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Communications in molecules: local and *multi*-configuration channels and their entropic descriptors of bond multiplicity and composition

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Abstract The Orbital Communication Theory of the chemical bond, in which molecules are treated as information systems transmitting "signals" of electron allocations to Atomic Orbitals, is extended to cover the local resolution level of electron distributions and the Configuration-Interaction (CI, *multi*-determinantal) description of molecular states. These communication systems generate the information-theoretic measures of both the absolute and relative multiplicities of chemical bonds, as well as the bond covalent (communication-noise) and ionic (information-flow) components. The orbital/local communications via the CI ensembles of the occupied molecular orbitals in such generalized molecular states are investigated. Illustrative *two*-orbital model and its prototype *Valence-Bond* structures are examined in a more detail.

Keywords Chemical bonds · Communication systems · Covalent/ionic components · Entropic bond multiplicities · Information theory · Local information propagation · Orbital communications

1 Introduction

The *Information Theory* (IT) [1–8] has been successfully applied to explore the electron probabilities and patterns of chemical bonds they generate in molecules, e.g., [9–21]. In Schrödinger's quantum mechanics the electronic state is determined by the system wave-function, the (complex) amplitude of the particle probability distribution, which carries the *classical* part of the overall information content. Both the electron density or its shape factor, the *probability* distribution determined by the wave-function *modulus*, and the system *current* distribution, related to the gradient

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of the wave-function *phase*, ultimately contribute to the *resultant* (quantum) information content of molecular states. The former reveals the classical information content, while the latter determines its *non*-classical complement in the overall information measure [9,10,20–23].

The *non*-classical information terms, due to the electron current (or the wave-function phase), introduce a *non*-vanishing information *source* into the associated entropy/information continuity equation, which expresses a local balance of the resultant information density [10,13]. Since the extremum principles of these generalized information measures ultimately determine the molecular equilibria implied by the Schrödinger equation [2,13], this quantum IT treatment of the molecular electronic structure is thus equivalent to the standard quantum-mechanical description. The *vertical* information principles [20–23], for the fixed electron density, were shown to closely parallel the familiar energy and entropy principles of the ordinary thermodynamics.

Elsewhere it has been argued that many classical problems of theoretical chemistry can be approached afresh using the IT perspective [9–21]. For example, the displacements of the classical information distribution in a molecule, relative to the *promolecular* reference consisting of its *non*-bonded constituent atoms, have been investigated [11–15,17–21,24–26] and the least biased partition of the molecular electron distributions into subsystem contributions, e.g., densities of bonded atoms, has been examined [11–13,27–34]. This IT approach has been shown to lead to the "stockholder" *Atoms-in-Molecules* (AIM) of Hirshfeld [35]. These optimum density pieces can be derived from alternative global and local variational principles of IT. They have been also generalized in a related problem of the AIM partitioning of *two*-electron densities [11,32–34].

The spatial localization of specific chemical bonds present another challenging problem to be tackled by this novel treatment of molecular systems. Another diagnostic problem of the molecular electronic structure deals with the shell structure and electron localization in atoms and molecules. The *non*-additive Fisher information in the *Atomic Orbital* (AO) resolution has been recently used as the *Contra-Gradience* (CG) criterion for localizing the bonding regions in molecules [11–21,25–38], while the related information density in the *Molecular Orbital* (MO) resolution has been shown [11,39] to determine the vital ingredient of the *Electron-Localization Function* (ELF) [40–42].

The *Communication Theory of the Chemical Bond* (CTCB), which uses the entropic descriptors of the molecular information (communication) channels in the AIM, orbital and local resolutions of the electron probability distributions, has also been developed [11–13,43–60]. The same bond descriptors have been used to provide the information-scattering perspective on the intermediate stages in the electron redistribution processes [61], including the atom "promotion" via the orbital hybridization [62], and the communication theory for the excited electron configurations has been developed [63]. Moreover, the phenomenological description of equilibria in molecular subsystems has been proposed [11,64–66], which formally resembles that developed in ordinary thermodynamics [67].

Entropic probes of the electronic structure have already provided attractive tools for describing the chemical bond phenomenon in information terms. For an exploration of the chemical bond multiplicities in the orbitally-resolved communication theory [13,58–60,68–71] it is vital to examine how the input information is propa-

gated between AO, the typical basis functions used to describe the *bonding* (occupied) MO subspace. In fact, the molecular system can be regarded as an *information system* determined by the communication network of the electronic *conditional* probabilities, in which the elementary "units" relevant to the resolution level in question emit and/or receive the electron-allocation signals [13]. This *classical* information scattering and flow processes can be characterized by standard tools of the Shannon's theory of communication [3,4,7,8,11–13], thus providing a novel class of descriptors of molecular "connectivities" between AIM.

In particular, the communication *noise*, measured by the network average *conditional entropy* (scattered information), reflects the AO *indeterminism* in a molecule, and hence also the electron *delocalization* effect synonymous with the chemical *covalency* concept. The complementary bond component, chemical *iconicity*, is similarly probed by the channel average *mutual information* (information *flow*) descriptor, which reflects the AO *deterministic* (localization) aspect of the probability propagation in a molecule. These two IT components complement each other: the more ionic (deterministic) is the molecular communication system, the less covalent (indeterministic) is its probability propagation in the given AO basis. This reflects a competition between these two bond components for the available basis functions.

The *classical* (probability) entropic probes have been applied to interpret the molecular electron distributions in chemical terms. These communication descriptors have been derived from the classical information channels determined by the conditional *probabilities* of the AO events in the *stationary* (*non*-degenerate) molecular state, for which the spatial-*phase* component, and hence also the associated probability current, both identically vanish. The truly *quantum* channel, capable of the communication interference [72], calls for the information system of the probability-*amplitude* propagation, with the scattering amplitudes then explicitly depending on phases of the emitting and monitoring complex *event*-states. Such an *amplitude* channel, corresponding to the quantum scattering between complex basis functions in the complex molecular state, still awaits a more thorough examination [21].

The IT approach introduces into the theory of electronic structure of molecular systems the novel *entropy*-representation [10–23], which complements the familiar *energy*-representation of the molecular quantum mechanics. Such a dual perspective parallels that known from the ordinary thermodynamics [67]. It establishes the equivalent energy and entropy/information principles governing the molecular equilibria, provides a new unifying perspective on molecular electronic structure, extends the variety of tools for probing chemical processes, and enriches the range of available descriptors of the bonding patterns in molecules. It increases our understanding of the classical (intuitive) chemical concepts, e.g., the identity of AIM, bond localization, sources and measures of bond-order, its covalent/ionic composition, etc. The novel, through-*bridge* mechanism of the (*intermediate*) orbital interactions in molecules has been identified [73–77], which complements the familiar through-*space* (direct) bond contributions. The IT approach also covers changes in the bond pattern effected by chemical reactions [78,79]. The equivalence of the *vertical* (*density*-constrained) energy and entropy/information rules in quantum mechanics parallels that of the complementary energy and entropy principles of thermodynamics.

In this work we intend to examine the local communications in molecules and their bond-multiplicity descriptors. We shall also attempt to generalize the AO formulation of CTCB, called the *Orbital Communication Theory* (OCT) [12,13,58–60,68–71], into the *multi*-determinantal expansions of electronic states encountered in the *Configuration-Interaction* (CI) treatment. Previous *one*-determinantal MO approach, e.g., within the Hartree-Fock (HF) or Kohn-Sham (KS) Self-Consistent Field (SCF) MO theories, will be extended to cover the *multi*-determinantal states of CI theory. The molecular networks for the electronic information delocalization among basis functions, both classical (probability propagation) and quantum (amplitude scattering), will then also cover the CI MO-ensembles. This treatment extends the previous *Natural Orbital* (NO) analysis [45] of the homonuclear bond in H_2 within the Shull model [80–83]. The information dissipation/flow phenomena will be investigated using both the local and CI orbital descriptions, and the bond multiplicity/composition descriptors in prototype *Valence-Bond* (VB) structures will be reexamined.

Throughout the article the following tensor notation is used: A denotes a scalar quantity, $\boldsymbol{A}$ stands for the *row*- or *column*-vector, and $\mathbf{A}$ represents a square or rectangular matrix. The logarithm of the Shannon-type information measure is taken to an arbitrary but fixed base. In keeping with the custom in works on IT the logarithm taken to base 2 corresponds to the information measured in *bits* (binary digits), while selecting log = ln expresses the amount of information in *nats* (natural units): 1 nat = 1.44 bits.

