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ORIGINAL PAPER

Entropy/information coupling between orbital-communications in molecular subsystems

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Abstract The information coupling between chemical bonds in molecular fragments, e.g., distinct parts of a single molecule or reactants in the bimolecular system, is investigated within the orbital communication theory. The relevant overlap measures of the joint/conditional "probabilities" of simultaneous *two*-orbital probability scatterings on different sites are established within the standard restricted Hartree-Fock (SCF LCAO MO) theory and the associated entropy/information descriptors of the chemical interactions between the bond/reactivity phenomena in such molecular subsystems are explored. The relevant *four*-orbital bond-projections measure the *external* dependencies between the associated *intra*-fragment communications between atomic orbitals on each fragment, thus effectively accounting for the external communication couplings between the internal chemical bonds in each subsystem.

Keywords Bond descriptors · Chemical bond theory · Entropy covalency · Information ionicity · Information theory · *Many*-orbital bond projections · Molecular information channels · Molecular subsystems · Orbital communications in molecules

1 Introduction

Use of standard techniques of the *information theory* (IT) [1–8] gives a valuable insight into the entropic origins and the IT-covalent (communication-noise) and

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Throughout the paper A denotes a *scalar* quantity, $\boldsymbol{A}$ stands for a *row-vector*, and $\mathbf{A}$ represents a *square/rectangular* matrix. The numerical entropies are reported in *bits*, which correspond to the base 2 in the logarithmic measure of information.

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IT-ionic (information-flow) components of the chemical bonds in molecular systems, e.g. [9–19]. The Shannon theory of communication [4–6] has been successfully applied to probe the bonding patterns in molecules within the *communication theory of the chemical bond* (CTCB) [9,19–34]. Its latest realization, called the *orbital communication theory* (OCT) [10,31–34] has been shown to provide efficient tools for exploring bonding patterns in molecules and tackling diverse problems in the theory of molecular electronic structure. The *electron localization function* (ELF) [35] has been shown to explore the *non*-additive part of the Fisher information [1–3] in the *molecular orbital* (MO) resolution [9,10,36], while a similar approach in the *atomic orbital* (AO) representation generates the so called *contra-gradience* (CG) descriptors of chemical bonds, which are related to the AO matrix representation of the electronic kinetic-energy [10,37–39].

The key concept of OCT is the information system in the basis function resolution, exploring the associated (condensed) electron probabilities of AO as carriers of information in the molecular system under consideration. The adopted basis functions (AO) of the standard *restricted Hartree-Fock* (RHF) theory in its analytical SCF LCAO MO realization then determine the underlying elementary "events" determining the channel *inputs* $\boldsymbol{a} = \{a_i\}$ and *outputs* $\boldsymbol{b} = \{b_j\}$, and the associated probabilities of finding an electron on these functions $\boldsymbol{P}(\boldsymbol{a}) = \{P(a_i) = p_i\} = \boldsymbol{p}$ and $\boldsymbol{P}(\boldsymbol{b}) = \{P(b_j) = q_j\} = \boldsymbol{q}$. The orbital information networks describing the orbital communications in the molecule are then determined by the conditional entropies of the channel outputs given inputs, $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(b_j|a_i) = P(j|i)\}$. They describe the probability propagation *via* the system chemical bonds and are characterized by the standard quantities developed in IT for real communication devices.

Due to the electron delocalization throughout the network of the occupied MO the transmission of "signals" about the electronic AO-events becomes randomly disturbed, thus exhibiting a typical communication "noise". Indeed, an electron initially attributed to the given orbital in the channel "input" $\boldsymbol{a}$ can be later found with a *non*-zero probability at several AO in the molecular "output" $\boldsymbol{b}$. This feature of the electron delocalization is embodied in the probability spread in each row of $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a})$. In OCT these conditional probabilities follow from the quantum-mechanical superposition principle [40] supplemented by the "physical" projection onto the subspace of the system occupied MO, which determine the molecular pattern of chemical bonds [10,32,41]. In this formulation of CTCB the *off*-diagonal orbital communications have been shown to be proportional to the corresponding Wiberg [42] bond-orders or the related quadratic indices of the chemical bond multiplicity [43–52]. The *intra*-atomic probability scatterings determines the *additive* channel, responsible for the atomic valence polarization (promotion) in the molecule, while the *inter*-atomic communications determine the *non*-additive channel generating the external charge-transfer/delocalization phenomena [10,53].

In order to characterize the *external* couplings between the *internal* AO-communications located on different molecular sites the *four*-orbital probabilities are required [10,41]. It is the main goal of the present work to explore the relevant *inter*-subsystems communications reflecting the information coupling between the *intra*-fragment channels. The corresponding overlap/projection measures of the conditional "probabilities", of the AO-communications on one fragment conditional on the AO-communications in another fragment, and their associated entropy/information descriptors will be examined. Although the emphasis will be placed on the methodological issues in developing basic elements of the communication theory of such *inter*-fragment couplings in the bond system of the molecule, diverse molecular scenarios, to which this extension can be applied, will be also commented upon.

2 Orbital information channels

We begin with a short summary of the molecular communication systems in the AO/basis-function resolution and their *covalency* (noise) and *ionicity* (information-flow) descriptors [9,10]. In the standard RHF description of the molecular electronic structure the network of chemical bonds between constituent atoms is determined by the occupied *molecular orbitals* (MO) in the system ground-state. Assuming, for simplicity, the *closed*-shell electron configuration of $N = 2n$ electronic system, thus identifies the n lowest (*doubly*-occupied, orthonormal) MO, $\boldsymbol{\phi} = (\phi_1, \phi_2, \ldots, \phi_n) = \{\phi_s\}$, as the origins of the bond descriptors in the molecular system under consideration, both global (in the system as a whole) and regional (in molecular fragments). In the familiar LCAO MO approach they are generated as linear combinations (LC) $\boldsymbol{\phi} = \boldsymbol{\chi}\mathbf{C}$ of the adopted basis functions (AO), $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m) = \{\chi_i\}$, $\langle \boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$, e.g., Löwdin's symmetrically orthogonalized orbitals. Here, the rectangular matrix $\mathbf{C} = \{C_{i,s}\} = \langle \boldsymbol{\chi}|\,\boldsymbol{\phi}\rangle$ groups the LCAO MO coefficients, to be determined from the energy variational approach using the *self-consistent field* (SCF) procedure.

The key concept of this standard orbital description is the *first*-order density matrix $\boldsymbol{\gamma}$ in the AO representation, also called the *charge-and-bond-order* (CBO) matrix. It represents the projection operator onto the subspace of all doubly occupied MO, $\hat{\mathrm{P}}_{\boldsymbol{\phi}} = |\boldsymbol{\phi}\rangle\langle\boldsymbol{\phi}| = \sum_s |\phi_s\rangle\langle\phi_s| \equiv \sum_s \hat{\mathrm{P}}_s$,

$$\begin{aligned}\boldsymbol{\gamma} &= 2\,\langle \boldsymbol{\chi}|\,\boldsymbol{\phi}\rangle\,\langle \boldsymbol{\phi}\,|\boldsymbol{\chi}\rangle = 2\mathbf{C}\mathbf{C}^{\dagger} \equiv 2\,\langle \boldsymbol{\chi}|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|\boldsymbol{\chi}\rangle \\ &= \left\{\gamma_{i,j} = 2\,\langle \chi_i|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,\middle|\chi_j\right\rangle \equiv 2\,\langle i|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|j\rangle\Big\},\end{aligned} \tag{1}$$

thus satisfying the idempotency relation:

$$(\boldsymbol{\gamma})^2 = 4\,\langle \boldsymbol{\chi}|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|\boldsymbol{\chi}\rangle\,\langle \boldsymbol{\chi}|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|\boldsymbol{\chi}\rangle = 4\,\langle \boldsymbol{\chi}|\,\hat{\mathrm{P}}^2_{\boldsymbol{\phi}}\,|\boldsymbol{\chi}\rangle = 4\,\langle \boldsymbol{\chi}|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|\boldsymbol{\chi}\rangle = 2\boldsymbol{\gamma}. \tag{2}$$

The CBO matrix reflects the promoted (valence) state of AO in the molecule. Its diagonal elements reflect the effective electron occupations of the basis functions in the ground-state, $\{N_i = \gamma_{i,i} = Np_i\}$, where $\boldsymbol{p} = \{p_i \equiv P(i) = \gamma_{i,i}/N\}$ stand for the molecularly normalized probabilities of the AO being occupied in the molecule: $\sum_i p_i = 1$. This matrix also determines the system electron density

$$\rho(\boldsymbol{r}) = 2\boldsymbol{\phi}(\boldsymbol{r})\boldsymbol{\phi}^{\dagger}(\boldsymbol{r}) = \boldsymbol{\chi}(\boldsymbol{r})[2\mathbf{C}\mathbf{C}^{\dagger}]\boldsymbol{\chi}^{\dagger}(\boldsymbol{r}) \equiv \boldsymbol{\chi}(\boldsymbol{r})\boldsymbol{\gamma}\boldsymbol{\chi}^{\dagger}(\boldsymbol{r}) = Np(\boldsymbol{r}), \tag{3}$$

and hence also the *one*-electron probability distribution $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$, the *shape* factor of ρ.

