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Entropy/information descriptors of the chemical bond revisited

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Abstract   Information-theoretic (IT) indexing of the chemical bond multiplicities and their covalent/ionic contributions in the Orbital Communication Theory is reexamined. The molecules are interpreted as information channels in the Atomic Orbital (AO) resolution, in which the signals (probabilities) of the electron-allocation to AO events are propagated between the channel "inputs" and "outputs". The *molecular* conditional-entropy descriptor of such a probability network measures the average communication "noise" due to electron delocalization *via* the framework of all occupied molecular orbitals (MO) and provides a measure (in bits) of the bond IT-covalent component. The complementary IT-ionic bond multiplicity has been previously characterized by the channel average mutual-information (information-capacity, flow) descriptor, between the *promolecular* input and *molecular* output distributions, which reflects a degree of the deterministic character of such AO communications. The consistency of using this promolecule $\rightarrow$ molecule channel, reflecting the "history" of the bond formation process, as the stationary information network is validated using the classical cascade of the sequential molecular channels, effecting the multiple probability propagations. The "normalization" of the global bond descriptor of this channel to the sum of the molecular Shannon entropy and the information distance between the two compared AO distributions is demonstrated analytically and tested numerically. The promolecule (M^0) $\rightarrow$ molecule (M) *transition channel* is formulated in the general basis set case and its overall bond multiplicity index is determined. The *mixed channels* are examined, with different sets of the input and output events. The displacement in the density matrix reflecting the $M^0 \rightarrow M$ transition provides

Here the symbols A, $\boldsymbol{A}$, and $\mathbf{A}$ describe the scalar quantity, the row vector and a rectangular matrix, respectively.

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the AO representation of the corresponding difference between the molecular and pro-molecular density operators. Finally, the closed *communication loops* are proposed, consisting of the molecular and promolecular cascades, respectively, which generate the difference entropy/information descriptors of the system chemical bonds, between the corresponding molecular indices and their promolecular analogs, with the latter reflecting the internal communications in the isolated atoms.

1 Introduction

The Information Theory (IT) [1–7] of Fisher [1] and Shannon [2,3] has been effectively used as a unifying concept in physics [8] and in an exploration of the electronic structure of molecules M [9–11], to probe an effective state of bonded atoms relative to the corresponding free atoms defining the *promolecule* M^0 [12–19], which led to a theoretical justification of the stockholder principle of Hirshfeld [20] of partitioning the molecular electron distribution, and to detect/index the system chemical bonds [9–11,21–28]. The associated molecular displacements of the entropy/information quantities due to bond formation, relative to the *initial* (promolecular) densities and their free-atom components, have been employed as descriptors of the chemical bond. It has been argued that a network of the system chemical bonds, determined by the occupied Molecular Orbitals (MO), determines the communication channels for the probability/information delocalization throughout the whole molecular system [9–11,29–36]. It generates the communication noise in the probability propagation between atomic orbitals (AO) and gives rise to an effective flow of information contained in the electron probability distributions. The former has been linked to the molecular bond *IT-covalency*, while the latter reflects the channel *IT-ionicity*, which together index the bond overall IT-multiplicity (in bits) [6,7,9–11,29–36].

It has been demonstrated that changes in the entropic content of the electron distribution due to chemical bonds, as reflected by the corresponding information measures of Fisher [1], Shannon [2], Kullback and Leibler [4,5], can indeed be used as reliable diagnostic tools for probing the chemical bonds in a molecule [9–19]. For example, the *non*-additive part of the Fisher information in MO resolution [24] has been shown to generate the familiar Electron Localization Function (ELF) [37–39], while the associated AO-resolved measure provides the basis of the *Contra-Gradient* (CG) probe [10,11,25] of the chemical bond localization in molecular systems [10,11,25–28]. These novel IT criteria complement the familiar density difference analysis of quantum chemistry, e.g. [21]. The reconstruction of the initial densities of free atoms is effected through the polarization of the constituent atoms and the charge-transfer (CT) between them. In accordance with this prevailing perspective on the bond-formation process, it is said that the free atoms of the AP are "promoted" to their effective "valence-state" in a molecule. These flows of electrons, both inside and between

constituent atoms, modify the electron densities and the associated probability distributions relative to the corresponding free-atoms. The resulting small displacements in the molecular electronic structure, mainly in the valence shell, determine all properties of the system chemical bonds.

The promolecular reference, of the *non*-bonded atoms in their molecular positions, constitutes a natural initial stage in the bond-formation process. It has to be used to determine the difference aspects of the chemical bond, which depend upon the "history" of the bond formation. A use of the AO resolved information channels also allows to connect to the standard orbital theories and SCF MO computations of molecular electronic structure, e.g., Hartree-Fock (HF) or Kohn-Sham (KS). Thus, the molecular channel reflecting the probability scattering between the basis functions, e.g., the Gaussian expansions of AO, and its average *noise* (covalency) and information *flow* (ionicity) descriptors have been established as convenient tools for characterizing the chemical bonds in the *Orbital Communication Theory* (OCT) [10,11,30–36].

To summarize, in such an IT approach the molecule is viewed as the communication channel, in which "*signals*" conveying a message about the electron distribution among AO are transmitted from the molecular/promolecular "*source*" (input) $a = \{\chi_i \equiv i\}$, to the molecular "*receiver*" (output) $b = \{\chi_j \equiv j\}$, both consisting of all basis functions (AO) $\chi = \{\chi_k \equiv k\}$ (row vector) used to represent MO. The elements of OCT have recently been developed and the information quantities of the communication theory have been successfully used as new tools for probing the overall chemical bond multiplicities in molecules and their fragments, as well as their ionic and covalent components. It should be emphasized that the multiple (cascade) scatterings are also admissible, since each AO in the molecular system both emits and receives signals of electron allocations [12,13,40–44]. The conditional probabilities $\mathbf{P}(b|a) = \{P(j|i) \equiv P(i \rightarrow j) = P(i \wedge j)/p_i\}$ for the *single* stages in the transmission of information between AO, which generate the so called *direct* bond multiplicities, have been identified and the *multiple* scattering effects, responsible for the *indirect* bonds realized through the AO intermediaries, have been explored [40–44].

For example, in an elementary interaction between two AO located on different atoms, each contributing a single electron to form the chemical bond, the conditional entropy of the outputs-given-inputs, which reflects the average *noise* (IT-covalency) measure, reaches the highest value for the *maximum-delocalization* limit of the equal participation of the two basis functions in their occupied (bonding) combination, for which the mutual information in the two sets of events, which quantifies the channel *information capacity* (IT-ionicity), exactly vanishes. Accordingly, in the *lone-pair* (*lp*) limit, when the two AO do not mix, it is this "ionicity" descriptor which is maximized, while the IT-covalency exactly vanishes. Thus, the IT-ionicity reflects a degree of determinism (localization) in the probability scattering of the electron-assignment signals to AO in the molecular channel, with its maximum value corresponding to the conditional probabilities between AO basis functions represented by the identity matrix, $\mathbf{P}^{lp}(b|a) = \{\delta_{i,j}\} = \mathbf{I}$, when they do not effectively combine into MO. Therefore, the mutual information in the *promolecular* input and the *molecular* output of the molecular channel to a large extent reflects the *lp* (*non*-interacting) aspect of AO communications as well as some CT (*ion-pair*) contribution, which is customarily associated with the ionic (difference) bond component.

The mutual-information (difference) descriptor of the bond IT ionicity involves the promolecular input and molecular output signals, respectively, in the molecular information channel. The use of such channels as "stationary" communication systems awaits a more thorough justification. The bond components compete with one another: increase in one facet brings about a decrease in the other, complementary bond multiplicity. Indeed, the AO-coupling (delocalization, covalency) phenomenon complements the AO-decoupling (localization, lone-pair) aspect of the molecular communications. Although the latter effectively reflects the localization feature of AO communications, which is a part of the ionicity phenomenon, it remains unclear how it accounts for the *difference* (CT) aspect of the chemical bonding, between final (molecular) and initial (promolecular) information densities. This displacement aspect of the electron distributions constitutes another important ingredient of the IT ionic bond component and requires a closer examination in OCT. Of interest also are the communication channels and their entropy/information descriptors, which reflect the $M^0 \rightarrow M$ transition and connect different set of orbital events, which appear in typical SCF MO calculations of the molecular electronic structure, e.g., the primitive Gaussians, AO, MO, etc.