2 Communication channels and their information descriptors

We begin with some rudiments on the molecular information networks and the entropy/information descriptors of a transmission of the electron-assignment "signals" in molecular *communication systems* [11–13,46–63]. The basic elements of such a "device" are shown in Fig. 1. The signal emitted from n "inputs" $\boldsymbol{a} = (a_1, a_2, \ldots, a_n)$ of the channel *source* $\mathbf{A}$ is characterized by the probability distribution $\boldsymbol{P(a)} = \boldsymbol{p} = (p_1, p_2, \ldots, p_n)$. It can be received at m "outputs" $\boldsymbol{b} = (b_1, b_2, \ldots, b_m)$ of

Input (Source): $\mathbf{A}$	Communication network: $\mathbf{P(b\|a)}$	*Output* (Receiver): $\mathbf{B}$

$$a_1 \qquad\qquad\qquad\qquad\qquad\qquad b_1$$
$$a_2 \qquad\qquad\qquad\qquad\qquad\qquad b_2$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$p_i \rightarrow a_i \;\rule{1cm}{0.4pt}\; P(b_j|a_i) \equiv P(j|i) \;\rule{1cm}{0.4pt}\!\!\rightarrow\; b_j \rightarrow q_j$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
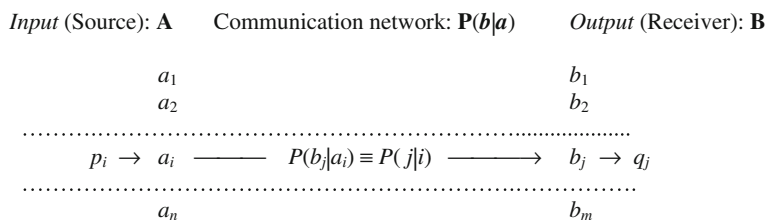$$a_n \qquad\qquad\qquad\qquad\qquad\qquad b_m$$

Fig. 1 Schematic diagram of the communication system characterized by two probability vectors: $\boldsymbol{P(a)} = \{P(a_i)\} = \boldsymbol{p} = (p_1, \ldots, p_n)$, of the channel "input" events $\boldsymbol{a} = (a_1, \ldots, a_n)$ in the system source $\mathbf{A}$, and $\boldsymbol{P(b)} = \{P(b_j)\} = \boldsymbol{q} = (q_1, \ldots, q_m)$, of the "output" events $\boldsymbol{b} = (b_1, \ldots, b_m)$ in the system receiver $\mathbf{B}$. The transmission of signals in this communication channel is described by the $(n \times m)$-matrix of the conditional probabilities $\mathbf{P(b|a)} = \{P(b_j|a_i) \equiv P(j|i) = P(i, j)/p_i\} \equiv \mathbf{P(q|p)}$ of observing different "outputs" (*columns*, $j = 1, 2, \ldots, m$), given the specified "inputs" (*rows*, $i = 1, 2, \ldots, n$). For clarity, only a single scattering $a_i \rightarrow b_j$ is shown in the diagram

the system *receiver* **B**. The transmission of signals in the channel is randomly disturbed thus exhibiting a communication *noise*. The signal propagation is described by the conditional probabilities of the "outputs-given-inputs", $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(b_j|a_i) = P(a_i \wedge b_j)/P(a_i) \equiv P(j|i)\} \equiv \mathbf{P}(\boldsymbol{q}|\boldsymbol{p})$; here $\mathbf{P}(\boldsymbol{a},\boldsymbol{b}) = \{P(a_i \wedge b_j) \equiv P(i,j)\}$ groups probabilities of a joint occurrence of the specified pair of the input and output events. The relevant normalization conditions of these probabilities read:

$$\sum_j P(i,j) = p_i, \quad \sum_i P(i,j) = q_j,$$

$$\sum_i \sum_j P(i,j) = 1; \quad \sum_j P(j|i) = 1, \quad i = 1, 2, \ldots \tag{1}$$

The distribution of the output signal $\boldsymbol{P}(\boldsymbol{b}) = \boldsymbol{q}$ among the detection "events" $\boldsymbol{b}$ is given by the output probability distribution $\boldsymbol{q} = (q_1, q_2, \ldots, q_m) = \boldsymbol{P}(\boldsymbol{a})\boldsymbol{P}(\boldsymbol{b}|\boldsymbol{a}) = \boldsymbol{p}\mathbf{P}(\boldsymbol{q}|\boldsymbol{p})$.

The Shannon entropy of the "product" distribution $\mathbf{P}(\boldsymbol{a},\boldsymbol{b})$ can be expressed as the sum of the average entropy in the marginal (input) probability distribution $\boldsymbol{p}$,

$$S(\boldsymbol{p}) = -\sum_i p_i \log p_i \tag{2}$$

and the average *conditional entropy* in $\boldsymbol{q}$ given $\boldsymbol{p}$ (see Fig. 2),

$$S(\boldsymbol{q}|\boldsymbol{p}) = -\sum_i \sum_j P(i,j) \log P(j|i)], \tag{3}$$
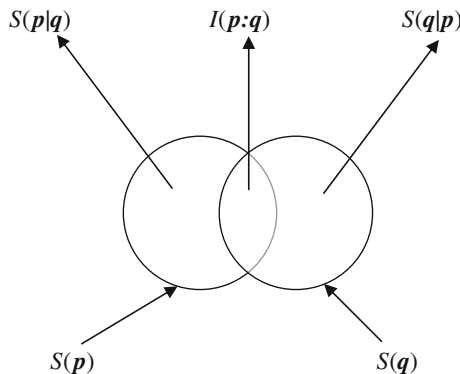

Fig. 2 Diagram of the *conditional-entropy* and *mutual-information* quantities for two dependent probability distributions $\boldsymbol{p}$ and $\boldsymbol{q}$ of Fig. 1. *Two circles* enclose areas representing the entropies $S(\boldsymbol{p})$ and $S(\boldsymbol{q})$ of two separate probability vectors/schemes, while their common (overlap) area corresponds to the mutual information $I(\boldsymbol{p}{:}\boldsymbol{q})$ in these two distributions. The remaining part of *each circle* represents the corresponding conditional entropy, $S(\boldsymbol{p}|\boldsymbol{q})$ or $S(\boldsymbol{q}|\boldsymbol{p})$, measuring the residual uncertainty about events in one set, when one has the full knowledge of the occurrence of events in the other set of outcomes. The area enclosed by the envelope of two circles thus represents the entropy of the "product" (joint) distribution: $S(\mathbf{P}(\boldsymbol{a},\boldsymbol{b})) = S(\boldsymbol{p}) + S(\boldsymbol{q}) - I(\boldsymbol{p}:\boldsymbol{q}) = S(\boldsymbol{p}) + S(\boldsymbol{q}|\boldsymbol{p}) = S(\boldsymbol{q}) + S(\boldsymbol{p}|\boldsymbol{q})$

$$S[\mathbf{P}(\boldsymbol{a},\boldsymbol{b})] = -\sum_i \sum_j P(i,j) \log P(i,j)$$

$$= -\sum_i \sum_j p_i P(j|i) \left[\log p_i + \log P(j|i)\right]$$

$$= -\left[\sum_j P(j|i)\right] \sum_i p_i \log p_i - \sum_i p_i \left[\sum_j P(j|i) \log P(j|i)\right]$$

$$\equiv S(\boldsymbol{p}) + S(\boldsymbol{q}|\boldsymbol{p}), \tag{4}$$

The latter represents the extra amount of the information about the occurrence of events $\boldsymbol{b}$, given that the events $\boldsymbol{a}$ are known to have occurred. In other words: the amount of information obtained as a result of simultaneously observing the events $\boldsymbol{a}$ and $\boldsymbol{b}$ of two discrete probability distributions equals to the amount of information in one set, say $\boldsymbol{a}$, supplemented by the extra information provided by the occurrence of events in the other set $\boldsymbol{b}$, when $\boldsymbol{a}$ are known to have occurred already.

The common amount of information in two dependent events a_i and b_j, $I(i:j)$, measuring the information about a_i provided by the occurrence of b_j or the information about b_j provided by the occurrence of a_i, determines the *mutual information* in these two events:

$$I(i:j) = \log\left[P(i,j)/(p_i q_j)\right] = \log\left[P(i|j)/p_i\right] \equiv \log\left[P(j|i)/q_j\right]$$

$$= I(j:i). \tag{5}$$

It vanishes, when both events are independent, i.e., when the occurrence of one event does not influence (or condition) the probability of the occurrence of the other event, and it is negative, when the occurrence of one event makes a *non*-occurrence of the other event more likely. It also follows from the preceding equation that

$$I(i:j) = I(i) - I(i|j) = I(j) - I(j|i) = I(i) + I(j) - I(i,j) \quad \text{or}$$

$$I(i,j) = I(i) + I(j) - I(i:j), \tag{6}$$

where the *self*-information of the joint event $I(i,j) = -\log P(i,j)$. Thus, the information in the joint occurrence of two events a_i and b_j is the information in the occurrence of a_i plus that in the occurrence of b_j minus the mutual information. Clearly, for independent events, when $P^{ind.}(i,j) = p_i q_j$, $I^{ind.}(i:j) = 0$ and hence $I^{ind.}(i,j) = I(i) + I(j)$.

