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ORIGINAL PAPER

Additive and non-additive information channels in orbital communication theory of the chemical bond

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Abstract The molecular communication system in the resolution of the basis functions $\boldsymbol{\chi} = \{\boldsymbol{\chi}_{\mathrm{X}}\}$ contributed by the molecule constituent atoms $\{\mathrm{X}\}$, the key concept of the Orbital Communication Theory (OCT) of the chemical bond, is introduced and its information-theoretic (IT) bond descriptors are summarized. The additive and *non*-additive components of these molecular information channels are identified. The former involve only the *internal* (*one*-center) communications $\{\mathrm{X} \rightarrow \mathrm{X}\}$ between the basis functions $\boldsymbol{\chi}_{\mathrm{X}}$ of each bonded atom X, determined by the associated (diagonal) block $\mathbf{P}(\boldsymbol{\chi}_{\mathrm{X}}|\boldsymbol{\chi}_{\mathrm{X}})$ of the molecular conditional probabilities, which are responsible for the *intra*-atom promotion to its effective *valence* state. The latter accordingly involve only the *external* (*two*-center) communications between the contributed AO of each pair of bonded atoms, $\{\mathrm{Y} \rightarrow \mathrm{X}$ and $\mathrm{X} \rightarrow \mathrm{Y}\}$, generated by the off-diagonal blocks of conditional probabilities $\mathbf{P}(\boldsymbol{\chi}_{\mathrm{X}}|\boldsymbol{\chi}_{\mathrm{Y}})$ and $\mathbf{P}(\boldsymbol{\chi}_{\mathrm{Y}}|\boldsymbol{\chi}_{\mathrm{X}})$, $\mathrm{X} \neq \mathrm{Y}$, respectively, which are responsible for the *inter*-atomic bonding effects in the molecule. Both these probability scatterings ultimately determine the resultant multiplicities of the system chemical bonds. The *input*-ensemble average value of the channel conditional-entropy, which measures its communication "noise" due to electron delocalization via all chemical bonds, measures the IT-*covalency* in the molecule, while the complementary descriptor of the ensemble average value of the network mutual-information (information-capacity) reflects the electron localization effects and measures the system IT-*ionic* component. The illustrative example of the localized chemical bond originating from the interaction between two atomic orbitals is reexamined in some detail and the bond-weighted ensemble approach to chemical interactions in diatomic molecular fragments

Throughout the article the symbols **X**, *X*, and *X*, respectively denote a square (rectangular) matrix, a *row* vector, and a scalar quantity.

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is discussed within the standard Restricted Hartree-Fock theory. In diatomic systems such treatment exactly reproduces the familiar bond index of Wiberg and provides its resolution into the complementary IT-covalent and IT-ionic components. The operator formulation of the probability-scattering phenomena in molecules is given and the probability-amplitude channel defined by the first-order density matrix is introduced. The AIM internal and external eigenvalue problems of this *Charge-and-Bond-Order* matrix are introduced and a similar approach to probability propagation matrices/operators is suggested.

Keywords Additive/non-additive subchannels · Bond ionicity/covalency · Chemical bond multiplicities · Entropy/information bond descriptors · Information theory · Orbital communication theory · Wiberg bond index

1 Introduction

The concepts and techniques of Information Theory (IT) [1–8] have been successfully used to explore the chemical properties of molecules and their fragments, and to examine the bonding patterns in molecular and reactive systems, e.g., [9,10]. The *non*-additive Fisher information in *Atomic Orbital* (AO) resolution has been recently used to define the *Contra-Gradience* (CG) criterion for localizing the bonding regions in molecules [10–13], while the related information density in the *Molecular Orbital* (MO) resolution has been shown [9,14] to determine the key ingredient of the *Electron-Localization Function* (ELF) [15]. The *Communication Theory of the Chemical Bond* (CTCB) has been developed using the basic entropy/information descriptors of the molecular information (communication) channels in the bonded-atom, orbital and local resolution levels of the electron probability distributions [9,10,16–32]. The same bond descriptors have been used to provide the information-scattering perspective on the intermediate stages in the electron redistribution processes [33], including the atom promotion via the orbital hybridization [34], and the communication theory for excited electron configurations has been developed [35–37]. To summarize, the entropic probes of the molecular electronic structure have provided novel, attractive tools for describing the chemical bond phenomenon in information terms.

Each level of resolving the molecular electron density (ρ) or probability ($p = \rho/N$) distribution of N electrons into the system constituent fragments, $\rho = \sum_\alpha \rho_\alpha$, e.g., the pieces $\boldsymbol{\rho} = \{\rho_\alpha\}$ attributed to *Atoms-in-Molecules* (AIM), *Molecular Orbitals* (MO) or the *Atomic-Orbital* (AO) basis functions, implies the associated division of the molecular (*total*) physical quantity $A[\rho]$ into its additive, $A^{add.}[\boldsymbol{\rho}]$, and *non-additive*, $A^{nadd.}[\boldsymbol{\rho}]$, contributions:

$$A[\rho] \equiv A^{total}[\boldsymbol{\rho}] = A^{add.}[\boldsymbol{\rho}] + A^{nadd.}[\boldsymbol{\rho}], \quad A^{add.}[\boldsymbol{\rho}] = \sum_\alpha A[\rho_\alpha]. \tag{1}$$

We have indicated above that in the underlying "multi-component" system $A[\rho]$ becomes the functional of the whole vector of the subsystem densities: $A[\rho] = A^{total}[\boldsymbol{\rho}]$ [38]. For example, this Gordon-Kim-type division [39] of the kinetic energy functional defines the non-additive contribution, which constitutes the basis of the DFT-embedding concept of Cortona and Wesołowski [40–43].

Such a division can be also used to partition the information quantities themselves [9–14]. In particular, the inverse of the *non*-additive Fisher information in the MO resolution has been shown to define the IT-ELF concept [14], in the spirit of the original Becke and Edgecombe formulation [15], while the related quantity in the AO resolution of the *Self-Consistent Field* (SCF) or *Kohn-Sham* (KS) [44] MO theories offers the key CG criterion for localizing the chemical bonds [11–13].

The key concept of CTCB is the molecular information system, which can be constructed at alternative levels of resolving the electron probabilities into contributions corresponding to the underlying elementary "events" determining the channel *inputs* $\boldsymbol{a} = \{a_i\}$ and *outputs* $\boldsymbol{b} = \{b_j\}$, e.g., the finding of an electron on the specified AO, MO, AIM, molecular fragment, *etc*. Such communication channels can be generated within both the *local* and *condensed* descriptions of electronic probabilities. These networks describe the probability/information propagation in the molecule and can be characterized by the standard entropic quantities developed in IT for real communication devices [3,4,7,8].

Due to the electron delocalization throughout the network of chemical bonds in the molecule the transmission of "signals" about the electron-assignment to the underlying events of the resolution in question becomes randomly disturbed, thus exhibiting typical communication "noise". Indeed, an electron initially attributed to the given AO in the channel "input" $\boldsymbol{a}$ (molecular, promolecular, or the "ensemble" tailored) can be later found with a *non*-zero probability at several locations in the molecular "output" $\boldsymbol{b}$. This feature of the electron delocalization is embodied in the system conditional probabilities of the *outputs-given-inputs*, $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(b_j|a_i) \equiv P(j|i)\}$, which define the molecular information network. In the *one*-electron approach of OCT [30–32,35–37] one constructs this matrix using the *superposition-principle* of quantum mechanics [45], appropriately supplemented by the "physical" projection onto the subspace of the system occupied MO, which determine the pattern of chemical bonds [30–32]. Both the molecule as a whole and its constituent subsystems can be adequately described using the OCT bond indices. The internal and external indices of molecular fragments (groups of AO) can be efficiently generated using the appropriate *reduction* of the molecular channel, by combining selected outputs into larger fragment(s) [31].

Recent developments in CTCB include its orbital formulation, called the *Orbital Communication Theory* (OCT) [30–32,38,39], which was shown to be capable of reproducing the chemical (Wiberg [46]) bond orders in diatomic molecules [37]. In view of the importance of the *non*-additive information terms in describing bonding effects in molecules [10–14] a similar partition of the molecular communication systems into their *additive* and *non-additive* sub-channels has recently been suggested [10]. This division of molecular information channels separates their additive (*one*-center) communications between AO, which give rise to the *non*-bonding promotion of bonded atoms, from the *non*-additive (*two*-center) probability scattering, which generates the truly bonding effects in molecules. Clearly, both these types of the probability propagation ultimately affect the resultant IT bond descriptors. It is the main purpose of the present work to explore and further develop this novel perspective on the information-redistribution processes in molecular systems.

2 Molecular communication systems in atomic orbital resolution

In OCT the *off*-diagonal orbital communications have been recently shown [30] to be proportional to the Wiberg [46] or related quadratic indices of the chemical bond multiplicity [47–56], all formulated within the standard SCF LCAO MO theory. The Wiberg-calibrated IT indices of diatomic interactions in molecules, generated using the bond-weighted ensemble approach, which adopts the flexible ("ensemble") input probabilities to probe the localized bond in the molecule, have been successfully implemented in the RHF MO theory [37]. The resulting IT descriptors been shown to account for the chemical intuition quite well, at the same time providing the resolution of diatomic bond-multiplicities into the complementary IT-covalent and IT-ionic components. In the same study the need for recognizing the signs of the off-diagonal matrix elements of the CBO matrix has been stressed, in order to properly account for the so called "occupation" decoupling, when the *anti*-bonding MO become populated, e.g., in the excited electron configurations.

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

The system electron density,

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

and hence also the *one*-electron probability distribution $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$, representing the *shape*-factor of ρ, are both determined by the one-electron density matrix $\boldsymbol{\gamma}$, called the *Charge-and-Bond-Order* (CBO) matrix, which constitutes the AO representation of the projection operator $\hat{\mathrm{P}}_{\boldsymbol{\varphi}} = |\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}| = \sum_s |\varphi_s\rangle\langle\varphi_s| \equiv \sum_s \hat{\mathrm{P}}_s$ onto the subspace of all occupied MO:

$$\begin{aligned} \boldsymbol{\gamma} &= 2\,\langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle \langle \boldsymbol{\varphi} | \boldsymbol{\chi} \rangle = 2\mathbf{C}\mathbf{C}^\dagger \equiv 2\,\langle \boldsymbol{\chi} | \hat{\mathrm{P}}_{\boldsymbol{\varphi}} | \boldsymbol{\chi} \rangle \\ &= \left\{ \gamma_{i,j} = 2\,\langle \chi_i | \hat{\mathrm{P}}_{\boldsymbol{\varphi}} \left| \chi_j \right\rangle \equiv 2\,\langle i | \hat{\mathrm{P}}_{\boldsymbol{\varphi}} | j \rangle \right\}. \end{aligned} \tag{3}$$

It satisfies the following idempotency relation:

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

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

The molecular information system in the (condensed) orbital resolution involves the AO events $\boldsymbol{\chi}$ in its input $\boldsymbol{a} = \{\chi_i\} \equiv \{i\}$ and output $\boldsymbol{b} = \{\chi_j\} \equiv \{j\}$. It represents the effective communication promotion of these basis functions in the molecule *via* the probability/information scattering described by the conditional probabilities of the AO-outputs given the AO-inputs, identified by the *row* (input) and *column* (output) indices i and j, respectively. In this *one*-electron description the AO→AO communication network is determined by the conditional probabilities of the output AO-events, given the input AO-events [9,30],

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(\chi_j|\chi_i) \equiv P(j|i) = P(i \wedge j)/p_i\} \equiv \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\chi}), \quad \sum_j P(j|i) = 1, \tag{5}$$

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

$$\sum_i P(i \wedge j) = p_j, \quad \sum_j P(i \wedge j) = p_i, \quad \sum_i \sum_j P(i \wedge j) = 1. \tag{6}$$

The conditional probabilities of Eq. (5) define the probability scattering in the AO-promotion channel of the molecule, in which the "signals" of the molecular electron allocations to basis functions are transmitted between the AO inputs and outputs. Such information system constitutes the basis of the OCT of the chemical bond.

