sigma = -1$: $S_{A\text{-}C}(\mathbf{B}^r\,|\,\mathbf{A}^r) = 0$, $I_{A\text{-}C}(\mathbf{A}^r{:}\mathbf{B}^r) = 1$, $N_{A\text{-}C}^{\,r} = 1$;

(b) $\Sigma = 1$: $S_{A\text{-}C}(\mathbf{B}^r\,|\,\mathbf{A}^r) = 1$, $I_{A\text{-}C}(\mathbf{A}^r{:}\mathbf{B}^r) = 0$, $N_{A\text{-}C}^{\,r} = 1$;

(c) $\Sigma = ⅓$: $S_{A\text{-}C}(\mathbf{B}^r\,|\,\mathbf{A}^r) = 0.946$, $I_{A\text{-}C}(\mathbf{A}^r{:}\mathbf{B}^r) = 0.054$, $N_{A\text{-}C}^{\,r} = 1$.

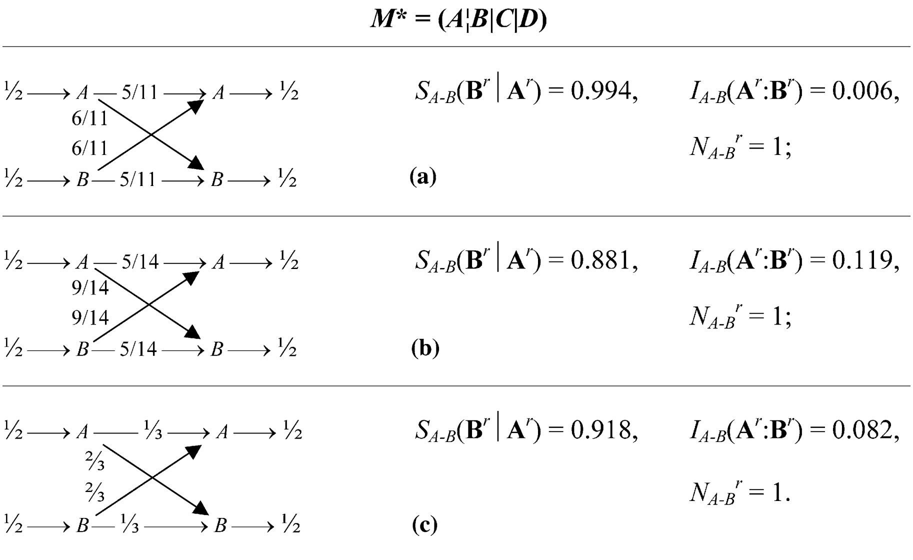
Scheme 6. Renormalized communication systems of the $A - C$ fragment in $M^*(A, C) = (A¦C|B)$, for $q = 1$ and $\Sigma = -1(a)$, $1(b)$, and 1/3 (c), in the 3-OAO model of the symmetric TS.

the localized (single) π electrons on each of the remaining non-bonded (closed) carbon atoms in the benzene ring.

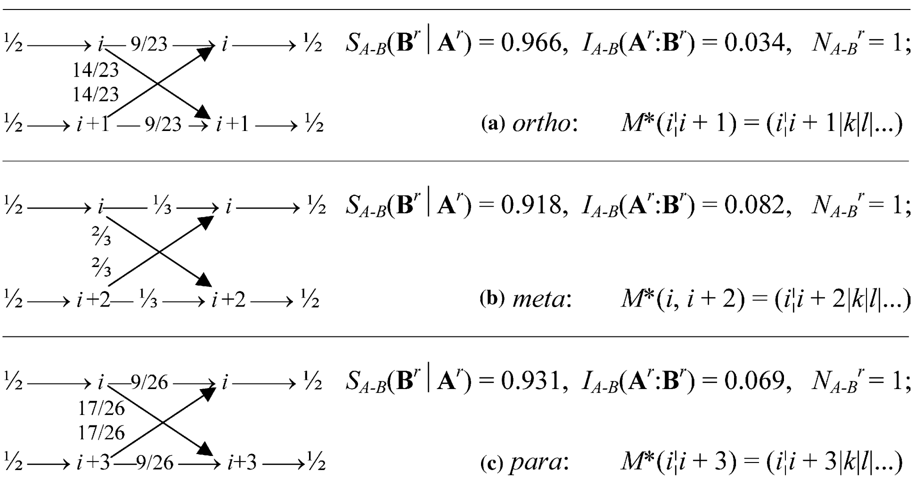
A reference to scheme 8 indicates that all these hypothetical (localized) π bonds in the benzene ring are strongly covalent and exhibit only a residual information ionicity below 10%. The highest entropy covalency (lowest information ionicity) is found for the mutual *ortho*-position of the two carbon atoms, while the lowest covalency (highest ionicity) is observed for the *meta*-pairs or the ring AIM; the *para* C–C interaction exhibits intermediate levels of the two bond components, which are relatively closer to the *meta* than *ortho* predictions.

