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Chemical bonds through probability scattering: Information channels for intermediate-orbital stages*

Roman F. Nalewajski

Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland
E-mail: nalewajs@chemia.uj.edu.pl

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The information-theoretic (IT) approach to chemical bonds, based upon the molecular probability-scattering channels in orbital resolution, is developed to cover both the overall promotion of atomic orbitals (AO) and the partial communication systems due to typical intermediate stages of reconstructing the system electronic structure, due to the orbital hybridization, orthogonalization, mixing into the molecular orbitals (MO), etc. The geometric and physical orbital promotion channels are distinguished, with the former taking into account solely the elementary channels due to the orbital-mixing, and the latter additionally including the MO-occupation term, which effectively projects-out the orbital promotion via the occupied MO only. This IT development generates the complementary descriptors of the molecular communication channel, *viz.*, its conditional entropy (IT-covalency) and mutual-information (IT-ionicity), which add up to the total IT bond-order. These components provide a transparent description of the covalent/ionic competition for the valence electrons of constituent atoms. Their orbital-promotion contributions, from the elementary sub-channels reflecting the familiar intermediate stages of the bond-formation process, offer a novel information-scattering perspective on the relative roles played by these partial transformations of orbitals in shaping the resultant entropy/information descriptors of the system chemical bonds. The combination (grouping) rules for the consecutive and parallel arrangements of the elementary sub-channels are summarized and the stage-additivity of the IT bond-descriptors in the molecular sequential cascade of the elementary sub-channels for the intermediate sets of orbitals is examined in a more detail. A distinction between the molecular information channels describing the separated atoms and the free-atoms in the system atomic promolecule, respectively, is stressed and their entropy/information descriptors are briefly summarized. The associated difference descriptors of the overall IT bond-orders with respect to the promolecular reference are introduced and similar displacement measures are designed for the molecular promotion of intermediate orbitals. The illustrative results for the simplest model of a single chemical bond originating from an interaction between two *overlapping* atomic orbitals are presented. In particular, the bond-increments due to the orthogonalization and de-orthogonalization sub-channels of the overall AO-promotion cascade will be investigated.

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

KEY WORDS: bond components; chemical bonds; covalent/ionic bond-indices; electronic structure theory; information flow in molecules; information theory; molecular communication systems; multiplicities of chemical bonds; orbital description; orbital hybridization; orbital orthogonalization; probability scattering in molecules

1. Introduction

The information-theory (IT) [1–4] has been shown to generate a novel class of the entropy/information descriptors of chemical bonds in molecular systems, including the valence numbers of bonded atoms, the overall IT bond multiplicities and their covalent and ionic components [5–18]. This IT approach provides a complementary, information scattering (flow) perspective on the familiar covalent and ionic bond components, which was shown to be in a general accord with the chemical intuition. In several illustrative orbital models and π-electron systems these communication channels were shown to give rise to the IT bond-orders which compare favourably with bond indices from the molecular orbital (MO) theory.

The IT description was shown to give a transparent account of the competition between these two bond components, which also accords with the chemical intuitive expectations. The resulting entropy/information indices of chemical bonds have been shown to give rise to the dichotomous covalent and ionic components, which conserve the overall bond-order in several model systems [6, 9, 14]. The communication theory also generates several alternative strategies for determining the internal and external bonds of molecular fragments [7, 10, 11, 14].

In this communication theory approach to chemical bonds the molecular system is interpreted as an information channel [2, 4], in which the molecular or "promolecular" electron probabilities are "scattered" via the network of the chemical bonds connecting the system constituent atoms [14], due to the system occupied MO. The bond *entropy-covalency* (conditional entropy) descriptor of such a molecular information channel then measures its average communication "noise" reflecting the extra uncertainty in the distribution of the system valence electrons due to their delocalization via the network of the occupied MO. Accordingly, the bond *information-ionicity* (mutual information) index measures the amount of information flowing through this communication system, which survives against the this noise generated by the probability scattering implied by this electron spreading throughout the molecule.

The MO description, against which one ultimately compares the alternative treatments of chemical bonds in molecules and their fragments, generates the standard interpretation of the bond origin and provides useful measures of its multiplicity ("order"), e.g., the so called "quadratic" valence indices [19–28]. It has been recently demonstrated [9] that the so called probability-partitioning scheme gives rise within both MO and communication theories to similar trends in atomic contributions to the overall bond multiplicity and atomic valence-numbers in the simplest model of a single chemical bond, which results from an interaction between two atomic orbitals (AO). This standard perspective usually refers to AO of constituent atoms, the basis functions for majority of the quantum mechanical calculations determining the system electronic structure, as the starting point (source) of the bond-formation process. They define the associated "promolecule", consisting of the "frozen" (ground-state) atoms placed in their respective positions in the molecule, which constitutes the standard reference for extracting effects due to the chemical bonds, e.g., in the density-difference diagrams and the Hirshfeld ("stockholder") partition of the molecular electron density into pieces attributed to bonded atoms [29]. They are usually expressed in terms of some arbitrary functions, e.g., the elementary Gaussian- or Slater-type orbitals.

Therefore, the AO framework, which constitutes the basis for the contemporary "language" of chemistry, also defines the *canonical* (standard) level of resolution of the electron distribution in the communication theory of the chemical bond. In view of this importance of the orbital description in the electronic structure theory, the molecular information channels in orbital resolution have been introduced [16–18]. These communication systems reflect the molecular scattering of the AO electron probabilities of the constituent non-bonded atoms of the system promolecule, manifesting the bonded-atom promotion relative to the corresponding free atom reference, due to the presence of the remaining AIM. Indeed, as a result of the electron delocalization throughout the system chemical bonds, which are embodied in both the shapes of MO and their occupations in the electron configuration under consideration, the AO are effectively "promoted" to their effective occupations in the molecule.

The two main types of the orbital information channels have been identified [17, 18]. The so called *geometrical* channels explore the molecular AO probability scattering via the network of all (equally weighted) MO, both occupied and virtual, while in the *physical* channels the chemical bonds are probed through the occupied MO only [17, 18]. They generate the associated IT-measures of the system covalent and ionic components. They both involve the conditional probabilities of AO, given MO (or of MO, given AO), which directly follow from the quantum-mechanical superposition principle as squares of the relevant expansion coefficients. These elementary electron-delocalization sub-channels are supplemented in the physical probability-scattering network with the relevant MO-occupation sub-channel reflecting the actual MO occupations in the electron configuration under consideration.

More specifically, the molecular information system reflecting the "geometric" AO-promotion involves a sequence (cascade) of the AO $\rightarrow$ MO and MO $\rightarrow$ AO sub-channels, in which the initial (promolecular, *input*) probabilities are propagated via all (equi-weighted) MO in the adopted AO basis set, both occupied and virtual for the molecular electron configuration in question. This geometric (AO-mixing) probability-cascade, AO → MO(all) → AO, gives rise to the entropy/information descriptors of the overall "rotation" of the MO-vectors relative to those representing AO in the molecular Hilbert space. Therefore, they provide the global IT measures of the AO promotion in the whole MO-space. However, the physical probability scattering and the resulting AO promotion in the molecule are determined only by the subset of the configuration occupied MO, which solely determine the network of chemical bonds in the system. The associated information cascade AO → MO(occupied) → AO determines the resultant physical AO-promotion channel, which includes the effect of the actual occupations of MO on the overall IT bond-order index and its covalent/ionic components.

Extracting reliable entropic descriptors of chemical bonds in excited electronic configurations of molecular systems has also been tackled [15, 18]. An adequate treatment of bond-multiplicities in excited electronic configurations presents a challenge in the probability-based IT approach, since electron probabilities do not reflect the relative phases of AO in the occupied MO, thus loosing the "memory" about the MO nodal structure. The chemically acceptable descriptors of bond-orders in such states must account for an expected reduction of bond multiplicities upon electron excitations from the ground-state occupied (bonding) to virtual (antibonding) MO, which effectively decrease the configuration overall "bonding" character. In a more recent development [18] this has been achieved by supplementing the communication theory with the orbital probability-conditioning schemes using appropriate occupation-weighted projections onto the relevant orbital subspaces.

The original, *two*-electron development [5–15] has explored the electron communication links measured by the joint (conditional) probabilities of finding one electron on the specific atom-in-a-molecule (AIM), given the specified atomic location of the other electron. The molecular information channels in orbital resolution are *one*-electron in character, since they explore the conditional probabilities of a single electron. Therefore this *one*-electron description should be distinguished from the previous IT bond-order measures of the molecular information channels in atomic resolution [5–15], quadratic valence indices [22–28], or the average Fermi-hole measures [30], which all probe the system joint *two*-electron probabilities in atomic resolution.

The *one*-electron perspective of the orbital information systems is similar to that adopted in the local Hirshfeld-channels [6, 29] and in the IT justification [14, 16, 32–36] of the stockholder partitioning [36]. Indeed, the electron densities of the Hirshfeld atoms have been shown to generate the unbiased AIM components of the given molecular electron distribution which exhibit the smallest information-distance (entropy deficiency, missing information) relative to the corresponding free atoms of the system promolecule [32]. The unbiased orbital contributions to electron distributions of these stockholder AIM have also been established using a similar IT principle [16]. Finally, the IT partitioning has been extended to the molecular *two*-electron distributions (pair-densities), yielding the effective electron densities of the associated *two*-electron stockholder AIM [14, 34, 37, 38].

However, several issues of the orbital communication theory of the chemical bond still await further investigation. For example, one would like to understand, how the intermediate stages of the bond-formation process, e.g., the AO orthogonalization and hybridization, which are often invoked in the chemical interpretation of bonding effects, influence the resultant scattering of orbital probabilities in molecules. The combined channel of the AO-promotion appears as the *sequential* series (cascades) of the probability/information scatterings in elementary stages involving various intermediate sets of orbitals. Their relevant sequences also define the effective information channels for the molecular promotion of electrons occupying these orbitals, in a similar manner to that used to generate the physical promotion cascade for AO. This is in contrast to the partial sub-channels discussed elsewhere [7, 10, 14]. Indeed, the molecular system constitutes the *parallel* arrangement of such communication systems of molecular fragments.

It is a main purpose of this work to examine in a more detail the role played by the intermediate orbitals, which are part of all *ab initio* calculations of the molecular electronic structure in the AO basis set. The grouping rules for combining the entropic descriptors of sub-channels into those of the system as a whole will be reexamined, for both sequential and parallel cases. The difference approach to bond indices of the elementary and the orbital-promotion communication systems will be developed and the stage-increments of the IT bond indices will be introduced. The illustrative application will examine the role of the AO-orthogonalization. This will be done analytically using the simplest model of a diatomic consisting of two valence electrons occupying two overlapping AO. Throughout the paper the entropic quantities are reported in bits, corresponding to the base 2 in the familiar logarithmic measure of information [2–4].

2. Overall promotion of orbital probabilities in bonded atoms

In what follows the real AO, the basis functions for the typical Self-Consistent Field (SCF) calculations of the molecular electronic structure, will be identified by indices (k, l), while their symmetrically (Löwdin) orthogonalized analogs (OAO) will be indexed by $(\tilde{k}, \tilde{l})$. The MO will be similarly distinguished by indices (i, j), while other subscripts, e.g., (n, m) or$(\tilde{m}, \tilde{n})$, will be used to denote intermediate sets of orbitals and their orthogonalized variety, respectively.

The electron occupation numbers $\boldsymbol{N} = \{N_k\}$ of AO $\boldsymbol{\chi} = \{\chi_k\}$ are modified in the molecular ground-state relative to the corresponding free-atom values $\boldsymbol{N}^0 = \{N_k^0\}$ characterizing the iso-electronic "promolecule", due to electron delocalization and/or charge transfer (CT) via the system chemical bonds. This physical promotion of bonded atoms also affects the associated AO probabilities, $\boldsymbol{P}_\chi = \{P_k = N_k/N\} \neq \boldsymbol{P}_\chi^0 = \{P_k^0 = N_k^0/N^0\}$, where the overall number of electrons $N = \sum_k N_k = N^0 = \sum_k N_k^0$. As a result of the AO mixing into the molecular orbitals (MO), $\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C} = \{\varphi_i\}$, where $\mathbf{C} = \{C_{k,i}\}$ groups the LCAO MO coefficients, the system occupied MO give rise to the displaced effective occupations of AO in atoms-in-molecules (AIM), and to the concomitant redistribution of electron probabilities. It further implies the associated changes in the entropy/information descriptors of the system electronic structure in the AO resolution, which can be used as probes of the system chemical bonds. Indeed, the effective "scattering" of electrons among all basis set functions is tantamount to the effective promotion of AO and readjustment of the information contained in the molecular electron distribution among the system AO, compared to that characterizing the initial (promolecular) AO occupations.

In this section we shall first briefly outline the molecular communication systems in orbital resolution, which describe the flow of information accompanying the geometrical and physical promotion of AIM. The associated IT measures of the system bond-orders will then be summarized, including the complementary indices of the of the conditional-entropy (IT-covalency) and mutual-information (IT-ionicity). These quantities respectively reflect the extra information "noise" created by the electron delocalization via the "communication" networks determined by either all MO (geometrical promotion) or their occupied subset (physical promotion), respectively, and the corresponding amounts of information flowing through such orbital channels. The overall AO-promotion channel, reflecting the resultant effect of the probability scattering through the system MO will be expressed as the corresponding cascade involving the elementary geometrical AO $\to$ MO and MO $\to$ AO sub-channels, as well as the relevant occupational MO $\to$ MO sub-channel. Similar information cascades and the resultant orbital promotion systems will be defined for all intermediate stages in adjusting the system electronic structure, e.g., the orbital hybridization, orthogonalization, mixing into MO, etc.

It directly follows from the familiar superposition principle of quantum mechanics that the squares of the moduli of the LCAO MO coefficients $\mathbf{C} = \{C_{k,i} = \langle \chi_k | \psi_i \rangle\}$, representing the AO—MO projections, generate the molecular Hilbert-space probabilities of one set of orbitals, conditional on the other set:

$$\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \{P(i|k) = \langle \varphi_i|\chi_k\rangle\langle\chi_k|\varphi_i\rangle \equiv \langle\varphi_i|\hat{\mathrm{P}}_k|\varphi_i\rangle = \langle\chi_k|\varphi_i\rangle\langle\varphi_i|\chi_k\rangle \equiv \langle\chi_k|\hat{\mathrm{P}}_i|\chi_k\rangle\},$$

$$\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\varphi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})^{\mathrm{T}} = \{P(k|i)\}, \quad \sum_i^{MO} P(i|k) = \sum_k^{\mathrm{AO}} P(k|i) = 1. \tag{1}$$

Above, these probabilities have been expressed as expectation values, either for ith MO of the AO projection operator $\hat{\mathrm{P}}_k = |\chi_k\rangle\langle\chi_k|$, or for kth AO of the MO projector $\hat{\mathrm{P}}_i = |\varphi_i\rangle\langle\varphi_i|$. Here $P(k|i)$ stands for the conditional probability of χ_k, given φ_i, while $P(i|k)$ denotes the conditional probability of φ_i, given χ_k. The normalization conditions in equation (1) involve the summation of the conditional probabilities over all orbital events in one (variable) set, for the fixed orbital events in the other (parameter) set. By convention the variable index, e.g., k in $P(k|i)$, denotes the *column* in the conditional probability matrix $\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\varphi})$, while the parameter index, e.g., i in $P(k|i)$, identifies *row* in this matrix.

These geometric probabilities of the molecular Hilbert space in orbital approximation define implicitly the associated joint AO—MO probabilities of simultaneously observing the specified (AO, MO)-pair. The AO-"event" in these joint orbital probabilities may either refer to the bonded atom in the molecule [17], when the molecular input probabilities of AO, $\boldsymbol{P}_\chi$, are used to probe the system IT-covalency [5, 6, 14],

$$\mathbf{P}(\boldsymbol{\chi}, \boldsymbol{\varphi}) = \{P(i,k) = P(i|k)P_k = P(k,i) = P(k|i)P_i\}, \tag{2a}$$

or to the free atom of the promolecule [18], when the molecular communication system is probed with the initial AO probabilities $\boldsymbol{P}^0_{\boldsymbol{\chi}}$ of non-bonded atoms [18] to extract the system IT-ionicity [5, 6, 14]:

$$\mathbf{P}(\boldsymbol{\chi}^0, \boldsymbol{\varphi}) = \{P(i,k^0) = P(i|k^0)P^0_k = P(k^0,i) = P(k^0|i)P_i\}. \tag{2b}$$

Moreover, since the AO projectors in equation (1) are common to both AIM and free-atoms in the promolecule, $\{P(i|k) = P(i|k^0)\} = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}^0)$, and hence

$$P(i,k)/P(i,k^0) = P_k/P^0_k. \tag{2c}$$

The partial normalizations of these joint probabilities generate the relevant AO and MO probabilities:

$$\boldsymbol{P}_{\boldsymbol{\chi}} = \left\{P_k = \sum_i^{\mathrm{MO}} P(k,i)\right\}, \qquad \boldsymbol{P}^0_{\boldsymbol{\chi}} = \left\{P^0_k = \sum_i^{\mathrm{MO}} P(k^0,i)\right\},$$
$$\boldsymbol{P}_{\boldsymbol{\varphi}} = \left\{P_i = \sum_k^{\mathrm{AO}} P(i,k) = \sum_k^{\mathrm{AO}} P(i,k^0)\right\}, \tag{3}$$

also normalized: $\sum_k^{\mathrm{AO}} P_k = \sum_k^{\mathrm{AO}} P^0_k = \sum_i^{\mathrm{MO}} P_i = 1$. The free-atom probabilities $\boldsymbol{P}^0_{\boldsymbol{\chi}} = \{P^0_k = N^0_k/N\}$ reflect the initial AO occupations $\boldsymbol{N}^0 = \{N^0_k\}$ in the promolecular reference, before the bond formation. The MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}} = \{P_i = n_i/N\}$ similarly reflect the MO occupations $n = \{n_i\}$ in the molecular ground-state.

In the conventional orbital approximation of the MO theory the resultant effect of chemical bonds in a given molecular system is an effective excitation of electrons from the occupied to empty AO, relative to occupations of

$$P_\chi^0 \longrightarrow \chi \xrightarrow{\mathbf{P}(\varphi|\chi)} \varphi \xrightarrow{\mathbf{P}(\varphi^*|\varphi)} \varphi^* \xrightarrow{\mathbf{P}(\chi^*|\varphi^*)} \chi^* \longrightarrow P_\chi \quad \textbf{(a)}$$

$$P_\chi^0 \longrightarrow \chi^0 \longrightarrow \mathbf{P}(\chi^*|\chi^0) \longrightarrow \chi^* \longrightarrow P_\chi \quad \textbf{(b)}$$

$$P_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\chi^*|\chi) \longrightarrow \chi^* \longrightarrow P_\chi \quad \textbf{(c)}$$

Scheme 1. The *physical* probability scattering, $\boldsymbol{\chi} \to \boldsymbol{\varphi} \to \boldsymbol{\varphi}^* \to \boldsymbol{\chi}^*$, from the initial (input) probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}^0$, of AO in the non-bonded atoms of the promolecule (Panels a, b) or $\boldsymbol{P}_{\boldsymbol{\chi}}$, of AO in AIM (Panel c), via the ground-state occupied MO $\boldsymbol{\varphi}$ to the effective probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}$ of the promoted AO $\boldsymbol{\chi}^*$ in bonded atoms (molecular output). In Part a the three elementary stages of this information cascade are shown, giving-rise to the resultant AO-promotion channel b and c. This probability network involves two *geometrical* (orbital-mixing) stages of the $\boldsymbol{\chi} \to \boldsymbol{\varphi} = \boldsymbol{\chi}^0 \to \boldsymbol{\varphi}$ and $\boldsymbol{\varphi}^* \to \boldsymbol{\chi}^*$ probability scatterings reflected by the conditional probabilities $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}^0)$ and $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})^{\mathrm{T}}$, respectively, and the MO-occupation stage $\boldsymbol{\varphi} \to \boldsymbol{\varphi}^*$ described by the $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$ matrix of the MO probabilities in the molecule.

the non-bonded constituent atoms. In bonded-atoms electrons are redistributed due to both AO mixing into MO, and the energetically most favuorable occupations of MO in the ground-state of the molecule. These two aspect are depicted in Scheme 1, where the effective physical promotion of AO in the molecule [17] involves both the geometrical probabilities of the molecular Hilbert space, reflecting the optimum *shapes* of MO, and the populational probabilities reflecting the *occupations* of MO in the system ground-state. The effective information system for the promotion of AO in a molecule can thus be viewed as a succession (cascade) of Scheme 1a [17, 18] consisting of the three elementary sub-channels of the probability propagation: geometrical AO → MO (AO mixing into MO), the occupational MO(all) → MO(occupied), and the geometrical MO → AO (MO mixing into AO). Wile the first and third stage of this sequence reflect the geometric property of the MO Hilbert space in the adopted AO basis set, the second step attributes the physical meaning only to the occupied MO sub-space and projects out the virtual MO sub-space [17, 18].

The effective conditional probabilities $\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\chi}) = \{P(l|k)\}$, of χ_l in the channel output, given χ_k in the channel input, which determine the resultant (physical) AO-promotion channel of Scheme 1b, are thus generated by the product of conditional probabilities determining these three elementary stages in the information cascade of Scheme 1a:

$$\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*) = \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}^0). \tag{4}$$

The first term $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})$ accounts for the geometrical AO → MO probability scattering due to the mixing of AO into MO. The second, occupational factor $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$ extracts the effects due to the system occupied MO, thus accounting for the actual involvement of each MO in the ground-state Slater determinant. Thus, in this matrix all elements in columns, which correspond to the virtual MO in the electron configuration under consideration, by definition vanish identically. Finally, the third contribution, $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*)$, represents the MO $\rightarrow$ AO (geometrical) probability scattering, due to the MO mixing into AO.