The mutual information of an event with itself defines its *self*-information: $I(i:i) \equiv I(i) = \log[P(i|i)/p_i] = -\log p_i$, since $P(i|i) = 1$. It vanishes, when $p_i = 1$, i.e., when there is no uncertainty about the occurrence of a_i, so that the occurrence of this event removes no uncertainty, hence conveys no information. This quantity provides a measure of the uncertainty about the occurrence of the event itself, i.e., the information received when this event actually occurs. The Shannon entropy of Eq. (2) can be thus interpreted as the mean value of *self*-informations $\{I(i) = -\log p_i\}$ in individual events: $S(\boldsymbol{p}) = \sum_i p_i I(i)$. One similarly defines the average *mutual*

information in two probability distributions (see Fig. 2) as the mean value of the mutual information quantities for individual joint events:

$$I(\boldsymbol{p} : \boldsymbol{q}) = \sum_i \sum_j P(i, j) I(i : j) = \sum_i \sum_j P(i, j) \log \left[P(i, j) / P^{ind.}(i, j) \right]$$
$$= S(\boldsymbol{p}) + S(\boldsymbol{q}) - S[\mathbf{P}(\boldsymbol{a}, \boldsymbol{b})] = S(\boldsymbol{p}) - S(\boldsymbol{p}|\boldsymbol{q}) = S(\boldsymbol{q}) - S(\boldsymbol{q}|\boldsymbol{p}) \geq 0, \quad (7)$$

where equality holds for independent distributions. Indeed, the amount of uncertainty in $\boldsymbol{q}$ can only decrease when $\boldsymbol{p}$ has been known beforehand, $S(\boldsymbol{q}) \geq S(\boldsymbol{q}|\boldsymbol{p}) = S(\boldsymbol{q}) - I(\boldsymbol{p} : \boldsymbol{q})$, with equality being observed only when the two sets of events are independent, thus giving *non*-overlapping entropy circles in Fig. 2.

The average mutual information is also an example of the entropy deficiency (cross entropy, missing information, information distance, directed divergence) of Kullback and Leibler [5,6]. For example, in the discrete probability scheme identified by events $\boldsymbol{a} = \{a_i\}$ and their probabilities $P(\boldsymbol{a}) = \boldsymbol{p}$, this discrimination information in $\boldsymbol{p}$ with respect to the reference distribution $P(\boldsymbol{a}_0) = \boldsymbol{p}_0 = \{p_i^0\}$ reads:

$$\Delta S(\boldsymbol{p}|\boldsymbol{p}_0) = \sum_i p_i \log(p_i/p_i^0) \equiv \sum_i p_i I_i \geq 0. \quad (8)$$

This quantity provides a measure of the information resemblance between the two compared probability schemes. The more the two distributions differ from one another, the larger this information distance. For individual events the logarithm of the probability ratio $I_i = \log(p_i/p_i^0)$, called the probability *surprisal*, provides a measure of the event information in the current distribution relative to that in the reference distribution. Notice that the equality in the preceding equation takes place only for the vanishing surprisals in all events, i.e., when the two probability distributions are identical.

Indeed, the average mutual information of Eq. (7) measures the missing information between the joint probabilities $\mathbf{P}(\boldsymbol{a}, \boldsymbol{b}) \equiv \boldsymbol{\pi}$ of the *dependent* events $\boldsymbol{a}$ and $\boldsymbol{b}$, and the joint probabilities $\mathbf{P}^{ind.}(\boldsymbol{a}, \boldsymbol{b}) = \boldsymbol{\pi}_0 = \boldsymbol{p}^{\mathrm{T}} \boldsymbol{q}$ for the *independent* joint events: $I(\boldsymbol{p} : \boldsymbol{q}) = \Delta S(\boldsymbol{\pi}|\boldsymbol{\pi}_0)$. The average mutual information thus reflects a degree of a dependence between events defining the two probability schemes. A similar information-distance interpretation can be attributed to the average conditional entropy of Eq. (3): $S(\boldsymbol{p}|\boldsymbol{q}) = S(\boldsymbol{p}) - \Delta S(\boldsymbol{\pi}|\boldsymbol{\pi}_0)$.

3 Orbital channels in a single electron configuration

In OCT the orbital channels [3,4,6,11–13] propagate probabilities of electron assignments to basis functions of SCF MO calculations, e.g., *Atomic Orbitals* (AO) $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m)$. The underlying conditional probabilities of the *output* orbital events, given the input orbitals, $\mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \{P(\chi_j|\chi_i) \equiv P(j|i) \equiv P_{i \to j} = A(j|i)^2 = (A_{i \to j})^2\}$, or the associated scattering amplitudes $\mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \{A(j|i) = A_{i \to j}\}$ of the *emitting* (input) states $\boldsymbol{a} = |\boldsymbol{\chi}\rangle = \{|\chi_i\rangle\}$ among the *monitoring/receiving* (output) states $\boldsymbol{b} = |\boldsymbol{\chi}'\rangle = \{|\chi_j\rangle\}$, results from the (bond-projected) superposition principle of

quantum mechanics [58–60,68–72,84]. The local description, which we shall examine in the present analysis, uses basis functions $\{|r\rangle\}$ of the position representation identified by the continuous labels of spatial coordinates determining the location r of an electron. They determine both the input $a = \{|r\rangle\}$ and output $b = \{|r'\rangle\}$ of the *local* molecular channel determined by the relevant conditional probabilities $\{P(r'|r) = P_{r \to r'} = (A_{r \to r'})^2\}$.

The entropy/information indices of the covalent/ionic components of chemical bonds represent the complementary descriptors of the average communication *noise* and of the amount of information *flow*, respectively, in the molecular orbital channel. One observes that the *molecular* input $P(a) \equiv p$ generates the same distribution in the output of the molecular channel, $q = pP(b|a) = \{\sum_i p_i P(j|i) \equiv \sum_i P(i \wedge j) = p_j\} = p$, thus identifying p as the *stationary* vector of AO-probabilities in the molecular ground state. This purely molecular communication channel is devoid of any reference (history) of the chemical bond formation and generates the average noise index of the IT bond-*covalency* measured by the *conditional-entropy* of the system outputs given inputs: $S(P(b)|P(a)) = S(q|p) \equiv S$.

The AO channel with the *promolecular* input signal, $P(a_0) = p_0 = \{p_i^0\}$, of to the system *free* constituent atoms, refers to the initial stage in the bond-formation process. It corresponds to the ground-state (fractional) occupations of the AO contributed by the system constituent atoms, before their mixing into *Molecular Orbitals* (MO). These input probabilities give rise to the average information *flow* index of the system IT bond-*ionicity*, given by the *mutual-information* in the channel promolecular inputs and molecular outputs [44]:

$$I(P(a_0):P(b)) = I(p_0:q) = \sum_i \sum_j P(i,j) \log\left[p_i P(i,j)/(p_i p_j p_i^0) \right]$$
$$= \sum_i \sum_j P(i,j)\left[-\log p_j + \log\left(p_i/p_i^0 \right) + \log P(j|i) \right]$$
$$= S(q) + \Delta S(p|p_0) - S \equiv I_0. \tag{9}$$

This amount of information reflects the fraction of the initial (promolecular) information content $S(p_0)$ which has not been dissipated as noise in the molecular communication system. In particlular, for the molecular input, when $p_0 = p$ and hence the vanishing information distance $\Delta S(p|p_0) = 0$,

$$I(p:q) = S(q) - S \equiv I. \tag{10}$$

The sum of these two bond components, e.g.,

$$M(P(a_0);P(b)) = M(p_0;q) = S + I^0 = S(q) + \Delta S(p|p_0) \equiv M_0, \tag{11}$$

measures the *absolute* overall IT bond-multiplicity, of all bonds in the molecular system under consideration, relative to the *promolecular* reference. For the *molecular* input this quantity preserves the Shannon entropy of the molecular input probabilities:

$$M(\boldsymbol{p}\,;\boldsymbol{q}) = S(\boldsymbol{q}|\boldsymbol{p}) + I(\boldsymbol{p}:\boldsymbol{q}) = S(\boldsymbol{q}) \equiv M. \tag{12}$$

The *relative* index,

$$\Delta M = M - M_0 = \Delta S(\boldsymbol{p}|\boldsymbol{p}_0), \tag{13}$$

reflecting changes due to the chemical bonds alone, is then interaction dependent. It correctly vanishes in the atomic dissociation limit of *separated atoms*, when $\boldsymbol{p}_0$ and $\boldsymbol{p}$ become identical. The entropy deficiency index $\Delta S(\boldsymbol{p}|\boldsymbol{p}_0)$, reflecting the information distance between the molecular electron density, generated by the constituent bonded atoms, and promolecular density, due to molecularly placed non-bonded constituent atoms, thus represents the overall IT difference-index of the system chemical bonds. Another interaction-dependent approach has been proposed within the *Natural Orbital* (NO) description of H_2 [45].