3. Mutually separated groups of AIM

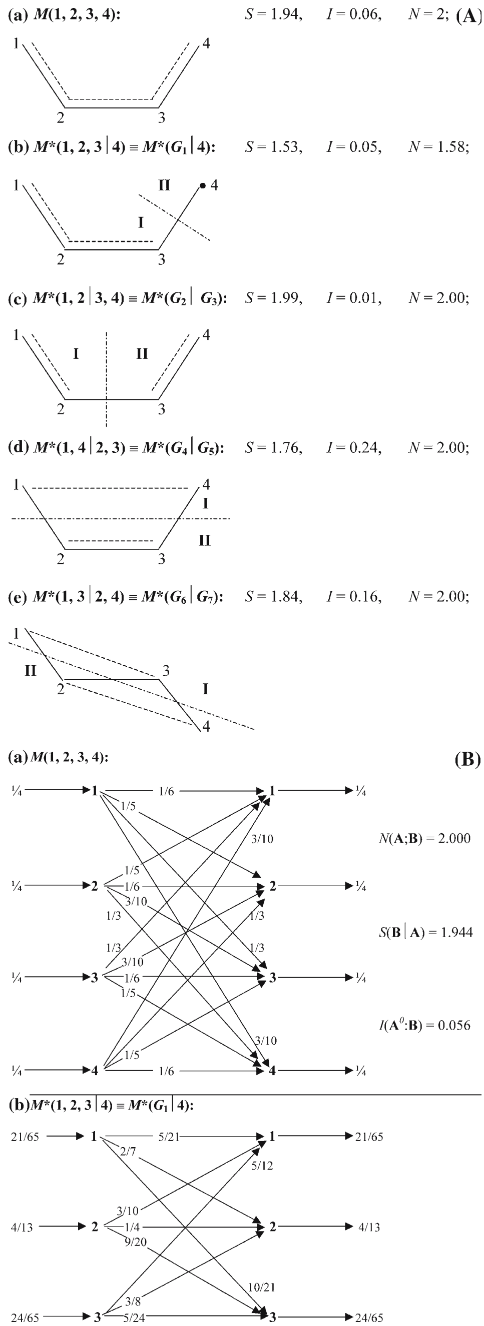
One can also consider several mutually separated (disconnected, closed, non-bonded) groups $\boldsymbol{G}=\{G_i\}$, each consisting of the chemically interacting (connected, open, bonded) subset of constituent atoms, with the chemical bonds being allowed exclusively within each group, e.g., $M^*(G_1|G_2|G_3) = (i¦j¦\ldots|k¦l¦\ldots|m¦n¦\ldots) \equiv M^*(i, j, \ldots|k, l, \ldots|m, n, \ldots)$. Examples of such a division of the π-bond systems in butadiene and benzene are shown in schemes



Scheme 7. Renormalized communication systems for the $A - B$–fragment in the biradical butadiene $M^*(A, B) = (A|B|C|D)$ in the Hückel approximation: $A - B$ ={1–2 or 3–4} (panel *a*), {2–3) or (1–4)} (panel *b*), and {1–3 or 2–4} (panel *c*). The closed carbon atoms C and D, which are hypothetically excluded from forming the π-bonds in the carbon chain, are not shown in these diagrams.



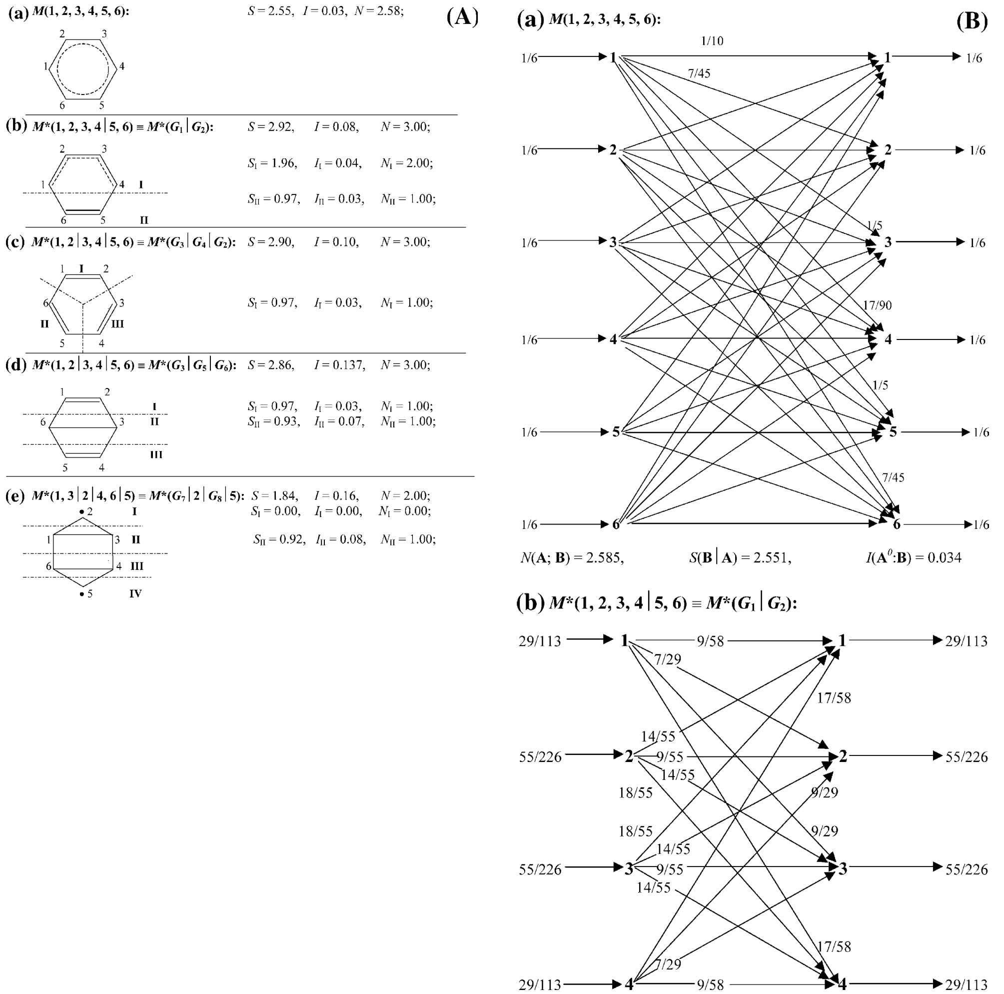
Scheme 8. Renormalized, separated π-electron communication systems for alternative pairs $i - j$ of carbon atoms in benzene, $M^*(i, j) = (i|j|k|l|...)$: $j = i + 1$ (panel *a*), $i + 2$ (panel *b*), and $i + 3$ (panel *c*), in the Hückel approximation. The closed carbon atoms $k \neq (i, j)$, which are hypothetically excluded from forming π-bonds with the system remainder, are not shown in the diagrams.



