

# ***Many-orbital probabilities and their entropy/ information descriptors in orbital communication theory of the chemical bond***

Roman F. Nalewajski

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**Abstract** The joint/conditional “probability” measures of simultaneous *many-orbital* events in chemical bonds, which involve several basis functions, are derived within standard SCF LCAO MO description of molecular systems. These generalized projection/overlap quantities satisfy the symmetry properties and sum rules of the ordinary probabilities, but can exhibit negative values. The associated information-theoretic descriptors of chemical bonds for a general case of several (dependent) orbital probability schemes are examined. The *many-orbital* theory extends the range of applications of the orbital communication theory to many classical issues in the theory of molecular electronic structure and chemical reactivity. Such probabilities are required in several molecular scenarios, e.g., bimolecular and catalytic reactivity, directing influence of ligands/substituents, the three-centre bonds, etc., which are also identified. Such an approach implies the effect of the IT-*ionic* activation of the chemisorbed reactants in catalytic systems.

**Keywords** Bond descriptors · Catalytic systems · Chemical bond theory · Entropy covalency · Information ionicity · Information theory · *Many-orbital probabilities* · Molecular information systems · Orbital communications in molecules

## **1 Introduction**

The *information theory* (IT) [1–8] has recently been shown to provide efficient tools for tackling diverse problems in the theory of molecular electronic structure [9–41].

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Throughout the paper  $P$  denotes a *scalar* quantity,  $\mathbf{P}$  stands for a *row-vector*, and  $\mathbf{P}$  represents a square/rectangular matrix.

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R. F. Nalewajski (✉)  
Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland  
e-mail: nalewajs@chemia.uj.edu.pl

For example, the IT-definition of *atoms-in-molecules* (AIM) has been reexamined [9–13] and the information content of electronic distributions in molecules as well as the entropic origins of the chemical bond have been approached anew [9–18]. Moreover, the Shannon theory of communication [4–6] has been applied to probe the bonding patterns in molecules within the *communication theory of the chemical bond* (CTCB) [9, 19–36] and thermodynamic-like description of the electronic “gas” in molecular systems has been explored [9, 37–39]. The CTCB bonding patterns in both the ground and excited electron configurations have been tackled and the valence-state promotion of atoms due to the orbital hybridization has been characterized. This development has widely explored the use of the average communication-noise (delocalization, indeterminacy) and information-flow (localization, determinacy) indices as novel descriptors of the overall IT covalency and ionicity, respectively, of all chemical bonds in the molecular system as a whole, as well as the internal bonds present in its constituent subsystems and the external, inter-fragment bonds. The electron localization function [40] has been shown to explore the non-additive part of the Fisher information [1–3] in the *molecular orbital* (MO) resolution [9, 41], while a similar approach in the *atomic orbital* (AO) representation generates the so called *contra-gradient* (CG) descriptors of chemical bonds, which are related to the matrix representation of the electronic kinetic-energy [42–44]. The molecular quantum mechanics and IT are related through the Fisher (locality) measure of information [1–3], which represents the gradient content of the system wave-function, thus being proportional to the average kinetic energy of electrons. The stationary Schrödinger equation indeed marks the optimum probability amplitude of the associated Fisher-information principle including the additional constraint of the fixed value of the system potential energy [42, 45–50].

The key concept of CTCB is the molecular information system, which can be constructed at alternative levels of resolving the electron probabilities into the underlying elementary “events” determining the channel inputs  $\mathbf{a} = \{a_i\}$  and outputs  $\mathbf{b} = \{b_j\}$ , of finding an electron on the basis-set orbital, AIM, molecular fragment, etc. They can be generated within both the local and condensed descriptions of electronic probabilities in a molecule. Such molecular information networks describe the probability/information propagation in a molecule and can be characterized by the standard quantities developed in IT for real communication devices. Due to electron delocalization throughout the network of chemical bonds in a molecule the transmission of “signals” about the electron allocations to these (mutually exclusive) events becomes randomly disturbed, thus exhibiting the communication “noise”. Indeed, an electron initially attributed to the given atom/orbital in the channel “input”  $\mathbf{a}$  (molecular or promolecular) can be later found with a non-zero probability at several locations in the molecular “output”  $\mathbf{b}$ . This feature of the electron delocalization is embodied in the conditional probabilities of outputs given inputs,  $\mathbf{P}(\mathbf{b} | \mathbf{a}) = \{P(b_j | a_i)\}$ , which define the molecular communication network.

In the *orbital-communication theory* (OCT) [33–36] these conditional probabilities are defined in the basis-function resolution. They follow from the quantum-mechanical superposition principle [51] supplemented by the “physical” projection onto the subspace of the system occupied MO, which determine the molecular pattern of chemical bonds. In this formulation of CTCB the off-diagonal orbital communications have

been shown to be proportional to the corresponding Wiberg [52] or related quadratic indices of the chemical bond [53–62]. It is the main goal of the present work to extend this *two*-orbital development into the simultaneous *many*-orbital events in molecular chemical bonds, in order to generate the entropy/information descriptors involving several (dependent) probability distributions. The molecular scenarios, in which such IT indices are required will be identified and briefly discussed.

## 2 Molecular information channels in atomic orbital resolution

In MO theory the network of chemical bonds is determined by the occupied MO's in the system ground-state. Let us assume, for simplicity, the closed-shell (*cs*) electron configuration of  $N = 2n$  electronic system, in the standard *Restricted Hartree-Fock* (RHF) description, which involves the  $n$  lowest (doubly occupied, orthonormal) MO. In the LCAO MO approach they are generated as linear combinations (LC) of the appropriate (orthogonalized) basis functions  $\chi = (\chi_1, \chi_2, \dots, \chi_m) = \{\chi_i\}$ ,  $\langle \chi | \chi \rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$ , e.g., Löwdin's symmetrically orthogonalized Atomic Orbitals (AO),  $\varphi = (\varphi_1, \varphi_2, \dots, \varphi_n) = \{\varphi_s\} = \chi \mathbf{C}$ , where the rectangular matrix  $\mathbf{C} = \{C_{i,s}\} = \langle \chi | \varphi \rangle$  groups the relevant LCAO MO expansion coefficients, to be determined using the familiar *self-consistent field* (SCF) approach.