An exploration of the chemical bond system in electronic states indeed calls for the AO resolution determined by the basis functions $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m)$ of typical SCF LCAO MO calculations. The occupied MO of the familiar Hartree-Fock (HF) theory define the *bonding subspace* $\boldsymbol{\varphi}^0 = \boldsymbol{\chi}\mathbf{C}^0\{\varphi_s^0 = \phi_s^0\xi_s, s = 1, 2, \ldots, N\}$ of the (*singly*-occupied) *spin*-MO (SMO) in the molecular ground-state of N electrons given by the Slater determinant consisting of N-lowest SMO:

$$\Psi_0(N) = \det\left[\boldsymbol{\varphi}^0\right] \equiv |\varphi_1^0, \varphi_2^0, \ldots, \varphi_N^0|. \tag{14}$$

Here, $\varphi_s^0(\boldsymbol{r}, \sigma) = \phi_s^0(\boldsymbol{r})\xi_s^0(\sigma)$, ϕ_s^0 denotes the *spatial* MO, and ξ_s^0 stands for one of two admissible spin states of an electron: $\xi_s^0 \in \{\alpha(\text{spin-}up), \beta(\text{spin-}down)\}$. One recalls at this point, that—rigorously speaking—in the Kohn-Sham (KS) theory such determinant of the method orbitals, which provides quite an adequate description of the system chemical bonds, e.g., [11–13], defines the *hypothetical* state of *non*-interacting electrons, which generates the same density as the (Coulomb-correlated) ground state of the *real* (interacting) system.

In this simplest, *one*-determinantal orbital approximation one thus takes into account only a single orbital configuration, e.g., the ground-state $\Psi_0(N)$, the occupied SMO of which give rise to all physical properties of the system under consideration. This configuration is thus uniquely identified by its *singly*-occupied (physical) SMO subspace $\boldsymbol{\varphi}^0 = (\varphi_1^0, \varphi_2^0, \ldots, \varphi_N^0)$, or by the associated spatial MO, $\boldsymbol{\phi}^0 = (\phi_1^0, \phi_2^0, \ldots, \phi_N^0) = \boldsymbol{\chi}\mathbf{C}^0$, which define the corresponding (idempotent) projectors:

$$\hat{P}_{\boldsymbol{\varphi}}^0 \equiv \sum_{s=1}^{N}\left|\phi_s^0\right\rangle\left\langle\phi_s^0\right| = |\boldsymbol{\varphi}^0\rangle\langle\boldsymbol{\varphi}^0|, \quad (\hat{P}_{\boldsymbol{\varphi}}^0)^2 = \hat{P}_{\boldsymbol{\varphi}}^0; \quad \hat{P}_{\boldsymbol{\phi}}^0 \equiv |\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|, \quad (\hat{P}_{\boldsymbol{\phi}}^0)^2 = \hat{P}_{\boldsymbol{\phi}}^0. \tag{15}$$

They generate the configuration *Charge-and-Bond-Order* (CBO) matrix, i.e., the *one*-electron *density matrix* in the AO representation:

$$\boldsymbol{\gamma}^0 = \left\langle \chi \middle| \boldsymbol{\varphi}^0 \right\rangle \left\langle \boldsymbol{\varphi}^0 \middle| \chi \right\rangle \equiv \langle \chi | \hat{\mathrm{P}}^0_{\boldsymbol{\varphi}} | \chi \rangle = \mathbf{C}^0 \mathbf{C}^{0\dagger} = \{\gamma_{k,l}(0)\}, \quad \mathrm{tr}\, \boldsymbol{\gamma}^0 \equiv \sum_i \gamma_{i,i}(0) = N,$$

(16)

where the rectangular matrix of the LCAO MO expansion coefficients $\mathbf{C}^0 = \langle \chi | \boldsymbol{\varphi}^0 \rangle = \langle \chi | \boldsymbol{\phi}^0 \rangle$. For the complete AO basis, when $|\chi\rangle\langle\chi| = 1$, the CBO matrix is also idempotent: $(\boldsymbol{\gamma}^0)^2 = \boldsymbol{\gamma}^0$.

The conditional probabilities of AO communications in this ground-state configuration, via its occupied MO,

$$\mathbf{P}^0(\chi'|\chi) = \{P^0(j|i) \equiv P_{i \to j}(0) = A^0(j|i)^2 = [A_{i \to j}(0)]^2$$
$$= \gamma_{i,j}(0)\gamma_{j,i}(0)/\gamma_{i,i}(0)\},$$

(17)

then determine the associated *joint*-probability matrix:

$$\mathbf{P}^0(\chi, \chi') = \{P^0(i, j) = p_i(0)P^0(j|i) = \gamma_{i,j}(0)\gamma_{j,i}(0)/N\},$$

(18)

where the configuration AO probabilities $\boldsymbol{p}^0 = \{p_i(0) = \gamma_{i,i}(0)/N\}$. It can be straightforwardly verified that for the complete basis set they satisfy the normalization conditions of Eq. (1), e.g.,

$$\sum_j P^0(i, j) = (1/N) \sum_j \gamma_{i,j}(0)\gamma_{j,i}(0) = \gamma_{i,i}(0)/N = p_i(0).$$

The associated communication amplitudes then read:

$$\mathbf{A}^0(\chi'|\chi) = \left\{ A^0(j|i) = A_{i \to j}(0) = \gamma_{i,j}(0)/[\gamma_{i,i}(0)]^{1/2} \right\}.$$

(19)

They are dependent upon phases of the CBO matrix elements thus being capable of the communication "interference" [72,85].

4 Local communications in single electron configuration

A deeper understanding of the molecular electronic structure ultimately calls for the (*continuous*) *fine*-grained, local description [86], to complement the (*discrete*) *coarse*-grained AO resolution adopted in OCT. One observes that the above orbital-communication development can indeed be naturally generalized into such an extreme resolution level of resolving the electron distributions in molecules, when one examines the information propagations between infinitesimal volume elements around $\boldsymbol{r} \in \mathfrak{R}$ in the channel input and $\boldsymbol{r}' \in \mathfrak{R}'$ in its output, respectively, where $\mathfrak{R}$ or $\mathfrak{R}'$ denote the whole physical space.

As alredy mentioned in the preceding section, in such an approach one adopts the local basis set of the precise localization states $\{|\boldsymbol{r}\rangle\}$ of an electron, in which the MO projectors of Eq. (15) give rise to the ordinary (idempotent) *one*-electron density

matrix. For example, for the *single*, say ground-state Slater determinant [Eq. (14)] in HF or KS theories one finds:

$$\gamma^0(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r}|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\mathbf{r}'\rangle = \langle \mathbf{r}|\hat{P}_{\boldsymbol{\phi}}^0|\mathbf{r}'\rangle = \sum_s \phi_s^0(\mathbf{r})\phi_s^0(\mathbf{r}')^*,$$

$$\mathrm{tr}\gamma^0 \equiv \int \gamma^0(\mathbf{r}, \mathbf{r})d\mathbf{r} = \int \rho^0(\mathbf{r})d\mathbf{r} = N, \tag{20}$$

$$\int \gamma^0(\mathbf{r}, \mathbf{r}')\gamma^0(\mathbf{r}', \mathbf{r}'')d\mathbf{r}' = \int \langle \mathbf{r}|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\mathbf{r}'\rangle\langle \mathbf{r}'|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\mathbf{r}''\rangle d\mathbf{r}'$$

$$= \langle \mathbf{r}|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\mathbf{r}''\rangle = \langle \mathbf{r}|\boldsymbol{\phi}^0\rangle\langle\boldsymbol{\phi}^0|\mathbf{r}''\rangle = \gamma^0(\mathbf{r}, \mathbf{r}''). \tag{21}$$

Above we have used the basis set completeness, $\int d\mathbf{r}'|\mathbf{r}'\rangle\langle\mathbf{r}'| = 1$, the MO orthonormality, $\langle\boldsymbol{\phi}^0|\boldsymbol{\phi}^0\rangle = \mathbf{I}$, $\rho^0(\mathbf{r}) = Np^0(\mathbf{r})$ stands for molecular electron density, while $p^0(\mathbf{r}) = \gamma^0(\mathbf{r}, \mathbf{r})/N$ denotes its "shape" (probability) factor.

