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Basis set dependence of molecular information channels and their entropic bond descriptors

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Abstract   Information channels from SCF MO calculations using different basis sets and their entropic bond descriptors are compared within the orbital communication theory. In this information-theoretic (IT) treatment of communications between basis functions the overall covalency and ionicity bond components reflect the average communication noise and information flow, respectively, in the resolution level specified by the adopted set of basis functions. The basis-set dependence of the orbital conditional probabilities and their entropic descriptors of the information covalency/ionicity content is explored. Compared to the minimum set χ of the occupied *atomic orbitals* of the separated constituent atoms, the extended basis sets of Gaussian orbitals and/or their formal contractions generally give rise to a higher IT-covalency and lower IT-ionicity descriptors of the system chemical bonds. In the augmented set case, $\chi^{aug.} = (\chi, \psi)$, containing the polarization function complement ψ of χ, the use of only $\chi \rightarrow \chi$ communications is advocated in a semi-quantitative chemical interpretation of the IT bond indices. The *maximum-overlap criterion* is used to transform the general (ortho-normal) extended basis ξ to its *semi*-augmented form $\widetilde{\chi}^{aug.} = \widetilde{\xi} = (\widetilde{\chi}, \widetilde{\psi})$, in which $\widetilde{\chi} \approx \chi$ and $\widetilde{\psi} \approx \psi$, which facilitates the near minimum basis set interpretation of bond descriptors and extraction of communications involving the polarization functions $\widetilde{\psi}$. A similar transformation using the minimum information distance criterion can be

Throughout the paper A, *A* and **A** denote the scalar quantity, *row*-vector and square/rectangular matrix, respectively.

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also envisaged. The effect of the atomic reduction of the molecular channels, which misses the effect of the "internal" communications (bonds) on constituent atoms, is also examined. As intuitively expected, the IT descriptors of such reduced channels are found to be less sensitive to the basis set enlargement.

1 Introduction

The information theory (IT) [1–7] has recently been effectively used as a unifying concept in physics [8] and in an exploration of the electronic structure of molecules [9–11]. The effective state of bonded atoms relative to the corresponding free atoms defining the system *promolecule* has been probed [12–20] and the IT justification [10–20] of the stockholder principle of Hirshfeld [21] for partitioning the molecular electron distribution into atomic pieces was given. The IT approach has also been applied to detect/index the system chemical bonds [9–11,22–29]. The molecular displacements of the entropy/information quantities due to bond formation, relative to the *initial* (promolecular) densities and their free-atom components, have been advocated as efficient probes of the chemical bonds [22–29].

It has also been argued that a network of the system chemical bonds, generated by the occupied molecular orbitals (MO), determines the communication channels for the probability/information delocalization throughout the whole molecular system [9–11,30–38]. It generates the communication noise in the ground-state propagation of signals of the electron allocations to basis functions of SCF MO calculations, e.g., the (orthogonalized) 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 overall bond-*covalency*, while the latter reflects the associated bond-*ionicity*. Together they index the resultant IT bond multiplicity (in bits) [6,7,9–11,30–38].

The entropic manifestations of electron redistributions due to chemical bonds, e.g., those reflected by the Fisher [1], Shannon [2] or Kullback-Leibler [4,5] measures of the information content, have been used in probing the chemical bonds of a molecule [9–20]. For example, the *non*-additive part of the Fisher information in MO resolution [25] has been shown to generate the familiar *electron localization function* (ELF) [39–41], while the associated AO-resolved measure provides the basis of the *Contra-gradient* (CG) probe [10,11,26] of the chemical bond localization in molecular systems [10,11,26–29]. These novel IT criteria complement the familiar density-difference analysis reflecting the reconstruction of the initial densities of free atoms of the promolecule through the polarization (promotion) of the constituent atoms and the charge-transfer (CT) between them.

The molecular channel is defined by the conditional probabilities between the elementary events of ascribing electrons to the basis functions in the "input" and "output"

of the communication network. It reflects the probability propagation between these elementary functions, e.g., those of the Gaussian expansion of AO. Its average *noise* (covalency, delocalization) and information *flow* (ionicity, localization) descriptors, defined by the complementary *conditional-entropy* and *mutual-information* quantities, then measure the "scattering" and "deterministic" aspects of the information system in question. They have been established as convenient tools for characterizing the chemical bonds in the *orbital communication theory* (OCT) [10,11,31–38]. 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 aspect of the chemical bond, i.e., the "history" of the bond formation. A use of the AO-resolved information channels also allows one to connect to the standard orbital interpretations and SCF LCAO MO computations of molecular electronic structure, in both the Hartree-Fock (HF) or Kohn-Sham (KS) theories.

These molecular communications can be explored within any type of the basis set, e.g., the primitive Gaussians and/or their formal contractions. Since each selection of the basis functions determines its own set of the electron-allocation events in OCT their entropy/information descriptors are by definition basis set dependent. It is the main purpose of the present work to examine this dependence in some detail and propose adequate platforms for their comparison in the chemically meaningful terms and a subsequent interpretation of the information origins of the chemical bond.

More specifically, the orbital *maximum overlap* and the *minimum information-distance* criteria can be used to transform the arbitrary basis functions to equivalent orbitals resembling AO, and to produce the associated, chemically relevant communication systems. In this numerical analysis both the fully resolved and reduced channels [9,42] of communications between the atomically-centered basis functions will be compared. The entropic descriptors are measured in bits, the unit corresponding to the basis 2 of the logarithmic measure of information.

2 Molecular conditional probabilities and their information descriptors

In OCT using the given (othonormal) basis $\chi = \{\chi_k \equiv |k\rangle\}$ the molecule is viewed as the communication channel (see Fig. 1), in which *"signals"* conveying a message about the electron distribution among these elementary functions are transmitted from the molecular *"source"* (input) $a = \{\chi_i \equiv |i\rangle\} = \chi$, to the molecular *"receiver"* (output) $b = \{\chi_j \equiv |j\rangle\} = \chi'$, both consisting of all basis functions used to represent the system MO. It should be emphasized, that the multiple (cascade) scatterings are also admissible, since each AO in the molecular system both emits and receives

Fig. 1 The information channels for determining the (molecular) IT-covalency (**a**) and the (difference) IT-ionicity (**b**) bond descriptors in OCT
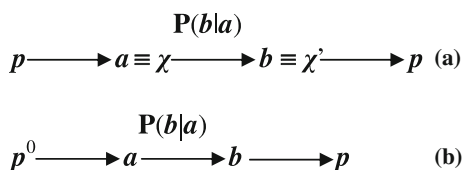
signals of electron allocations [11,43–47]. The conditional probabilities for the *direct* (*single*-stage) in such a transmission of information,

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

where p_i stands for the molecular probability of the χ_i occupancy and $P(i \wedge j)$ denotes the joint probability of observing the two orbitals in the occupied MO subspace of the molecule, then generate the so called *direct* bond multiplicities and their covalency (noise) and ionicity (deterministic) components. They have been generated [31–36] from the quatum mechanical superposition principle [48] and the *multiple* scattering effects, responsible for the *indirect* bonds realized through the AO intermediaries, have been explored [43–47,49].

In the *restricted* HF (RHF) approximation these direct-scattering probabilities $\mathbf{P}(b|a)$, for the *closed*-shell molecular configuration of $N = 2r$ electrons can be expressed in terms of elements of the (idempotent) *charge-and-bond-order* (CBO), density matrix

$$\begin{aligned} \boldsymbol{\gamma} &= \langle \boldsymbol{\chi}|\boldsymbol{\varphi}\rangle \mathbf{n}^0 \langle \boldsymbol{\varphi}|\boldsymbol{\chi}\rangle \equiv N \langle \boldsymbol{\chi}|\hat{\mathrm{D}}|\boldsymbol{\chi}\rangle \\ &= 2\langle \boldsymbol{\chi}|\boldsymbol{\varphi^o}\rangle \langle \boldsymbol{\varphi^o}|\boldsymbol{\chi}\rangle \equiv 2\langle \boldsymbol{\chi}|\hat{\mathrm{P}}_b|\boldsymbol{\chi}\rangle = \{\gamma_{i,j}\}, \quad \boldsymbol{\gamma}^2 = 2\boldsymbol{\gamma}, \end{aligned} \quad (2)$$

where the (diagonal) matrix $\mathbf{n}^0 = \{n_s \delta_{s,t}\}$ groups MO occupations in the molecular ground-state, $\hat{\mathrm{D}} = |\boldsymbol{\varphi}\rangle (\mathbf{n}^0/N)\langle \boldsymbol{\varphi}| = |\boldsymbol{\varphi}\rangle \mathbf{p}^{0,\varphi}\langle \boldsymbol{\varphi}|$ stands for the density operator of the associated MO ensemble, and $\hat{\mathrm{P}}_b = |\boldsymbol{\varphi^o}\rangle \langle \boldsymbol{\varphi^o}|$ denotes the projection onto the bonding subspace $|\boldsymbol{\varphi^o}\rangle = \{\varphi_1, \varphi_2, \ldots, \varphi_r\}$ of r occupied MO in the molecular ground-state.