2.1. Alternative representations of the MO-occupation channel

Let us now briefly reexamine the MO-occupation conditional probabilities, $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi}) = \{P(j|i)\}$, where $P(j|i)$ stands for the probability of φ_j^* in the output of the (physical) MO-occupation sub-channel, given φ_i in its input. Therefore, only the columns j corresponding to the occupied MO, for which $P_j = n_j/N \neq 0$, can exhibit a non-vanishing values of $P(j|i)$. By definition, this matrix must generate in the output of the second sub-channel in Scheme 1a the molecular (ground-state) MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}} = \{P_i\}$,

$$\boldsymbol{P}_{\boldsymbol{\varphi}} = \boldsymbol{P}_{\boldsymbol{\varphi}}^{\text{inp.}} \mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi}), \tag{5}$$

where the input MO probabilities,

$$\boldsymbol{P}_{\boldsymbol{\varphi}}^{\text{inp.}} = \boldsymbol{P}_{\boldsymbol{\chi}}^{0} \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \left\{ P_i^{\text{inp.}} = \sum_k^{\text{AO}} P_k^0 P(i|k) \right\}, \tag{6}$$

group the output MO probabilities of the geometrical stage AO $\rightarrow$ MO in probability propagation, which precedes the occupational step in the physical AO-promotion information system of Scheme 1a.

This requirement alone cannot specify uniquely the communication network of conditional probabilities $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$. For example, one could explore the simplest *diagonal* (disconnected) representation $\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$ of this probability matrix, which has been adopted in previous studies [17, 18]. It represents the noiseless probability scattering at the MO-occupation stage, i.e., with the probability entering the input φ_i being directed towards a single output φ_i^* only. This further implies the diagonal form of the joint two-MO probabilities,

$$\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}, \boldsymbol{\varphi}^*) = \{\tilde{P}(i, j) = P_j \delta_{i,j}\}, \tag{7}$$

which automatically satisfies the required overall normalization,

$$\sum_i^{\text{MO}} \sum_j^{\text{MO}} \tilde{P}(i, j) = \sum_i P_i = 1. \tag{8}$$

The associated conditional probabilities at this MO-occupation stage thus read:

$$\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^*|\boldsymbol{\varphi}) = \{\tilde{P}(j|i) = (P_j/P_j^{\text{inp.}})\delta_{i,j}\}. \tag{9}$$

They satisfy the partial (row) normalizations, which are expected of the true conditional probabilities, only for the "stationary" channel, when $\boldsymbol{P}_{\boldsymbol{\varphi}}^{\mathrm{inp.}} = \boldsymbol{P}_{\boldsymbol{\varphi}}$:

$$\sum_{j}^{\mathrm{MO}} \tilde{P}(j|i) = \frac{P_i}{P_i^{\mathrm{inp.}}} = 1, \quad i = 1, 2, \ldots \tag{10}$$

Indeed, in the diagonal (disconnected) representation the constraints of the correct row normalizations imply the trivial (deterministic, noiseless) channel corresponding to the identity matrix: $\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^*|\boldsymbol{\varphi}) = \{\delta_{i,j}\} \equiv \mathbf{I}$. As we shall argue below such populational stage characterizes the purely geometric promotion of AO, with equally weighted contributions from all MO (occupied and virtual).

Substituting equation (9) into equation (4) gives the associated AO-promotion probabilities $\tilde{\mathbf{P}}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*) = \{\tilde{P}(l|k)\}$, where

$$\begin{aligned}\tilde{P}(l|k) &= \sum_{i,j}^{\mathrm{MO}} P(i|k)\tilde{P}(j|i)P(l|j) = \sum_{i,j}^{\mathrm{MO}} P(i|k)\frac{P_j}{P_j^{\mathrm{inp.}}}\delta_{i,j}P(l|j) \\ &= \sum_{i}^{\mathrm{MO}} P(l|i)\frac{P_i}{P_i^{\mathrm{inp.}}}P(i|k).\end{aligned} \tag{11}$$

It is of interest to examine the resulting output probabilities of the promoted AO (Scheme 1b) in this representation [see equations (3) and (6)]:

$$\begin{aligned}\tilde{P}_l &\equiv \sum_{k}^{\mathrm{AO}} P_k^0 \tilde{P}(l|k) = \sum_{i}^{\mathrm{MO}} P(l|i)\frac{P_i}{P_i^{\mathrm{inp.}}}\left[\sum_{k}^{\mathrm{AO}} P_k^0 P(i|k)\right] = \sum_{i}^{\mathrm{MO}} P(l|i)P_i \\ &= \sum_{i}^{\mathrm{MO}} P(l,i) = P_l.\end{aligned} \tag{12}$$

Therefore, the AO-promotion channel resulting from the diagonal MO-occupation network predicts the molecular AO probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}$ in the output of Scheme 1b.

It should be stressed, that the conditional AO-promotion probabilities of equation (11) are input-dependent, through $\boldsymbol{P}_{\boldsymbol{\varphi}}^{\mathrm{inp.}}(\boldsymbol{P}_{\boldsymbol{\chi}}^0)$ [equation (6)]. Therefore, they describe the effectively dependent two-AO events in the AO-promotion channel 1b, defining the associated two-AO probabilities [see equation (2)]:

$$\tilde{\mathbf{P}}(\boldsymbol{\chi}, \boldsymbol{\chi}^*) = \left\{ \tilde{P}(k,l) = P_k \tilde{P}(l|k) = \sum_{i}^{\mathrm{MO}} P(l,i)\frac{1}{P_i^{\mathrm{inp.}}}P(i,k) \right\}. \tag{13}$$

They satisfy the correct partial normalization for the stationary MO-occupation channel, when $\{P_i = P_i^{\text{inp.}}\}$:

$$\sum_{k}^{\text{AO}} \tilde{P}(k,l) = \sum_{i}^{\text{MO}} P(l,i) \frac{P_i}{P_i^{\text{inp.}}} = P_l. \tag{14}$$

The normalization conditions (8) and (10) can be automatically satisfied, for any admissible input probability vector, within the appropriate *non-diagonal* (connected) form of $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$. For the *independent* MO events in the input and output of the MO-occupation network the joint *two*-MO probabilities read:

$$\mathbf{P}(\boldsymbol{\varphi}, \boldsymbol{\varphi}^*) = \{P(i,j) = P_i^{\text{inp.}} P_j\}, \tag{15}$$

where $P(i,j)$ is the probability of φ_i in the channel input and φ_j in its output. They give rise to the associated non-diagonal form of the MO conditional probabilities,

$$\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi}) = \{P(j|i) = P(j,i)/P_i^{\text{inp.}} = P_j\}, \tag{16}$$

which determines the information scattering in the MO-occupation sub-channel in Scheme 1a. This matrix is seen to contain identical rows defined by the MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}}$.

This representation gives rise to the following conditional probabilities of the physical AO-promotion in the molecule [equation (4)]:

$$\begin{aligned} P(l|k) &= \sum_{i}^{\text{MO}} \sum_{j}^{\text{MO}} P(i|k) P(j|i) P(l|j) = \left[\sum_{i}^{\text{MO}} P(i|k) \right] \sum_{j}^{\text{MO}} P_j P(l|j) \\ &= \sum_{j}^{\text{MO}} P(l,j) = P_l, \end{aligned} \tag{17}$$

which guarantees the correct partial normalizations of equation (10),

$$\sum_{l}^{\text{AO}} P(l|k) = \sum_{l}^{\text{AO}} P_l = 1, \quad k = 1, 2, \ldots \tag{18}$$

Hence, the output AO probabilities of Scheme 1b are identical with those resulting from the diagonal representation of the MO-occupation channel [equation (12)]:

$$P_l = \sum_{k}^{\text{AO}} P_k^0 P(l|k). \tag{19}$$

In equation (17) we have used the normalization condition of the geometrical probabilities of MO conditional on AO [equation (1)] and the associated relation (3) for the joint probabilities $\mathbf{P}(\boldsymbol{\chi}, \boldsymbol{\varphi}) = \{P(l, j)\}$ [equation (2)] of the simultaneous (AO, MO)-events. As we shall demonstrate in the next section, these conditional probabilities of the resultant (physical) AO-promotion in the molecule reproduce the molecular information channel and the resulting entropy/information bond-orders in the simplest 2-AO model of the chemical bond, which have been generated using the two-electron (AIM-resolved) approach [5, 6, 9, 14].

The conditional probabilities of equation (17) are seen to be input-independent, exhibiting purely molecular character, independent of the promolecular bond origin. Hence, the joint effective two-AO probabilities resulting from this *one*-electron perspective, of simultaneously observing χ_k in the promolecular input and χ_l in the molecular output, read:

$$\mathbf{P}(\boldsymbol{\chi}, \boldsymbol{\chi}^*) = \{P(k, l) = P(l\,|k)\,P_k^0 = P_l\,P_k^0\}. \tag{20}$$

They describe the independent input–output AO-events and satisfy all relevant partial and overall normalizations:

$$\sum_k^{\mathrm{AO}} P(k, l) = P_l, \quad \sum_l^{\mathrm{AO}} P(k, l) = P_k^0, \quad \sum_k^{\mathrm{AO}} \sum_l^{\mathrm{AO}} P(k, l) = 1. \tag{21}$$

2.2. *Overall indices of chemical bonds*

In determining the overall entropy/information indices of the covalent and ionic bond components and the associated total IT bond-order in the molecule one can follow two alternative approaches. The two-input approach used within the two-electron development in atomic resolution [5, 6, 14] adopts the molecular AO probabilities in the channel input (Scheme 1c) to extract average measure of the system average communication "noise", which describes the molecular covalency as purely molecular phenomenon. At the same time the promolecular AO probabilities are used (Scheme 1b) to determine the information-distance measure of the amount of information flowing through the channel, between the non-bonded atoms in the channel input and AIM in the channel output, which indexes the molecular ionicity as the difference phenomenon. Alternatively, the resultant communication system of Scheme 1b can be used to estimate both bond components [18], since this information-scattering network has a double-input interpretation in the present orbital development [equation (4)]: $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}^0)$. Both approaches give-rise to slightly different "normalization" of the total bond-order: in the two-input approach it amounts to the Shannon entropy of the promolecular AO probabilities, while in the single-input approach the total bond-multiplicity equals the Shannon entropy of the molecular probabilities of the promoted AO.

Within the two-input development the molecular conditional entropy indices of IT [2, 4], of the promoted (molecular) AO output given the initial (molecular) AO input [5, 6, 14], read for the two representations of the preceding section:

$$\tilde{S}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) = -\sum_{k}^{\mathrm{AO}}\sum_{l}^{\mathrm{AO}} \tilde{P}(l,k)\log\frac{\tilde{P}(l,k)}{P_k} = \tilde{S}(\boldsymbol{\chi},\boldsymbol{\chi}^{*}) - S(\boldsymbol{\chi}^{*}),$$

$$S(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) = -\sum_{k}^{\mathrm{AO}}\sum_{l}^{\mathrm{AO}} P(l,k)\log\frac{P(l,k)}{P_k} = S(\boldsymbol{\chi},\boldsymbol{\chi}^{*}) - S(\boldsymbol{\chi}^{*}) = S(\boldsymbol{\chi}^{*}). \quad (22a)$$

They measure differences between the corresponding Shannon entropies:

(i) of the joint *two*-AO probabilities:

$$\tilde{S}(\boldsymbol{\chi},\boldsymbol{\chi}^{*}) = -\sum_{k}^{\mathrm{AO}}\sum_{l}^{\mathrm{AO}} \tilde{P}(l,k)\log\tilde{P}(l,k) \text{ or}$$

$$S(\boldsymbol{\chi},\boldsymbol{\chi}^{*}) = -\sum_{k}^{\mathrm{AO}}\sum_{l}^{\mathrm{AO}} P(l,k)\log P(l,k) = 2S(\boldsymbol{\chi}^{*}), \quad (23)$$

(ii) of the *single*-AO (molecular) probabilities:

$$S(\boldsymbol{\chi}^{*}) = -\sum_{l}^{\mathrm{AO}} P_l \log P_l. \quad (24)$$

This index reflects the average communication "noise" in the resultant information channel of Scheme 1b. In previous applications of the AIM- and orbitally resolved theories to simple models of chemical bonds [5–18] it has been shown to provide a realistic IT descriptor of the molecular bond-covalency. Indeed, this component is intuitively associated with an extra uncertainty in the distribution of electrons of the constituent atoms created by their delocalization throughout the network of the system chemical bonds generated by the occupied MO. It thus reflects an effective "sharing" of the free-atom electrons between all constituent atoms, as intuitively expected of the realistic covalent measure. This spreading (scattering) of the electron probability throughout the molecule implies an accompanying redistribution of the information contained in the electron distribution, thus increasing the average communication noise (conditional entropy) and decreasing the channel complementary descriptor (mutual information) indexing the ionic bond multiplicity.

As argued elsewhere [5, 6, 14] the IT-ionic component in the AO-resolved molecular communication system is reflected by the *mutual information* index:

$$\tilde{I}(\boldsymbol{\chi}^{0}:\boldsymbol{\chi}^{*}) = S(\boldsymbol{\chi}^{0}) - \tilde{S}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) \text{ or}$$

$$I(\boldsymbol{\chi}^{0}:\boldsymbol{\chi}^{*}) = S(\boldsymbol{\chi}^{0}) - S(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) = S(\boldsymbol{\chi}^{0}) - S(\boldsymbol{\chi}^{*}), \quad (25a)$$

where $S(\boldsymbol{\chi}^0)$ stands for the Shannon entropy of the initial AO probabilities

$$S(\boldsymbol{\chi}^0) = -\sum_k^{\mathrm{AO}} P_k^0 \log P_k^0. \tag{26}$$

The mutual information descriptor reflects the joint information contained in probabilities of the initial (promolecular) input $\boldsymbol{\chi}^0$ and the final (molecular) output $\boldsymbol{\chi}^*$, respectively. It has been expressed in equation (25a) as the difference between the promolecular entropy in the AO resolution and the relevant average-noise (conditional entropy) index, with the latter measuring the information loss due to electron delocalization in the molecule. A reference to this equation also shows that the information-difference $I(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*)$ amounts to the negative shift in the molecular Shannon entropy of bonded-atoms, relative to that of the free atoms. In the AO-promotion channel of Scheme 1b the mutual-information descriptor between the promolecular input and the molecular output thus probes the net amount of information flowing through the communication system, which survives the information loss due to the noise.

It has also been argued elsewhere [5–18] that this index, complementary to the conditional entropy of equation (22a), reflects the bond "ionicity" reaching the maximum value for the noiseless channel, when there is no effective probability scattering: $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{I}$, $S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = 0$, $I(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^0)$. It represent the difference (displacement) aspect of the molecular communication channel, relative to the initial free-atom reference. This quantity also reflects the entropy-deficiency (missing information, relative entropy) of Kullback and Leibler [12], between probabilities of the dependent (molecular) and independent (promolecule-molecule) 2-AO events [14].

It follows from equation (25a) that the entropy-covalency and information-ionicity indices compete against each other for a fraction of the initial information $S(\boldsymbol{\chi}^0)$, which marks the overall IT bond-order in the orbital communication system [5–14]:

$$\begin{aligned}\tilde{N}(\boldsymbol{\chi}^0; \boldsymbol{\chi}^*) &= \tilde{S}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) + \tilde{I}(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*) = N(\boldsymbol{\chi}^0; \boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) + I(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*)\\ &= S^0(\boldsymbol{\chi}).\end{aligned} \tag{27a}$$

This overall bond-order conservation accords with the actual competition between the electron-sharing (covalent) and electron-transfer (ionic) attributes of the chemical bond [9, 14].

This promolecular "normalization" of the overall bond-order is changed in the single-input approach [18] to the corresponding molecular Shannon entropy of equation (24). Denoting the resulting indices with bars gives:

$$\bar{S}(\chi^*|\chi^0) = -\sum_k^{AO}\sum_l^{AO} P(l,k^0)\log\frac{P(l,k^0)}{P_k^0} = -\sum_k^{AO} P_k^0 \sum_l^{AO} P(l|k)\log P(l|k)$$
$$= S(\chi^0,\chi^*) - S(\chi^0), \tag{22b}$$

$$\bar{I}(\chi^0\colon \chi^*) = \sum_k^{AO}\sum_l^{AO} P(l,k^0)\log\frac{P(l,k^0)}{P_k^0 P_l} = S(\chi^*) + S(\chi^0) - S(\chi^0,\chi^*)$$
$$= S(\chi^*) - \bar{S}(\chi^*|\chi^0), \tag{25b}$$

$$\bar{N}(\chi^0;\chi^*) = \bar{S}(\chi^*|\chi^0) + \bar{I}(\chi^0\colon \chi^*) = S(\chi^*). \tag{27b}$$

It should be stressed that the effective electron excitation (promotion) from the occupied to virtual AO of the promolecule implies a higher degree of uncertainty in the electron distribution of the bonded atoms: $S(\chi^*) \geqslant S(\chi^0)$. Therefore, one should in general expect a slightly higher overall IT bond-index in the single-input approach, compared to that resulting from the two-input scheme. The equality takes place in these rare systems, e.g., π-electron systems of the alternant hydrocarbons, in which the promolecular and molecular AO probabilities are identical.

2.3. Geometrical AO-promotion channel and its bond descriptors

The purely geometric aspect of the information scattering in the molecular Hilbert-space [17] corresponds to the deterministic, noiseless MO-occupation sub-channel in Scheme 1a: $\mathbf{P}^g(\varphi^+|\varphi) = \mathbf{I}$. It involves all (equally weighted) MO and does not introduce any extra noise into the AO-promotion communications. The associated purely geometrical promotion of AO due to their mixing into MO is thus given by the conditional probabilities:

$$\mathbf{P}^g(\chi^+|\chi) = \mathbf{P}(\varphi|\chi)\mathbf{P}^g(\varphi^+|\varphi)\mathbf{P}(\chi^+|\varphi^+) \equiv \mathbf{P}(\varphi|\chi)\mathbf{P}(\chi^+|\varphi)$$
$$= \left\{ P^g(l|k) = \sum_i^{MO} P(i|k)P(l|i) = \sum_i^{MO} |\langle k|i\rangle|^2\, |\langle l|i\rangle|^2 \right.$$
$$\left. = \sum_i^{MO} |C_{k,i}|^2\, |C_{l,i}|^2 \right\}. \tag{28}$$

It should be emphasized, that the output AO probabilities in the geometric-promotion channel, $\boldsymbol{P}_{\chi}^{+} = \boldsymbol{P}_{\chi}^{0}\mathbf{P}^{g}(\chi^{+}|\chi) = \{P_l^{+}\}$, in general differ from those resulting from the effective physical-promotion system, $\boldsymbol{P}_{\chi} = \boldsymbol{P}_{\chi}^{0}\mathbf{P}(\chi^{*}|\chi) = \{P_l\}$ [17]. More specifically, equation (28) gives [see equation (6)]:

$$P_l^{+} = \sum_{k}^{\mathrm{AO}} P_k^0 P^g(l\,|k) = \sum_{i}^{\mathrm{MO}} \left[\sum_{k}^{\mathrm{AO}} P_k^0 P(i|k) \right] P(l\,|i) = \sum_{i}^{\mathrm{MO}} P_i^{\mathrm{inp.}} P(l\,|i)$$
$$\equiv \sum_{i}^{\mathrm{MO}} P(l, i^{\mathrm{inp.}}) \neq P_l = \sum_{i}^{\mathrm{MO}} P_i P(l\,|i) \equiv \sum_{i}^{\mathrm{MO}} P(l, i). \tag{29}$$

The geometric channel gives rise to the associated entropy/information indices describing the effective probability/information scattering in the molecular Hilbert-space,

$$S^g(\chi^{+}|\chi) = -\sum_{k}^{\mathrm{AO}} P_k^{+} \sum_{l}^{\mathrm{AO}} P^g(l\,|k) \log P^g(l\,|k),$$
$$I^g(\chi^0\!: \chi^{+}) = S(\chi^0) - S^g(\chi^{+}|\chi),$$
$$N^g(\chi^0; \chi^{+}) = S^g(\chi^{+}|\chi) + I^g(\chi^0\!: \chi^{+}) = S(\chi^0), \tag{30}$$

obtained from equations (22a), (25a), and (27a) by replacing $\mathbf{P}(\chi^{*}|\chi)$ with $\mathbf{P}^g(\chi^{+}|\chi) = \mathbf{I}$. These "bond" descriptors reflect the complementary aspects of the AO-promotion created only by the AO mixing into MO: the extra communication "noise", the amount of information flowing through the geometric channel, and the overall IT bond index measuring the Shannon entropy of the input probabilities, respectively.

The physical IT bond indices of the preceding section reflect the resultant effects of both the MO shapes and their ground-state occupations, while their geometric analogs describe only the former aspect of the probability propagation in the molecular AO-promotion information system. Therefore, the difference between the corresponding physical and geometric descriptors provides a measure of the *occupational* (o) contribution only:

$$S^o(\chi^{*}|\chi) = S(\chi^{*}|\chi) - S^g(\chi^{+}|\chi), \tag{31}$$
$$I^o(\chi^0\!: \chi^{+}) = I(\chi^0\!: \chi^{*}) - I^g(\chi^0\!: \chi^{+}).$$

Since the total bond indices measure the Shannon entropy of the promolecular input the occupational contribution to the overall bond measure vanishes identically:

$$N^o(\chi^0; \chi^{*}) = N(\chi^0; \chi^{*}) - N^g(\chi^0; \chi^{+}) = 0. \tag{32}$$

Therefore, the overall IT bond indices resulting from the geometrical and physical information channels are identical, with the occupational aspect of the physical channel influencing only the proportions between the IT-covalent and IT-ionic bond components. In the next section we shall illustrate the two AO-promotion channels and their IT indices for the chemical bond formed by two OAO of bonded atoms in a diatomic molecule A—B.