It is the main goal of the present analysis to reexamine in OCT the previously applied concept of the mutual-information between promolecular-input and molecular-output signals as measure of the bond ionicity, as well as to extend the concept of the molecular communication channels into the "transition" or "mixed" systems and "loops" of the elementary probability propagations. We shall also examine the relevant "normalizations" of the associated IT descriptors of such communication systems. The validity of using the *promolecular*-input and *molecular*-output probabilities in the molecular channel to determine the information capacity measure of the bond IT-ionicity will be demonstrated by constructing the sequential cascade of molecular channels which transforms the promolecular input signal into the molecular output distribution. The need of using the stationary molecular network of direct communications between AO will be then emphasized, as required by the superposition of the probability amplitudes in such sequential cascade. It will be argued that this "determinicity" descriptor of the bond ionicity contains the CT term explicitly related to the $M^0 \rightarrow M$ charge redistribution and measuring the *entropy-deficiency* (missing information, cross entropy, directed divergence) of Kullback and Leibler [4,5] in the molecule relative to its promolecule, which quantifies the information similarity between the molecular and promolecular distributions of electrons. We recall, that its density bears a strong resemblance to the familiar density difference function of quantum chemistry [9–11,21–23], between molecular and promolecular distributions of electrons, which explicitly reveals the charge rearrangement due to the chemical bond formation.

Finally, the explicit difference approach to the IT-indexing of the chemical bonds in OCT will be explored, which directly addresses changes in the nature of AO communications before and after the chemical bond formation. They are defined by the conditional probabilities of the AO events in these two "physical" limits, which are generated by the promolecular and molecular density matrices, respectively. The $M \rightarrow M^0$ "transition" channel will be introduced, the mixed channels consisting of different sets of the input and output events will be examined, and the closed loops of the molecular

and promolecular information channels (or their sequential cascades) will be proposed, which give rise to the explicit "difference" entropy/information descriptors of the system chemical bonds.

2 Multiple molecular propagations of the promolecular signal

The promolecular input probabilities $p^0 = \{p_i^0\}$ of AO in the molecular channel defined by the conditional probabilities $\mathbf{P}(b|a)$ produces the output distribution $p^* = \{p_i^*\} = p^0 \mathbf{P}(b|a)$, which generally differs from the (stationary) molecular probabilities $p = \{p_i\} = p\mathbf{P}(b|a)$. A natural question then arises about a possible existence of an *effective* molecular channel in AO resolution, $\mathbf{P}^{eff.}(b|a)$, for which the molecular output resulting from the promolecular input is assured: $p = p^0 \mathbf{P}^{eff.}(b|a)$. In this section we shall demonstrate that such a classical transformation of the initial (promolecular) distribution of electrons, in the ground-states of the separated constituent atoms, into the final effective AO occupations in the molecule can indeed be effected *via* the (infinite) sequential cascade of the molecular channels.

Consider a sequence of the molecular AO communications in the infinite cascade of molecular channels, at each stage involving all (orthonormal) basis functions χ, in which the output signal from the preceding stage constitutes the input signal of the next stage in such an indirect probability propagation among AO. In every intermediate molecular channel each AO both receives and emits the signals of the electron allocations to AO, so that all communications are propagated *via* many stages until the stationary distribution of electrons is established.

There are two possible ways to approach the information scattering in such AO-resolved cascade of the molecular channels. The *quantum-mechanical* (amplitude) cascade, which recognizes the wave aspect of the electronic distributions, propagates the probability amplitudes, while its *classical* analog constitutes a sequence of several molecular channels of the direct scattering of conditional probabilities. As demonstrated elsewhere [42,43], in the *amplitude-cascade* the multiple (n) probability scattering *via* the interference of the conditional-probability amplitudes, at each stage involving all basis functions, preserves the direct probabilities defining the molecular channel:

$$\mathbf{P}(\chi_1 \to \chi_2 \to \cdots \to \chi_{n-1} \to \chi_n) = \mathbf{P}(\chi \to \chi') \equiv \mathbf{P}(b|a). \tag{1}$$

In the *Restricted Hartree-Fock* (RHF) approximation these direct scattering probabilities for the *closed*-shell molecular configuration of $N = 2m$ electrons, which we assume for reasons of simplicity, $\mathbf{P}(b|a)$ can be expressed in terms of elements of the *Charge-and-Bond-Order* (CBO), density matrix

$$\boldsymbol{\gamma} = \langle \chi | \varphi \rangle \mathbf{n}^0 \langle \varphi | \chi \rangle \equiv N \langle \chi | \hat{D} | \chi \rangle = 2 \langle \chi | \varphi^o \rangle \langle \varphi^o | \chi \rangle \equiv 2 \langle \chi | \hat{P}_b | \chi \rangle; \tag{2a}$$

$$\begin{array}{ccccccccc}
& \mathbf{P}(b_1|a_1) & & & & \mathbf{P}(b_2|a_2) & & & \\
\boldsymbol{p}^0 \longrightarrow [a_1 \equiv \chi \longrightarrow b_1] & \longrightarrow \boldsymbol{p}^{(1)} \longrightarrow [a_2 \longrightarrow b_2] & \longrightarrow \boldsymbol{p}^{(2)} \longrightarrow
\end{array}$$

$$\begin{array}{cccc}
& & \mathbf{P}(b_n|a_n) & \\
\ldots \longrightarrow \boldsymbol{p}^{(n-1)} \longrightarrow [a_n \longrightarrow b_n \equiv \chi`] & \longrightarrow \boldsymbol{p}^{(n)}
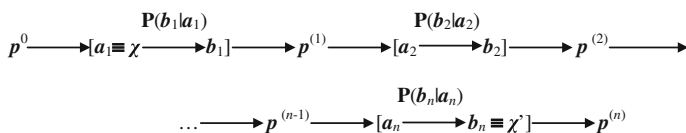\end{array}$$

Fig. 1 The sequential (classical) *probability-cascade* of n molecular channels $\{\chi_l \equiv a_l \to \chi'_l \equiv b_l\}$, each described by the direct conditional probabilities $\mathbf{P}(b_l|a_l) = \mathbf{P}(b|a)$ between all basis functions (AO), in which the promolecular signal $\boldsymbol{p}^0$ of the cascade opening stage is gradually transformed into the stationary signal $\boldsymbol{p}^{(n)}$ in its closing $(n \to \infty)$ channel

here the (diagonal) matrix $\mathbf{n}^0 = \{n_s \delta_{s,t}\}$ groups MO occupations in the molecular ground-state, $\hat{\mathrm{D}} = |\boldsymbol{\varphi}\rangle \left(\mathbf{n}^0/N\right) \langle\boldsymbol{\varphi}| = |\boldsymbol{\varphi}\rangle \mathbf{p}^{0,\varphi} \langle\boldsymbol{\varphi}|$ stands for the density operator of the associated MO ensemble, and $\hat{\mathrm{P}}_b$ denotes the projection onto the bonding (occupied) MO subspace in the molecular ground-state. The normalized probability $P(j|i) \equiv P(i \to j)$ from the quantum superposition principle [45] applied to the occupied subspace of MO then reads [30]:

$$P(i \to j) \equiv P(i \wedge j)/p_i = (2\gamma_{i,i})^{-1} \gamma_{i,j} \gamma_{j,i}, \tag{3}$$

where the joint probability of two orbital events

$$P(i \wedge j) = \gamma_{i,j} \gamma_{j,i}/(2N), \quad \sum_i P(i \wedge j) = p_j, \quad \sum_j P(i \wedge j) = p_i,$$

$$\sum_i \sum_j P(i \wedge j) = 1. \tag{4}$$

In considering the spreading of a general input signal $\boldsymbol{p}^0$ in the molecular channel one can also envisage the multiple sequence (probability-cascade) of molecular channels (shown in Fig. 1), in the limit $n \to \infty$. In this sequence the output signal of the preceding stage forms the input signal for the consecutive stage in the chain. One observes that for a general input signal, e.g., the promolecular distribution $\boldsymbol{p}^0$, any single stage in this cascade of molecular channels produces a slightly different, molecularly shifted output signal.

On one hand, each propagation stage can be expected to contribute to an increase in the noise content of the resultant AO communications, so that such a classical probability cascade may produce the fully equalized output probabilities marking the maximum uncertainty in the stationary signal resulting from this *classical*, probability cascade. On the other hand one would hope that sufficiently close to the equilibrium (molecular) distribution, when $\boldsymbol{p}^0 = \{\gamma_{a,a}^0/N\} \cong \boldsymbol{p} = \{\gamma_{a,a}/N\}$, i.e., $\{\gamma_{a,a}^0/\gamma_{a,a}\} \cong \{1(0)$ for the occupied (unoccupied) AO\} in this *Separated-Atoms-Limit* (SAL), the output signal in each consecutive step of this sequence should resemble the molecular distribution even more closely compared to the current channel input. Here, $\boldsymbol{p}^0 = \{\gamma_{a,a}^0/N\}$ and the promolecular CBO matrix, of the *non*-bonded (isolated) atoms in their molecular positions,

$$\gamma^0 = \langle \chi | \psi \rangle \, v^0 \, \langle \psi | \chi \rangle \equiv N \langle \chi | \hat{D}^0 | \chi \rangle, \tag{2b}$$

where $v^0 = \{v_a \delta_{a,b}\}$ groups the ground-state AO occupations in the promolecular reference state. The indicated mixture of the canonical AO $\psi = \{\psi_a\}$ in the promolecule determines the associated density operator defining the promolecular AO ensemble: $\hat{D}^0 = | \psi \rangle (v^0/N) \langle \psi | = | \psi \rangle \mathbf{p}^{0,\psi} \langle \psi |$.

