Journal of Mathematical Chemistry, Vol. 43, No. 1, January 2008 (© 2006)
DOI: 10.1007/s10910-006-9194-6

Entropic bond indices from molecular information channels in orbital resolution: ground-state systems

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Received 10 August 2006; accepted 16 September 2006

The molecular communication channels of Information Theory (IT) are constructed within the orbital description of molecular electronic structure using the superposition principle of quantum mechanics. Two types of such information systems are introduced, called the "*geometric*" and "*physical*" channels. The communication network of the former is determined by all molecular orbitals (MO), occupied and virtual, which result from the specified set of atomic orbitals (AO). The geometric channel thus reflects the relative "rotation" of MO relative to AO in the molecular Hilbert space, and the associated "promotion" of AO in the molecule due to the probability scattering via the communication network generated by the complete set of MO. They are devoid of the physical content embodied in the MO-occupations, which distinguish one electron configuration of the molecule from another. The latter information is included in the physical AO-promotion channels, which involve the probability scattering via the occupied MO alone. The probability conditioning is shown to be related to the appropriate projection in the orbital Hilbert space. The geometric and the physical (ground-state) bond indices of the *conditional-entropy* (IT-covalency) and *mutual-information* (IT-ionicity) are generated for the 2-AO model and selected π-electron systems (ethylene, allyl, butadiene, and benzene) in the Hückel approximation. They are shown to compare favorably with the previously reported IT bond-orders obtained from the two-electron molecular information channels in atomic resolution.

KEY WORDS: bond multiplicities, conditional probabilities in orbital resolution, covalent/ionic bond components, information theory of molecules, molecular information channels, orbital description, superposition principle

1. Introduction

The molecular orbital (MO) approach to chemical bonds gives a transparent interpretation of their origin and provides useful measures of their multiplicity ("order") [1–13]. It generates the standard description of the bonding patterns in molecules and their constituent fragments, against which one ultimately compares the alternative treatments. The information-theory (IT) has recently been shown [14–25] to generate the adequate entropy/information descriptors of the chemical bonds, e.g., the valence numbers of bonded atoms, the overall IT bond multiplicity and its covalent and ionic components. They emerge in the *communication theory* of the chemical bond, with the molecule is interpreted as the information channel of IT, with the molecular or promolecular electron probabilities being scattered via the network of the chemical bonds between the system constituent atoms. It has recently been demonstrated [18] that both MO and communication theories give rise to similar atomic contributions to the overall bond multiplicity and valence-numbers in the simplest 2-AO model of a single chemical bond resulting from the interaction between two atomic orbitals (AO). This novel approach provides a complementary information-scattering (-flow) interpretation to the covalent and ionic bond components.

The molecular information channel in orbital resolution [25] uses the conditional probabilities of AO given MO, or of MO given AO. They are obtained from the quantum-mechanical superposition principle. This *one*-electron perspective is similar to that adopted in the local communication systems implied by the Hirshfeld [26] division of the molecular electron distributions into densities of atoms-in-molecules (AIM) [15, 27]. It is in contrast to the *two*-electron approach, e.g., those determining the bond descriptors from the communication channels in atomic resolution [14–23], the so called quadratic valence indices [6–11], and the average Fermi-hole measures [12, 13]. The two-electron IT approach (see, e.g., [23] and refs therein) includes the electron-correlation effects and gives rise to the novel communication interpretation of the familiar electronic structures of the classical valence-bond theory [28, 29]. The entropy/information bond indices have been shown to give rise to the dichotomous covalent and ionic components, which conserve the overall bond-order in several model systems [15, 17, 18, 23]. The communication theory also generates several alternative strategies for determining the internal and external bonds of molecular fragments [16, 19, 20, 23].

Several issues, however, still remain to be solved in a more satisfactory manner. For example, the reduction of the entropic bond-orders in the excited electronic configurations [15, 22–24], which populate the *anti*-bonding MO more strongly compared to the ground-state, presents a challenging problem within the IT approach. Indeed, these indices are formulated in terms of the electron probabilities alone, i.e., the diagonal elements of the density matrices in orbital resolution, which do not reflect the relative phases of AO in the occupied MO, thus loosing the "memory" about the MO nodal structure. It is the main purpose of this and future works to tackle some of these problems by using the relevant probability-conditioning schemes, defined by the corresponding projections in the orbital Hilbert space of the molecular system under consideration. The connection can be made with the quadratic bond multiplicities of the MO theory [6–11], by examining the separate orbital *sub*-channels corresponding to the electron-"promotion" and probability-"survival" in the molecule, respectively, relative to the free-atoms of the "promolecule" [26].

The *conditional-entropy* descriptors of the system bond covalency and the *mutual-information* measures of the system bond-ionicity, which result from the communication channels in orbital resolution, will be compared with the bond multiplicities obtained from the associated two-electron information channels in atomic resolution. These novel concepts will be illustrated for the previously explored 2-AO model and selected π-bond systems in the Hückel description. Throughout the paper the entropic quantities are reported in bits, which correspond to the base 2 of the logarithmic measure of information.

2. The molecular communication channels in orbital resolution

2.1. Conditional probabilities

Let the row vector $\boldsymbol{\psi} = \{\psi_i\} = \boldsymbol{\chi}\mathbf{C}$ groups the MO defined in the (orthogonalized) AO basis set $\boldsymbol{\chi} = \{\chi_k\}$, $\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \{\langle\chi_k|\chi_l\rangle = \delta_{k,l}\} = \mathbf{I}$. Here the rectangular matrix $\mathbf{C} = \{C_{k,i}\} = (\mathbf{C}^{\text{occ.}}, \mathbf{C}^{\text{virt.}})$ groups the corresponding expansion coefficients for both the occupied ($\mathbf{C}^{\text{occ.}}$) and empty ($\mathbf{C}^{\text{virt.}}$) MO. For example, the $\boldsymbol{\psi}$ may represent spatial parts of molecular spin-orbitals from the Kohn–Sham (KS) or unrestricted Hartree–Fock (UHF) theories. In the spin-resolved approaches one identifies MO of the spin-up and spin-down sets: $\boldsymbol{\psi} = \{\boldsymbol{\psi}^\sigma\}$, $\boldsymbol{\psi}^\sigma = \{\boldsymbol{\psi}_i^\sigma\} = \boldsymbol{\chi}\mathbf{C}^\sigma$, $\sigma = (\uparrow, \downarrow)$. The LCAO coefficients represent projections of MO on AO: $\mathbf{C} = \langle\boldsymbol{\chi}|\boldsymbol{\psi}\rangle$ or $\mathbf{C}^\sigma = \langle\boldsymbol{\chi}|\boldsymbol{\psi}^\sigma\rangle$.