The normalized probability $P(j|i) \equiv P(i \to j)$ derived from the quantum superposition principle [48] applied to the occupied subspace of MO then reads [31]:

$$\begin{aligned} P(j|i) &= \mathcal{N}_i \, |\, \langle i|\hat{\mathrm{P}}_b|j\rangle \,|^2 \\ &= \mathcal{N}_i \langle j|\hat{\mathrm{P}}_b \hat{\mathrm{P}}_i \hat{\mathrm{P}}_b|j\rangle \equiv \mathcal{N}_i \langle j|\hat{\mathrm{S}}_i|j\rangle = (2\gamma_{i,i})^{-1}\gamma_{i,j}\gamma_{j,i}, \end{aligned} \quad (3)$$

where $\hat{\mathrm{P}}_i = |i\rangle\langle i|$ and $\mathcal{N}_i = 2/\gamma_{i,i}$ stands for the normalization constant satisfying the relevant sum rule:

$$\sum_j P(j|i) = (\mathcal{N}_i/4) \sum_j \gamma_{i,j}\gamma_{j,i} = (\mathcal{N}_i/2)\gamma_{i,i} = 1. \quad (4)$$

This probability is seen to be determined by the expectation value in the *final* (variable, output) state χ_j of the scattering operator $\hat{\mathrm{S}}_i$ from the *initial* (reference, input) state χ_i:

$$\hat{\mathrm{S}}_i = \hat{\mathrm{P}}_b|i\rangle\langle i|\hat{\mathrm{P}}_b = \hat{\mathrm{P}}_b\hat{\mathrm{P}}_i\hat{\mathrm{P}}_b \equiv |i^b\rangle\langle i^b| \equiv \hat{\mathrm{P}}_i^b, \quad (5)$$

where $|i^b\rangle = \hat{\mathrm{P}}_b|i\rangle$ stands for the projection of χ_i onto the $\boldsymbol{\varphi}^o$ subspace. Hence, recognizing the molecular probabilities of basis functions $\boldsymbol{p} = \{p_i = \gamma_{i,i}/N\}$ gives the

following joint probability of simultaneously observing two functions in the molecular bond system:

$$P(i \wedge j) = p_i P(j|i) = (2N)^{-1} \gamma_{i,j} \gamma_{j,i}, \tag{6}$$

which satisfy the required partial and overall normalizations:

$$\sum_i P(i \wedge j) = p_j, \quad \sum_j P(i \wedge j) = p_i, \quad \sum_i \sum_j P(i \wedge j) = 1. \tag{7}$$

The molecular *conditional entropy* of the outputs-given-inputs in Fig. 1a,

$$
\begin{aligned}
S(\boldsymbol{b}|\boldsymbol{a}) &= -\sum_{i \in \chi} p_i \sum_{j \in \chi'} P_{i \to j} \log_2 P_{i \to j} \\
&= -\sum_{i \in \chi} \sum_{j \in \chi'} P(i \wedge j) \log_2 \frac{P(i \wedge j)}{p_i} \equiv S^{\chi},
\end{aligned} \tag{8}
$$

reflects the average *noise* (IT-covalency), while the the *mutual information* in the *promolecular* input and the *molecular* output signals of Fig. 1b,

$$
\begin{aligned}
I(\boldsymbol{a}^0 : \boldsymbol{b}) &= \sum_{i \in \chi} \sum_{j \in \chi'} P(i \wedge j) \log_2 \frac{P(i \wedge j)}{p_i^0 p_j} \\
&= \sum_{i \in \chi} \sum_{j \in \chi'} P(i \wedge j) \log_2 \left[\frac{P(i \wedge j)}{p_i p_j} \left(\frac{p_i}{p_i^0} \right) \right] \\
&= \sum_{i \in \chi} p_i \sum_{j \in \chi'} P_{i \to j} \left[\log_2 \left(\frac{p_i}{p_i^0} \right) - \log_2 p_j + \log_2 P_{i \to j} \right] \\
&= \sum_{i \in \chi} p_i \log_2 \left(\frac{p_i}{p_i^0} \right) \left(\sum_{j \in \chi'} P_{i \to j} \right) - \sum_{j \in \chi'} \left(\sum_{i \in \chi} P(i \wedge j) \right) \log_2 p_j - S(\boldsymbol{b}|\boldsymbol{a}) \\
&= \Delta S(\boldsymbol{p}|\boldsymbol{p}^0) + S(\boldsymbol{p}) - S(\boldsymbol{b}|\boldsymbol{a}),
\end{aligned} \tag{9}
$$

measures the channel IT ionicity (*information capacity*) [9–11,30–38]. In the preceding equation we have recognized the relevant normalization conditions of the molecular probabilities,

$$\Delta S(\boldsymbol{p}|\boldsymbol{p}^0) = \sum_{i \in \chi} p_i \log_2 \left(\frac{p_i}{p_i^0} \right) \tag{10}$$

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

$$S(\boldsymbol{p}) = -\sum_{j \in \boldsymbol{\chi}'} p_j \log_2 p_j \tag{11}$$

denotes the familiar Shannon entropy [2,3] of the molecular probabilities of basis functions.

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

$$N(\boldsymbol{a}^0; \boldsymbol{b}) \equiv S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a}^0 : \boldsymbol{b}) = S(\boldsymbol{p}) + \Delta S(\boldsymbol{p} \,|\, \boldsymbol{p}^0). \tag{12}$$

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 ground-state probability distribution $\boldsymbol{p}$. The second, difference term measured by the information "distance" between molecular and promolecular AO probabilities reflects the CT changes due to bond formation. Thus, Eq. (12) 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 the final electronic probability density from its initial, promolecular analog.

One also observes that the mutual-information quantity estimated from the purely molecular channel of Fig. 1a,

$$I(\boldsymbol{a} : \boldsymbol{b}) = S(\boldsymbol{p}) - S(\boldsymbol{b}|\boldsymbol{a}) \equiv I^{\chi}, \tag{13}$$

gives rise to the modified overall index

$$N(\boldsymbol{a} ; \boldsymbol{b}) \equiv S(\boldsymbol{b}|\boldsymbol{a}) + I(\boldsymbol{a} : \boldsymbol{b}) = S(\boldsymbol{p}), \tag{14}$$

and hence:

$$N(\boldsymbol{a}^0; \boldsymbol{b}) - N(\boldsymbol{a} ; \boldsymbol{b}) = \Delta S(\boldsymbol{p} \,|\, \boldsymbol{p}^0). \tag{15}$$

In Table 1 we have compared for four representative molecules the illustrative IT bond descriptors (Eqs. 8, 13 and 14) resulting from the AO-channel, generated by RHF calculations in the minimum STO-3G basis set, and from the contracted basis set channel, determined by SCF MO calculations in the extended 6-31G* basis set. These predictions demonstrate the basis set dependence of entropic bond indices: relative to the minimum basis AO description the extended set is seen to increase the communication noise (*indeterminacy*) descriptor of the bond covalency, while diminishing the complementary information-flow (*determinacy*) measure of the bond ionicity. In the next section we shall develop a common platform for comparing such seemingly diverse predictions in OCT and establish appropriate means for their the chemically meaningful interpretation.