3. An illustration: interaction of two orthonormal orbitals in the chemical bond

The simplest (*two*-electron) model involves the interaction of two (real) valence OAO, $\tilde{\boldsymbol{\chi}} = (\tilde{\chi}_A, \tilde{\chi}_B) \equiv (\tilde{A}, \tilde{B})$, contributed by atoms A and B, respectively. The assumed (covalent) promolecule $M^0 = (A^0|B^0)$ involves a single valence electron occupying each free atom, i.e., $\boldsymbol{P}^0_{\boldsymbol{\chi}} = (1/2, 1/2) = P^0_{\tilde{\chi}}$. This model provides a realistic description of both the symmetric covalent bond, when $\boldsymbol{P}_{\boldsymbol{\chi}} = (P, Q) = \boldsymbol{P}^0_{\boldsymbol{\chi}}$, e.g., the π-bond in ethylene and the σ-bond in H_2, and of the polarized chemical bonds, for $P \neq Q$ [5–18].

In this 2-OAO model the two mutually orthogonal combinations, $\tilde{\boldsymbol{\chi}} = (\tilde{\chi}_A, \tilde{\chi}_B) = \boldsymbol{\chi}\mathbf{S}_{\chi}^{-1/2}$, of the original (overlapping) AO, $\boldsymbol{\chi} = (\chi_A, \chi_B)$, where $\mathbf{S}_{\boldsymbol{\chi}} = \langle \boldsymbol{\chi}|\boldsymbol{\chi}\rangle \neq \mathbf{I}$, are subsequently mixed into the (orthonormal) bonding (b) and anti-bonding (a) MO expressed in terms of the complementary OAO probabilities P and Q:

$$\varphi_b = \sqrt{P}\tilde{\chi}_A + \sqrt{Q}\tilde{\chi}_B \quad \text{and} \quad \varphi_a = -\sqrt{Q}\tilde{\chi}_A + \sqrt{P}\tilde{\chi}_B, \quad P + Q = 1. \tag{33}$$

In the joint matrix notation this transformation reads:

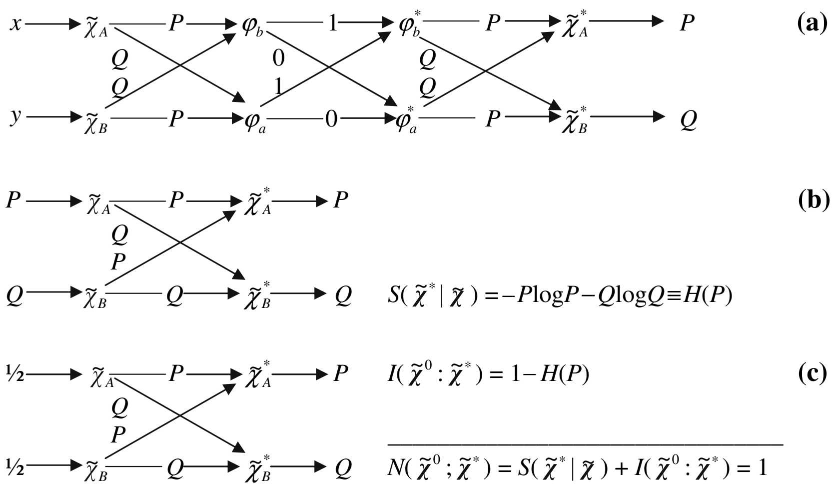
$$\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C} = (\boldsymbol{\chi}\mathbf{S}_{\chi}^{-1/2})\mathbf{O} = \tilde{\boldsymbol{\chi}}\mathbf{O}, \quad \mathbf{O} = \begin{bmatrix} \sqrt{P} & -\sqrt{Q} \\ \sqrt{Q} & \sqrt{P} \end{bmatrix}, \quad \mathbf{O}^{\mathrm{T}}\mathbf{O} = \mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} = \mathbf{I}. \tag{34}$$

Therefore, the OAO-mixing (probability) parameter $0 \leqslant P \leqslant 1$ measures the conditional probabilities $P(\tilde{A}|b) = P(\tilde{B}|a) = P$, of detecting $\tilde{\chi}_A$ in φ_b or $\tilde{\chi}_B$ in φ_a, respectively. The complementary probability $Q = 1 - P$ similarly reflects $P(\tilde{A}|a) = P(\tilde{B}|b) = Q$.

Again, the squares of the matrix elements in $\mathbf{O} = \{O_{\tilde{k},i}\}$ generate the conditional probabilities of $\boldsymbol{\varphi}$ into $\tilde{\boldsymbol{\chi}}$, $\tilde{\boldsymbol{\chi}} = \boldsymbol{\varphi}\mathbf{O}^{\mathrm{T}}$, the [see equation (1)]:

$$\mathbf{P}(\boldsymbol{\varphi}|\tilde{\chi}) = \left\{P(i|\tilde{k}) = O^2_{\tilde{k},i}\right\} = \begin{bmatrix} P & Q \\ Q & P \end{bmatrix} = \mathbf{P}(\tilde{\boldsymbol{\chi}}|\boldsymbol{\varphi})^{\mathrm{T}} = \{P(\tilde{k}|i) = O^2_{i,\tilde{k}}\}. \tag{35}$$

Indeed, since $\mathbf{O}^{\mathrm{T}} = \mathbf{O}^{-1}$ reversely transforms $\boldsymbol{\varphi}$ into $\tilde{\boldsymbol{\chi}}$, $\tilde{\boldsymbol{\chi}} = \boldsymbol{\varphi}\mathbf{O}^{\mathrm{T}}$, the squares of these expansion coefficients also provide conditional probabilities of OAO conditional on MO: $\mathbf{P}(\tilde{\boldsymbol{\chi}}|\boldsymbol{\varphi}) = \mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\chi}})^{\mathrm{T}}$.



Scheme 2. The physical OAO-promotion in the ground-state of the two-orbital model for the *non*-diagonal representation of the MO-occupation sub-channel. Panel a shows the information cascade for the general input-probability vector $\boldsymbol{P}_{\boldsymbol{\chi}}^{0}(x) = (x, y = 1 - x)$. It involves a succession of the geometrical (OAO → MO), occupational (MO → MO), and geometrical (MO → OAO) probability-scattering networks, which determines the resultant communication system of Panels b and c for the effective OAO promotion in the molecular ground-state. In the stationary channel of Panel b, which probes the entropy-covalency $S(\tilde{\boldsymbol{\chi}}^* | \tilde{\boldsymbol{\chi}})$ [5, 6, 14], the molecular OAO probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}(P) = (P, Q = 1 - P)$ shape the system input "signal". The non-stationary channel of Panel c uses in its input the OAO probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}^{0} = (1/2, 1/2)$ of the covalent promolecule, which is needed to extract the bond information-ionicity $I(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*)$ reflecting the difference (displacement) aspect of the chemical bond. These indices conserve the overall single-bond multiplicity: $N(\tilde{\boldsymbol{\chi}}^0; \tilde{\boldsymbol{\chi}}^*) = S(\tilde{\boldsymbol{\chi}}^* | \tilde{\boldsymbol{\chi}}) + I(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*) = S(\tilde{\boldsymbol{\chi}}^0) = 1$ bit.

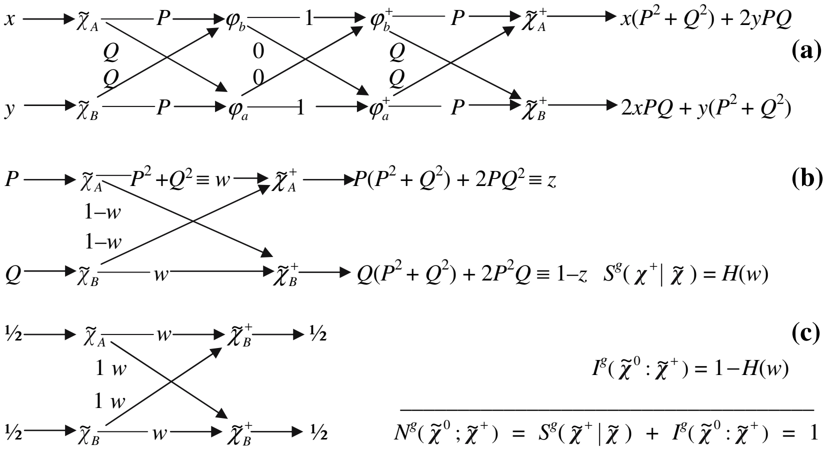
These conditional probabilities determine the geometric OAO → MO and MO → MO sub-channels in Scheme 1a. The ground-state (singlet) MO occupations $\boldsymbol{n} = \{n_b, n_a\} = (2, 0)$, or the MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}} = \{P_b, P_a\} = (1, 0)$, determine the MO-occupation sub-channels [equations (9) and (16)]:

$$\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^* | \boldsymbol{\varphi}) = \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix} \quad \text{or} \quad \mathbf{P}(\boldsymbol{\varphi}^* | \boldsymbol{\varphi}) = \begin{bmatrix} 1 & 0 \\ 1 & 0 \end{bmatrix}. \tag{36}$$

Finally, the product of equation (4) generates the associated effective OAO-promotion probabilities [equations (11) and (17)]:

$$\tilde{\mathbf{P}}(\tilde{\boldsymbol{\chi}}^* | \tilde{\boldsymbol{\chi}}) = \begin{bmatrix} 2P^2 & 2PQ \\ 2PQ & 2Q^2 \end{bmatrix} \quad \text{or} \quad \mathbf{P}(\tilde{\boldsymbol{\chi}}^* | \tilde{\boldsymbol{\chi}}) = \begin{bmatrix} P & Q \\ P & Q \end{bmatrix}. \tag{37}$$

The OAO promotion cascades and the resultant channels for the diagonal representation of the MO-occupation sub-channel, both physical and geometric, have been discussed elsewhere [17]. For the symmetrical MO, when $P = Q = 1/2$,



Scheme 3. The geometrical OAO-promotion in the two-orbital model. Panel a shows the information cascade involving a succession of two geometrical (OAO $\to$ MO) and (MO $\to$ OAO) sub-channels being separated by the deterministic (noiseless) MO-occupation sub-channel $\mathbf{P}^g(\boldsymbol{\varphi}^+|\boldsymbol{\varphi}) = \mathbf{I}$. It determines the resultant communicational system of Panels b and c, for the effective OAO-promotion in the molecular Hilbert space. In the non-stationary channel b, which probes the geometric entropy-covalency $S^g(\tilde{\boldsymbol{\chi}}^+|\tilde{\boldsymbol{\chi}})$, the molecular OAO probabilities shape the system input "signal", while the stationary channel c uses the input OAO probabilities of the atomic promolecule to extract the geometric information-ionicity $I^g(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^+)$. Again, the overall bond-order measure is conserved at the 1 bit level marking a single chemical bond: $N^g(\tilde{\boldsymbol{\chi}}^0; \tilde{\boldsymbol{\chi}}^+) = S^g(\tilde{\boldsymbol{\chi}}^+|\tilde{\boldsymbol{\chi}}) + I^g(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^+) = S(\tilde{\boldsymbol{\chi}}^0) = 1$ bit.

they both were shown to correctly predict the IT-single, purely covalent chemical bond:

$$\tilde{N}(\tilde{\boldsymbol{\chi}}^0; \tilde{\boldsymbol{\chi}}^*) = \tilde{S}(\tilde{\boldsymbol{\chi}}^*|\tilde{\boldsymbol{\chi}}) = N^g(\tilde{\boldsymbol{\chi}}^0; \tilde{\boldsymbol{\chi}}^*) = S^g(\tilde{\boldsymbol{\chi}}^*|\tilde{\boldsymbol{\chi}}) = 1\,\text{bit},$$
$$\tilde{I}(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*) = I^g(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*) = 0.$$

The physical OAO-promotion of the two-orbital model for the new, non-diagonal representation of the MO-occupation sub-channel is summarized in Scheme 2. The relevant $\tilde{\boldsymbol{\chi}} \to \boldsymbol{\varphi} \to \boldsymbol{\varphi}^* \to \tilde{\boldsymbol{\chi}}^*$ cascade is shown in Scheme 2a. It defines the resultant OAO-promotion channel of Scheme 2b and 2c, reported for the molecular and promolecular input probabililities, respectively, together with the relevant entropy-covalency and information-ionicity indices.

This non-symmetrical orbital channel is identical with the AIM-resolved channel of the previous *two*-electron approach (see, e.g., [5, 6, 14]). As already reported in Scheme 2, its entropy/information descriptors (in bits) of the model chemical bond, from equations (22a), (25a), and (27a), read: $S(\tilde{\boldsymbol{\chi}}^*|\tilde{\boldsymbol{\chi}}) = -P\log P - Q\log Q \equiv H(P)$ (Scheme 2b), $I(\tilde{\boldsymbol{\chi}}^0{:}\tilde{\boldsymbol{\chi}}^*) = 1 - H(P)$ (Scheme 2c), and hence $N(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*) = S(\tilde{\boldsymbol{\chi}}^*|\tilde{\boldsymbol{\chi}}) + I(\tilde{\boldsymbol{\chi}}^0 : \tilde{\boldsymbol{\chi}}^*) = S(\tilde{\boldsymbol{\chi}}^0) = 1$. Therefore, when the bonding MO is polarized in the whole range $0 \leqslant P \leqslant 1$ of the AO-probability parameter P controlling the OAO mixing into MO the overall IT bond-order is preserved at the 1 bit level, while the complementary IT-covalency and IT-ionicity descriptors of this single chemical bond compete for the initial entropy/information $S(\tilde{\chi}^0)$ contained in the promolecular electron distribution among the two OAO. As expected, for the symmetrical MO, when $P = Q = 1/2$, one again diagnoses the purely-covalent chemical bond in the model: $N(\tilde{\chi}^0{:}\tilde{\chi}^*) = S(\tilde{\chi}^*|\tilde{\chi}) = 1$ and $I(\tilde{\chi}^0 : \tilde{\chi}^*) = 0$.

These entropy/information indices of the model chemical bond are in accord with the chemical intuition. They give rise to the conserved overall bond multiplicity and correctly reflect the competition between the complementary bond components. Indeed, the greater a degree of the electron "sharing" between the bonded atoms (the covalent aspect), i.e., the greater average "noise" in the molecular information channel, the smaller the "localization" and/or CT of the valence electrons in molecules (the ionic aspect), as measured by the mutual information of the molecular communication system, which has survived despite the information loss due to the noise. The partial-channel approach [7, 14] to this OAO-promotion information network then generates transparent perspective on a subtle interplay of various AIM-resolved contributions to this conserved single bond-order [9, 14].

In Scheme 3 the geometrical OAO-promotion in the model is summarized. As reported in the Panels b and c the sum of the complementary conditional-entropy and mutual-information descriptors of the channel IT covalency and ionicity, respectively, again conserves the overall index of the Hilbert space promotion of AO due to their mixing into MO: $N^g(\tilde{\chi}^0; \tilde{\chi}^+) = S^g(\tilde{\chi}^+|\tilde{\chi}) + I^g(\tilde{\chi}^0 : \tilde{\chi}^+) = S(\tilde{\chi}^0) = 1$ bit. It also follows from the expressions for the bond components reported in Scheme 3b and 3c that for the symmetric bonding MO, for $P = Q = 1/2$ and hence $w = z = 1/2$, $S^g = 1$ and $I^g = 0$. Therefore, in this symmetric case the occupational contributions of equation (31) to the conserved overall bond order identically vanish: $S^o(\tilde{\chi}^*|\tilde{\chi}) = I^o(\tilde{\chi}^0 : \tilde{\chi}^*) = 0$.

4. Molecular promotion channels of intermediate orbitals

In this section we provide an overview of the communication systems representing the physical and geometric promotions for the intermediate sets of orbitals, which connect to the customary stages of the electronic structure readjustments accompanying the chemical bond formation. An example of the effective physical promotion, which combines the geometric and populational sub-channels is represented by the AO → MO(*occd.*) → AO probability scatterings [17, 18] shown in Schemes 1a and 2a, which give rise to the resultant channels of Schemes 1b and 2(b, c), respectively. These effective information systems are seen to represent the communication cascades involving two geometrical (orbital mixing) sub-channels, with the information scattering determined by the conditional probabilities $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})$ [or $\mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\chi}})$] and $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*)$ [or $\mathbf{P}(\tilde{\boldsymbol{\chi}}^*|\boldsymbol{\varphi}^*)$], respectively, and the MO electron population sub-channel described by the $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$ [or $\tilde{\mathbf{P}}^d(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$] matrix of conditional probabilities reflecting the ground-state occupations of MO.

The effective information channels of Schemes 1b and 2(b, c) amount to the *resultant* (physical) promotion of AO, from the *initial* (promolecular or molecular) AO probabilities to the *final* effective probabilities of interacting orbitals of constituent atoms in the molecular ground-state. Similar communication channels can be constructed for all admissible *intermediate* stages of the orbital promotion in molecules. They should also involve the information systems representing the elementary orbital-occupation and orbital-mixing “displacements” in the system electronic structure. Examples of such *partial* channels involving solely the (intermediate) OAO basis set have been given in the preceding section.

Such elementary promotion cascades for intermediate stages of shaping the final, equilibrium molecular electronic structure also involve changes in the effective electron occupations of the given set of orbitals, giving rise to their purely *occupational*-promotion, e.g., in the atomic excitations from their ground-states to the specified valence-states in the molecule, or in occupying MO in accordance with the principle of the least orbital energy. The orbital-mixing stages, for the fixed occupations of the original set, generate the purely geometric, *delocalizational*-promotion, e.g., due to the AO-mixing into the “directed” hybrid orbitals (HO), their subsequent transformation into orthogonal HO (OHO), combining the OHO into MO, mixing the canonical MO of the SCF LCAO MO theory into the natural orbitals (NO) in the familiar configuration-interaction (CI) scheme, etc. These partial geometric transformations modify the shapes of initial orbitals, thus changing orientations of the associated state-vectors in the molecular Hilbert-space.

These elementary channels subsequently combine into the physical or geometrical sequences (cascades), which reflect the effective promotions of the chosen set of orbitals $\boldsymbol{\psi} =$ AO, HO, OHO, MO, NO. The physical cascade for orbitals $\boldsymbol{\psi}$ reflects the effective $\boldsymbol{\psi} \to \boldsymbol{\psi}^*$ probability scattering via the system occupied MO, $\boldsymbol{\psi} \to \mathrm{MO}(occd.) \to \boldsymbol{\psi}^*$ or $\boldsymbol{\psi} \to (\boldsymbol{\varphi} \to \boldsymbol{\varphi}^*) \to \boldsymbol{\psi}^*$. It is defined by the conditional probabilities [see equation (4)]

$$\mathbf{P}(\boldsymbol{\psi}^*|\boldsymbol{\psi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\psi})\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})\mathbf{P}(\boldsymbol{\psi}^*|\boldsymbol{\varphi}^*). \tag{38}$$

In general, the geometric factors $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\psi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\varphi})^{\mathrm{T}}$ may involve several intermediate steps of the orbital-transformation leading from $\boldsymbol{\psi}$ to $\boldsymbol{\varphi}$:$\boldsymbol{\psi} \to \cdots \to \boldsymbol{\varphi} \equiv \boldsymbol{\psi} \to \boldsymbol{\varphi}$. The associated geometrical cascade $\boldsymbol{\psi} \to \mathrm{MO}(all) \to \boldsymbol{\psi}^*$ or $\boldsymbol{\psi} \to (\boldsymbol{\varphi} \to \boldsymbol{\varphi}^+)^g \to \boldsymbol{\psi}^+ \equiv \boldsymbol{\psi} \to \boldsymbol{\varphi} \to \boldsymbol{\psi}^+$, corresponds to the identity sub-channel for the MO-occupation step, $\mathbf{P}^g(\boldsymbol{\varphi}^+|\boldsymbol{\varphi}) = \mathbf{I}$, in the probability product of the preceding equation. It thus refers to the $\boldsymbol{\psi}$-promotion due to all (equally weighted) MO in the adopted AO basis set [see equation (28)]:

$$\boldsymbol{P}_{\varphi}{}^{\text{inp.}} \longrightarrow \varphi \longrightarrow \mathbf{P}(\varphi^{*}|\varphi) \longrightarrow \varphi^{*} \longrightarrow \boldsymbol{P}_{\varphi} \qquad \textbf{(a)}$$

$$\boldsymbol{P}_{\psi}{}^{\text{inp.}} \longrightarrow \psi \longrightarrow \mathbf{P}(\psi^{*}|\psi) \longrightarrow \psi^{*} \longrightarrow \boldsymbol{P}_{\psi} \qquad \textbf{(b)}$$

$$\boldsymbol{P}_{\chi}{}^{0} \longrightarrow \chi \longrightarrow \mathbf{P}(\psi|\chi) \longrightarrow \psi \longrightarrow \boldsymbol{P}_{\psi}{}^{g} \qquad \textbf{(c)}$$

$$\boldsymbol{P}_{\psi} \longrightarrow \psi \longrightarrow \mathbf{P}(\chi|\psi) \longrightarrow \chi \longrightarrow \boldsymbol{P}_{\chi}{}^{g} \qquad \textbf{(d)}$$

Scheme 4. The elementary occupational (Panels a and b) and geometrical (Panels c and d) channels of the orbital-promotion cascades: for the MO-occupation promotion $\boldsymbol{\varphi} \to \boldsymbol{\varphi}^{*}$ (Panel a), the physical $\boldsymbol{\psi}$-occupation $\boldsymbol{\psi} \to \boldsymbol{\psi}^{*}$ (Panel b), and the two, mutually reverse, orbital-mixing transformations: $\boldsymbol{\chi} \to \boldsymbol{\psi}$ (Panel c) and $\boldsymbol{\psi} \to \boldsymbol{\chi}$ (Panel d). In the third channel the initial, free-atom probabilities $\boldsymbol{P}^{0}_{\boldsymbol{\chi}}$ of AO in the promolecular input give rise to the geometrically promoted probabilities $\boldsymbol{P}^{g}_{\boldsymbol{\psi}}$, while in the fourth channel the molecular input probabilities $\boldsymbol{P}_{\boldsymbol{\psi}}$ are transformed into the geometrical average probabilities $\boldsymbol{P}^{g}_{\boldsymbol{\chi}}$.

$$\mathbf{P}^{g}(\boldsymbol{\psi}^{+}|\boldsymbol{\psi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\psi})\mathbf{P}^{g}(\boldsymbol{\varphi}^{+}|\boldsymbol{\varphi})\mathbf{P}(\boldsymbol{\psi}^{+}|\boldsymbol{\varphi}^{+}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\psi})\mathbf{P}(\boldsymbol{\psi}^{+}|\boldsymbol{\varphi}). \tag{39}$$

Each factor in the probability products of equations (38) and (39) determines itself the elementary channel describing the given transformation of orbitals or the specified displacements in their effective occupations. For example, it follows from equation (5) that the (physical) MO-occupation conditional probabilities $\mathbf{P}(\boldsymbol{\varphi}^{*}|\boldsymbol{\varphi})$ define the elementary channel transforming the input (geometric) probability vector of MO, $\boldsymbol{P}^{\text{inp.}}_{\boldsymbol{\varphi}}$, into the ground-state MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}}$, thus defining the *elementary* channel of Scheme 4a. Similarly, the conditional probabilities $\mathbf{P}(\boldsymbol{\psi}^{*}|\boldsymbol{\psi})$ define the effective channel for the physical, *occupation*-promotion of $\boldsymbol{\psi}$ in the molecule, shown in Scheme 4b, involving the probability scattering from the initial probabilities due to the preceding orbital-mixing stage(s), $\boldsymbol{P}^{\text{inp.}}_{\boldsymbol{\psi}} = \boldsymbol{P}^{0}_{\boldsymbol{\chi}}\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})$, to their effective physical probabilities in the molecule: $\boldsymbol{P}_{\boldsymbol{\psi}} = \boldsymbol{P}^{\text{inp.}}_{\boldsymbol{\psi}}\mathbf{P}(\boldsymbol{\psi}^{*}|\boldsymbol{\psi})$.