Scheme 9. The mutually separated groups of AIM in the butadiene π-chain (part A) and their entropy/information indices (in bits). In part B the communication channels are shown for the butadiene as a whole and for the triatomic allyl chain $G_1 = (1, 2, 3)$. The corresponding channels for the diatomic fragments have been reported in scheme 7.

9 and 10, respectively, where the relevant channels (in the Hückel theory approximation) of both the system as a whole and of its separated fragments are reported together with the corresponding entropy/information indices. Due to the mutually disconnected character of these subsets of bonded atoms, the global indices of such hypothetically partitioned "molecular" systems are the corresponding sums of additive intra-group contributions. It follows from scheme 9 that the entropy/information indices of the overall bond multiplicity $N=S+I$ and its covalent (S) and ionic (I) components generally agree with intuitive chemical estimates for both the molecular and hypothetical ("valence") structures in butadiene. For example, a diminished information bond order for $M^*(1,2,3|4) = M^*(G_1|4)$ (panel A*b*) agrees with the 3/2-bit, i.e., 3/2 bond, expected for the allyl fragment G_1, with the remaining structures (panels A*c*–*e*), involving divisions into separate diatomic subsystems, all giving rise to the conserved, 2-bit (double) total π-bond index. The differences in "strengths" of the corresponding localized bonds are also well reflected by the bond composition. The lowest covalent component $N^{\mathrm{cov}} = 1.76$ bits is predicted in panel A*d*, for bonds corresponding to pairs of the terminal and middle carbon atoms, respectively, while the two pairs of neighboring atoms in panel A*c* generate almost purely covalent bond, $N^{\mathrm{cov}} = 1.99$ bits. The second-neighbor pairs in panel A*e* give rise to the bond composition, which is intermediate between these two extreme electronic structures.

Similar conclusions follow from the corresponding results for the "valence" structures in benzene, reported in scheme 10. Limiting the electron delocalization to the consecutive four carbon atoms in the benzene ring (panel A*b*) in $M^*(1,2,3,4|5,6)=M^*(G_1|G_2)$ gives the total 3-bit (triple) π-bond in the system, in a general agreement with the chemical expectation. The bond composition in the G_1 fragment is almost identical to that in butadiene, with effectively two almost purely covalent conjugated π-bonds; the 1-bit (single) bond in G_2 is also seen to be almost exclusively covalent in character. A comparison of these predictions with the entropy/information indices of the system as a whole (panel A*a*) indicates that the overall index, again of almost exclusively conditional entropy origin, becomes lowered, when the hypothetical barriers for the electron delocalization in the carbon ring are lifted. Indeed, the extra inter-group connections present in the molecular communication system of panel B*a*, relative to those resulting from the separate fragment channels of schemes 10B*b* and 8*a*, effectively lower the overall indeterminancy exhibited by the molecular π-electron probabilities. The entropic indices for the remaining partitions of panels A*c*–*e*, into the separate diatomic and atomic subsystems, are also seen to be in accord with the chemical intuition. The diatomic interactions across the benzene ring are diagnosed as generating a slightly higher information ionicity (panels A*d*,*e*), in comparison to those between the nearest neighbors (panels A*b*,*c*).