Let us examine the representative opening stages of this multiple sequence of the probability propagation in some detail. For ith output event in the general basis set resolution $\chi = \{\chi_i\}$ of the first (closed-shell) molecular propagation one finds

$$p_i^{(1)} = \sum_k^{AO} p_k^0 P(k \to i) = \frac{1}{2N} \sum_k^{AO} \left(\frac{\gamma_{k,k}^0}{\gamma_{k,k}} \right) \gamma_{k,i} \gamma_{i,k} \cong \frac{1}{2N} \sum_k^{AO} \gamma_{i,k} \gamma_{k,i} = \frac{\gamma_{i,i}}{N} = p_i, \tag{5}$$

where we have used the idempotency of γ:

$$\gamma^2 = 2\gamma. \tag{6}$$

Hence the ratio

$$\frac{p_i^{(1)}}{p_i} = \sum_k^{SAL} \left(\frac{\gamma_{k,i} \gamma_{i,k}}{2\gamma_{i,i}} \right) \left(\frac{\gamma_{k,k}^0}{\gamma_{k,k}} \right) = \sum_k^{SAL} P(i \to k) \left(\frac{p_k^0 p_k}{p_k^2} \right)$$

$$= \sum_k^{SAL} P(i \to k) \left(\frac{p_k^g(0)}{p_k} \right)^2. \tag{7}$$

It should be compared with the initial relative input $p_i^{(0)}/p_i = \gamma_{i,i}^{(0)}/\gamma_{i,i}$. Sufficiently close to the molecular occupations of MO the geometric average of the initial and molecular probability in Eq. (7),

$$p_k^g(0) = (p_k^0 p_k)^{1/2} = (\gamma_{k,k}^0 \gamma_{k,k})^{1/2}/N, \tag{8}$$

is indeed close to the stationary molecular probability of the minimum basis set (SAL occupied), $\{p_k^g(0) = (p_k^0 p_k)^{1/2} \cong p_k\}$, and hence

$$p_i^{(1)}/p_i \cong \sum_k^{SAL} P(i \to k) \equiv P(i \to SAL) \approx 1, \tag{9}$$

since in the extended basis set only a small part of the valence electrons of the SAL electron configuration is scattered into the polarization functions.

In the second propagation stage one similarly finds:

$$p_i^{(2)} = \sum_l^{AO} p_l^{(1)} P(l \to i) \cong \sum_l^{AO} p_l P(l \to i) = \sum_l^{AO} P(i \wedge l) = p_i, \qquad (10)$$

where we have used the familiar partial normalization condition of the joint probabilities, $\sum_j^{AO} P(i \wedge j) = p_i$, which can be directly verified using Eqs. (4) and (6). Therefore,

$$\frac{p_i^{(2)}}{p_i} = \sum_l^{AO} P(i \to l) \left(\frac{p_l^{(1)} p_l}{p_l^2} \right) = \sum_l^{AO} P(i \to l) \left(\frac{p_l^g(1)}{p_l} \right)^2. \qquad (11)$$

Obviously, the new geometric average

$$p_l^g(1) = (p_l^{(1)} p_l)^{1/2} = (\gamma_{l,l}^0)^{1/4} (\gamma_{l,l})^{3/4} / N, \qquad (12)$$

is even closer to p_l than $p_l^g(0)$ and hence

$$\frac{p_i^{(2)}}{p_i} \cong \sum_l^{AO} P(i \to l) = 1. \qquad (13)$$

The same conclusion follows for each of the subsequent $n > 2$ stages,

$$p_i^{(n)} = \sum_m^{AO} p_m^{(n-1)} P(m \to i) \cong \sum_m^{AO} p_m P(m \to i) = \sum_m^{AO} P(i \wedge m) = p_i, \qquad (14)$$

for which

$$\frac{p_i^{(n)}}{p_i} = \sum_m^{AO} P(i \to m) \left(\frac{p_m^{(n-1)} p_m}{p_m^2} \right)$$
$$= \sum_l^{AO} P(i \to m) \left(\frac{p_m^g(n-1)}{p_m} \right)^2 \cong \sum_m^{AO} P(i \to m) = 1. \qquad (15)$$

One also observes that with the growing order n of this probability cascade the general geometric average

$$p_m^g(n) = (p_m^{(n)} p_m)^{1/2} = (\gamma_{m,m}^0)^{1/2^n} (\gamma_{m,m})^{(2^n-1)/2^n} / N, \qquad (16)$$

fast approaches the molecular probability $p_m = \gamma_{m,m}/N$ of the basis function χ_m.

In this way the molecular stationary distribution of electrons can be ultimately viewed as the limit of the probability/information propagation *via* the infinite (*classical*) sequential cascade of any (*non*-stationary) input signal, e.g., the promolecular
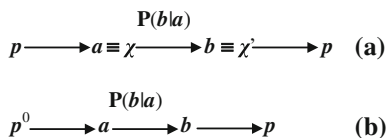
$$p \xrightarrow{\hspace{1.5cm}} a \equiv \chi \xrightarrow{\mathbf{P}(b|a)} b \equiv \chi' \xrightarrow{\hspace{1.5cm}} p \quad \textbf{(a)}$$

$$p^0 \xrightarrow{\hspace{1.5cm}} a \xrightarrow{\mathbf{P}(b|a)} b \xrightarrow{\hspace{1.5cm}} p \quad \textbf{(b)}$$

Fig. 2 The (quantum) information channels for determining the (molecular) IT-covalency (**a**) and the (difference) IT-ionicity (**b**) bond descriptors in OCT

distribution p^0 for the initial AO events with $\chi = a$, the input of the opening channel for $n = 1$, which is ultimately transformed into the stationary (molecular) distribution p for the molecular AO events $\chi' = b$, the output probabilities of the closing channel for $n \to \infty$:

$$\lim_{n \to \infty} p^0 \prod_{l=1}^{n} \mathbf{P}(b_l|a_l) \equiv p^0 \mathbf{P}^{\infty}(b|a) = p. \tag{17}$$

Notice, however, that in general $\mathbf{P}^{eff \cdot}(b|a) = \mathbf{P}^{\infty}(b|a) \neq \mathbf{P}(b|a)$; only for the *idempotent* molecular channels, for which $[\mathbf{P}(b|a)]^n = \mathbf{P}(b|a)$, $\mathbf{P}^{eff \cdot}(b|a) = \mathbf{P}(b|a)$. We have thus explicitly demonstrated that the molecular output is not inconsistent with the promolecular input in the molecular communication network, even classically, provided that the *multi*-stage (cascade) propagations are considered.

However, this *multi*-stage propagation of electronic probabilities contradicts the quantum superposition of the associated amplitudes $\mathbf{A}(a \to b) = \{A_{i \to j}\}$ [see also Eq. 1], which correctly identifies $\mathbf{P}(b|a) = \{P_{i \to j} \equiv |A_{i \to j}|^2\}$ as combining the stationary communication links between basis functions, established as a result of the *multi*-stage scattering of the probability amplitudes [42,43]. The previous use of the classically *non*-stationary probability channel $p^0 \to \mathbf{P}(b|a) \to p$ in determining the bond IT-ionicity descriptor is thus validated in this more realistic, quantum interference of the molecular probability amplitudes.

Therefore, in what follows we shall consistently apply the molecular (quantum) stationary information channel in determining both the (molecular) IT-covalency (Fig. 2a) and the (difference) IT-ionicity (Fig. 2b) indices of communications between the adopted basis functions, in accordance with the previous practice of OCT. It should be stressed that "freezing" the molecular channel for the propagation of the promolecular input signal implies preserving the molecular conditional probabilities from the bond-projected superposition principle (Eq. 3), from which the joint probabilities of Eq. 4 are subsequently derived.

The resultant cascade transformation in Eq. 17, of the promolecular AO probabilities into their molecular counterparts, complements the associated transformation of orbitals. Both these transformations are required to describe the transition between the associated density operators, from $\hat{D}^0$ to $\hat{D}$ (see Eqs. 2a, b), which determine the associated ensembles of the occupied AO and MO in the initial (promolecular) and final (molecular) ground states, respectively.