The local information system involves these strict-localization events in both its input $\boldsymbol{a} = \{|\mathbf{r}\rangle\}$ and output $\boldsymbol{b} = \{|\mathbf{r}'\rangle\}$. It is determined by the conditional-probability kernel

$$P^0(\mathbf{r}'|\mathbf{r}) = P_{\mathbf{r}\to\mathbf{r}'}(0) = \gamma^0(\mathbf{r}, \mathbf{r}')\gamma^0(\mathbf{r}', \mathbf{r})/\gamma^0(\mathbf{r}, \mathbf{r}) \equiv [A_{\mathbf{r}\to\mathbf{r}'}(0)]^2, \tag{22}$$

the square of the associated scattering amplitude:

$$A_{\mathbf{r}\to\mathbf{r}'}(0) = \gamma^0(\mathbf{r}, \mathbf{r})/[\rho^0(\mathbf{r})]^{1/2}. \tag{23}$$

The corresponding *joint*-probability distribution thus reads:

$$P^0(\mathbf{r}, \mathbf{r}') = p^0(\mathbf{r})P^0(\mathbf{r}'|\mathbf{r}) = \gamma^0(\mathbf{r}, \mathbf{r}')\gamma^0(\mathbf{r}', \mathbf{r})/N. \tag{24}$$

One again directly verifies their normalizations using the idempotency property of the density matrix [Eq. (21)]:

$$\int P^0(\mathbf{r}', \mathbf{r}')d\mathbf{r}' = (1/N)\int \gamma^0(\mathbf{r}, \mathbf{r}')\gamma^0(\mathbf{r}', \mathbf{r})d\mathbf{r}' \equiv (1/N)\int \Omega^0(\mathbf{r}, \mathbf{r}')d\mathbf{r}'$$

$$= \gamma^0(\mathbf{r}, \mathbf{r})/N = p^0(\mathbf{r}), \tag{25}$$

$$\int P^0(\mathbf{r}'|\mathbf{r})d\mathbf{r}' = [\rho^0(\mathbf{r})]^{-1}\int \gamma^0(\mathbf{r}, \mathbf{r}')\gamma^0(\mathbf{r}', \mathbf{r})d\mathbf{r}' = \gamma^0(\mathbf{r}, \mathbf{r})/\rho^0(\mathbf{r}) = 1. \tag{26}$$

Therefore, the molecular density matrix uniquely determines all local communications between the system infinitesimal volume-elements, *via* the subspace of the configuration occupied SMO,

$$\{P^0(\mathbf{r}, \mathbf{r}') = P_{\mathbf{r},\mathbf{r}'}[\gamma^0]\}, \ \{P^0(\mathbf{r}'|\mathbf{r}) = P_{\mathbf{r}\to\mathbf{r}'}[\gamma^0]\} \quad \text{and} \quad \{A^0(\mathbf{r}'|\mathbf{r}) = A_{\mathbf{r}\to\mathbf{r}'}[\gamma^0]\}. \tag{27}$$

While probabilities of the local conditional probabilities are independent of the phases of the "*off*-diagonal" part of γ^0, for $\mathbf{r}' \neq \mathbf{r}$, their amplitudes are seen to be explicitly dependent upon phases of the local basis functions.

5 Entropy/information descriptors of local channels

The overall conditional entropy descriptor [Eq. (3)] of the local channel defined by the *two*-point probabilities of Eqs. (22) and (24), is given by the following functional of the density matrix γ^0 of the molecular ground-state configuration $\Psi_0(N)$ [see Eq. (21)],

$$
\begin{aligned}
S^0(\mathfrak{R}'|\mathfrak{R}) &= -\iint P^0(\boldsymbol{r}, \boldsymbol{r}') \log P^0(\boldsymbol{r}'|\boldsymbol{r}) d\boldsymbol{r}\, d\boldsymbol{r}' \\
&= -\iint P_{\boldsymbol{r},\boldsymbol{r}'}[\gamma^0] \log P_{\boldsymbol{r}\to\boldsymbol{r}'}[\gamma^0] d\boldsymbol{r} d\boldsymbol{r}' \equiv S_{\mathfrak{R}\to\mathfrak{R}'}[\gamma^0] \\
&= -N^{-1} \iint \gamma^0(\boldsymbol{r}, \boldsymbol{r}')\gamma^0(\boldsymbol{r}', \boldsymbol{r})\{\log[\gamma^0(\boldsymbol{r}, \boldsymbol{r}')\gamma^0(\boldsymbol{r}', \boldsymbol{r})] - \log\gamma^0(\boldsymbol{r}, \boldsymbol{r})\} d\boldsymbol{r}'\, d\boldsymbol{r} \\
&\equiv -N^{-1} \iint \Omega^0(\boldsymbol{r}, \boldsymbol{r}') \log\Omega^0(\boldsymbol{r}, \boldsymbol{r}') d\boldsymbol{r}'\, d\boldsymbol{r} \\
&\quad + N^{-1} \int[\int \Omega^0(\boldsymbol{r}, \boldsymbol{r}') d\boldsymbol{r}'] \log\rho^0(\boldsymbol{r}) d\boldsymbol{r} \\
&= N^{-1}(S[\Omega^0] - S[\rho^0]).
\end{aligned}
\tag{28}
$$

It thus reflects the difference between the Shannon-entropy

$$
S[\Omega^0] = -\iint \Omega^0\left(\boldsymbol{r}, \boldsymbol{r}'\right) \log\Omega^0\left(\boldsymbol{r}, \boldsymbol{r}'\right) d\boldsymbol{r} d\boldsymbol{r}'
\tag{29}
$$

of the *two*-point distribution of Eq. (25),

$$
\Omega^0(\boldsymbol{r}, \boldsymbol{r}') = \Omega^0_{\boldsymbol{r},\boldsymbol{r}'}[\gamma^0] = \gamma^0(\boldsymbol{r}, \boldsymbol{r}')\gamma^0(\boldsymbol{r}', \boldsymbol{r}) = N P^0(\boldsymbol{r}, \boldsymbol{r}'),
\tag{30}
$$

and the entropy of the electron density $\rho^0(\boldsymbol{r}) = N p^0(\boldsymbol{r})$,

$$
\begin{aligned}
S[\rho^0] &= -\int \rho^0(\boldsymbol{r}) \log\rho^0(\boldsymbol{r}) d\boldsymbol{r} = -N \int p^0(\boldsymbol{r})[\log N + \log p^0(\boldsymbol{r})] d\boldsymbol{r} \\
&= -N\log N + N S[p^0].
\end{aligned}
\tag{31}
$$

The deterministic contribution $S^0(diag.)$ of $S[\Omega^0]$ originates from its "diagonal" scatterings $\{\boldsymbol{r} \to \boldsymbol{r}\}$, when $\Omega^0(\boldsymbol{r}, \boldsymbol{r}) = [\rho^0(\boldsymbol{r})]^2$ and hence:

$$
\begin{aligned}
S^{diag.}[\Omega^0] &= -\int \Omega^0(\boldsymbol{r}, \boldsymbol{r}) \log\Omega^0(\boldsymbol{r}, \boldsymbol{r}) d\boldsymbol{r} = -\int[\rho^0(\boldsymbol{r})]^2\log[\rho^0(\boldsymbol{r})]^2 d\boldsymbol{r} = S[(\rho^0)^2] \\
&= -2N^2 \int[p^0(\boldsymbol{r})]^2\log[N p^0(\boldsymbol{r})] d\boldsymbol{r},
\end{aligned}
\tag{32}
$$

i.e., by the diagonal contribution to $S_{\mathfrak{R}\to\mathfrak{R}'}[\gamma^0]$:

$$
S^0(diag.) = N^{-1}\left\{S^{diag.}[\Omega^0] - S[\rho^0]\right\} = N^{-1}\left\{S[(\rho^0)^2] - S[\rho^0]\right\}.
\tag{33}
$$

Accordingly, the "scattering" aspect of $S[\Omega^0]$ is revealed by its *off*-diagonal part

$$
S^{ndiag.}[\Omega^0] = S[\Omega^0] - S^{diag.}[\Omega^0],
\tag{34}
$$

or by the associated contribution to $S_{\mathfrak{R}\to\mathfrak{R}'}[\gamma^0]$:

$$
S^0(ndiag.) = S^0(\mathfrak{R}'|\mathfrak{R}) - S^0(diag.) = N^{-1} S^{ndiag.}[\Omega^0].
\tag{35}
$$