By the superposition principle of quantum mechanics the squares of the moduli of these orbital projections generate the *conditional* probabilities of MO given AO:

$$\begin{aligned}\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \{P(i|k) \equiv P_{i,k}/P_k &= \langle\psi_i|\chi_k\rangle\langle\chi_k|\psi_i\rangle \equiv \langle\psi_i|\hat{\mathrm{P}}_k|\psi_i\rangle \\ &= \langle\chi_k|\psi_i\rangle\langle\psi_i|\chi_k\rangle \equiv \langle\chi_k|\hat{\mathrm{P}}_i|\chi_k\rangle\}, \\ &\sum_i^{\text{all}} P(i \mid k) = 1. \end{aligned} \tag{1}$$

Above, they have been expressed as the relevant expectation values: of the AO projection operator $\hat{\mathrm{P}}_k = |\chi_k\rangle\langle\chi_k|$ for ith MO, or of the MO projector $\hat{\mathrm{P}}_i = |\psi_i\rangle\langle\psi_i|$ for kth AO. The implicitly defined joint AO–MO probabilities,

$$\mathbf{P}(\boldsymbol{\chi} \wedge \boldsymbol{\psi}) = \{P(\chi_k \wedge \psi_i) \equiv P_{k,i} = P(k|i)P_i \equiv P_{i,k} = P(i|k)P_k\} \tag{2}$$

give rise to the normalized AO and MO probabilities, overall and spin-resolved:

$$\boldsymbol{P}_{\chi} = \left\{ P_k = \sum_i^{\text{all}} P_{i,k} = \sum_i^{\text{all}} \sum_\sigma P_{i,k}^\sigma \equiv \sum_\sigma P_k^\sigma \right\}, \quad \sum_k P_k = \sum_k \sum_\sigma P_k^\sigma = 1,$$

$$\boldsymbol{P}_{\psi} = \{ P_i = \sum_k P_{i,k} = \sum_\sigma \sum_k P_{i,k}^\sigma \equiv \sum_\sigma P_i^\sigma \}, \quad \sum_i^{\text{all}} P_i = \sum_i^{\text{all}} \sum_\sigma P_i^\sigma = 1. \tag{3}$$

It also follows from Equation (2) that

$$P(k|i)/P(i|k) = P_k/P_i. \tag{4}$$

The AO probabilities $\boldsymbol{P}_{\chi} = \{P_k = N_k/N\}$, where $N = \sum_k N_k$ is the system overall number of electrons, reflect the initial AO occupations $\boldsymbol{N} = \{N_k\}$. For example, the ground-state occupations of the free constituent atoms determine the reference (promolecular) input probabilities in AO resolution, $\boldsymbol{P}_{\chi}^{0}$, before the bond formation. In Equation (3) we have introduced the joint AO–MO probabilities, for specific molecular spin-orbitals (MSO), e.g., in the UHF or LSDA theories,

$$\mathbf{P}(\boldsymbol{\chi} \wedge \boldsymbol{\psi}^\sigma) = \{P(\chi_k \wedge \psi_i^\sigma) \equiv P_{k,i}^\sigma = P(k|i^\sigma)P_i^\sigma \equiv P_{i,k}^\sigma = P(i^\sigma|k)P_k\}. \tag{5}$$

They are implicitly defined by the associated conditional probabilities in the spin-resolved MO representation,

$$\begin{aligned}\mathbf{P}(\boldsymbol{\psi}^\sigma|\boldsymbol{\chi}) = \{P(i^\sigma|k) \equiv P_{i,k}^\sigma/P_k &= \langle\psi_i^\sigma|\chi_k\rangle\langle\chi_k|\psi_i^\sigma\rangle \equiv \langle\psi_i^\sigma|\hat{\mathrm{P}}_k|\psi_i^\sigma\rangle \\ &= \langle\chi_k|\psi_i^\sigma\rangle\langle\psi_i^\sigma|\chi_k\rangle \equiv \langle\chi_k|\hat{\mathrm{P}}_i^\sigma|\chi_k\rangle\}, \\ &\sum_i^{\text{all}} P(i^\sigma|k) = 1.\end{aligned} \tag{6}$$

Here, $P(k|i^\sigma)]$ stands for the probability of χ_k given ψ_i^σ, while $P(i^\sigma|k)$ is the probability of ψ_i^σ given χ_k. These two sets of conditional probabilities are related (compare equations (2) and (4)):

$$P(k|i^\sigma)/P(i^\sigma|k) = P_k/P_i^\sigma. \tag{7}$$

The spin resolution can be carried out also for atomic orbitals, by separating the atomic SO (ASO), singly occupied by the spin-up and spin-down electrons, respectively: $\boldsymbol{\chi} = \{\boldsymbol{\chi}^\sigma\}$, $\boldsymbol{\chi}^\sigma = \{\chi_k^\sigma\}$, $\sigma = (\uparrow, \downarrow)$ (see Equation (3)). The spin-resolved AO probabilities $\mathbf{P}_\chi^\sigma = \{P_k^\sigma = N_k^\sigma/N\}$ then reflect the initial occupations $\mathbf{N}^\sigma = \{N_k^\sigma\}$ of ASO in the promolecular reference. The renormalized ASO probability vector,

$$\bar{P}_\chi^\sigma = \{\bar{P}_k^\sigma = P_k^\sigma(N/N^\sigma) \equiv P_k^\sigma/P^\sigma \equiv P(k|\sigma) = N_k^\sigma/N^\sigma\}, \sum_k \bar{P}_k^\sigma = 1, \tag{8}$$

groups the conditional probabilities $\bar{P}_k^\sigma$ of observing the ASO, χ_k^σ, i.e., χ_k in the subsystem of ASO occupied by electrons with the spin orientation σ. They satisfy the appropriate σ-subsystem normalization requirement.

The AO index k in $P(i|k)$ and $P(i^\sigma|k)$ represents a parameter, while the MO (or MSO) index i (or i^σ) is a variable, as indeed reflected by the normalization relation in equations (1) and (6), which involve summations over all MO constructed in the given AO space $\boldsymbol{\chi}$, both occupied and virtual. These roles are reversed in the other set of conditional probabilities, of AO given MO (or MSO):

$$\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})^T = \{P(k|i) \equiv P_{k,i}/P_i = P(i|k)(P_k/P_i)\}, \sum_k P(k|i) = 1, \quad (9)$$

$$\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}^\sigma) = \mathbf{P}(\boldsymbol{\psi}^\sigma|\boldsymbol{\chi})^T = \{P(k|i^\sigma) \equiv P_{k,i}^\sigma/P_i^\sigma = P(i^\sigma|k)(P_k/P_i^\sigma)\},$$
$$\sum_k P(k|i^\sigma) = 1. \quad (10)$$

2.2. Geometrical information channels

In IT, the two sets of orbitals, $\boldsymbol{\chi}$ and $\boldsymbol{\psi}$, define the AO-*inputs* and MO-*outputs* of the information system shown in figure 1, with the conditional probabilities $\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})$ or $\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi})$ determining the "communication" connections between the corresponding orbital events. This channel involves all MO $\boldsymbol{\psi}$ constructed within the given basis set $\boldsymbol{\chi}$, both occupied and virtual in the specified electron configuration of the molecule. It solely reflects the "geometry" of the orbital Hilbert-space, being devoid of any information about the actual distribution of electrons among AO or MO. Its communication "noise" thus probes the probability scattering due to the overlaps (projections) between all AO and MO, which measure the electron delocalization due to the network of MO for the specified input probability distribution $\boldsymbol{P}_\chi$. The latter characterizes the electron configuration of the free atoms of the promolecule, marking either the ground- or promoted-states of such non-bonded atoms. This promolecular reference defines the bond origins, against which the molecular electronic structure and the associated effective electron configuration of bonded atoms will be compared.

$$\boldsymbol{P}_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\psi|\chi) \longrightarrow \psi \longrightarrow \boldsymbol{P}_\psi$$

Figure 1. The "geometric" AO→MO information channel defined by the spinless conditional probabilities of Equation (1). The AO probabilities $\boldsymbol{P}_\chi$ (Equation (3)) determine the distribution of the *input* signals, in the channel "source," while the MO probabilities $\boldsymbol{P}_\psi = \boldsymbol{P}_\chi \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})$ (Equation (3)) define the associated probabilities of the *ouput* signals, in the channel "receiver." The input probabilities reflect the initial (promolecular) occupations $\boldsymbol{N}$ of AO in the non-bonded atoms.