3 Bond descriptors in OCT

When basis functions χ, say AO, do not interact chemically, thus representing a collection of the isolated (separated) subsystems χ^0, their conditional probability matrix is given by the identity matrix, $\mathbf{P}(\boldsymbol{b}^0|\boldsymbol{a}^0) = \{\delta_{i,j}\} = \mathbf{I}$, since only the deterministic (diagonal) communications between these orbital events $\boldsymbol{a}^0 = \chi^0$ and $\boldsymbol{b}^0 = \chi'^0$ are then admissible. When χ are arranged into subsets grouping the AO basis functions from constituent atoms $\{X\}$, $\chi = \{\chi_X\}$, these communications between AO in the SAL assume the block diagonal form, $\mathbf{P}^0(\boldsymbol{b}|\boldsymbol{a}) = \{\mathbf{P}^0(\boldsymbol{b}_Y|\boldsymbol{a}_X)\delta_{X,Y}\}$, since only the *intra*-atomic probability scatterings are allowed in this promolecular, SAL limit, due to the *non*-vanishing blocks of the associated density matrix $\gamma^0 = \{\gamma^0_{X,X}\delta_{X,Y}\}$. It should be emphasized that the ground-state configurations of the separated atoms often involve open shells, for which the closed-shell expression of Eqs. (3) and (4) should be appropriately modified [34]. Finally, due to the formation of the chemical bonds, the *non*-vanishing *inter*-atomic blocks of AO probability propagations appear in the molecule, $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(i \to j)\} = \{\mathbf{P}(\boldsymbol{b}_Y|\boldsymbol{a}_X)\}$, reflecting the related full block structure of the CBO matrix: $\gamma = \{\gamma_{X,Y}\}$.

In the standard LCAO MO treatment the complete description of the system bond *covalency*, i.e., the common possession of the valence electrons in the molecule by the system constituent atoms (the purely *molecular* phenomenon), is provided by γ, the AO representation of the projection operator $\hat{P}_b$ onto the bonding (occupied) subspace $\varphi^o = \{\varphi_1, \varphi_2, \ldots, \varphi_m\}$ of MO (Eq. 2a). Notice, however, that its purely *inter*-atomic facet should require the *difference* approach, relative to the promolecule reference γ^0, the AO representation of the projection onto the subspace of the occupied (canonical) AO of the constituent atoms in the SAL.

In OCT this covalency aspect of all chemical bonds in the system under consideration is measured by the average communication noise (in bits) in the molecular AO channel, i.e., the entropy in $\boldsymbol{b}$ conditional on $\boldsymbol{a}$:

$$
\begin{aligned}
S(\boldsymbol{b}|\boldsymbol{a}) &= -\sum_{i\in\chi} p_i \sum_{j\in\chi'} P_{i\to j} \log_2 P_{i\to j} \equiv \sum_{i\in\chi} p_i \sum_{j\in\chi'} S(j|i) \\
&= -\sum_{i\in\chi} \sum_{j\in\chi'} P(i \wedge j) \log_2 \frac{P(i \wedge j)}{p_i}.
\end{aligned}
\tag{18}
$$

One could similarly interpret the average communication noise of the promolecular channel as reflecting the internal IT-covalency of the separated atoms:

$$
\begin{aligned}
S^0(\boldsymbol{b}|\boldsymbol{a}) &= -\sum_{i\in\chi} p_i^0 \sum_{j\in\chi'} P_{i\to j}^0 \log_2 P_{i\to j}^0 \\
&= -\sum_{i\in\chi} \sum_{j\in\chi'} P^0(i \wedge j) \log_2 \frac{P^0(i \wedge j)}{p_i^0}.
\end{aligned}
\tag{19}
$$

Therefore, the truly bonding, *inter*-atomic measure of the bond covalency in OCT is provided by the difference of these two conditional entropies:

$$\Delta S(\boldsymbol{b}|\boldsymbol{a}) = S(\boldsymbol{b}|\boldsymbol{a}) - S^0(\boldsymbol{b}|\boldsymbol{a}). \tag{20}$$

The corresponding measure of the mutual-information in the promolecular input and the molecular output similarly gives:

$$
\begin{aligned}
I\left(\boldsymbol{a}^0 : \boldsymbol{b}\right) &= \sum_{i \in \chi} \sum_{j \in \chi'} P(i \wedge j) \log_2 \frac{P(i \wedge j)}{p_i^0 p_j} \\
&= \sum_{i \in \chi} \sum_{j \in \chi'} P(i \wedge j) \log_2 \left[\frac{P(i \wedge j)}{p_i p_j} \left(\frac{p_i}{p_i^0} \right) \right] \\
&= \sum_{i \in \chi} p_i \sum_{j \in \chi'} P_{i \to j} \left[\log_2 \left(\frac{p_i}{p_i^0} \right) - \log_2 p_j + \log_2 P_{i \to j} \right] \\
&= \sum_{i \in \chi} p_i \log_2 \left(\frac{p_i}{p_i^0} \right) \left(\sum_{j \in \chi'} P_{i \to j} \right) \\
&\quad - \sum_{j \in \chi'} \left(\sum_{i \in \chi} P(i \wedge j) \right) \log_2 p_j - S(\boldsymbol{b}|\boldsymbol{a}) \\
&= \Delta S(\boldsymbol{p}|\boldsymbol{p}^0) + S(\boldsymbol{p}) - S(\boldsymbol{b}|\boldsymbol{a}), \tag{21}
\end{aligned}
$$

where we have recognized the relevant normalization conditions of the molecular probabilities. Here,

$$\Delta S(\boldsymbol{p}|\boldsymbol{p}^0) = \sum_{i \in \chi} p_i \log_2 \left(\frac{p_i}{p_i^0} \right) \tag{22}$$

stands for the cross entropy (entropy deficiency, missing information) of Kullback and Leibler [4,5], measuring the information similarity between the molecular and promolecular distributions of AO probabilities, and

$$S(\boldsymbol{p}) = - \sum_{j \in \chi'} p_j \log_2 p_j \tag{23}$$

stands for the Shannon entropy [2,3] of the molecular probabilities.

Therefore, the overall IT-bond index, which combines these entropy-covalency and information-ionicity components, gives

$$N(\boldsymbol{a}^0;\boldsymbol{b}) = S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a}^0;\boldsymbol{b}) = S(\boldsymbol{p}) + \Delta S(\boldsymbol{p}|\boldsymbol{p}^0). \tag{24}$$

This equation determines the overall "normalization" of the global bond-multiplicity index of the IT description in OCT. The first, molecular contribution measures the overall uncertainty content in the electron probability distribution, measured by the Shannon entropy of the molecular probabilities. The second, difference term reflects the CT changes due to bond formation, being measured by the information "distance" between molecular and promolecular AO probabilities. This equation thus explicitly separates the overall molecular delocalization ("covalency") measure $S(\boldsymbol{p})$ from the average entropic displacement ("ionicity") effect $\Delta S(\boldsymbol{p}|\boldsymbol{p}^0)$ due to the global displacement of electronic probabilities from the promolecular distribution.

Finally, correcting the IT-covalency for the *intra*-atomic covalency of Eq. (19) gives the associated *inter*-atomic index of all chemical bonds in the system under consideration:

$$\Delta N(\boldsymbol{a}^0; \boldsymbol{b}) = \Delta S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a}^0 : \boldsymbol{b}) = S(\boldsymbol{p}) + \Delta S(\boldsymbol{p}|\boldsymbol{p}^0) - S^0(\boldsymbol{b}|\boldsymbol{a}). \qquad (25)$$

It should be recalled that the mutual-information quantity estimated from the purely molecular channel,

$$I(\boldsymbol{a} : \boldsymbol{b}) = S(\boldsymbol{p}) - S(\boldsymbol{b}|\boldsymbol{a}), \qquad (26)$$

gives rise to the associated overall bond-multiplicity index

$$N(\boldsymbol{a}; \boldsymbol{b}) = S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a} : \boldsymbol{b}) = S(\boldsymbol{p}) \qquad (27)$$

and hence:

$$N(\boldsymbol{a}^0; \boldsymbol{b}) - N(\boldsymbol{a}; \boldsymbol{b}) = \Delta S(\boldsymbol{p}|\boldsymbol{p}^0). \qquad (28)$$

This new interpretation of the global bond-multiplicity in the IT description of electron probabilities thus identifies the CT (difference) index of the cross-entropy $\Delta S(\boldsymbol{p}|\boldsymbol{p}^0)$ as the difference between the overall IT bond-order of the molecular orbital channel for the promolecular and molecular orbital input signals, respectively. The molecular estimate of Eq. 27 thus reflects the global uncertainty contained in the AO-resolved probabilities, while its promolecular counterpart of Eq. (24) additionally contains the entropy deficiency between the two AO distributions, reflecting a displacement in the information content due to the bond formation process.