The system electron density  $\rho(\mathbf{r})$ , and hence also the *one*-electron probability distribution  $p(\mathbf{r}) = \rho(\mathbf{r})/N$ , the *shape*-factor of  $\rho$ , are determined by the first-order density matrix  $\gamma$  in the AO representation, also called the *charge-and-bond-order* (CBO) matrix,

$$\rho(\mathbf{r}) = 2\varphi(\mathbf{r})\varphi^\dagger(\mathbf{r}) = \chi(\mathbf{r})[2\mathbf{C}\mathbf{C}^\dagger]\chi^\dagger(\mathbf{r}) \equiv \chi(\mathbf{r})\boldsymbol{\gamma}\chi^\dagger(\mathbf{r}) = Np(\mathbf{r}). \quad (1)$$

It represents the projection operator  $\hat{\mathbf{P}}_\varphi = |\varphi\rangle\langle\varphi| = \sum_s |\varphi_s\rangle\langle\varphi_s| \equiv \sum_s \hat{\mathbf{P}}_s$  onto the subspace of all doubly occupied MO,

$$\begin{aligned} \boldsymbol{\gamma} &= 2\langle \chi | \varphi \rangle \langle \varphi | \chi \rangle = 2\mathbf{C}\mathbf{C}^\dagger \equiv 2\langle \chi | \hat{\mathbf{P}}_\varphi | \chi \rangle \\ &= \{\gamma_{i,j} = 2\langle \chi_i | \hat{\mathbf{P}}_\varphi | \chi_j \rangle \equiv 2\langle i | \hat{\mathbf{P}}_\varphi | j \rangle\} \end{aligned} \quad (2)$$

thus satisfying the appropriate idempotency relation:

$$(\boldsymbol{\gamma})^2 = 4\langle \chi | \hat{\mathbf{P}}_\varphi | \chi \rangle \langle \chi | \hat{\mathbf{P}}_\varphi | \chi \rangle = 4\langle \chi | \hat{\mathbf{P}}_\varphi^2 | \chi \rangle = 4\langle \chi | \hat{\mathbf{P}}_\varphi | \chi \rangle = 2\boldsymbol{\gamma}. \quad (3)$$

The CBO matrix reflects the promoted, valence-state of AO in the molecule, with the diagonal elements measuring the effective electron occupations of the basis functions,  $\{N_i = \gamma_{i,i} = Np_i\}$ , with the probabilities of AO being occupied in the molecule  $\mathbf{p} = \{p_i = \gamma_{i,i}/N\}$ ,  $\sum_i p_i = 1$ .

The molecular information system in the (condensed) orbital resolution involves the AO events  $\chi$  in its input  $\mathbf{a} = \{\chi_i\}$  and output  $\mathbf{b} = \{\chi_j\}$ . 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,

respectively. In this *one*-electron description the AO→AO communication network is determined by the conditional probabilities of the output AO-events, given the input AO-events,

$$\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(\chi_j|\chi_i) \equiv P(j|i) = P(i \wedge j)/p_i\}, \quad \sum_j P(j|i) = 1, \quad (4)$$

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

$$\sum_i P(i \wedge j) = p_j, \quad \sum_j P(i \wedge j) = p_i, \quad \sum_i \sum_j P(i \wedge j) = 1. \quad (5)$$

These conditional probabilities define the probability scattering in the AO-promotion 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.

As argued elsewhere [34], by using the generalized superposition principle of quantum mechanics [51], this matrix of (*physical*) conditional probabilities involves the squares of corresponding elements of the CBO matrix:

$$\mathbf{P}(\mathbf{b}|\mathbf{a}) = \{P(j|i) = \mathcal{N}_i | \langle i | \hat{P}_\phi | j \rangle |^2 = (2\gamma_{i,i})^{-1} \gamma_{i,j} \gamma_{j,i} \geq 0\}, \quad (6)$$

where the closed-shell normalization constant  $\mathcal{N}_i = (2\gamma_{i,i})^{-1}$  follows directly from Eq. (3) (for the open-shell generalization see [35, 36]). These probabilities explore the dependencies between AO resulting from their participation in the system occupied MO, i.e., their involvement in the entire network of chemical bonds in a molecule. This molecular channel can be probed using both the promolecular ( $\mathbf{p}^0 = \{p_i^0\}$ ) and molecular ( $\mathbf{p}$ ) input probabilities, in order to extract the IT-multiplicities of the *ionic* and *covalent* bond components, respectively.

The off-diagonal conditional probability of *j*th AO-output given *i*th AO-input is thus proportional to the squared element of the CBO matrix linking the two AO,  $\gamma_{j,i} = \gamma_{i,j}$ , thus being also proportional to the corresponding AO contribution  $\mathcal{M}_{i,j} = \gamma_{i,j}^2$  to the Wiberg [52] index of the overall chemical bond order between two atoms A and B in the molecule,

$$\mathcal{M}(\mathbf{A}, \mathbf{B}) = \sum_{i \in \mathbf{A}} \sum_{j \in \mathbf{B}} \mathcal{M}_{i,j}, \quad (7)$$

or to related, generalized quadratic descriptors of molecular bond-multiplicities [53–62].

It can be straightforwardly verified using the idempotency relation of Eq. (3) that the associated probability matrix of the joint *two*-orbital events,

$$\begin{aligned} \mathbf{P}(\mathbf{a} \wedge \mathbf{b}) &= \{P(i \wedge j) = P(i \wedge j | \boldsymbol{\varphi}) = |A(i \wedge j | \boldsymbol{\varphi})|^2 = p_i P(j | i) \\ &= (2N)^{-1} \gamma_{i,j} \gamma_{j,i} = (2N)^{-1} \langle i | \hat{\mathbf{P}}_{\boldsymbol{\varphi}} | j \rangle \langle j | \hat{\mathbf{P}}_{\boldsymbol{\varphi}} | i \rangle \geq 0\}, \end{aligned} \quad (8)$$

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

$$\sum_i P(i \wedge j) = (2N)^{-1} \sum_i \gamma_{j,i} \gamma_{i,j} = (2N)^{-1} 2\gamma_{j,j} = p_j. \quad (9)$$

It also follows from Eq. (8) that the amplitude  $A(i \wedge j | \boldsymbol{\varphi})$  of this *two*-orbital probability, conditional on the subspace  $\boldsymbol{\varphi}$  of the occupied MO, is proportional to the matrix element  $\gamma_{i,j} = 2\langle i | \hat{\mathbf{P}}_{\boldsymbol{\varphi}} | j \rangle = 2 \left( \langle i | \hat{\mathbf{P}}_{\boldsymbol{\varphi}} \right) \left( \hat{\mathbf{P}}_{\boldsymbol{\varphi}} | j \right) = 2\langle i_{\boldsymbol{\varphi}} | j_{\boldsymbol{\varphi}} \rangle$ , measuring the scalar product of projections of the two AO onto the subspace  $\boldsymbol{\varphi}$ .