The freedom to manipulate the input probabilities allows one to account for the "history" of the bond-formation process [14, 15, 23]. For example, in the simplest 2-AO model a given (molecular) electron distribution may give rise to different bond descriptors relative to the electron-sharing (*covalent*) or the pair-sharing (*coordination*) references, thus distinguishing the ordinary covalent bonds, when two atoms contribute a single electron each to form the chemical bond, from the donor–acceptor (DA) reference, when the two electrons have been donated by the basic atom [23].

The conditional probabilities of Equations (9) and (10) correspond to the "reverse" communication scenario, involving the MO-inputs and AO-outputs. In the actual molecular system, the input probabilities $\boldsymbol{P}_\psi = \{P_i = n_i/N\}$ reflect the MO occupations $\boldsymbol{n} = \{n_i\}$ in the molecular electron configuration of interest, thus specifying the "physical" initial probabilities. However, when probing the purely geometric probability scattering in orbital resolution one could explore the whole MO space in the specified basis set, without any "physical" information about the MO occupations, e.g., by using the output probabilities of figure 1. Such information system is schematically shown in figure 2. The information cascade consisting of the geometrical communication channels shown in figures 1 and 2 is shown in figure 3. It determines the effective geometrical AO→AO$^+$ promotion in the whole MO Hilbert space in the specified AO basis set. The associated effective information system is shown in figure 4.

The geometric AO→AO$^+$ promotion of figure 4 is defined by the resultant conditional probability matrix

$$\mathbf{P}(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) \equiv \{P(l^+|k) = \sum_i P(l|i)P(i|k)$$
$$= \sum_i \langle\psi_i|\hat{\mathrm{P}}_l|\psi_i\rangle\langle\psi_i|\hat{\mathrm{P}}_k|\psi_i\rangle \equiv \sum_i \langle\psi_i|\hat{\mathrm{P}}_l\hat{\mathrm{P}}_i\hat{\mathrm{P}}_k|\psi_i\rangle\}. \tag{11}$$

It should be observed that in the given basis set the projection on the whole orbital space can be equivalently expressed in terms of AO, MO, and MSO [see equations (1) and (6)]:

$$\sum_k^{\mathrm{AO}} \hat{\mathrm{P}}_k = \sum_i^{\mathrm{MO}} \hat{\mathrm{P}}_i = \sum_i^{\mathrm{MSO}} \hat{\mathrm{P}}_i^\sigma. \tag{12}$$

$$\boldsymbol{P}_\psi \longrightarrow \boldsymbol{\psi} \longrightarrow \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) \longrightarrow \boldsymbol{\chi}^+ \longrightarrow \boldsymbol{P}_\chi^+$$

Figure 2. The *geometric* MO→AO information channel defined by the spinless conditional probabilities of Equation (9). The MO probabilities $\boldsymbol{P}_\psi$ of figure 1 now determine the distribution of the MO-*input* signals, including both the occupied and virtual MO, while the product $\boldsymbol{P}_\chi^+ = \boldsymbol{P}_\psi\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) = \boldsymbol{N}^+/N$ defines the probabilities of the AO-*ouput* "signals," which reflect the *geometrically* "promoted" occupations $\boldsymbol{N}^+$ of AO in the molecule.

$$\boldsymbol{P}_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\psi|\chi) \longrightarrow \psi \longrightarrow \boldsymbol{P}_\psi \longrightarrow \mathbf{P}(\chi|\psi) \longrightarrow \chi^+ \longrightarrow \boldsymbol{P}_\chi^+$$

Figure 3. The information "cascade," from the initial AO probabilities $\boldsymbol{P}_\chi$ of non-bonded atoms (input) to the *geometrically* promoted AO probabilities $\boldsymbol{P}_\chi^+$ in the MO Hilbert space.

This AO→AO$^+$ probability scattering generates the communication "noise" measured by the *conditional entropy* [23, 30] of the geometrically promoted AO-outputs $\boldsymbol{\chi}^+$, given the promolecular AO-inputs $\boldsymbol{\chi}$,

$$S(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = -\sum_k P_k \sum_l P(l^+|k) \log P(l^+|k), \tag{13}$$

which reflects the extra uncertainty due to the electron delocalization among AO, via the whole system of MO. It should be stressed that these geometrical channels give equal emphasis to all MO in the specified basis set, thus formally corresponding to an *equi*-ensemble of MO, in which the unbiased (uniform) MO probabilities (occupations) are equalized.

The complementary IT descriptor of the communication system in figure 4, called the *mutual-information* [23, 30] in system AO-inputs and AO$^+$-outputs,

$$I(\boldsymbol{\chi}:\boldsymbol{\chi}^+) = \sum_k P_k \sum_l P(l^+|k) \log[P(l^+|k)/P_l^+] = S(\boldsymbol{\chi}^+) - S(\boldsymbol{\chi}^+|\boldsymbol{\chi}), \tag{14}$$

where the Shannon entropy [23, 30, 31] of the output AO probabilities

$$S(\boldsymbol{\chi}^+) = -\sum_l P_l^+ \log P_l^+, \tag{15}$$

measures the amount of information flowing through the channel. We have used in equation (14) the partial normalization of the joint probabilities $\mathbf{P}^+ = \mathbf{P}(\boldsymbol{\chi} \wedge \boldsymbol{\chi}^+) = \{P_k P(l^+|k) \equiv P_{k,l}^+\}$:

$$\sum_k P_{k,l}^+ = P_l^+. \tag{16}$$

The geometric-promotion channels reflect "rotation" of MO relative to AO in the molecular Hilbert space. They are devoid of any physical content embodied

$$\boldsymbol{P}_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\psi|\chi)\,\mathbf{P}(\chi|\psi) \longrightarrow \chi^+ \longrightarrow \boldsymbol{P}_\chi^+$$

Figure 4. The effective probability scattering from the initial AO probabilities $\boldsymbol{P}_\chi$ of non-bonded atoms (input) to the geometrically promoted AO probabilities $\boldsymbol{P}_\chi^+$ in the MO Hilbert space.

in the MO-occupations, which distinguish one electron configuration of the molecule from another. In what follows we shall examine the configuration physical-promotion channels, due to the probability scattering via the occupied MO alone.

2.3. Physical information channels

In the specified state of the molecule only the occupied MO of the given electron configuration (c) of the molecule influence the *physical* promotion of the free-atom electrons from the occupied to unoccupied AO. In order to separate out the configuration virtual MO in the orbital communication system shown in figure 5, the physical analog of the information channel of figure 2, one has to take into account the configuration MO-probability vector, $\boldsymbol{P}_{\psi}^{c} = \{P_i^c = n_i^c/N\}$, defined by the MO occupations $\boldsymbol{n}^c = \{n_i^c\}$, which now determine the physical input distribution.