Scheme 10. The mutually separated groups of bonded carbon atoms in the π-bond ring of benzene (part A) and the normalized communication channels (part B) for the system as a whole (panel *a*) and the four atom fragment G_1(panel b) (see panels A (*a*,*b*)). The relevant two-atom channels of the separate bonds are summarized in scheme 8. In part a the predicted overall and group entropy/information indices (in bits) of the covalent and ionic bond components and the resulting overall bond index are listed. In the molecular channel of Panel B*a* only the first column $\mathbf{P}(\mathbf{B}|1)$ of the conditional probability matrix $\mathbf{P}(\mathbf{B}|\mathbf{A})$ is shown in the diagram; the remaining columns are uniquely determined by symmetry and represent permutations of the elements of the first column.

4. Combining the subsystem entropies into the global information indices

The renormalized probabilities of molecular subsystems (equation (5)) and communication channels of schemes 2, 5–10 are the fragment-conditional.

Indeed, the sum of equation (4),

$$\wp_{i-j} \equiv \wp_K = \wp_K(i) + \wp_K(j), \tag{7}$$

denotes the probability that a pair of electrons has been located in the molecule on the diatomic fragment $K = (i, j)$, with the partial sum $\wp_K(n)$ thus representing the probability that an electron of this pair on K will be found on nth AIM of K. Similarly, the group one-electron input probabilities of scheme 1 (see also equation (5)),

$$Q_K^r(n) = \wp_K(n)/\wp_K \equiv Q(n|K), \quad n \in K, \quad \Sigma_{n\in K} Q(n|K) = 1, \tag{8}$$

denotes the *conditional* probability of finding an electron on atom n in K. This conditional character of the subsystem renormalized distributions is also reflected by their respective normalizations, e.g., that in the preceding equation. A similar conditional interpretation applies to the output one-electron probabilities of scheme 1:

$$R_K^r(n) = Q_K^r(i)P_K^r(n|i) + Q_K^r(j)P_K^r(n|j) = P_K^r(n,i) + P_K^r(n,j) = Q(n|K). \tag{9}$$

The subsystem renormalized two-electron probabilities of equation (5) also have the conditional meaning. More specifically, for $\{m, n\} \in K$,

$$P_K^r(m,n) = P_{m,n}/\wp_K = P(m,n|K), \quad \Sigma_{m\in K}\Sigma_{n\in K} P(m,n|K) = 1. \tag{10}$$

This conditional interpretation of the subsystem renormalized probabilities naturally connects the above separated subsystem development to the scenario of the familiar *Grouping Axiom* of the IT [1b]. Let us consider a general discrete probability distribution $\boldsymbol{p} = \{p_i\} = \{\boldsymbol{p}_K\}$, where probabilities $\boldsymbol{p}_K = \{p_{i\in K}\}$ correspond to the exclusive groups of outcomes $\boldsymbol{G} = \{G_K \equiv K\}$ and

$$\Sigma_i p_i = \Sigma_K \left(\Sigma_{j\in K} p_j\right) \equiv \Sigma_K P_K = 1. \tag{11}$$

Here the vector $\boldsymbol{P}^G = \{P_K\}$ combines the normalized *condensed* probabilities P_K, of the molecular outcome in group K, which in turn define the fragment-conditional, intra-group probabilities:

$$\boldsymbol{\pi}_K = \{\pi(i \in K|K) = p_{i\in K}/P_K\}, \quad \Sigma_{i\in K}\pi(i|K) = 1. \tag{12}$$

The Grouping Axiom states that the inter- and intra-group entropies should be combined into the entropy of the whole probability distribution in the following way:

$$S(\boldsymbol{p}) = S(\boldsymbol{P}^G) + \Sigma_K P_K S(\boldsymbol{\pi}_K). \tag{13}$$

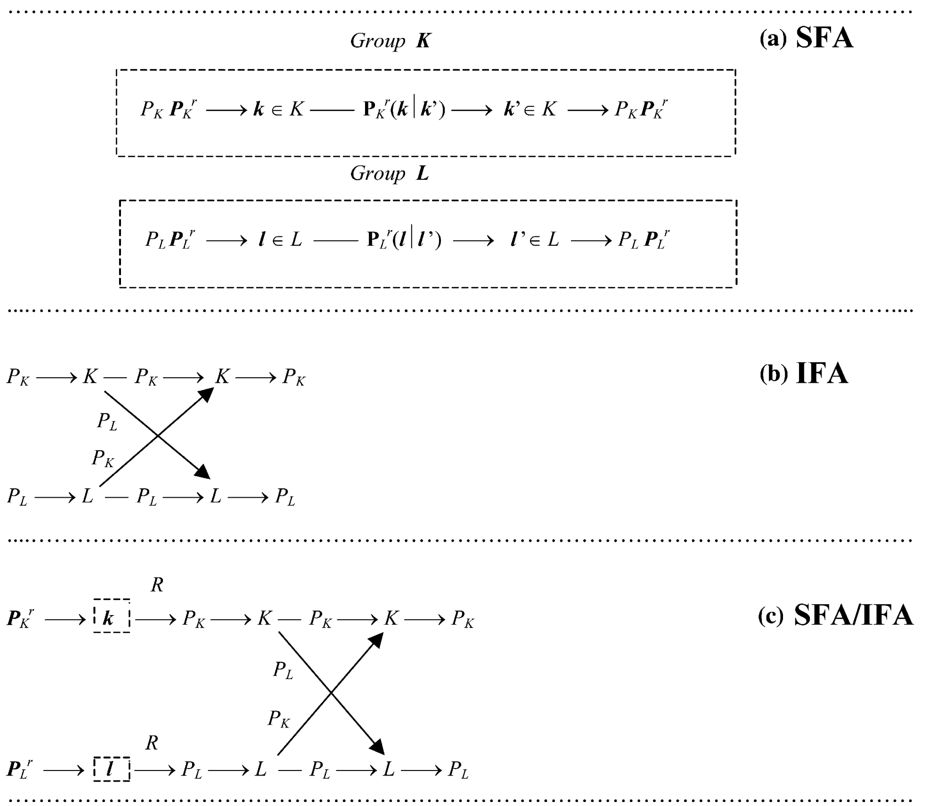
In other words, the entropy of the distribution $\boldsymbol{p}$ is the sum of the *inter-group* entropy $S(\boldsymbol{P}^G)$, solely determined by the condensed probabilities of the groups of outcomes, and the mean of the *intra-group* entropies $\{S(\boldsymbol{\pi}_K)\}$, generated by the fragment-conditional intra-group probabilities with the group probabilities $\boldsymbol{P}^G$ providing the "weights" in the average. This condition is indeed satisfied by the Shannon entropy, since using the normalization condition of equation (12) gives:

$$\begin{aligned} S(\boldsymbol{p}) &= -\Sigma_i p_i \log p_i = -\Sigma_K \Sigma_{j\in K} p_j \log p_j = -\Sigma_K P_K \Sigma_{j\in K} \pi(j|K) \log[P_K \pi(j|K)] \\ &= -\Sigma_K P_K \log P_K - \Sigma_K P_K [\Sigma_{j\in K} \pi(j|K) \log \pi(j|K)] \\ &= S(\boldsymbol{P}) + \Sigma_K P_K S(\boldsymbol{\pi}_K). \end{aligned} \tag{14}$$

We now seek similar *Combination Rules* for the global entropy/information indices of the chemical bond covalency and ionicity in terms of the internal bond indices of the *Separated Fragment Approximation* (SFA). Clearly, the disconnected character of the separated fragments misses the external (inter-fragment) part of the chemical communications between AIM. Therefore, the internal bond indices have to be supplemented by a realistic representation of contributions due to bonds between the groups of atoms defining the partition. The simplest is the *Independent Fragment Approximation* (IFA), in which the inter-subsystem two-electron probabilities, treated in the condensed subsystem resolution, are products of the condensed one-electron probabilities of the independent fragments (see scheme 11). In this approximation the inter-fragment mutual information index, measuring the information *ionicity* of these interactions vanishes identically (zero overlap case of scheme 1). In other words the IFA amounts to an assumption of a purely *covalent* character of the inter-group interactions. Therefore, it should be quite adequate in partitions involving practically neutral parts of the molecule, exhibiting negligible overall net charges. For example, this is the case in the π electron systems of butadiene and benzene, on which the resulting combination rules for bond indices will be tested.

When combining (mutually opening) the molecular subsystems in the *inter-subsystem* communication stage of scheme 11*b*, this combined SFA/IFA approach uses the AIM-resolved, molecular intra-subsystem two-electron probabilities at the separated subsystem stage of scheme 11*a*, and it views the inter-subsystem events, as involving the independent molecular fragments treated as whole units, or equivalently – the *average* bonded atoms on each fragment. The cascade of these two molecular channels, shown in scheme 11*c*, then determines the desired combination rule for generating the molecular bond indices from the condensed group probabilities and the intra-group entropies of the separated subsystems in the molecule.

Schemes 11*a*,*b* reflect two levels of acquiring the entropy/information characteristics of the whole molecular system, which are finally combined in the approximate molecular channel of scheme 11*c*. More specifically, the AIM resolved first panel extracts from the known molecular probabilities the internal bond indices of each separate (isolated) fragment at atomic level, while



Scheme 11. Combining the AIM-resolved channels of the separated fragments in $M^* = (\boldsymbol{k}|\boldsymbol{l}) = (K|L)$ (in boxes, panel a) with the subsystem-resolved channel of the independent molecular fragments in $M = (K, L)$ (panel b) into an effective molecular "cascade" (panel c). The effective channel of panel c allows one to use the subsystem entropy/information indices to generate the approximate global bond indices, of the open atoms in $M = (\boldsymbol{k}\boldsymbol{l})$. The symbol R in the last panel denotes the channel reduction, in which the separate AIM outputs of a given molecular fragment are "condensed" into a single output of the subsystem as a whole.

the less resolved IFA channel generates the complementary entropy/information measures characterizing the fragment-in-molecule.