As argued elsewhere [30–32,37] this matrix of the (*physical*) conditional probabilities involves the squares of corresponding elements of the CBO matrix:

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \left\{ P(j|i) = \mathcal{N}_i \left| \langle i | \hat{\mathbf{P}}_{\boldsymbol{\varphi}} | j \rangle \right|^2 = (2\gamma_{i,i})^{-1} \gamma_{i,j}\gamma_{j,i} \right\}, \tag{7}$$

where the closed-shell normalization constant $\mathcal{N}_i = (2\gamma_{i,i})^{-1}$ follows directly from Eq. (4) (for the open-shell generalization see [37]). These probabilities explore the dependencies between AO resulting from their participation in the framework of the occupied MO, i.e. their involvement in the entire network of chemical bonds in the molecule.

This AO-resolved channel can be probed using the *promolecular* ($\boldsymbol{p}^0 = \{p_i^0\}$) or molecular input probabilities, with the former corresponding to a collection of the "frozen" densities of the free (*non*-bonded) atoms placed in their molecular positions. Alternatively, some arbitrary (ensemble) input signals can be used to extract the "weighted" IT indices of bond multiplicities in molecular fragments and in the system as a whole, as well as their *ionic* and *covalent* components [9,37]. One also observes that the molecular input $\boldsymbol{P}(\boldsymbol{a}) \equiv \boldsymbol{p}$ generates the same distribution in the output of the molecular channel,

$$\boldsymbol{p}\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{P}(\boldsymbol{b}) \equiv \boldsymbol{q} = \left\{ \sum_i p_i P(j|i) \equiv \sum_i P(i \wedge j) = p_j \right\} = \boldsymbol{p}, \tag{8}$$

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

The associated joint probability matrix,

$$\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b}) = \Big\{P(i \wedge j) = p_i P(j|i) = (2N)^{-1}\,\gamma_{i,j}\gamma_{j,i} \\ = (2/N)\,\langle i|\,\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|j\rangle\,\langle j|\,\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|i\rangle \equiv (2/N)\,\langle i|\,\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_j\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|i\rangle\Big\}, \tag{9}$$

then satisfies the normalization conditions of Eq. (6), e.g.,

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

The off-diagonal conditional probability of jth AO-output given ith AO-input is thus proportional to the squared element of the CBO matrix linking the two AO, $\gamma_{j,i} = \gamma_{i,j}$, thus being also proportional to the corresponding AO contribution $\mathcal{M}_{i,j} = \gamma_{i,j}^2$ to Wiberg's [46–49] index of the overall chemical bond order between two atoms A and B in the molecule,

$$\mathcal{M}(\mathrm{A}, \mathrm{B}) = \sum_{i\in\mathrm{A}}\sum_{j\in\mathrm{B}} \mathcal{M}_{i,j}, \tag{11}$$

or to its generalized analogs in MO theory [50–56]. Hence, the vanishing communication between AO marks the absence of any chemical interaction between them. Therefore, the information channel in the promolecular reference state can exhibit only the diagonal *one*-center (*intra*-atomic) communications, while the presence of both the *one*- and *two*-center (*inter*-atomic) probability propagations marks the collection of AIM.

In OCT the entropy/information indices of the covalent/ionic components of all chemical bonds in the given molecular system represent the complementary descriptors of the average communication *noise* and the associated amount of information *flow* in the molecular information channel. The purely molecular communication channel, with $\boldsymbol{p}$ defining its input signal, is devoid of any reference (history) of the chemical bond formation and generates the average-noise index of the molecular IT *bond-covalency*, measured by the *conditional*-entropy of the system outputs given inputs:

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

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

$$S = -\sum_i \sum_j P(i \wedge j) \log P(i \wedge j) + \sum_i p_i \log p_i \equiv S(\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b})) - S(\mathbf{P}(\boldsymbol{a})). \tag{13}$$

The AO channel with the promolecular (reference) input “signal” $\boldsymbol{P}(a^0) = \boldsymbol{p}^0$ refers to the initial state in the bond-formation process. It corresponds to the ground-state (fractional) occupations of the AO contributed by the system constituent free-atoms, before their mixing into MO, and gives rise to the average information-flow descriptor of the system IT bond-ionicity, measured by the *mutual*-information in the channel inputs and outputs:

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

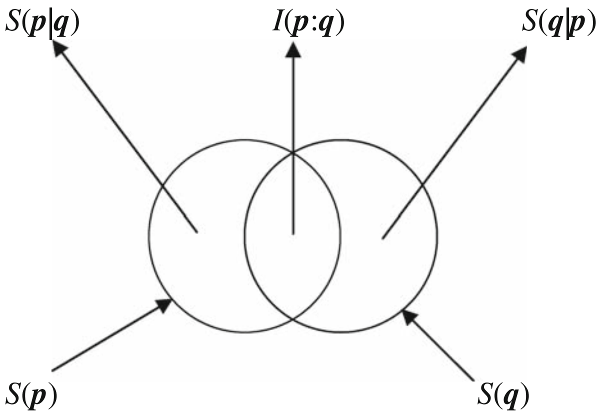
This amount of information reflects the fraction of the initial (promolecular) information content $S(\boldsymbol{p}^0)$, which has not been dissipated as noise in the molecular communication system. In particlular, for the molecular input signal, when $\boldsymbol{p}^0 = \boldsymbol{p}$,

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

Finally, the sum of these two bond components, e.g.,

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

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



Scheme 1 A qualitative diagram of the conditional entropy and mutual information quantities of two dependent probability distributions $\boldsymbol{p}$ and $\boldsymbol{q}$. Two *circles* enclose the areas representing the entropies $S(\boldsymbol{p})$ and $S(\boldsymbol{q})$ of the two *separate* distributions. The common (overlap) area of the *circles* corresponds to the mutual information in two distributions: $I(\boldsymbol{p}:\boldsymbol{q}) = S(\boldsymbol{p}) - S(\boldsymbol{p}|\boldsymbol{q}) = S(\boldsymbol{q}) - S(\boldsymbol{q}|\boldsymbol{p})$. The remaining parts of the *circles* represent the corresponding conditional entropies $S(\boldsymbol{p}|\boldsymbol{q})$ and $S(\boldsymbol{q}|\boldsymbol{p})$, measuring the residual uncertainty about events in one set, when one has the full knowledge of the occurrence of the events in the other set of outcomes. The area enclosed by the envelope of the two overlapping *circles* then represents the entropy of the "product" (joint) distribution: $S(\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b})) = S(\boldsymbol{p}) + S(\boldsymbol{q}) - I(\boldsymbol{p}:\boldsymbol{q}) = S(\boldsymbol{p}) + S(\boldsymbol{q}|\boldsymbol{p}) = S(\boldsymbol{q}) + S(\boldsymbol{p}|\boldsymbol{q})$

$$\begin{aligned} \mathcal{N}(\boldsymbol{P}(\boldsymbol{a}); \boldsymbol{P}(\boldsymbol{b})) &= S(\boldsymbol{P}(\boldsymbol{b})|\boldsymbol{P}(\boldsymbol{a})) + I(\boldsymbol{P}(\boldsymbol{a}) : \boldsymbol{P}(\boldsymbol{b})) \\ &= \sum_i p_i \,(S_i + I_i) \equiv \sum_i p_i \mathcal{N}_i = S(\boldsymbol{P}(\boldsymbol{a})) = S(\boldsymbol{p}). \end{aligned} \tag{17}$$

In the qualitative diagram of Scheme 1 illustrating the entropy/information quantities of two dependent probability distributions $\boldsymbol{p}$ and $\boldsymbol{q}$, the common (overlap) area of the associated entropy circles corresponds to the mutual information in both distributions, $I(\boldsymbol{P}(\boldsymbol{a}) : \boldsymbol{P}(\boldsymbol{b})) = I(\boldsymbol{p} : \boldsymbol{q})$, while the remaining parts of individual circles represent the corresponding conditional entropies $S(\boldsymbol{P}(\boldsymbol{b})|\boldsymbol{P}(\boldsymbol{a})) = S(\boldsymbol{q}|\boldsymbol{p})$ or $S(\boldsymbol{P}(\boldsymbol{a})|\boldsymbol{P}(\boldsymbol{b})) = S(\boldsymbol{p}|\boldsymbol{q})$. The latter measure the residual uncertainty about events in one set, when one has the full knowledge of the occurrence of the events in the other set of events. Accordingly, the area enclosed by the envelope of these two overlapping circles represents the entropy in the joint distribution of the two sets of outcomes:

$$S(\boldsymbol{p} \wedge \boldsymbol{q}) = S(\boldsymbol{p}) + S(\boldsymbol{q}) - I(\boldsymbol{p} : \boldsymbol{q}) = S(\boldsymbol{p}) + S(\boldsymbol{q}|\boldsymbol{p}) = S(\boldsymbol{q}) + S(\boldsymbol{p}|\boldsymbol{q}). \tag{18}$$

Troughout the paper the logarithm is taken to an arbitrary but fixed base: when $\log = \log_2$, the information is measured in *bits*, while selecting log = ln expresses the information content of the probability distribution in *nats*: 1 nat = 1.44 bits.

3 Additive and non-additive components of molecular channels

Let us combine the molecular basis functions of typical LCAO MO calculations into the corresponding atomic subsets:

$$\chi = \{\chi_X\} = (\chi_A, \chi_B, \chi_C, \ldots) \equiv \chi^{AIM}. \tag{19}$$

This arrangement determines the associated block structure of the AO conditional probability matrix of Eqs. (5) and (7):

$$\mathbf{P}(\chi^{AIM}|\chi^{AIM}) = \left\{\mathbf{P}(\chi_X|\chi_Y)\right\}, (X,Y) \in A, B, C, \ldots \tag{20}$$

Here, the diagonal block $\mathbf{P}(\chi_X|\chi_X)$ determines the *internal* (*one*-center) communications $X \to X$ in atom X alone, which are responsible for the AIM promotion to its bonding (*valence*) state in the molecule. The *off*-diagonal blocks $\mathbf{P}(\chi_X|\chi_Y)$ and $\mathbf{P}(\chi_Y|\chi_X)$, $X \neq Y$, similarly generate the external (*two*-center) communications $Y \to X$ and $X \to Y$, respectively, between the contributed AO of both atoms, which are ultimately responsible for the truly bonding effects in the overall IT multiplicities of the localized chemical bonds between the specified pairs of AIM [10]. It should be emphasized, however, that the chemical values of diatomic bond multiplicities combine both the *one*- and *two*-center effects, of the *intra*-atom promotion and *inter*-atomic delocalization and *Charge-Transfer* (CT) effects, respectively [9,10,50–56].