Similar elementary channels are defined by any of the admissible geometrical (orbital-mixing) stages or their successions (cascades). For example, the resultant $\boldsymbol{\chi} \to \cdots \to \boldsymbol{\psi} \equiv \boldsymbol{\chi} \to \boldsymbol{\psi}$ orbital-mixing transformation, from the initial (AO) set $\boldsymbol{\chi}$ to the intermediate functions $\boldsymbol{\psi}$, generates the conditional probabilities $\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \{P(m|k)\} = \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi})^{\mathrm{T}}$, of observing ψ_m, given χ_k, in the molecular Hilbert space. They define the elementary geometrical channels of Schemes 4(b, c).

It should be observed that probabilities $\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})$ also give rise to the associated average (geometric) populations of $\boldsymbol{\psi}$, $\boldsymbol{N}^{g}_{\boldsymbol{\psi}} = \{N^{g}_{m}\}$, and their effective probabilities, $\boldsymbol{P}^{g}_{\boldsymbol{\psi}} = \boldsymbol{N}^{g}_{\boldsymbol{\psi}}/N = \{P^{g}_{m}\}$, which result from the elementary $\boldsymbol{\chi} \to \boldsymbol{\psi}$ transformation of the initial (promolecular) AO occupations $\boldsymbol{N}^{0}_{\boldsymbol{\chi}} = \{N^{0}_{k}\}$ and probabilities $\boldsymbol{P}^{0}_{\boldsymbol{\chi}} = \boldsymbol{N}^{0}_{\boldsymbol{\chi}}/N = \{P^{0}_{k}\}$:

$$P_\chi^{\ 0} \longrightarrow \chi \xrightarrow{\quad \mathbf{P}(\psi|\chi) \quad} \psi \xrightarrow{\quad \mathbf{P}(\psi^*|\psi) \quad} \psi \xrightarrow{\quad \mathbf{P}(\chi^*|\psi^*) \quad} \chi^* \longrightarrow \boldsymbol{P}_\chi \qquad \textbf{(a)}$$

$$P_\chi^{\ 0} \longrightarrow \chi \xrightarrow{\quad \mathbf{P}(\psi|\chi) \quad} \psi \xrightarrow{\quad \mathbf{P}^g(\psi^+|\psi) \quad} \psi^+ \xrightarrow{\quad \mathbf{P}(\chi^+|\psi^+) \quad} \chi^+ \longrightarrow \boldsymbol{P}_\chi^{\ +} \qquad \textbf{(b)}$$

$$P_\chi^{\ 0} \longrightarrow \chi \xrightarrow{\quad \mathbf{P}(\psi|\chi) \quad} \psi \xrightarrow{\quad \mathbf{P}(\chi^+|\psi) \quad} \chi^+ \longrightarrow \boldsymbol{P}_\chi^{\ +} \qquad \textbf{(c)}$$

Scheme 5. The physical (Panel a) and geometrical (Panels b and c) cascades $\chi \to (\psi \to \psi^*) \to \chi^*$ and $\chi \to (\psi \to \psi^+)^g \to \chi^+ \equiv \chi \to \psi \to \chi^+$ of the AO-promotion via the intermediate orbitals ψ, from the initial (promolecular) probabilities $\boldsymbol{P}_\chi^0$ to the promoted (molecular) probabilities $\boldsymbol{P}_\chi$ or $\boldsymbol{P}_\chi^+$, respectively.

$$\boldsymbol{N}_\psi^g = \boldsymbol{N}_\chi^0 \mathbf{P}(\psi|\chi) \quad \text{and} \quad \boldsymbol{P}_\psi^g = \boldsymbol{P}_\chi^0 \mathbf{P}(\psi|\chi). \tag{40}$$

The "reverse" geometrical channel, defined by conditional probabilities $\mathbf{P}(\chi|\psi) = \mathbf{P}(\psi|\chi)^{\mathrm{T}}$, similarly propagates the input probabilities $\boldsymbol{P}_\psi$ or occupations $\boldsymbol{N}_\psi$ into the average (geometric) AO quantities, e.g., $\boldsymbol{P}_\psi^g$ into $\boldsymbol{P}_\chi^0$ or $\boldsymbol{N}_\psi^g$ into $\boldsymbol{N}_\chi^0$. The molecular physical occupations $\boldsymbol{N}_\psi$ and the associated probabilities $\boldsymbol{P}_\psi = \boldsymbol{N}_\psi / N$ are similarly transformed into the corresponding AO (geometrical) averages (Scheme 4d):

$$\boldsymbol{N}_\chi^g = \boldsymbol{N}_\psi \mathbf{P}(\chi|\psi), \qquad \boldsymbol{P}_\chi^g = \boldsymbol{P}_\psi \mathbf{P}(\chi|\psi) = \boldsymbol{N}_\chi^g / N. \tag{41}$$

It should be realized, that the physical AO-promotion cascade of Scheme 5a, $\chi \to [\psi \to (\varphi \to \varphi^*) \to \psi^*] \to \chi^* \equiv \chi \to (\psi \to \psi^*) \to \chi^*$, which involves the two geometrical sub-channels of Scheme 4(c, d) and the physical ψ-population channel of Scheme 4b, generated by the conditional probabilities of equation (38) describing the effective promotion of ψ through the system occupied MO, amounts to the resultant AO-promotion system of Scheme 1b:

$$\mathbf{P}(\chi^*|\chi) = \mathbf{P}(\psi|\chi)\mathbf{P}(\psi^*|\psi)\mathbf{P}(\chi^*|\psi^*) \equiv \mathbf{P}_{\chi \to \varphi}(\chi^*|\chi), \tag{42}$$

where the notation $\mathbf{P}_{\chi \to \varphi}(\chi^*|\chi)$ reflects the fact that these promotion probabilities include contributions from all intermediate stages in orbital transformations from AO to MO.

Again, combining the geometrical conditional probabilities of equation (39) with the elementary geometrical channels of Scheme 4(c, d), in the information cascade $\chi \to [\psi \to (\varphi \to \varphi^+)^g \to \psi^+] \to \chi^+ \equiv \chi \to (\psi \to \psi^+)^g \to \chi^+$, reconstructs the communication network defined by the Hilbert-space probabilities of equation (28), for the resultant geometrical promotion of AO in the molecule:

$$\mathbf{P}^g(\chi^+|\chi) = \mathbf{P}(\psi|\chi)\mathbf{P}^g(\psi^+|\psi)\mathbf{P}(\chi^+|\psi^+) \equiv \mathbf{P}_{\chi \to \varphi}^g(\chi^+|\chi). \tag{43}$$

Multiplying the last two equations by $\mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi})$ from the left and by $\mathbf{P}^{-1}(\boldsymbol{\chi}^{+}|\boldsymbol{\psi}^{+}) = \mathbf{P}^{-1}(\boldsymbol{\chi}^{*}|\boldsymbol{\psi}^{*})$ from the right, allows one to formally express the conditional probabilities embodying the physical and geometric promotion of orbitals $\boldsymbol{\psi}$ in terms of the corresponding (resultant) AO-promotion probabilities:

$$\mathbf{P}(\boldsymbol{\psi}^{*}|\boldsymbol{\psi}) = \mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi})\mathbf{P}^{-1}(\boldsymbol{\chi}^{*}|\boldsymbol{\psi}^{*}),$$
$$\mathbf{P}^{g}(\boldsymbol{\psi}^{+}|\boldsymbol{\psi}) = \mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}^{g}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi})\mathbf{P}^{-1}(\boldsymbol{\chi}^{+}|\boldsymbol{\psi}^{+}). \quad (44)$$

It should be realized, that $\mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi}) \neq \mathbf{P}^{\mathrm{T}}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi})$. Indeed, the inverse matrix of the conditional probabilities (positive) must contain negative elements and thus cannot be interpreted as probability matrix. Therefore, $\mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi})$, for which $\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \mathbf{P}^{-1}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \mathbf{I}$, does not describe the probability propagation $\boldsymbol{\psi} \to \boldsymbol{\chi}$, which is embodied by $\mathbf{P}^{\mathrm{T}}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi})$.

Finally, the product

$$\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}^{\mathrm{T}}(\boldsymbol{\psi}|\boldsymbol{\chi}^{+}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}^{+}|\boldsymbol{\psi}) \equiv \mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) \quad (45)$$

generates the fraction of the resultant (geometric) AO-promotion due to the transformation linking $\boldsymbol{\chi}$ and $\boldsymbol{\psi}$. This probability scattering also follows from equation (43) by formally putting $\mathbf{P}^{g}(\boldsymbol{\psi}^{+}|\boldsymbol{\psi}) = \mathbf{I}$, i.e., by neglecting the remaining $\boldsymbol{\chi}$-promotion contribution $\mathbf{P}^{g}_{\chi \to \varphi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi})$ resulting from the geometric probability scattering of the $\boldsymbol{\psi}$-promotion due to the effective transformations between $\boldsymbol{\psi}$ and $\boldsymbol{\varphi}$ [equation (39)]:

$$\mathbf{P}^{g}_{\psi \to \varphi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) \equiv \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})[\mathbf{P}^{g}(\boldsymbol{\psi}^{+}|\boldsymbol{\psi}) - \mathbf{I}]\mathbf{P}(\boldsymbol{\chi}^{+}|\boldsymbol{\psi}) = \mathbf{P}^{g}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) - \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}^{+}|\boldsymbol{\psi})$$
$$= \mathbf{P}^{g}_{\chi \to \varphi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) - \mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}). \quad (46)$$

The stage-additivity of the AO-promotion probabilities, $\mathbf{P}^{g}_{\chi \to \varphi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) = \mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi}) + \mathbf{P}^{g}_{\psi \to \varphi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi})$, also extends to the physical promotion of AO in the molecule. The relevant combination rule, $\mathbf{P}_{\chi \to \varphi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) = \mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) + \mathbf{P}_{\psi \to \varphi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi})$, now involves the geometric contribution due to $\mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{+}|\boldsymbol{\chi})$ information-scattering of equation (45), and the remaining physical part of the resultant probability-propagation $\boldsymbol{\psi} \to (\boldsymbol{\varphi} \to \boldsymbol{\varphi}^{*}) \to \boldsymbol{\psi}^{*}$, which involves the system occupied MO:

$$\mathbf{P}_{\psi \to \varphi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) \equiv \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})[\mathbf{P}(\boldsymbol{\psi}^{*}|\boldsymbol{\psi}) - \mathbf{I}]\mathbf{P}(\boldsymbol{\chi}^{*}|\boldsymbol{\psi}) = \mathbf{P}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) - \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}^{*}|\boldsymbol{\psi})$$
$$= \mathbf{P}_{\chi \to \varphi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}) - \mathbf{P}^{g}_{\chi \to \psi}(\boldsymbol{\chi}^{*}|\boldsymbol{\chi}). \quad (47)$$

To summarize, the resultant information channels representing the geometric or physical promotion of AO in molecules can be additively decomposed for any admissible Intermediate Orbitals (IO) in terms of the complementary sub-channels representing the AO → IO and IO → MO orbital transformations, respectively. This further implies a similar additive decomposition of the entropy/information indices of the system chemical bonds, generated by these sub-channels. In the next section we shall investigate these combination-rules for the IT bond-indices in the orbitally resolved communication theory of the chemical bond.

5. Elementary steps in probability-scattering networks

The overall probability-scattering matrix $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \{P(l^*|k)\}$, which defines the resultant promotion of AO in molecules, as well as the effective promotion probabilities $\mathbf{P}(\boldsymbol{\psi}^*|\boldsymbol{\psi})$ for intermediate orbitals $\boldsymbol{\psi}$, can be alternatively viewed as the information "cascades" composed of the consecutive sub-channels in the relevant chain of m elementary information scatterings involving orbitals:

$$\boldsymbol{\phi}^{(s)} = (\boldsymbol{\chi}, \tilde{\boldsymbol{\chi}}, \ldots, \boldsymbol{\psi}, \ldots, \boldsymbol{\varphi}, \boldsymbol{\varphi}^*, \ldots, \boldsymbol{\psi}^*, \ldots, \tilde{\boldsymbol{\chi}}^*, \boldsymbol{\chi}^*), \quad \text{for} \quad s = 0, 1, 2, \ldots, m, \ \text{ respectively,} \tag{48}$$

where $\boldsymbol{\psi}$ and $\boldsymbol{\psi}^*$ stand for the molecular geometrically and physically promoted sets, respectively. At stage $s > 0$ they are determined by the conditional probabilities of the current set of orbitals $\boldsymbol{\phi}^{(s)}$, conditional on orbitals $\boldsymbol{\phi}^{(s-1)}$ of the preceding stage: $\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)}) = \{P(n^{(s)}|m^{(s-1)})\}$. Examples of such elementary information networks are provided by the MO-occupation channel $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\varphi}^*)$ of Sect. 2.1, and the geometrical steps of the orthogonalization of AO into OAO, $\mathbf{P}(\tilde{\boldsymbol{\chi}}|\boldsymbol{\chi})$, and of the reverse transformation, $\mathbf{P}(\boldsymbol{\chi}|\tilde{\boldsymbol{\chi}})$.

In Scheme 6 we have illustrated such a succession of elementary probability propagations which lead from the initial AO probabilities $\boldsymbol{P}^0_{\boldsymbol{\chi}}$, for $s = 0$, to the final (molecular) probabilities $\boldsymbol{P}^*_{\boldsymbol{\chi}}$ for $s = m$, with the output signal of the preceding stage providing the input signal for the next stage. The whole series amounts to the overall physical promotion of AO in molecules:

$$\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \prod_{t=1}^{m} \mathbf{P}(\boldsymbol{\phi}^{(t)}|\boldsymbol{\phi}^{(t-1)}) \equiv \mathbf{P}(\boldsymbol{\phi}^{(m)}|\boldsymbol{\phi}^{(0)}),$$
$$\sum_n P(n^{(t)}\left|m^{(t-1)}\right.) = \sum_n P(n^{(t)}|k) = 1, \quad t = 1, 2, \ldots, s, \ldots, m. \tag{49}$$

The effective output probabilities after consecutive stages in this scheme thus read:

$$\begin{aligned}
\boldsymbol{P}^{(1)}_{\boldsymbol{\phi}} &= \boldsymbol{P}^0_{\boldsymbol{\phi}}\mathbf{P}(\boldsymbol{\phi}^{(1)}|\boldsymbol{\phi}^{(0)}) \equiv \boldsymbol{P}^0_{\boldsymbol{\chi}}\mathbf{P}(\tilde{\boldsymbol{\chi}}|\boldsymbol{\chi}) \equiv P^g_{\tilde{\boldsymbol{\chi}}},\\
\boldsymbol{P}^{(2)}_{\boldsymbol{\phi}} &= \boldsymbol{P}^{(1)}_{\boldsymbol{\phi}}\mathbf{P}(\boldsymbol{\phi}^{(2)}|\boldsymbol{\phi}^{(1)}) = \boldsymbol{P}^0_{\boldsymbol{\chi}}[\mathbf{P}(\tilde{\boldsymbol{\chi}}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\phi}^{(2)}|\tilde{\boldsymbol{\chi}})] \equiv \boldsymbol{P}^0_{\boldsymbol{\chi}}\mathbf{P}(\boldsymbol{\phi}^{(2)}|\boldsymbol{\chi}),\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
\boldsymbol{P}^{(m)}_{\boldsymbol{\phi}} &= \boldsymbol{P}^{(m-1)}_{\boldsymbol{\phi}}\mathbf{P}(\boldsymbol{\phi}^{(m)}|\boldsymbol{\phi}^{(m-1)}) = \cdots = \boldsymbol{P}^0_{\boldsymbol{\chi}}\prod_{t=1}^{m}\mathbf{P}(\boldsymbol{\phi}^{(t)}|\boldsymbol{\phi}^{(t-1)}) \equiv \boldsymbol{P}^0_{\boldsymbol{\chi}}\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi})\\
&= \boldsymbol{P}^*_{\boldsymbol{\chi}},
\end{aligned} \tag{50}$$

$$\boldsymbol{P}_{\chi}^{0} \longrightarrow \underbrace{\boxed{\chi \rightarrow \mathbf{P}(\chi|\chi) \rightarrow \chi = \phi^{(1)}}}_{}\!\!\!\!\overset{\phi^{(0)}\rightarrow\phi^{(1)}}{} \longrightarrow \boldsymbol{P}_{\phi}^{(1)} \longrightarrow \overset{\phi^{(1)}\rightarrow\phi^{(2)}}{\boxed{\phi^{(1)} \rightarrow \mathbf{P}(\phi^{(2)}|\phi^{(1)}) \rightarrow \phi^{(2)}}} \ldots$$

$$\ldots \longrightarrow \boldsymbol{P}_{\phi}^{(m-1)} \longrightarrow \overset{\phi^{(m-1)}\rightarrow\phi^{(m)}}{\boxed{\phi^{(m-1)} \rightarrow \mathbf{P}(\phi^{(m)}|\phi^{(m-1)}) \rightarrow \phi^{(m)}}} \longrightarrow \boldsymbol{P}_{\phi}^{(m)} \equiv \boldsymbol{P}_{\chi}^{*}$$

Scheme 6. The molecular information-cascade resulting from the consecutive arrangement of information channels $\{\mathbf{P}(\boldsymbol{\phi}^{(t)}|\boldsymbol{\phi}^{(t-1)})\}, t = 1, 2, \ldots, s, \ldots, m,$ of the elementary reconstructions in the system electronic structure leading from the promolecular AO probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}^{0} = \boldsymbol{P}_{\boldsymbol{\phi}}^{(0)}$ to the molecular AO probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}^{*} = \boldsymbol{P}_{\boldsymbol{\phi}}^{(m)}$.

where $\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) = \{P(n^{(s)}|k)\}$ groups the probabilities of $\boldsymbol{\varphi}^{(s)}$ conditional on AO, i.e., the combined effect of probability propagations via all preceding steps $t = (1, 2, \ldots, s)$.

For example, in typical SCF LCAO MO calculations the atomic ground-state populations of AO can be modified, to account for the populational promotion of atoms to the relevant valence-state configuration. Such initially promoted basis set functions can then be subject to the appropriate (one-centre) hybridization, to be subsequently (many-centre) orthogonalized, and finally –"rotated" in the system orbital Hilbert-space into the optimum MO. All these stages generate specific contributions to the IT indices of chemical bonds, e.g., the entropy/information descriptors of the intermediate-orbital promotion channels of the preceding section, or those describing the elementary stages of equation (50) and Scheme 6.