In Table 1 we have reported representative numerical results for four illustrative molecules. They have been obtained from the standard SCF MO (RHF) calculations using the minimum basis set of AO or their valence subspace, respectively. It follows from these bond indices that they do not reflect the chemical (intuitive) bond multiplicities too closely. Only the diatomic bond-order measures from the flexible input approach [34], originating from communications in the diatomic fragment of interest, provide a satisfactory representation of the accepted intuitive estimates of the chemical bond multiplicity. Nevertheless, the increasing trend exhibited by the bond multiplicities per hydrogen ligand in the full basis variant of the table,

$$N(\text{C–H}) = 0.80, \quad N(\text{N–H}) = 0.99, \quad N(\text{O–H}) = 1.38,$$

Table 1 The entropy/information indices (in bits) of the overall bond multiplicity and its covalent/ionic composition for selected small molecules

Molecule	Minimum basis set of AO					Valence AO only				
	$N(a^0;b)$	$S(b\|a)$	$I(a^0:b)$	$S(p)$	$\Delta S(p\|p^0)$	$N(a^0;b)$	$S(b\|a)$	$I(a^0:b)$	$S(p)$	$\Delta S(p\|p^0)$
CH_4	3.208	1.546	1.662	3.122	0.086	3.106	1.897	1.209	2.999	0.107
NH_3	2.981	1.201	1.780	2.934	0.047	2.823	1.480	1.343	2.764	0.059
H_2O	2.763	0.813	1.951	2.734	0.029	2.552	1.005	1.547	2.515	0.037
CO	3.246	0.716	2.530	3.224	0.022	2.938	0.993	1.944	2.908	0.030
CO_2	3.844	0.865	2.979	3.817	0.027	3.587	1.177	2.410	3.541	0.046

and a similar trend observed in the reported IT-ionicity indices $I(a^0:b)$ both reflect the growing chemical bond ionicity, due to higher electronegativity of the heavy atom. This component is seen to compete with the system IT-covalency, which exhibits a diminishing trend in this series. It should be realized, that ionicity index in OCT accounts for both the increased determinism in molecular communications, mainly due to the lone-pair/hybridization effects on the heavy atom, and the increased uncertainty (communication noise) due to electron spreading throughout these localized-bonds.

It also follows from the table, that removing the inner $1s$ shells in the valence basis set calculations gives a similar IT descrition of the chemical bonds, compared to the corresponding full-basis analog. One observes, however, a diminished ionicity (increased covalency) in the valence-only calculations compared to the full minimum-basis results. This trend should be expected, since the valence pattern misses the lone (inner) electronic pair, thus predicting more noisy (less deterministic) molecular communications between AO.

4 $M^0 \rightarrow M$ transition channel

Consider now a general set of the (orthonormal) basis functions χ, e.g., the primitive Gaussians (GTO) or their formal contractions, which are not directly related to AO. The separate SCF MO calculations for the isolated atoms $\{X^0\}$, which define the system promolecule M^0 and the molecule M itself, then determine the ground-state occupations $\mathbf{v}^0 = \{v_a\delta_{a,b}\}$ of canonical AO $\boldsymbol{\psi} = \{\psi_a\}$, and $\mathbf{n}^0 = \{n_s\delta_{s,t}\}$ of canonical MO $\boldsymbol{\varphi} = \{\varphi_s\}$, respectively. They also give the corresponding (unitary) transformations $\mathbf{C}^0 = \langle\chi|\psi\rangle$ and $\mathbf{C} = \langle\chi|\varphi\rangle$ of these basis functions into the AO and MO sets, respectively,

$$\boldsymbol{\psi} = \chi\mathbf{C}^0 \quad \text{or} \quad \boldsymbol{\psi}\mathbf{C}^{0\dagger} = \chi \quad \text{and} \quad \boldsymbol{\varphi} = \chi\mathbf{C} \quad \text{or} \quad \boldsymbol{\varphi}\mathbf{C}^\dagger = \chi, \tag{29}$$

from which one subsequently extracts the explicit "rotations" between these two sets of the "physical" states:

$$\boldsymbol{\varphi} = \left(\boldsymbol{\psi}\mathbf{C}^{0\dagger}\right)\mathbf{C} \equiv \boldsymbol{\psi}\mathbf{D} \quad \text{and} \quad \boldsymbol{\varphi}\mathbf{D}^\dagger = \boldsymbol{\varphi}(\mathbf{C}^\dagger\mathbf{C}^0) = \boldsymbol{\psi}. \tag{30}$$

The relevant expressions for the expansion coefficients in Eq. (29) in terms of the transformation $\mathbf{D} = \langle \boldsymbol{\psi} | \boldsymbol{\varphi} \rangle = \mathbf{C}^{0\dagger} \mathbf{C}$ then read:

$$\mathbf{C} = \langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle = \langle \boldsymbol{\chi} | \boldsymbol{\psi} \rangle \langle \boldsymbol{\psi} | \boldsymbol{\varphi} \rangle = \mathbf{C}^0 \mathbf{D} \quad \text{and} \quad \mathbf{C}^0 = \langle \boldsymbol{\chi} | \boldsymbol{\psi} \rangle = \langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle \langle \boldsymbol{\varphi} | \boldsymbol{\psi} \rangle = \mathbf{C} \mathbf{D}^\dagger.$$
(31)

This matrix and the associated ground-state occupations of AO and MO, in the SAL and molecule, respectively, provide the required transformation of orbitals and their occupations, which together define the two density operators involved in the $M \rightarrow M^0$ transition.

The CBO matrices of Eqs. (2a), (2b),

$$\begin{aligned}
\boldsymbol{\gamma} &= \langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle \, \mathbf{n}^0 \, \langle \boldsymbol{\varphi} | \boldsymbol{\chi} \rangle = \mathbf{C} \mathbf{n}^0 \mathbf{C}^\dagger = \mathbf{C}^0 \left(\mathbf{D} \mathbf{n}^0 \mathbf{D}^\dagger \right) \mathbf{C}^{0\dagger} \\
&= \langle \boldsymbol{\chi} | \boldsymbol{\psi} \rangle \left[\langle \boldsymbol{\psi} | \boldsymbol{\varphi} \rangle \, \mathbf{n}^0 \, \langle \boldsymbol{\varphi} | \boldsymbol{\psi} \rangle \right] \langle \boldsymbol{\psi} | \boldsymbol{\chi} \rangle \equiv \mathbf{C}^0 \boldsymbol{\gamma}^{\boldsymbol{\psi}} \mathbf{C}^{0\dagger}, \\
\boldsymbol{\gamma}^0 &= \langle \boldsymbol{\chi} | \hat{\mathrm{D}}^0 | \boldsymbol{\chi} \rangle = \langle \boldsymbol{\chi} | \boldsymbol{\psi} \rangle \, \mathbf{v}^0 \, \langle \boldsymbol{\psi} | \boldsymbol{\chi} \rangle = \mathbf{C}^0 \mathbf{v}^0 \mathbf{C}^{0\dagger} = \mathbf{C} \left(\mathbf{D}^\dagger \mathbf{v}^0 \mathbf{D} \right) \mathbf{C}^\dagger \\
&= \langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle \left[\langle \boldsymbol{\varphi} | \boldsymbol{\psi} \rangle \, \mathbf{v}^0 \, \langle \boldsymbol{\psi} | \boldsymbol{\varphi} \rangle \right] \langle \boldsymbol{\varphi} | \boldsymbol{\chi} \rangle \equiv \mathbf{C} \boldsymbol{\gamma}^{0,\boldsymbol{\varphi}} \mathbf{C}^\dagger,
\end{aligned}$$
(32)

identify the "mixed" representations of the two density operators involved in this transition: the molecular CBO matrix in AO representation, $\boldsymbol{\gamma}^{\boldsymbol{\psi}} = N \langle \boldsymbol{\psi} | \hat{\mathrm{D}} | \boldsymbol{\psi} \rangle = \mathbf{D} \mathbf{n}^0 \mathbf{D}^\dagger$, and the promolecular density matrix in MO representation, $\boldsymbol{\gamma}^{0,\boldsymbol{\varphi}} = N \langle \boldsymbol{\varphi} | \hat{\mathrm{D}}^0 | \boldsymbol{\varphi} \rangle = \mathbf{D}^\dagger \mathbf{v}^0 \mathbf{D}$. They complement their canonical (diagonal) analogs:

$$\begin{aligned}
\boldsymbol{\gamma}^{0,\boldsymbol{\psi}} &= N \langle \boldsymbol{\psi} | \hat{\mathrm{D}}^0 | \boldsymbol{\psi} \rangle = \langle \boldsymbol{\psi} | \boldsymbol{\psi} \rangle \, \mathbf{v}^0 \, \langle \boldsymbol{\psi} | \boldsymbol{\psi} \rangle = \mathbf{v}^0 \quad \text{and} \\
\boldsymbol{\gamma}^{\boldsymbol{\varphi}} &= N \langle \boldsymbol{\varphi} | \hat{\mathrm{D}} | \boldsymbol{\varphi} \rangle = \langle \boldsymbol{\varphi} | \boldsymbol{\varphi} \rangle \, \mathbf{n}^0 \, \langle \boldsymbol{\varphi} | \boldsymbol{\varphi} \rangle = \mathbf{n}^0.
\end{aligned}$$
(33)

Thus, the diagonal CBO matrix, in terms of the canonical orbitals defining the reference in question, becomes *non*-diagonal in the mixed representation of the other reference state.