This physical MO$\rightarrow$AO communication system explores only the active part of the geometrical channel, the so called physical subchannel representing the active part of the whole geometric information system for the molecular electron configuration in question. This projection of the occupied MO scattering can be accomplished geometrically through the physical MO-projection (density operator) defined in terms of the diagonal matrix of the MO occupations, $\mathbf{n}^{c} = \{n_i^c \delta_{i,j}\}$:

$$\begin{aligned}\hat{\mathrm{D}}^c &= |\boldsymbol{\psi}\rangle\ \mathbf{n}^c \langle\boldsymbol{\psi}| = \sum_i |\psi_i\rangle\ n_i^c\ \langle\psi_i| \equiv \sum_i \hat{\mathrm{D}}_i^c \\ &= \sum_\sigma |\boldsymbol{\psi}_c^\sigma\rangle\ \mathbf{n}_c^\sigma \langle\boldsymbol{\psi}_c^\sigma| = \sum_\sigma\sum_i |\psi_i^\sigma\rangle\ n_i^\sigma \langle\psi_i^\sigma| = \sum_\sigma\sum_i \hat{\mathrm{D}}_i^\sigma = \sum_\sigma \hat{\mathrm{D}}_c^\sigma. \quad (17)\end{aligned}$$

Its matrix representation in the adopted AO basis set defines the MO-ensemble density matrix,

$$\begin{aligned}\mathrm{D}^c &= \langle\boldsymbol{\chi}|\hat{\mathrm{D}}^c|\boldsymbol{\chi}\rangle = \mathbf{C}\mathbf{n}^c\mathbf{C}^\dagger \equiv \langle\boldsymbol{\chi}|\sum_\sigma \hat{\mathrm{D}}_c^\sigma|\boldsymbol{\chi}\rangle = (\mathbf{D}_c^\alpha + \mathbf{D}_c^\beta) \\ &= \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}^c) = \{P^c(k|i)\}, \quad (18)\end{aligned}$$

where $\boldsymbol{\psi}^c = \{\psi_i^c\}$ groups the configuration occupied MO. It represents the spinless *charge-and-bond-order* (CBO) matrix of the LCAO MO theory, the sum of its two spin components $\{\mathbf{D}_c^\sigma\}$. As also indicated in equation (18) the density matrix

$$\boldsymbol{n}_{\psi}^{c} \longrightarrow \boldsymbol{\psi}^{c} \longrightarrow \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}^{c}) \longrightarrow \boldsymbol{\chi}^{*} \longrightarrow \boldsymbol{N}_{c}^{*}$$

Figure 5. The *physical* MO$\rightarrow$AO information channel for the molecular electron configuration $\boldsymbol{n}^c = \{n_i^c\}$ with the MO-input $\boldsymbol{n}_\psi^c = \boldsymbol{n}^c$. The product $\boldsymbol{P}_{\boldsymbol{\chi}}^* = \boldsymbol{n}_\psi^c \mathbf{P}(\chi|\boldsymbol{\psi}^c) = \boldsymbol{N}_c^*$, where $\boldsymbol{\psi}^c$ denotes the configuration occupied MO, defines the effective, promoted occupations $\boldsymbol{N}^*$ of AO in the specified molecular state.

$\mathbf{D}^c$ represents the conditional probabilities determining the information channel of figure 5, which represents the configuration physical (active) part of the whole geometrical communication network. The configuration unoccupied part $\boldsymbol{\psi}^u$ of the complete set of MO $\boldsymbol{\psi} = (\boldsymbol{\psi}^c, \boldsymbol{\psi}^u)$ represent the unphysical part of the whole geometric channel, which remains inactive in the configuration MO$\to$AO probability scattering (see figure 6).

The physical AO $\to$ AO* probability promotion in the given molecular electron configuration is thus obtained by combining the geometric AO $\to$ MO channel of figure 1 with the physical subchannel of figure 5. The resulting information cascade in orbital resolution is shown in figure 6.

The initial AO occupations are changed in the molecule, due to delocalization of electrons via a network of the occupied MO, to the physically "promoted" occupations $\boldsymbol{N}_c^* = \{N_k^*\}$. This combined channel defines the resultant physical AO $\to$ AO* probability scattering shown in figure 7.

This effective physical channel linking the promolecule occupied AO $\boldsymbol{\chi}$ and the molecule occupied AO $\boldsymbol{\chi}^*$ is thus determined by the conditional probability matrix:

$$\begin{aligned}\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\psi}^c|\boldsymbol{\chi})\mathbf{n}^c\mathbf{P}(\boldsymbol{\chi}^*|\boldsymbol{\psi}^c) &\equiv \{P(l^*|k) = \sum_i^c P(l^*|i)\, n_i^c P(i|k) \\ &= \sum_i \langle\psi_i|\hat{\mathrm{P}}_l|\psi_i\rangle n_i^c \langle\psi_i|\hat{\mathrm{P}}_k|\psi_i\rangle \equiv \sum_i \langle\psi_i|\hat{\mathrm{P}}_l\hat{\mathrm{D}}_i^c\hat{\mathrm{P}}_k|\psi_i\rangle\},\end{aligned} \tag{19}$$

where we have used the occupation-weighted MO projections $\{\hat{\mathrm{D}}_i^c = n_i^c\hat{\mathrm{P}}_i\}$ of equation (17).

The conditional-entropy of the promoted (molecular) AO output, given the initial (promolecular) AO intput (see equation (13)),

$$S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = -\sum_k^o P_k \sum_l^c P(l^*|k)\ \log P(l^*|k) \tag{20}$$

measures the average communication "noise" in the information channel of figure 7. It was shown previously [14–23] to represent a realistic IT descriptor of the molecular entropy-covalency. It reflects the extra uncertainty in the molecular electron distribution, due to AO delocalization effects in the system occupied

$$\boldsymbol{P}_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\psi\,\chi) \longrightarrow \begin{bmatrix} \psi^c \to \mathbf{P}(\chi|\psi^c) \to \chi^* \\ \psi^u \to \mathbf{0}(\chi|\psi^u) \to \chi^* \end{bmatrix} \longrightarrow \boldsymbol{N}_c^*$$

Figure 6. The orbitally resolved molecular information "cascade," from the initial AO probabilities $\boldsymbol{P}_\chi$ of the non-bonded atoms (input) to the physically promoted AO occupations $\boldsymbol{N}_c^*$ in the molecule. Here, $\mathbf{0}(\boldsymbol{\chi}|\boldsymbol{\psi}^u)$ denotes the zero rectangular matrix of conditional probabilities of AO given the virtual MO in configuration c.

$$\boldsymbol{P}_\chi \longrightarrow \chi \longrightarrow \mathbf{P}(\psi^c|\chi^o)\, \mathbf{n}^c\, \mathbf{P}(\chi^c|\psi^c) \longrightarrow \chi^c \longrightarrow \boldsymbol{N}_c^*$$

Figure 7. The resultant probability scattering from the initial AO probabilities $\boldsymbol{P}_\chi$ of the occupied AO $\boldsymbol{\chi}$ of the non-bonded atoms in the promolecular reference (input) to the effective (promoted) AO occupations N_c^* in the molecular electron configuration c (output) exhibiting the MO occupations $\mathbf{n}^c$.

MO, i.e., a sharing of the free-atom electrons among all constituent AO. This spreading of the electron probability (density) throughout the whole molecular system is indeed intuitively associated with the covalent component of the chemical bond.