Table 1 Basis set dependence of the entropy/information descriptors of the molecular communication channels for four illustrative molecules: RHF results in the minimum (STO-3G) and extended (6-31G*) basis sets

Molecule	STO-3G			6-31G*		
	$S(\boldsymbol{p}|\boldsymbol{p}')$	$I(\boldsymbol{p}:\boldsymbol{p}')$	$N(\boldsymbol{p};\boldsymbol{p}')$	$S(\boldsymbol{p}|\boldsymbol{p}')$	$I(\boldsymbol{p}:\boldsymbol{p}')$	$N(\boldsymbol{p};\boldsymbol{p}')$
CH_4	1.546	1.576	3.122	2.371	1.153	3.525
NH_3	1.201	1.733	2.934	2.102	1.253	3.335
H_2O	0.813	1.921	2.734	1.716	1.237	2.953
CO	0.720	2.506	3.226	1.780	0.923	2.703

The molecular input signal has been used to determine both the conditional-entropy and mutual-information data (Fig. 1a)

3 Molecular communications in the minimum and augmented bases

In the OCT exploration of the molecular bond structure one thus faces the problem of comparing the orbitally resolved information channels resulting from SCF LCAO MO calculations using different basis sets. Their conditional-entropy (IT-covalency) and information-capacity (IT-ionicity) descriptors are sensitive to the type and the number of basis functions used to represent the occupied MO subspace, which fully determines the system chemical bonds. Indeed, each basis set determines its own electron-assignment events in both the input and output of the molecular information channel. Therefore, a natural question arrises: how to compare communication systems generated in a small basis

$$\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m), \tag{16}$$

and a larger set

$$\boldsymbol{\chi}^{aug.} = [(\chi_1, \chi_2, \ldots, \chi_m), (\psi_{m+1}, \psi_{m+2}, \ldots, \psi_{m+n})] = (\boldsymbol{\chi}, \boldsymbol{\psi}), \tag{17}$$

in which m functions of the smaller basis $\boldsymbol{\chi}$ are augmented by n polarization functions $\boldsymbol{\psi}$.

For example, one can envisage a typical scenario, when $\boldsymbol{\chi}$ stands for the orthogonalized *minimum* basis of AO, which are occupied in the ground-state of separated atoms, with $\boldsymbol{\psi}$ then denoting the polarization functions required to account for the lowered symmetry of *atoms-in-molecules* (AIM) due to their molecular environment. Of interest also are the associated entropy/information descriptors of the system chemical bonds and their covalent/ionic components that these channels generate. For reasons of simplicity the closed-shell molecular ground-state is assumed throughout. The minimum basis set $\boldsymbol{\chi}$ delineates the bonding capabilities offered by the *active* AO of separated atoms, which are occupied in their respective ground-states, while the polarization complement $\boldsymbol{\psi}$ embodies all purely molecular sources of chemical bonding, for which atomic promotion to higher (ground-state unoccupied) AO is required.
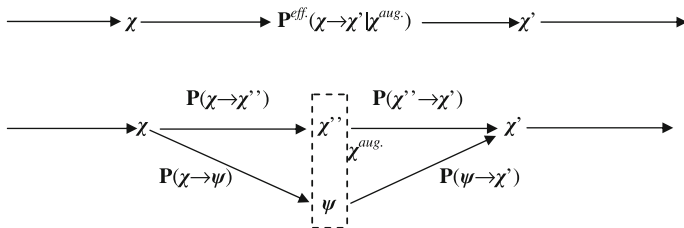
Fig. 2 Effective conditional probabilities $\mathbf{P}^{eff.}(\chi \to \chi'|\chi^{aug.})$ of communications between functions of the small basis set generated from the cascade scattering involving large (augmented) basis set $\chi^{aug.} = (\chi, \psi)$

One way to transform the communication system for a large basis set $\chi^{aug.}$ into an effective probability propagation between basis functions of a small set χ is *via* the propability propagation in the *information cascade* $\chi \to \chi^{aug.} \to \chi'$ (shown in Fig. 2). The large basis calculations generate the associated CBO matrix $\gamma^{aug.}$ (double the density matrix $\mathbf{d}^{aug.}$),

$$
\begin{aligned}
\gamma^{aug.} &= 2\langle\chi^{aug.}|\hat{\mathsf{P}}_b|\chi^{aug.}\rangle \equiv 2\mathbf{d}^{aug.} = 2\begin{bmatrix} \langle\chi|\hat{\mathsf{P}}_b|\chi\rangle & \langle\chi|\hat{\mathsf{P}}_b|\psi\rangle \\ \langle\psi|\hat{\mathsf{P}}_b|\chi\rangle & \langle\psi|\hat{\mathsf{P}}_b|\psi\rangle \end{bmatrix} \\
&\equiv \begin{bmatrix} \gamma^{aug.}_{\chi,\chi} \equiv \{\gamma_{i,j}\} & \gamma^{aug.}_{\chi,\psi} \equiv \{\gamma_{i,l}\} \\ \gamma^{aug.}_{\psi,\chi} \equiv \{\gamma_{k,j}\} & \gamma^{aug.}_{\psi,\psi} \equiv \{\gamma_{k,l}\} \end{bmatrix},
\end{aligned} \tag{18}
$$

where $\hat{\mathsf{P}}_b$ again stands for the bond projector into the subspace of the (doubly occupied) MO. Its blocks determine all elementary stages of the cascade communications of Fig. 2:

$$
\begin{aligned}
\mathbf{P}(\chi \to \chi'') &= \{P_{i \to j} = \gamma^2_{i,j}/(2\gamma_{i,i}) = d^2_{i,j}/d_{i,i}\} = \mathbf{P}(\chi'' \to \chi')^{\mathrm{T}}, \\
\mathbf{P}(\chi \to \psi) &= \{P_{i \to l} = \gamma^2_{i,l}/(2\gamma_{i,i}) = d^2_{i,l}/d_{i,i}\}, \\
\mathbf{P}(\psi \to \chi') &= \{P_{l \to j} = \gamma^2_{l,j}/(2\gamma_{l,l}) = d^2_{l,j}/d_{l,l}\}.
\end{aligned} \tag{19}
$$

These direct-scattering blocks define the associated (rectangular) matrices $\mathbf{P}(\chi \to \chi^{aug.})$ and $\mathbf{P}(\chi^{aug.} \to \chi')$ of the stage-prababilities in the cascade:

$$
\begin{aligned}
\mathbf{P}(\chi \to \chi^{aug.}) &= [\mathbf{P}(\chi \to \chi''), \mathbf{P}(\chi \to \psi)] \text{ and} \\
\mathbf{P}(\chi^{aug.} \to \chi') &= \begin{bmatrix} \mathbf{P}(\chi'' \to \chi') \\ \mathbf{P}(\psi \to \chi') \end{bmatrix},
\end{aligned} \tag{20}
$$

thus determining the effective probabilities $\mathbf{P}^{eff.}(\chi \to \chi'|\chi^{aug.})$ resulting from the cascade $\chi \to \chi^{aug.} \to \chi' \equiv \chi \to [\chi'', \psi] \to \chi'$:

$$
\begin{aligned}
\mathbf{P}^{eff\cdot}(\chi \to \chi'|\chi^{aug\cdot}) &= \mathbf{P}(\chi \to \chi^{aug\cdot})\mathbf{P}(\chi^{aug\cdot} \to \chi') \\
&= \mathbf{P}(\chi \to \chi'')\mathbf{P}(\chi'' \to \chi') + \mathbf{P}(\chi \to \psi)\mathbf{P}(\psi \to \chi') \\
&= \left\{ \sum_k P(i \to j'|k); i \in \chi, j' \in \chi', k \in \chi^{aug\cdot} \right\}. \quad (21)
\end{aligned}
$$

This information channel involves the *extended*-set of basis functions as intermediates in the effective communications between the *minimum*-set AO in the cascade input and output, which are occupied in the *promolecule* combining the free atoms placed in their molecular positions. Therefore, in this cascade information system one effectively accounts for contributions to propagations between basis functions χ and χ' originating from the polarization functions ψ. This retains the minimum-basis framework for the subsequent, chemically meaningfull interpretation of bond-multiplicities. In this way the (*implicit*) supplement ψ in the extended set of the intermediate stage of the cascade intervenes only in calculating the effective molecular communications between the (*explicit*) minimum basis AO.