In OCT the entropy/information indices of the covalent/ionic components of all chemical bonds in the given molecular system represent the complementary descriptors of the average communication noise and the amount of information-flow in the molecular information channel. The molecular input  $\mathbf{p}(\mathbf{a}) \equiv \mathbf{p}$  generates the same distribution in the output of the molecular channel [see Eq. (5)],

$$\mathbf{p}\mathbf{P}(\mathbf{b}|\mathbf{a}) = \left\{ \sum_i p_i P(j|i) \equiv \sum_i P(i \wedge j) = p_j \right\} = \mathbf{p}, \quad (10)$$

thus identifying  $\mathbf{p}$  as the *stationary* probability vector for the molecular ground state, while the promolecular input  $\mathbf{p}(\mathbf{a}^0) \equiv \mathbf{p}^0$  in general produces different output probability  $\mathbf{p}^0\mathbf{P}(\mathbf{b}|\mathbf{a}) = \mathbf{p}^*(\mathbf{a}^0) = \{p_j^*\} = \mathbf{p}^* \neq \mathbf{p}$ .

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

$$\begin{aligned} S(\mathbf{b}|\mathbf{a}) &= - \sum_i \sum_j P(i \wedge j) \log [P(i \wedge j) / p_i] \\ &= \sum_i p_i \left[ - \sum_j P(j|i) \log P(j|i) \right] \equiv \sum_i p_i S_i \equiv S[\mathbf{p}|\mathbf{p}] \equiv S. \end{aligned} \quad (11)$$

This average-noise descriptor thus expresses the difference between the Shannon entropies of the molecular *one*- and *two*-orbital probabilities,

$$\begin{aligned} S &= H[\mathbf{P}(\mathbf{a} \wedge \mathbf{b})] - H[\mathbf{p}]; \\ H[\mathbf{p}] &= - \sum_i p_i \log p_i \equiv H(\mathbf{a}) \equiv H(\mathbf{b}), \\ H[\mathbf{P}(\mathbf{a} \wedge \mathbf{b})] &= - \sum_i \sum_j P(i \wedge j) \log P(i \wedge j) \equiv H(\mathbf{a} \wedge \mathbf{b}). \end{aligned} \quad (12)$$

Hence, for the *independent* input and output events, when  $\mathbf{P}^{ind.}(\mathbf{a} \wedge \mathbf{b}) = \{p_i p_j\}$ ,  $H[\mathbf{P}^{ind.}(\mathbf{a} \wedge \mathbf{b})] = 2H[\mathbf{p}]$ , and hence  $S^{ind.} = H[\mathbf{p}]$ .

The molecular channel with  $\mathbf{p}^0$  determining its input “signal” probability refers to the initial-state in the bond-formation process, describing the *promolecule*—a collection of non-bonded (free atoms) in their respective positions in a 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-ion-icity, given by the *mutual-information* in the channel inputs and outputs:

$$\begin{aligned} I(\mathbf{a}^0; \mathbf{b}) &= \sum_i \sum_j P(i \wedge j) \log[P(i \wedge j)/(p_j p_i^0)] \\ &= \sum_i p_i \left\{ \sum_j P(j|i) \log[P(j|i)/p_i^0] \right\} \\ &\equiv \sum_i p_i I_i = H(\mathbf{b}) + H(\mathbf{a}^0) - H(\mathbf{a} \wedge \mathbf{b}) = H[\mathbf{p}^0] - S \equiv I[\mathbf{p}^0; \mathbf{p}] \equiv I. \end{aligned} \quad (13)$$

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

$$I(\mathbf{a}; \mathbf{b}) = \sum_i \sum_j P(i, j) \log[P(i, j)/(p_j p_i)] = H[\mathbf{p}] - S \equiv I[\mathbf{p}; \mathbf{p}]. \quad (14)$$

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

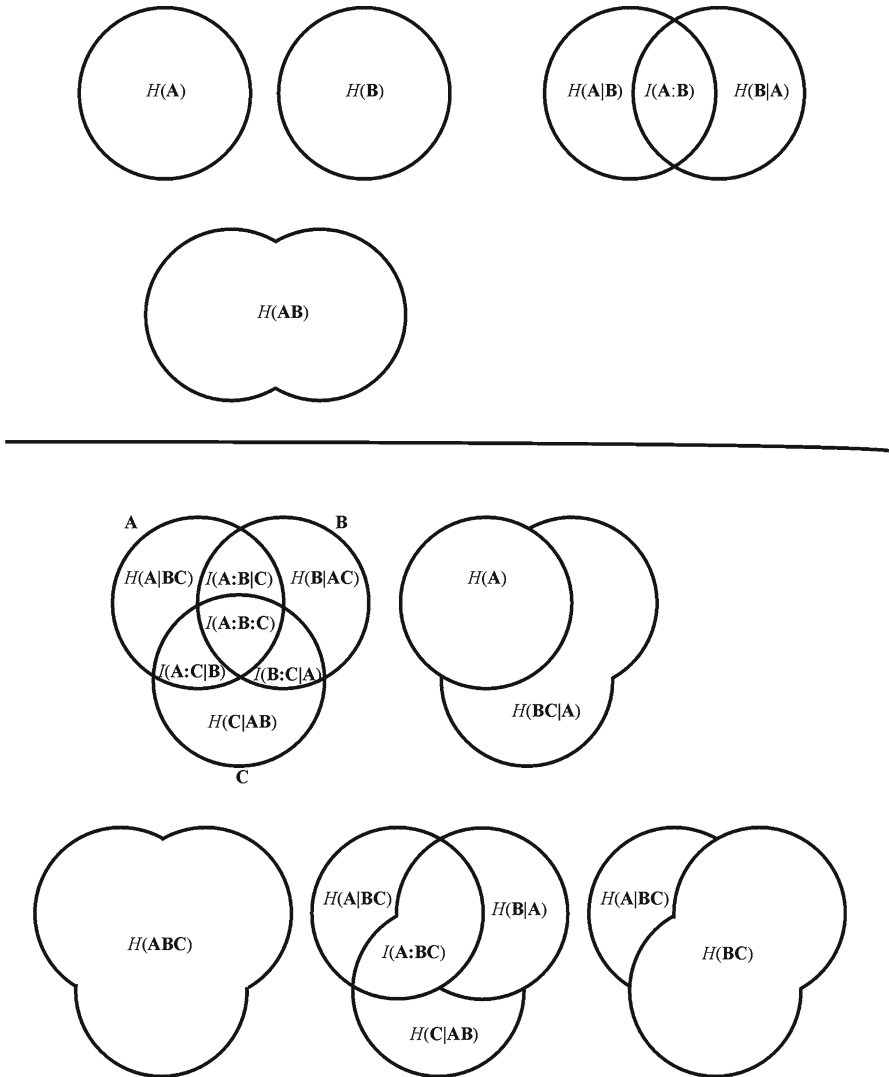
Finally, the sum of these two bond components,

$$\begin{aligned} \mathcal{N}(\mathbf{a}^0; \mathbf{b}) &= S + I \equiv \mathcal{N}[\mathbf{p}^0; \mathbf{p}] \equiv \mathcal{N} = H[\mathbf{p}^0] \\ &= \sum_i p_i (S_i + I_i) \equiv \sum_i p_i \mathcal{N}_i, \end{aligned} \quad (15a)$$

where  $\mathcal{N}_i = -\log p_i^0$  stands for the *self-information* in the promolecular AO-input event  $\chi_i$ , 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  $\mathbf{p}(\mathbf{a}) = \mathbf{p}$ , this quantity preserves the Shannon entropy of the molecular input probabilities:

$$\mathcal{N}(\mathbf{a}; \mathbf{b}) = S(\mathbf{b}|\mathbf{a}) + I(\mathbf{a}; \mathbf{b}) = H(\mathbf{a}) = H[\mathbf{p}]. \quad (15b)$$