As we have already remarked above, the *inter*-atomic communications in the molecular channel reflect the chemical interactions between different atoms [9,10], so that the collection of *non*-bonded (separated) atoms of the promolecule exhibits only the *intra*-atomic probability propagations. The same principle can be used to naturally partition the molecular AO communication system of the AIM-arranged basis set χ^{AIM} into its *additive* and *non-additive sub*-channels [10] [see also Eq. (1)]:

$$\mathbf{P}^{total}\left(\chi^{AIM}\middle|\chi^{AIM}\right) = \mathbf{P}^{add.}\left(\chi^{AIM}\middle|\chi^{AIM}\right) + \mathbf{P}^{nadd.}\left(\chi^{AIM}\middle|\chi^{AIM}\right). \tag{21}$$

As illustrated in Scheme 2, the former combines all internal (*intra*-atomic) communications within each (chemically decoupled) AIM, thus being solely determined by the diagonal, atomic blocks of the molecular conditional probabilities $\mathbf{P}(\chi^{AIM}|\chi^{AIM})$,

$$\mathbf{P}^{int.}\left(\chi^{AIM}\middle|\chi^{AIM}\right) = \left\{\mathbf{P}\left(\chi_X|\chi_X\right)\delta_{X,Y}\right\} \equiv \mathbf{P}^{add.}\left(\chi^{AIM}\middle|\chi^{AIM}\right), \tag{22}$$

while the latter groups all *external* (*inter*-atomic) probability propagations in the (chemically coupled) diatomic fragments of the molecular system under consideration:

$$\mathbf{P}^{ext.}\left(\chi^{AIM}\middle|\chi^{AIM}\right) = \{\mathbf{P}\left(\chi_X|\chi_Y\right)(1-\delta_{X,Y})\} \equiv \mathbf{P}^{nadd.}\left(\chi^{AIM}\middle|\chi^{AIM}\right). \tag{23}$$

It should be stressed at this point that the *sub*-channel scattering probabilities originating from the given input do no longer sum up to 1, since this normalization condition

$$\begin{bmatrix} \mathbf{P}(\chi_A|\chi_A) & \mathbf{P}(\chi_B|\chi_A) & \mathbf{P}(\chi_C|\chi_A) & \cdots \\ \mathbf{P}(\chi_A|\chi_B) & \mathbf{P}(\chi_B|\chi_B) & \mathbf{P}(\chi_C|\chi_B) & \cdots \\ \mathbf{P}(\chi_A|\chi_C) & \mathbf{P}(\chi_B|\chi_C) & \mathbf{P}(\chi_C|\chi_C) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} = \begin{bmatrix} \mathbf{P}(\chi_A|\chi_A) & \mathbf{0} & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{P}(\chi_B|\chi_B) & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{0} & \mathbf{P}(\chi_C|\chi_C) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} + \begin{bmatrix} \mathbf{0} & \mathbf{P}(\chi_B|\chi_A) & \mathbf{P}(\chi_C|\chi_A) & \cdots \\ \mathbf{P}(\chi_A|\chi_B) & \mathbf{0} & \mathbf{P}(\chi_C|\chi_B) & \cdots \\ \mathbf{P}(\chi_A|\chi_C) & \mathbf{P}(\chi_B|\chi_C) & \mathbf{0} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix}$$

$$= \begin{bmatrix} A\rightarrow A & \mathbf{0} & \mathbf{0} & \cdots \\ \mathbf{0} & B\rightarrow B & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{0} & C\rightarrow C & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} + \begin{bmatrix} \mathbf{0} & A\rightarrow B & A\rightarrow C & \cdots \\ B\rightarrow A & \mathbf{0} & B\rightarrow B & \cdots \\ C\rightarrow A & C\rightarrow B & \mathbf{0} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix}$$

total internal (additive) external (*non*-additive)

Scheme 2 Partitioning of the molecular information system in the AO resolution into the *one*-center (AIM-internal, additive) and *two*-center (AIM-external, *non*-additive) *sub*-channels, and the underlying communications between the constituent bonded atoms

applies only to the total matrix of molecular conditional probabilities involving both the AIM diagonal and off-diagonal communications. In the CTCB/OCT approaches only the *full* list of the AIM/AO inputs determines the complete *origins* (sources) of all chemical bonds in the molecule. Therefore, both atomic and diatomic entropy/information terms, involving the *intra*-atom and *inter*-atom communications to both constituent AIM of the diatomic molecular fragment under consideration, ultimately contribute to the overall IT bond index in the molecular system in question, which describes the resultant chemical connectivity between the two bonded atoms. Indeed, the chemical bond concept combines both the atom-promotion (polarization) and the inter-atomic delocalization/CT phenomenona.

However, as demonstrated elsewhere [37], the probability scatterings in the given diatomic fragment of the molecule, which originate from the specified AO input, have to be weighted by the *two*-center (AO-AIM) joint probabilities, in order to exclude the effects of the *lone*-pair electrons in the resultant bond descriptors. These *one*-center, *non*-bonding features of the molecular electronic structure can artificially rise the magnitudes of the overall bond-multiplicities, thus preventing an acceptable agreement with chemical intuition and the related MO descriptors.

As we have already argued in the preceding section (see also [10,37]), the promoted (valence) state of each bonded atom is determined by the associated diagonal block of molecular conditional probabilities. Important though it is for the full characterization of the AIM valence preparation in the molecule and the resultant, chemical bond multiplicities, which are reflected by the resultant IT bond-multiplicities and their covalent/ionic components, it has no direct relevance for the pattern of diatomic interactions between bonded atoms. Therefore, the partition of Eqs. (21–23) again emphasizes the importance of separating the additive and *non*-additive *sub*-channels, for distinguishing the chemical *one*-center promotion of AIM from the *two*-center, interaction phenomena in OCT of the chemical bond.

Clearly, in the canonical AO representation there are some *internal* covalency ("noise") and ionicity (information flow) contributions involved in the atomic promotion processes [34]. One also observes that in the *Natural Hybrid Orbital* (NHO) freamework, in which the atomic (diagonal) blocks of the *first*-order density matrix become diagonal, the *intra*-atomic communications become deterministic in character, so that the *one*-center (additive) IT-covalency identically vanishes. As in the CG probe of the chemical bond localization [10–13], the entropic bond descriptors of diatomic interactions are then seen to be solely determined by the *non*-additive *sub*-channel, which combines the communications between AO originating from *different* atoms. When supplemented by the atom-promotion communications and the bond-weighting in the channel input ensemble, this separation exactly reproduces the Wiberg [46] bond-orders in diatomic molecules [10,37] and fully account for the bond-differentiation patterns in diatomic fragments of typical molecules (see Sect. 5).

4 Chemical interaction between two orbitals revisited

Consider the illustrative problem of combining the two Löwdin-orthogonalized AO (OAO), $A(\boldsymbol{r})$ and $B(\boldsymbol{r})$, say, two orthogonalized 1s orbitals centered on atoms A and B, respectively, each contributing a single electron to form the chemical bond A—B: $\boldsymbol{p}^0 = (½, ½)$. The two basis functions $\boldsymbol{\chi} = (A, B)$ form the bonding (φ_b) and *anti*-bonding (φ_a) MO combinations $\boldsymbol{\varphi} = (\varphi_b, \varphi_a) \equiv \boldsymbol{\chi}\mathbf{C} \equiv (\boldsymbol{\chi}\boldsymbol{C}_b^T, \boldsymbol{\chi}\boldsymbol{C}_a^T)$:

$$\varphi_b = \sqrt{P}A + \sqrt{Q}B \equiv \sum_{k=A,B} \chi_k C_{k,b}, \qquad \varphi_a = -\sqrt{Q}A + \sqrt{P}B \equiv \sum_{k=A,B} \chi_k C_{k,a},$$
$$P + Q = 1; \tag{24}$$

here the square matrix $\mathbf{C} = (\boldsymbol{C}_b^T|\boldsymbol{C}_a^T)$ groups the LCAO MO expansion coefficients, with columns $\boldsymbol{C}_b^T$ and $\boldsymbol{C}_a^T$ defining the individual MO, expressed in terms of the complementary probabilities P and $Q = 1 - P$, with P marking the conditional probabilities $P(A|\varphi_b) = P(B|\varphi_a) = P$, and Q measuring the remaining matrix elements of the molecular conditional probability matrix: $P(B|\varphi_b) = P(A|\varphi_a) = Q$.

In the ground-state (*bonding*) configuration $\Psi_0 = [\varphi_b^2]$ of this 2-OAO model the CBO matrix of Eq. (3) reads:

$$\boldsymbol{\gamma}_0 = 2\begin{bmatrix} P & \sqrt{PQ} \\ \sqrt{PQ} & Q \end{bmatrix}. \tag{25}$$

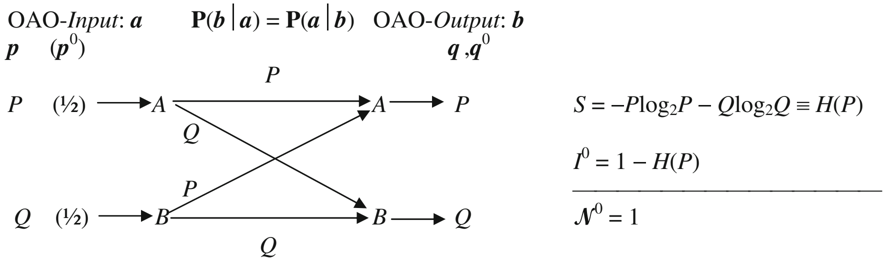
Using Eq. (7) then gives the associated matrices of the joint and conditional probabilities of the two AO in this model chemical bond:

$$\mathbf{P}_0(\boldsymbol{a} \wedge \boldsymbol{b}) = \begin{bmatrix} P^2 & PQ \\ PQ & Q^2 \end{bmatrix}, \quad \mathbf{P}_0(\boldsymbol{b}|\boldsymbol{a}) = \mathbf{P}_0(\boldsymbol{a}|\boldsymbol{b}) = \begin{bmatrix} P & Q \\ P & Q \end{bmatrix}. \tag{26}$$

The latter defines the *non*-symmetric binary communication channel shown in Scheme 3. As also indicated there, the channel IT-covalency (in bits) is determined by the binary entropy function

$$S = H(P) = -P\log_2 P - Q\log_2 Q, \tag{27}$$

while the associated IT-ionicity descriptor $I^0 = S(\boldsymbol{p}^0) - S = 1 - H(P)$. Together they give rise to the conserved overall ("single") bond index in the model: $\mathcal{N}^0 = 1$ bit. The



Scheme 3 The *non*-symmetric binary channel of the 2-OAO model of the chemical bond with the molecular, $\boldsymbol{p} = (P, Q)$, and promolecular, $\boldsymbol{p}^0 = (½, ½)$, input probabilities and the molecular output probabilities $\boldsymbol{q} = \boldsymbol{p}$. The associated entropy/information descriptors (in bits), giving rise to the conserved overall bond order $\mathcal{N}^0 = 1$, are also reported [30]

model correctly predicts the purely covalent bond for the maximum-delocalization (symmetrical) MO, when $P = Q = ½$, and the purely ionic bond for the limiting *ion*-pair configurations $[A^+B^-](P = 0)$ or $[A^-B^+](Q = 0)$, which involve the lone electron pairs on a single AIM [9,30].

The simplest way to identify the *additive* (internal) and *non-additive* (external) bond contributions, which conserve the overall perspective of Scheme 3 as the *total* description in the AO-AIM resolution of Eq. (19), is to separate the *one*-center and *two*-center contributions to the entropy/information indices of Scheme 3:

$$\begin{aligned} S &= (-P^2 \log_2 P - Q^2 \log_2 Q) + (-PQ \log_2 Q - QP \log_2 P) \equiv S^{add.} + S^{nadd.}, \\ I^0 &= \left[P^2 \log_2(2P) + Q^2 \log_2(2Q)\right] + \left[PQ \log(2P) + QP \log_2(2Q)\right] \\ &\equiv I^{0,add.} + I^{0,nadd.}, \\ \mathcal{N}^0 &= \left(S^{add.} + I^{0,add.}\right) + \left(S^{nadd.} + I^{0,nadd.}\right) = \mathcal{N}^{0,add.} + \mathcal{N}^{0,nadd.} = \mathcal{N}^{0,total}. \end{aligned} \tag{28}$$

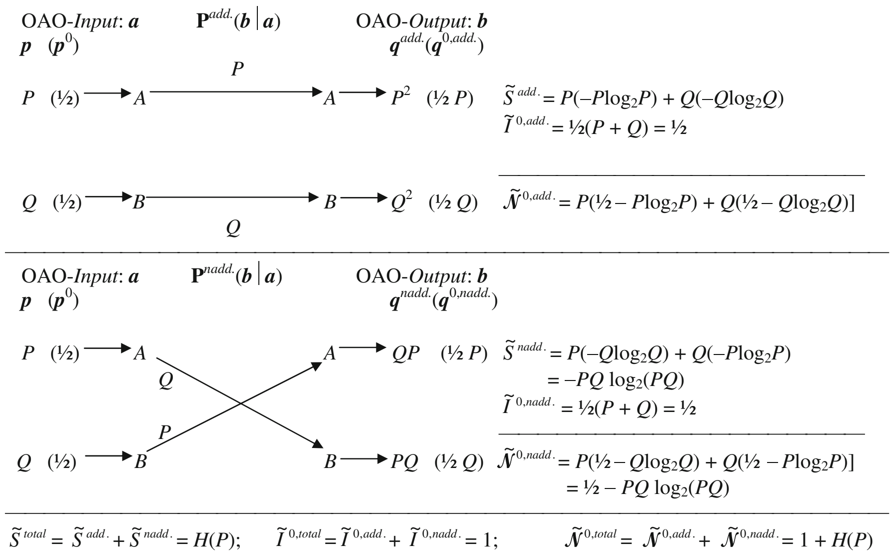
For the limiting configurations $P = (½, 1, 0)$ this partition gives the following resolution of the total indices reported in Scheme 3:

It follows from Table 1 that for the purely covalent configuration of $P = ½$ this division attributes a half of the overall entropy-covalency $S^{total} = 1$ bit to the *one*-center (additive) covalency and the other half to the *two*-center (non-additive) covalency in the model.