The mutual-information descriptor of this effective physical channel (see equation (14)),

$$I(\boldsymbol{\chi}:\boldsymbol{\chi}^*) = \sum_k^0 P_k \sum_l^c P(l^*|k)\ \log[P(l^*|k)/P_l^*] = S(\boldsymbol{\chi}^*) - S(\boldsymbol{\chi}^*|\boldsymbol{\chi}), \tag{21}$$

where $S(\boldsymbol{\chi}^*)$ stands for the Shannon entropy (equation (15)) of the promoted output AO probabilities in the specified molecular electron-configuration,

$$S(\boldsymbol{\chi}^*) = -\sum_l^c P_l^* \log P_l^*, \tag{22}$$

should reflect the information bond-ionicity [14–23]. It follows from equations (20) and (21) that the overall IT-descriptor of the AO channel of figure 7 equals the Shannon entropy of the physically promoted AO probabilities:

$$N(\boldsymbol{\chi};\boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) + I(\boldsymbol{\chi}:\boldsymbol{\chi}^*) = S(\boldsymbol{\chi}^*). \tag{23}$$

Clearly, similar molecular information subchannels can be constructed for the two spin orientations $\sigma = (\uparrow, \downarrow)$. The spin-resolved input is then determined by the ASO occupations $\boldsymbol{N}_c^\sigma$ and the MSO probabilities $\boldsymbol{p}_c^\sigma = \{p_i^\sigma = n_i^\sigma/N\}$ or $\bar{\mathbf{p}}_c^\sigma = \{\bar{p}_i^\sigma = n_i^\sigma/N^\sigma\}$, defining the associated diagonal matrices $\{\mathbf{n}_c^\sigma\} = \{n_i^\sigma \delta_{i,j}\}$, $\mathbf{p}_c^\sigma = \{p_i^\sigma \delta_{i,j}\}$ or $\bar{\mathbf{p}}_c^\sigma = \{\bar{p}_i^\sigma \delta_{i,j}\}$. The physical AO → AO* scattering is then determined by the spin-resolved conditional probabilities $\mathbf{P}(\boldsymbol{\psi}^\sigma|\boldsymbol{\chi})$ (equation (6)) and the relevant MSO occupations.

3. Illustrative ground-state applications

3.1. 2-AO model

The simplest model of the chemical bond [5–8, 14–18, 23] involves the interaction between the two orthogonal AO, $\boldsymbol{\chi} = (a, b)$, originating from atoms A

and B, respectively, which give rise to the two ortho-normal combinations, $\boldsymbol{\psi} = (\psi_{\mathrm{b}}, \psi_{\mathrm{a}})$, representing the bonding (ψ_{b}) and antibonding (ψ_{a}) MO:

$$\psi_{\mathrm{b}} = P^{1/2}a + Q^{1/2}b, \qquad \psi_{\mathrm{a}} = -Q^{1/2}a + P^{1/2}b, \quad P + Q = 1. \tag{24}$$

The shape of both MO is controlled by a single parameter, e.g., the conditional probability $P(a|\psi_{\mathrm{b}}) = P(b|\psi_{\mathrm{a}}) = P$.

From the quantum-mechanical superposition principle one determines the following (geometric) conditional probability matrix:

$$\mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) = \begin{bmatrix} P & Q \\ Q & P \end{bmatrix}. \tag{25}$$

In the covalent (*cov.*) promolecule each free atom contributes a single electron each to form the chemical bond in the molecule AB, while in the coordination (*coord.*), DA-promolecule the two electrons originate from the *donor* (basic) atom B. Therefore, the initial AO probability distributions in these two references read: $\boldsymbol{P}_{\chi}^{cov.} = (1/2, 1/2)$ and $\boldsymbol{P}_{\chi}^{DA.} = (0, 1)$. In the ground-state (singlet) configuration $[\psi_{\mathrm{b}}^2]$ the bonding MO is doubly occupied: $\boldsymbol{n}^0 = (2, 0)$.

The conditional probabilities of equation (25) define the symmetric binary channel of the geometric AO $\rightarrow$ MO probability scattering, which is shown in figure 8 for a general AO input probabilities $\boldsymbol{P}_{\chi} = (x, y = 1 - x)$. The corresponding MO $\rightarrow$ AO$^+$ geometric channel for a general MO input probabilities $\boldsymbol{P}_{\psi} = (u, v = 1 - u)$ is shown in figure 9. They give rise to the effective AO $\rightarrow$ MO $\rightarrow$ AO$^+$ cascade of figure 10, which determines the effective geometrical AO $\rightarrow$ AO$^+$-promotion channel shown in figure 11. Its communication connections are defined by the conditional probabilities (see equations (11) and (25)):

$$\mathbf{P}(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) = \begin{bmatrix} P^2 + Q^2 & 2PQ \\ 2PQ & P^2 + Q^2 \end{bmatrix}. \tag{26}$$

Next, we shall examine the IT-descriptors of equations (13) and (14) of the geometric AO promotion channel (figure 11), which, respectively, reflect the entropy "covalency" and information "ionicity" of the whole orbital Hilbert space. It follows from equations (13) and (26) that the conditional entropy of the geometrically promoted output $\boldsymbol{P}_{\chi}^+$, given the promolecular distribution $\boldsymbol{P}_{\chi} = (x, y)$,

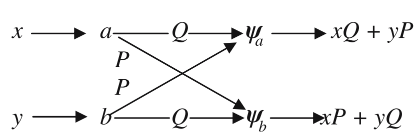

Figure 8. The geometric AO $\rightarrow$ MO channel in the 2-AO model (see figure 1).

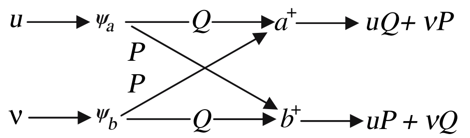

Figure 9. The geometric MO → AO$^+$ communication channel in 2-AO model (see figure 2).

is input-independent:

$$S(\chi^+|\chi) = -(P^2 + Q^2)\log(P^2 + Q^2) - 2PQ\,\log(2PQ) \equiv S(P). \qquad (27)$$

For the non-bonding polarization of MO, e.g., $P = 0 (Q = 1)$, when $\psi_b = b$, $\psi_a = -a$, or $P = 1 (Q = 0)$, when $\psi_b = a$, $\psi_a = b$, this index identically vanishes: $S(0) = S(1) = 0$. Its maximum value is reached for the symmetrical/anti-symmetrical/antisymmetrical MO, $P = Q = 1/2 : S(1/2) = 1$.

Therefore, as intuitively expected, the maximum entropy-covalency contained in the shapes of MO, compared to the original AO, is exhibited by the symmetrical combinations of AO, e.g., in the minimum-basis description of the σ-bond in H_2 or π-bond in ethylene. Such absence of the bond polarization is interpreted in chemistry as manifestation of the vanishing bond ionicity. Indeed, the input-dependent information-ionicity index of equation (14) can be shown to vanish for such non-polarized shapes of MO. More specifically, the Shannon entropy of the promoted AO-output distribution (equation (15) then reads (see figure 11):

$$S(\chi^+) = -s(x, P)\log s(x, P) - [1 - s(x, P)]\log[1 - s(x, P)] \equiv H(s), \qquad (28)$$

where $H(s)$ denotes the familiar *binary-entropy* function. It reaches the maximum value for $s = 1/2$, $H(1/2) = 1$, and vanishes for $s = (0, 1)$. It also follows from the expressions defining the output probabilities $\boldsymbol{P}_\chi^+ = (s, t)$ in figure 11 that $s(1/2, P) = t(1/2, P) = 1/2$, so that the output probability for the uniform input is independent of the current polarization P of MO: $H(s(1/2, P)) = H(1/2) = 1$. For the coordination promolecular input $(x = 0, y = 1)$ the output probabilities $(s = 2PQ, t = P^2 + Q^2)$ give rise to $H(s) = S(P)$ (equation (27)), and hence (see equation (14)): $I(\chi : \chi^+) = H(s(x, P)) - S(P) \equiv I(x, P) = 0$.