The resultant conditional probabilities of the s-chain in this probability propagation, including all stages from $t = 1$ to $t = s$ in Scheme 6,

$$\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) \equiv \{P(n^{(s)}|k)\} = \prod_{t=1}^{s} \mathbf{P}(\boldsymbol{\phi}^{(t)}|\boldsymbol{\phi}^{(t-1)}) = \mathbf{P}(\boldsymbol{\phi}^{(s-1)}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)}), \quad (51)$$

generates the associated IT bond-indices of Eqs. (22a), (25a), and (27a):

$$S^{(s)} = S(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) = -\sum_{k}^{\mathrm{AO}}\sum_{n}^{(s)} P_k P(n^{(s)}|k) \log P(n^{(s)}|k) = S(\boldsymbol{\chi}, \boldsymbol{\phi}^{(s)}) - S(\boldsymbol{\chi}),$$
$$I^{(s)} = I(\boldsymbol{\chi}^0 : \boldsymbol{\phi}^{(s)}) = S(\boldsymbol{\phi}^{(s)}) - S^{(s)}, \; N^{(s)} = S^{(s)} + I^{(s)} = N(\boldsymbol{\chi}; \boldsymbol{\phi}^{(s)}) = S(\boldsymbol{\phi}^{(s)}). \quad (52)$$

They reflect the resultant entropy-covalency, information-ionicity and total bond multiplicity, acquired in all elementary stages $1 \leqslant t \leqslant s$. Only for $s = m$ the full measures of the molecular (physical) promotion of AO are recovered:

$$\begin{aligned} S^{(m)} &= S(\boldsymbol{\chi}^*|\boldsymbol{\chi}), \quad I^{(m)} = I(\boldsymbol{\chi}^0: \boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*) - S^{(m)}, \\ N^{(m)} &= N(\boldsymbol{\chi}^0; \boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*). \end{aligned} \tag{53}$$

Since each elementary channel introduces extra communication "noise" into these probability-scattering networks, the acquired uncertainty at stage s cannot be smaller than that at preceding stage:

$$S^{(s)} \geqslant S^{(s-1)} \geqslant S^{(s-2)} \geqslant \ldots \geqslant S^{(1)} \geqslant S^{(0)} = 0. \tag{54a}$$

with the equality $S^{(s)} = S^{(s-1)}$ corresponding to the noiseless (deterministic) identity-channel at stage s, $\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)}) = \mathbf{I}$, i.e., $\boldsymbol{\phi}^{(s)} = \boldsymbol{\phi}^{(s-1)}$. Moreover, since $I^{(s)} = S(\boldsymbol{\phi}^{(s)}) - S^{(s)}$, equation (54a) implies a monotonic decrease of the IT-ionicity index in successive steps of the consecutive information cascade in molecular systems,

$$I^{(s)} \leqslant I^{(s-1)} \leqslant I^{(s-2)} \leqslant \ldots \leqslant I^{(1)} \leqslant I^{(0)} = S(\boldsymbol{\chi}^0), \tag{54b}$$

where the initial reference values $S^{(0)} = 0$ and $I^{(0)} = S(\boldsymbol{\chi}^0)$ characterize the promolecular channels discussed in Sect. 8. This decrease in $I^{(s)}$ is expected to be slower compared to increase in $S^{(s)}$, since $N^{(s)} = S(\boldsymbol{\phi}^{(s)})$ should also slowly increase with the growing electron delocalization in successive stages of the probability propagation in molecules.

Of interest also are the entropy/information systems for each elementary step in the cascade of Scheme 6. The relevant communication system of stage s involves in its input the output probability of the preceding stage, $\boldsymbol{P}_{\boldsymbol{\phi}}^{(s-1)}$ [equation (50)] the communication links characterized by the conditional probability matrix $\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)})$ of equation (51), which generates the output probabilities at step s: $\boldsymbol{P}_{\boldsymbol{\phi}}^{(s)} = \boldsymbol{P}_{\boldsymbol{\phi}}^{(s-1)}\mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)})$. The information indices of this elementary channel of sth stage in the orbital-probability scattering read:

$$\begin{aligned} S_s &= S(\boldsymbol{\phi}^{(s)}|\boldsymbol{\phi}^{(s-1)}) = -\sum_m^{(s-1)} \sum_n^{(s)} P_m^{(s-1)} P(n^{(s)}|m^{(s-1)}) \log P(n^{(s)}|m^{(s-1)}) \\ &= -\sum_m^{(s-1)} \sum_n^{(s)} P(m^{(s-1)}, n^{(s)}) \log \frac{P(m^{(s-1)}, n^{(s)})}{P_m^{(s-1)}} = S(\boldsymbol{\phi}^{(s-1)}, \boldsymbol{\phi}^{(s)}) - S(\boldsymbol{\phi}^{(s-1)}), \\ I_s &= I(\boldsymbol{\phi}^{(s-1)} : \boldsymbol{\phi}^{(s)}) = S(\boldsymbol{\phi}^{(s)}) + [S(\boldsymbol{\phi}^{(s-1)}) - S(\boldsymbol{\phi}^{(s-1)}, \boldsymbol{\phi}^{(s)})] = S(\boldsymbol{\phi}^{(s)}) - S_s, \\ N_s &= N(\boldsymbol{\phi}^{(s-1)}; \boldsymbol{\phi}^{(s)}) = I_s + S_s = S(\boldsymbol{\phi}^{(s)}). \end{aligned} \tag{55}$$

A reference to equation (52) thus indicates the total IT bond-order preservation: $N^{(s)} = N_s = S(\boldsymbol{\phi}^{(s)})$. In other words, in the sequential series of elementary channels the total bond-multiplicity acquired after s consecutive steps is the same as that reached in the last stage of the series.

6. Stage-additivity of bond-indices

In the consecutive-cascade of elementary information sub-channels of Scheme 6 the role of the preceding step in the series is limited to shaping the input probabilities of the next step. Indeed, should these probabilities be known, one could forget altogether about the existence of all earlier steps in the sequence. Therefore, the essence of this arrangement is that the probabilities of the current probability-scattering stage are directly coupled only to probabilities of the preceding stage.

This feature of the sequential information cascade is illustrated in Figure 1 for the simplest case of two sub-channels $\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A}) \equiv \{\pi(j|i)\}$ and $\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) \equiv \{\pi(k|j)\}$ in the series

$$\boldsymbol{A} \to \mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A}) \to \boldsymbol{B} \to P_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) \to \boldsymbol{C}, \tag{56}$$

with $\boldsymbol{A} = \{A_i\}$, $\boldsymbol{B} = \{B_j\}$, and $\boldsymbol{C} = \{C_k\}$ grouping the input, intermediate, and output probabilities, respectively. The effective output probabilities of the cascade as a whole is determined by the intermediate set of probabilities $\boldsymbol{B} = \boldsymbol{A}\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})$:

$$\boldsymbol{C} = \boldsymbol{B}\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) = \boldsymbol{A}[\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B})] \equiv \boldsymbol{A}\mathbf{P}_{\mathrm{III}}(\boldsymbol{C}|\boldsymbol{A}), \tag{57}$$

were the conditional probabilities $\mathbf{P}_{\mathrm{III}}(\boldsymbol{C}|\boldsymbol{A}) \equiv \{\pi(k|i)\}$ determine the communication links between the cascade input and output "events".

In figure 1 the mutual dependence between probabilities is reflected by the overlap between the corresponding circles representing the associated Shannon entropies $S(\boldsymbol{A})$, $S(\boldsymbol{B})$ and $S(\boldsymbol{C})$ of the three probability vectors involved [4]. Their mutual arrangement in the consecutive cascade is depicted in Panel a, while Panel d illustrates conditional-entropy (S) and mutual-information (I) quantities, which appear in a general case of three dependent probability distributions [4]. As seen in the figure, in the sequential cascade the mutual-information $I(\boldsymbol{A}:\boldsymbol{C})$, as reflected by the overlap between $S(\boldsymbol{A})$ and $S(C)$, must be totally included in the mutual information in $I(\boldsymbol{A}:\boldsymbol{B})$, again represented by the overlap between $S(\boldsymbol{A})$ and $S(\boldsymbol{B})$, since the whole dependence of $\boldsymbol{C}$ on $\boldsymbol{A}$ originates from $\boldsymbol{B}$. Therefore the mutual information in the peripheral distributions must be equal to the mutual information in all three distributions involved:

$$I(\boldsymbol{A}:\boldsymbol{C}) = I(\boldsymbol{A}:\boldsymbol{B}:\boldsymbol{C}) \leqslant I(\boldsymbol{A}:\boldsymbol{B}) < S(\boldsymbol{A}). \tag{58a}$$

The inequality in the preceding equation, which is well illustrated in figure 1, expresses the fact that the amount of information at the exit of the cascade, $I(\boldsymbol{A}:\boldsymbol{C})$, is less than that at the exit of its first sub-channel, $I(\boldsymbol{A}:\boldsymbol{B})$. The latter is also seen to preserve only a fraction of the initial information content $S(\boldsymbol{A})$

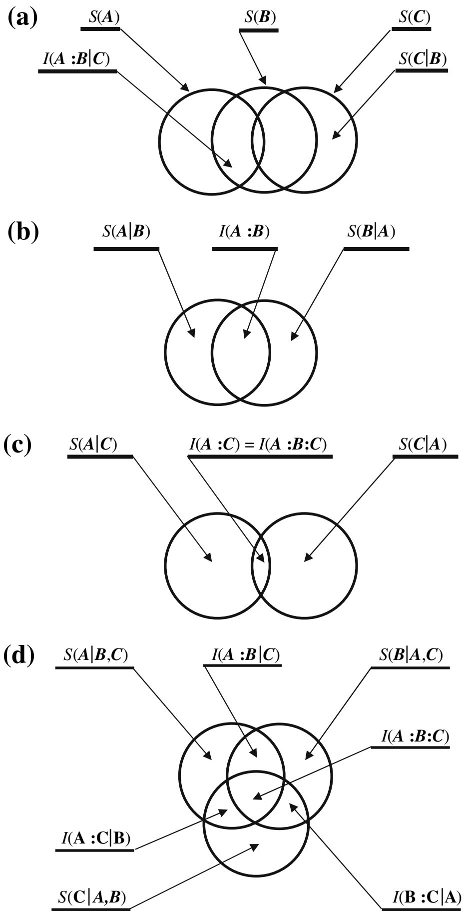


Figure 1. Dependent probability distributions $\boldsymbol{A}=\{A_i\}$, $\boldsymbol{B}=\{B_j\}$, and $\boldsymbol{C}=\{C_k\}$ of the two-step information channel, $\boldsymbol{A}\rightarrow \mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A}) \rightarrow \boldsymbol{B} \rightarrow P_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) \rightarrow \boldsymbol{C}$, which consists of the consecutive arrangement of two sub-channels $\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})$ and $\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B})$ giving rise to the resultant channel $\mathbf{P}_{\mathrm{III}}(\boldsymbol{C}|\boldsymbol{A})=\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{A})$. These 3 channels give rise to the overlapping Shannon entropies $S(\boldsymbol{A})$, $S(\boldsymbol{B})$, and $S(\boldsymbol{C})$ of Panels (a)–(c), which depict their mutual arrangement for the specific case of the sequential arrangement of the two sub-channels, when the output of the first channel constitutes the input of the second channel in the series. Therefore, a dependence $\boldsymbol{C}(\boldsymbol{A})$ is only implicit in character, $\boldsymbol{C}(\boldsymbol{B}(\boldsymbol{A}))$, as schematically shown in Panel a. This diagram shows that the overlap region between $S(\boldsymbol{A})$ and $S(\mathbf{C})$, representing the mutual information $I(\boldsymbol{A}{:}\boldsymbol{C})=I(\boldsymbol{A}{:}\boldsymbol{B}{:}\boldsymbol{C})+I(\boldsymbol{A}{:}\boldsymbol{C}|\boldsymbol{B})$ (Panels a, c), is completely contained in $I(\boldsymbol{A}{:}\boldsymbol{B})$ (Panels a, b), thus implying the vanishing mutual information in $\boldsymbol{A}$ and $\boldsymbol{C}$, conditional on $\boldsymbol{B}{:}I(\boldsymbol{A}{:}\boldsymbol{C}|\boldsymbol{B})=0$. In other words, for the series arrangement of two sub-channels $I(\boldsymbol{A}{:}\boldsymbol{C})=I(\boldsymbol{A}{:}\boldsymbol{B}{:}\boldsymbol{C})$, the mutual information in the peripheral probabilities is equal to that in three probability distributions: $I(\boldsymbol{A}{:}\boldsymbol{C}) = I(\boldsymbol{A}{:}\boldsymbol{B}{:}\boldsymbol{C})$. This is not the case for general dependencies between three probability vectors, which correspond to the mutual arrangement of three subsystem entropies shown in Panel d. The diagram *b* and *c* show a gradual loss of information (increase in entropy) at each step, as reflected by the difference between conditional-entropies $S(\boldsymbol{A}|\boldsymbol{C}) > S(\boldsymbol{A}|\boldsymbol{B})$. It implies the associated lowering of the amount of information flowing through the cascade, measured by the corresponding mutual-information quantities, $I(\boldsymbol{A}{:}\boldsymbol{B}) > I(\boldsymbol{A}{:}\boldsymbol{C})$, fractions of the initial amount of information $S(\boldsymbol{A})$ at the cascade input.

in the cascade input probabilities. This successive loss of information is alternatively represented by the associated inequalities between the direct measures of the missing information at each step, which is provided by the relevant conditional-entropy indices, which are also shown in the figure:

$$S(\boldsymbol{A}|\boldsymbol{C}) = S(\boldsymbol{A}) - I(\boldsymbol{A}:\boldsymbol{C}) > S(\boldsymbol{A}|\boldsymbol{B}) = S(\boldsymbol{A}) - I(\boldsymbol{A}:\boldsymbol{B}). \tag{58b}$$

The first index measures the information loss for the cascade as a whole, while the second reflects the information lost in its first sub-channel.

These inequalities can be derived analytically, by considering the elementary information quantities of figure 1d, in terms of which the overall information loss in the cascade can be expressed in terms of the information loss due to the preceding stage:

$$\begin{aligned} S(\boldsymbol{A}|\boldsymbol{C}) &= S(\boldsymbol{A}|\boldsymbol{B}) + I(\boldsymbol{A}:\boldsymbol{B}|\boldsymbol{C}) - I(\boldsymbol{A}:\boldsymbol{C}|\boldsymbol{B}) \\ &= S(\boldsymbol{A}|\boldsymbol{B}) + I(\boldsymbol{A}:\boldsymbol{B}|\boldsymbol{C}), \end{aligned} \tag{59}$$

since for the consecutive sub-channels the explicit dependence between peripheral probabilities, which does not result from their dependence on $\boldsymbol{B}$, identically vanishes: $I(\boldsymbol{A}:\boldsymbol{C}|\boldsymbol{B}) = 0$. The preceding equation expressed the so called *stage-additivity* of the information loss (conditional entropy) in the sequential cascade.

Thus, the mutual information $I(\boldsymbol{A}:\boldsymbol{B}|\boldsymbol{C})$, reflecting a dependence of $\boldsymbol{A}$ on $\boldsymbol{C}$ which cannot be attributed to $\boldsymbol{A}[\boldsymbol{C}(\boldsymbol{B})]$, represents the extra loss of the initial information in the second sub-channel. It represents a fraction of $I(\boldsymbol{A}:\boldsymbol{B})$, of the initial information content $S(\boldsymbol{A})$, which has survived at the exit of the first sub-channel.

Returning now to the stage-covalency index S_s of the preceding section, the above stage-additivity of the conditional-entropies reveals that by the very construction of the information cascade of Scheme 6 this IT-index of the elementary channel defining step s in the series can be alternatively expressed as the corresponding difference between the successive resultant indices of equation (52):

$$S_s = S^{(s)} - S^{(s-1)} = S(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) - S(\boldsymbol{\phi}^{(s-1)}|\boldsymbol{\chi}) = S(\boldsymbol{\phi}^{(s)}, \boldsymbol{\chi}) - S(\boldsymbol{\chi}, \boldsymbol{\phi}^{(s-1)}). \tag{60}$$

In the specific case of the two-step cascade of fig. 1 these entropies read: $S^{(\mathrm{I})} = S(\boldsymbol{A}|\boldsymbol{B}) = S_{\mathrm{I}}$, $S^{(\mathrm{II})} = S(\boldsymbol{A}|\boldsymbol{C})$, and hence $S_2 = S^{(\mathrm{II})} - S^{(\mathrm{I})} = I(\boldsymbol{A}:\boldsymbol{B}|\boldsymbol{C})$. A similar additivity rule holds for the complementary mutual-information indices of stage s:

$$\begin{aligned} I_s = I^{(s)} - I^{(s-1)} &= I(\boldsymbol{\chi}:\boldsymbol{\phi}^{(s)}) - I(\boldsymbol{\chi}:\boldsymbol{\phi}^{(s-1)}) \\ &= S(\boldsymbol{\phi}^{(s-1)}|\boldsymbol{\chi}) - S(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) = -S_s, \end{aligned} \tag{61}$$

and hence: $N_s = N^{(s)} - N^{(s-1)} = 0$. This total bond-order preservation at successive steps of the sequential series of elementary probability-scattering sub-channels is also illustrated in figure 1: $N_{\mathrm{I}} = S(\boldsymbol{A}|\boldsymbol{B}) + I(\boldsymbol{A}:\boldsymbol{B}) \equiv S_I + I_I = S(\boldsymbol{A}|\boldsymbol{C}) + I(\boldsymbol{A}:\boldsymbol{C}) \equiv S_{\mathrm{II}} + I_{\mathrm{II}} = S(\boldsymbol{A})$.

To summarize, each next step in the sequential cascade increases the conditional-entropy (information loss) index, while decreasing by the same amount the mutual-information (information flow) index, thus preserving their sum, measuring the overall IT bond-multiplicity, at the cascade initial entropy level.

Different grouping rules for these IT bond indices apply in the communication system consisting of elementary sub-channels combined in the parallel manner. They are summarized in the Appendix.

7. Orbital transformations in typical molecular calculations

Consider the familiar scenario in the quantum-mechanical calculations of the molecular electronic structure involving the multi-step transformation of the initial (real) AO into the optimum MO for the system ground-state:

$$\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C} = (\boldsymbol{\chi}\mathbf{U})\mathbf{S}_{\boldsymbol{\psi}}^{-1/2}\mathbf{O} \equiv (\boldsymbol{\psi}\mathbf{S}_{\boldsymbol{\psi}}^{-1/2})\mathbf{O} = \tilde{\boldsymbol{\psi}}\mathbf{O}, \quad \mathbf{U}\mathbf{U}^{\mathrm{T}} = \mathbf{O}\mathbf{O}^{\mathrm{T}} = \mathbf{I},$$
$$\mathbf{S}_{\boldsymbol{\psi}} = \langle \boldsymbol{\psi} | \, \boldsymbol{\psi} \rangle \,. \tag{62}$$

Here, the atomic "rotations" $\mathbf{U} = \{\{U_{x\in X, t\in X}\}\delta_{X,Y}\} = \{\mathbf{U}_X\delta_{X,Y}\}$ transform the mutually orthogonal, canonical AO on atom X, $\boldsymbol{\chi}_X = \{\chi_{x\in X}\}$, into the appropriate hybrids (HO), $\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{U} = \{\psi_t\} = \{\boldsymbol{\psi}^X = \boldsymbol{\chi}_X\mathbf{U}_X\}$. For this "directed" (localized) set of atomic orbitals $\mathbf{S}_{\boldsymbol{\psi}}^{-1/2} = \{H_{t,\tilde{t}}\} \equiv \mathbf{H}$ and $\mathbf{S}_{\boldsymbol{\psi}}^{1/2} = \{h_{\tilde{t},t}\} \equiv \mathbf{h} = \mathbf{H}^{-1}$ provide the relevant transformations between HO and their symmetrically orthogonalized analogs (OHO): $\tilde{\boldsymbol{\psi}} = \boldsymbol{\psi}\mathbf{H}$ and $\boldsymbol{\psi} = \tilde{\boldsymbol{\psi}}\mathbf{h}$. The latter are finally "rotated" into MO using the LCOHO (orthogonal) transformation $\mathbf{O} = \{O_{\tilde{t},i}\}$, $\boldsymbol{\varphi} = \tilde{\boldsymbol{\psi}}\mathbf{O}$, and hence $\tilde{\boldsymbol{\psi}} = \boldsymbol{\varphi}\mathbf{O}^{\mathrm{T}}$.