In the qualitative diagrams of the upper part of Fig. 1, referring to two dependent probability schemes, the common (overlap) area of the associated entropy circles corresponds to the mutual information in both distributions,  $I(\mathbf{a}; \mathbf{b})$ , while the remaining



**Fig. 1** A qualitative diagram showing a variety of the conditional-entropy and mutual-information quantities characterizing two (*upper part*) and three (*lower part*) dependent probability schemes  $\{X = \begin{bmatrix} x \\ p_X(x) \end{bmatrix}\} = A, B, C$ , combining events  $x = \{x_i\} = (a, b, c)$  and their probabilities  $p_X(x) = \{p_X(x_i)\}$  [6]; here, the individual circles  $H(A) = H[p(a)] = H(a)$ ,  $H(B) = H[p(b)] = H(b)$  and  $H(C) = H[p(c)] = H(c)$  represent the Shannon entropies of the separate probability distributions,  $H(AB) = H(a \wedge b)$ ,  $H(B|A) = S(b|a)$ ,  $I(A:B) = I(a : b)$ , etc

parts of individual circles represent the corresponding conditional entropies  $S(b|a)$  or  $S(a|b)$ . The latter measure the residual uncertainty about events in one set, when one has the full knowledge of the occurrence of the events in the other set of events. Accordingly, the area enclosed by the envelope of these two overlapping circles represents the entropy in the joint distribution of these two sets of outcomes:

$$H(\mathbf{a} \wedge \mathbf{b}) = H(\mathbf{a}) + H(\mathbf{b}) - I(\mathbf{a} : \mathbf{b}) = H(\mathbf{a}) + S(\mathbf{bla}) = H(\mathbf{b}) + S(\mathbf{alb}). \quad (16)$$

### 3 Many-orbital extension

To determine the entropy/information quantities of three dependent probability distributions, which are schematically shown in diagrams of the lower part of Fig. 1, the joint probabilities of the occurrence of the simultaneous *three*-orbital events in the molecular chemical bond system are required, which define the associated conditional probabilities,

$$\begin{aligned} & \mathbf{P}(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}) \\ &= \{P(i \wedge j \wedge k) = p_k P(i \wedge j | k) = p_j P(i \wedge k | j) = p_i P(j \wedge k | i)\}. \end{aligned} \quad (17)$$

These quantities must be symmetrical with respect to exchanges of AO labels. This can be assured by the appropriate symmetrization,

$$P(i \wedge j \wedge k) = \frac{1}{3!} \sum_p P[p(i, j, k) \equiv (i_p, j_p, k_p)], \quad (18)$$

where the summation is over all permutations of  $(i, j, k)$ :  $p = p(i, j, k) = (i_p, j_p, k_p)$ . These joint and conditional probabilities have to satisfy the relevant partial and total normalization conditions formulated in the following sum-rules:

$$\begin{aligned} \sum_i \sum_j P(i \wedge j | k) &= \sum_i \sum_k P(i \wedge k | j) = \sum_j \sum_k P(j \wedge k | i) = 1, \\ \sum_i P(i \wedge j \wedge k) &= P(j \wedge k), \\ \sum_j P(i \wedge j \wedge k) &= P(i \wedge k), \\ \sum_k P(i \wedge j \wedge k) &= P(i \wedge j), \text{ etc.} \end{aligned} \quad (19)$$

It follows from Eq. (8) that the amplitude  $A(i \wedge j | \varphi)$  of the joint *two*-orbital probability is proportional to the relevant CBO matrix element coupling the two orbitals. It reflects the product of the AO projections onto the occupied subspace of MO:  $A(i \wedge j | \varphi) \propto \gamma_{i,j} = 2\langle i_\varphi | j_\varphi \rangle$ . One also observes that the probability  $P(i \wedge j | \varphi) = |A(i \wedge j | \varphi)|^2$  can be expressed as the expectation value in the projected state  $|i_\varphi\rangle$  of the projection operator  $\hat{P}_{(j|\varphi)}$  onto  $|j_\varphi\rangle$ :

$$P(i \wedge j | \varphi) = (2N)^{-1} \gamma_{i,j} \gamma_{j,i} = (2/N) \langle i_\varphi | j_\varphi \rangle \langle j_\varphi | i_\varphi \rangle = (2/N) \left\langle i_\varphi \left| \hat{P}_{(j|\varphi)} \right| i_\varphi \right\rangle \geq 0. \quad (20a)$$



This expression is equivalent to the associated *permutation*-symmetrized form:

$$\begin{aligned}
 P(i \wedge j | \varphi) &= (2N)^{-1} \gamma_{i,j} \gamma_{j,i} = (2/N) \frac{1}{2!} \sum_p \langle i_p^\varphi | \hat{P}_{j_p} | i_p^\varphi \rangle \\
 &= (2/N) \left\{ \frac{1}{2!} \left[ \langle i_\varphi | j_\varphi \rangle \langle j_\varphi | i_\varphi \rangle + \langle j_\varphi | i_\varphi \rangle \langle i_\varphi | j_\varphi \rangle \right] \right\} \\
 &= \frac{1}{N} \left( \langle i_\varphi | \hat{P}_{(j|\varphi)} | i_\varphi \rangle + \langle j_\varphi | \hat{P}_{(i|\varphi)} | j_\varphi \rangle \right). \quad (20b)
 \end{aligned}$$

In what follows we present an extension of this projection technique, which covers the simultaneous *many*-AO events in the bond system of the molecule.