The occupied MO also determine the key modes of the information propagation in the molecule [30,32]. The molecular information system in the (condensed) orbital resolution involves the full list of the AO-*events* $\boldsymbol{\chi}$ in its "*input*" $\boldsymbol{a} = \{\chi_i\}$ and "*output*" $\boldsymbol{b} = \{\chi_j\}$. It represents the effective communication promotion of these basis functions in the molecule, *via* the probability/ information scattering described by the conditional probabilities of the AO-outputs given the AO-inputs, identified by the *row* (input) and *column* (output) indices i and j, respectively. In OCT the entropy/information indices of the covalent and ionic components of all chemical bonds in the given molecular system represent the complementary descriptors of the average communication-*noise* and information-*flow* in the molecular information channel [9,31–34,41].

In this orbital description the AO $\rightarrow$ AO communication network is thus fully characterized by the *conditional* probabilities of the output AO-events, given the input AO-events,

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \left\{P(\chi_j|\chi_i) \equiv P(j|i) = P(i \wedge j)/P(i)\right\}, \qquad \sum_j P(j|i) = 1, \tag{4}$$

where the associated *joint* probabilities of simultaneously observing two AO in the system chemical bonds $\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b}) = \{P(i \wedge j)\}$ satisfy the following partial and overall normalization relations:

$$\sum_i P(i \wedge j) = P(j), \qquad \sum_j P(i \wedge j) = P(i), \qquad \sum_i \sum_j P(i \wedge j) = 1. \tag{5}$$

The conditional probabilities of Eq. (4) explore the dependencies between AO resulting from their simultaneous participation in the system occupied MO, *i.e.*, their involvement in the entire network of chemical bonds in a molecule. They define the probability scattering in the AO-channel of the molecule, in which the "signals" of the molecular/promolecular electron allocations to basis functions are transmitted between the AO inputs and outputs. Such information system constitutes the basis of OCT of the chemical bond. Due to the electron delocalization in the molecule via the system occupied MO this information network exhibits a communication "noise" reflecting a degree of indeterminacy in this electron probability propagation between AO.

This molecular channel can be probed using both the promolecular ($\boldsymbol{p}^0 = \{p_i^0\}$) and molecular ($\boldsymbol{p}$) input probabilities, in order to extract the IT-multiplicities of the *ionic* and *covalent* bond components, respectively. The atomic promolecule consists of the "frozen" *free*-atoms building the molecule brought to their final (molecular) locations. Their AO probabilities $\boldsymbol{p}^0$ thus reflect the corresponding ground-states of the system constituent atoms and can be regarded as defining the initial state in the bond-formation process, in the spirit of the familiar *deformation-density* diagrams,

$$\Delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho^0(\boldsymbol{r}) = N\left[p(\boldsymbol{r}) - p^0(\boldsymbol{r})\right], \tag{6}$$

where $\rho^0(\boldsymbol{r})$ and $p^0(\boldsymbol{r})$ stand for the promolecular electron density and its shape/probability factor, respectively.

As argued elsewhere [31], using the generalized superposition principle of quantum mechanics [40] allows one to relate these conditional probabilities to the squares of the corresponding elements of the density matrix:

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \left\{P(j|i) = (2\gamma_{i,i})^{-1}\gamma_{i,j}\gamma_{j,i} = (2\gamma_{i,i})^{-1}\gamma_{i,j}^2\right\}. \tag{7}$$

The *off*-diagonal conditional probability of jth AO-output given ith AO-input is thus proportional to the square of the CBO matrix element linking the two AO, $\gamma_{j,i} = \gamma_{i,j}$. Therefore, it is also proportional to the corresponding AO contribution $\mathscr{M}_{i,j} = \gamma_{i,j}^2$ to the Wiberg [42,43] index of the chemical *bond*-order between two atoms A and B in the molecule,

$$\mathscr{M}(\mathrm{A,B}) = \sum_{i\in\mathrm{A}}\sum_{j\in\mathrm{B}} \mathscr{M}_{i,j}, \tag{8}$$

and to related, generalized *quadratic* descriptors of the molecular bond-multiplicities [44–52].

It can be readily verified using Eq. (2) that the associated joint-probability matrix,

$$\begin{aligned}\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b}) = \Big\{P(i\wedge j) &= P(i)\,P(j|i) = (2N)^{-1}\,\gamma_{i,j}\gamma_{j,i} \\ &= (2N)^{-1}\,\langle i|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|j\rangle\,\langle j|\,\hat{\mathrm{P}}_{\boldsymbol{\phi}}\,|i\rangle \equiv (2N)^{-1}\,\langle i|\,\hat{P}_{\boldsymbol{\phi}}\hat{P}_j\hat{P}_{\boldsymbol{\phi}}\,|i\rangle \\ &= (2N)^{-1}\,\langle j|\,\hat{P}_{\boldsymbol{\phi}}\,|i\rangle\,\langle i|\,\hat{P}_{\boldsymbol{\phi}}\,|j\rangle \equiv (2N)^{-1}\,\langle j|\,\hat{P}_{\boldsymbol{\phi}}\hat{P}_i\hat{P}_{\boldsymbol{\phi}}\,|j\rangle\Big\},\end{aligned} \tag{9}$$

indeed satisfies the normalization conditions of Eq. (5), e.g.,

$$\sum_i P(i\wedge j) = (2N)^{-1}\sum_i \gamma_{j,i}\gamma_{i,j} = (2N)^{-1}\,2\gamma_{j,j} = P(j). \tag{10}$$

These relations also imply that molecular input probabilities $\boldsymbol{p}(\boldsymbol{a}) \equiv \boldsymbol{p}$ generate the same probabilities in the output of the molecular channel,

$$\boldsymbol{p}\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{p}, \tag{11}$$

thus reflecting the stationary character of this distribution.

The molecular channel with $\boldsymbol{p}$ defining its input signal is thus devoid of any reference (history) of the chemical bond formation and generates the average noise index of the molecular bond IT-covalency measured by the *conditional-entropy* of the system outputs given inputs:

$$\begin{aligned}S(\boldsymbol{b}|\boldsymbol{a}) &= -\sum_i\sum_j P(i\wedge j)\log[P(i\wedge j)/P(i)] \\ &= \sum_i P(i)\left[-\sum_j P(j|i)\log P(j|i)\right] \equiv \sum_i P(i)S_i \equiv S[\boldsymbol{p}|\boldsymbol{p}] \equiv S.\end{aligned} \tag{12}$$

This average-noise descriptor thus expresses the difference between the Shannon entropies of the molecular *one*- and *two*-orbital probability distributions:

$$
\begin{aligned}
S &= H[\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b})] - H[\boldsymbol{p}],\\
H[\boldsymbol{p}] &= -\sum_i p_i \log p_i \equiv H(\boldsymbol{a}) \equiv H(\boldsymbol{b}),\\
H[\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b})] &= -\sum_i \sum_j P(i\wedge j)\log P(i\wedge j) \equiv H(\boldsymbol{a}\wedge\boldsymbol{b}).
\end{aligned}
\tag{13}
$$

Hence, for the *independent* input and output events, when $\mathbf{P}^{\text{ind.}}(\boldsymbol{a}\wedge\boldsymbol{b}) = \{p_i p_j\}$, $H[\mathbf{P}^{\text{ind.}}(\boldsymbol{a}\wedge\boldsymbol{b})] = 2H[\boldsymbol{p}]$, and hence $S^{\text{ind.}} = H[\boldsymbol{p}]$, the whole input entropy $H[\boldsymbol{p}]$ is transformed into the communication noise (bond covalency) of the molecular information system.

The molecular channel with $\boldsymbol{p}^0$ determining its input "signal" probability refers to the initial-state in the bond-formation process, described by the atomic promolecule, a collection of the *non*-bonded (*free* atoms) in their respective positions in the molecule. In other words, it corresponds to the ground-state (fractional) occupations of the AO contributed by the system constituent free atoms, before their mixing into MO. This input signal gives rise to the average information-flow descriptor of the system IT bond-ionicity, relative to this reference, as given by the *mutual-information* in the channel inputs and outputs:

$$
\begin{aligned}
I\left(\boldsymbol{a}^0:\boldsymbol{b}\right) &= \sum_i\sum_j P(i\wedge j)\log\left[P(i\wedge j)/\left(p_j p_i^0\right)\right]\\
&= \sum_i p_i\left\{\sum_j P(j|i)\log\left[P\left(i|j\right)/p_i^0\right]\right\} \equiv \sum_i p_i I_i\\
&= H(\boldsymbol{b}) + H\left(\boldsymbol{a}^0\right) - H(\boldsymbol{a}\wedge\boldsymbol{b})\\
&= H\left[\boldsymbol{p}^0\right] - S \equiv I\left[\boldsymbol{p}^0:\boldsymbol{p}\right] \equiv I.
\end{aligned}
\tag{14}
$$

This amount of information reflects the fraction of the initial (promolecular) information content $H[\boldsymbol{p}^0]$, which has not been dissipated as noise in the molecular communication system. In particlular, for the molecular input, when $\boldsymbol{p}^0 = \boldsymbol{p}$,

$$
I(\boldsymbol{a}:\boldsymbol{b}) = \sum_i\sum_j P(i\wedge j)\log\left[P(i\wedge j)/\left(p_j p_i\right)\right] = H[\boldsymbol{p}] - S \equiv I[\boldsymbol{p}:\boldsymbol{p}]. \tag{15}
$$

Hence, for the independent input and output events $I^{\text{ind.}}(\boldsymbol{a}:\boldsymbol{b}) = 0$.