The extremum of $I(x, P)$ with respect to the input probability x determines the so called *information capacity* [23, 30] of this geometric-promotion channel. Since the conditional-entropy part of this difference is input-independent, the

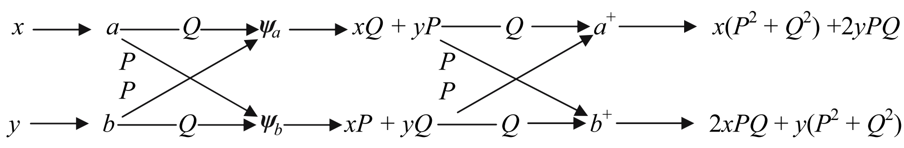

Figure 10. The geometric AO → MO→ AO$^+$ information cascade in 2-AO model (figure 3).

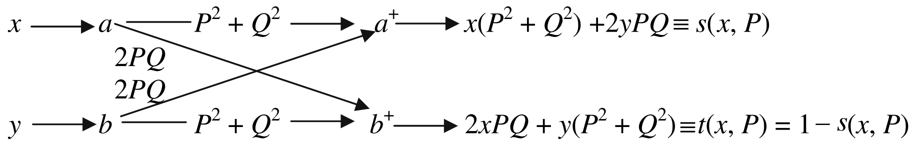

Figure 11. The geometric AO $\to$ AO$^+$ promotion channel in 2-AO model (figures 4 and 10).

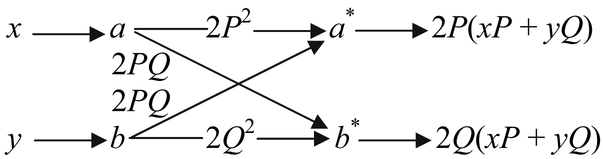

Figure 12. The physical AO $\to$ AO* promotion channel in 2-AO model (see figure 7).

maximum of $I(x, P)$ is determined by the condition of the maximum of the output entropy $H(s(x, P))$,

$$\frac{\partial H}{\partial x} = \frac{\partial H}{\partial s}\frac{\partial s}{\partial x} = (P - Q)^2 \log\left(\frac{1-s}{s}\right) = 0. \tag{29}$$

Hence the extremum of the geometric information-ionicity index $I(x, P)$ is observed for non-polarized MO, $P = Q = 1/2$, when $s = t = 1/2$ for any admissible value of the input-probability parameter $0 \leqslant x \leqslant 1$, and hence $I(x, P = 1/2) = 0$. The output probabilities are then independent of the input probabilities, as indeed manifested by the vanishing value of their mutual information index, which marks the zero amount of information flowing through the geometric promotion channel.

In the ground-state (singlet) electron configuration $\Psi^0 = |\psi_b^+ \psi_b^-|$ both electrons occupy the bonding MO: $\boldsymbol{n}^0 = (2, 0)$. The effective conditional probabilities of the physical-promotion channel in AO resolution (see equation (19) and figure 7) then read:

$$\mathbf{P}^0(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = \mathbf{P}(\boldsymbol{\psi}|\boldsymbol{\chi})\mathbf{n}^0\mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\psi}) = 2\begin{bmatrix} P^2 & PQ \\ PQ & Q^2 \end{bmatrix}. \tag{30}$$

They determine the physical AO-promotion channel shown in figure 12, which probes only the electron delocalization via the bonding MO.

The relevant functions of the conditional-entropy S (IT-covalency), mutual-information I (IT-ionicity), and overall bond-order $N = I + S$ (IT-bond-multiplicity) for the covalent (electron-sharing) input $x = y = 1/2$ in this physical AO-promotion channel read:

$$S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = 2H(P) - 1, \qquad I(\boldsymbol{\chi} : \boldsymbol{\chi}^*) = 1 - H(P), \qquad N(\boldsymbol{\chi}; \boldsymbol{\chi}^*) = H(P). \tag{31}$$

For the symmetrical bonding-MO, $P = Q = 1/2$, when $H(P) = 1$, e.g., in H_2 or the π-bond in ethylene, this gives: $S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = 1$, $I(\boldsymbol{\chi} : \boldsymbol{\chi}^*) = 0$, and $N(\boldsymbol{\chi}; \boldsymbol{\chi}^*) = 1$, thus correctly marking the single, purely covalent bond in these two prototype systems. These predictions are only in partial agreement with the corresponding IT-indices obtained from the two-electron molecular information system in atomic resolution [14–23], which generate the conserved "single" overall bond in the model:

$$S^{\mathrm{AIM}} = H(P), \qquad I^{\mathrm{AIM}} = 1 - H(P), \qquad N^{\mathrm{AIM}} = 1. \tag{32}$$

The symmetrical AO combination $P = Q = 1/2$ again gives a single, purely covalent bond-order, $S^{\mathrm{AIM}} = N^{\mathrm{AIM}} = 1$ bit and $I^{\mathrm{AIM}} = 0$, in full agreement with the present orbital-channel predictions.

Consider now the extreme polarization $P = 1$, when $H(P) = 0$ and $\psi_{\mathrm{b}} = a$ (no chemical interaction between the two AO), so that the two electrons are located on atom A in the molecule. One then finds: $S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = -1$, $I(\boldsymbol{\chi} : \boldsymbol{\chi}^*) = 1$, and $N(\boldsymbol{\chi}; \boldsymbol{\chi}^*) = 0$. Therefore, this IT-diagnosis of the lone-pair molecular configuration predicts no overall bond in the model. The IT-ionicity index reflects the electron transfer relative to the promolecule, while the negative IT-covalency identifies the non-bonding electron pair. This diagnosis differs from the AIM-resolved two-electron description (equation (32)) of this electron configuration [14–23], which predicts the conserved overall bond-order relative to the covalent promolecule, when the bonding MO becomes polarized to AO of the acceptor (acidic) atom A: $S^{\mathrm{AIM}} = 0$, $I^{\mathrm{AIM}} = 1$, $N^{\mathrm{AIM}} = 1$.

Let us next examine the IT-descriptors generated by the physical AO-promotion channel for the DA (pair-sharing) promolecule, for $x = 0$, when the free (basic) atom B^0 donates two electrons to form the coordination bond $B \rightarrow A$ in the molecule. Since in this case the output entropy $S(\boldsymbol{\chi}^*)$ is exactly equal to the conditional entropy $S(\boldsymbol{\chi}^*|\boldsymbol{\chi})$, the information-ionicity index vanishes for all admissible MO polarizations P:

$$S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = N(\boldsymbol{\chi}; \boldsymbol{\chi}^*) = 2Q[H(P) - \log Q - 1], \qquad I(\boldsymbol{\chi} : \boldsymbol{\chi}^*) = 0. \tag{33}$$

Thus, the covalent component amounts to the total bond index in this orbital description. In the coordination-bond case it is in fact impossible to separate the bond *covalency*, resulting from the charge transfer between atoms, from its *ionicity*, which originates from the same effect. Therefore, attributing the whole bond-multiplicity to the covalent component alone gives a more transparent description of the coordination bond. These results are more in line with the accepted chemical intuition, compared to the previously designed two-electron indices from the AIM-channel [14–23], in which the covalent (positive) and ionic (negative) components give rise to the vanishing overall index:

$$S^{\mathrm{AIM}} = -I^{\mathrm{AIM}} = H(P), \qquad N^{\mathrm{AIM}} = 0. \tag{34}$$

For the maximum-covalency bond polarization $P = Q = 1/2$ one again obtains from equation (33) $S = N = 1$ (a single coordination bond), which accords with the accepted chemical viewpoint. As shown in the DA orbital diagram of figure 13, the coordination promolecule reference ($x = 0$), with two electrons originating from atom B, differs from the bond-dissociation limit ($P = 1$), in which the lone-pair of electrons is located on atom A. This bond-breaking configuration indeed gives $S = I = N = 0$, in full accord with the chemical intuition.