Consider first the simultaneous *three*-orbital events in the molecular framework of chemical bonds. A straightforward extension of the projection principle of the preceding equation gives:

$$\begin{aligned}
 P(i \wedge j \wedge k) &= P(i \wedge j \wedge k | \varphi) = (2/N) \frac{1}{3!} \sum_p \langle i_p^\varphi | \hat{P}_{j_p} \hat{P}_{k_p} | i_p^\varphi \rangle \\
 &\equiv (2/N) \frac{1}{3!} \sum_p \langle i_p^\varphi | \hat{P}_{j_p k_p}^\varphi | i_p^\varphi \rangle \\
 &= [(\gamma_{i,j} \gamma_{j,k} \gamma_{k,i} + \gamma_{j,k} \gamma_{k,i} \gamma_{i,j}) + (\gamma_{i,k} \gamma_{k,j} \gamma_{j,i} + \gamma_{k,j} \gamma_{j,i} \gamma_{i,k}) \\
 &\quad + (\gamma_{k,j} \gamma_{j,i} \gamma_{i,k} + \gamma_{j,i} \gamma_{i,k} \gamma_{k,j})] / (24N) \\
 &= (\gamma_{i,j} \gamma_{j,k} \gamma_{k,i} + \gamma_{i,k} \gamma_{k,j} \gamma_{j,i} + \gamma_{k,j} \gamma_{j,i} \gamma_{i,k}) / (12N) \\
 &= \gamma_{i,j} \gamma_{j,k} \gamma_{k,i} / (4N) = (2/N) \langle i | \hat{P}_\varphi | j \rangle \langle j | \hat{P}_\varphi | k \rangle \langle k | \hat{P}_\varphi | i \rangle, \quad (21)
 \end{aligned}$$

where we have recognized the symmetrical character of  $\boldsymbol{\gamma}$ :  $\boldsymbol{\gamma} = \boldsymbol{\gamma}^T$ . These probability-related quantities define the associated *three*-dimensional matrix  $\mathbf{P}(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}) = \{P(i \wedge j \wedge k)\}$ . One can directly verify the normalizations of Eq. (19) by using the idempotency relation of Eq. (3), e.g.,

$$\begin{aligned}
 \sum_i P(i \wedge j \wedge k) &= (12N)^{-1} \left[ \left( \sum_i \gamma_{k,i} \gamma_{i,j} \right) \gamma_{j,k} + \left( \sum_i \gamma_{j,i} \gamma_{i,k} \right) \gamma_{k,j} \right. \\
 &\quad \left. + \gamma_{k,j} \left( \sum_i \gamma_{j,i} \gamma_{i,k} \right) \right] = [(2N)^{-1} \gamma_{k,j} \gamma_{j,k}] = P(j \wedge k). \quad (22)
 \end{aligned}$$

It should be emphasized, however, that these *three*-AO projection quantities can exhibit negative values, e.g., when in the bond system two pairs of orbitals are effectively bonded, say  $\gamma_{i,j} > 0$  and  $\gamma_{j,k} > 0$ , while the third pair remains effectively *anti*-bonded:  $\gamma_{k,i} < 0$ . Therefore, since the genuine probabilities have to be positive, these *bond*-conditioned quantities can at best be regarded as generalized *probability indices*, which satisfy all symmetry properties and sum rules expected of the true probability measures. As such they are expected to generate adequate *average*

entropy/information indices of molecular channels, when used in standard IT expressions, capable of reflecting diverse couplings between chemical bonds in molecular fragments, reactants, etc. Alternatively, they can be regarded as *relative* probability measures, in reference to the system promolecule, with the negative three-orbital *displacements* then signifying that an accumulation of joint probabilities in the bonded pairs of AO is associated with its lowering in the *anti*-bonded pair of orbitals.

This property of the projected *many*-orbital “probabilities”, conditional on the molecular chemical bonds, reflects the mutual *competition* between AO for the system valence electrons, with the higher “probability” of the bonded pairs of AO being associated with the lower probability in *anti*-bonded interaction. This is in perfect agreement with chemical intuition and the elementary quantum-mechanical description of the chemical bond. We resort to these generalized “probability” quantities in order to reflect the familiar *interference phenomena* exhibited by the probability amplitudes (wave functions) of quantum mechanics.

The “probabilities” of Eq. (21) in turn generate the associated “probability” indices of the 2-AO bond events conditional on the third basis function [see Eq. (17)]:

$$\begin{aligned} \mathbf{P}(\mathbf{a} \wedge \mathbf{b}|\mathbf{c}) &= \{P(i \wedge j|k) = P(i \wedge j \wedge k)/p_k = (4\gamma_{k,k})^{-1} \gamma_{k,i} \gamma_{i,j} \gamma_{j,k}\}, \\ \mathbf{P}(\mathbf{b} \wedge \mathbf{c}|\mathbf{a}) &= \{P(j \wedge k|i) = P(i \wedge j \wedge k)/p_i = (4\gamma_{i,i})^{-1} \gamma_{i,j} \gamma_{j,k} \gamma_{k,i}\}, \quad (23) \\ \mathbf{P}(\mathbf{a} \wedge \mathbf{c}|\mathbf{b}) &= \{P(i \wedge k|j) = P(i \wedge j \wedge k)/p_j = (4\gamma_{j,j})^{-1} \gamma_{j,k} \gamma_{k,i} \gamma_{i,j}\}. \end{aligned}$$

These expressions also represent natural extensions of their *two*-AO analogs of Eq. (6) and satisfy the relevant normalization constraints of Eq. (19), e.g.,

$$\begin{aligned} \sum_i \sum_j P(i \wedge j|k) &= (4\gamma_{k,k})^{-1} \sum_j \left( \sum_i \gamma_{k,i} \gamma_{i,j} \right) \gamma_{j,k} \\ &= (2\gamma_{k,k})^{-1} \left( \sum_j \gamma_{k,j} \gamma_{j,k} \right) = \gamma_{k,k} / \gamma_{k,k} = 1. \end{aligned}$$

One similarly generates from the first-order reduced density matrix of Eq. (2) the joint probabilities of the simultaneous *four*-AO events or the associated AO conditional probabilities of the simultaneous *three*-AO events in the molecular system of chemical bonds,

$$\mathbf{P}(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c} \wedge \mathbf{d}) = \{P(i \wedge j \wedge k \wedge l) = P(i \wedge j \wedge k \wedge l | \varphi) = p_l P(i \wedge j \wedge k | l), \text{ etc.}\}, \quad (24)$$

for which the relevant normalization relations read:

$$\sum_i \sum_j \sum_k P(i \wedge j \wedge k | l) = 1, \quad \sum_l P(i \wedge j \wedge k \wedge l) = P(i \wedge j \wedge k), \text{ etc.} \quad (25)$$