The sum of these two bond components,

$$
\begin{aligned}
\mathcal{N}\left(\boldsymbol{a}^0;\boldsymbol{b}\right) &= S + I \equiv \mathcal{N}\left[\boldsymbol{p}^0;\boldsymbol{p}\right] \equiv \mathcal{N} = H\left[\boldsymbol{p}^0\right]\\
&= \sum_i p_i\left(S_i + I_i\right) \equiv \sum_i p_i \mathcal{N}_i,
\end{aligned}
\tag{16}
$$

where $\mathcal{N}_i = -\log p_i^0$ stands for the *self-information* in the promolecular AO-event χ_i, measures the overall IT bond-multiplicity of all bonds in the molecular system under consideration. It is seen to be conserved at the promolecular-entropy level, which marks the initial information content of AO probabilities. Alternatively, for the molecular input, when $\boldsymbol{p}(\boldsymbol{a}) = \boldsymbol{p}$, this quantity preserves the Shannon entropy of the molecular input probabilities:

$$\mathcal{N}(\boldsymbol{a}; \boldsymbol{b}) = S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a} : \boldsymbol{b}) = H(\boldsymbol{a}) = H[\boldsymbol{p}]. \tag{17}$$

3 Information couplings between probability-propagations in molecular fragments

It follows from the OCT outline presented in the preceding section that in this communication approach the chemical bonds originate from the probability scattering between the basis functions. The *two*-center probability propagations result in the *external* bond phenomena, including the *charge-transfer* (CT) and electron delocalization between bonded atoms, while the *one*-center communications are responsible for the *internal* polarization (P) of *atoms-in-molecules* (AIM), i.e., their promotion to an effective valence state in the molecular environment [53]. In this section we aim at determining the *inter*-subsystems communications which reflect the information coupling between the *intra*-fragment channels, e.g., in the chemically bonded fragments of a molecule or in weakly interacting molecular reactants. Such development should facilitate an extension of OCT to the bond-coupling phenomena in molecules and reactive systems.

Clearly, the extraction of such dependencies between AO-communications on different subsystems, which reflect the influence of chemical bonds in one part of the molecule on those in another fragment, requires the *four*-orbital probabilities in the overall bond system [10,41], since it combines the *two*-orbital events on both subsystems. The corresponding *joint* probabilities of the simultaneous *four*-orbital events generate in turn the associated probabilities of the AO-communications in one fragment conditional on the AO-communications in another fragment, which reflect the information coupling of interest. We shall explore alternative sets of the *doubly*- and *triply*-conditional "probability" measures, which can be derived from the canonical *four*-AO projections. The graph representation of these functions of the CBO matrix elements will be developed and the entropy/information descriptors of such probability propagations, *inter*-subsystem induced in the molecular chemical bond system, from the *input*-pairs of AO to the *output*-pairs of basis functions, will also be examined.

3.1 Probabilities

In OCT of the interactions between molecular subsystems one introduces the generalized "probability" quantities reflecting the products of the AO projections onto the occupied subspace of MO, which determine the resultant bonding pattern of the molecule [41]. These bond-conditional (projected) measures of the overlap between many basis functions can assume negative values, but they exhibit all the symmetry properties and sum-rules of the genuine *many*-AO probabilities. As such they are expected to generate useful *average* entropy/information indices, from the standard communication-noise and information-flow descriptors of the molecular information channels in orbital resolution, which reflect the bond-coupling in molecular fragments and between reactants. In what follows these generalized "probabilities", conditional on the molecular bond system, will be used to determine the associated AO-conditional quantities capable of indexing the dependence between communications (conditional 2-AO events) on different molecular sites.

As demonstrated elsewhere, the overlap measures of the bond "probabilities" of simultaneous *four*-orbital events, of finding an electron in the system of chemical bonds of the molecule simultaneously on the basis functions $(\chi_i \in \boldsymbol{a}) \wedge (\chi_j \in \boldsymbol{b}) \wedge (\chi_k \in \boldsymbol{c}) \wedge (\chi_l \in \boldsymbol{d})$, where $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}, \boldsymbol{d}) = \boldsymbol{\chi}$, is proportional to the following product of the four CBO matrix elements:

$$P(i \wedge j \wedge k \wedge l) = (8N)^{-1}\, \gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}. \tag{18}$$

They satisfy the appropriate normalization conditions:

$$\begin{aligned}\sum_i \sum_j \sum_k \sum_l P(i \wedge j \wedge k \wedge l) &= \sum_i \sum_j \sum_k P(i \wedge j \wedge k)\\ &= \sum_i \sum_j P(i \wedge j)\\ &= \sum_i P(i) = 1,\end{aligned} \tag{19}$$

where the bond probability of the simultaneous *three*-orbital event [10,41]:

$$P(i \wedge j \wedge k) = (4N)^{-1}\, \gamma_{i,j}\gamma_{j,k}\gamma_{k,i}. \tag{20}$$

This formula can be straightforwardly extended to larger numbers of AO determining the elementary events [41], e.g.,

$$P(i \wedge j \wedge k \wedge l \wedge m) = (16N)^{-1}\, \gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,m}\gamma_{m,i}. \tag{21}$$

Thus, the joint probabilities of Eq. (18) are of the *fourth*-order in terms of the CBO matrix elements. Should the AO (χ_i, χ_j) be located in the fragment A of the molecule and the basis functions (χ_k, χ_l) on another fragment B, the product determining the probability $P([i \wedge j] \wedge [k \wedge l])$ coupling A and B is seen to include both the *intra*-fragment bond-orders, $\gamma_{i,j}$ and $\gamma_{k,l}$, as well as the *inter*-fragment CBO matrix elements: $\gamma_{j,k}$ and $\gamma_{l,i}$. For the weakly coupled fragments, e.g., in molecular reactants at large separations interacting *via* the van der Waals forces, before they interact chemically, the system MO strongly resemble those of the separated fragments, so that $\gamma_{j,k}$ and $\gamma_{l,i}$ become very small indeed, thus giving rise to practically vanishing *inter*-subsystem joint probabilities. The latter are thus expected to assume appreciable magnitudes only for the strongly (chemically) interacting subsystems.

The joint "probabilities" of the simultaneous *many*-orbital events generate in turn the associated conditional "probabilities" of the electron communications *via* the chemical-bond system of the molecule. The usual (*single*) probability-conditioning is effected by dividing the joint r-AO probability $P(\chi_1, \chi_2, \ldots, \chi_s, \chi_{s+1}, \ldots, \chi_r) \equiv P(p_1, p_2, \ldots, p_s, v_1, v_2, \ldots, v_{r-s})$ by another joint probability of s AO, $P(\chi_1, \chi_2, \ldots, \chi_s) \equiv P(p_1, p_2, \ldots, p_s)$,

$$P(v_1, v_2, \ldots, v_{r-s}|p_1, p_2, \ldots, p_s) \\ = P(p_1, p_2, \ldots, p_s, v_1, v_2, \ldots, v_{r-s}) / P(p_1, p_2, \ldots, p_s). \tag{22}$$

Here, the list of AO in the reference, *parameter* (p) list of s AO, $(p_1, p_2, \ldots, p_s)$, in the ratio denominator, includes only a subset of r orbitals appearing in the numerator, with the remaining r–s orbitals $(v_1, v_2, \ldots, v_{r-s})$ then determining the *variable* (v) subset of AO. This conditional probability then satisfies the obvious normalization condition involving summations over AO in the variable-list only:

$$\sum_{v_1}\sum_{v_2}\cdots\sum_{v_{r-s}} P(v_1, v_2, \ldots, v_{r-s}\,|p_1, p_2, \ldots, p_s\,) = 1. \tag{23}$$

Alternatively, this conditioning procedure can be viewed as the AO "grouping" scheme, since it distinguishes the complementary variable and parameter subsets of orbitals:

$$(p_1, p_2, \ldots, p_s, v_1, v_2, \ldots, v_{r-s}) \rightarrow \left[(p_1, p_2, \ldots, p_s), (v_1, v_2, \ldots, v_{r-s})\right]. \tag{24}$$