It should be emphasized that this partition of the molecular IT-indices of the chemical bond into *one*- and *two*-center contributions does not refer to any specific additive and *non*-additive *sub*-channels of propagating the normalized AO probabilities in the

Table 1 Comparison of the limiting values of IT bond descriptors (in bits) of Schemes 3 and 4

P	$S = S^{total}$	$I^0 = I^{0,total}$	$\mathcal{N}^0 = \mathcal{N}^{0,total}$	$S^{nadd.}$	$I^{0,nadd.}$	$\mathcal{N}^{0,nadd.}$	$S^{add.}$	$I^{0,add.}$	$\mathcal{N}^{0,add.}$
P = 1/2	1	0	1	1/2	0	1/2	1/2	0	1/2
P = 0, 1	0	1	1	0	0	0	0	1	1



Scheme 4 The additive (*upper*) and *non*-additive (*lower*) *sub*-channels in the 2-OAO model of the chemical bond obtained by fixing the molecular *conditional* probabilities $\{P(j|i)\}$. The molecular, $\boldsymbol{p} = (P, Q)$, and promolecular, $\boldsymbol{p}^0 = (½, ½)$, input probabilities, are used to determine the IT covalency and ionicity indices (in bits), respectively, which are also reported together with their partial and total sums

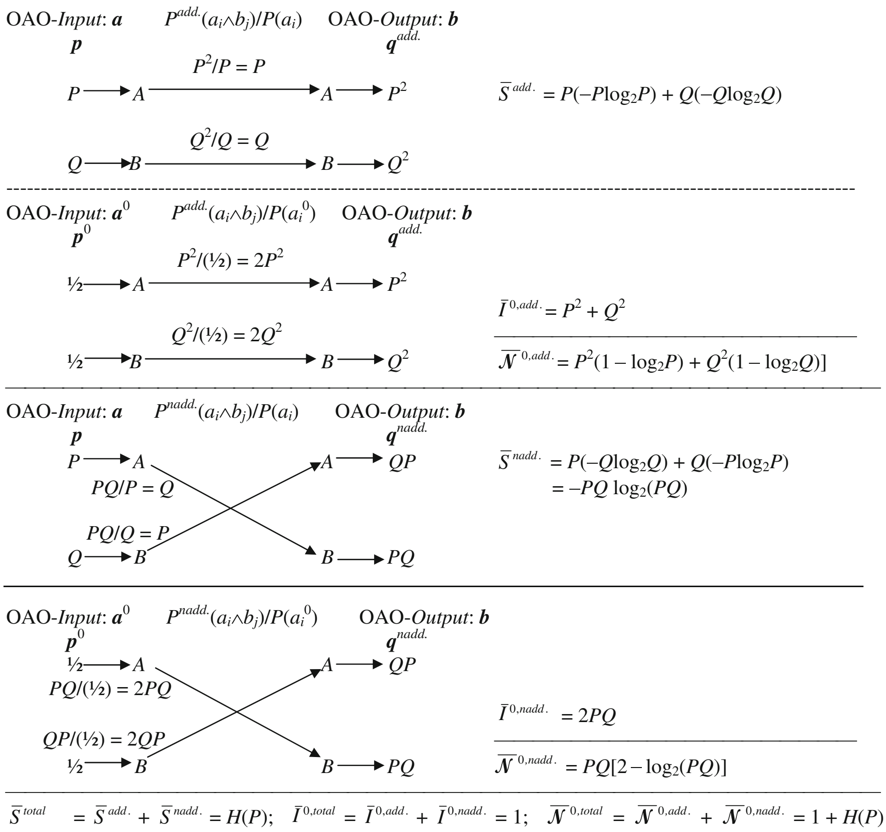
2-OAO system. There are two alternative ways of defining such properly normalized *sub*-channels in the model. The one fixing the molecular *conditional* probabilities of Eq. (26) is summarized in Scheme 4 while the other, which preserves the molecular *joint* probabilities of Eq. (26), is examined in Scheme 5.

Since the partial networks involve the *non*-normalized subsets of communications originating from the specified AO/AIM input, the direct summations of Eqs. (12) and (14) over the *non*-vanishing probability scatterings will be applied to determine the associated entropy/information descriptors. Let us first examine the conditional-entropy and mutual-information descriptors of the additive and *non*-additive *sub*-channels shown in Scheme 4. The additive (*one*-center) descriptors then read:

$$\begin{aligned}\tilde{S}^{add.} &\equiv S(\boldsymbol{q}^{add.}|\boldsymbol{p}) = -P^2\log_2 P - Q^2\log_2 Q = P(-P\log_2 P) + Q(-Q\log_2 Q),\\ \tilde{I}^{0,add.} &\equiv I(\boldsymbol{p}^0 : \boldsymbol{q}^{0,add.}) = ½P\log_2[P/(½P)] + ½Q\log_2[Q/(½Q)]\\ &\qquad = ½(P+Q) = ½,\end{aligned}$$

$$\tilde{\mathcal{N}}^{0,add.} = \tilde{S}^{add.} + \tilde{I}^{0,add.} = ½[P(1 - 2P\log_2 P) + Q(1 - 2Q\log_2 Q)]. \quad (29)$$

These partial descriptors are seen to be composed of the molecular probability weighted contributions to the binary entropy of Eq. (27), besides the constant term in the information-flow component. As we have already emphasized in the preceding section, the above *intra*-atomic information quantities reflect only the AIM promotion in the model, and have no implications for the chemical interaction between the two atoms. The latter is described by the associated *non*-additive (*two*-center) terms of Scheme 4:



Scheme 5 The additive (*upper part*) and *non*-additive (*lower part*) *sub*-channels in the 2-OAO model of the chemical bond obtained by fixing the molecular joint probabilities $\{P(i \wedge j)\}$. Again, the molecular, $\boldsymbol{p} = (P, Q)$, and promolecular, $\boldsymbol{p}^0 = (½, ½)$, input probabilities, are used to determine the entropy-covalency and information-ionicity descriptors, respectively

$$\begin{aligned}
\tilde{S}^{nadd.} &\equiv S(\boldsymbol{q}^{nadd.}|\boldsymbol{p}) = P(-Q\log_2 Q) + Q(-P\log_2 P) = -PQ\log_2(PQ)\,,\\
\tilde{I}^{0,nadd.} &\equiv I(\boldsymbol{p}^0 : \boldsymbol{q}^{0,nadd.}) = ½Q\log_2[Q/(½Q)] + ½P\log_2[P/(½P)]\\
&= ½(Q+P) = ½,\\
\tilde{\mathcal{N}}^{0,add.} &= \tilde{S}^{nadd.} + \tilde{I}^{0,nadd.} = ½ - PQ\log_2(PQ)\,.
\end{aligned} \tag{30}$$

As also shown in Scheme 4, the total indices combining these additive and *non*-additive bond-order terms then read:

$$\begin{aligned}
\tilde{S}^{total} &= \tilde{S}^{add.} + \tilde{S}^{nadd.} = H(P),\\
\tilde{I}^{0,total} &= \tilde{I}^{0,add.} + \tilde{I}^{0,nadd.} = 1,\\
\mathcal{N}^{0,total} &= \tilde{\mathcal{N}}^{0,add.} + \tilde{\mathcal{N}}^{0,nadd.} = 1 + H(P)\,.
\end{aligned} \tag{31}$$

Table 2 Comparison of the limiting values of IT bond descriptors (in bits) of Schemes 3 and 4

P	S	I^0	$\mathcal{N}^0$	$\tilde{S}^{nadd.}$	$\tilde{I}^{0,nadd.}$	$\tilde{\mathcal{N}}^{0,nadd.}$	$\tilde{S}^{add.}$	$\tilde{I}^{0,add.}$	$\tilde{\mathcal{N}}^{0,nadd.}$	$\tilde{S}^{total}$	$\tilde{I}^{0,total}$	$\tilde{\mathcal{N}}^{0,total}$
$P = ½$	1	0	1	½	½	1	½	½	1	1	1	2
$P = 0, 1$	0	1	1	0	½	½	0	½	½	0	1	1

Table 3 Comparison of the limiting values of IT bond descriptors (in bits) of Schemes 3 and 5

P	S	I^0	$\mathcal{N}^0$	$\overline{S}^{nadd.}$	$\overline{I}^{0,nadd.}$	$\overline{\mathcal{N}}^{0,nadd.}$	$\overline{S}^{add.}$	$\overline{I}^{0,add.}$	$\overline{\mathcal{N}}^{0,nadd.}$	$\overline{S}^{total}$	$\overline{I}^{0,total}$	$\overline{\mathcal{N}}^{0,total}$
$P = ½$	1	0	1	½	½	1	½	½	1	1	1	2
$P = 0, 1$	0	1	1	0	0	0	0	1	1	0	1	1

A comparison of these overall entropy/information quantities with those reported in Scheme 3 (see Table 2) reveals a different bond composition in this *sub*-channel approach, with only the IT-covalency (noise) component being identical in both descriptions. One now observes that the overall index $\tilde{\mathcal{N}}^{0,total}$ is no longer conserved with changing polarization of MO. It should be also emphasized, that the truly bonding *non*-additive terms of Eq. (30) give rise to different composition of the *non*-conserved *two*-center IT bond-order $\tilde{\mathcal{N}}^{0,nadd.} = 1$ in the maximum-delocalization/covalency ($P = ½$) and $\tilde{\mathcal{N}}^{0,nadd.} = ½$ in the lone-pair [$P = 1, 0$ (ion-pair)] configurations, compared to the conserved value $\mathcal{N}^{0,total} = 1$ predicted by the overall channel of Scheme 3.

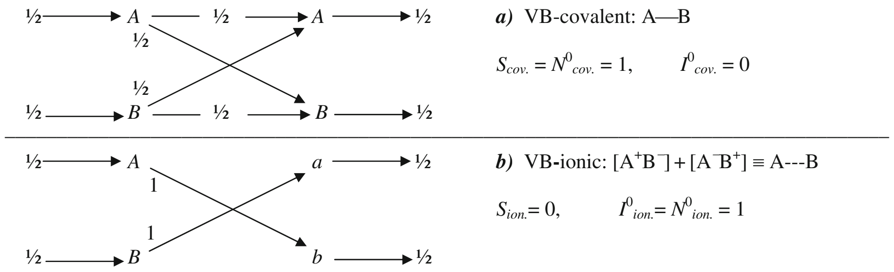
One similarly derives the entropy/information descriptors for the *sub*-channels reported in Scheme 5. The comparison between the bond descriptors it generates for the three limiting configurations with those predicted by the molecular channel of Scheme 3 is given in Table 3. It follows from Tables 1, 2 and 3 that for the ion-pair configurations $P = (0, 1)$ the *sub*-channel overall descriptors of Tables 2 and 3 give the same IT bond indices as those resulting from the molecular channel (see Table 1), while for the maximum covalency ($P = ½$) bonding MO of H_2, the additional 1bit of IT-ionicity is generated in the sub-channel description, due to the renormalization of the input probabilities in the partial communication channels.