The specific expressions follow from generalizing by induction Eqs. (8) and (21):

$$\begin{aligned} \mathbf{P}(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c} \wedge \mathbf{d}) &= \{P(i \wedge j \wedge k \wedge l) = (2/N) \frac{1}{4!} \sum_p \langle i_p^\varphi | \hat{P}_{j_p}^\varphi \hat{P}_{k_p}^\varphi \hat{P}_{l_p}^\varphi | i_p^\varphi \rangle \\ &\equiv (2/N) \frac{1}{4!} \sum_p \langle i_p^\varphi | \hat{P}_{j_p k_p l_p}^\varphi | i_p^\varphi \rangle = (8N)^{-1} \gamma_{i,j} \gamma_{j,k} \gamma_{k,l} \gamma_{l,i} \\ &= (2/N) \langle i | \hat{P}_\varphi | j \rangle \langle j | \hat{P}_\varphi | k \rangle \langle k | \hat{P}_\varphi | l \rangle \langle l | \hat{P}_\varphi | i \rangle, \end{aligned} \quad (26)$$

$$\mathbf{P}(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c} | \mathbf{d}) = \{P(i \wedge j \wedge k | l) = P(i \wedge j \wedge k \wedge l) / pl = (8\gamma_{l,i})^{-1} \gamma_{i,j} \gamma_{j,k} \gamma_{k,l} \gamma_{l,i}\}. \quad (27)$$

The fulfillment of the normalization relations of Eq. (25) is again guaranteed by the idempotency condition of Eq. (3):

$$\begin{aligned} \sum_i \sum_j \sum_k P(i \wedge j \wedge k | l) &= (8\gamma_{l,i})^{-1} \sum_i \sum_j \left( \sum_k \gamma_{j,k} \gamma_{k,l} \right) \gamma_{i,j} \gamma_{l,i} \\ &= (4\gamma_{l,i})^{-1} \sum_i \left( \sum_j \gamma_{i,j} \gamma_{j,l} \right) \gamma_{l,i} \\ &= (2\gamma_{l,i})^{-1} \left( \sum_i \gamma_{l,i} \gamma_{i,l} \right) = \gamma_{l,i} / \gamma_{l,i} = 1, \end{aligned} \quad (28)$$

$$\begin{aligned} \sum_l P(i \wedge j \wedge k \wedge l) &= (8N)^{-1} \left( \sum_l \gamma_{k,l} \gamma_{l,i} \right) \gamma_{i,j} \gamma_{j,k} \\ &= (4N)^{-1} \gamma_{k,i} \gamma_{i,j} \gamma_{j,k} = P(i \wedge j \wedge k). \end{aligned} \quad (29)$$

Clearly, this development can be straightforwardly extended to cover a general case of the  $n$ -orbital distributions  $\mathbf{P}(\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \dots \wedge \mathbf{a}_n)$  and  $\mathbf{P}(\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \dots \wedge \mathbf{a}_{n-1} | \mathbf{a}_n)$ :

$$\begin{aligned} \mathbf{P}(\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \dots \wedge \mathbf{a}_n) &= \{P(i_1 \wedge i_2 \wedge \dots \wedge i_n | \varphi) = P(i_1 \wedge i_2 \wedge \dots \wedge i_n) \\ &= (2^{n-1} N)^{-1} \gamma_{i_1, i_2} \gamma_{i_2, i_3} \dots \gamma_{i_{n-1}, i_n} \gamma_{i_n, i_1} \\ &= (2^{n-1} N)^{-1} \langle i_1 | \hat{P}_\varphi | i_2 \rangle \langle i_2 | \hat{P}_\varphi | i_3 \rangle \dots \\ &\quad \langle i_{n-1} | \hat{P}_\varphi | i_n \rangle \langle i_n | \hat{P}_\varphi | i_1 \rangle\}, \end{aligned} \quad (30)$$

$$\begin{aligned} \mathbf{P}(\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \dots \wedge \mathbf{a}_{n-1} | \mathbf{a}_n) &= \{P(i_1 \wedge i_2 \wedge \dots \wedge i_{n-1} | i_n) \\ &= (2^{n-1} \gamma_{i_n, i_n})^{-1} \gamma_{i_1, i_2} \gamma_{i_2, i_3} \dots \gamma_{i_{n-1}, i_n} \gamma_{i_n, i_1}\}. \end{aligned} \quad (31)$$

The joint *many*-orbital events in the familiar *one*-electron description of the SCF LCAO MO method require some comment. Obviously, the electron occupying a given MO  $\varphi_s = \chi C_s$  where  $C_s = \{C_{i,s}\}$  stands for the  $s$ -th column in  $\mathbf{C} = \{C_s\}$ , is simultaneously observed in all AO which participate in this linear combination, i.e., on all

basis functions exhibiting a non-vanishing expansion coefficient  $C_{i,s} \neq 0$ . The resultant effect from all occupied MO, which determine the network of chemical bonds in the molecule, on such simultaneous probabilities of several AO is obtained in Eq. (30) by applying the projector  $\hat{P}_\varphi$  onto the occupied subspace of MO, which then links such physical-projection measures of probabilities to the relevant product of the CBO matrix elements.

#### 4 Entropic indices of several probability distributions

In the lower part of Fig. 1 a variety of the entropy/information descriptors is depicted for the case of three dependent (“overlapping”) probability schemes

$$\left\{ \mathbf{X} = \begin{bmatrix} \mathbf{x} \\ \mathbf{p}_{\mathbf{X}}(\mathbf{x}) \end{bmatrix} \right\} = (\mathbf{A}, \mathbf{B}, \mathbf{C}), \quad (32)$$

involving the corresponding AO “events”  $\mathbf{x} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$  in the adopted basis set  $\chi = (\chi_1, \chi_2, \dots, \chi_m)$  or in its alternative subsets and the associated probabilities  $\{\mathbf{p}_{\mathbf{X}}(\mathbf{x})\}$ . These IT quantities, some of them negative, now involve the conditional (relative) entropies with respect to a single or two probability schemes, the mutual information contained in two or three probability distributions, and the conditional mutual-information characteristics of these three probability schemes.

These diagrams demonstrate the *additivity* of the information quantities in the *three*-probability scenario, which may involve two *output*-signals resulting from a single *input*-signal in the molecular channel, or the repeated, two *input*-signals transmitted in the noisy information channel. For example, the amount of information about the input signal **A** obtained by observing two output signals **B** and **C** is measured by the mutual information quantity given by the difference of the Shannon (*a priori*) entropy  $H(\mathbf{A})$  and the conditional (double *a posteriori*) entropy in **A** given **B** and **C**, i.e., the indeterminacy of **A** relative to **B** and **C**,

$$\begin{aligned} I(\mathbf{A} : \mathbf{BC}) &= \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b \wedge c)}{p(a)P(b \wedge c)} \\ &= \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a|b \wedge c)}{p(a)} \\ &= H(\mathbf{A}) - H(\mathbf{A}|\mathbf{BC}) \equiv I(\mathbf{a}\mathbf{b} \wedge \mathbf{c}) = H(a) - S(\mathbf{a}|\mathbf{b} \wedge \mathbf{c}), \quad (33) \end{aligned}$$

where

$$H(\mathbf{A}|\mathbf{BC}) \equiv S(\mathbf{a}|\mathbf{b} \wedge \mathbf{c}) = - \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log P(a|b \wedge c). \quad (34)$$