The electron distribution of the system *promolecule* [11,35] is described by the sum of the molecularly placed electron densities $\{\rho_0^X(r)\}$ of the free constituent atoms,

$$\rho_0(r) = Np_0(r) = \sum_X \rho_X^0(r), \tag{36}$$

determining the diagonal part $\rho_0(r) = \gamma_0(r, r)$ of the promolecular density matrix

$$\gamma_0(r, r') = \sum_X \gamma_X^0(r, r). \tag{37}$$

The shape factor $p_0(r)$ provides the reference input signal for establishing the corresponding descriptor of the information-*flow* in the local channel, given by the mutual information quantity of Eqs. (7) and (9):

$$
\begin{aligned}
I^0(\Re_0 : \Re') &= N^{-1} \int [\int P^0(r, r')] \log[P^0(r'|r)/p_0(r)] dr' dr \equiv I_{\Re \to \Re'}^0[\gamma^0, \gamma_0] \\
&= -S_{\Re \to \Re'}[\gamma^0] - N^{-1} \int [\int \Omega^0(r, r') dr'] \log p_0(r)\} dr \\
&\equiv -S_{\Re \to \Re'}[\gamma^0] + S[p^0] + \Delta S[p^0|p_0],
\end{aligned}
\tag{38}
$$

where the entropy deficiency in the molecular (ground-state) probability p^0 relative to the promolecular distribution p_0 [compare Eq. (8)],

$$\Delta S[p^0|p_0] = \int p^0(r) \log[p^0(r)/p_0(r)] dr \equiv \int p^0(r) I(r) dr, \tag{39}$$

measures the average value of the local surprisal function $I(r)$, which reflects the information distance between the two distributions. It generally constitutes a relatively minor contribution, since $p^0(r)$ and $p_0(r)$ strongly resemble one another, being distinguished only by relatively minor displacements in the AIM valence shells. This similarity index exactly disappears for the molecular input signal $p^0(r)$, $\Delta S[p^0|p^0] = 0$, thus giving a modified value of the average mutual information of the local channel [Eq. (10)]:

$$I^0(\Re : \Re') = -S_{\Re \to \Re'}[\gamma^0] + S[p^0]. \tag{40}$$

The corresponding overall bond multiplicity indices of Eqs. (11) and (12) then read:

$$
\begin{aligned}
M^0(\Re_0; \Re') &= S^0(\Re'|\Re) + I^0(\Re_0; \Re') = S[p^0] + \Delta S[p^0|p_0], \\
M^0(\Re; \Re') &= S^0(\Re'|\Re) + I^0(\Re; \Re') = S[p^0].
\end{aligned}
\tag{41}
$$

Therefore, the overall IT multiplicity of the molecular local channel probed by the molecular signal again recovers the Shannon entropy of the ground-state probability of electrons [compare Eq. (12)]. The difference index of Eq. (13),

$$\Delta M = M^0(\Re; \Re') - M^0(\Re_0; \Re') = \Delta S[p^0|p_0], \tag{42}$$

again reflects the overall similarity between the molecular probability distribution p^0 and the promolecular reference p_0; it correctly disappears in the *Separated Atoms Limit* (SAL), where the two distributions become identical.

6 Average orbital communications in CI MO-ensembles

Consider next the familiar (*single*-reference) *Configuration Interaction* (CI) expansion of the molecular ground-state $\Psi^{CI}(N)$ into n_c Slater determinants (electron configurations) $\boldsymbol{\Psi}(N) = \{\Psi_\alpha(N)\}$:

$$\Psi^{CI}(N) = \sum_\alpha \Psi_\alpha(N)c_\alpha \equiv \boldsymbol{\Psi}(N)\boldsymbol{c},$$

$$\boldsymbol{c} = \{c_\alpha = \langle \Psi_\alpha(N)|\Psi^{CI}(N)\rangle, \ \alpha = 0, 1, \ldots, n_c\} = \langle \boldsymbol{\Psi}(N)|\Psi^{CI}(N)\rangle,$$

$$\langle \Psi_\alpha(N)|\Psi_\beta(N)\rangle = \delta_{\alpha,\beta} \ \text{or} \ \langle \boldsymbol{\Psi}(N)|\boldsymbol{\Psi}(N)\rangle = \mathbf{I}, \tag{43}$$

with $\alpha = 0$ corresponding to the ground-state (HF or KS) configuration $\Psi_0(N)$, which usually dominates. The *single*-configuration approximation of Eq. (14), for $|c_0| = 1$ or $p_0 = |c_0|^2 = 1$, can be thus regarded as the limiting case of the CI expansion truncated after this first HF/KS configuration. A typical strong dominance of the CI wave function by the HF/KS ground-state configuration, $p_{\alpha=0} >> p_{\alpha>0}$, implies that most of the AO communications are indeed carried out *via* the SMO occupied in the HF/KS Slater determinant, which generally provides quite satisfactory description of gross patterns of chemical bonds, e.g., [11–21].

The (orthonormal) configurations $\boldsymbol{\Psi}(N) = \{\Psi_\alpha(N) = \det[\boldsymbol{\varphi}^\alpha]\}$ are uniquely determined by the subspaces of N *singly*-occupied SMO, $\boldsymbol{\varphi}^\alpha$, or by their AO expansions, $\boldsymbol{\varphi}^\alpha = \boldsymbol{\chi}\mathbf{C}^\alpha = \{\varphi_s(\alpha) = \boldsymbol{\chi}\,C_s^\alpha\}$, $\mathbf{C}^\alpha = \{C_{i,s}(\alpha) = \langle \chi_i|\varphi_s(\alpha)\rangle\}$, which give rise to the associated CBO matrices [see Eq. (16)],

$$\boldsymbol{\gamma}^\alpha = \langle \boldsymbol{\chi}|\boldsymbol{\varphi}^\alpha\rangle\langle \boldsymbol{\varphi}^\alpha|\boldsymbol{\chi}\rangle = \mathbf{C}^\alpha \mathbf{C}^{\alpha\dagger} = \mathbf{C}\boldsymbol{v}^\alpha \mathbf{C}^\dagger. \tag{44}$$

Here, the (diagonal) matrix of SMO-occupations in the configuration $\Psi_\alpha(N)$,

$$\boldsymbol{v}^\alpha = \{[1 \ (occupied \ \text{MO}) \ \text{or} \ 0 \ (virtual \ \text{MO})]\delta_{s,s'} = \upsilon_s(\alpha)\delta_{s,s'}\}, \tag{45}$$

and the *full* LCAO matrix $\mathbf{C} = (\mathbf{C}^\alpha|\mathbf{C}^{v,\alpha})$ combines expansion coefficients of all m MO:

$$\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C} = (\boldsymbol{\varphi}^\alpha, \boldsymbol{\varphi}^{v,\alpha}) = \{\varphi_s\}, \tag{46}$$

occupied, $\boldsymbol{\varphi}^\alpha$, and virtual, $\boldsymbol{\varphi}^{v,\alpha} = \boldsymbol{\chi}\mathbf{C}^{v,\alpha}$, obtained in the given basis set $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m)$. The diagonal elements of $\boldsymbol{\gamma}^\alpha$ represent the configuration effective AO occupations $\{n_i(\alpha) = \gamma_{i,i}(\alpha)\}$, while the *off*-diagonal elements similarly determine the configuration "bond-orders" between different AO: $\{n_{i,j}(\alpha) = \gamma_{i,j}(\alpha), i \neq j\}$.

Therefore, each configuration can be associated with the related MO-ensemble defined by the idempotent SMO-projector $\hat{P}_\alpha = |\varphi^\alpha\rangle\langle\varphi^\alpha|$:

$$\hat{d}_\alpha = \sum_s [\upsilon_s(\alpha)/N]\,|\phi_s\rangle\,\langle\phi_s| \equiv \sum_s \pi_s(\alpha)\hat{P}_s = (1/N)\,|\varphi^\alpha\rangle\langle\varphi^\alpha|$$

$$= (1/N)\,\hat{P}_\alpha; \quad \sum_s \pi_s(\alpha) = 1. \tag{47}$$

In other words, each determinant $\Psi_\alpha(N)$ implies the associated ensemble of the configuration occupied SMO (*single*-particle states). It is defined by the density operator $\hat{d}_\alpha$ with *equal* probabilities of the occupied (physical) SMO in $\Psi_\alpha(N)$, $\{\pi_{s\in\alpha} = 1/N\}$, through which the electron probabilities are scattered (delocalized) between m basis functions in the underlying AO information system. One further observes that the CBO (density) matrix $\boldsymbol{\gamma}^\alpha$ is proportional to the AO representation of $\hat{d}_\alpha$,

$$\mathbf{d}^\alpha \equiv \langle\boldsymbol{\chi}|\,\hat{d}_\alpha\,|\boldsymbol{\chi}\rangle = N^{-1}\boldsymbol{\gamma}^\alpha. \tag{48}$$