It should be finally observed that this simple RHF description of the model ground-state gives rise to the (equal) statistical mixture of the *covalent* (off-diagonal) and ionic (diagonal) *Valence-Bond* (VB) structures, which determine the system resultant electronic structure. The underlying conditional probabilities,

$$\mathbf{P}_{cov.}(\boldsymbol{b}|\boldsymbol{a}) = \begin{bmatrix} ½ & ½ \\ ½ & ½ \end{bmatrix} \quad \text{and} \quad \mathbf{P}_{ion.}(\boldsymbol{b}|\boldsymbol{a}) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{32}$$

which define these partial VB-channels [27], shown in Scheme 6, can be used to resolve the molecular communications $\mathbf{P}_0(\boldsymbol{b}|\boldsymbol{a})$ of Eq. (26):

$$\mathbf{P}_0(\boldsymbol{b}|\boldsymbol{a}) = ½[\mathbf{P}_{cov.}(\boldsymbol{b}|\boldsymbol{a}) + \mathbf{P}_{ion.}(\boldsymbol{b}|\boldsymbol{a})]. \tag{33}$$



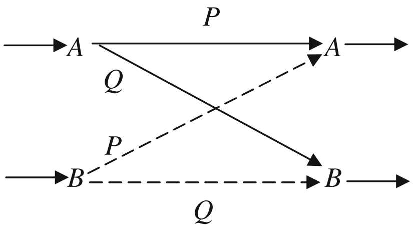
Scheme 6 The elementary VB communication channels for the homonuclear-diatomic A—B and their IT bond indices [27]

Using the grouping (combination) theorem for IT descriptors of such parallel arrangement [27] of these partial channels then expresses the molecular conditional information descriptor as the arithmetic average of the corresponding indices listed in Scheme 6, while the associated average mutual information quantity has to be increased by the Shannon entropy of the "ensemble" probabilities. Hence, for $P = ½$ one obtains, $S_{av.} = ½$, $I^0_{av.} = 3/2$, and hence $\mathcal{N}^0_{av.} = 2$, which reproduces the total indices reported in Tables 2 and 3. Similarly, for $P = (0, 1)$ one finds: $S_{av.} = 0$, $I^0_{av.} = 1$, $\mathcal{N}^0_{av.} = 1$, again in agreement with the total values listed in these tables.

This observation indicates that all these total IT descriptors of the underlying *sub*-channels include 1 bit of the spurious *group*-entropy in the IT-ionicity component, which has no relevance for the bonding interaction between AO, thus again leaving 1 bit of the truly bonding information measure for the purely covalent MO at $P = ½$, and the vanishing entropy/information bond-order for the lone-pair configurations at $P = (0, 1)$.

5 Bond-weighted channels and the Wiberg index

In typical SCF LCAO MO calculations the lone pairs of the *valence*- and/or *inner*-shell electrons can strongly affect the IT descriptors of chemical bonds. It has been argued elsewhere [10,37], that the elimination of such *lone*-pair contributions to the resultant IT bond indices of diatomic fragments in molecules requires an ensemble approach with the orbital input probabilities derived from the joint probabilities of two orbitals centered on different atoms. Indeed, the contributions due to each AO input should be weighted using the corresponding joint (*two*-orbital) probabilities, which reflect the actual simultaneous participation of the given pair of basis functions in the system chemical bonds, thus effectively projecting out the spurious contributions due to the inner- and outer-shell AO, which are excluded from mixing into delocalized MO combinations. This probability-weighting procedure, known as the flexible input approach, has been shown to be capable of reproducing the Wiberg bond order in diatomics [46–49], at the same time providing the IT-covalent/ionic resolution of this index. The diatomic bond multiplicities are determined by the constituent AO of both atoms, $\boldsymbol{\chi}_{AB} = (\boldsymbol{\chi}_A, \boldsymbol{\chi}_B)$. This partial basis corresponds to the diatomic block $\boldsymbol{\gamma}_{AB} = \{\boldsymbol{\gamma}_{X,Y}, (X, Y) = A, B\}$ of the molecular density matrix and



$$S_{AB}(\chi_{AB}|A) = S_{AB}(\chi_{AB}|B) = H(P)$$

$$I^0_{AB}(A{:}\chi_{AB}) = I^0_{AB}(B{:}\chi_{AB}) = 1 - H(P)$$

Scheme 7 The elementary (*row*) *sub*-channels [9] due to inputs A (*solid lines*) and B (*broken lines*) in the 2-OAO model of the chemical bond

the associated part of the conditional probabilities between AO contributed by both atoms: $\mathbf{P}_{AB}(\chi_{AB}|\chi_{AB}) = \{\mathbf{P}(\chi_Y|\chi_X), (X, Y) = A, B\}$. The former determines the effective number of electrons on AB in the molecule given by the partial trace $N_{AB} = \sum_{i\in AB}\gamma_{i,i}$.

We begin this section by applying this weighting procedure to the 2-OAO model of the preceding section. In the bond-weighted approach [10,37] one separates the molecular channel of Scheme 3 into the elementary (*row*) *sub*-channels due to each OAO input [9] (see Scheme 7). The conditional-entropy and mutual-information quantities for these partial communication systems, $\{S_{AB}(\chi_{AB}|i)\}$ and $\{I^0_{AB}(i{:}\chi_{AB})\}$, respectively, with the latter being determined for the covalent-reference probabilities $\boldsymbol{p}^0 = (½, ½)$ marking the single electrons contributed by each OAO to the diatomic chemical bond, are also listed in the diagram. They represent the IT indices *per electron*, so that these contributions have to be multiplied by $N_{AB} = 2$ in the corresponding resultant measures.

Therefore, using the *off*-diagonal joint probability $P_0(A \wedge B) = P_0(B \wedge A) = PQ = \gamma_{A,B}\gamma_{B,A}/4$ as the ensemble probability for both OAO inputs gives the following average quantities for the model diatomic bond (see Fig. 1):

$$\begin{aligned} S_{AB} &= N_{AB}\left[P_0(A\wedge B)S_{AB}(\chi_{AB}|A) + P_0(B\wedge A)S_{AB}(\chi_{AB}|B)\right] \\ &= 4PQH(P) = \mathcal{M}_{A,B}H(P), \\ I^0_{AB} &= N_{AB}\left[P_0(A\wedge B)I^0_{AB}(A:\chi_{AB}) + P_0(B\wedge A)I^0_{AB}(B:\chi_{AB})\right] \\ &= 4PQ[1-H(P)] = \mathcal{M}_{A,B}\,[1-H(P)], \\ \mathcal{N}^0_{AB} &= S_{AB} + I^0_{AB} = 4PQ = (\gamma_{A,B})^2 = \mathcal{M}_{A,B}. \end{aligned} \tag{34}$$

We have thus recovered the Wiberg index as the overall IT descriptor of the chemical bond in 2-OAO model, $\mathcal{N}^0_{AB} = \mathcal{M}_{A,B}$, at the same time establishing its covalent, $S_{AB} = \mathcal{M}_{A,B}H(P)$, and ionic, $I^0_{AB} = \mathcal{M}_{A,B}[1-H(P)]$, contributions. It follows from Fig. 1 that these IT-covalency and IT-ionicity components compete with one another while conserving the Wiberg bond-order of the model as the overall information measure of the bond multiplicity.

This development can be straightforwardly generalized to a general case of several basis functions contributed by each bonded atom [37]. The molecular probability scattering in the specified diatomic fragment (A, B) involving the basis functions $\chi_{AB} = (\chi_A, \chi_B)$ contributed by these atoms to the overall set of AO, $\chi = \{\chi_X\}$,

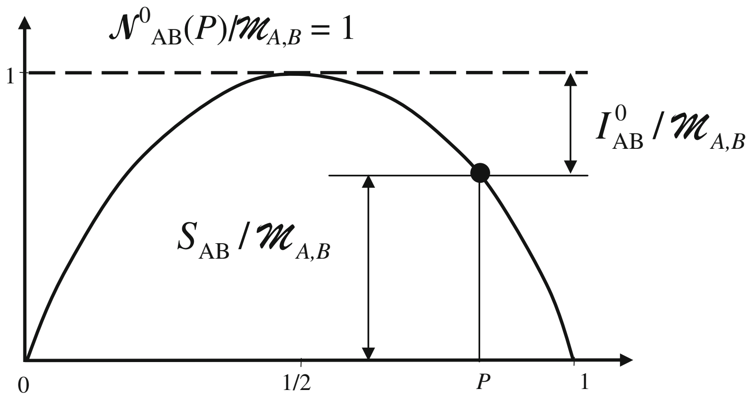


Fig. 1 The variations of the IT-covalent $[S_{AB}(P)]$ and and IT-ionic $[I^0_{AB}(P)]$ components in the 2-OAO model of the chemical bond, in $\mathcal{M}_{A,B}$ units, with changing MO polarization P and the conservation of the relative total bond-order $\mathcal{N}^0_{AB}(P)/\mathcal{M}_{A,B} = 1$

is fully characterized by the corresponding block $\mathbf{P}_{AB}(\boldsymbol{\chi}_{AB}|\boldsymbol{\chi}_{AB})$ of the molecular conditional probability matrix. It contains only the *intra*-diatomic communications, missing the probability propagations originating from AO of the remaining constituent atoms $\boldsymbol{\chi}_Z \notin \boldsymbol{\chi}_{AB}$, thus being perfectly capable of describing the *localized* chemical interactions between A and B.

The atomic *output*-reduction [9] of $\mathbf{P}(\boldsymbol{\chi}_{AB}|\boldsymbol{\chi}_{AB})$, carried out by combining the AO events $\boldsymbol{\chi}_X$ into a single atomic event X in the output of the molecular channel, gives the associated *condensed* conditional probabilities of such a partially reduced information system of diatomic fragment,

$$\begin{aligned} \boldsymbol{P}_{AB}(\boldsymbol{X}_{AB}|\boldsymbol{\chi}_{AB}) &= \left[\boldsymbol{P}(\mathrm{A}|\boldsymbol{\chi}_{AB}), \boldsymbol{P}(\mathrm{B}|\boldsymbol{\chi}_{AB})\right] \\ &= \{P\,(\mathrm{X}|i)\} = \sum_{j\in \mathrm{X}} \boldsymbol{P}(j|\,\boldsymbol{\chi}_{AB});\ \chi_i \in \boldsymbol{\chi}_{AB}, \mathrm{X} = \mathrm{A,B}\}. \end{aligned} \tag{35}$$

Here, $P(X|i)$ measures the conditional probability that an electron originating from χ_i will be found on atom X in the molecule. The sum of these conditional probabilities over all AO contributed by the two atoms then determines the communication connections $\{P(\mathrm{AB|i})\}$ linking the condensed diatomic output AB and the given AO input χ_i in the communication system of the diatomic fragment under consideration:

$$\begin{aligned} &\boldsymbol{P}(\mathrm{A}|\boldsymbol{\chi}_{AB}) + \boldsymbol{P}(\mathrm{B}|\boldsymbol{\chi}_{AB}) = \boldsymbol{P}(\mathrm{AB}|\boldsymbol{\chi}_{AB}) \\ &\quad = \left\{ P(\mathrm{AB}|i) = P(\mathrm{A}|i) + P(\mathrm{B}|i) = \sum_{j\in(\mathrm{A,B})} P(j|\,i) \le 1 \right\}. \end{aligned} \tag{36}$$

In other words, $P(\mathrm{AB|i})$ measures the probability that an electron occupying χ_i will be detected in the diatomic fragment AB of the molecule. The inequality in the preceding equation reflects the fact that the atomic basis functions participate in chemical bonds with all constituent atoms, with the equality sign corresponding only to the diatomic molecule, when $\boldsymbol{\chi}_{\mathrm{AB}} = \boldsymbol{\chi}$.