Moreover, since we have explicitly demonstrated in Sect. 2 that the cascade propagation of AO communications in molecules ultimately brings the required transition of AO probabilities from their SAL ($\tilde{\boldsymbol{p}}^0 = \{\tilde{p}_a^0 = v_a/N\}$) to the molecular $\tilde{\boldsymbol{p}} = \{\tilde{p}_a = \tilde{\gamma}_{a,a}/N\}$ AO values, where $\tilde{\boldsymbol{\gamma}} = \{\tilde{\gamma}_{a,b}\} = \mathbf{D} \mathbf{n}^0 \mathbf{D}^\dagger = \boldsymbol{\gamma}^{\boldsymbol{\psi}}$, this displacement of AO occupations in the $M^0 \rightarrow M$ transition can be compactly described by the diagonal conditional-probability matrix:

$$\boldsymbol{\pi}(\tilde{\boldsymbol{p}}^0 \rightarrow \tilde{\boldsymbol{p}}) = \{ (\tilde{p}_a/\tilde{p}_a^0) \delta_{a,b} \}, \quad \tilde{\boldsymbol{p}}^0 \boldsymbol{\pi}(\tilde{\boldsymbol{p}}^0 \rightarrow \tilde{\boldsymbol{p}}) = \tilde{\boldsymbol{p}}.$$
(34)

Therefore, we now have two necessary ingredients, which fully describe in the familiar MO approximation changes in electronic AO probabilities in the course of a transition from the promolecule to molecule: the transformation matrix $\mathbf{D}$, of the

"rotation" of $\boldsymbol{\psi}$ into $\boldsymbol{\varphi}$, accounts for changes in the shapes of orbitals, while matrix $\boldsymbol{\pi}(\tilde{\boldsymbol{p}}^0 \to \tilde{\boldsymbol{p}})$ effects the associated displacements in AO occupations. These two stages describe the sequential cascade for this joint transition in the system electronic structure,

$$\tilde{\boldsymbol{p}}^0 \longrightarrow [\boldsymbol{\pi}(\tilde{\boldsymbol{p}}^0 \to \tilde{\boldsymbol{p}}) \longrightarrow \tilde{\mathbf{P}}(\boldsymbol{\psi} \to \boldsymbol{\psi}')] \longrightarrow \tilde{\boldsymbol{p}}, \tag{35}$$

where the conditional probabilities, for the *closed*-shell molecular configuration,

$$\tilde{\mathbf{P}}(\boldsymbol{\psi} \to \boldsymbol{\psi}') = \{\tilde{P}_{a \to b} \equiv \tilde{P}(a \wedge b)/\tilde{p}_a = (2\tilde{\gamma}_{a,a})^{-1}\tilde{\gamma}_{a,b}\tilde{\gamma}_{b,a}\}, \tag{36}$$

are defined in terms of elements of the density matrix $\boldsymbol{\gamma}^\psi$ of Eq. (32), which also defines the AO probabilities (occupations) $\tilde{\boldsymbol{p}}$ in the molecule. Therefore, this double cascade, with the promolecular probabilities $\tilde{\boldsymbol{p}}^0$ in its initial (promolecular) AO input ($\boldsymbol{\psi}^0$) and probabilities $\tilde{\boldsymbol{p}}$ in its final (molecular) AO output ($\boldsymbol{\psi}'$), gives rise to the resultant conditional probabilities

$$\begin{aligned}\tilde{\mathbf{P}}(\boldsymbol{\psi}^0 \to \boldsymbol{\psi}') &= \boldsymbol{\pi}(\tilde{\boldsymbol{p}}^0 \to \tilde{\boldsymbol{p}})\tilde{\mathbf{P}}(\boldsymbol{\psi} \to \boldsymbol{\psi}') \\ &= \{\tilde{P}_{a^0 \to b} \equiv \tilde{P}(a \wedge b)/\tilde{p}_a^0 = (2v_a)^{-1}\tilde{\gamma}_{a,b}\tilde{\gamma}_{b,a}\}\end{aligned} \tag{37}$$

where $\tilde{P}(a \wedge b) = (2N)^{-1}\tilde{\gamma}_{a,b}\tilde{\gamma}_{b,a}$. Using the idempotency of $\tilde{\boldsymbol{\gamma}}$, $\tilde{\boldsymbol{\gamma}}^2 = 2\tilde{\boldsymbol{\gamma}}$, one can then explicitly verify Eq. (35),

$$\begin{aligned}&\tilde{\boldsymbol{p}}^0 \tilde{\mathbf{P}}(\boldsymbol{\psi}^0 \to \boldsymbol{\psi}') \\ &= \left\{\sum_a^{\text{AO}} \tilde{p}_a^0 \tilde{P}_{a^0 \to b} = \sum_a^{\text{AO}} \tilde{P}(a \wedge b) = (2N)^{-1}\sum_a^{\text{AO}} \tilde{\gamma}_{b,a}\tilde{\gamma}_{a,b} = \tilde{\gamma}_{b,b}/N = \tilde{p}_b\right\}, \end{aligned} \tag{38}$$

and derive the modified "normalization" of probabilities determining this effective "transition" channel:

$$\sum_b^{\text{AO}} \tilde{P}_{a^0 \to b} = (2v_a)^{-1}\sum_b^{\text{AO}} \tilde{\gamma}_{a,b}\tilde{\gamma}_{b,a} = \tilde{\gamma}_{a,a}/v_a = \tilde{p}_a/\tilde{p}_a^0. \tag{39}$$

The cascade channel of Eq. 35 generates the following communication-noise index of the chemical bond covalency in OCT:

$$\begin{aligned}\tilde{S}(\boldsymbol{\psi}'|\boldsymbol{\psi}^0) &= -\sum_{a \in \boldsymbol{\psi}^0} \tilde{p}_a^0 \sum_{b \in \boldsymbol{\psi}'} \tilde{P}_{a^0 \to b} \log_2 \tilde{P}_{a^0 \to b} \\ &= -\sum_{a \in \boldsymbol{\psi}^0} \sum_{b \in \boldsymbol{\psi}'} \tilde{P}(a \wedge b) \log_2 \frac{\tilde{P}(a \wedge b)}{\tilde{p}_a^0}.\end{aligned} \tag{40}$$

For the corresponding index reflecting the mutual-information in $\tilde{\boldsymbol{p}}^0$ and $\tilde{\boldsymbol{p}}$ one obtains

$$\tilde{\boldsymbol{I}}(\boldsymbol{\psi}^0 : \boldsymbol{\psi}') = \sum_{a \in \boldsymbol{\psi}^0} \tilde{p}_a^0 \sum_{b \in \boldsymbol{\psi}'} \tilde{P}_{a^0 \to l} \log_2 \frac{\tilde{P}_{a^0 \to b}}{\tilde{p}_b} = S(\tilde{\boldsymbol{p}}) - \tilde{S}(\boldsymbol{\psi}'|\boldsymbol{\psi}^0) \qquad (41)$$

and hence the overall index reads:

$$\tilde{N}(\boldsymbol{\psi}^0; \boldsymbol{\psi}') = \tilde{S}(\boldsymbol{\psi}'|\boldsymbol{\psi}^0) + \tilde{\boldsymbol{I}}(\boldsymbol{\psi}^0 : \boldsymbol{\psi}') = S(\tilde{\boldsymbol{p}}). \qquad (42)$$

Hence, the overall IT bond index in the transition communication channel of Eq. 35 amounts to the Shannon entropy of the molecular AO probabilities.

5 Mixed channels

In molecular information networks the lists of events in the channel input and output, respectively, may differ from one another, e.g., when examining communications between different set of orbitals, e.g., $\chi \to \psi$ and $\chi \to \varphi$ or the associated channels simultaneously involving AO and MO. In OCT the "mixed" information channel $\psi \to \varphi$, from the AO (input) to MO (output), is defined by the conditional probabilities $\mathbf{P}(\psi \to \varphi) = \mathbf{P}(\varphi|\psi) = \{P_{a \to s} = P(s|a)\}$. In this section we express the mixed probabilities in terms of the corresponding expansion coefficients and density matrices and examine the entropic descriptors of the illustrative GTO $\to$ AO and AO $\to$ MO channels as well as those of the resultant communications in their sequential cascade of the bond formation process, GTO $\to$ AO $\to$ MO, which describes the communications in the double cascade $\chi \to \psi \to \varphi$ of the *stage* evolution of the primitive basis functions χ into AO and the subsequent transformation of the latter into MO. The product

$$\mathbf{P}(\chi \to \varphi|\psi) = \mathbf{P}(\chi \to \psi)\mathbf{P}(\psi \to \varphi) = \{P_{i \to s|a}\} \qquad (43)$$

thus determines the "bridge" communications from χ to φ *via* ψ intermediates [40–43]. One also observes that the "physical" conditional probabilities $\mathbf{P}(\chi \to \psi)$ and $\mathbf{P}(\psi \to \varphi)$ are defined in the "bond" subspaces of the occupied AO in M^0 and of the occupied MO in M, respectively. Indeed, the virtual AO ($a = b$) are effectively excluded as intermediates in the ground-state of the promolecule, since the amplitude of the output signal from the GTO $\to$ AO stage of the bridge cascade, i.e., the input signal for its second AO $\to$ MO stage, then identically vanishes: $A_{i \to b} = 0$. The same is true for the second stage of the cascade: the communications to the virtual MO $s = t$ give rise to the vanishing amplitudes: $A_{a \to t} = 0$.