Let us now examine the combination rule for the conditional entropy measure of the system global bond covalency. First, we exhaustively divide the constituent bonded atoms $\boldsymbol{i} = \{i\}$ of the molecule, $\boldsymbol{M} = (i, j, \ldots)$, among the exclusive groups of AIM in $M^* = (\boldsymbol{k}|\boldsymbol{l}|\ldots) \equiv (K|L|\ldots)$, representing the separated molecular fragments $\boldsymbol{K} = \{K\}$ (see scheme 11a). This partition defines the associated division of the molecular one-and two-electron probabilities: $\boldsymbol{P}=\{\boldsymbol{P}_K=\{P_k\}\equiv\boldsymbol{P}(\boldsymbol{k})\}$ and $\mathbf{P}=\{\mathbf{P}_{K,L}=\{P_{k,l}\}\equiv\mathbf{P}(\boldsymbol{k},\boldsymbol{l})\}$, where $k \in \boldsymbol{k}$, $l \in \boldsymbol{l}$, etc. The global conditional entropy index can then be transformed into the corresponding subsystem-resolved expression:

$$\begin{aligned} S(\mathbf{B}|\mathbf{A}) &= S(\boldsymbol{j}|\boldsymbol{i}) = -\Sigma_i \Sigma_j P_{i,j} \log(P_{i,j}/P_i) \\ &= -\Sigma_K \Sigma_L P_{K,L} \Sigma_{k\in K} \Sigma_{l\in L} (P_{k,l}/P_{K,L}) \log\{(P_{k,l}/P_{K,L})(P_{K,L}/P_K)/(P_k/P_K)]\} \\ &\equiv -\Sigma_K \Sigma_L P_{K,L} \Sigma_{k\in K} \Sigma_{l\in L} P(k,l|K,L) \log[P(k,l|K,L)P(L|K)/P(k|K)], \end{aligned} \tag{15}$$

where $\boldsymbol{P}^G = \{P_K = \Sigma_{k\in K} P_k\} \equiv \mathbf{P}(\boldsymbol{K})$ and $\{P_{K,L} = \Sigma_{k\in K} \Sigma_{l\in L} P_{k,l}\} \equiv \mathbf{P}(\boldsymbol{K}, \boldsymbol{K}')$. Here, $P(L|K)$ is the molecular condensed conditional probability of finding an electron on fragment L, when another electron has already been located on subsystem K, $\boldsymbol{P}^r_K \equiv P(\boldsymbol{k}|K) = \{P(k|K)\}$ groups the AIM-resolved subsystem conditional probabilities of finding an electron of group K on its constituent AIM $\boldsymbol{k}$, while $\mathbf{P}(\boldsymbol{k}, \boldsymbol{l}|K, L) = \{P(k, l|K, L)\} = \mathbf{P}^r_{K,L}(\boldsymbol{l}|\boldsymbol{k})$ groups the joint conditional probabilities that one electron of fragment K will be located on atoms $\boldsymbol{k} \in K$, when simultaneously another electron of L will be found on atoms $\boldsymbol{l} \in L$.

Next, let us examine the conditional entropy of the SFA channel of $M^* = (\boldsymbol{k}|\boldsymbol{l}|...)$ shown in scheme 11a. It consists of the separate (mutually closed, disconnected) group channels in atomic resolution, thus neglecting all the inter-subsystem two-electron connections, and involves the molecular input and output probabilities of the group constituent atoms: $\boldsymbol{P} = \{\boldsymbol{P}_K = P_K \boldsymbol{P}(\boldsymbol{k}|K)\}$. Therefore, in this SFA the overall conditional entropy of the channel 11a is the sum of additive group contributions weighted in accordance with the respective group probabilities in M:

$$\begin{aligned} S(\mathbf{B}^{SFA}|\mathbf{A}^{SFA}) &= -\Sigma_K P^{SFA}_{K,K} \Sigma_{k\in K} \Sigma_{k'\in K} P(k,k'|K) \log[P(K|K)^{SFA} P(k,k'|K)/P(k|K)] \\ &= -\Sigma_K P^{SFA}_{K,K} \log P(K|K)^{SFA} \\ &\quad -\Sigma_K P^{SFA}_{K,K} \Sigma_{k\in K} \Sigma_{k'\in K} P(k,k'|K) \log[P(k,k'|K)/P(k|K)] \\ &= \Sigma_K P_K S_K(\boldsymbol{k}|\boldsymbol{k}') \end{aligned} \tag{16}$$

where $P(K|K)^{SFA} = P^{SFA}_{K,K}/P_K \equiv \wp_K/P_K$, $\wp_K = \Sigma_{k\in K} \Sigma_{k'\in K} P_{k,k'} \equiv \Sigma_{k\in K} \wp_K(k)$, and $P(k,k'|K) \equiv P(k,k'|K,K)$. We have used in the preceding equation the normalization condition for the group two-electron conditional entropies (equation (10)) and recognized that the signal entering the subsystem K in the input must be received with certainty by the same subsystem in the output, so that in the overall subsystem resolution of scheme 11a $P(K|K)^{SFA} = P^{SFA}_{K,K}/P_K = 1$, thus giving rise to the vanishing first sum in the second line of the equation.

Therefore, the conditional entropy $S(\mathbf{B}^{SFA}|\mathbf{A}^{SFA})$, measuring the overall internal covalency in a collection of separated fragments in M^* (channel 8a), is the mean of the intra-subsystem covalencies, weighted in accordance with the molecular group probabilities $\boldsymbol{P}^G$. In other words, the SFA channel represents an ensemble of the fragment channels, with the subsystem condensed probabilities providing the corresponding ensemble probabilities, i.e., the weighting factors for calculating the average molecular uncertainties.