The mutual information quantity of Eq. (33) can be alternatively expressed in terms of other entropic quantities shown in the qualitative diagrams of the figure. For example, it is seen to measure the sum of elementary amounts of information in the three or

two probability schemes, and it can be alternatively expressed in terms of the relevant entropies:

$$\begin{aligned}
 I(\mathbf{A}:\mathbf{BC}) &= I(\mathbf{A}:\mathbf{B}|\mathbf{C}) + I(\mathbf{A}:\mathbf{C}|\mathbf{B}) + I(\mathbf{A}:\mathbf{B}:\mathbf{C}) \equiv I(\mathbf{a}:\mathbf{b}|c) + I(\mathbf{a}:c|b) + I(\mathbf{a}:\mathbf{b}:c) \\
 &= I(\mathbf{A}:\mathbf{B}) + I(\mathbf{A}:\mathbf{C}|\mathbf{B}) \equiv I(\mathbf{a}:\mathbf{b}) + I(\mathbf{a}:c|b) \\
 &= H(\mathbf{AB}) - H(\mathbf{A}|\mathbf{BC}) - H(\mathbf{B}|\mathbf{A}) \equiv H(\mathbf{a} \wedge \mathbf{b}) - S(\mathbf{alb} \wedge c) - S(\mathbf{bla}); \quad (35)
 \end{aligned}$$

here the mutual information in two probability distributions given the third distribution,

$$\begin{aligned}
 I(\mathbf{A}:\mathbf{B}|\mathbf{C}) &= H(\mathbf{A}|\mathbf{C}) - H(\mathbf{A}|\mathbf{BC}) = \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a|b \wedge c)}{P(a|c)} \\
 &= \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b|c)}{P(a|c)P(b|c)} \\
 &= \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b \wedge c)p(c)}{P(a \wedge c)P(b \wedge c)}, \quad (36)
 \end{aligned}$$

and the mutual information in three probability schemes,

$$\begin{aligned}
 I(\mathbf{a}:\mathbf{b}:c) &= I(\mathbf{a}:\mathbf{b}) - I(\mathbf{a}:\mathbf{b}|c) = I(\mathbf{a}:c) - I(\mathbf{a}:c|\mathbf{b}) = I(\mathbf{b}:c) - I(\mathbf{b}:c|\mathbf{a}) \\
 &= \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b)P(a \wedge c)P(b \wedge c)}{p(a)p(b)p(c)P(a \wedge b \wedge c)} \\
 &= H(\mathbf{a}) + H(\mathbf{b}) + H(\mathbf{c}) - H(\mathbf{a} \wedge \mathbf{b}) - H(\mathbf{a} \wedge \mathbf{c}) \\
 &\quad - H(\mathbf{b} \wedge \mathbf{c}) + H(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}), \quad (37)
 \end{aligned}$$

which may assume negative values, is represented in Fig. 1 by the common area of the three entropy circles. This expression can be straightforwardly generalized for a larger number of probability schemes. For example, for the four dependent probability distributions one finds:

$$\begin{aligned}
 I(\mathbf{a}:\mathbf{b}:c:\mathbf{d}) &= I(\mathbf{a}:\mathbf{b}:c) - I(\mathbf{a}:\mathbf{b}:c|\mathbf{d}) = H(\mathbf{a}) + H(\mathbf{b}) + H(\mathbf{c}) + H(\mathbf{d}) \\
 &\quad - H(\mathbf{a} \wedge \mathbf{b}) - H(\mathbf{a} \wedge \mathbf{c}) - H(\mathbf{a} \wedge \mathbf{d}) \\
 &\quad - H(\mathbf{b} \wedge \mathbf{c}) - H(\mathbf{b} \wedge \mathbf{d}) - H(\mathbf{c} \wedge \mathbf{d}) \\
 &\quad + H(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}) + H(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{d}) + H(\mathbf{a} \wedge \mathbf{c} \wedge \mathbf{d}) \\
 &\quad + H(\mathbf{b} \wedge \mathbf{c} \wedge \mathbf{d}) - H(\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c} \wedge \mathbf{d}). \quad (38)
 \end{aligned}$$

The conditional entropy of Eq. (34),

$$H(\mathbf{A}|\mathbf{BC}) \equiv H(\mathbf{A}|\mathbf{D}) = H(\mathbf{AD}) - H(\mathbf{D}) = S(\mathbf{ald}) \equiv S(\mathbf{ald}), \quad (39)$$

measures the average noise in the  $(\mathbf{d} \equiv \mathbf{b} \wedge \mathbf{c}) \rightarrow \mathbf{a}$  propagation of information in the underlying communication system. This entropy can be compared (see Fig. 1) with

the two-scheme relative entropy  $H(\mathbf{A}|\mathbf{B}) = H(\mathbf{A}) - I(\mathbf{A}:\mathbf{B})$ , which measures the communication noise in the  $\mathbf{b} \rightarrow \mathbf{a}$  probability scattering [see also Eq. (33)]:

$$\begin{aligned} H(\mathbf{A}|\mathbf{BC}) &= - \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b \wedge c)}{P(b \wedge c)} \\ &= - \sum_{a \in \mathbf{a}} \sum_{b \in \mathbf{b}} \sum_{c \in \mathbf{c}} P(a \wedge b \wedge c) \log \frac{P(a \wedge b \wedge c)p(a)}{p(a)P(b \wedge c)} \\ &= H(\mathbf{A}) - I(\mathbf{A}:\mathbf{BC}) < H(\mathbf{A}|\mathbf{B}), \end{aligned} \quad (40)$$

since  $I(\mathbf{A}:\mathbf{D}) > I(\mathbf{A}:\mathbf{B})$ . Thus, the information propagation from the product events in the  $\mathbf{d} \rightarrow \mathbf{a}$  channel results in less noise (IT covalency) compared to that characterizing the  $\mathbf{b} \rightarrow \mathbf{a}$  network. Hence, the opposite trend is detected in the complementary mutual information quantities of Eq. (33):

$$I(\mathbf{A}:\mathbf{BC}) = H(\mathbf{A}) - H(\mathbf{A}|\mathbf{D}) > I(\mathbf{A}:\mathbf{B}) = H(\mathbf{A}) - H(\mathbf{A}|\mathbf{B}). \quad (41)$$

The product-event scattering thus preserves in  $\mathbf{D} = \mathbf{BC}$  a larger portion of the information content of  $\mathbf{A}$ , compared to that conserved in the scheme  $\mathbf{B}$  alone, due to the extra information in  $\mathbf{C}$  about  $\mathbf{A}$  given  $\mathbf{B}$ , as measured by  $I(\mathbf{A}:\mathbf{C}|\mathbf{B})$ . In other words, the  $\mathbf{d} \rightarrow \mathbf{a}$  probability propagation results in a larger IT-ionic component, compared to the  $\mathbf{b} \rightarrow \mathbf{a}$  scattering.