Therefore, the cascade of Fig. 2 fully accounts for the effects of ψ-intermediaries in shaping the resultant communication network between the *minimum*-set of basis functions. The effective probabilities of Eq. 21 represent the parallel arrangement of all *single*-AO "bridges" $\{P(i \to j'|k)\}$, which have recently been introduced to investigate the implicit (bridge) bond orders realized *via* the AO intermediaries [43–47]. It should be observed, that the full conditional probability matrix in the large basis $\chi^{aug\cdot}$, of the direct $\chi^{aug\cdot} \to \chi^{aug\cdot'}$ communications,

$$
\mathbf{P}(\chi^{aug\cdot} \to \chi^{aug\cdot'}) = \begin{bmatrix} \mathbf{P}(\chi \to \chi') & \mathbf{P}(\chi \to \psi') \\ \mathbf{P}(\psi \to \chi') & \mathbf{P}(\psi \to \psi') \end{bmatrix}, \quad (22)
$$

combines the three blocks of Eq. 19 and the scatterings between polarization functions themselves:

$$
\mathbf{P}(\psi \to \psi') = \{P_{k \to l} = \gamma_{k,l}^2/(2\gamma_{k,k}) = d_{k,l}^2/d_{k,k}\}. \quad (23)
$$

It has been also demonstrated elsewhere [46,47,49], that applying the idempotency property of the density matrix to the superposition of amplitudes of the elementary bridge-probabilities $\{P(i \to j'|k)\}$, predicts for such a parallel propagation through the *complete* bridge $\chi^{aug\cdot}$, consisting of all (parallel) *single*-AO bridges,

$$
\mathbf{P}(\chi^{aug\cdot} \to \chi^{aug\cdot'}|\chi^{aug\cdot''}) \equiv \sum_{k''} \mathbf{P}(\chi^{aug\cdot} \to \chi^{aug\cdot'}|k'') = \mathbf{P}(\chi^{aug\cdot} \to \chi^{aug\cdot'}).
$$

$$
(24)
$$

However, the effective probabilities $\mathbf{P}^{eff\cdot}(\chi \to \chi'|\chi^{aug\cdot})$ should slightly differ from their minimum basis analogs $\mathbf{P}(\chi \to \chi')$ by additionally incorporating all purely molecular origins of chemical bonding which are not admissible in the smaller set:

$$
\mathbf{P}^{eff\cdot}(\chi \to \chi'|\chi^{aug\cdot}) \approx \mathbf{P}(\chi \to \chi'). \quad (25)
$$

In the numerical part of this work we shall compare the conditional-entropy (noise) descriptors of the overall bond covalency in these two communication networks, in order to extract terms due to these polarizational *degrees-of-freedom*.

4 Use of the maximum overlap criterion

In a general case of the extended (*non*-orthogonal) basis $\boldsymbol{\zeta}$, $\langle \boldsymbol{\zeta} | \boldsymbol{\zeta} \rangle = \mathbf{S}$, of say *Gaussian* (G) orbitals or their formal contractions, we first transform the basis functions to their symmetrically orthogonalized analogs $\boldsymbol{\xi} = \boldsymbol{\zeta} \mathbf{S}^{-1/2}$, $\langle \boldsymbol{\xi} | \boldsymbol{\xi} \rangle = \mathbf{I}$. Since in comparing the communication channels for $\boldsymbol{\xi}$ and $\boldsymbol{\chi}$ the larger set cannot be directly related to the minimum basis $\boldsymbol{\chi}$ of the free-atom occupied AO, e.g., of the STO-nG type, one should again rotate functions $\boldsymbol{\xi}$ into their optimum (orthonormal) linear combinations,

$$\widetilde{\boldsymbol{\xi}} = (\widetilde{\boldsymbol{\chi}}, \widetilde{\boldsymbol{\psi}}) = \boldsymbol{\xi}\mathbf{U} = \boldsymbol{\xi}[\mathbf{U}_\chi | \mathbf{U}_\psi] = \boldsymbol{\zeta}\mathbf{C}, \quad \mathbf{C} = \mathbf{S}^{-1/2}\mathbf{U} \quad \text{or} \quad \mathbf{U} = \mathbf{S}^{1/2}\mathbf{C}, \quad (26)$$

which generate the m-dimensional subspace $\widetilde{\boldsymbol{\chi}} = \boldsymbol{\xi}\mathbf{U}_\chi$ of orbitals exhibiting the maximum pairwise resemblance (overlap) with their minimum basis analogs:

$$\text{tr}_\chi \, \langle \boldsymbol{\chi} | \, \widetilde{\boldsymbol{\chi}} \rangle = \sum_{i=1}^{m} \langle \boldsymbol{\chi}_i | \widetilde{\boldsymbol{\chi}}_i \rangle \equiv \text{tr}\widetilde{\boldsymbol{\Delta}}_\chi = \text{maximum}. \quad (27)$$

The relevant Euler equations for this *maximum overlap criterion* (MOC) are well known, e.g. [50–52], giving the following optimum transformation in terms of the rectangular matrix $\boldsymbol{\Delta} = \langle \boldsymbol{\chi} | \boldsymbol{\xi} \rangle$ of the overlap integrals between functions in these two basis sets:

$$\widetilde{\boldsymbol{\chi}} = \boldsymbol{\xi} \left[\boldsymbol{\Delta}^{\mathrm{T}}(\boldsymbol{\Delta}\boldsymbol{\Delta}^{\mathrm{T}})^{-1/2} \right] = \boldsymbol{\xi}\mathbf{U}_\chi. \quad (28)$$

The associated representation of the bond-subspace projector of Eq. 18,

$$\boldsymbol{\gamma}^{\widetilde{\chi}} = 2\langle \widetilde{\boldsymbol{\chi}} | \hat{\mathrm{P}}_b | \widetilde{\boldsymbol{\chi}} \rangle \equiv 2\mathbf{d}^{\widetilde{\chi}} = 2\mathbf{U}_\chi^\dagger \langle \boldsymbol{\xi} | \hat{\mathrm{P}}_b | \boldsymbol{\xi} \rangle \mathbf{U}_\chi = \mathbf{U}_\chi^\dagger \boldsymbol{\gamma}^\xi \mathbf{U}_\chi \equiv \{\widetilde{\gamma}_{i,j} = 2\widetilde{d}_{i,j}\}, \quad (29)$$

then determines the effective communications between optimum functions $\widetilde{\boldsymbol{\chi}}$ in the input and output of the molecular information channel:

$$\widetilde{\mathbf{P}}(\widetilde{\boldsymbol{\chi}} \rightarrow \widetilde{\boldsymbol{\chi}}') = \{P(\widetilde{\chi}_i \rightarrow \widetilde{\chi}_j') = \widetilde{\gamma}_{i,j}^2/(2\widetilde{\gamma}_{i,i}) = \widetilde{d}_{i,j}^2/\widetilde{d}_{i,i}\}. \quad (30)$$

These communications provide the effective minimum-basis description of the probability propagations in the general extended basis. The IT bond descriptors of this channel should then be compared with those resulting from the reference basis set $\boldsymbol{\chi}$.

The remaining blocks of the full CBO matrix in the transformed basis $\widetilde{\boldsymbol{\xi}}$ read:

$$
\begin{aligned}
\boldsymbol{\gamma}^{\widetilde{\boldsymbol{\xi}}} &= 2\langle\widetilde{\boldsymbol{\xi}}|\hat{P}_b|\widetilde{\boldsymbol{\xi}}\rangle = 2\mathbf{U}^\dagger\langle\boldsymbol{\xi}|\hat{P}_b|\boldsymbol{\xi}\rangle\mathbf{U} = \mathbf{U}^\dagger\boldsymbol{\gamma}^\varphi\mathbf{U} \equiv \{\widetilde{\gamma}_{r,s} = 2\widetilde{d}_{r,s}\} \\
&= 2\begin{bmatrix} \langle\widetilde{\boldsymbol{\chi}}|\hat{P}_b|\widetilde{\boldsymbol{\chi}}\rangle & \langle\widetilde{\boldsymbol{\chi}}|\hat{P}_b|\widetilde{\boldsymbol{\psi}}\rangle \\ \langle\widetilde{\boldsymbol{\psi}}|\hat{P}_b|\widetilde{\boldsymbol{\chi}}\rangle & \langle\widetilde{\boldsymbol{\psi}}|\hat{P}_b|\widetilde{\boldsymbol{\psi}}\rangle \end{bmatrix} \equiv \begin{bmatrix} \boldsymbol{\gamma}^{\widetilde{\boldsymbol{\xi}}}_{\widetilde{\boldsymbol{\chi}},\widetilde{\boldsymbol{\chi}}} \equiv \boldsymbol{\gamma}^{\widetilde{\boldsymbol{\chi}}} & \boldsymbol{\gamma}^{\widetilde{\boldsymbol{\xi}}}_{\widetilde{\boldsymbol{\chi}},\widetilde{\boldsymbol{\psi}}} \equiv \{\widetilde{\gamma}_{i,l}\} \\ \boldsymbol{\gamma}^{\widetilde{\boldsymbol{\xi}}}_{\widetilde{\boldsymbol{\psi}},\widetilde{\boldsymbol{\chi}}} \equiv \{\widetilde{\gamma}_{k,j}\} & \boldsymbol{\gamma}^{\widetilde{\boldsymbol{\xi}}}_{\widetilde{\boldsymbol{\psi}},\widetilde{\boldsymbol{\psi}}} \equiv \{\widetilde{\gamma}_{k,l}\} \end{bmatrix}.
\end{aligned} \quad (31)
$$