Since in general these electron occupations may involve open shells the corresponding (weighted) bond "projections" now represent the associated density operators $\hat{\mathrm{D}}^0$ and $\hat{\mathrm{D}}$,

$$\hat{D}^0 = |\psi\rangle \left(\mathbf{v}^0/N\right) \langle\psi| \equiv |\psi\rangle \, \mathbf{p}^0 \, \langle\psi| \quad \text{and} \quad \hat{D} = |\varphi\rangle \left(\mathbf{n}^0/N\right) \langle\varphi| \equiv |\varphi\rangle \, \mathbf{p} \, \langle\varphi|,$$
(44)

which respectively define the promolecular and molecular (ground-state) *bond ensembles* with the diagonal matrices of orbital probabilities: $\mathbf{p}^0 = \{\tilde{p}^0_{a,b}\delta_{a,b}\}$ and $\mathbf{p} = \{p_s\delta_{s,t}\}$. Their χ-representations define the CBO matrices of Eq. (32):

$$\gamma^0 = N\langle\chi|\hat{D}^0|\chi\rangle \equiv N\mathbf{d}^0 \quad \text{and} \quad \gamma = N\langle\chi|\hat{D}|\chi\rangle \equiv N\mathbf{d}.$$

In accordance with the superposition principle of quantum mechanics [30,45] the communications $\chi \to \psi$, in the "bond" system of the promolecule, and $\psi \to \varphi$, in the bond system of the molecule, are proportional to the square of the corresponding (weighted) projections (scattering amplitudes) between the two sets of the orbitals involved:

$$\mathbf{A}_{\chi\to\psi} = \{A_{i\to a} = \langle i|\hat{D}^0|a\rangle\} = \langle\chi|\hat{D}^0|\psi\rangle = \langle\chi|\hat{D}^0|\chi\rangle\mathbf{C}^0 = \gamma^0\mathbf{C}^0 \text{ and}$$
$$\mathbf{A}_{\psi\to\varphi} = \{A_{a\to s} = \langle a|\hat{D}|s\rangle\} = \langle\psi|\hat{D}|\varphi\rangle = \langle\psi|\hat{D}|\psi\rangle\mathbf{D} = \gamma^\psi\mathbf{D}.$$
(45)

Their squares accordingly determine the corresponding conditional probabilities between different sets of the orbital events involved:

$$\begin{aligned}
P_{i\to a} &= \mathcal{N}_i|A_{i\to a}|^2 = \mathcal{N}_i\langle a|\hat{D}^0|i\rangle\langle i|\hat{D}^0|a\rangle \equiv \mathcal{N}_i\langle a|\hat{S}^0_i|a\rangle \\
&= \mathcal{N}_i|(\mathbf{d}^0\mathbf{C}^0)_{i,a}|^2 \equiv \mathcal{N}_i|G^0_{i,a}|^2, \\
P_{a\to s} &= |A_{a\to s}|^2 = \mathcal{N}_a\langle s|\hat{D}|a\rangle\langle a|\hat{D}|s\rangle \equiv \mathcal{N}_a\langle s|\hat{S}_a|s\rangle \\
&= \mathcal{N}_a|(\mathbf{d}\mathbf{C})_{a\to s}|^2 \equiv \mathcal{N}_a|G_{a\to s}|^2,
\end{aligned}$$
(46)

where $\hat{S}^0_i$ and $\hat{S}_a$ stand for the relevant *scattering operators*: from $|i\rangle$, in the promolecular ensemble, and from $|a\rangle$, in the molecular ensemble, respectively. The normalization constants are determined from the associated sum rules: $\Sigma_a P_{i\to a} = \Sigma_s P_{a\to s} = 1$:

$$\begin{aligned}
\mathcal{N}_i &= (\langle i|(\hat{D}^0)^2|i\rangle)^{-1} = 1/[(\mathbf{d}^0)^2]_{i,i} \quad \text{and} \\
\mathcal{N}_a &= (\langle a|\hat{D}^2|a\rangle)^{-1} = 1/[(\mathbf{d})^2]_{a,a},
\end{aligned}$$
(47)

where we have observed that in the Hilbert space spanned by the adopted set of GTO $\sum_a |a\rangle\langle a| = \sum_s |s\rangle\langle s| = 1$. This normalization then assures that summation over the complete list of the final outputs in the combined GTO → AO → MO channel recovers the probability of the preceding stage in this double cascade: $\Sigma_s P_{i\to s|a} = P_{i\to a}$.

Let us examine the entropy/information descriptors of the combined mixed channel $\chi \to \psi \to \varphi$. Using the relevant normalizations it can be demonstrated that the overall measure of the average conditional entropy (of the bond covalency) in such product (bridge) propagations is given by the sum of the noise descriptors of each stage of the double cascade:

$$S(\chi \to \varphi|\psi) = -\sum_i^{GTO}\sum_a^{AO}\sum_s^{MO} P(i \wedge s|a) \log P(i \to s|a)$$

$$= -\sum_i^{GTO}\sum_a^{AO}\sum_s^{MO} P(i \wedge a)P(a \to s)[\log P(i \to a) + \log P(a \to s)]$$

$$= -\sum_i^{GTO}\sum_a^{AO} P(i \wedge a) \log P(i \to a) - \sum_a^{AO}\sum_s^{MO} P(a \wedge s) \log P(a \to s)]$$

$$= S(\chi \to \psi) + S(\psi \to \varphi). \tag{48}$$

The corresponding expression for the channel information ionicity then reads:

$$I(\chi : \varphi|\psi) = \sum_i^{GTO}\sum_a^{AO}\sum_s^{MO} P(i \wedge s|a) \log[P(i \to s|a)/p_s]$$

$$= -S(\chi \to \varphi|\psi) - \sum_s^{MO}\sum_a^{AO} \left(\sum_i^{GTO} P(i \wedge s|a)\right) \log p_s$$

$$= -S(\chi \to \varphi|\psi) - \sum_a^{AO}\sum_s^{MO} \left(\sum_i^{GTO} P(i \wedge a)\right) P(a \to s) \log p_s$$

$$= -S(\chi \to \varphi|\psi) - \sum_s^{MO} \left(\sum_a^{AO} P(a \wedge s)\right) \log p_s$$

$$= -S(\chi \to \varphi|\psi) + S(\{p_s\}), \tag{49}$$

where $S(\{p_s\})$ denotes the Shannon entropy of the MO probabilities in the molecular ground-state ensemble. Hence, the latter also determines the overall IT bond index of this double cascade:

$$N(\chi; \varphi|\psi) = S(\chi \to \varphi|\psi) + I(\chi : \varphi|\psi) = S(\{p_s\}). \tag{50}$$

The AO resolution thus provides a natural framework to discuss and understand the bond-formation process. It fixes the ψ representation, in which $\gamma^{0,\psi} = v^0$ is diagonal, while the effective molecular occupations of AO are given by the diagonal part of a *non*-diagonal matrix γ^ψ. As we have already argued in Sect. 4, the transformation of the *non*-bonded (separated) atoms of the promolecular reference into the bonded *Atoms-in-Molecules* (AIM), which is ultimately responsible for the *inter*-atomic part of the overall chemical bond phenomenon, is described by the expansion (LCAO MO) coefficients $\mathbf{D} = \langle \psi|\varphi\rangle$ of the "rotation" of $|\psi\rangle$ (AO) into $|\varphi\rangle$ (MO). For this $M^0 \to M$ transition they also generate the relevant *displacement* of the CBO matrix in AO representation:

$$\Delta\boldsymbol{\gamma}(M^0 \to M) = \Delta\boldsymbol{\gamma}^{\psi} = \boldsymbol{\gamma}^{\psi} - \boldsymbol{\gamma}^{0,\psi} = \{\Delta\gamma_{a,b}\} = \mathbf{D}\Delta\boldsymbol{\gamma}^{\varphi}\mathbf{D}^{\dagger}$$
$$= N\langle\boldsymbol{\psi}|\hat{\mathbf{D}} - \hat{\mathbf{D}}^0|\boldsymbol{\psi}\rangle \equiv N\langle\boldsymbol{\psi}|\Delta\hat{\mathbf{D}}|\boldsymbol{\psi}\rangle = N(\mathbf{d}^{\psi} - \mathbf{d}^{0,\psi}) \equiv N\Delta\mathbf{d}^{\psi}.$$
$$\tag{51}$$

This AO $\to$ MO "transition" density matrix is thus fully described by the molecular CBO-displacement in the AO representation relative to the promolecular reference,

$$\Delta\boldsymbol{\gamma}^{\psi} = \mathbf{D}\,\mathbf{n}^0\mathbf{D}^{\dagger} - \mathbf{v}^0 \equiv \{\gamma_{a\to b} - \gamma_{a,b}^0 = \Delta\gamma_{a,b}\}. \tag{52}$$