To summarize, the  $(\mathbf{d} = \mathbf{b} \wedge \mathbf{c}) \rightarrow \mathbf{a}$  communications appear less noisy (more deterministic) compared to  $\mathbf{b} \rightarrow \mathbf{a}$ . Therefore, the a posteriori indeterminacy of  $\mathbf{A}$  relative to  $\mathbf{B}$ ,  $H(\mathbf{A}|\mathbf{B})$ , exceeds the double a posteriori entropy  $H(\mathbf{A}|\mathbf{BC})$ , which measures the indeterminacy of  $\mathbf{A}$  relative to  $\mathbf{B}$  and  $\mathbf{C}$ , while the information about  $\mathbf{A}$  provided by  $\mathbf{B}$  alone,  $I(\mathbf{A}:\mathbf{B})$ , is lower than  $I(\mathbf{A}:\mathbf{BC})$  by the extra amount of information about  $\mathbf{A}$  provided by  $\mathbf{C}$ , when  $\mathbf{B}$  is known beforehand,  $I(\mathbf{A}:\mathbf{C}|\mathbf{B})$ .

## 5 Prospective molecular applications

The IT quantities of *many*-AO probability distributions have recently been used to characterize the molecular similarity trends in the sequential-cascade approach of CTCB [27]. The ensemble IT indices generated by several probability distributions have also emerged within the *flexible-input* generalization of OCT [36]. In the remaining part of this section we shall briefly examine other potential applications of these generalized bond descriptors in describing the bonding patterns of molecular/reactive systems and their fragments. For simplicity, we shall limit our discussion to IT quantities involving three probability schemes in AO resolution (see Fig. 1), for which the joint probabilities of Eq. (21) are required.

We first observe that a possible molecular scenario invoking such three-scheme quantities may involve three separate species A, B and C, e.g., two reactants A and B and a catalyst/surface C, with the corresponding sets of the AO-events ( $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ ) of the associated probability schemes ( $\mathbf{A}$ ,  $\mathbf{B}$ ,  $\mathbf{C}$ ) then referring to the basis functions provided by the constituent atoms of each reactant. Alternatively, three molecular fragments can

be involved. The three-orbital development then enables one to discuss the influence of one reactant/fragment, say C, on the bond structure (or reactivity) of two remaining fragments A and B. For example, one could address a natural question: how the electronic/bonding structure of the catalyst affects the structure/reactivity patterns of two adsorbed species, and ultimately assess directly the cooperation effects between the catalyst-adsorbate bonds (A–C, B–C) and the A–B bond linking the two adsorbates.

More specifically, the conditional three-scheme entropy of Eq. (34) (see also Fig. 1),  $S(\mathbf{b}|\mathbf{a}\wedge\mathbf{c}) = H(\mathbf{B}|\mathbf{AC}) = H(\mathbf{B}|\mathbf{A}) - I(\mathbf{B}:\mathbf{C}|\mathbf{A})$ , i.e., the indeterminacy of the molecular AO-output events  $\mathbf{b}$  with respect to the double AO-input (product) events  $\mathbf{a}\wedge\mathbf{c}$ , now reflects only a *part* of the overall IT-covalency (noise) in the  $\mathbf{a} \rightarrow \mathbf{b}$  communications, measured by the indeterminacy of  $\mathbf{b}$  with respect to  $\mathbf{a}$  alone,  $H(\mathbf{B}|\mathbf{A}) = S(\mathbf{b}|\mathbf{a})$ , which reflects the *overall* information loss in the  $\mathbf{a} \rightarrow \mathbf{b}$  probability scattering. The mutual-information contribution  $I(\mathbf{B}:\mathbf{C}|\mathbf{A})$ , by which  $H(\mathbf{B}|\mathbf{AC})$  is decreased relative to  $H(\mathbf{B}|\mathbf{A})$  and by which  $I(\mathbf{B}:\mathbf{AC})$  is increased relative to  $I(\mathbf{A}:\mathbf{B})$ , should be now be attributed to the influence of the catalyst C. In fact, the mutual information in A and C given B describes the effect of an increased ionic (deterministic) character of chemical interactions between the chemisorbed reactants A and B, compared to the AO communications in the separate species.

This ionic “activation” of adsorbates, as a result of forming the partial A–C and B–C chemical bonds on active sites of the catalytic surface, also manifests the *competition effect* between these surface bonds and the inter-adsorbate bond A–B in the catalytic system: the more heavily are the valence electrons of A and B involved in the chemical bonds with C, the less noisy (more deterministic) are their mutual communications, thus giving rise to less covalent (more ionic) interactions between the *chemisorbed species*. The *physical* adsorption of these reactants should be marked by a relatively small value of  $I(\mathbf{B}:\mathbf{C}|\mathbf{A})$ , since then the dependencies (“overlaps”) between (B, A) and C, should be small, thus grossly diminishing the ionic activation effect generated by the presence of the catalyst. Indeed, the surface *chemical* bond between a given adsorbate and the catalyst should be strongly felt at the position of the other adsorbate, and hence the information “coupling” between probability distributions of the chemisorbed species and that of the catalyst should be relatively strong.

Another molecular scenario, in which the three-scheme entropy/information descriptors are expected to be useful, is the influence of one reactive site in a molecule upon another, e.g., in the contexts of subtle reactivity preferences in the *donor–acceptor* (DA) reactive systems implied by the *hard and soft acids and bases* (HSAB) rule [63–71], and particularly its regional formulation for predicting the regioselectivity trends in cyclization reactions [72], the *maximum complementarity* principle [73], and the bond-length variation rules of Gutmann [74]. Such cooperative interaction between different sites in a molecule is also responsible for the directing *trans/cis influence* of ligands in transition metal complexes and the familiar *substituent effect* in aromatic systems. The IT description of the AIM cooperation in the *many-centre* bonds, e.g., in boron hydrides or propellanes, is also expected to require the entropy/information indices involving several probability schemes.

It should be emphasized that an extraction of the information couplings between probability propagations in two different molecular fragments requires the *four-orbital* “probabilities” in the system as a whole. They in turn generate the associated prob-

abilities of the AO-communications (conditional *two*-AO events) in one fragment, conditional on the AO-communications (conditional *two*-AO events) in another part of the molecule. These *triply*-conditional bond probabilities and their alternative molecular applications will be examined in a separate study [75].

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