They in turn determine the "external" communications $\widetilde{\boldsymbol{\chi}} \to \widetilde{\boldsymbol{\psi}}'$, $\widetilde{\boldsymbol{\psi}} \to \widetilde{\boldsymbol{\chi}}'$ and $\widetilde{\boldsymbol{\psi}} \to \widetilde{\boldsymbol{\psi}}'$ in the MOC-transformed $\widetilde{\boldsymbol{\xi}}$ channel,

$$
\begin{aligned}
\widetilde{\mathbf{P}}(\widetilde{\boldsymbol{\chi}} \to \widetilde{\boldsymbol{\psi}}') &= \{P(\widetilde{\chi}_i \to \widetilde{\psi}_l') = \widetilde{\gamma}_{i,l}^2/(2\widetilde{\gamma}_{i,i})\}, \\
\widetilde{\mathbf{P}}(\widetilde{\boldsymbol{\psi}} \to \widetilde{\boldsymbol{\chi}}') &= \{P(\widetilde{\psi}_k \to \widetilde{\chi}_j') = \widetilde{\gamma}_{k,j}^2/(2\widetilde{\gamma}_{k,k})\}, \\
\widetilde{\mathbf{P}}(\widetilde{\boldsymbol{\psi}} \to \widetilde{\boldsymbol{\psi}}') &= \{P(\widetilde{\psi}_k \to \widetilde{\psi}_l') = \widetilde{\gamma}_{k,l}^2/(2\widetilde{\gamma}_{k,k})\},
\end{aligned}
$$

which generate the associated polarization/promotion contributions to the system IT bond indices.

To summarize, in a general case of the (orthogonalized) basis set $\boldsymbol{\xi}$, in which the minimum set $\boldsymbol{\chi}$ is not directly augmented by its complement $\boldsymbol{\psi}$ of polarization functions, one first interprets the molecular CBO/probability data in terms of the equivalent, *semi*-augmented basis $\widetilde{\boldsymbol{\xi}}$, in which the subspaces $\widetilde{\boldsymbol{\chi}}$ (strongly resembling $\boldsymbol{\chi}$) and hence also $\widetilde{\boldsymbol{\psi}}$ (approximating $\boldsymbol{\psi}$) have been established using MOC. This procedure also offers some interpretative advantages, by separating the near minimum-basis (internal) and the remaining polarization (external) communication links and generating their associated IT bond multiplicities due to polarization (promotion) in bonded atoms. A more detailed analysis of chemical implications of these "external" communications will be the subject of a separate study. The minimum-basis sources of the chemical bond, due to the internal communications in $\widetilde{\boldsymbol{\chi}}$, are then determined by the diagonal block $\boldsymbol{\gamma}^{\widetilde{\boldsymbol{\chi}}}$ of the transformed CBO data [Eq. (31)].

Clearly, this MOC procedure can be also regarded as generating the optimum augmented set $\widetilde{\boldsymbol{\chi}}^{aug\cdot} = \widetilde{\boldsymbol{\xi}} = (\widetilde{\boldsymbol{\chi}}, \widetilde{\boldsymbol{\psi}})$ from the initial extended set $\boldsymbol{\xi}$. Indeed, the MOC procedure by determining the optimum subspace $\widetilde{\boldsymbol{\chi}}$ also defines, implicitly, the complementary subspace $\widetilde{\boldsymbol{\psi}}$, i.e., the best polarization/diffuse complement of $\widetilde{\boldsymbol{\chi}}$, which can be derived within the given extended basis $\boldsymbol{\xi}$.

The performance of this criterion and the quality of the derived MOC fits can be tested by first comparing some elementary chemical descriptors of the molecular electronic structure from standard RHF calculations, e.g., the Wiberg [53] bond-orders

$$
W_{\text{A}-\text{B}} = \sum_{i\in\text{A}}\sum_{j\in\text{B}}(\gamma_{i,j})^2 \quad (32)
$$

(see Table 2), in each (ortho-normal) basis set considered. In these numerical tests performed for illustrative molecules the reference minimum basis set $\boldsymbol{\chi}$ contains the

Table 2 Wiberg [53] bond-orders $\{W_{A-B}\}$ for illustrative molecules: RHF results in the extended (ξ) and minimum (χ and $\widetilde{\chi}$) basis sets

Molecule	A—B	W_{A-B}^{ξ}	W_{A-B}^{χ}	$W_{A-B}^{\widetilde{\chi}}$	Molecule	A—B	W_{A-B}^{ξ}	W_{A-B}^{χ}	$W_{A-B}^{\widetilde{\chi}}$
H_2	H—H	1.000	1.000	1.000	C_2H_6	C—C	1.099	1.024	1.027
HF	H—F	1.049	0.977	0.886		C—H	0.971	0.991	0.990
F_2	F—F	1.214	1.000	1.000	C_2H_2	C—C	3.083	3.003	3.001
NaCl	Na—Cl	1.122	1.049	0.834		C—H	0.939	0.992	0.981
H_2O	O—H	1.028	0.983	0.943	C_6H_6	o C—C	1.488	1.444	1.444
CO_2	C—O	2.348	1.983	1.942		m C—C	0.059	0.001	0.001
NH_3	N—H	1.007	0.989	0.977		p C—C	0.111	0.116	0.115
CH_4	C—H	0.989	0.998	0.998		C— H	0.933	0.981	0.980

STO-3G expansions, to which the general extended set ξ of the 6-31G** type is then MOC adjusted to determine the $\widetilde{\chi}$ subset itself.

5 Atomic reductions and diatomic subchannels

The channel reduction [9,42], by combining contributions due to group of orbitals, can be used to separate the *intra*-atomic bond contributions from the truly bonding, *inter*-atomic ones. For example, adding molecular probabilities due to orbitals $\chi_X = \{\chi_j, j \in X\}$ from atom X allows one to generate the corresponding condensed probability data $\{P_X = \sum_{x \in X} p_x\}$ for the atoms as whole building blocks in a molecule. This *atomic reduction* can be performed in the *input* and *output* of the molecular communication system. As a result the constituent AIM, acting as whole units, then determine the admissible emitters and receivers of the electron assignment signals in the molecular communication system. Such AIM-resolved description, which we call the *atomic-frame* of the MO channel, can be generated for any adopted basis set. The question then arises, how sensitive are the entropy/information descriptors of the scattering and deterministic aspects of the information propagation in such atomic channels to the basis set quality. It should be realized, that the given *deterministic* communication X → Y, with $P(Y|X) = 1$, becomes "noisy" in the underlying orbital resolution $\{\chi_X \to \chi_Y\}$, with communications defined by $\mathbf{P}(\chi_Y|\chi_X)$, where $\sum_{x \in X} \sum_{y \in Y} P(y|x) = 1$. The AIM *input*-reduction scheme thus determines the group *sources* of the the chemical bonds which are counted by the accompanying atomic *output*-reduction. In this section we briefly summarize the reduction process of conditional probabilities of the original (fully resolved) communication channel in the given basis set $\chi = \{\chi_k \equiv k\}$ to the associated atomic-frame.

We recall that these elementary communication links have been expressed as the expectation values in the *output*-orbital $|j\rangle$ of the scattering operator from the *input*-orbital $|i\rangle$ (Eq. 5) representing its bond-subspace projector $\hat{S}_i = |i^b\rangle\langle i^b| = \hat{P}_i^b$,

$$P_{i \to j} = \mathcal{N}_i \langle j^b | \hat{P}_i^b | j^b \rangle = \mathcal{N}_i \gamma_{i,j} \gamma_{j,i}/4 = (2\gamma_{i,i})^{-1} \gamma_{i,j} \gamma_{j,i}. \qquad (33)$$

The atomic input-reduction for atom A thus involves the summation over the input orbitals $|i\rangle \in \chi_A$, which defines the scattering operator in the molecular bonding subspace from this atomic unit as a whole:

$$\hat{S}_A = \sum_{i \in A} |i^b\rangle\langle i^b| = \hat{P}_A^b, \tag{34}$$

and the associated input-condensed probabilities:

$$P(j|A) = P_{A \to j} = \mathcal{N}_A \langle j^b | \hat{P}_A^b | j^b \rangle = \mathcal{N}_A \sum_{i \in A} \gamma_{j,i} \gamma_{i,j}/4$$
$$= (2N_A)^{-1} \sum_{i \in A} \gamma_{j,i} \gamma_{i,j}, \tag{35}$$

where $N_A = \sum_{i \in A} \gamma_{i,i}$ stands for the effective electron population of atom A, and the normalization constant $\mathcal{N}_A = 2/N_A$ satisfies the condition of Eq. 4:

$$\sum_j P(j|A) = \sum_A (\mathcal{N}_A/4) \sum_{i \in A} \gamma_{j,i} \gamma_{i,j} = 1. \tag{36}$$