The combination of configurations in the ground state $\Psi^{CI}(N)$ [Eq. (43)] similarly determines the CI MO-ensemble corresponding to *non*-equal SMO probabilities, $\{\pi_s = \sum_\alpha p_\alpha\pi_s(\alpha)\}$,

$$\hat{d}^{CI} = \sum_{s=1}^{m} \pi_s\hat{P}_s, \quad \sum_s \pi_s = 1, \tag{49}$$

where the conditional probability p_α of the configuration $\Psi_\alpha(N)$ in $\Psi^{CI}(N)$ results from the superposition principle:

$$p_\alpha \equiv P(\Psi_\alpha|\Psi^{CI}) = |c_\alpha|^2, \quad \sum_\alpha p_\alpha = 1. \tag{50}$$

This CI density operator of MO subsequently determines its AO representation,

$$\mathbf{d}^{CI} \equiv \langle\boldsymbol{\chi}|\,\hat{d}^{CI}\,|\boldsymbol{\chi}\rangle \equiv N^{-1}\boldsymbol{\gamma}^{CI}, \tag{51}$$

proportional to the CI-*average* density matrix matrix:

$$\boldsymbol{\gamma}^{CI} = \sum_\alpha p_\alpha\boldsymbol{\gamma}^\alpha \equiv \langle\boldsymbol{\gamma}\rangle_{ens.}. \tag{52}$$

The latter combines the diagonal elements $\{\gamma_{i,i}(\alpha) = n_i(\alpha)\}$, the average AO occupations in the configurations involved in the *CI ensemble* defined by the density operator

$$\hat{D}^{CI} = \sum_\alpha |\Psi_\alpha\rangle p_\alpha\,\langle\Psi_\alpha| = \sum_\alpha p_\alpha\hat{P}_\alpha, \tag{53}$$

defined by sum of the configuration projections $\{\hat{P}_\alpha\}$ weighted by the associated probabilities $\boldsymbol{p}^{ens.} = \{p_\alpha\}$,

$$n_i^{\text{CI}} = \langle n_i \rangle_{ens.} = \sum_\alpha p_\alpha n_i(\alpha) \equiv \langle \gamma_{i,i} \rangle_{ens.} = \sum_\alpha p_\alpha \gamma_{i,i}(\alpha), \quad i = 1, 2, \ldots, \quad (54)$$

and the *off*-diagonal elements reflecting the CI-average "bond-orders" between pairs of basis functions:

$$n_{i,j}^{\text{CI}} = \langle n_{i,j} \rangle_{ens.} = \sum_\alpha p_\alpha n_{i,j}(\alpha) = \sum_\alpha p_\alpha \gamma_{i,j}(\alpha) = \langle \gamma_{i,j} \rangle_{ens.}, \quad i \neq j. \quad (55)$$

In principle there are two admissible ways of extending the molecular AO communications into the above CI scenario involving several electronic configurations: the *classical* (probability) and *quantum* (amplitude) averaging in the ground-state CI SMO-ensemble. Both ultimately reproduce the *single*-configuration development of the preceding section as their limiting case, but only the latter is capable of accounting for the interference phenomena between AO communications in the configurations used in the CI expansion of the system ground state. Evaluating capabilities of these two treatments in interpreting the prototype bond patterns should in principle allow one to select the most suitable approach for chemical applications, to be used for an understanding of the information content of molecular electronic structure, patterns of chemical bonds, bond multiplicities and their covalent/ionic composition.

The classical (*probability*) CI channel thus involves the averaging over the configuration AO probabilities themselves:

$$\langle P(j|i) \rangle_{ens.} \equiv \sum_\alpha p_\alpha P^\alpha(j|i) \equiv \sum_\alpha p_\alpha P_{i \to j}(\alpha)$$
$$= \langle N_i \rangle_{ens.} \sum_\alpha p_\alpha \gamma_{i,j}(\alpha) \gamma_{j,i}(\alpha),$$
$$\sum_j \langle P(j|i) \rangle_{ens.} = 1 \Rightarrow \langle N_i \rangle_{ens.} = 1/\langle n_i \rangle_{ens.}. \quad (56)$$

Here the elements of the AO conditional-probability matrix in configuration $\Psi_\alpha(N)$ [see Eq. (17)],

$$\mathbf{P}^\alpha(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \{P^\alpha(j|i) \equiv P_{i \to j}(\alpha)$$
$$= |A_{i \to j}(\alpha)|^2 = |\gamma_{i,j}(\alpha)|^2/\gamma_{i,i}(\alpha) \equiv N_i(\alpha)\gamma_{i,j}(\alpha)^2\},$$
$$\alpha = 0, 1, \ldots, n_c, \quad (57)$$

determine the configuration *a posteriori* (classical) amplitudes [see Eq. (19)]:

$$\mathbf{A}^\alpha(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \Big\{ A^\alpha(j|i) \equiv A_{i \to j}(\alpha) \equiv [P^\alpha(j|i)]^{1/2} = \gamma_{i,j}(\alpha)/[\gamma_{i,i}(\alpha)]^{1/2}$$
$$= [N_i(\alpha)]^{1/2} \gamma_{i,j}(\alpha) \Big\}. \quad (58)$$

The average probabilities $\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{ens.} = \{\langle P(j|i) \rangle_{ens.} \equiv \langle P_{i \to j} \rangle_{ens.}\}$ generate the *classical* (probability) network of the "*single*-input" summation (parallel) CI arrangement [85]:

$$\chi \to \{p_\alpha \to \mathbf{P}^\alpha(\chi'|\chi)\} \to \chi' \Rightarrow \chi \to \langle \mathbf{P}(\chi'|\chi)\rangle_{ens.} \to \chi',$$

$$\langle \mathbf{P}(\chi'|\chi)\rangle_{ens.} = \sum_\alpha p_\alpha \mathbf{P}^\alpha(\chi'|\chi) \equiv \{[\langle A_{i\to j}\rangle_{ens.}]^2\}, \qquad (59)$$

where $\langle A_{i\to j}\rangle_{ens.}$ denotes the *a posteriori* CI amplitude for the $\chi_i \to \chi_j$ communication. In this approximation the ensemble-average quantity $\langle P(j|i)\rangle_{ens.}$ describes the classical $\chi_i \to \chi_j$ AO probability propagation in the ground-state CI combination of configurations. It misses the amplitude-superposition terms, which reflect quantum effects of the *direct* AO communications (bonds) in a molecule. This direct CI averaging of the configuration AO communications also involves an effective MO-ensemble defined by the (*non*-idempotent) density operator of Eq. (49),

$$\hat{\mathrm{d}}^{\mathrm{CI}} = \sum_\alpha p_\alpha \hat{\mathrm{d}}_\alpha = \sum_s \left\{ \sum_\alpha p_\alpha [\upsilon_s(\alpha)/N] \right\} |\phi_s\rangle \langle \phi_s| \equiv \sum_s \pi_s \hat{\mathrm{P}}_s, \quad \sum_s \pi_s = 1, \qquad (60)$$

exhibiting *non-equal* probabilities of SMO, $\{\pi_s = \upsilon_s^{\mathrm{CI}}/N\}$, which reflect the effective (fractional) average occupations $\{\upsilon_s^{\mathrm{CI}} = \sum_\alpha p_\alpha \upsilon_s(\alpha)\}$ of SMO in the CI-ensemble. As also indicated in Eq. (59) the square root of each probability $\langle P(j|i)\rangle_{ens.}$ determines the corresponding classical CI amplitude $\langle A(j|i)\rangle_{ens.} = [\langle P(j|i)\rangle_{ens.}]^{1/2}$.