A variety of such *singly*-conditional quantities can be defined for the alternative *variable* and *parameter* subsets of AO, corresponding to both the molecular and fragment normalizations. For example, the molecular set of probabilities conditioning a single AO on larger groups ("clusters") of basis functions read [see also Eqs. (4) and (7)]:

$$\begin{aligned} P(i|j\wedge k) &= P(i\wedge j\wedge k)/P(j\wedge k) = \gamma_{i,j}\gamma_{k,i}/(2\gamma_{k,j}), \\ &\sum_i P(i|k\wedge l) = 1; \\ P(i|j\wedge k\wedge l) &= P(i\wedge j\wedge k\wedge l)/P(j\wedge k\wedge l) = \gamma_{i,j}\gamma_{l,i}/(2\gamma_{l,j}), \\ &\sum_i P(i|j\wedge k\wedge l) = 1; \\ P(i|j\wedge k\wedge l\wedge m) &= P(i\wedge j\wedge k\wedge l\wedge m)/P(j\wedge k\wedge l\wedge m) = \gamma_{i,j}\gamma_{m,i}/(2\gamma_{m,j}), \\ &\sum_i P(i|j\wedge k\wedge l\wedge m) = 1. \end{aligned} \tag{25}$$

One similarly defines the conditional probabilities for the AO-pair in the variable list:

$$\begin{aligned} P(i\wedge j|k) &= P(i\wedge j\wedge k)/P(k) = {}^1\!/_4\gamma_{i,j}\gamma_{j,k}\gamma_{k,i}/\gamma_{k,k}, \\ &\sum_i\sum_j P(i\wedge j|k) = 1; \end{aligned}$$

$$P(i\wedge j|k\wedge l) = P(i\wedge j\wedge k\wedge l)/P(k\wedge l) = {}^1\!/_4\gamma_{i,j}\gamma_{j,k}\gamma_{l,i}/\gamma_{l,k},$$
$$\sum_i\sum_j P(i\wedge j|k\wedge l) = 1;$$
$$P(i\wedge j|k\wedge l\wedge m) = P(i\wedge j\wedge k\wedge l\wedge m)/P(k\wedge l\wedge m) = {}^1\!/_4\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}/\gamma_{m,k},$$
$$\sum_i\sum_j P(i\wedge j|k\wedge l\wedge m) = 1. \tag{26}$$

The second line of the preceding equation conditions one *two*-orbital event $(i\wedge j)$ on another *two*-orbital event $(k\wedge l)$. Again, in the above scenario of weakly-coupled subsystems this probability directly connects to the *configuration interaction* (CI) representation of the van der Waals interactions, with both events then corresponding to the coupled *two*-orbital events (electron configurations) on the separate subsystems. In OCT these probabilities determine the molecular communications between the *two*-orbital outputs $\{i\wedge j\}$ and *two*-orbital inputs $\{k\wedge l\}$, with the *off*-diagonal block of probability propagations, $\{i\wedge j\}\in$ A and $\{k\wedge l\}\in$ B, then specifically reflecting the chemical interactions between the molecular subsystems A and B.

Accordingly for the *three*- and *four*-AO variable sets one finds:

$$P(i\wedge j\wedge k|l) = P(i\wedge j\wedge k\wedge l)/P\,(l) = \gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}/(8\gamma_{l,l}),$$
$$\sum_i\sum_j\sum_k P(i\wedge j\wedge k|l) = 1;$$
$$P(i\wedge j\wedge k|l\wedge m) = P(i\wedge j\wedge k\wedge l\wedge m)/P(l\wedge m) = \gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}/(8\gamma_{m,l}),$$
$$\sum_i\sum_j\sum_k P(i\wedge j\wedge k|l\wedge m) = 1;$$
$$P(i\wedge j\wedge k\wedge l|m) = P(i\wedge j\wedge k\wedge l\wedge m)/P(m) = \gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,m}\gamma_{m,i}/(16\gamma_{m,m}),$$
$$\sum_i\sum_j\sum_k P(i\wedge j\wedge k|l\wedge m) = 1. \tag{27}$$

It should be observed, however, that the IT bond descriptors are generated from the molecular communications between the input and output AO, quantified by the conditional probabilities of Eqs. (4) and (7). Therefore, in order to directly connect to this information-system description one has to generate the *triply*-conditional probability

$$\begin{aligned}P(l|k\|j|i) &= P(i\wedge j\wedge k\wedge l)/[P\,(i)\;P(i\wedge j)P(k)]\\ &\equiv P(k\wedge l\|i\wedge j)/\,[P\,(i)\;P(k)] = \left(\frac{N^2}{4}\right)\frac{\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{i,i}\gamma_{j,i}\gamma_{k,k}},\end{aligned} \tag{28}$$

and the associated *doubly*-conditional joint probability

$$\begin{aligned}P[(j|i)\wedge(l|k)] &= P(l|k\|j|i)P(i\wedge j) = P(i\wedge j\wedge k\wedge l)/\,[P\,(i)\;P(k)]\\ &= \left(\frac{N}{8}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{i,i}\gamma_{k,k}},\end{aligned} \tag{29}$$

which relate the output conditional event $(l|k)$, of the $k \rightarrow l$ communication, to the input event $(j|i)$, of the $i \rightarrow j$ communication. Again, in the CI description these two sets of *two*-orbital events can be thought of as being related to the formal excitations $i \rightarrow j$ and $k \rightarrow l$ in the molecular bond system, with the probability $P(l|k\|j|i)$ then reflecting the information coupling, per $P(j|i) = 1$, between these elementary AO excitations.

Therefore [see Eq. (29)], the *triply*-conditional probability is given by the ratio of joint probability $P[(j|i)\wedge(l|k)]$ of two conditional (input/output) events, $(j|i)$ and $(l|k)$, respectively, and the input-cluster probability $P(i\wedge j)$, which conditions the variable, output-cluster $(k\wedge l)$ of AO on the parameter, input-cluster $(i\wedge j)$:

$$P(l|k\|j|i) = P[(j|i)\wedge(l|k)]/P(i\wedge j). \tag{30}$$

The probability of Eq. (28) distinguishes the input (parameter) 2-AO group $(i\wedge j)$ from the complementary output (variable) 2-AO event $(k\wedge l)$, by the *inter*-group conditioning factor $P(i\wedge j)$ in the ratio denominator, giving rise to the *singly*-conditional probability $P(k\wedge l\|i\wedge j)$, denoted by the double vertical line separating the two subsets of AO, and then introduces the extra, *intra*-group conditioning in both subsets, via the denominator factors $P(i)$ and $P(k)$, respectively, denoted by single vertical lines. Therefore, this probability indeed conditions the output (conditional) event $(l|k)$ on the input (conditional) event $(j|i)$, with their joint probability given by Eq. (29). The latter is seen to fulfill the normalization condition involving the summation over the variable AO of both conditional events:

$$\sum_j \sum_l P[(j|i)\wedge(l|k)] = P(i\wedge k)/\,[P\,(i)\;P(k)] \equiv P(i\wedge k)/P^{\text{ind.}}(i,k). \tag{31}$$

This ratio thus measures the *correlation* between the two parameter AO, as reflected by the ratio of the joint probability of two AO in the molecular bond system to the reference joint probability of two *independent* orbitals.

One can also relate the joint 2-AO event to the conditional 2-AO event. Consider first the conditional-*parameter* case, of the conditional event $\{(j|i)\}$, for which the relevant *doubly*-conditional probability reads:

$$\begin{aligned} P(k\wedge l\|j|i) &= P(i\wedge j\wedge k\wedge l)/P(i\wedge j)P(i) = P(k\wedge l\|i\wedge j)/P(i) \\ &= \left(\frac{N^2}{4}\right)\frac{\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{i,i}\gamma_{j,i}}. \end{aligned} \tag{32}$$

Hence, the associated (*singly*-conditional) joint probability,

$$\begin{aligned} P[(j|i)\wedge(k\wedge l)] &= P(k\wedge l\|j|i)P(i\wedge j) = P(i\wedge j\wedge k\wedge l)/P\,(i) \\ &= \left(\frac{N}{8}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{i,i}}, \end{aligned} \tag{33}$$

satisfies the following normalization relation:

$$\sum_j \sum_k \sum_l P[(j|i) \wedge (k \wedge l)] = 1. \tag{34}$$

Another set of the *doubly*-conditional molecular probabilities

$$\begin{aligned} P(l|k\|i \wedge j) &= P(k \wedge l\|i \wedge j)/P(k) = P(i \wedge j \wedge k \wedge l)/[P(k)P(i \wedge j)] \\ &= \left(\frac{N}{4}\right) \frac{\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{j,i}\gamma_{k,k}} \end{aligned} \tag{35}$$

involves the conditional-*variable* case, with the "output" *two*-orbital event $(l|k)$, and defines the associated *singly*-conditional joint probability

$$\begin{aligned} P[(i \wedge j) \wedge (l|k)] &= P(l|k\|i \wedge j)P(i \wedge j) = P(i \wedge j \wedge k \wedge l)/P(k) \\ &= \left(\frac{N}{8}\right) \frac{\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}}{\gamma_{k,k}}, \\ &\sum_i \sum_j \sum_l P[(i \wedge j) \wedge (l|k)] = 1. \end{aligned} \tag{36}$$

3.2 Diagrammatic representation

In the MO approximation all bond-projected *many*-orbital "probabilities" can be expressed in terms of the corresponding CBO matrix elements (see the preceding section) by using the explicit expressions for the joint probabilities of Eqs. (9, 18, 20) and (21). As shown in Table 1 these functions can be systematized by using a simple diagrammatic technique, in which the *off*-diagonal density-matrix element is represented by an arrow connecting the two AO labels, solid—when it appears in numerator, and broken—when the bond-order is a part of the denominator, with the corresponding circles representing the diagonal elements. In these graphs the numerical factors are disregarded. This convention becomes self-explanatory, when one compares the algebraic expressions and their associated diagrammatic representations shown in the table.