The corresponding output-reduction for atom B involves straightforward summations of the canonical probabilities of Eq. 33 over the output orbitals $|j\rangle \in \chi_B$:

$$P(B|i) = P_{i \to B} = \mathcal{N}_i \langle j^b | \hat{P}_i^b | j^b \rangle = (2\gamma_{i,i})^{-1} \sum_{j \in B} \gamma_{j,i} \gamma_{i,j},$$
$$\sum_B P(B|i) = \sum_j P(j|i) = 1. \tag{37}$$

Finally, the simultaneous input and output atomic reductions of the MO channel, which allows one to determine the IT indices describing the global atomic sources of the *inter*-atomic bonds, involve both these condensations of the fully resolved conditional probabilities:

$$P(B|A) = P_{A \to B} = \mathcal{N}_A \sum_{j \in B} \langle j^b | \hat{P}_A^b | j^b \rangle$$
$$= (2N_A)^{-1} \sum_{i \in A} \sum_{j \in B} \gamma_{j,i} \gamma_{i,j}, \quad \sum_B P(B|A) = 1. \tag{38}$$

They define the associated conditional-entropy (average "noise") descriptor

$$S^\chi(AB) = -\sum_{X \in AB} P_X \sum_{Y \in AB} P(Y|X) \log P(Y|X). \tag{39}$$

It should be emphasized that this totally reduced channel misses some contributions to these interatomic IT connectivities [9,42], since in the reduced input the atoms are

treated as whole subsystems thus missing the intra-atomic bond sources due to the AIM polarization/ promotion. Moreover, since in polyatomics $P_A + P_B < 1$, these diatomic descriptors have to be eventually renormalized to ensure that the diatomic input signal is complete.

It has been argued elsewhere [36] that by focusing on communications $\mathbf{P}(\boldsymbol{\chi}_{XY}|\boldsymbol{\chi}_{XY})$ in diatomic fragments XY of the molecule, between their constituent orbitals $\boldsymbol{\chi}_{XY} = (\boldsymbol{\chi}_X, \boldsymbol{\chi}_Y)$, one can derive useful entropy/information indices of the localized bond X—Y, e.g.,

$$
\begin{aligned}
S(\boldsymbol{\chi}_{XY}|\boldsymbol{\chi}_{XY}) \equiv S^{\chi}_{XY} &= - \sum_{i \in \chi_{XY}} p_i \sum_{j \in \chi_{XY}} P_{i \to j} \log_2 P_{i \to j} \\
&= - \sum_{Z \in (X,Y)} \sum_{i \in \chi_Z} p_i \sum_{j \in \chi_Z} P_{i \to j} \log_2 P_{i \to j} \\
&\quad - \left[\sum_{i \in \chi_X} p_i \sum_{j \in \chi_Y} P_{i \to j} \log_2 P_{i \to j} \right. \\
&\quad \left. + \sum_{i \in \chi_Y} p_i \sum_{j \in \chi_X} P_{i \to j} \log_2 P_{i \to j} \right] \\
&\equiv S^{\chi}_{XY}(int.) + S^{\chi}_{XY}(ext.).
\end{aligned}
\tag{40}
$$

Here, the internal, $S^{\chi}_{XY}(int.)$, and external, $S^{\chi}_{XY}(ext.)$, contributions reflect the communication noise generated by the intra- and inter-atomic communication in diatomic fragment XY. They respectively involve the atom diagonal $\{\mathbf{P}(\boldsymbol{\chi}_X|\boldsymbol{\chi}_X), \mathbf{P}(\boldsymbol{\chi}_Y|\boldsymbol{\chi}_Y)\}$ and off-diagonal $\{\mathbf{P}(\boldsymbol{\chi}_Y|\boldsymbol{\chi}_X), \mathbf{P}(\boldsymbol{\chi}_X|\boldsymbol{\chi}_Y)\}$ probability scatterings. The latter generate the conditional entropies which can be expected to be more directly related to the Wiberg bond multiplicities of the SCF MO theory.

6 Maximum information-similarity criterion

In determining the optimum transformation of a general (orthonortmal) basis set $\boldsymbol{\xi}$ of Section 4 to the approximate augmented set $\widetilde{\boldsymbol{\xi}} = (\widetilde{\boldsymbol{\chi}}, \widetilde{\boldsymbol{\psi}})$, in which the subspace $\widetilde{\boldsymbol{\chi}} = \boldsymbol{\xi} \mathbf{U}_{\chi}$ is to resemble as much as possible the minimum set $\boldsymbol{\chi}$ of the occupied AO of the separated constituent atoms, one can also use the relevant information criteria. For example, one can require the minimum entropy deficiency (information distance) [4,5] between the electron probability distributions $p^0(\boldsymbol{r})$ and $\widetilde{p}^0(\boldsymbol{r})$ generated by the atomically occupied basis sets $\boldsymbol{\chi}$ and $\widetilde{\boldsymbol{\chi}}$, respectively,

$$
\Delta S[\widetilde{p}^0 | p] = \int \widetilde{p}^0(\boldsymbol{r}) \log \frac{\widetilde{p}^0(\boldsymbol{r})}{p^0(\boldsymbol{r})} d\boldsymbol{r} = \text{minimum}.
\tag{41}
$$

The reference (orthonormal) AO $\boldsymbol{\chi} = \boldsymbol{\xi} \mathbf{F}$ and their ground-state occupations $\boldsymbol{v}^0 = \{v_i \delta_{i,j}\}$ result from the separate SCF MO calculations on the (isolated) constituent atoms. They generate the associated atomic (canonical) CBO matrix, $\boldsymbol{\gamma}^0 = \langle \boldsymbol{\xi} | \boldsymbol{\chi} \rangle \boldsymbol{v}^0 \langle \boldsymbol{\chi} | \boldsymbol{\xi} \rangle \equiv N \langle \boldsymbol{\xi} | \hat{\mathrm{D}}^0 | \boldsymbol{\xi} \rangle = \mathbf{F} \boldsymbol{v}^0 \mathbf{F}^{\dagger}$, the associated promolecular electron density

$$\rho^0(r) = \chi(r)v^0\chi^\dagger(r) = \xi(r)\gamma^0\xi^\dagger(r)$$
$$= \sum_{r,s} \gamma^0_{r,s}\xi^*_s(r)\xi_r(r) \equiv \sum_{r,s} \gamma^0_{r,s}\Omega_{s,r}(r) = \text{tr}[\gamma^0\boldsymbol{\Omega}(r)] \qquad (42)$$

and its probability distribution (shape-factor) $p^0(r) = \rho^0(r)/N$. Attributing the same occupations to the approximate orbitals $\widetilde{\chi}$ then gives the corresponding variational densities:

$$\widetilde{\rho}^0(r) = N\widetilde{p}^0(r) = \widetilde{\chi}(r)v^0\widetilde{\chi}^\dagger(r) = \xi(r)(\mathbf{U}_\chi v^0\mathbf{U}^\dagger_\chi)\xi^\dagger(r) \equiv \xi(r)\widetilde{\gamma}^0\xi^\dagger(r)$$
$$= \sum_{r,s} \widetilde{\gamma}^0_{r,s}\Omega_{s,r}(r) = \text{tr}[\widetilde{\gamma}^0\boldsymbol{\Omega}(r)]. \qquad (43)$$

One further observes that for the nonbonded atoms $\{X^0\}$ of the promolecule $M^0 = (X^0|Y^0|\ldots)$ both CBO matrices assume the block-diagonal forms $\gamma^0 = \{\gamma^0_X\delta_{X,Y}\}$ and $\widetilde{\gamma}^0 = \{\widetilde{\gamma}^0_X\delta_{X,Y}\}$ in terms of the atomically arranged basis set $\xi = \{\xi_X\}$ with $\mathbf{U}_\chi = \{\mathbf{U}_X\}$ determining $\{\widetilde{\chi}_X = \xi_X\mathbf{U}_X\}$. Here, ξ_X combines the basis functions contributed by atom X, $\mathbf{U}_X$ groups the relevant expansion coefficients determining its canonical AO. In this arrangement the basis function distributions $\boldsymbol{\Omega}(r) = \{\Omega_{r,s}(r)\} = \{\boldsymbol{\Omega}_{X,Y}(r) = \xi^\dagger_X(r)\xi_Y(r)\}$. Therefore, the above promolecular traces are given by the sum of the associated atomic traces,

$$\rho^0(r) = \sum_X \text{tr}[\gamma^0_X\boldsymbol{\Omega}_{X,X}(r)] = \sum_X \rho^0_X(r),$$
$$\widetilde{\rho}^0(r) = \sum_X \text{tr}[\widetilde{\gamma}^0_X\boldsymbol{\Omega}_{X,X}(r)] = \sum_X \widetilde{\rho}^0_X(r), \qquad (44)$$

where the promolecular densities of nonbonded atoms read: $\rho^0_X(r) = \sum_{x\in X} \nu_x|\chi_x(r)|^2 \equiv N p^0_X(r)$ and $\widetilde{\rho}^0_X(r) \equiv N\widetilde{p}^0_X(r) = \sum_{x\in X} \nu_x|\widetilde{\chi}_x(r)|^2 \equiv \sum_{x\in X} \widetilde{\rho}^0_x(r)$.