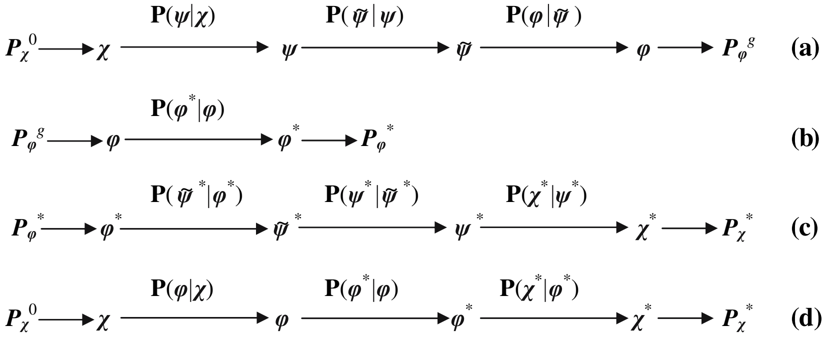
Therefore, for this particular selection of intermediate stages in determining the effective (physical) AO promotion in molecules various sets of orbitals of equation (48), determining the elementary information-propagation sub-channels read: $\boldsymbol{\phi}^{(s)} = (\boldsymbol{\chi}, \boldsymbol{\psi}, \tilde{\boldsymbol{\psi}}, \boldsymbol{\varphi}, \boldsymbol{\varphi}^*, \tilde{\boldsymbol{\psi}}^*, \boldsymbol{\psi}^*, \boldsymbol{\chi}^*)$, for $s = 0, 1, 2, \ldots, 7$, respectively. These partial transformations of orbitals in typical MO calculations generate the associated conditional probabilities for each orbital transformation stage, which determine the elementary communication systems in Panels a and c of Scheme 7:

$$\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \{\{P(t|x) = (U_{x,t})^2\}\delta_{X,Y}\} = \{\mathbf{P}(\boldsymbol{\psi}_X|\boldsymbol{\chi}_X)\delta_{X,Y}\} = \mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\psi}^*)^{\mathrm{T}} \tag{63}$$

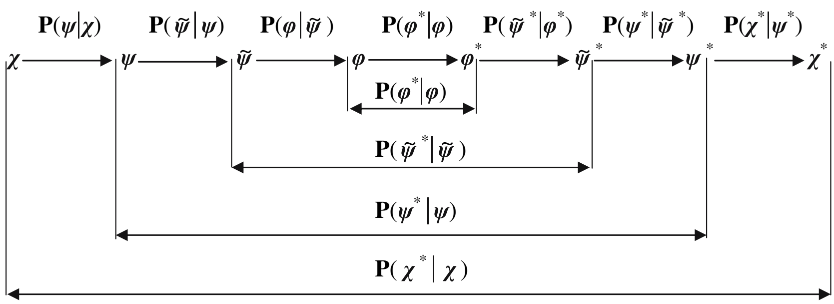
$$\mathbf{P}(\boldsymbol{\psi}^*|\tilde{\boldsymbol{\psi}}^*) = \{P(t|\tilde{t}) = (h_{\tilde{t},t})^2\} = \mathbf{P}(\tilde{\boldsymbol{\psi}}|\boldsymbol{\psi})^{\mathrm{T}}, \tag{64}$$

$$\mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\psi}}) = \{P(i|\tilde{t}) = (O_{\tilde{t},i})^2\} = \mathbf{P}(\tilde{\boldsymbol{\psi}}^*|\boldsymbol{\varphi}^*)^{\mathrm{T}}. \tag{65}$$

The resultant (physical) AO-promotion channel $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi})$ of Scheme 1 also involves the MO-population sub-channel $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$ of Eq. 16 [see also Schemes 1a and 7b], which formally transforms the input MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}}^{\mathrm{inp.}}$, from



Scheme 7. The partial communication systems behind the effective AO-promotion channel of Scheme 1: the AO → MO probability-scattering cascade (Panel a), consisting of three elementary channels $\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}), \mathbf{P}(\tilde{\boldsymbol{\psi}}|\boldsymbol{\psi})$, and $\mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\psi}})$: $\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\tilde{\boldsymbol{\psi}}|\boldsymbol{\psi})\mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\psi}})$; the MO-occupation sub-channel $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$, from the initial (*geometrical*) MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}}^{g\cdot} = \boldsymbol{P}_{\boldsymbol{\chi}}^{0}\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})$ to the physical MO probabilities $\boldsymbol{P}_{\boldsymbol{\varphi}}$ of the system ground-state electron configuration (Panel b); the MO* → AO* probability-propagation cascade: $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*) = \mathbf{P}(\tilde{\boldsymbol{\psi}}^*|\boldsymbol{\varphi}^*)\mathbf{P}(\boldsymbol{\psi}^*|\tilde{\boldsymbol{\psi}}^*)\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\psi}^*) = \mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\psi}})^{\mathrm{T}}\mathbf{P}(\tilde{\boldsymbol{\psi}}|\boldsymbol{\psi})^{\mathrm{T}}\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})^{\mathrm{T}}$ (Panel c). Each of the partial AO → MO and MO* → AO* cascades involves the elementary channels of the AO-hybridization into HO, HO-orthogonalization into OHO, and OHO-"rotation", respectively. The (physical) AO promotion channel of Scheme 1 represents the resultant effect of a succession (Panel d) of the partial channels of Panels a-c, $\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\varphi}^*)^{\mathrm{T}}$, consisting of seven elementary sub-channels shown in Scheme 8.



Scheme 8. The probability-propagation ranges in the physical-promotion cascades for orbitals $\{\boldsymbol{\chi}(\mathrm{AO}), \boldsymbol{\psi}(\mathrm{HO}), \tilde{\boldsymbol{\psi}}(\mathrm{OHO})\} = \{\boldsymbol{\phi}^{(s)}, s = 0, 1, 2\}$. The elementary MO-occupation sub-channel $\mathbf{P}(\boldsymbol{\varphi}^*|\boldsymbol{\varphi})$, for $s = 3$, is also marked as representing the physical promotion of MO in the molecule.

the output of the preceding AO → MO part of the whole AO-promotion cascade [equation (5)],

$$\boldsymbol{P}_{\boldsymbol{\varphi}}^{g} = \boldsymbol{P}_{\boldsymbol{\chi}}^{0}\mathbf{P}(\boldsymbol{\varphi}|\boldsymbol{\chi}) = \{P_i^g\} \equiv \boldsymbol{P}_{\boldsymbol{\varphi}}^{\mathrm{inp.}}. \tag{66}$$

The conditional probabilities of equations (63)–(66) and (30) also represent the elementary stages in Scheme 6, thus defining the sub-channels of the "chain-rule" product of equation (49), for $m = 7$:

$$\mathbf{P}(\boldsymbol{\phi}^{(1)}|\boldsymbol{\phi}^{(0)}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}), \quad \mathbf{P}(\boldsymbol{\phi}^{(2)}|\boldsymbol{\phi}^{(1)}) = \mathbf{P}(\tilde{\boldsymbol{\psi}}|\boldsymbol{\psi}), \quad \mathbf{P}(\boldsymbol{\phi}^{(3)}|\boldsymbol{\phi}^{(2)}) = \mathbf{P}(\boldsymbol{\varphi}|\tilde{\boldsymbol{\psi}}),$$
$$\mathbf{P}(\boldsymbol{\phi}^{(4)}|\boldsymbol{\phi}^{(3)}) = \mathbf{P}(\boldsymbol{\varphi}^{*}|\boldsymbol{\varphi}), \quad \mathbf{P}(\boldsymbol{\phi}^{(5)}|\boldsymbol{\phi}^{(4)}) = \mathbf{P}(\tilde{\boldsymbol{\psi}}^{*}|\boldsymbol{\varphi}^{*}), \quad \mathbf{P}(\boldsymbol{\phi}^{(6)}|\boldsymbol{\phi}^{(5)}) = \mathbf{P}(\boldsymbol{\psi}^{*}|\tilde{\boldsymbol{\psi}}^{*}),$$
$$\mathbf{P}(\boldsymbol{\phi}^{(7)}|\boldsymbol{\phi}^{(6)}) = \mathbf{P}(\boldsymbol{\chi}^{*}|\boldsymbol{\psi}^{*}). \tag{67}$$

The corresponding cascades $\mathbf{P}(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)})$, $s = 0, 1, 2, 3$ of equation (38), for the physical promotion of orbitals $\{\boldsymbol{\chi}, \boldsymbol{\psi}, \tilde{\boldsymbol{\psi}}, \boldsymbol{\varphi}\}$ are delineated in Scheme 8. The bond indices generated by these effective orbital-promotion channels,

$$\begin{aligned}
S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) &= -\sum_{m}^{(s)} P_m^{(s)} \sum_{n}^{(s)} P(n^{(s)*}|m^{(s)}) \log P(n^{(s)*}|m^{(s)}),\\
I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*}) &= \sum_{m}^{(s)} P_m^{(s)} \sum_{n}^{(s)} P(n^{(s)*}|m^{(s)}) \log\left[P(n^{(s)*}|m^{(s)})/P_n^{(s)}\right]\\
&= S(\boldsymbol{\phi}^{(s)}) - S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}),\\
N(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)*}) &= S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) + I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*}) = S(\boldsymbol{\phi}^{(s)})\\
&= -\sum_{n}^{(s)} P_n^{(s)} \log P_n^{(s)},\ s = 1, 2, 3,
\end{aligned} \tag{68}$$

describe the IT-bond-multiplicities generated at the $\boldsymbol{\varphi}^{(s)}$-orbital stage of the AO transformation into MO.

8. Free-atom references

Let us now briefly comment on the initial values of the IT indices, calculated for the non-scattered conditional probabilities $\mathbf{P}^{(0)}(\boldsymbol{\chi}^{(0)}|\boldsymbol{\chi}^{(0)}) = \mathbf{I}$, which represent the "disconnected" AO of the free constituent atoms (A^0, B^0, $C^0, \ldots$) in the promolecule $M^0 = (A^0|B^0|C^0|\ldots)$, where the vertical *solid* line separating the atomic labels signifies the non-bonded (disconnected, mutually closed) status of atomic fragments. The unity normalized input probabilities $\boldsymbol{P}_{\boldsymbol{\chi}}^{0}$ in Scheme 1 also correspond to this reference distribution. In the promolecule the free atoms and the AO they contribute to form the chemical bonds in the molecule $M = (A^{*}\mathbin{¦}B^{*}\mathbin{¦}C^{*}\mathbin{¦}\ldots)$, where the *broken* vertical lines signify the bonded (connected, mutually open) status of AIM (A^{*}, B^{*}, $C^{*}, \ldots$), are fragments of the overall promolecular collection of atoms, as indeed reflected by the normalization of these initial AO probabilities. It should be observed, that in the communication theory of the chemical bond this promolecular reference carries the overall non-vanishing information-ionicity component, equal to the Shannon entropy of $\boldsymbol{P}^0_{\chi}$, although the associated entropy-covalency contribution identically vanishes:

$$S^{(0)}(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0)=0 \quad \text{and} \quad I^{(0)}(\boldsymbol{\chi}^0\!: \boldsymbol{\chi}^0)=N^{(0)}(\boldsymbol{\chi}^0; \boldsymbol{\chi}^0)=S(\boldsymbol{\chi}^0)= -\sum_{l}^{\mathrm{AO}} P_l^0 \log P_l^0. \tag{69}$$

The alternative, truly non-bonded reference for diagnosing chemical-bond multiplicities in molecular systems is provided by the collection of the infinitely distant (separated) atoms, corresponding to the dissociation of M into the free constituent atoms in this *Separated Atom Limit* (SAL): $M^{\infty}=(A^0+B^0+C^0+\ldots)$. In accordance with the familiar grouping approach of IT [7, 10, 14] (see also the Appendix), let us first consider a division of the promolecular system into the *separate* atomic communication systems, characterized by the unit input signal on each constituent atom:

$$\sum_{x\in X}^{\mathrm{AO}} \pi^0_{x,X}=1, \qquad X=A, B, C, \ldots \tag{70}$$

Here $\boldsymbol{\pi}^0_X=\{\pi^0_{x,X}=P^0(x \in X|X)=P^0_x/P^0_X\}$ groups the ground-state *conditional* probabilities of AO on the separate atom X, while the condensed probability of X^0 in M^0, $P^0_X=\sum_{x\in X} P^0_x=N^0_X/N$, where $N^0_X=Z_X$ is the overall number of electrons on neutral atom X, equal to the atomic number Z_X of the nucleus.

The IT bond-indices for the individual separate channels of atomic fragments in this limit explore the intra-atom "communications" measured by the conditional probabilities of AO on the same free atom $\mathbf{P}^0_X(\boldsymbol{\chi}^0_X\,|\boldsymbol{\chi}^0_X)=\{P^0_X(x'|x),\ x, x' \in X\}$, $X^0=A^0, B^0, \ldots$ The entropy/information indices of the separated atoms in AO resolution read:

$$\begin{aligned}
S^{(0)}_X(\boldsymbol{\chi}^0_X|\boldsymbol{\chi}^0_X) &= -\sum_{x\in X} P^0(x|X) \sum_{x'\in X} P^0_X(x'|x) \log P^0_X(x'|x)=S(\boldsymbol{\chi}^0_X, \boldsymbol{\chi}^0_X)-S(\boldsymbol{\chi}^0_X),\\
I^{(0)}_X(\boldsymbol{\chi}^0_X : \boldsymbol{\chi}^0_X) &= \sum_{x\in X} P^0(x|X) \sum_{x'\in X} P^0_X(x'|x) \log \frac{P^0_X(x'|x)}{P^0(x'|X)}=S(\boldsymbol{\chi}^0_X)-S^0_X(\boldsymbol{\chi}^0_X|\boldsymbol{\chi}^0_X),\\
N^{(0)}_X(\boldsymbol{\chi}^0_X; \boldsymbol{\chi}^0_X) &= S^{(0)}_X(\boldsymbol{\chi}^0_X|\boldsymbol{\chi}^0_X)+I^{(0)}_X(\boldsymbol{\chi}^0_X : \boldsymbol{\chi}^0_X)=S(\boldsymbol{\chi}^0_X)\equiv -\sum_{x\in X}^{\mathrm{AO}} \pi^0_{x,X} \log \pi^0_{x,X},
\end{aligned} \tag{71}$$

where the $S(\boldsymbol{\chi}^0_X, \boldsymbol{\chi}^0_X)$ denotes the Shannon entropy of equation (23) for the joint (two-AO) probabilities $\mathbf{P}(\boldsymbol{\chi}^0_X, \boldsymbol{\chi}^0_X)=\{P^0_X(x, x')=P^0(x|X)P^0_X(x'|x), x, x' \in X\}$, normalized to orbital probabilities $\boldsymbol{\pi}^0_X$:

$$\sum_{x' \in X} P_X^0(x, x') = P^0(x\,|X) = \pi_{x,X}^0. \tag{72}$$

However, since $\langle x|x'\rangle = \delta_{x,x'}$ and the AO occupations of the (ground-state) free atoms are fixed, the intra-atomic conditional probabilities $\mathbf{P}_X^0(\boldsymbol{\chi}_X^0\,|\boldsymbol{\chi}_X^0) = \mathbf{I}_X$ and hence:

$$S_X^{(0)}(\boldsymbol{\chi}_X^0|\boldsymbol{\chi}_X^0) = 0 \quad \text{and} \quad I_X^{(0)}(\boldsymbol{\chi}_X^0 : \boldsymbol{\chi}_X^0) = N_X^{(0)}(\boldsymbol{\chi}_X^0; \boldsymbol{\chi}_X^0) = S(\boldsymbol{\chi}_X^0). \tag{73}$$

The above entropy/information quantities characterize the isolated atomic systems, in the absence of all remaining atoms of the promolecule. In order to generate the corresponding quantities characterizing the *collection* of the infinitely-distant, separated atoms in M^∞, the quantities of equation (71) have to be combined using the appropriate grouping rules of IT (see the Appendix), with the overall (group) probabilities $P_{\text{AIM}}^0 = \{P_X^0\}$ providing the promolecular weights of the free atomic subsystems:

$$\begin{aligned}
S^{(\infty)}(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0) &= -\sum_X P_X^0 \sum_{x,x' \in X} P^0(x\,|X) P_X^0(x'\,|x) \log P_X^0(x'\,|x) \\
&= \sum_X P_X^0 S_X^{(0)}(\boldsymbol{\chi}_X^0|\boldsymbol{\chi}_X^0) = 0, \\
I^{(\infty)}(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^0) &= \sum_X P_X^0 \sum_{x,x' \in X} P^0(x\,|X) P_X^0(x'\,|x) \log \frac{P_X^0(x'\,|x)}{P_X^0 P^0(x'\,|X)} \\
&= \sum_X P_X^0 I_X^{(0)}(\boldsymbol{\chi}_X^0 : \boldsymbol{\chi}_X^0) \\
&= S(\boldsymbol{\chi}^0) - S^{(\infty)}(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0) = S(\boldsymbol{\chi}^0), \\
N^{(\infty)}(\boldsymbol{\chi}^0; \boldsymbol{\chi}^0) &= S^{(\infty)}(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0) + I^{(\infty)}(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^0) = S(\boldsymbol{\chi}^0),
\end{aligned} \tag{74}$$

where we have observed that the Shannon entropy of AO in a collection of separated atoms is again given by the promolecular entropy of equation (26) and (69):

$$\begin{aligned}
S^{(\infty)}(\boldsymbol{\chi}^0) &\equiv -\sum_X \sum_{x \in X} [P_X^0 P^0(x\,|X)] \log[P_X^0 P^0(x\,|X)] \\
&= -\sum_k P_k^0 \log P_k^0 = S(\boldsymbol{\chi}^0).
\end{aligned} \tag{75}$$

These entropy/information descriptors of atomic subsystems in M^∞ measure the *internal* IT-covalency, IT-ionicity, and overall IT-index of the free atoms in the dissociation limit, against which the corresponding molecular quantities, describing bonded atoms, can be compared.

In a separate analysis the present development will be applied to diatomics using both the minimum basis set *ab initio* calculations and realistic model considerations. The orbital models have been selected to get a better insight into a

Table 1
The entropy/information descriptors (in bits) of the AO-promotion channels for the minimum basis sets of the canonical AO of the free atoms in the promolecular and SAL references.

Atom			Promolecule: $(A^0\|B^0)$			Dissociation promolecule: (A^0+B^0)				SAL: A^0+B^0		
	$S_X^{(0)}$	$I_X^{(0)}, N_X^{(0)}$		$S^{(0)}$	$I^{(0)}, N^{(0)}$		$S^{(\infty)}$	$I^{(\infty)}$	$N^{(\infty)}$		S^{SAL}	$I^{\mathrm{SAL}}, N^{\mathrm{SAL}}$
H^0	0.00	0.00	$(H^0\|H^0)$	0.00	1.00	(H^0+H^0)	1.00	0.00	1.00	H^0+H^0	0.00	0.00
Li^0	0.00	0.92	$(Li^0\|H^0)$	0.00	1.50	(Li^0+H^0)	0.81	0.69	1.50	Li^0+H^0	0.00	0.92
C^0	0.00	1.92	$(H^0\|F^0)$	0.00	2.52	(H^0+F^0)	0.47	2.05	2.52	H^0+F^0	0.00	2.28
O^0	0.00	2.25	$(Li^0\|F^0)$	0.00	2.75	(Li^0+F^0)	0.81	1.94	2.75	Li^0+F^0	0.00	3.20
F^0	0.00	2.28	$(C^0\|O^0)$	0.00	3.09	(C^0+O^0)	0.98	2.11	3.09	C^0+O^0	0.00	4.17

relative importance of the familiar effects of the effective AO promotion due to: electron excitation and/or AO hybridization, orthogonality, and their mixing into MO. The selected diatomics exhibit both single (H_2, LiH, HF, LiF) and multiple (CO) chemical bonds. They involve different numbers of the valence- and inner-shell lone pairs of electrons on constituent atoms, and cover the *sp*-hybridization effects (HF, LiF, CO). In Table 1 we have listed the representative values of the reference quantities for constituent free atoms of these illustrative diatomics.

It follows from the table that the overall bond-index of the promolecular, $(A^0|B^0)$ and $(A^0 + B^0)$, channels of the AO promotion in free atoms is conserved, in accordance with equations (69) and (74). Only the entropy-covalency and information-ionicity are redistributed for this preserved sum of the two bond components. It should be observed that the finite conditional-entropy contribution in the dissociation-promolecule represents the "group" entropy, of atomic fragments in the collection of all dissociated atoms, while the intra-group entropies $S_X^{(0)}$ identically vanish since $\mathbf{P}^0(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0) = \{\mathbf{P}_X^0(\boldsymbol{\chi}_X^0\,|\boldsymbol{\chi}_X^0)\delta_{X,Y}\} = \mathbf{I}$.

Yet another free-atom reference is provided by the sum of communication channels for isolated atoms, $M^{\mathrm{SAL}} = A^0 + B^0 + C^0 + \ldots$, with each atomic subsystem processing the unit input signal, thus representing a separate communication channel. These true-SAL indices are generated by the sums of atomic indices of equation (73). A reference to Table 1 shows that these dissociation-limit quantities exhibit the vanishing conditional entropy index and generally higher mutual-information ionicities, compared to those for $(A^0 + B^0)$, due to the missing weights P^0_{AIM}.

These promolecular and SAL reference states of the mutually non-bonded (disconnected) atoms correctly predict the vanishing entropy-covalency of the separate atomic communication systems of free-atoms, while in the dissociation-promolecule, in which the free-atoms communicate the atom-assignment signals as whole condensed (IT-reduced) units at the inter-atom stage of the probability grouping, the finite entropy-covalency reflects the free atom being a part of a larger system. Therefore, in IT this reference channel cannot be considered as representing truly non-bonded atoms, since it allows for the condensed ("reduced") communications between the free-atoms.

To summarize, in the communication-theory approach to chemical bonds these reference states on non-bonded atoms are distinguished by the input "signal" and/or the atomic grouping of AO probabilities. As a result they all can be distinguished by different sets of the initial entropy/information descriptors, with respect to which the proper bonding contributions to IT indices can be extracted in the appropriately defined difference measures of bond multiplicity.

9. Difference approach to entropic bond indices

In this section we shall briefly examine *relative* bond descriptors, measuring the difference between the IT bond-orders for communication channels of the effective promotion of AO in a given molecular system, and those describing the promolecular reference system, consisting of the "frozen" electron distributions of isolated atoms brought to their respective positions in the molecule. Such difference measures reflect the bonding effects due to the actual chemical interactions between AIM. Similar difference approaches have also been used in the past, e.g., in designing the bond-orders from changes in the two-electron density matrix [22–28], and in generating the familiar density-difference diagrams for diagnosing the effects due to chemical bonds. Also, it should be recalled that the atomic promolecule plays a vital role in justifying the "stockholder" partitioning [29] of the molecular electron density into the localized AIM contributions, by using the minimum entropy-deficiency principle of IT [32–38].