The table also includes other *multi*-conditional probabilities, reflecting the information couplings between the chemical bonds in molecular subsystems, besides those already discussed in Sect. 3.1. For example, the *doubly*-conditional case involving the conditional event $(j|i)$ in the *variable*-part and the joint event $(k \wedge l \wedge m)$ in the *parameter*-list exhibits the "probability"

$$P(j|i\|k \wedge l \wedge m) = P(i \wedge j\|k \wedge l \wedge m)/P\ (i) = \left(\frac{N}{4}\right) \frac{\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}}{\gamma_{i,i}\gamma_{m,k}}. \tag{37}$$

The associated probability of the *variable*-event $(i \wedge j \wedge k)$ conditional on the *parameter*-event $(l|m)$ reads:

Table 1 Graphical representations of selected overlap/projection measures of *many*-orbital probabilities expressed in terms of the CBO-matrix elements

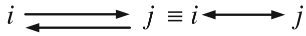
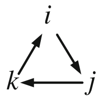
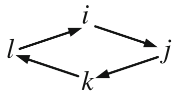
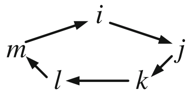
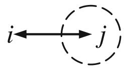
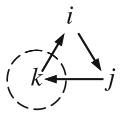
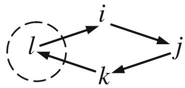
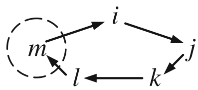
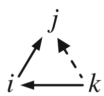
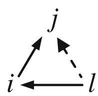
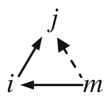
Algebraic functions	Diagrammatic representation
A. Joint probabilities	
$P(i \wedge j) = (2N)^{-1}\gamma_{i,j}\gamma_{j,i}$	
$P(i \wedge j \wedge k) = (4N)^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,i}$	
$P(i \wedge j \wedge k \wedge l) = (8N)^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}$	
$P(i \wedge j \wedge k \wedge l \wedge m) = (16N)^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,m}\gamma_{m,i}$	
B. *Singly*-conditional probabilities	
B.1. *Single AO in parameter-list*	
$P(i\vert j) = (2\gamma_{j,j})^{-1}\gamma_{i,j}\gamma_{j,i}$	
$P(i \wedge j\vert k) = (4\gamma_{k,k})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,i}$	
$P(i \wedge j \wedge k\vert l) = (8\gamma_{l,l})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,i}$	
$P(i \wedge j \wedge k \wedge l\vert m) = (16\gamma_{m,m})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{l,m}\gamma_{m,i}$	
B.2. *Single AO in variable-list*	
$P(i\vert j \wedge k) = (2\gamma_{k,j})^{-1}\gamma_{i,j}\gamma_{k,i}$	
$P(i\vert j \wedge k \wedge l) = (2\gamma_{l,j})^{-1}\gamma_{i,j}\gamma_{l,i}$	
$P(i\vert j \wedge k \wedge l \wedge m) = (2\gamma_{m,j})^{-1}\gamma_{i,j}\gamma_{m,i}$	

Table 1 continued

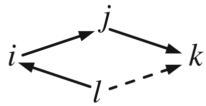
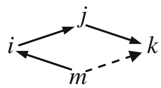
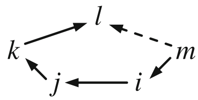
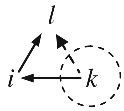
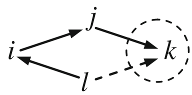
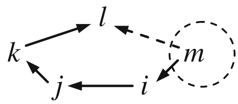
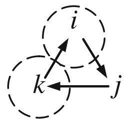
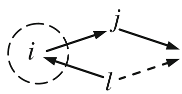
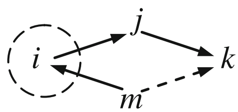
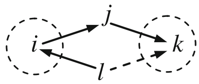
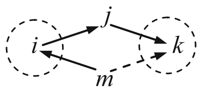
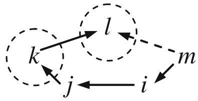
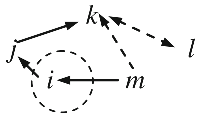
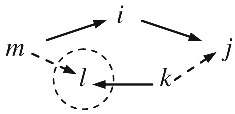
Algebraic functions	Diagrammatic representation
B.3. *Many AO in both lists*	
$P(i \wedge j \| k \wedge l) = (4\gamma_{l,k})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{l,i}$	
$P(i \wedge j \| k \wedge l \wedge m) = (4\gamma_{m,k})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}$	
$P(i \wedge j \wedge k \| l \wedge m) = (8\gamma_{m,l})^{-1}\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}$	
C. *Doubly*-conditional probabilities	
C.1. *Conditional in the parameter-list*	
$P(i \\| l \| k) = (N/2)\gamma_{i,l}\gamma_{k,i}(\gamma_{k,k}\gamma_{k,l})^{-1}$	
$P(i \wedge j \\| l \| k) = (N/4)\gamma_{i,j}\gamma_{j,k}\gamma_{l,i}(\gamma_{l,k}\gamma_{k,k})^{-1}$	
$P(i \wedge j \wedge k \\| l \| m) = (N/8)\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}(\gamma_{m,l}\gamma_{m,m})^{-1}$	
C.2. *Conditional in the variable-list*	
$P(j \| i \\| k) = (N/4)\gamma_{i,j}\gamma_{j,k}\gamma_{k,i}(\gamma_{i,i}\gamma_{k,k})^{-1}$	
$P(j \| i \\| k \wedge l) = (N/4)\gamma_{i,j}\gamma_{j,k}\gamma_{l,i}(\gamma_{i,i}\gamma_{l,k})^{-1}$	
$P(j \| i \\| k \wedge l \wedge m) = (N/4)\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}(\gamma_{i,i}\gamma_{m,k})^{-1}$	

Table 1 continued

Algebraic functions	Diagrammatic representation
D. *Triply*-conditional probabilities	
$P(j\|i\\|l\|k) = (N^2/4)\gamma_{i,j}\gamma_{j,k}\gamma_{l,i}(\gamma_{k,k}\gamma_{l,k}\gamma_{i,i})^{-1}$	
$P(j\|i\\|l\wedge m\|k) = (N^2/4)\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}(\gamma_{i,i}\gamma_{m,k}\gamma_{k,k})^{-1}$	
$P(i\wedge j\|k\\|m\|l) = (N^2/8)\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}(\gamma_{k,k}\gamma_{m,l}\gamma_{l,l})^{-1}$	
$P(j\|i\\|m\|k\wedge l) = (N^2/8)\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}(\gamma_{i,i}\gamma_{m,k}\gamma_{k,l}\gamma_{l,k})^{-1}$	
$P(i\|j\wedge k\\|m\|l) = (N^2/4)\gamma_{i,j}\gamma_{k,l}\gamma_{m,i}(\gamma_{k,j}\gamma_{m,l}\gamma_{l,l})^{-1}$	

$$P(i\wedge j\wedge k\|l|m) = P(i\wedge j\wedge k\|l\wedge m)/P(m) = \left(\frac{N}{8}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}}{\gamma_{m,m}\gamma_{m,l}}. \tag{38}$$

In the final part of the table we have also listed the diagrams for the probability expressions of the following *triply*-conditional, 5-AO events:

$$\begin{aligned} P(j|i\|l\wedge m|k) &= P(i\wedge j\|k\wedge l\wedge m)/[P(i)P(k)] \\ &= \left(\frac{N^2}{4}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}}{\gamma_{i,i}\gamma_{m,k}\gamma_{k,k}}, \end{aligned} \tag{39}$$