It should be emphasized that in the optimum basis augmentation scheme we are actually interested in the maximum similarity of each atom $\widetilde{X}^0$, described by $\widetilde{\gamma}^0_X$, to its reference X^0, described by γ^0_X, so that the overall information similarity criterion of Eq. (41) should be replaced by its atomically resolved analog:

$$\Delta S[\widetilde{X}^0|X^0] = \sum_X \int \widetilde{p}^0_X(r)\log\frac{\widetilde{p}^0_X(r)}{p^0_X(r)}dr$$
$$= \sum_X \Delta S[\widetilde{p}^0_X|p^0_X] = \frac{1}{N}\sum_X \Delta S[\widetilde{\rho}^0_X|\rho^0_X] = \text{minimum}, \qquad (45)$$

$$\text{or} \quad \Delta S[\widetilde{\rho}^0_X|\rho^0_X] = \text{minimum}, \qquad X = A, B, \ldots \qquad (46)$$

In the variational principle the additive functional $\Delta S[\widetilde{X}^0|X^0]$ must be supplemented by the associated (canonical) constraints enforcing the prescribed AO occupations and/or orbital normalization.

Should the whole basis $\boldsymbol{\xi}$ be used in SCF MO calculations on the ground-states of the system separated (molecularly placed) atoms, giving the reference orbitals $\chi_X = \boldsymbol{\xi} \mathbf{U}_X$, as in determining the *counterpoise correction* to molecular interactions [54], then the optimum augmentation scheme should exactly recover the minimum basis set and the orbital/atomic densities it generates. Indeed, including in this exact augmentation scheme the relevant constraints of the prescribed atomic numbers of electrons, $N_X^0 = \int \widetilde{\rho}_X^0(\boldsymbol{r}) d\boldsymbol{r} = \sum_{x \in X} \nu_x$, in the atomically resolved variational principle of Eq. 45,

$$\delta \left(\sum_X \Delta S[\widetilde{\rho}_X^0 | \rho_X^0] - \sum_X \lambda_X \int \widetilde{\rho}_X^0(\boldsymbol{r}) d\boldsymbol{r} \right) \equiv \delta \Theta[\{\widetilde{\rho}_X^0\}] = 0. \tag{47}$$

then reconstructs these densities through the corresponding Euler equations:

$$\frac{\delta \Theta[\{\widetilde{\rho}_X^0\}]}{\delta \widetilde{\rho}_X^0(\boldsymbol{r})} = \ln \frac{\widetilde{\rho}_X^0(\boldsymbol{r})}{\rho_X^0(\boldsymbol{r})} + 1 - \lambda_X \equiv f_X(\boldsymbol{r}) - \lambda_X \equiv \ln \frac{\widetilde{\rho}_X^0(\boldsymbol{r})}{G_X \rho_X^0(\boldsymbol{r})} = 0. \tag{48}$$

Indeed, applying the corresponding constraint value gives $G_X = 1$ and hence $\widetilde{\rho}_X^0(\boldsymbol{r}) = \rho_X^0(\boldsymbol{r})$.

Clearly, by adopting different bases $\{\widetilde{\boldsymbol{\xi}}_X\}$ and $\{\boldsymbol{\xi}_X\}$ in the atomic and molecular calculations, respectively, i.e., $\{\chi_X = \widetilde{\boldsymbol{\xi}}_X \mathbf{U}_X\}$ and $\{\widetilde{\chi}_X = \boldsymbol{\xi} \mathbf{U}_X\}$, can only produce $\widetilde{\chi}$ resembling χ: $\{\widetilde{\chi}_X \approx \chi_X\}$. The independent variational principles for determining the minimum cross-entropies $\{\Delta S[\widetilde{\rho}_X^0 | \rho_X^0], X = A, B, \ldots\}$ for the optimum expansion coefficients $\mathbf{U}_X = (\boldsymbol{U}_x | \boldsymbol{U}_{x'} | \ldots)$ of $\widetilde{\rho}_X^0(\boldsymbol{r}) = \widetilde{\rho}_X^0[\mathbf{U}_X; \boldsymbol{r}]$ (Eq. 44) of the approximate (canonical) AO should include the relevant normalization constraints of orbitals $\widetilde{\chi}_X = \{\widetilde{\chi}_x\}$ or their electron densities $\widetilde{\boldsymbol{\rho}}_X = \{\widetilde{\rho}_x^0(\boldsymbol{r})\}$,

$$\int |\widetilde{\chi}_x(\boldsymbol{r})|^2 d\boldsymbol{r} \equiv \langle \widetilde{x} | \widetilde{x} \rangle = 1 = \boldsymbol{U}_x^\dagger \boldsymbol{U}_x \quad \text{or}$$

$$\int \widetilde{\rho}_x^0(\boldsymbol{r}) d\boldsymbol{r} = \nu_x \int |\widetilde{\chi}_x(\boldsymbol{r})|^2 d\boldsymbol{r} = \nu_x, \quad x \in X, \tag{49}$$

$$\delta \{\Delta S[\widetilde{\rho}_X^0 | \rho_X^0] - \sum_{x \in X} \mu_x \int \widetilde{\rho}_x^0(\boldsymbol{r}) d\boldsymbol{r}\} = 0. \tag{50}$$

The associated Euler equations for the optimum unknowns $\boldsymbol{U}_x = \{U_{r,x}\}$ then assume the form of the eigenvalue problem of the Hermitian matrix $\mathbf{H}^X = \int f_X(\boldsymbol{r}) \boldsymbol{\Omega}(\boldsymbol{r}) d\boldsymbol{r}$:

$$\mathbf{H}^X \boldsymbol{U}_x = \mu_x \boldsymbol{U}_x, \quad x \in X, \tag{51}$$

and hence:

$$\mu_x = \frac{\delta \Delta S[\widetilde{\rho}_X^0 | \rho_X^0]}{\delta \nu_x} \bigg|_{\widetilde{\chi}_x} = \boldsymbol{U}_x^\dagger \mathbf{H}^X \boldsymbol{U}_x. \tag{52}$$

7 Numerical calculations

The adopted (reference) minimum set χ is the familiar STO-3G basis used in GAMESS system, while the representative extended set ξ is the split-valence contracted basis 6-31G** also involving a single shell of polarization functions on each element. The experimental geometries have been used throughout. The results in the extended set have been subsequently transcribed into the effective minimum set $\widetilde{\chi}$, by using the maximum overlap criterion of Eqs. (27) and (28).

The reported Wiberg indices of bond multiplicities in Table 2 are seen to reflect the accepted chemical intuition quite well in all basis-set variants reported, but the two minimum sets are somewhat superior in recognizing the accepted values of the single, multiple and "half" bonds of the textbook chemistry. For example, as in the Hückel approximation, these basis sets predict practically 3/2 bond between two *ortho*-carbons, vanishing *direct* chemical bonding between the two *meta*-carbons, and approximately 0.1 cross-ring bond between *para*-carbons in benzene. One also detects a slight basis-set dependence of these bond-orders, particularly for CO_2 and F_2.

A comparison of Table 3 indicates that the MOC of Eq. (27) is indeed quite efficient in extracting the effective minimum-basis (*chemical*) interpretation from the extended basis results. It should also be noticed, that it is the entropy-covalency descriptor S which exhibits the strongest basis set dependence, with the information-ionicity component I remaining practically unaffected by specific choices of basis functions. The justification of this trend comes from Eq. (9). Indeed, taking into account that for the given basis set the information distance $\Delta S(p|p) = 0$, one predicts an increased invariance of $I(p:p) = S(p) - S(p|p)$, due to an expected cancellation of increases in these two entropies accompanying the basis-set enlargement.