It should be observed that equation (16) represents the conditional entropy analog of the second, intra-group term in the Shannon theorem of equations (13) and (14). Its first term, for the groups as wholes, is generated by the inter-subsystem (external) IFA network shown in scheme 11*b*,

$$\begin{aligned} S(\boldsymbol{L}^{IFA}|\boldsymbol{K}^{IFA}) &= -\Sigma_K \Sigma_L P_{K,L}^{IFA} \log(P_{K,L}^{IFA}/P_K) \\ &= -\Sigma_L(\Sigma_K P_{K,L}^{IFA}) \log P_L = -\Sigma_L P_L \log P_L, \end{aligned} \tag{17}$$

since $P_{K,L}^{IFA} = P_K P_L$ and hence $P(L|K)^{IFA} = P_{K,L}^{IFA}/P_K = P_L$. Therefore, adding this *external* IFA entropy term to the corresponding SFA *internal* contribution of equation (16) gives rise to the following combination rule for the global conditional entropy (bond covalency) index in terms of the relevant quantities characterizing molecular fragments:

$$\begin{aligned} S(\mathbf{B}|\mathbf{A}) = S(\boldsymbol{j}|\boldsymbol{i}) &\cong S(\boldsymbol{L}^{IFA}|\boldsymbol{K}^{IFA}) + S(\mathbf{B}^{SFA}|\mathbf{A}^{SFA}) \\ &= S(\boldsymbol{P}^G) + \Sigma_K P_K S_K(\boldsymbol{k}|\boldsymbol{k}'), \end{aligned} \tag{18}$$

in the spirit of the Grouping Axiom of equation (13).

The corresponding combination rule for the global mutual information index, measuring the overall bond ionicity in the molecule as a whole, can be derived in a similar way. We start from the exact definition in the AIM resolution of molecular probabilities for $\mathbf{A}^0 = \mathbf{A}$, as is the case in all illustrative systems used in this analysis,

$$\begin{aligned} I(\mathbf{B}:\mathbf{A}) = I(\boldsymbol{j}:\boldsymbol{i}) &= -\Sigma_i \Sigma_j P_{i,j} \log[P_{i,j}/(P_i P_j)] \\ &= -\Sigma_K \Sigma_L P_{K,L} \Sigma_{k\in K} \Sigma_{l\in L} (P_{k,l}/P_{K,L}) \log\{(P_{k,l}/P_{K,L})/(P_k P_l/P_{K,L})]\} \\ &\equiv -\Sigma_K \Sigma_L P_{K,L} \Sigma_{k\in K} \Sigma_{l\in L} P(k,l|K,L) \log[P(k,l|K,L)/P^0(k,l|K,L)], \end{aligned} \tag{19}$$

where $P^0(k,l|K,L)$ stands for the joint probabilities of independent AIM, conditional upon the specified molecular fragment origins of the two electrons. Invoking next the SFA of scheme 11*a* then gives:

$$\begin{aligned} I(\mathbf{B}:\mathbf{A}) \cong I(\mathbf{B}^{SFA}:\mathbf{A}^{SFA}) &= -\Sigma_K P_{K,K}^{SFA} \Sigma_{k\in K} \Sigma_{k'\in K} P(k,k'|K) \\ &\quad \times \log[P(k,k'|K)/P^0(k,k'|K)] \\ &= \Sigma_K P_K I_K(\boldsymbol{k}:\boldsymbol{k}'), \end{aligned} \tag{20}$$

where $I_K(\boldsymbol{k}:\boldsymbol{k}')$ denotes the amount of information flowing through the separated fragment K.

As we have already observed above, the mutual information contribution corresponding to scheme 11*b* vanishes identically in the IFA, since the input and output probabilities are assumed to be independent in this approximation at the fragment resolution level. Therefore, the preceding equation already represents the final combination rule for the system global information ionicity in the combined SFA/IFA treatment of scheme 11*c*. This global index is thus approximated by the mean value of the intra-subsystem ionicity indices, with the relevant weights reflecting the condensed one-electron probabilities of the molecular fragments defining the partition.

In table 1 we have tested the performance of the approximate combination rules of equations (18) and (20) for the π bonds in butadiene and benzene, in the Hückel theory approximation. The relevant partitions of the bonded carbon atoms into subsystems, the associated communication channels of the separated subsystems and their entropy/information indices are summarized in schemes 7–10. In these alternant hydrocarbons one-electron probabilities of carbon atoms are identical, so that the group probabilities are proportional to the number of atoms participating in the π-bond system in the molecule. Thus, for the fragment K consisting of m_K carbon atoms, $P_K = m_K/m$, where m denotes the overall number of carbon atoms in the π-electron system. The reference global entropy/information data in table 1, for the molecule as a whole, have been reported in parts B*a* of schemes 9 and 10.