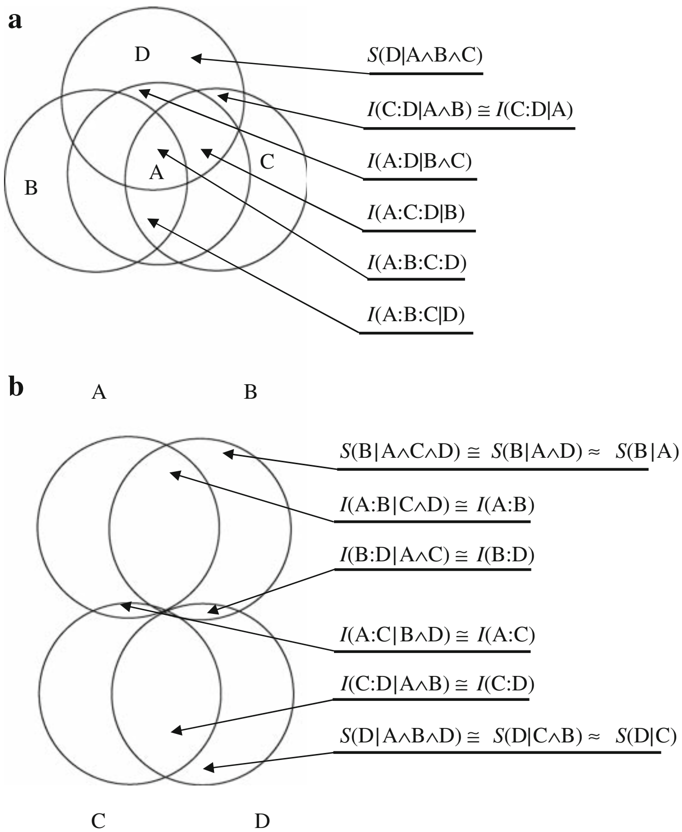
$$\begin{aligned} P(i\wedge j\,|k\|m|\,l) &= P(i\wedge j\wedge k\|l\wedge m)/[P(k)P(l)] \\ &= \left(\frac{N^2}{8}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{k,l}\gamma_{m,i}}{\gamma_{l,l}\gamma_{m,l}\gamma_{k,k}}, \end{aligned} \tag{40}$$

$$\begin{aligned} P(j\,|i\|m|\,k\wedge l) &= P(i\wedge j\|k\wedge l\wedge m)/[P\,(i)\;P(k\wedge l)] \\ &= \left(\frac{N^2}{2}\right)\frac{\gamma_{i,j}\gamma_{j,k}\gamma_{m,i}}{\gamma_{i,i}\gamma_{m,k}\gamma_{k,l}\gamma_{l,k}}, \end{aligned} \tag{41}$$

$$\begin{aligned} P(i|j\wedge k\|m|l) &= P(i\wedge j\wedge k\|l\wedge m)/[P(j\wedge k)P(l)] \\ &= \left(\frac{N^2}{4}\right)\frac{\gamma_{i,j}\gamma_{k,l}\gamma_{m,i}}{\gamma_{k,j}\gamma_{m,l}\gamma_{l,l}}. \end{aligned} \tag{42}$$

3.3 Entropy/information descriptors

In the qualitative diagram of Scheme 1a we have delineated areas representing various indices reflecting the entropy/information couplings between four dependent probability schemes, $\{X = (\boldsymbol{x}, \boldsymbol{P}(\boldsymbol{x})\} = (A, B, C, D)$, which combine the relevant sets of events, $\{\boldsymbol{x}\} = (\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}, \boldsymbol{d})$, and their probabilities, $\{\boldsymbol{P}(\boldsymbol{x})\} = [\boldsymbol{P}(\boldsymbol{a}), \boldsymbol{P}(\boldsymbol{b}), \boldsymbol{P}(\boldsymbol{c}), \boldsymbol{P}(\boldsymbol{d})]$. The Shannon entropies of the latter [Eq. (13)], $\{H(X) = H[\boldsymbol{P}(\boldsymbol{x})]\}$, are depicted by circles. For example, these partial events may refer to finding in the bond system of the molecule an electron on the basis functions $\{\boldsymbol{x} = \boldsymbol{\chi}_X\}$ contributed by molecular



Scheme 1 General entropy/information diagrams of four probability schemes (A, B, C, D) corresponding to the strongly (chemically) interacting AIM/orbitals (*Panel a*), and to weakly-interacting, internally-bonded pairs A–B and C–D (*Panel b*) in the reaction complex $\begin{bmatrix} \text{A—B} \\ | \quad\; | \\ | \quad\; | \\ \text{C—D} \end{bmatrix}$. The "areas" of selected conditional-entropy (S) and mutual-information (I) descriptors of the scheme mutual dependencies are also shown in these diagrams with $I(A : B : C : D) \cong 0$ in Panel b. The entropies of the separate probability distributions are represented by *circles*, the circle overlap area denotes the relevant mutual-information quantity, while the circle remainders, after removal of their overlap(s) with other *circle*(*s*), signifies the corresponding conditional-entropy descriptor

fragments {X}. The particular arrangement of these fragment entropies for the pair M_1----M_2 of the weakly-interacting species M_1 = A–B and M_2 = C–D, e.g., reactants in the bimolecular reactive system, is shown in Scheme 1b. In these diagrams the overlap areas between circles reflect the average mutual-information quantities, measuring the bond IT-ionicities, while the corresponding circle-remainders represent the complementary average conditional entropies, measuring the associated IT-covalency components. It should be emphasized at this point that some of these descriptors may assume negative values [6].

Consider, e.g., the conditional entropy of D, given A, B, and C,

$$\begin{aligned} S(\mathrm{D}|\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}) &= S[\boldsymbol{P}(\boldsymbol{d})|\boldsymbol{P}(\boldsymbol{a})\wedge\boldsymbol{P}(\boldsymbol{b})\wedge\boldsymbol{P}(\boldsymbol{c})] \\ &= -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log P(d|\,a\wedge b\wedge c), \end{aligned} \tag{43}$$

which is shown in Scheme 1a. It represents the residual uncertainty in D, when the events of the three remaining schemes are known to have occurred already. In the molecular fragment scenario it measures the overall IT-covalency of all bonds in fragment D, due to the basis functions of the remaining subsystems A, B, and C. The complementary IT-ionicity index reads [6],

$$\begin{aligned} I(\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}{:}\mathrm{D}) &= I[\boldsymbol{P}(\boldsymbol{a})\wedge\boldsymbol{P}(\boldsymbol{b})\wedge\boldsymbol{P}(\boldsymbol{c}):\boldsymbol{P}(\boldsymbol{d})] = H(\mathrm{D}) - S(\mathrm{D}|\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}) \\ &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log\frac{P(a\wedge b\wedge c\wedge d)}{P(d)P(a\wedge b\wedge c)} \\ &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log\frac{P(d|a\wedge b\wedge c)}{P(d)}, \end{aligned} \tag{44}$$

thus giving rise to the overall (conditional) bond index in D:

$$\mathcal{N}(\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C};\,\mathrm{D}) = S(\mathrm{D}|\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}) + I(\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}{:}\mathrm{D}) = H(\mathrm{D}). \tag{45}$$

Using the property of the information *additivity* [6] one can alternatively express the amount of information of Eq. (44) in terms of more elementary mutual information quantities generating the overlap area between the envelope of three overlapping circles (A, B, C) and D (see Scheme 1a):

$$\begin{aligned} I(\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}{:}\mathrm{D}) &= I(\mathrm{A}{:}\mathrm{D}) + I(\mathrm{B}{:}\mathrm{D}|\mathrm{A}\wedge\mathrm{C}) + I(\mathrm{C}{:}\mathrm{D}|\mathrm{A}\wedge\mathrm{B}) \\ &= I(\mathrm{A}{:}\mathrm{D}|\mathrm{B}\wedge\mathrm{C}) + I(\mathrm{B}{:}\mathrm{D}|\mathrm{A}\wedge\mathrm{C}) + I(\mathrm{C}{:}\mathrm{D}|\mathrm{A}\wedge\mathrm{B}) \\ &\quad + I(\mathrm{A}{:}\mathrm{C}{:}\mathrm{D}|\mathrm{B}) + I(\mathrm{A}{:}\mathrm{B}{:}\mathrm{D}|\mathrm{C}) + I(\mathrm{A}{:}\mathrm{B}{:}\mathrm{C}{:}\mathrm{D}). \end{aligned} \tag{46}$$

In particular, the *two*-scheme descriptors [see Eqs. (12) and (15)] read:

$$S(\mathrm{B}|\mathrm{A}) = -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}} P(a\wedge b)\log P(b|a),$$
$$I(\mathrm{A{:}B}) = \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}} P(a\wedge b)\log\frac{P(b|\,a)}{P(b)} = H(B) - S(\mathrm{B}|\mathrm{A}). \tag{47}$$