It is related to the $\boldsymbol{\psi}$ and $\boldsymbol{\varphi}$ representations of the *difference* density operator:

$$\Delta\hat{\mathbf{D}} = \hat{\mathbf{D}} - \hat{\mathbf{D}}^0 = |\boldsymbol{\psi}\rangle\Delta\boldsymbol{\gamma}^{\psi}\langle\boldsymbol{\psi}| = |\boldsymbol{\varphi}\rangle\Delta\boldsymbol{\gamma}^{\varphi}\langle\boldsymbol{\varphi}|, \quad \Delta\boldsymbol{\gamma}^{\varphi} = \boldsymbol{\gamma}^{\varphi} - \boldsymbol{\gamma}^{0,\varphi} = \mathbf{n}^0 - \mathbf{D}^{\dagger}\mathbf{v}^0\mathbf{D}.$$
$$\tag{53}$$

This equivalence can be straightforwardly demonstrated:

$$\mathbf{D}\Delta\boldsymbol{\gamma}^{\varphi}\mathbf{D}^{\dagger} = \langle\boldsymbol{\psi}|\boldsymbol{\varphi}\rangle[\mathbf{n}^0 - \mathbf{D}^{\dagger}\mathbf{v}^0\mathbf{D}]\langle\boldsymbol{\varphi}|\boldsymbol{\psi}\rangle = N\langle\boldsymbol{\psi}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\Delta\hat{\mathbf{D}}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{\psi}\rangle$$
$$= N\langle\boldsymbol{\psi}|\Delta\hat{\mathbf{D}}|\boldsymbol{\psi}\rangle = N\mathbf{d}^{\psi} = \Delta\boldsymbol{\gamma}^{\psi}, \tag{54}$$

since $|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{\psi}\rangle = |\boldsymbol{\psi}\rangle$ in the Hilbert space spanned by the basis vectors $|\boldsymbol{\chi}\rangle$.

The elements of this difference density matrix have a transparent "geometrical" interpretation in the molecular Hilbert space,

$$\Delta\boldsymbol{\gamma}^{\psi} = \left\{\Delta\gamma_{a,b} = \left[\langle a|\,\boldsymbol{\varphi}\rangle(\mathbf{n}^0)^{1/2}\right]\left[(\mathbf{n}^0)^{1/2}\langle\boldsymbol{\varphi}|\,b\rangle\right]\right.$$
$$- \left[\langle a|\,\boldsymbol{\psi}\rangle(\mathbf{v}^0)^{1/2}\right]\left[(\mathbf{v}^0)^{1/2}\langle\boldsymbol{\psi}|b\rangle\right]$$
$$\equiv \langle\bar{a}^b|\bar{b}^b\rangle - \langle\bar{a}^0|\bar{b}^0\rangle\Big\}, \tag{55}$$

where $|\bar{a}^b\rangle$ and $|\bar{a}^0\rangle$ denote the population-weighted projections of $|\psi_a\rangle$ onto the two compared occupied subspaces: ε^b, of MO in M, and ε^0, of AO in M^0, respectively. Thus, this representative matrix element measures the displacement in the scalar product between the specified pair of AO in the occupied subspaces of the canonical orbitals determining the ground-states of the molecule and its promolecule.

Therefore, the difference CBO matrix of Eqs. (51)–(54) fully describes in the orbital approximation the displacement aspect of the system electronic structure due to the $M^0 \to M$ transition, thus monitoring the bond formation effects. Its closure relation, $\mathrm{tr}\Delta\boldsymbol{\gamma}^{\psi} = \Sigma_a\Delta\gamma_{a,a} = 0$, reflects preservation of the overall number of electrons in this isoelectronic transition, while the trace of its square, $\mathrm{tr}(\Delta\boldsymbol{\gamma}^{\psi})^2 = \Sigma_a\Sigma_b\Delta\gamma_{a,b}\Delta\gamma_{b,a} \equiv \sigma^2$, determines the dispersion σ of elements in the molecular CBO matrix in AO representation relative to their promolecular analogs.
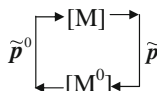
Fig. 3 The (stationary) closed loop of the molecular [M] and promolecular [M^0] information systems of Eqs. (56) and (57). When supplemented with the sign convention for the molecular and promolecular IT descriptors of the chemical bond, it generates the molecular difference indices of the system chemical bonds, relative to the promolecular reference

6 Information loop concept and the difference bond descriptors

In Sect. 2 we have demonstrated that the propagation of the promolecular AO signal $\tilde{\boldsymbol{p}}^0$ in the sequential cascade of the *molecular* channels, equivalent to the *direct* molecular scattering $\mathbf{P}(b^{\psi}|a^{\psi})$ related to γ^{ψ}, ultimately produces the molecular AO signal $\tilde{\boldsymbol{p}}$ in the channel output (Fig. 2b; see also Sect. 4):

$$\tilde{\boldsymbol{p}}^0 \to a^{\psi}\!-\!\mathbf{P}(b^{\psi}|a^{\psi}) \to b^{\psi} \to \tilde{\boldsymbol{p}} \quad \text{or} \quad \tilde{\boldsymbol{p}}^0 \to [\mathrm{M}] \to \tilde{\boldsymbol{p}}. \tag{56}$$

The same argument can be used to demonstrate that the molecular input $\tilde{\boldsymbol{p}}$ applied in the sequential cascade of the *promolecular* channels, equivalent to the direct promolecular network $\mathbf{P}^0(b^{\psi}|a^{\psi})$ derived from $\gamma^{0,\psi}$, ultimately generates the promolecular signal in its output:

$$\tilde{\boldsymbol{p}} \to a^{\psi}\!-\!\mathbf{P}^0(b^{\psi}|a^{\psi}) \to b^{\psi} \to \tilde{\boldsymbol{p}}^0 \quad \text{or} \quad \tilde{\boldsymbol{p}} \to \left[\mathrm{M}^0\right] \to \tilde{\boldsymbol{p}}^0. \tag{57}$$

These two channels can be arranged into the closed *information loop* shown in Fig. 3, in which the input of the molecular subchannel is simultaneously identified as the output of the promolecular subchannel, and the output of the partial molecular communication network simultaneously constitutes the input of the partial promolecular system. In this closed "cascade" the direction of the probability propagation in one subchannel is reversed relative to the other subchannel.

Should one adopt the convention ascribing to the molecular ("left–right") direction the "plus" sign of the associated entropy/information descriptors of Eqs. (40)–(42), and to the promolecular ("right–left") direction the "minus" sign of the corresponding *intra*-atomic indices,

$$\tilde{S}^0(\boldsymbol{\psi}^0|\boldsymbol{\psi}') = -\sum_{a\in\boldsymbol{\psi}'} \tilde{p}_a \sum_{b\in\boldsymbol{\psi}^0} \tilde{P}^0_{a\to b^0} \log_2 \tilde{P}^0_{a\to b^0}$$

$$= -\sum_{a\in\boldsymbol{\psi}'}\sum_{b\in\boldsymbol{\psi}^0} \tilde{P}^0(a\wedge b) \log_2 \frac{\tilde{P}^0(a\wedge b)}{\tilde{p}_a},$$

$$\tilde{I}^0(\boldsymbol{\psi}^0:\boldsymbol{\psi}') = \sum_{a\in\boldsymbol{\psi}'} \tilde{p}_a \sum_{b\in\boldsymbol{\psi}^0} \tilde{P}^0_{a\to b^0} \log_2 \frac{\tilde{P}^0_{a\to b^0}}{\tilde{p}^0_b} = S(\tilde{\boldsymbol{p}}^0) - \tilde{S}^0(\boldsymbol{\psi}^0|\boldsymbol{\psi}'),$$

$$\tilde{N}^0(\boldsymbol{\psi}^0;\boldsymbol{\psi}') = \tilde{S}(\boldsymbol{\psi}^0|\boldsymbol{\psi}') + \tilde{I}(\boldsymbol{\psi}^0:\boldsymbol{\psi}') = S(\tilde{\boldsymbol{p}}^0), \tag{58}$$

the resultant IT indices of such a molecular communication loop would then generate the associated difference descriptors of the chemical bonds in AO resolution:

$$\Delta \tilde{S}^{\psi} = \tilde{S}(\psi' \big| \psi^0) - \tilde{S}^0(\psi^0 \big| \psi'), \qquad \Delta \tilde{I}^{\psi} = \tilde{I}(\psi^0 : \psi') - \tilde{I}^0(\psi^0 : \psi'),$$
$$\Delta \tilde{N}^{\psi} = \tilde{N}(\psi^0; \psi') - \tilde{N}^0(\psi^0; \psi') = S(\tilde{p}) - S(\tilde{p}^0). \tag{59}$$

These displacements describe the net changes in the average communication noise and information flow in AO resolution, which accompany the chemical bond formation in the molecule. The associated overall indices are now seen to be normalized to the molecular shift in the Shannon entropy of AO probabilities relative to the promolecular reference value.

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