The associated *fragment*-normalized AO probabilities,

$$\tilde{\boldsymbol{p}}(\mathrm{AB}) = \left\{\tilde{p}_i(\mathrm{AB}) = \gamma_{i,i}/N_{\mathrm{AB}},\, \chi_i \in \boldsymbol{\chi}_{\mathrm{AB}}\right\}, \quad \sum_{i\in(\mathrm{A,B})} \tilde{p}_i(\mathrm{AB}) = 1, \tag{37}$$

where $N_{\mathrm{AB}} = \sum_{i\in(\mathrm{A,B})} \gamma_{i,i}$ stands for the number of electrons found in the molecule on the specified diatomic fragment and $\tilde{p}_i(\mathrm{AB})$ denotes the probability that one of them occupies $\chi_{i\in(A,B)}$, then determine the simultaneous probabilities of the joint two-orbital events:

$$\mathbf{P}_{\mathrm{AB}}(\boldsymbol{\chi}_{\mathrm{AB}} \wedge \boldsymbol{\chi}_{\mathrm{AB}}) = \{P_{\mathrm{AB}}(i \wedge j) = \tilde{p}_i(\mathrm{AB})P(j|i) = \gamma_{i,j}\gamma_{j,i}/\,(2N_{\mathrm{AB}})\}. \tag{38}$$

They in turn generate, *via* the relevant partial summations, the joint atom-orbital probabilities in AB, $\{P_{\mathrm{AB}}(\mathrm{X}, i)\}$:

$$\begin{aligned}\boldsymbol{P}_{\mathrm{AB}}(\boldsymbol{X}_{\mathrm{AB}} \wedge \boldsymbol{\chi}_{\mathrm{AB}}) &= \left[\boldsymbol{P}_{\mathrm{AB}}(\mathrm{A} \wedge \boldsymbol{\chi}_{\mathrm{AB}}), \boldsymbol{P}_{\mathrm{AB}}(\mathrm{B} \wedge \boldsymbol{\chi}_{\mathrm{AB}})\right]\\ &= \left\{P_{\mathrm{AB}}(\mathrm{X} \wedge i) = \sum_{j\in\mathrm{X}} P_{\mathrm{AB}}(i \wedge j) \equiv \tilde{p}_i(\mathrm{AB})P(\mathrm{X}|i), \quad \mathrm{X} = \mathrm{A,B}\right\}.\end{aligned} \tag{39}$$

For the closed-shell molecular systems one thus finds:

$$\begin{aligned}\boldsymbol{P}_{\mathrm{AB}}(\mathrm{X} \wedge \boldsymbol{\chi}_{\mathrm{AB}}) &= \left\{P_{\mathrm{AB}}(\mathrm{X} \wedge i) = \tilde{p}_i(\mathrm{AB}) \sum_{j\in\mathrm{X}} P(j|\,i) = \sum_{j\in\mathrm{X}} \frac{\gamma_{i,j}\gamma_{j,i}}{2N_{\mathrm{AB}}}\right\}\\ &\equiv \boldsymbol{P}_{\mathrm{AB}}(\boldsymbol{\chi}_{\mathrm{AB}} \wedge \mathrm{X})^{\mathrm{T}}, \quad \mathrm{X} = \mathrm{A,B}.\end{aligned} \tag{40}$$

These vectors of AO probabilities in the diatomic fragment AB subsequently define the condensed probabilities $\{P_X(\mathrm{AB})\}$ of both bonded atoms in this subsystem:

$$P_{\mathrm{X}}(\mathrm{AB}) = \frac{N_{\mathrm{X}}(\mathrm{AB})}{N_{\mathrm{AB}}} = \sum_{i\in(\mathrm{A,B})} P_{\mathrm{AB}}(\mathrm{X} \wedge i) = \sum_{i\in(\mathrm{A,B})} \sum_{j\in\mathrm{X}} \frac{\gamma_{i,j}\gamma_{j,i}}{2N_{\mathrm{AB}}}, \mathrm{X} = \mathrm{A,B}, \tag{41}$$

where the effective number of electrons $N_X(\mathrm{AB})$ on atom $\mathrm{X} \in (\mathrm{A, B})$ now reads:

$$N_{\mathrm{X}}(\mathrm{AB}) = \sum_{i\in(\mathrm{A,B})} \sum_{j\in\mathrm{X}} \frac{\gamma_{i,j}\gamma_{j,i}}{2}. \tag{42}$$

Therefore, in diatomic molecules, for which $\boldsymbol{\chi}_{\mathrm{AB}} = \boldsymbol{\chi}$, one finds using the idempotency relation of Eq. (4),

$$P_{\mathrm{X}}(\mathrm{AB}) = \sum_{j \in \mathrm{X}} \left(\sum_{i} \frac{\gamma_{j,i}\gamma_{i,j}}{2N_{\mathrm{AB}}} \right) = \sum_{j \in \mathrm{X}} \frac{\gamma_{j,j}}{N_{\mathrm{AB}}} = \sum_{j \in \mathrm{X}} \tilde{p}_j(\mathrm{AB}), \ \mathrm{X} = \mathrm{A}, \mathrm{B}, \quad (43)$$

and hence $P_{\mathrm{A}}(\mathrm{AB}) + P_{\mathrm{B}}(\mathrm{AB}) = 1$.

The relative importance of the basis functions of one atom in forming the chemical bonds with the other atom in the specified diatomic fragment is reflected by the joint *bond* (b) probabilities of the two atoms, defined only by the diatomic components of the simultaneous probabilities [37]:

$$\begin{aligned} P_b(\mathrm{A} \wedge \mathrm{B}) &\equiv \sum_{j \in \mathrm{B}} P_{\mathrm{AB}}(\mathrm{A} \wedge j) \equiv \sum_{i \in \mathrm{A}} P_{\mathrm{AB}}(i \wedge \mathrm{B}) \\ &= P_b(\mathrm{B} \wedge \mathrm{A}) = \sum_{i \in \mathrm{A}} \sum_{j \in \mathrm{B}} \frac{\gamma_{i,j}\gamma_{j,i}}{2N_{\mathrm{AB}}}. \end{aligned} \quad (44)$$

Indeed, the joint atom-orbital bond probabilities, $\{P_{\mathrm{AB}}(\mathrm{A} \wedge j),\ j \in \mathrm{B}\}$ and $\{P_{\mathrm{AB}}(i \wedge \mathrm{B},),\ i \in \mathrm{A}\}$, to be used as weighting factors in the average conditional-entropy (covalency) and mutual-information (ionicity) descriptors of the chemical bond(s) between A and B, assume appreciable magnitudes only when the electron occupying the atomic orbital χ_i of one atom is simultaneously found with a significant probability on the other atom, thus effectively excluding the contributions to the entropy/information bond descriptors due to the lone-pair electrons.

The *reference* bond probabilities of AO, to be used to calculate the *mutual*-information (IT-ionicity) bond index of the diatomic channel, have to be normalized to the corresponding sums $\boldsymbol{P}(\mathrm{AB}|\boldsymbol{\chi}_{\mathrm{AB}}) = \{\mathrm{P}(\mathrm{AB}|\mathrm{i})\}$ of Eq. (36). Since the bond probability concept of Eq. (44) symmetrically involves the two bonded atoms, one applies the same symmetry requirement in determining the associated reference bond probabilities of AO:

$$\{p_b(i) = P(\mathrm{AB}|i)/2; \quad i \in (\mathrm{A,B})\}, \quad (45)$$

where $P(\mathrm{AB}|\mathrm{i})$ denotes the probability that an electron originating from orbital χ_i will be found on atom A or B in the molecule.

In OCT the complementary quantities characterizing the average *noise* (conditional entropy of the channel output given input) and the information *flow* (mutual information in the channel output and the reference input) in the diatomic communication system defined by the AO conditional probabilities provide the overall descriptors of the fragment bond covalency and ionicity, respectively. Both molecular and promolecular reference (input) probability distributions have been used in the past to determine the information index characterizing the displacement (ionicity) aspect of the system chemical bonds. In the bond-weighted diatomic development the equal bond probabilities of Eq. (45) will be used as the input reference values.

In the A–B fragment development we similarly define the following (“ensemble”) average contributions of both constituent atoms to the diatomic-covalency (delocalization) entropy:

$$
\begin{aligned}
S_{AB}(\mathrm{B}|\boldsymbol{\chi}_{A}) &= \sum_{i \in \mathrm{A}} P_{AB}(i \wedge \mathrm{B}) S_{AB}(\boldsymbol{\chi}_{AB}|i), \\
S_{AB}(\mathrm{A}|\boldsymbol{\chi}_{B}) &= \sum_{i \in \mathrm{B}} P_{AB}(i \wedge \mathrm{A}) S_{AB}(\boldsymbol{\chi}_{AB}|i),
\end{aligned} \tag{46}
$$

where the Shannon entropy (in bits) of the conditional probabilities for the given AO input $\chi_i \in \boldsymbol{\chi}_{AB} = (\boldsymbol{\chi}_A, \boldsymbol{\chi}_B)$ in the diatomic channel:

$$
S_{AB}(\boldsymbol{\chi}_{AB}|i) = -\sum_{j \in (\mathrm{A},\mathrm{B})} P(j|i) \log_2 P(j|i). \tag{47}
$$

In Eq. (46), the conditional entropy $S_{AB}(\mathrm{Y}|\boldsymbol{\chi}_X)$ quantifies (in bits) the X→Y delocalization per electron, so that the total covalency in the diatomic fragment A–B reads:

$$
S_{AB} = N_{AB}\left[S_{AB}(\mathrm{B}|\boldsymbol{\chi}_A) + S_{AB}(\mathrm{A}|\boldsymbol{\chi}_B)\right]. \tag{48}
$$

The bond-weighted contributions to the average *mutual*-information quantities (in bits) of the two bonded atoms are similarly defined in reference to the unbiased bond probabilities of AO [Eq. (45)]:

$$
\begin{aligned}
I_{AB}(\boldsymbol{\chi}_A : \mathrm{B}) &= \sum_{i \in \mathrm{A}} P_{AB}(i \wedge \mathrm{B}) I(i : \boldsymbol{\chi}_{AB}), \\
I_{AB}(\mathrm{A} : \boldsymbol{\chi}_B) &= \sum_{i \in \mathrm{B}} P_{AB}(i \wedge \mathrm{A}) I(i : \boldsymbol{\chi}_{AB}), \\
I(\boldsymbol{\chi}_{AB} : i) &= \sum_{j \in (\mathrm{A},\mathrm{B})} P(j|i) \log_2 \left(\frac{P(j|i)}{p_b(j)}\right).
\end{aligned} \tag{49}
$$

They generate the total information ionicity of all chemical bonds in the diatomic fragment AB:

$$
\mathcal{I}_{AB} = N_{AB}[I_{AB}(\boldsymbol{\chi}_A : \mathrm{B}) + I_{AB}(\mathrm{A} : \boldsymbol{\chi}_B)]. \tag{50}
$$

Finally, the sum of the above total (diatomic) entropy-covalency and information-ionicity indices determines the overall information-theoretic bond multiplicity of the molecular fragment in question:

$$\mathcal{N}_{\mathrm{AB}} = \mathcal{S}_{\mathrm{AB}} + \mathcal{I}_{\mathrm{AB}}. \tag{51}$$

Again, the identity $\mathcal{N}_{\mathrm{AB}} = \mathcal{M}(\mathrm{A}, \mathrm{B})$ (Eq. 11) for diatomic molecules, for which $\boldsymbol{\chi}_{\mathrm{AB}} = \boldsymbol{\chi}$ and the reference probabilities $\{p_b(k) = P(\mathrm{AB}|k)/2 = ½\}$, can be readily demonstrated:

$$\begin{aligned}
\mathcal{N}_{\mathrm{AB}} = \mathcal{S}_{\mathrm{AB}} + \mathcal{I}_{\mathrm{AB}} = N_{\mathrm{AB}} \Bigg\{ & \sum_{i \in \mathrm{A}} P_{\mathrm{AB}}(i \wedge \mathrm{B})\, [S_{\mathrm{AB}}(\boldsymbol{\chi}\,|i) + I(i : \boldsymbol{\chi})] \\
& + \sum_{i \in \mathrm{B}} P_{\mathrm{AB}}(i \wedge \mathrm{A}) [S_{\mathrm{AB}}(\boldsymbol{\chi}\,|i) + I(i : \boldsymbol{\chi})] \Bigg\} \\
\equiv N_{\mathrm{AB}} & \left\{ \sum_{i \in \mathrm{A}} P_{\mathrm{AB}}(i \wedge \mathrm{B}) N(\boldsymbol{\chi}; i) + \sum_{i \in \mathrm{B}} P_{\mathrm{AB}}(i \wedge \mathrm{A}) N(\boldsymbol{\chi}; i) \right\} \\
= N_{\mathrm{AB}} & \left\{ \sum_{i \in \mathrm{A}} P_{\mathrm{AB}}(i \wedge \mathrm{B}) + \sum_{i \in \mathrm{B}} P_{\mathrm{AB}}(i \wedge \mathrm{A}) \right\} \\
= 2 N_{\mathrm{AB}} & P_b(\mathrm{A} \wedge \mathrm{B}) = \mathcal{M}(\mathrm{A},\mathrm{B}),
\end{aligned} \tag{52}$$

where we have observed that the conditional IT bond multiplicity due to the input χ_k (per single electron)

$$\begin{aligned}
N(\boldsymbol{\chi}; k) &= \sum_{l \in \chi} \left\{ -P(l\,|k) \log_2 P(l\,|k) + P(l\,|k) \log_2 [P(l\,|k)/p_b(l)] \right\} \\
&= \left[\sum_{l \in \chi} P(l\,|k) \right] \log_2 2 = 1.
\end{aligned} \tag{53}$$

In Table 4 we have compared the illustrative numerical results of the Restricted Hartree-Fock (RHF) calculations [37] using two choices of the basis set for the localized interactions in representative diatomic and polyatomic molecules, for their equilibrium geometries. In diatomic systems the trends exhibited by the entropic covalent and ionic components of the exactly conserved Wiberg overall bond order generally agree with intuitive expectations. For example, in the minimum basis set description, the roughly "single" chemical bond in F_2, HF and LiH is seen to be almost purely covalent, although a more substantial IT-ionicity is diagnosed in the extended basis set calculations in the fluorine compounds. For the most ionic LiF, which exhibits in the minimum basis set roughly 3/2 bond, consisting of approximately 1 covalent and ½ ionic bond multiplicities, the extended basis set give approximately a "single" bond-order estimate, with the information theory again predicting the ionic dominance over the covalent component of the resultant bond index. In CO, for which the extended basis set calculations have diagnosed approximately a "triple" bond, this chemical interaction is again seen to be predominantly covalent.