3.2. π-electron systems in Hückel theory

Consider next the π-MO, $\boldsymbol{\pi} = \{\pi_i\}$ of allyl radical in the Hückel approximation for the consecutive numbering of carbon atoms in the π-electron system,

$$\pi_1 = \frac{1}{2}(\chi_1 + \chi_3) + \frac{\sqrt{2}}{2}\chi_2, \qquad \pi_2 = \frac{\sqrt{2}}{2}(\chi_1 - \chi_3),$$
$$\pi_3 = \frac{1}{2}(\chi_1 + \chi_3) - \frac{\sqrt{2}}{2}\chi_2. \tag{35}$$

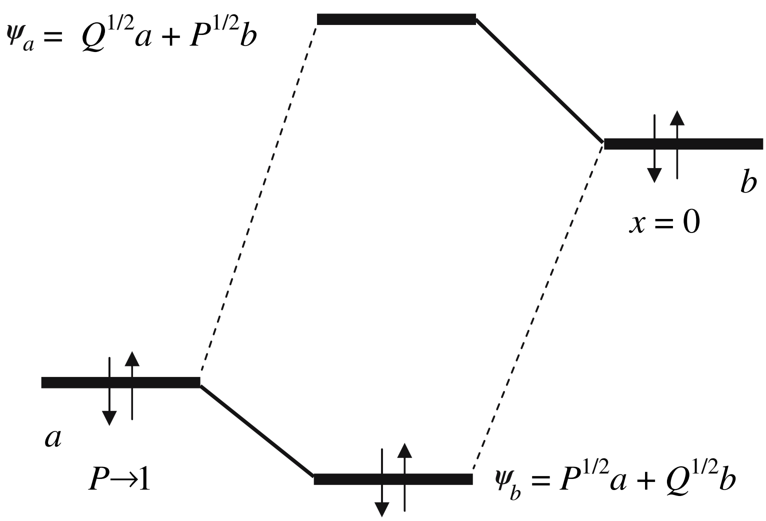

Figure 13. The interaction of two atomic orbitals a (from the acidic atom A) and b (from the basic atom A). The complementary MO probabilities P and $Q = 1 - P$, $P > Q$, determine the AO mixing in both MO. In this schematic orbital-energy diagram, the coordination promolecule is determined by the AO-input probability $x = 0$ (lone electron pair on B), while the bond-dissociation corresponds to $P \to 1$ limit (lone electron pair on A).

They generate the conditional probabilities of MO given AO, or AO given MO:

$$\mathbf{P}(\boldsymbol{\pi}|\boldsymbol{\chi}) = \begin{bmatrix} 1/4 & 1/2 & 1/4 \\ 1/2 & 0 & 1/2 \\ 1/4 & 1/2 & 1/4 \end{bmatrix} = \mathbf{P}(\boldsymbol{\chi}|\boldsymbol{\pi})^T, \tag{36}$$

which give rise to the associated π-electron AO → MO or MO → AO geometric channels. The resultant geometric-promotion probabilities,

$$\mathbf{P}(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = \begin{bmatrix} 3/8 & 1/4 & 3/8 \\ 1/4 & 1/2 & 1/4 \\ 3/8 & 1/4 & 3/8 \end{bmatrix} \tag{37}$$

then define the effective AO → AO$^+$ information system shown in figure 14. The resulting IT-indices of this geometric channel,

$$S(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = 1.541 = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}), \qquad I(\boldsymbol{\chi}:\boldsymbol{\chi}^+) = 0.044 = I(\boldsymbol{\chi}:\boldsymbol{\chi}^*),$$
$$N(\boldsymbol{\chi};\boldsymbol{\chi}^+) = 1.585 = N(\boldsymbol{\chi};\boldsymbol{\chi}^*), \tag{38}$$

again compare favorably with the previously reported entropy/information bond-indices obtained within the two-electron approach in atomic resolution [23]:

$$S^{\mathrm{AIM}} = 1.524, \qquad I^{\mathrm{AIM}} = 0.061, \qquad N^{\mathrm{AIM}} = 1.585. \tag{39}$$

They both predict roughly IT-(3/2) bond of mainly entropy-covalent character.

The ground-state MO occupations of this radical, $\boldsymbol{n}^0 = (2, 1, 0)$, give rise to the physical AO-promotion channel, which is found to be identical with the geometric channel of figure 14. Therefore, the physical-promotion IT descriptors of π-bonds in allyl are identical in the Hückel approximation with the corresponding geometric entropy/information indices (equation (38)), which were shown to semi-quantitatively reproduce the previously reported π bond-orders from the allyl two-electron AIM information system (equation (39)).

In butadiene the pairs of carbon AO, $\boldsymbol{G}_I = (\chi_1, \chi_4)$ and $\boldsymbol{G}_{II} = (\chi_2, \chi_3)$, group the basis functions related by symmetry. Let us now introduce the group

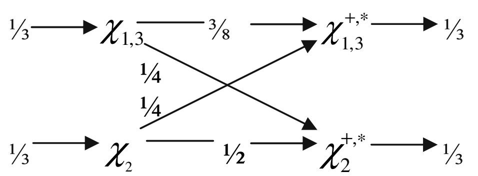

Figure 14. The geometric AO → AO$^+$ and physical (ground-state) AO → AO* promotion channel of π-electrons in allyl (Hückel theory).

complementary conditional probabilities (p, $q = 1 - p$) for the specified MO of π-electrons, $\{\pi_i, i = 1, \ldots, 4\}$,

$$\pi_1 = a(\chi_1 + \chi_4) + b(\chi_2 + \chi_3), \qquad \pi_2 = b(\chi_1 - \chi_4) + a(\chi_2 - \chi_3),$$
$$\pi_3 = b(\chi_1 + \chi_4) - a(\chi_2 + \chi_3), \qquad \pi_4 = a(\chi_1 - \chi_4) - b(\chi_2 - \chi_3),$$

$$a = \frac{1}{2}\sqrt{1 - 1/\sqrt{5}} = 0.37175, \qquad b = \frac{1}{2}\sqrt{1 + 1/\sqrt{5}} = 0.60150, \tag{40}$$

$$\begin{aligned} P(\mathrm{I}|\pi_1) = P(II|\pi_2) = P(II|\pi_3) = P(I|\pi_4) = 2a^2 \equiv p = 0.27639,\\ P(\mathrm{II}|\pi_1) = P(I|\pi_2) = P(I|\pi_3) = P(II|\pi_4) = 2b^2 \equiv q = 0.72361. \end{aligned} \tag{41}$$

These MO generate the geometric-promotion channel shown in figure 15. The corresponding geometric-promotion indices from IT are:

$$\begin{aligned} S(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = 1.971 = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}), \qquad I(\boldsymbol{\chi} : \boldsymbol{\chi}^+) = 0.029 = I(\boldsymbol{\chi} : \boldsymbol{\chi}^*),\\ N(\boldsymbol{\chi}; \boldsymbol{\chi}^+) = 2.000 = N(\boldsymbol{\chi}; \boldsymbol{\chi}^*). \end{aligned} \tag{42}$$

This result again compares favorably with the previously reported IT bond-orders from the π-communication channels in atomic resolution within the two-electron approach [14, 15, 21, 23]:

$$S^{\mathrm{AIM}} = 1.944, \qquad I^{\mathrm{AIM}} = 0.056, \qquad N^{\mathrm{AIM}} = 2.000. \tag{43}$$

They both predict 2-bits (IT-double) overall bond index of mainly entropy-covalent origin, in qualitative agreement with the chemical estimate.