The associated *many*-scheme quantities can be similarly expressed by the relevant probabilities [6,41]:

$$\begin{aligned} I(\mathrm{A{:}B{:}C}) &= I(\mathrm{A{:}B}) - I(\mathrm{A{:}B}|\mathrm{C}) \\ &= H(\mathrm{A}) + H(\mathrm{B}) + H(\mathrm{C}) - H(\mathrm{A}\wedge\mathrm{B}) - H(\mathrm{A}\wedge\mathrm{C}) \\ &\quad - H(\mathrm{B}\wedge\mathrm{C}) + H(\mathrm{A}\wedge\mathrm{B}\wedge\mathrm{C}) \\ &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}} P(a\wedge b\wedge c)\log\frac{P(c|a)P(c|b)}{P(c)P(c|a\wedge b)}, \end{aligned} \tag{48}$$

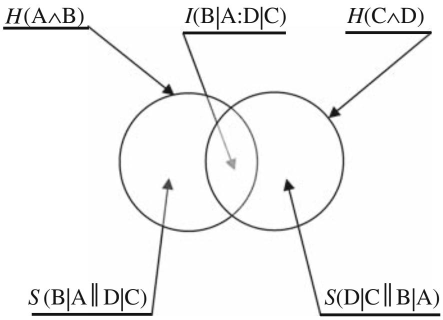
$$I(\mathrm{A{:}B}|\mathrm{C}) = S(\mathrm{A}|\mathrm{C}) - S(\mathrm{A}|\mathrm{B}\wedge\mathrm{C}) = \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}} P(a\wedge b\wedge c)\log\frac{P(a|b\wedge c)}{P(a|c)}, \tag{49}$$

$$\begin{aligned} &I(\mathrm{A} : \mathrm{B{:}C{:}D}) = I(\mathrm{A{:}B{:}C}) - I(\mathrm{A{:}B{:}C}|\mathrm{D}) \\ &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log\frac{P(d|a\wedge b\wedge c)P(d|a)P(d|b)P(d|c)}{P(d)P(d|a\wedge b)P(d|b\wedge c)P(d|a\wedge c)}, \end{aligned} \tag{50}$$

$$I(\mathrm{A{:}B{:}C}|\mathrm{D}) = I(\mathrm{A{:}B}|\mathrm{D}) - I(\mathrm{A{:}B}|\mathrm{C}\wedge\mathrm{D}), \tag{51}$$

$$\begin{aligned} I(\mathrm{A{:}B}|\mathrm{C}\wedge\mathrm{D}) &= S(\mathrm{A}|\mathrm{C}\wedge\mathrm{D}) - S(\mathrm{A}|\mathrm{B}\wedge\mathrm{C}\wedge\mathrm{D}) \\ &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log\frac{P(a|b\wedge c\wedge d)}{P(a|c\wedge d)}. \end{aligned} \tag{52}$$

In a similar manner one characterizes the IT-covalent and IT-ionic couplings between the orbital information systems of the complementary subsystems in $\mathrm{M} = (\mathrm{M}_1 ¦ \mathrm{M}_2)$ (see Scheme 2). Let the schemes A and B denote the AO input and outputs in M_1 with the remaining schemes C and D having a similar meaning for M_2. The fragment AO events extend over all basis functions contributed by its constituent atoms. One then defines the following entropy-information descriptors which reflect the influence of chemical bond(s) in M_1, originating from communications $\mathrm{A} \to \mathrm{B}$, on bonds in M_2, generated by the communications $\mathrm{C} \to \mathrm{D}$. The *intra*-fragment communications are thus characterized by the conditional probabilities $\mathbf{P}(\mathrm{B}|\mathrm{A}) = \{P(b|a)\}$



Scheme 2 Entropy/information diagrams of the interaction between communications A → B and C → D in the complementary fragments M_1 = A–B and M_2 = C–D of M = (M_1¦M_2)

and $\mathbf{P}(\mathrm{D|C}) = \{P(d|c)\}$, respectively, defining the associated *singly*-conditional probability schemes (B|A) and (D|C).

The mutual couplings of the complementary subsystems in M are described by the *triply*-conditional probabilities $\mathbf{P}(\mathrm{B|A\|D|C}) = \{P(b|a\|d|c)\}$. They are measured by the following average entropy/information descriptors describing the influence of one *intra*-fragment communication network on the other:

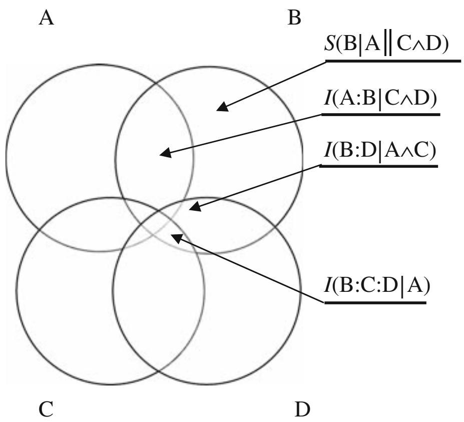
$$\begin{aligned}
S(\mathrm{B|A\|D|C}) &= -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log P(b|a\|d|c)\\
&= -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log \frac{P[(b|a)\wedge(d|c)]}{P(c\wedge d)},\\
S(\mathrm{D|C\|B|A}) &= -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log P(d|c\|b|a),\\
&= -\sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log \frac{P[(b|a)\wedge(d|c)]}{P(a\wedge b)},
\end{aligned}\tag{53}$$

$$\begin{aligned}
I(\mathrm{B|A{:}D|C}) &= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log \frac{P(b|a\|d|c)}{P(a\wedge b)}\\
&= \sum_{a\in\boldsymbol{a}}\sum_{b\in\boldsymbol{b}}\sum_{c\in\boldsymbol{c}}\sum_{d\in\boldsymbol{d}} P(a\wedge b\wedge c\wedge d)\log \frac{P[(b|a)\wedge(d|c)]}{P(a\wedge b)P(c\wedge d)}\\
&= H(\mathrm{A}\wedge\mathrm{B}) - S(\mathrm{B|A\|D|C}) = H(\mathrm{C}\wedge\mathrm{D}) - S(\mathrm{D|C\|B|A}),
\end{aligned}\tag{54}$$

thus giving rise to the associated overall indices of this interaction:

$$\begin{aligned}
\mathcal{N}(\mathrm{B|A;\,D|C}) &= S(\mathrm{B|A\|D|C}) + I(\mathrm{B|A:D|C}) = H(\mathrm{A}\wedge\mathrm{B}),\\
\mathcal{N}(\mathrm{D|C;\,B|A}) &= S(\mathrm{D|C\|B|A}) + I(\mathrm{B|A:D|C}) = H(\mathrm{C}\wedge\mathrm{D}).
\end{aligned}\tag{55}$$

These IT covalency and ionicity descriptors of the communication interaction between the two subsystems thus conserve the internal uncertainties in each molecular fragment (see Scheme 2), measured by the Shannon entropies in each subsystem, of the dependent probability schemes of their constituent parts:



Scheme 3 Entropy/information diagram for the chemically interacting subsystems $M_1 = A–B$ and $M_2 = C–D$ in $M = (M_1 \mathbin{\vert} M_2)$

$$H(A\wedge B) = H(A) + H(B) - I(A{:}B) \quad \text{and} \quad H(C\wedge D) = H(C) + H(D) - I(C{:}D). \tag{56}$$

Some of the entropy/information descriptors discussed in this section have direct implications for the chemical interactions between subsystems in $M = (M_1 \mathbin{\vert} M_2)$. As explicitly shown in Scheme 3, the mutual-information $I(A{:}B|C\wedge D)$ reflects the influence of M_2 on the IT-ionicity in M_1, while the associated conditional-entropy

$$S(B|A\|C\wedge D) = S(B|A) - I(B{:}D|A\wedge C) - I(B{:}C{:}D|A) \tag{57}$$

indexes the effect of the presence of M_2 on the internal IT-covalency in M_1.

Finally, attributing the four schemes A, B, C and D to the corresponding subsystems in the bimolecular reactive system

$$M_1\text{–}M_2 = \begin{bmatrix} A\text{—}B \\ | \quad\; | \\ | \quad\; | \\ C\text{—}D \end{bmatrix} \tag{58}$$

and using the approximate relations of Scheme 1b imply $I(A{:}B|C\wedge D) \cong I(A{:}B)$, $I(B{:}C{:}D|A) \cong 0$, and hence $S(B|A\|C\wedge D) \cong S(B|A) - I(B{:}D|A\wedge C) \approx S(B|A)$. Therefore, the weak M_1----M_2 interactions have practically vanishing effect on the internal ionicities of reactants, with only their internal covalencies being slightly affected.

It should be emphasized, that the above expressions for the IT descriptors apply only to the genuine (positive, fractional) *many*-AO probabilities, when the *non*-negative character of the logarithm argument is automatically assured. Since the overlaps between the bonding projections of AO can exhibit negative values, the *modulus* of the logarithm argument involving such projected quantities should be applied. For the fractional overlaps this prescription gives rise to the positive contributions in the bonding (enhancing) coupling of the subsystem communications, and the negative contributions for the *anti*-bonding coupling between the internal communications in each fragment. In the next section we shall briefly illustrate this point in the representative application of the present approach to the communication coupling between the diatomic fragments of the π-electron system in butadiene, and between alternative parts of the carbon chain in benzene, using the familiar Hückel MO.