The basis-set dependence of the predicted IT bond descriptors is seen to be relatively weak, with the extended basis calculations often giving rise to predictions exhibiting

Table 4 Comparison of the diatomic Wiberg index $\mathcal{M}(A, B)$ and entropy/information bond-multiplicities $\mathcal{N}_{AB}$, S_{AB} and $\mathcal{I}_{AB}$ of the *bond*-weighted channels for selected diatomic fragments A–B in representative molecules M: RHF results for equilibrium geometries in the minimum (STO-3G) and extended (6-31G*) basis sets (from [37])

M	A–B	$\mathcal{M}(A, B)$		$\mathcal{N}_{AB}$		S_{AB}		$\mathcal{I}_{AB}$	
		Min.	Ext.	Min.	Ext.	Min.	Ext.	Min.	Ext.
F_2	F–F	1.000	1.228	1.000	1.228	0.947	1.014	0.053	0.273
HF	H–F	0.980	0.816	0.980	0.816	0.887	0.598	0.093	0.218
LiH	Li–H	1.000	1.005	1.000	1.005	0.997	1.002	0.003	0.004
LiF	Li–F	1.592	1.121	1.592	1.121	0.973	0.494	0.619	0.627
CO	C–O	2.605	2.904	2.605	2.904	2.094	2.371	0.511	0.533
H_2O	O–H	0.986	0.878	1.009	0.896	0.859	0.662	0.151	0.234
AlF_3	Al–F	1.071	1.147	1.093	1.154	0.781	0.748	0.311	0.406
CH_4	C–H	0.998	0.976	1.025	1.002	0.934	0.921	0.091	0.081
C_2H_6	C–C	1.023	1.129	1.069	1.184	0.998	1.078	0.071	0.106
	C–H	0.991	0.955	1.018	0.985	0.939	0.879	0.079	0.106
C_2H_4	C–C	2.028	2.162	2.086	2.226	1.999	2.118	0.087	0.108
	C–H	0.984	0.935	1.013	0.967	0.947	0.878	0.066	0.089
C_2H_2	C–C	3.003	3.128	3.063	3.192	2.980	3.095	0.062	0.097
	C–H	0.991	0.908	1.021	0.943	0.976	0.878	0.045	0.065
$C_6H_6^a$	$C0_1$–C_2	1.444	1.507	1.526	1.592	1.412	1.473	0.144	0.119
	C_1–C_3	0.000	0.061	0.000	0.059	0.000	0.035	0.000	0.024
	C_1–C_4	0.116	0.114	0.119	0.117	0.084	0.081	0.035	0.035

[a] For the sequential numbering of carbon atoms in the benzene ring

slightly better agreement with intuitive chemical estimates. One also finds that in polyatomic systems the Wiberg bond-orders are very well reproduced by the overall IT descriptors. The carbon-carbon interactions in the benzene ring are seen to be properly differentiated and the intuitive multiplicities of the carbon-carbon chemical bonds in ethane, ethylene and acetylene are correctly accounted for.

The IT bond descriptors provide the covalent/ionic resolution of the Wiberg bond-order $\mathcal{M}(A, B)$, which has been customarily regarded as being of purely "covalent" origin. However, the LCAO MO coefficients carry the information about both the electron-sharing (covalent) and electron-separation/transfer (ionic) phenomena in the chemical bond. Therefore, this overall index in fact combines the covalent and ionic contributions, which remain to be separated. The present IT approach provides such a resolution of this in fact *resultant* bond-order.

6 Operator development and amplitude channels

The partitioning of the molecular channel, defined by the conditional probabilities $\mathbf{P}(\boldsymbol{\chi}^{AIM}|\boldsymbol{\chi}^{AIM})$ between AO, into the associated internal (additive) and external (*non*-additive) components of Scheme 2 is in the spirit of a similar division of the matrix representations of quantum-mechanical operators in a related context of the operator *internal* and *external* eigenvalue problems [57–60]. The latter approach has been applied to identify the partially-decoupled channels of the collective electron displacements in reactants [57–59], and it has been successfully used to precisely determine the *inter*-atomic flows of electrons in molecules [61–65].

Indeed, the probability-operator origin of the conditional probability matrix is also seen in Eq. (8): when acting on the input probability vector $\boldsymbol{p}$ it generates generally different distribution $\boldsymbol{q} = \boldsymbol{p}\mathbf{P}(\boldsymbol{b}|\boldsymbol{a})$. In order to interpret this matrix equation of the AO representation in terms of the equivalent operator ("geometric") equation formulated in the relevant probability vector space one first observes that the elementary propability propagation $i \to j$, from the AO input χ_i to the AO output χ_j in the communication network determined by all chemical bonds in the molecule, as reflected by the AO conditional probability $P(j|i)$, must be interpreted as the *expectation value* in state $|\chi_i\rangle = |i\rangle$ of the appropriate propagation operator $\hat{\mathrm{R}}_j = \hat{\hat{\mathrm{R}}}_j/N_i$, of scattering a single electron to state $|\chi_j\rangle = |j\rangle$. Using Eq. (7) then gives:

$$P(j|i) = \langle i|\,\hat{\mathrm{R}}_j\,|i\rangle = \frac{1}{2N_i}\left\langle i|\,\hat{\mathrm{P}}_{\varphi}\hat{\mathrm{P}}_j\hat{\mathrm{P}}_{\varphi}\right|i\Big\rangle, \qquad \hat{\mathrm{P}}_j = |j\rangle\,\langle j|\,, \tag{54}$$

and hence

$$\hat{\mathrm{R}}_j = \frac{\hat{\mathrm{P}}_{\varphi}\hat{\mathrm{P}}_j\hat{\mathrm{P}}_{\varphi}}{2}. \tag{55}$$

This equation provides a transparent interpretation of the propagation operator to the specified output state $|j\rangle$ as the (MO-projected) projection onto the final AO state in question. The set of all such scatterings defines the molecular probability propagations to all basis functions, $\{\hat{\mathrm{R}}_j\} = \hat{\mathbf{R}}$, the trace of which generates the molecular output-probability vector:

$$\mathrm{tr}(\hat{\mathrm{D}}\hat{\mathbf{R}}) = \sum_{i=1}^{m} p_i\,\langle i|\,\hat{\mathbf{R}}\,|i\rangle = \sum_{i=1}^{m} \boldsymbol{q}^{(i)} = \boldsymbol{q}, \tag{56}$$

where the input density-operator:

$$\hat{\mathrm{D}} = \sum_{i=1}^{m} |i\rangle\, p_i\, \langle i| = \sum_{i=1}^{m} p_i\hat{\mathrm{P}}_i. \tag{57}$$

The probability propagation equation thus acquires the following *ensemble*-average interpretation:

$$\boldsymbol{p}\mathbf{P}\,(\boldsymbol{b}|\boldsymbol{a}) = \left\{\sum_{i=1}^{m} p_i\,P(j\,|i\,) = \sum_{i=1}^{m} p_i\,\langle i|\,\hat{\mathrm{R}}_j\,|i\rangle \right.$$
$$\left. = \sum_{\mathrm{X}}\sum_{i\in\mathrm{X}} p_i\,\langle i|\,\hat{\mathrm{R}}_j\,|i\rangle \equiv \mathrm{tr}(\hat{\mathrm{D}}\hat{\mathrm{R}}_j) = q_j \right\} \equiv \boldsymbol{q}, \qquad (58)$$

Therefore, the output probability q_j represents the *input*-ensemble average of the probability-scattering operator $\hat{\mathrm{R}}_j$.

The additive (internal) probability propagation to the specified output $|j \in \mathrm{X}\rangle$, originating from $\{|i \in \mathrm{X}\rangle\}$, is then determined by the *intra*-atomic scattering component $\boldsymbol{q}^{int.}$ defined by the AIM-internal part of the trace:

$$\boldsymbol{p}\mathbf{P}^{add.}(\boldsymbol{b}|\boldsymbol{a}) = \left\{\sum_{i\in\mathrm{X}} p_i\,\langle i|\,\hat{\mathrm{R}}_{j\in\mathrm{X}}\,|i\rangle = q_j^{int.}\right\} \equiv \boldsymbol{q}^{int.}, \qquad (59)$$

while the complementary *non*-additive (external) part $\boldsymbol{q}^{ext.}$, originating from $\{|i \notin \mathrm{X}\rangle\}$ is given by the associated AIM-external part of the trace:

$$\boldsymbol{p}\mathbf{P}^{nadd.}(\boldsymbol{b}|\boldsymbol{a}) = \left\{\sum_{\mathrm{Y}\notin\mathrm{X}}\sum_{i\in\mathrm{Y}} p_i\,\langle i|\,\hat{\mathrm{R}}_{j\in\mathrm{X}}\,|i\rangle = q_j^{ext.}\right\} \equiv \boldsymbol{q}^{ext.},\quad \boldsymbol{q}^{int.} + \boldsymbol{q}^{ext.} = \boldsymbol{q}. \qquad (60)$$

Therefore, for the specified AO input $|i \in \mathrm{X}\rangle$ the corresponding internal and external scattering operators read:

$$\hat{\mathrm{R}}_{i\in\mathrm{X}}^{int.} = \sum_{j\in\mathrm{X}} \hat{\mathrm{R}}_j, \qquad \hat{\mathrm{R}}_{i\in\mathrm{X}}^{ext.} = \sum_{j\notin\mathrm{X}} \hat{\mathrm{R}}_j = \sum_{\mathrm{Y}\notin\mathrm{X}}\sum_{j\in\mathrm{Y}} \hat{\mathrm{R}}_j. \qquad (61)$$

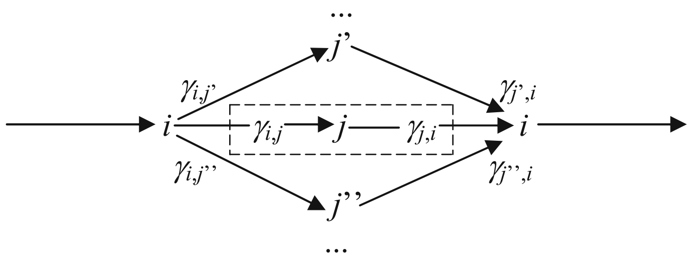
They determine the associated internal and external parts of the output-probability component due to this input [see Eq. (56)]:

$$\boldsymbol{q}^{(i)} = \{p_i\,P\,(j|i)\} = \{p_i\,\langle i|\,\hat{\mathrm{R}}_j\,|i\rangle\} = p_i\,\langle i|\,\hat{\mathrm{R}}_i^{int.}\,|i\rangle + p_i\,\langle i|\,\hat{\mathrm{R}}_i^{ext.}\,|i\rangle$$
$$\equiv \boldsymbol{q}^{(i),int.} + \boldsymbol{q}^{(i),ext.}, \quad \sum_{i=1}^{m} \boldsymbol{q}^{(i)} = \boldsymbol{q}. \qquad (62)$$

It thus directly follows from the normalization of conditional probabilities (Eq. 5) that

$$\sum_{j=1}^{m} P(\,j|\,i) = \sum_{j=1}^{m} \langle i|\,\hat{\mathrm{R}}_j\,|i\rangle = 1 \quad \text{or} \quad \hat{\mathrm{R}}_i^{int.} + \hat{\mathrm{R}}_i^{ext.} = \sum_{j=1}^{m} \hat{\mathrm{R}}_j = 1. \qquad (63)$$

This normalization, that the probability at the given AO input will be scattered with certainty to some of the AO outputs, expresses the conservation of electronic probabilities in the molecule.