By taking into account the ground-state occupation of these four MO, $\boldsymbol{n}^0 = (2, 2, 0, 0)$, one again finds that in the Hückel theory the ground-state physical AO-promotion is identical with the geometric information system of figure 15, thus giving rise to the same IT bond descriptors (equation (42)), which agree with intuitive chemical expectations.

As the final example of the geometric AO → AO$^+$ promotion we consider the π-electron ring in benzene [14, 15, 21, 23]. The familiar canonical MO from in

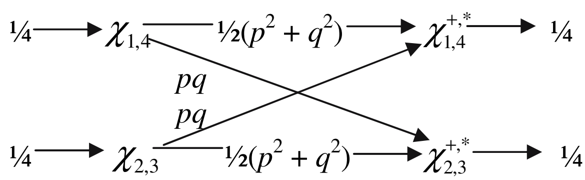

Figure 15. The geometric AO → AO$^+$ and physical (ground-state) AO → AO* promotion of π-electrons in butadiene (Hückel theory).

the Hückel method for the consecutive numbering of carbon atoms in the hexagonal π-ring,

$$\begin{aligned}
&\pi_1 = 6^{-1/2}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6),\\
&\pi_2 = 1/2(\chi_1+\chi_2-\chi_4-\chi_5), \qquad \pi_2' = 12^{-1/2}(\chi_1-\chi_2-2\chi_3-\chi_4+\chi_5+2\chi_6),\\
&\pi_3 = 1/2(\chi_1-\chi_2+\chi_4-\chi_5), \qquad \pi_3' = 12^{-1/2}(\chi_1+\chi_2-2\chi_3+\chi_4+\chi_5-2\chi_6),\\
&\pi_4 = 6^{-1/2}(\chi_1-\chi_2+\chi_3-\chi_4+\chi_5-\chi_6)
\end{aligned} \tag{44}$$

give rise to the geometric-promotion channel shown in figure 16. A subsequent inclusion of the ground-state MO-occupations $\boldsymbol{n}^0 = (2, 2, 2, 0, 0, 0)$ then shows that in the Hückel approximation the associated physical AO-promotion channel is identical with the geometric communication system of figure 16.

Their entropy/information descriptors,

$$\begin{aligned}
&S(\boldsymbol{\chi}^+|\boldsymbol{\chi}) = S(\boldsymbol{\chi}^*|\boldsymbol{\chi}) = 2.506, \qquad I(\boldsymbol{\chi}:\boldsymbol{\chi}^+) = I(\boldsymbol{\chi}:\boldsymbol{\chi}^*) = 0.079,\\
&N(\boldsymbol{\chi};\boldsymbol{\chi}^+) = N(\boldsymbol{\chi};\boldsymbol{\chi}^*) = 2.585,
\end{aligned} \tag{45}$$

again provide quite realistic representation of the related indices of the two-electron communication approach in atomic resolution:

$$S^{\mathrm{AIM}} = 2.551, \qquad I^{\mathrm{AIM}} = 0.035, \qquad N^{\mathrm{AIM}} = 2.585. \tag{46}$$

In both approaches the overall IT-index 2.585 is dominated by the entropy-covalency with the information-ionic component amounting to a minor correction in the resultant bond-multiplicity.

It should be stressed, that this overall IT bond-order falls short of the 3-bits measure predicted for the three separated π-bonds in cyclohexatriene [14, 15, 21, 23]. This result reflects the fact that in the symmetric hexagon structure, prevailed due to carbon–carbon σ-bonds, the system compromises the overall π-bond-order, which otherwise could reach higher values, should the bond alternation be allowed [32–34].

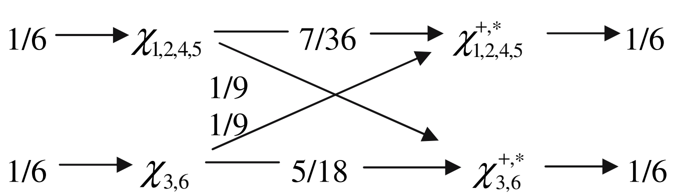

Figure 16. The geometric and physical (ground-state) AO $\rightarrow$ AO promotion of π-electrons in benzene (Hückel theory).

4. Conclusion

In this article, we have extended the communication theory of the chemical bond [23] by examining several molecular information channels within the MO description, which provides the standard framework for diagnosing the system bond network. They are determined by the conditional probabilities **P**(AO|MO) [or **P**(MO|AO)] from the superposition principle of quantum mechanics, which are defined by the relevant projection operators in the Hilbert space spanned by the AO basis set or – equivalently – by the complete set of the resulting MO.

The so-called "geometric" channels involve the AO → MO [or MO → AO] scattering of the initial (promolecular, input) probabilities via the whole set of MO, occupied and virtual in the molecular electron configuration in question. Throughout the associated AO → MO(all) → AO$^+$ probability cascade they determine the effective geometric AO → AO$^+$ "promotion," from the initial promolecular distribution to that characterizing the equally weighed MO. Its standard conditional-entropy and mutual-information descriptors in IT reflect the overall rotation of MO relative to AO in the molecular Hilbert space, thus providing the measures of the overall MO entropy-covalency and information-ionicity in the molecular system under consideration. The illustrative applications to the 2-AO model and π-electrons in simple alternant hydrocarbons have demonstrated that these IT-indices compare favorably with the previously reported entropy/information bond-orders developed within the two-electron approach in atomic resolution.

The other, "physical" set of molecular channels involves the MO-occupation weighted probability scattering. It distinguishes one electron configuration from another, thus providing a convenient framework for diagnosing the bonding pattern in the molecular excited states. This development will be described in the next paper of this series [35]. The "physical" (ground-state) AO→AO* promotion channel, resulting from the probability-scattering cascade AO→MO(occupied)→AO*, have also been shown to give a realistic account of the overall bond-multiplicities in the selected illustrative systems. In the Hückel theory description of the alternant hydrocarbons these physical-promotion channels have been found to be identical with the corresponding geometrical-promotion information systems, thus generating the same sets of the IT bond-indices.

This orbital development within the communication approach to chemical bonds in molecular systems provides their information-theoretic description, which complements the standard MO perspective [18]. It explores the AO probability scattering in molecules via the network of chemical bonds and generates the associated IT-measures of their covalent and ionic components. The bond-covalency measures the average communication-"noise" in the orbital channel, while the bond-ionicity reflects the amount of the promolecular information flowing through the channel, which has survived the increase in the orbital uncertainty due to the noise. This IT description gives a transparent account of the competition between these two bond components, which accords with the chemical intuitive expectations.

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