4 Illustrative example: communication couplings in the carbon chain of π-electron systems

For the consecutive numbering of the four $2p_\pi$ orbitals contributed by carbon atoms in the π-electron chain of butadiene, the CBO matrix in the Hückel MO theory reads:

$$\boldsymbol{\gamma} = \begin{bmatrix} 1 & 2/\sqrt{5} & 0 & -1/\sqrt{5} \\ 2/\sqrt{5} & 1 & 1/\sqrt{5} & 0 \\ 0 & 1/\sqrt{5} & 1 & 2/\sqrt{5} \\ -1/\sqrt{5} & 0 & 2/\sqrt{5} & 1 \end{bmatrix}, \tag{59}$$

thus giving rise to the following molecular *two*-AO probabilities:

$$\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b}) = \begin{bmatrix} 1/8 & 1/10 & 0 & 1/40 \\ 1/10 & 1/8 & 1/40 & 0 \\ 0 & 1/40 & 1/8 & 1/10 \\ 1/40 & 0 & 1/10 & 1/8 \end{bmatrix}, \mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \begin{bmatrix} 1/2 & 2/5 & 0 & 1/10 \\ 2/5 & 1/2 & 1/10 & 0 \\ 0 & 1/10 & 1/2 & 2/5 \\ 1/10 & 0 & 2/5 & 1/2 \end{bmatrix}, \tag{60}$$

with the conditional probability matrix $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a})$ defining the molecular communications between AO, which reflect the probability scattering (electron delocalization, "noise") pattern in the system as a whole. The corresponding predictions for the six AO in the benzene ring can be summarized as follows:

$$\begin{array}{llll} \gamma_{i,i} = 1, & \gamma_{i,i+1} = 2/3, & \gamma_{i,i+2} = 0, & \gamma_{i,i+3} = -1/3, \\ P(i\wedge i) = 1/12, & P[i\wedge(i+1)] = 1/27, & P[i\wedge(i+2)] = 0, & P[i\wedge(i+3)] = 1/108, \\ P(i|i) = 1/2, & P(i+1|i) = 2/9, & P(i+2|i) = 0, & P(i+3|i) = 1/18. \end{array} \tag{61}$$

Consider first alternative divisions of the butadiene basis set M $= (1, 2, 3, 4)$ into the complementary diatomic fragments, M $=$ [M$_1$, M$_2$], e.g., M $= [(1, 2), (3, 4)]$ or M $= [(1, 4), (2, 3)]$. For the first partition the input data of Eq. (59) generate the following *non*-vanishing coupling overlaps involving pairs of orbitals on different subsystems,

$$\begin{aligned} &P(1\wedge 1\wedge 4\wedge 4) = 1/160\,(\text{bonding}) \text{ and} \\ &P(1\wedge 2\wedge 3\wedge 4) = -1/200\,(\textit{anti}\text{-bonding})\,, \end{aligned} \tag{62}$$

and hence the associated conditional projections:

$$\begin{aligned} &P(1\wedge 1|4\wedge 4) = 1/20, && P(1\wedge 2|3\wedge 4) = -1/20,\\ &P[(1|1)\wedge(4|4)] = 1/10, && P[(1|2)\wedge(3|4)] = -2/25,\\ &P(1|1\|4|4) = 4/5, && P(1|2\|3|4) = -4/5. \end{aligned} \tag{63}$$

The *triply*-conditional probabilities of the preceding equation then generate the following entropic indices of the mutual communication couplings between carbon atoms of the two fragments of the π-chain in butadiene:

$$S(1\,|1\|4|\,4) = 0.0020, \quad S(1\,|2\|3|\,4) = -0.0016. \tag{64}$$

The predicted weak *anti*-bonding coupling between the internal *off*-diagonal communications in both subsystems and the bonding coupling between their diagonal scatterings both indicate that this interaction makes the internal communications in each fragment more deterministic (ionic) in character, thus giving rise to less electron delocalization (covalency) in each subsystem. This observation manifests the (symmetry-breaking) competition principle in the bonding pattern of the molecule: the larger the covalent component of the π-bond in one subsystem, the smaller the bond covalency in its complementary subsystem.

For the $M = [(1, 4), (2, 3)]$ partition one similarly finds a strong *anti*-bonding coupling entropies between the diagonal communications in peripheral and central atoms, respectively:

$$S(1|1\|2|2) = S(4|4\|3|3) = -0.0420. \tag{65}$$

It indicates that a more ionic character of the chemical bond in one subsystem generates less ionic bond in the complementary part of the molecule.

Next, let us examine the communication coupling between two diatomic fragments in benzene: $M_1 = (i, i + 1)$ and $M_2 = (i + 2, i + 3)$. The *non*-vanishing coupling entropies for such subsystems read:

$$S(i|i+1\|i+2|i+3) = 0.0021, \qquad S(i+1|i+1\|i+2|i+2) = -0.0185. \tag{66}$$

Therefore, the *off*-diagonal (delocalization) probability scatterings in both fragments enhance one another, while the opposite influence is predicted for the diagonal (localization) propagations in each subsystem. In other words, the more localized (stronger) the π-bond in one diatomic fragment, the stronger the π bonds in the remaining diatomics-in-the-molecule. This conjecture agrees with the recent thoughts on the competition between the σ (stronger) and π (weaker) bonds in the benzene ring, with the former forcing the regular hexagon structure of the benzene ring and the latter favoring the alternated pattern of the three localized π bonds of the cyclohexatriene [54,55].

5 Conclusion

In this work we have extended OCT by establishing the relevant theoretical framework for treating the chemical interactions between molecular subsystems, and in particular—for describing the influence of interactions between complementary parts of the molecule on their internal bonding patterns. The bond-conditioned measures of the *four*-AO "probabilities" required for determining the relevant entropy/information descriptors have been introduced and their explicit expressions in terms of elements of the molecular *first*-order reduced density matrix of the RHF theory have been given. The entropic descriptors describing the coupling between internal information channels of molecular fragments have been identified and their IT-ionic and IT-covalent components have been established.

Although the present approach uses the "overlaps" (projections) between AO-components in the subspace of the occupied MO as "probability" measures, it is expected to be nonetheless applicable to many classical problems in the theory of the molecular electronic structure and chemical reactivity. In fact, the generalized "probability" indices satisfy the symmetry properties of admissible AO-exchanges and they obey all sum/normalization rules of the genuine probabilities. Therefore, when used in the standard communication description to determine the *average* conditional-entropy (noise, covalency) and mutual-information (information-flow, ionicity) descriptors of the chemical bonds and their interactions they should provide a valuable IT bond indicators, for diagnosing the mutual influences of one molecular subsystem on another. In a sense, the generalized, many-AO overlap represents a more richer concept compared to the probability itself, by being capable of simultaneously describing the probability accumulation in all bonding interactions between AO, at the same time giving rise to the probability depletion in all *anti*-bonding interactions [41].

In chemistry one is often interested in predicting how the chemical bonds (reactivity) in one part of the molecule or *super*-molecule influence the bonding patterns (reactivity) in another part of the system under consideration. The present development facilitates future applications of OCT to such classical problems in the theory of molecular electronic structure and chemical reactivity. They may refer to the influence of the catalyst on the internal bonds in the chemisorbed species [41] or - to the coupling between regional reactivities of chemical species, e.g., [56–60].

Another intriguing question in this IT treatment of chemical bonds is the correspondence between the entropy/information descriptors of molecular and subsystem communication channels and the chemical concepts of the *hardness* and *softness* of the equilibrium, ground-state distribution of electrons [61–66]. The former reflects the "resistance" to polarization, while the latter, inverse notion indexes the "easiness" of effecting such a response to an external perturbation. The *soft* molecules generally exhibit the delocalized electrons of the constituent AIM, *via* the chemical bonds effected by AO in the atomic valence shells, while the *hard* species are characterized by valence electrons which are strongly localized on the bonded atoms/ions. In the information-channel description the electron delocalization generates a substantial noise (IT-covalency) in communications between basis function of the molecular quantum-mechanical calculations, while the localized electron distributions are synonymous with a substantial information-flow (IT-ionicity) component of the overall IT bond-order in question.

Therefore, it is natural to associate the conditional-information quantities with the corresponding measures of the molecular or regional softnesses, and to interpret the complementary mutual-information descriptors as providing entropic measures of the associated chemical hardnesses. An attempt to numerically validate this correspondence will be the subject of future quantum-mechanical study. As also indicated elsewhere [41], the *three*-orbital effects imply an extra IT-ionic activation of the chemisorbed species in catalytic reactions. A more detailed analysis of this prediction will be also a subject of a separate analysis.

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