Scheme 8 The AO probability propagation product $\gamma_{i,j}\gamma_{j,i}$ as communication link in the *sequential* cascade of two elementary CBO (amplitude) *sub*-channels, each defined by the density matrix $\boldsymbol{\gamma}$

It follows from Eq. (7) that in the closed-shell configurations $P(\chi_j|\chi_i) = P(j|i) = \gamma_{i,j}\gamma_{j,i}/(2\gamma_{i,i})$ and $P(\chi_i|\chi_j) = P(i|j) = \gamma_{j,i}\gamma_{i,j}/(2\gamma_{j,j})$. Hence the equality between the *renormalized* communications linking these two orbitals, proportional to the joint probability $P(i \wedge j)$ [see Eq. (9)],

$$\gamma_{i,i}P(j|i) \equiv \tilde{P}(j\,|i\,) = \gamma_{j,j}P(i|j) \equiv \tilde{P}(i\,|j\,) \\ = \gamma_{j,i}\gamma_{i,j}/2 = (\gamma_{i,j})^2/2 = NP(i \wedge j). \tag{64}$$

Using the idempotency relation of Eq. (4) one finds their partial-normalization relations:

$$\sum_{j=1}^{m} \tilde{P}(j\,|i\,) = \gamma_{i,i} \quad \text{and} \quad \sum_{i=1}^{m} \tilde{P}(j\,|i\,) = \gamma_{j,j}. \tag{65}$$

It also follows from Eq. (64) that the elements of the CBO matrix themselves determine the communication links in the associated *amplitude channel*. Indeed, $\gamma_{j,i}$ or $\gamma_{i,j}$ determine the amplitude of the renormalized joint-probability $\tilde{P}(j\,|i\,) = NP(i \wedge j)$:

$$\tilde{P}(j\,|i\,) = \left(\frac{\gamma_{i,j}}{\sqrt{2}}\right)^2 = [\tilde{A}(j\,|i\,)]^2. \tag{66}$$

Therefore, the conditional-probability amplitude $\tilde{A}(j\,|i\,)_\propto \gamma_{i,j}$ can be regarded as the amplitude propagation connection $\chi_i \to \chi_j$ in the underlying communication system called the *amplitude channel* of Scheme 8.

It thus follows that the elementary AO communication of Eq. (66) can be regarded as representing the resultant link $\chi_i \to \chi_j \to \chi_i$ in the *sequential* cascade consisting of two amplitude channels (see Scheme 8), with the AO *outputs* of the first information system constituting the *inputs* of the second system. A reference to the idempotency relations of Eq. (4) then shows that the sum over all such common inputs/outputs j of both subsystems in the combined communications $\{i \to j \to i\}$ of the sequential cascade generates, to a common multiplicative factor, the resultant (diagonal) amplitude propagation $i \to i$:

$$\sum_{i=1}^{m} \tilde{A}(j\,|i\,)\tilde{A}(i\,|j\,) = \frac{1}{2}\sum_{i=1}^{m} \gamma_{i,j}\gamma_{j,i} = \gamma_{i,i} = \sqrt{2}\tilde{A}(i\,|i\,). \tag{67}$$

7 Eigenvalue problems

In the familiar framework of the closed-shell RHF theory the MO $\boldsymbol{\varphi}(\boldsymbol{r}) = \langle \boldsymbol{r}|\boldsymbol{\varphi}\rangle = \langle \boldsymbol{r}|\boldsymbol{\chi}\rangle\mathbf{C} = \boldsymbol{\chi}(\boldsymbol{r})\mathbf{C}$, where the matrix of LCAO MO coefficients $\mathbf{C} = \langle\boldsymbol{\chi}|\boldsymbol{\varphi}\rangle = \{\langle\boldsymbol{\chi}|\varphi_i\rangle = \boldsymbol{C}_i^T\}$ combines projections of MO onto the (OAO) basis states $\boldsymbol{\chi}(\boldsymbol{r}) = \langle\boldsymbol{r}|\boldsymbol{\chi}\rangle$, diagonalize the CBO matrix $\boldsymbol{\gamma} = \langle\boldsymbol{\chi}|\boldsymbol{\varphi}\rangle\mathbf{d}\langle\boldsymbol{\varphi}|\boldsymbol{\chi}\rangle \equiv \langle\boldsymbol{\chi}|\hat{\gamma}|\boldsymbol{\chi}\rangle$, with the diagonal matrix of MO occupations $\mathbf{d} = \{n_i\delta_{i,j}\}$ representing the eigenvalues of the underlying matrix or operator equations:

$$\boldsymbol{\gamma}\boldsymbol{C}_i^{\mathrm{T}} = n_i\boldsymbol{C}_i^{\mathrm{T}} \qquad \text{or} \qquad \hat{\gamma}|\varphi_i\rangle = n_i|\varphi_i\rangle, \qquad i = 1, 2, \ldots, m. \tag{68}$$

Of interest also are [57–65] the associated *internal* and *external* eigenvalue problems of this density matrix in the AIM fragment resolution. They are respectively defined by the AIM-*diagonal* (additive, $\boldsymbol{\gamma}_{int.}^{\mathrm{AIM}}$) and AIM-*off-diagonal* (non-additive, $\boldsymbol{\gamma}_{ext.}^{\mathrm{AIM}}$) parts of $\boldsymbol{\gamma}^{\mathrm{AIM}} = \langle\boldsymbol{\chi}^{\mathrm{AIM}}|\hat{\gamma}|\boldsymbol{\chi}^{\mathrm{AIM}}\rangle$:

$$\boldsymbol{\gamma}^{\mathrm{AIM}} = \left\{\boldsymbol{\gamma}_{\mathrm{X,Y}}\right\} = \{\boldsymbol{\gamma}_{\mathrm{X,X}}\delta_{\mathrm{X,Y}}\} + \{\boldsymbol{\gamma}_{\mathrm{X,Y}}(1-\delta_{\mathrm{X,Y}})\} \equiv \boldsymbol{\gamma}_{int.}^{\mathrm{AIM}} + \boldsymbol{\gamma}_{ext.}^{\mathrm{AIM}}, \tag{69}$$

$$\boldsymbol{\gamma}_{int.}^{\mathrm{AIM}}\boldsymbol{D}_\alpha^{\mathrm{T}} = \nu_\alpha\boldsymbol{D}_\alpha^{\mathrm{T}}, \qquad \alpha = 1, 2, \ldots, m, \qquad \boldsymbol{D}_\alpha = \{\boldsymbol{D}_{\mathrm{X},\alpha\in\mathrm{X}}\} \qquad \text{and} \tag{70}$$

$$\boldsymbol{\gamma}_{ext.}^{\mathrm{AIM}}\boldsymbol{d}_\beta^{\mathrm{T}} = \omega_\beta\boldsymbol{d}_\beta^{\mathrm{T}}, \qquad \beta = 1, 2, \ldots, m. \tag{71}$$

The internal modes define the NHO of the externally-decoupled AIM,

$$\boldsymbol{\lambda}_{\mathrm{X}} = \{\lambda_{\mathrm{X},\alpha} = \boldsymbol{\chi}_{\mathrm{X}}\boldsymbol{D}_{\mathrm{X},\alpha}^{\mathrm{T}}\} \equiv \boldsymbol{\chi}_{\mathrm{X}}\mathbf{D}_{\mathrm{X}}, \qquad \mathrm{X} = \mathrm{A,B}, \ldots, \tag{72}$$

with $\{\nu_\alpha\}$ standing for the NHO occupations in the promoted, *valence*-state in the molecule, while the the external modes,

$$\boldsymbol{\psi}^{ext.} = \{\psi_\beta = \boldsymbol{\chi}^{\mathrm{AIM}}\boldsymbol{d}_\beta^{\mathrm{T}}\} \equiv \boldsymbol{\chi}^{\mathrm{AIM}}\mathbf{d}, \tag{73}$$

consisting of pairs of the delocalized (CT-active) modes $\{\psi_{-|\omega|}, \psi_{+|\omega|}\}$, for the non-vanishing eigenvalues $\{\omega_\beta\}$ measuring the electron-transfers $\{\psi_{-|\omega|} \to \psi_{+|\omega|}\}$ between atoms, and the zero-eigenvalue (atomic) modes, for the zero *inter*-atomic electron flows, representing the interaction-induced polarization of bonded atoms [57–65].

A similar block partitioning in the AIM-fragment perspective can be carried out for the scattering probabilities in the AO resolution, e.g., of the conditional probabilities [see Eqs. (22, 23) and Scheme 2] and their renormalized analogs for the joint AO events. The corresponding eigenvalue problems it generates would similarly determine the independent (decoupled) probability propagation modes, for the internal promotion of AIM and the external CT-active modes of bonded atoms, which provide the most compact description of the reconstruction of the information distribution in the bond-formation process, involving a transition from the initial state of the atomic promolecule to the real molecular system. Such an eigen-solution approach to communication systems in the AO resolution will be explored in future studies.

8 Conclusion

In this work we have outlined the key concepts of the OCT of the chemical bond, including the underlying *two*-orbital probabilities defining the molecular communications between AO and their entropy/information descriptors providing the IT measures of the overall bond multiplicity and its covalent (noise) and ionic (information flow) components. The additive (*intra*-atomic) and *non*-additive (*inter*-atomic) contributions to these molecular probability-propagation networks have been established and their role in the bonding phenomena has been examined for the illustrative case of the chemical interaction between two AO. This development is in spirit of the related studies stressing the importance of the *non*-additive information contributions for extracting the subtle changes due to the chemical bond formation [7–9, 12–14].

We have demonstrated in this and previous studies that the AO-resolved OCT using the ensempble (bond) input probabilities and recognizing the bonding/antibonding character of the orbital interactions in a molecule, reflected by the signs of the underlying CBO matrix elements, to a large extent remedies the problem of the insufficient bond differentiation observed in the AIM-resolved CTCB [9]. The *off*-diagonal conditional probabilities it generates are proportional to the quadratic (Wiberg) bond indices of the MO theory, and hence the strong inter-orbital communications correspond to strong bond-multiplicities. It also properly accounts for the increasing *populational*-decoupling of AO, when the anti-bonding MO become occupied [37]. It should be also emphasized, that the extra computation effort of this IT analysis of the molecular bonding patterns is negligible, compared to the standard computations of the molecular electronic structure, since all quantum-mechanical computations in the orbital approximation already determine the CBO data required by this generalized formulation of OCT.

The bond-weighted ensemble approach within OCT extends our understanding of the chemical bond from the complementary viewpoint of the Communication Theory. The bond-probability weighting of contributions due to separate AO inputs fully reproduces the bond differentiation in diatomic fragments of the molecule, as implied by the quadratic bond index of Wiberg, and gives rise to its resolution into the complementary IT-covalent and IT-ionic components. This has been illustrated using the two-orbital model and the representative RHF calculations for selected diatomic molecules and representative diatomic fragments in typical polyatomic systems.

The operator formulation of the probability-scattering phenomena in molecules has been given and the additive and *non*-additive contributions to the probabilities defining the molecular communication system have been identified as corresponding *input*-ensemble averages. The probability-amplitude channels defined by the CBO matrix itself have been introduced and examining the separate internal and external eigenvalue problems of molecular probability-scattering channels has been advocated.

The advantages of examining the *intra*- and *inter*-atom decoupled modes, determined by the separate internal and external eigenvalue problems of the molecular conditional probabilities, have been advocated as providing the most compact representations of the *intra*-atom promotion and *inter*-atomic delocalization/CT phenomena, respectively.

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