An inspection of table 1 shows, that the approximate combination rules for obtaining the global information indices of chemical bonds in the molecular system from the entropy/information descriptors of the separated molecular fragments work quite well indeed. They exactly reproduce the global information index N of all chemical bonds in the system and semi-quantitatively predict its covalent/ionic composition. It should be recalled that these rules have been derived using the SFA/IFA approximations, in which the molecular fragment data, acquired by treating each subsystem separately, are combined as the overall, independent units of the approximate molecular communication system. The success of these rules indicates that the entropy/information descriptors of molecular subsystems are relatively insensitive to the details of the fragment molecular environment. In other words, the internal bond indices of a given functional group established within the communication theory approach should be to a large extent "transferable" (in the combination rule sense of the word) from one molecule to another. The numerically validated adequacy of the IFA also implies,

Table 1
The performance of the combination rules for predicting the global entropy/information bond indices (in bits) from the separated molecular fragment data, for butadiene and benzene in the Hückel approximation.

		Butadiene (scheme 9)					Benzene (scheme 10)				
Bond index	Partition:	*a*	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
S		1.944	1.958	1.994	1.881	1.918	2.551	2.545	2.551	2.539	2.530
I		0.056	0.042	0.006	0.119	0.082	0.034	0.040	0.034	0.046	0.055
$N = S + I$		2.000	2.000	2.000	2.000	2.000	2.585	2.585	2.585	2.585	2.585

that the intra- and inter-fragment entropy/information indices of the molecular fragments are additive. This observation is in sharp contrast to the energetic characteristics of molecular subsystems, which are strongly non-additive.

In atomic resolution the ultimate partition of the atomic promolecular reference corresponds to the separated (disconnected) free atoms (scheme 4*d*). For this division scheme the intra-group entropy/information vanishes identically, thus predicting in the IFA the zero global mutual information, $I(\mathbf{B}:\mathbf{A}) = I(\mathbf{B}^{SFA}:\mathbf{A}^{SFA}) = I(\mathbf{B}^0:\mathbf{A}^0) = 0$, consistent with the independent status of each separated atom, and the global conditional entropy given by the group contribution $S(\mathbf{B}|\mathbf{A}) = (\boldsymbol{P}^G)$. In the 3-AO model ($q = 1$), butadiene, and benzene the probability of each atom in the molecular system is identical, $P_i = 1/m$, where m is the number or atoms. This gives $S(\mathbf{B}|\mathbf{A}) = N(\mathbf{A}; \mathbf{B}) = \log_2 m$(in bits).

5. Conclusion

We have explored the entropy/information descriptors of chemical bonds involving the *separated* molecular fragments. These *internal* (intra-group) contributions reflect the information bond indices of the inter-group disconnected communication channels of molecular subsystems. The complemenatry *external* (inter-group) terms, reflecting the fragment interaction with the molecular reminder, have been obtained by treating the whole (reduced) fragments as independent constituent parts of the molecule. This approximate combination rules parallel the familiar Grouping Axiom of IT and have been shown to give quantitatively correct predictions of the corresponding global quantities, characterizing the whole molecule. The present separated fragment development complements the alternative approaches, based upon the subsystem partial and reduced channels, which have been reported elsewhere [11,12].

It has been demonstrated, that the bonding patterns of the illustrative separated molecular subsystems, which emerge from the present communication theory approach, are generally in accord with the chemical intuition. Among others, it has been shown that in the benzene carbon ring an opening of the mutually closed diatomic fragments lowers the overall bond index, relative to that characterizing a collection of the disconnected fragments. Thus, the aromaticity of π electrons manifests itself by a *lowering* of the molecular entropy/information index relative to the hypothetical reference of the separated or partially delocalized π bonds. Thus, the natural tendency of the delocalized π electrons is to destabilize the regular hexagonal structure towards the distorted system. This is in accord with a modern outlook on the influence of the σ and π electrons on aromaticity, [20–22] in accordance to which the π bonds favor the distorted (cyclohexatriene-like) structures, while the σ bonds prefer the regular hexagon structure of the benzene ring.

The present entropy/information descriptors of the internal chemical bonds involving the mutually non-bonded (disconnected) molecular fragments complement the recently proposed bond indices of the mutually bonded (connected) subsystems [11,12]. The latter were shown to exhibit a high degree of equalization marking the information *equilibrium* of the ground-state distribution of electrons in the *entropy representation*, thus identifying the information "*intensities*" of the mutually bonded parts of the molecule. This is reminiscent of the electronegativity equalization principle, [23,24] which provides the equilibrium criterion in the familiar energy representation. It also follows from the present analysis, that the separated subsystem indices are also more equalized than the corresponding bond descriptors from the MO theory.

Clearly, the communication theory of chemical bonds in molecular systems and their fragments, based upon the calculated one- and two-electron probabilities in the atomic resolution, is conditional upon the applied AIM discretization scheme, which is not unique. This dependence will be the subject of an independent study. It has been argued recently [2,3] that the stockholder partitioning of the molecular one-and two-electron distributions offers the most objective division scheme in reference to the corresponding promolecular data, thus offering the unbiased framework for the subsequent extraction of information-theoretic bond indices. The orbital models, which we have used to illustrate the present SFA/IFA treatment, have been selected only to connect to the previous studies [8-12,17b,c] of the chemical bond multiplicities in these systems.

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