Consider the following displacements of the molecular IT bond indices relative to their initial values for the covalently non-bonded (disconnected) atoms of the system atomic promolecule [see equations (22a)–(27a)]:

$$\begin{aligned}
\Delta S(\chi^*|\chi) &= S(\chi^*|\chi) - S^{(0)}(\chi^0|\chi^0) = S(\chi^*|\chi) = S(\chi^*),\\
\Delta I(\chi^0 : \chi^*) &= I(\chi^0 : \chi^*) - I^{(0)}(\chi^0 : \chi^0) = I(\chi^0 : \chi^*) - S(\chi^0) = -S(\chi^*),\\
\Delta N(\chi^0 ; \chi^*) &= N(\chi^0 ; \chi^*) - N^{(0)}(\chi^0 ; \chi^0) = \Delta S(\chi^*|\chi) + \Delta I(\chi^0 : \chi^*)\\
&= S(\chi^*) - S(\chi^*) = 0.
\end{aligned} \tag{76}$$

Therefore, the displacement measure of the total IT bond-order, $\Delta N(\chi^0; \chi^*)$, vanishes identically, with the Shannon entropy of the effective probabilities of AO in the molecule determining both $\Delta S(\chi^*|\chi^0)$ and $|\Delta I(\chi^0 : \chi^*)|$. The negative value of the relative information-ionicity reflects the fact that due to the chemical "noise" in the molecule the amount of information flowing in the physical AO-promotion channel is lower than the maximum value $S(\chi^0)$ characterizing the noiseless promolecule. By the same amount increases the average communication noise, measuring the bond entropy-covalency created by this probability scattering. It manifests the extra uncertainty in the electron distributions among AO, compared to that already present in the promolecular electron distribution in the AO resolution. This effect of an electron-delocalization among all available AO of the adopted basis set, via the system occupied MO, which amounts to the AO-promotion in the molecular channel, has indeed been intuitively associated by chemists with the very notion of the *covalent* chemical bond.

Of interest also are relative bond-contributions due to each elementary probability-scattering step $1 \leqslant s \leqslant m$ (see Sect. 4.2) in the series of molecular reconstructions of electron probabilities, which ultimately generates the resultant probabilities of the promoted AO [see Schemes 6, 7, and equations (55), (60), (61)]:

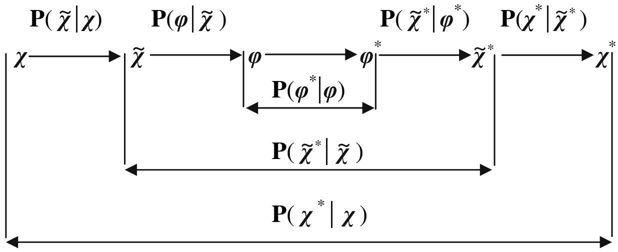
$$\Delta S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \sum_{t=1}^{m} S_t, \quad \Delta I(\boldsymbol{\chi}^0 \colon \boldsymbol{\chi}^*) = \sum_{t=1}^{m} I_t = -\Delta S(\boldsymbol{\chi}^*|\boldsymbol{\chi}),$$
$$\Delta N(\boldsymbol{\chi}^0; \boldsymbol{\chi}^*) = \sum_{t=1}^{m} N_t = 0, \tag{77}$$

These additive contributions to the overall difference measures of equation (76) reflect the stage-to-stage evolution of the cumulative bond indices of equation (52):

$$S^{(s)} = S^{(0)}(\boldsymbol{\chi}^0|\boldsymbol{\chi}^0) + \sum_{t=1}^{s} S_t = \sum_{t=1}^{s} S_t,$$
$$I^{(s)} = I^{(0)}(\boldsymbol{\chi}^0 \colon \boldsymbol{\chi}^0) + \sum_{t=1}^{s} I_t = S(\boldsymbol{\chi}^0) + \sum_{t=1}^{s} I_t = S(\boldsymbol{\phi}^{(s)}) - S^{(s)},$$
$$N^{(s)} = N^{(0)}(\boldsymbol{\chi}^0 \colon \boldsymbol{\chi}^0) + \sum_{t=1}^{s} N_t = S(\boldsymbol{\chi}^0) + \sum_{t=1}^{s} N_t = S(\boldsymbol{\phi}^{(s)}), \quad s = 1, 2, \ldots, m, \tag{78}$$

exhibiting a monotonic increase in $S^{(s)}$ and the accompanying decrease in $I^{(s)}$, which together determine at each stage the overall index of the IT bond-multiplicity at the $S(\boldsymbol{\varphi}^{(s)})$ level. These displacements in the bond-components generated by either the populational promotion or an effective mixing of orbitals due to their hybridization, orthogonalization, forming MO, etc., should allow one to evaluate relative roles played by these specific elementary processes in forming the system chemical bonds.

An alternative perspective on the entropy/information descriptors associated with the specific sets of orbitals $\boldsymbol{\phi}^{(s)}$, $s = 0, 1, 2, 3$, of Sect. 7, follows from the $\boldsymbol{\phi}^{(s)}$-promotion channels [see equation (38) and Schemes 4b, 8]. Now, instead of focusing on each elementary step in the probability-propagation



Scheme 9. The physical promotion of the overlapping orbitals in the 2-AO model of a chemical bond.

chain of Scheme 8, one first seeks the IT-indices of equation (68), for the $\boldsymbol{\phi}^{(s)} \to (\boldsymbol{\varphi} \to \boldsymbol{\varphi}^*) \to \boldsymbol{\phi}^{(s)*}$ (physical) promotion in the molecule. The differences between these entropy/information indices describing the consecutive sets of orbitals for $s = 1, 2, 3$, i.e., AO, HO, OHO, and MO,

$$\begin{aligned}
\Delta S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) &= S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) - S(\boldsymbol{\phi}^{(s-1)*}|\boldsymbol{\phi}^{(s-1)}) = S_s + S_{m-s+1},\\
\Delta I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*}) &= I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*}) - I(\boldsymbol{\phi}^{(s-1)} : \boldsymbol{\phi}^{(s-1)*}) = I_s + I_{m-s+1}\\
&= [S(\boldsymbol{\phi}^{(s)}) - S(\boldsymbol{\phi}^{(s-1)})] - \Delta S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)})\\
&\equiv \Delta S(\boldsymbol{\phi}^{(s)}) - \Delta S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}),\\
\Delta N(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)*}) &= N(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*}) - N(\boldsymbol{\phi}^{(s-1)}; \boldsymbol{\phi}^{(s-1)*})\\
&= \Delta S(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) + \Delta I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)*})\\
&= N_s + N_{m-s+1} = \Delta S(\boldsymbol{\phi}^{(s)}),
\end{aligned} \tag{79}$$

then measure the bond components due to physical promotion of $\boldsymbol{\chi}^{(s-1)}$, compared to those already present in the information channel for the molecular promotion of $\boldsymbol{\chi}^{(s)}$.

These entropy/information displacements provide complementary IT-indices of the bond-order contribution due to the $\boldsymbol{\phi}^{(s-1)} \to \boldsymbol{\phi}^{(s)}$ and $\boldsymbol{\phi}^{(s)*} \to \boldsymbol{\phi}^{(s-1)*}$ steps in the series of Scheme 8. It should be emphasized, however, that contrary to the difference measures S_s, I_s, and N_s [equations (55), (60) and (61)], which describe a single elementary step in the molecular probability propagation in Scheme 8, the entropy/information displacements of equation (79) characterize the above mentioned two steps involved in the molecular promotion of orbitals $\boldsymbol{\phi}^{(s-1)}$, which are missing in the promotion of orbitals $\boldsymbol{\phi}^{(s)}$.

We finally observe that the conditional probabilities $\mathbf{P}(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)})$ [equation (38)] reflect the physical promotion of orbitals $\boldsymbol{\phi}^{(s)*}$ in the molecule, via the system occupied MO, while the noiseless (geometric) matrix $\mathbf{P}^g(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) = \mathbf{I}$ represents the disconnected orbitals $\boldsymbol{\phi}^{(s)}$. The latter define yet another reference for calculating the difference IT indices. The reference entropy/information quantities determined by this separate-orbital channel, with the input and output probabilities $\boldsymbol{P}_{\boldsymbol{\phi}}^{(s)} = \boldsymbol{P}_{\boldsymbol{\chi}}^0 \mathbf{P}(\boldsymbol{\phi}^{(s)}|\boldsymbol{\chi}) = \boldsymbol{P}_{\boldsymbol{\phi}}^{(s)} \mathbf{P}^g(\boldsymbol{\phi}^{(s)*}|\boldsymbol{\phi}^{(s)}) = \{P_m^{(s)}\}$, are:

$$S^g(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) = 0, \quad I^g(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) = N^g(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)^*}) = S(\boldsymbol{\phi}^{(s)})$$
$$= -\sum_m^{(s)} P_m^{(s)} \log P_m^{(s)}. \tag{80}$$

This geometric $\boldsymbol{\phi}^{(s)}$-reference is thus characterized by the vanishing entropy-covalency and the information-ionicity and overall IT index reproducing the Shannon entropy contained in the input probability at stage s, shaped by all preceding orbital transformation stages $0 < t < s$. This channel effectively removes all bond contributions due to steps s+1, $s+2, \ldots, m-s$ in the series of Scheme 6. The relative IT-indices with respect to the reference values of equation (80), describing the disconnected (geometric) $\boldsymbol{\phi}^{(s)}$-reference channel of truly non-bonded orbitals $\boldsymbol{\phi}^{(s)}$, thus reflect changes due to chemical bonds due the electron delocalization among these orbitals in the molecule, via the system occupied MO. The associated difference measures of the overall entropy-covalency, information-ionicity read [see equation (68)]:

$$\begin{aligned}
\Delta S^g(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) &= S(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) - S^g(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) = S(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) \\
&= \sum_{t=s+1}^{m-s} S_s = S^{(m-s)} - S^{(s)}, \\
\Delta I^g(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) &= I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) - I^g(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) \\
&= I(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) - S(\boldsymbol{\phi}^{(s)}) = -S(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}), \\
\Delta N^g(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)^*}) &= N(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)^*}) - N^g(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)^*}) \\
&= \Delta S^g(\boldsymbol{\phi}^{(s)^*}|\boldsymbol{\phi}^{(s)}) + \Delta I^g(\boldsymbol{\phi}^{(s)} : \boldsymbol{\phi}^{(s)^*}) = 0.
\end{aligned} \tag{81}$$

Again, these relative entropy/information descriptors are seen to give rise to the vanishing total index $\Delta N^g(\boldsymbol{\phi}^{(s)}; \boldsymbol{\phi}^{(s)^*}) = 0$.

10. Single chemical bond from two *non*-orthogonal AO

In Sect. 3 we have summarized the communication channel of the physical and geometric promotions, due to a chemical interaction between two OAO,$\tilde{\boldsymbol{\chi}} = (\tilde{\chi}_A, \tilde{\chi}_B) \equiv (\tilde{A}, \tilde{B})$, which represent the symmetrically (Löwdin) orthogonalized analogs the overlapping AO$\boldsymbol{\chi} = (\chi_A, \chi_B)$ of two atoms (A, B). In this 2-OAO model of a single chemical bond the physical promotion of the basis orbitals counts only the $\tilde{\boldsymbol{\chi}} \to \boldsymbol{\varphi} \to \boldsymbol{\varphi}^* \to \tilde{\boldsymbol{\chi}}^*$ steps in the overall chain of the molecular probability propagation shown in Scheme 9, thus neglecting the two AO orthogonalization/de-orthogonalization steps $\boldsymbol{\chi} \to \tilde{\boldsymbol{\chi}}$ and $\tilde{\boldsymbol{\chi}}^* \to \boldsymbol{\chi}^*$, respectively, of the effective AO-promotion in the molecule. It is the main purpose of this section to examine the effect of this hitherto missing stages on the overall bond-multiplicity and its IT covalent/ionic composition.

The non-orthogonal (normalized) AO give rise to the non-diagonal overlap matrix $\mathbf{S}_\chi = \langle \chi|\chi\rangle \neq \mathbf{I}$. Its eigenvalue (diagonalization) problem determines the matrices $\mathbf{S}_\chi^{\pm 1/2}$, which represent transformations between AO and OAO, $\chi = \tilde{\chi}\mathbf{S}_\chi^{1/2}$, $\tilde{\chi} = \chi\mathbf{S}_\chi^{-1/2}$, e.g.,

$$\mathbf{S}_\chi = \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix}, S > 0; \mathbf{U}^{\mathrm{T}}\mathbf{S}_\chi\mathbf{U} = \mathbf{s} = \{s_i\delta_{i,j}\} = \begin{bmatrix} 1+S & 0 \\ 0 & 1-S \end{bmatrix},$$
$$\mathbf{U} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}; \mathbf{S}_\chi^{1/2} = \mathbf{U}\ \mathbf{s}^{1/2}\mathbf{U}^{\mathrm{T}} = \begin{bmatrix} a & b \\ b & a \end{bmatrix}, \quad a = \frac{1}{2}\left(s_1^{1/2} + s_2^{1/2}\right),$$
$$b = \frac{1}{2}\left(s_1^{1/2} - s_2^{1/2}\right). \tag{82}$$

It again follows from the superposition principle of quantum mechanics that the squares of elements in $\mathbf{S}_\chi^{1/2} \equiv \{\sigma_{\tilde{k},l}\}$ determine the probabilities of AO conditional on OAO:

$$\mathbf{P}(\chi|\tilde{\chi}) = \mathbf{P}(\chi^*|\tilde{\chi}^*) = \{P(l|\tilde{k}) = \sigma_{\tilde{k},l}^2\} = \begin{bmatrix} c & d \\ d & c \end{bmatrix} = \mathbf{P}(\tilde{\chi}|\chi)^{\mathrm{T}},$$
$$c = 1/2(1+\sqrt{1-S^2}), \qquad d = 1/2(1-\sqrt{1-S^2}) = 1-c. \tag{83}$$

In Scheme 10 we have summarized the relevant communication channels of the physical AO-promotion in the complete model of the AO-orthogonalization augmented channel of Scheme 2(b, c). A reference to this scheme shows that the molecularly promoted probabilities of AO, which result from scattering of the assumed molecular probabilities of OAO, $P_{\tilde{\chi}} = (P, Q)$ [see equation (33)],

$$P_\chi^* = (P_A^*, P_B^* = 1 - P_A^*) = P_{\tilde{\chi}}\mathbf{P}(\chi^*|\tilde{\chi}^*) = (Pc + Qd, Pd + Qc), \tag{84}$$

fully determine the effective conditional probabilities [see equation (83) and Scheme 2, for $\mathbf{P}(\tilde{\chi}^*|\tilde{\chi})$]

$$\mathbf{P}(\chi^*|\chi) = \mathbf{P}(\tilde{\chi}|\chi)\mathbf{P}(\tilde{\chi}^*|\tilde{\chi})\mathbf{P}(\chi^*|\tilde{\chi}^*) = \begin{bmatrix} P_A^* & P_B^* \\ P_A^* & P_B^* \end{bmatrix}, \tag{85}$$

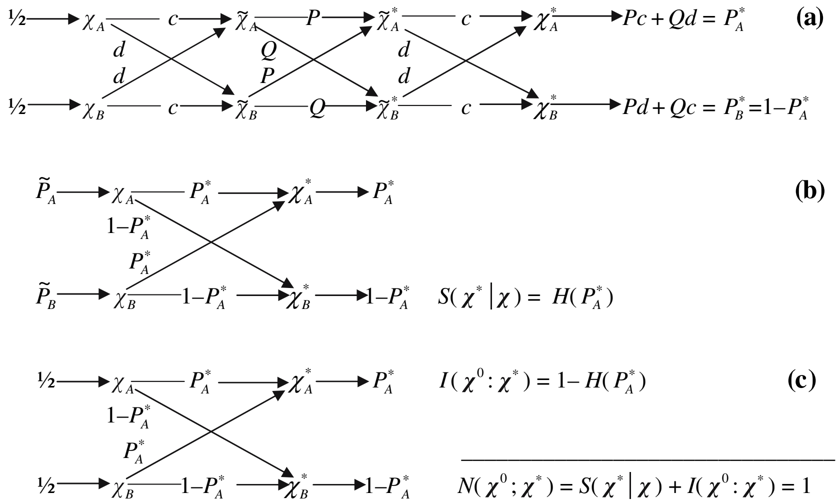
thus giving rise to the IT-indices of the resultant channel listed in Scheme 10.

The AO → OAO ($s = 1$, orthogonalization) stage (see Scheme 11) in the covalent-channel of Scheme 10b must produce the output probabilities

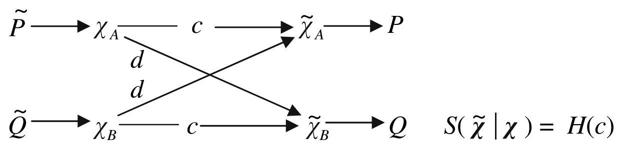
$$\boldsymbol{P}_{\tilde{\chi}} = (P, Q) \equiv \boldsymbol{P}_\chi^{\mathrm{inp.}}\mathbf{P}(\tilde{\chi}|\chi). \tag{86}$$

Therefore, its input probabilities read:

$$\boldsymbol{P}_\chi^{\mathrm{inp.}} = (\tilde{P}, \tilde{Q}) = \boldsymbol{P}_{\tilde{\chi}}\mathbf{P}(\tilde{\chi}|\chi)^{-1}$$
$$= (c^2 - d^2)^{-1}(Pc - Qd, Qc - Pd), \quad \tilde{P} + \tilde{Q} = 1. \tag{87}$$



Scheme 10. The physical AO-promotion in the ground-state of the 2-AO model (non-orthogonal orbitals) for the *non*-diagonal representation of the MO-occupation sub-channel (compare Scheme 2). The corresponding bond components, the entropy-covalency $S(\boldsymbol{\chi}^*|\boldsymbol{\chi})$, from Panel b, and information-ionicity $I(\boldsymbol{\chi}^0{:}\boldsymbol{\chi}^*)$, from Panel c, conserve the single-bond multiplicity: $N(\boldsymbol{\chi}^0;\boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) + I(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^0) = 1$.



Scheme 11. A single *orthogonalization* step $\boldsymbol{\chi} \to \tilde{\boldsymbol{\chi}}$, for $s = 1$, in the covalent AO-promotion chain giving rise to the conditional entropy (IT covalency) $S(\tilde{\boldsymbol{\chi}}|\boldsymbol{\chi}) = H(c)$.

It follows from the diagrams of Scheme 10 that, have the overlap dependent probabilities of equation (84) been determined, the binary entropy function $H(P_A^*)$ determines the channel conditional entropy (IT-covalency), while its complement to the preserved 1 bit of the overall IT bond-order, $1 - H(P_A^*)$, measures the channel mutual information (IT-ionicity). Therefore, the orbital overlap S does not influence predictions for the symmetric bonding MO, for which $P_A^* = P_B^* = 1/2$ and hence $S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = H(1/2) = 1$ bit and $I(\boldsymbol{\chi}^0 : \boldsymbol{\chi}^*) = 0$. One thus correctly predicts in this symmetric case a single, purely covalent bond, e.g., the σ bond in H_2 or the π bond in ethylene.

In Table 2 we have examined how the controlled degree of the AO non-orthogonality, reflected by the overlap integral $S = \langle \chi_A|\chi_B\rangle$, influences the entropy-covalency of the full molecular channel of Scheme 10 for the physical AO promotion in the model ground-state, compared to Scheme 2, which reflects only its $\tilde{\boldsymbol{\chi}} \to \boldsymbol{\varphi} \to \boldsymbol{\varphi}^* \to \tilde{\boldsymbol{\chi}}^*$ stages. This analysis has been carried out for three

Table 2
The effects of the non-vanishing overlap between AO, $S=\langle\chi_A|\chi_B\rangle$, and the MO-polarization parameter P measuring the conditional probability $P(\tilde{A}|b)$ [see equation (33)], on the predicted output probability P_A^* and the entropy-covalency $H(P_A^*)$ (in bits) in the 2-AO model of a single chemical bond A—B.

		$P=0.6,\ H(P)=0.971$			$P=0.75,\ H(P)=0.811$			$P=1,\ H(P)=0$	
S	$c(S)$	P_A^*	$H(P_A^*)$	$S_5=-I_1$	P_A^*	$H(P_A^*)$	$S_5=-I_1$	P_A^*	$H(P_A^*)=H(c)=S_5=-I_5$
0.1	1.00	0.599	0.971	−0.946	0.749	0.813	−0.786	0.998	0.025
0.2	0.99	0.598	0.972	−0.889	0.745	0.819	−0.729	0.990	0.082
0.3	0.98	0.595	0.974	−0.813	0.739	0.829	−0.653	0.977	0.158
0.4	0.96	0.592	0.976	−0.721	0.729	0.843	−0.561	0.958	0.250
0.5	0.93	0.589	0.978	−0.616	0.717	0.860	−0.456	0.933	0.355
0.6	0.90	0.580	0.982	−0.502	0.700	0.881	−0.342	0.900	0.469
0.7	0.86	0.571	0.985	−0.379	0.679	0.906	−0.219	0.857	0.592
0.8	0.80	0.560	0.990	−0.249	0.650	0.934	−0.089	0.800	0.722
0.9	0.72	0.544	0.995	−0.113	0.609	0.966	0.047	0.718	0.858

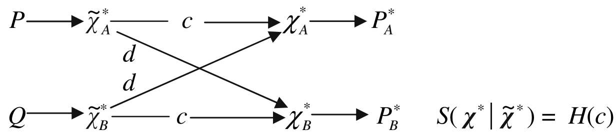
illustrative polarizations of the bonding MO, as reflected by parameter $P > 1/2$ [equation (33)] measuring the probability of $\tilde{\chi}_A$ in the occupied (bonding) MO, with atom A representing the acidic (acceptor) AIM in a diatomic:

$$P=\{0.6 \text{ (weak polarization)}, 0.75 \text{ (medium polarization)}, 1 \text{ (total polarization into ion-pair, } A^-B^+)\}.$$

A reference to this table indeed shows that for a growing weight P of atom A the index $H(P)$, measuring the bond OAO-covalency, gradually decreases reaching zero for the ion-pair configuration, which exhibits a lone electron pair on acidic atom A.