A similar conclusion follows from examining Table 4, where the corresponding IT descriptors of diatomic channels-in-molecules are displayed, both atomically reduced

Table 3 Comparison of the average noise (S) and information-flow (I) descriptors of the orbital communications in alternative minimum (χ, $\widetilde{\chi}$) and extended (ξ) basis sets

Molecule	S^{ξ}	S^{χ}	$S^{\widetilde{\chi}}$	I^{ξ}	I^{χ}	$I^{\widetilde{\chi}}$	ΔS	ΔI
H_2	2.1061	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HF	1.3822	0.3361	0.3209	2.1650	2.1913	2.1910	−0.0152	−0.0003
F_2	1.2664	0.1700	0.1735	3.0092	3.1147	3.1114	0.0035	−0.0033
NaCl	0.6172	0.2897	0.2390	3.6895	3.6876	3.7093	−0.0507	0.0217
H_2O	1.8818	0.8174	0.7782	1.9218	1.9157	1.9396	−0.0392	0.0239
CO_2	1.8695	0.8810	0.8548	2.9669	2.9735	2.9897	−0.0292	0.0162
NH_3	2.2851	1.1822	1.1618	1.7280	1.7495	1.7628	−0.0204	0.0133
CH_4	2.6874	1.6254	1.6208	1.4774	1.4971	1.5013	−0.0046	0.0042
C_2H_6	2.5343	1.4337	1.4338	2.4307	2.5151	2.5148	0.0001	−0.0003
C_2H_2	2.0478	1.0306	1.0294	2.4334	2.4917	2.4910	−0.0012	−0.0007
C_6H_6	2.5063	1.4248	1.4215	3.5600	3.6835	3.6864	−0.0033	0.0029

The last two columns report deviations in entropic indices: $\Delta S = S^{\widetilde{\chi}} - S^{\chi}$, $\Delta I = I^{\widetilde{\chi}} - I^{\chi}$

Table 4 The conditional entropies of diatomic fragments in molecules reported in Table 2, obtained from the RHF calculations for the experimental geometries in the extended (ξ) and minimum ($\chi, \widetilde{\chi}$)) basis sets: columns 3 and 4 report the average diatomic noise descriptors of the reduced molecular channel in atomic resolution, while columns 5–8 describe the two fully resolved diatomic communications in the specified AO bases

Molecule	A—B	S^ξ (AB)	S^χ (AB)	S_{AB}^ξ	S_{AB}^χ	$S_{AB}^{\widetilde{\chi}}$	ΔS_{AB}
H_2	H—H	1.0000	1.0000	2.1062	1.0000	1.0000	0.0000
HF	H—F	0.3532	0.3584	1.3822	0.3361	0.3209	−0.0152
F_2	F—F	0.3562	0.3096	1.2664	0.1700	0.1735	0.0035
NaCl	Na—Cl	0.2409	0.2288	0.6172	0.2897	0.2390	−0.0507
H_2O	O—H	0.4175	0.4194	1.3977	0.5138	0.4878	−0.0260
CO_2	C—O	0.4642	0.4269	0.9834	0.4464	0.4365	−0.0099
NH_3	N—H	0.4703	0.4720	1.2525	0.5283	0.5188	−0.0095
CH_4	C—H	0.5081	0.5122	1.0818	0.5685	0.5669	−0.0016
C_2H_6	C—C	0.4815	0.4638	0.8694	0.3991	0.3991	0.0000
	C—H	0.2834	0.2841	0.5465	0.2703	0.2694	−0.0009
C_2H_2	C—C	0.7822	0.7675	1.4088	0.6715	0.6761	0.0046
	C—H	0.3555	0.3614	0.6647	0.3308	0.3289	−0.0019
C_6H_6	o C—C	0.2243	0.2168	0.4098	0.2199	0.2199	0.0000
	m C—C	0.1274	0.1118	0.2565	0.1021	0.1020	−0.0001
	p C—C	0.1344	0.1300	0.2584	0.1141	0.1138	−0.0003
	C—H	0.1210	0.1213	0.2130	0.1083	0.1078	−0.0005

The last column reports the difference ΔS between these AO-resolved diatomic networks: $\Delta S_{AB} = S_{AB}^{\widetilde{\chi}} - S_{AB}^\chi$

and in full basis set resolution, respectively. In particular, the entries of the table last column again demonstrate the MOC efficiency in bringing the extended basis descriptors to an equivalent minimum basis representation. As expected, the bond components resulting from the AIM-reduced channels are similar in all representations. Therefore, they have been numerically validated as practical invariants of any SCF MO calculations. One also observes that for diatomics in Table 4, for which $P_H + P_X = 1, X = H, N, O, F$, one indeed detects a monotonic decrease in the entropy-covalency index, as intuitively expected from the increasing electronegativity of the hydrogen companion.

In the final comparison of Table 5 the overall IT-covalent (unreduced) indices of Table 4 have been partitioned into the *intra*-atomic and *inter*-atomic contributions of Eq. (40). In terms of these complementary components the basic conclusion drawn from preceding quantitities still holds: the two minimum variants of the basis set generate quite similar conditional-entropy descriptors. One also detects, that in these small-basis descriptions the internal/external communications in or between the two AIM are comparable, while the large-basis network generates a dramatic increase in the average noise due to the associated intra-atomic communications alone.

Table 5 The *intra-* and *inter-*atomic components $S_{XY}^{\zeta}(int.)$ and $S_{XY}^{\zeta}(ext.)$ of the conditional entropies S_{XY}^{ζ}, $\zeta = \xi$, χ and $\tilde{\chi}$, reported in Table 4

Molecule	A—B	$S_{AB}^{\xi}(int.)$	$S_{AB}^{\chi}(int.)$	$S_{AB}^{\tilde{\chi}}(int.)$	$S_{AB}^{\xi}(ext.)$	$S_{AB}^{\chi}(ext.)$	$S_{AB}^{\tilde{\chi}}(ext.)$
H_2	H—H	1.0531	0.5000	0.5000	1.0531	0.5000	0.5000
HF	H—F	1.0496	0.1629	0.1444	0.3326	0.1732	0.1765
F_2	F—F	1.0472	0.0858	0.0876	0.2192	0.0842	0.0859
NaCl	Na—Cl	0.4502	0.1684	0.1327	0.1670	0.1213	0.1063
H_2O	O—H	1.0009	0.2566	0.2381	0.3968	0.2572	0.2497
CO_2	C—O	0.5898	0.2032	0.1954	0.3936	0.2432	0.2411
NH_3	N—H	0.8912	0.3020	0.2949	0.3613	0.2263	0.2239
CH_4	C—H	0.6576	0.2658	0.2644	0.4242	0.3027	0.3025
C_2H_6	C—C	0.6172	0.2396	0.2380	0.2522	0.1595	0.1611
	C—H	0.3586	0.1471	0.1463	0.1879	0.1232	0.1231
C_2H_2	C—C	0.7590	0.3051	0.3080	0.6498	0.3664	0.3681
	C—H	0.4380	0.1866	0.1867	0.2267	0.1442	0.1422
C_6H_6	o C—C	0.2448	0.1018	0.1017	0.1650	0.1181	0.1182
	m C—C	0.2448	0.1018	0.1017	0.0117	0.0003	0.0003
	p C—C	0.2433	0.1018	0.1017	0.0151	0.0123	0.0121
	C—H	0.1426	0.0626	0.0624	0.0704	0.0457	0.0454

8 Conclusions

It was the main goal of the present analysis to find satisfactory tools for interpreting the entropic descriptors of the molecular information channels in orbital resolution, which are known to be strongly basis-set dependent. The minimum basis of AO occupied in the system "promolecule" generates the most "chemical" account of the bond covalency or ionicity and its resultant multiplicity, and gives understanding of diverse factors conditioning the efficiency of the orbital interaction, which can be linked to the familiar MO diagrams of the textbook chemistry.

Therefore, in this work we have proposed to transform the large-basis communications into probability propagations in an equivalent (augmented) set, comprising of the effective minimum set of AO determined from the MOC. We have also numerically confirmed that this fitted small basis and the reference minimum AO set indeed generate practically identical global and diatomic IT-indices, as well as their entropy-covalent/information-ionic composition and the internal (*intra*-atomic)/external (*inter*-atomic) contributions. As expected, the AIM-reduced channels were shown to be quite insensitive to basis set enlargement, so that the bond descriptors they generate provide another set of invariants in OCT of the chemical bond.

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