It should be observed that probabilities of equation (84) also reflect the exit probabilities of a single de-orthogonalization step $\tilde{\boldsymbol{\chi}}^* \to \boldsymbol{\chi}^*$ of Scheme 12, for $s=5$, in the overall sequence $\boldsymbol{\chi}\to\tilde{\boldsymbol{\chi}}\to\boldsymbol{\varphi}\to\boldsymbol{\varphi}^*\to\tilde{\boldsymbol{\chi}}^*\to\boldsymbol{\chi}^*$ consisting of $m=5$ elementary stages. Its conditional-entropy index $H(c)$, identical with that characterizing the orthogonalization step for $s=1$ (Scheme 11), reflects the resultant IT-covalency of equation (52) for $s=5$. It also follows from equation (84) that for the ultimate MO polarization $P=1(Q=0)$ of the ion-pair A^-B^+:$P_A^*(P=1)=c$ and $P_B^*(P=1)=d$. Hence, for the current value of the overlap integral S, the entropy $H(P_A^*(S))$ in the last column of Table 2 is equal to $H(c(S))$.

A comparison between the $H(P)$ and $H(P_A^*)$ entries in the table reveals that with increasing overlap between the two AO the peripheral (orthogonalization) steps $s=(1, 5)$ in the chain of Scheme 9 create an increasing amount of the extra entropy-covalency (communication noise) in the AO-promotion channel, compared to that already present in the OAO-promotion case. This effect is strength-



Scheme 12. A single *de-orthogonalization* step $\tilde{\chi}^* \rightarrow \chi^*$, for $s = 5$, in the AO-promotion chain giving rise to the conditional entropy (IT covalency) $S(\chi^* | \tilde{\chi}^*) = H(c)$.

ened still further, when the MO polarization gradually increases, being the strongest in the limiting case of the ion-pair configuration, for which the bond covalency of the mutually orthogonal orbitals identically vanishes. One also observes a steadily growing erosion of differences in the OAO probabilities $(P, Q = 1 - P)$. They become more equalized in the AO representation, $(P_A^*, P_B^* = 1 - P_A^*)$. This creates an extra uncertainty in the electron distribution between the two AO, compared to OAO. It is responsible for the above mentioned growth in the IT-covalency in the AO-promotion channel, which includes the two orthogonalization steps.

To summarize, the more the two atomic orbitals overlap, the more the Löwdin orbital probabilities of OAO differ from those characterizing the promoted AO, with the latter exhibiting an increasing degree of equalization and hence - more entropy-covalency. With respect to OAO the overlapping orbitals thus exhibit an extra delocalization of electrons between the two atoms. One would indeed expect this effect to be felt most in the extreme MO-polarization case, for which both electrons occupy the OAO of the acidic atom A, thus giving rise the vanishing IT-covalency at the OAO stage of the orbital promotion. Moreover, this orthogonalization increment for $P = 1$, when $\varphi_b = \tilde{\chi}_A$ and $\varphi_b = \tilde{\chi}_B$, has to be always positive (increasing the electron uncertainty), since it implies a displacement from the perfectly orbital-localized distribution of two electrons towards a partly delocalized pattern.

For a weak polarization of the bonding MO, this extra spreading of electrons between the two atomic orbitals remains relatively small, particularly in the small overlap regime, with the distribution of electrons between AO being somewhat constrained by a near-symmetry of the system electronic Hamiltonian. The orbital probabilities $P_A^* \cong P_B^* \cong 1/2$ are then in the vicinity of the maximum of the binary entropy function for $H(P_A^* = 1/2)$, where it changes very slowly. The strong effect of the AO orthogonalization on the resultant IT bond-entropies is observed in the limiting case of the ion-pair configuration in the OAO-representation, which corresponds to the fast-changing region of $H(P_A^* \leqslant 1)$.

Next, let us examine the relevant entropy-information descriptors characterizing the orthogonalization/de-orthogonalization steps alone. The input (promolecular) probabilities $\boldsymbol{P}_\chi^0 = (1/2, 1/2)$ determine the initial amount of information

$H(1/2)=1$ bit, at the start of the probability cascade of Scheme 10a. At this $s=0$ stage, $S^{(0)}=0$, since there has been no information-loss at the (absent) preceding steps; also, $I^{(0)}=1$, since the whole initial amount of information of the ionic channel (Scheme 10c), $S(\boldsymbol{\chi}^0)=1$, is available at the start of the AO-promotion cascade.

Similarly, at the exit of the first, orthogonalization step in the probability propagation cascade:

$$\begin{aligned}&S^{(1)}=S(\boldsymbol{\phi}^{(1)}|\boldsymbol{\phi}^{(0)})=H(c), \quad I^{(1)}=I(\boldsymbol{\phi}^{(0)}:\boldsymbol{\phi}^{(1)})=1-H(c),\\&N^{(1)}=S^{(1)}+I^{(1)}=1.\end{aligned} \tag{88}$$

The first quantity measures the information-dissipation in the elementary channel of Scheme 11, while the second, complementary index reflects the amount of information which survives the communication noise created by this orthogonalization step. Hence, these $s=1$ quantities determine the corresponding increments due to a single orthogonalization stage:

$$\begin{aligned}&S_1=S^{(1)}-S^{(0)}=S^{(1)}, \quad I_1=I^{(1)}-I^{(0)}=-S^{(1)},\\&N_1=N^{(1)}-N^{(0)}=S_1+I_1=0.\end{aligned} \tag{89}$$

These displacements are seen to conserve the overall bond-order $N^{(0)}=N^{(1)}=1$ bit, or $N_1=0$.

These entropy/information increments refer to the promolecular input $P^0_{\boldsymbol{\chi}}$, used in Scheme 10(a, c). Should the effective probabilities $P^{\mathrm{inp.}}_{\boldsymbol{\chi}}$ of equation (87) be used in the input of step $s=1$, e.g., in the single, molecular-channel approach to estimate the average noise and the mutual information quantities (see Scheme 10b), the input information content $H(\tilde{P}_A)$ would then be partly scattered to the amount $S^{(1)}(\tilde{P}_A)=H(c)$ and partly preserved to the amount $I^{(1)}(\tilde{P}_A)=H(\tilde{P}_A)-H(c)$, thus again conserving the overall entropy index: $N^{(1)}(\tilde{P}_A)=S^{(1)}(\tilde{P}_A)+I^{(1)}(\tilde{P}_A)=H(\tilde{P}_A)$. The corresponding entropy/information increments due to step $s=1$, relative to $S^{(0)}(\tilde{P}_A)\equiv 0$ and $I^{(0)}(\tilde{P}_A)\equiv H(\tilde{P}_A)$ then read: $S_1(\tilde{P}_A)=S^{(1)}(\tilde{P}_A)-S^{(0)}(\tilde{P}_A)=H(c)$, $I_1(\tilde{P}_A)=I^{(1)}(\tilde{P}_A)-I^{(0)}(\tilde{P}_A)=-H(c)$, and hence again $N_1(\tilde{P}_A)=S_1(\tilde{P}_A)+I_1(\tilde{P}_A)=0$.

The "reverse", de-orthogonalization step, from the assumed probabilities of OAO, $P_{\tilde{\chi}}=(P, Q)$, to those describing the overlapping AO (see Scheme 11) in the molecule, $P^*_{\boldsymbol{\chi}}=(P^*_A, P^*_B)$, gives the molecular estimate of the information noise $S^{(5)}=S(\boldsymbol{\chi}^*|\tilde{\boldsymbol{\chi}}^*)=H(c)$, which diminishes the initial information content $S(\tilde{\boldsymbol{\chi}})=H(P)$, thus predicting the surviving fraction $I^{(5)}=I(\tilde{\boldsymbol{\chi}}^*:\boldsymbol{\chi}^*)=H(P)-H(c)$ of the initial information $H(P)$ contained in $\boldsymbol{P}_{\tilde{\chi}}$, which marks the stage overall bond-order.

The IT-covalency index of the last sub-channel in the sequential series also represents the resultant covalency of the AO-promotion cascade. The resultant conditional-probabilities for the series $s = 1 \div 4$, ending with the preceding step $s = 4$, is determined by the product

$$\mathbf{P}(\tilde{\boldsymbol{\chi}}^* | \boldsymbol{\chi}) = \mathbf{P}(\tilde{\boldsymbol{\chi}} | \boldsymbol{\chi}) \mathbf{P}(\tilde{\boldsymbol{\chi}}^* | \tilde{\boldsymbol{\chi}}) = \begin{bmatrix} P & Q \\ P & Q \end{bmatrix}, \tag{90}$$

which generates $S^{(4)} = H(P)$ (see Scheme 2b). Therefore, the increment of the conditional entropy index in the last, de-orthogonalization step reads:

$$S_5 = S^{(5)} - S^{(4)} = H(c) - H(P). \tag{91}$$

Hence, since $H(1) = 0$, the last column in Table 2 also reflects the increments S_5 for the ion pair electron configuration.

It follows from Table 2 that this de-orthogonalization increment S_5, for the $\tilde{\boldsymbol{\chi}}^* \to \boldsymbol{\chi}^*$ step of the probability propagation in the model, exhibits negative sign at small and medium MO-polarizations, for both small and large overlap S between the two atomic orbitals. It implies that the representative covalency index associated with this step alone lowers the system conditional-entropy component, thus increasing the complementary descriptor of the mutual-information. Indeed, as one observes in Table 2, that for $P = (0.6, 0.75)$ the two complementary conditional-probabilities of equation (83), $[c(S),\ d(S) = 1 - c(S)]$, are in general [except for the $(S = 0.9, P = 0.75)$ case] distinctively more differentiated than $\boldsymbol{P}_{\tilde{\chi}} = (P, Q)$, and hence: $H(c) < H(P)$. In the ion-pair case the opposite is true, thus giving rise to the positive de-orthogonalization increment of the IT-covalency in the model. The first of these conditional probabilities measures the probability of electron surviving on the orbital in question, $c = P(\chi_A^* | \tilde{\chi}_A^*) = P(\chi_B^* | \tilde{\chi}_B^*)$, while the other represents the scattering probability: $d = P(\chi_B^* | \tilde{\chi}_A^*) = P(\chi_A^* | \tilde{\chi}_B^*)$. It follows from Table 2 that $c > d$, so that in the orthogonalization channels the electron survival on a given orbital is more probable than its transfer to the other orbital.

11. Conclusion

This development of the communication theory of the chemical bond in orbital resolution has explored several resultant information cascades and their elementary channels for intermediate sets of orbitals, e.g., OAO, HO (OHO), etc. The entropy/ information descriptors of these communication networks have been proposed as bond-indices for the familiar stages in terms of which the electronic structure of molecules is interpreted by chemists. In particular, the entropy/information increments of the covalent and ionic bond components at each intermediate step of the resultant orbital transformation, from AO to MO, have been examined. The sequential cascades of the probability (information) scattering in molecular systems have been designed for typical orbital-transformation steps in *ab initio* calculations. They allow one to describe the physical promotion of these orbital-intermediates, thus characterizing the role of these sets of orbitals in shaping the resultant bonding-patterns in the molecule. The IT-indices for each step alone similarly index the stage-to-stage evolution of the entropy/information bond-orders in the molecular ground-state.

The illustrative application to the two-orbital model of a single bond has extracted specific channels and the associated bond contributions due to the orbital overlap. This effect has been discussed in the past, e.g., within the Valence-Bond theory. It has been demonstrated that for the symmetrical bond in H_2 or the π bond in ethylene the IT predictions from the molecular orbital-promotion channels in the overlapping AO representation are the same as those in the orthogonal OAO representation. It has been shown that both the bond polarization and a degree of the orbital overlap influence these orbital-orthogonalization contributions to the entropy/information bond indices measuring the effective AO promotion in molecules. They increase bond-covalency, measured by the average information noise, and diminish bond-ionicity, reflected by the mutual information between the promolecular and molecular AO probabilities. This effect is particularly strong in the pure-ionic bond in the OAO representation.

The stage-additivity rule for consecutive series of molecular sub-channels has been compared with the grouping (combination) principles for the parallel arrangement of partial molecular channels [10, 14]. In the spirit of the predominant chemical thinking, which views the chemical bond as the difference-phenomenon, relative to the promolecular reference of a collection of free atoms, the bond-indexing has also been approached from this relative perspective, with the novel IT-indices now measuring displacements relative to the corresponding promolecular values.

In the future studies these alternative sources of the orbital promotion of orbitals in bonded atoms will be investigated using both *ab initio* calculations and more realistic semi-qiantitative models in terms of hybrid orbitals, which realistically represent chemical bonds in selected diatomics, for which interpretations of both the bond character and its multiplicity are well understood in the MO theory.

It would be particularly interesting to examine the effect on the overall bond descriptors of typical features of the molecular electronic structure, e.g., the presence of a single or multiple chemical bonds, lone electron pairs of the valence and/or core electrons, etc. The contributions to the IT bond multiplicities due to specific “displacements” in the orbital shapes and/or occupations could be also extracted, in order to evaluate the relative importance of the intermediate orbitals and their displaced occupations for the resultant pattern of the system chemical bonds and their covalent/ionic composition.

Appendix: Parallel arrangement of information sub-channels

As a comparison to the simplest sequential series of two elementary sub-channels, which we have examined in Sect. 6, let us briefly summarize the corresponding results for the parallel arrangement of figure A1. The separate (disconnected) sub-channels I and II of its Panel a, generated by the *intra*-group conditional probabilities $\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}^{\mathrm{I}}|\boldsymbol{A}^{\mathrm{I}})$ and $\mathbf{P}_{\mathrm{II}}(\boldsymbol{B}^{\mathrm{II}}|\boldsymbol{A}^{\mathrm{II}})$, respectively, are subsequently combined in a parallel manner [10, 14] into a single channel of Panel b, defined by the effective conditional probabilities $\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A})$. In the combined parallel channel the input *group* probabilities, $\boldsymbol{P}_G = (P_{\mathrm{I}}, P_{\mathrm{II}}) = (\lambda, 1-\lambda)$, reflect the overall probabilities of each subsystem in the system as a whole. Therefore, the normalized input and output probabilities of the combined channel read:

$$\boldsymbol{A}(\lambda) = [\lambda \boldsymbol{A}^{\mathrm{I}}, (1-\lambda)\boldsymbol{A}^{\mathrm{II}}], \tag{A1}$$

$$\boldsymbol{B}(\lambda) = [\lambda \boldsymbol{A}^{\mathrm{I}}\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}^{\mathrm{I}}|\boldsymbol{A}^{\mathrm{I}}), (1-\lambda)\boldsymbol{A}^{\mathrm{II}}\mathbf{P}_{\mathrm{II}}(\boldsymbol{B}^{\mathrm{II}}|\boldsymbol{A}^{\mathrm{II}})] = [\lambda \boldsymbol{B}^{\mathrm{I}}, (1-\lambda)\boldsymbol{B}^{\mathrm{II}}]. \tag{A2}$$

Hence, the conditional probabilities $\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A})$ of the combined channel,

$$\boldsymbol{A}(\lambda)\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A}) = \boldsymbol{B}(\lambda), \tag{A3}$$

assume the block-diagonal form:

$$\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A}) = \begin{bmatrix} \mathbf{P}_I\left(\boldsymbol{B}^{\mathrm{I}}|\boldsymbol{A}^{\mathrm{I}}\right) & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_{\mathrm{II}}\left(\boldsymbol{B}^{\mathrm{II}}|\boldsymbol{A}^{\mathrm{II}}\right) \end{bmatrix}, \tag{A4}$$

marking the *inter*-group disconnected communication network of figure A1b.

Such parallel arrangements of elementary channels has already been discussed elsewhere [7, 10, 14], within the fragment development of the molecular information channels in atomic resolution, where the relevant grouping rules for the overall IT bond indices in terms of these describing molecular fragments have been established. This parallel scenario would be also called for within the localized-orbital resolution of bonded atoms, e.g., the stockholder AIM [16].

These combination rules are in the spirit of the group-resolved expression for the Shannon entropy of the input-probabilities of equation (A1):

$$\begin{aligned} S(\boldsymbol{A}(\lambda)) &= -\sum_{\alpha=\mathrm{I,II}}\sum_{k\in\alpha} P_\alpha P(k\,|\alpha)\log[P_\alpha P(k\,|\alpha)] \\ &= -\sum_{\alpha=\mathrm{I,II}} P_\alpha \log P_\alpha - \sum_{\alpha=\mathrm{I,II}} P_\alpha \sum_{k\in\alpha} P(k\,|\alpha)\log P(k\,|\alpha) \\ &\equiv S(\boldsymbol{P}_G) + [\lambda S(\boldsymbol{A}^{\mathrm{I}}) + (1-\lambda)S(\boldsymbol{A}^{\mathrm{II}})], \end{aligned} \tag{A5}$$

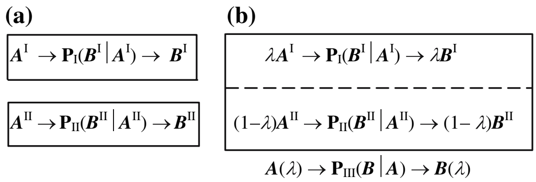


Figure A1. The parallel arrangement of two partial (disconnected) information systems (Panel a), defined by the intra-group conditional probabilities $\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}^{I}|\boldsymbol{A}^{\mathrm{I}})$ and $\mathbf{P}_{\mathrm{II}}(\boldsymbol{B}^{\mathrm{II}}|\boldsymbol{A}^{\mathrm{II}})$, respectively, into the combined information system (Panel b), characterized by $\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A})$. The inputs(outputs) of the parallel system combine those of separate subsystems. It should be observed that the normalized input probabilities $\boldsymbol{A}^{\mathrm{I}} = \{A_i^{\mathrm{I}}\}$ and $\boldsymbol{A}^{\mathrm{II}} = \{A_j^{\mathrm{II}}\}$ of the separate sub-channels represent the conditional (*intra*-group) probabilities in the combined system: $A_i^{\mathrm{I}} \equiv P(i|\mathrm{I})$ and $A_j^{\mathrm{II}} \equiv P(j|\mathrm{II})$, which thus exhibit the correct normalizations: $\sum_i P(i|\mathrm{I}) = \sum_j P(j|\mathrm{II}) = 1$. The absolute values of these probabilities are obtained by multiplying these conditional probabilities by appropriate group probability in the system as a whole: $\boldsymbol{A}(\lambda) = [\{A_i = P_{\mathrm{I}}P(i|\mathrm{I}) = \lambda A_i^{\mathrm{I}}\}, \{A_j = P_{\mathrm{II}}P(j|\mathrm{II}) = (1-\lambda)A_j^{\mathrm{II}}\}$. They give rise to the channel output probabilities $\boldsymbol{B}(\lambda) = \boldsymbol{A}(\lambda)\mathbf{P}_{\mathrm{III}}(\boldsymbol{B}|\boldsymbol{A}) = [\lambda \boldsymbol{B}^{\mathrm{I}}, (1-\lambda)\boldsymbol{B}^{\mathrm{II}}]$.

where the first term $S(\boldsymbol{P}_G) = H(\lambda)$ represents the group-uncertainty, while the rest measures the mean value (group-probability weighted) of the intra-group (conditional) probabilities for each subsystem. These contributions describe the experiment of removing the uncertainty, and thus of acquiring the information, about the whole system. First one identifies the group the experiment outcome is in, which removes the $S(\boldsymbol{P}_G)$ measure of uncertainty. The second term is thus associated with the uncertainties $S(\boldsymbol{A}^{\mathrm{I}})$ and $(\boldsymbol{A}^{\mathrm{II}})$ of outcomes within each group, which have to weighted in accordance with group probabilities $\boldsymbol{P}_G$.

The combination formulas for the system conditional entropy (IT-covalency) and mutual-information (IT-ionicity) of such separated fragments read:

$$
\begin{aligned}
S(\boldsymbol{B}(\lambda)|\boldsymbol{A}(\lambda)) &= -\sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda) \sum_{k,l\in\alpha} P(k|\alpha)P_\alpha(l|k)\log P_\alpha(l|k) \\
&= \sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda) S(\boldsymbol{B}^\alpha|\boldsymbol{A}^\alpha), \qquad \text{(A6)}\\
I(\boldsymbol{A}(\lambda):\boldsymbol{B}(\lambda)) &= \sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda) \sum_{k,l\in\alpha} P(k|\alpha)P_\alpha(l|k)\log \frac{P_\alpha(l|k)}{P_\alpha(\lambda)P(l|\alpha)} \\
&= \sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda) I(\boldsymbol{A}^\alpha:\boldsymbol{B}^\alpha) + S(\boldsymbol{P}_G). \qquad \text{(A7)}
\end{aligned}
$$

Hence the grouping rule for the total bond index:

$$\begin{aligned} N(\boldsymbol{A}(\lambda) : \boldsymbol{B}(\lambda)) &= S(\boldsymbol{B}(\lambda)|\boldsymbol{A}(\lambda)) + I(\boldsymbol{A}(\lambda) : \boldsymbol{B}(\lambda)) \\ &= S(\boldsymbol{P}_G(\lambda)) + \sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda)[S(\boldsymbol{B}^\alpha|\boldsymbol{A}^\alpha) + I(A^\alpha : B^\alpha)] \\ &\equiv S(\boldsymbol{P}_G(\lambda)) + \sum_{\alpha=\mathrm{I,II}} P_\alpha(\lambda) N(\boldsymbol{A}^\alpha : \boldsymbol{B}^\alpha). \end{aligned} \tag{A8}$$

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