In the *quantum*, amplitude-averaging scheme the elements of $\langle \boldsymbol{\gamma}\rangle_{ens.}$ are first used to determine the resultant (*a priori*) amplitudes $\{\langle A_{i\to j}\rangle_{av.}\}$ of the average communications between AO in this CI-ensemble of SMO. In full analogy to Eq. (19) this resultant communication amplitude is shaped by the ensemble average of the corresponding CBO element,

$$\langle A(j|i)\rangle_{av.} \equiv \langle A_{i\to j}\rangle_{av.} = [\langle N_i\rangle_{av.}]^{1/2}\langle \gamma_{i,j}\rangle_{ens.} = [\langle N_i\rangle_{av.}]^{1/2}\sum_\alpha p_\alpha \gamma_{i,j}(\alpha) \quad \text{or}$$

$$\langle \mathbf{A}(\chi'|\chi)\rangle_{av.} = \sum_\alpha p_\alpha \mathbf{A}^\alpha(\chi'|\chi) = \left\{ \langle A(j|i)\rangle_{av.} \equiv \langle A_{i\to j}\rangle_{av.} \right\}, \qquad (61)$$

with $\langle N_i\rangle_{av.}$ standing for the normalization factor of the resultant (average) conditional probabilities

$$\begin{aligned} \langle P(j|i)\rangle_{av.} &\equiv |\langle A_{i\to j}\rangle_{av.}|^2 = \langle N_i\rangle_{av.}\langle \gamma_{i,j}\rangle_{ens.}\langle \gamma_{j,i}\rangle_{ens.} \\ &= \langle N_i\rangle_{av.} \sum_\alpha \sum_\beta p_\alpha p_\beta \gamma_{i,j}(\alpha)\gamma_{j,i}(\beta) \\ &\equiv \sum_\alpha \sum_\beta p_\alpha p_\beta P_{i\to j}(\alpha, \beta), \end{aligned} \qquad (62)$$

now containing terms responsible for the interference between configurations. The normalization constant $\langle N_i\rangle_{av.}$ is again obtained from the requirement $\sum_j \langle P(j|i)\rangle_{av.} = 1$:

$$\langle N_i \rangle_{av.} = \left\{ \sum_\alpha \sum_\beta p_\alpha p_\beta \left[\sum_j \gamma_{i,j}(\alpha) \gamma_{j,i}(\beta) \right] \right\}^{-1}. \tag{63}$$

For the complete basis, when $\sum_j |\chi_j\rangle\langle\chi_j| = 1$, it reads:

$$\langle N_i \rangle_{av.} = \left\{ \left\langle \chi_i \left| \left[\sum_s \left| \varphi_s \right\rangle (\upsilon_s^{CI})^2 \left\langle \varphi_s \right| \right] \right| \chi_i \right\rangle \right\}^{-1}. \tag{64}$$

The resultant amplitudes of Eq. (61) define the *quantum* (amplitude) channel in the CI ground-state,

$$|\boldsymbol{\chi}\rangle \to \{p_\alpha \to \mathbf{A}^\alpha(\boldsymbol{\chi}'|\boldsymbol{\chi})\} \to |\boldsymbol{\chi}'\rangle \ \Rightarrow \ |\boldsymbol{\chi}\rangle \to \langle \mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} \to |\boldsymbol{\chi}'\rangle, \tag{65}$$

while the average probabilities of Eq. (62), $\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} = \{\langle P_{i \to j}\rangle_{av.}\}$, the squares of these average amplitudes, generate the associated quantum probability network. The latter is seen to be determined by the following "*double*-input" (parallel) system of the amplitude propagations in the CI MO-ensemble,

$$|\boldsymbol{\chi}\rangle \to \{p_\alpha \to \mathbf{A}^\alpha(\boldsymbol{\chi}'|\boldsymbol{\chi})\} \to |\boldsymbol{\chi}'\rangle \leftarrow \{\mathbf{A}^\beta(\boldsymbol{\chi}'|\boldsymbol{\chi}'') \leftarrow p_\beta\} \leftarrow |\boldsymbol{\chi}''\rangle$$
$$\Rightarrow |\boldsymbol{\chi}\rangle \to \langle \mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} \to |\boldsymbol{\chi}'\rangle \leftarrow \langle \mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi}'')\rangle_{av.} \leftarrow |\boldsymbol{\chi}''\rangle. \tag{66}$$

In short notation, for $\boldsymbol{\chi} = \boldsymbol{\chi}''$, it gives rise to the resultant probability propagation of Eq. (62):

$$\boldsymbol{\chi} \to \langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} \to \boldsymbol{\chi}'. \tag{67}$$

Therefore, the average probability $\langle P(j|i)\rangle_{av.}$ describes the parallel, *double*-input scatterings via the average propagation amplitudes:

$$|\chi_i\rangle \to \{p_\alpha \to A_{i \to j}(\alpha)\} \to |\chi_j\rangle \leftarrow \{A_{j \leftarrow i}(\beta) \leftarrow p_\beta\} \leftarrow |\chi_i\rangle$$
$$\Rightarrow |\chi_i\rangle \to \langle A_{i \to j}\rangle_{av.} \to |\chi_j\rangle \leftarrow \langle A_{i \to j}\rangle_{av.} \leftarrow |\chi_i\rangle \ \text{ or } \ \chi_i \to \langle P_{i \to j}\rangle_{av.} \to \chi_j. \tag{68}$$

The average probability $\langle P_{i \to j}\rangle_{av.}$ thus represents the resultant effect of the *double* amplitude propagations $|\chi_i\rangle \to |\chi_j\rangle \leftarrow |\chi_i\rangle$ and differs, by communication contributions reflecting the *inter*-configuration-interference, from the *direct* ensemble-average $\langle P_{i \to j}\rangle_{ens.}$ of the configuration conditional probabilities.

To summarize, the classical interpretation of molecular conditional probabilities, defining the ensemble-average AO communications of the CI configurations, is *phase*-independent since both the ensemble weights $\{p_\alpha\}$ and the configuration probabilities $\{\mathbf{P}^\alpha(\boldsymbol{\chi}'|\boldsymbol{\chi})\}$ loose memory about the phase content of both the CI coefficients $\{c_\alpha\}$ and the CBO matrix elements. In order to predict the interference effects between communication amplitudes of configurations in the resultant AO probabilities, one first combines the relevant elementary amplitudes due to

each determinant into $\langle\mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} = \{\langle A_{i \to j}\rangle_{av.}\}$ before determining the CI average communication probabilities as the squared moduli of the resultant amplitudes, $\langle\mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi})\rangle_{av.} = \{\langle P(j|i)\rangle_{av.} \equiv |\langle A_{i \to j}\rangle_{ens.}|^2\}$. As we have argued above, this *probability* channel can be related to the *double*-input amplitude propagations between AO.

The *classical* (probability) channel in the CI SMO-ensemble involves only n_c elementary (*intra*-configuration) probability communications $\{P_{i \to j}(\alpha)\}$, while the *quantum* (amplitude) network explores both the *intra*- and *inter*-configuration propagations between basis functions, and exhibits an explicit phase dependence. The latter requires n_c^2 elementary probability networks $\{P_{i \to j}(\alpha, \beta)\}$ which imply more indeterminacy in molecular communications between AO compared to the classical channel. Therefore, the quantum treatment of the orbital communications is expected to generate an increased fraction of the "noise" (electron AO delocalization, IT-covalency) content, and hence a decreased level of the communication "determinicity" (electron AO localization, IT-ionicity), compared to those characterizing the classical channel.

7 Illustrative example: *two*-orbital model of chemical bond

As an illustrative case consider the simplest 2-AO model consisting of the two orthonormal basis functions, e.g., two symmetrically (Löwdin) orthogonalized (real) AO contributed by different atoms A and B: $\boldsymbol{\chi} = \boldsymbol{\chi}' = (\chi_1, \chi_2) \equiv (\chi_A, \chi_B)$. They give rise to two independent (spatial) MO combinations $\boldsymbol{\phi} = (\phi_b, \phi_a)$, which can be expressed in terms of the complementary AO probabilities P and $Q = 1 - P$,

bonding, $\phi_b = \chi_A C_{A,b} + \chi_B C_{B,b} \equiv \chi_A (P)^{1/2} + \chi_B (Q)^{1/2} \equiv \boldsymbol{\chi} C_b$, and

$anti$-bonding, $\phi_a^{(1)} = \chi_A C_{A,a}^{(1)} + \chi_B C_{B,a}^{(1)} \equiv -\chi_A (Q)^{1/2} + \chi_B (P)^{1/2} \equiv \boldsymbol{\chi} C_a^{(1)}$,

$$(69)$$

or in the compact joint notation:

$$\boldsymbol{\phi}^{(1)} = \boldsymbol{\chi}[C_b|C_a^{(1)}] \equiv \boldsymbol{\chi}\mathbf{C}^{(1)}, \quad \mathbf{C}^{(1)} = \begin{bmatrix} \sqrt{P} & -\sqrt{Q} \\ \sqrt{Q} & \sqrt{P} \end{bmatrix}, \quad (70)$$

The magnitudes of LCAO MO coefficients are thus shaped by the conditional probabilities,

$$P = P(\chi_A|\phi_b) = (C_{A,b})^2 = P(\chi_B|\phi_a^{(1)}) = [C_{B,a}^{(1)}]^2, \quad \text{and}$$

$$Q = P(\chi_B|\phi_b) = (C_{B,b})^2 = P(\chi_A|\phi_a^{(1)}) = [C_{A,a}^{(1)}]^2 = 1 - P. \quad (71)$$

It can be straightforwardly verified that these two MO combinations indeed satisfy the MO-orthonormality relations:

$$\langle\boldsymbol{\phi}^{(1)}|\boldsymbol{\phi}^{(1)}\rangle = \mathbf{C}^{(1)T}\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle\mathbf{C}^{(1)} = \mathbf{C}^{(1)T}\mathbf{C}^{(1)} = \mathbf{I}, \quad (72)$$

where we have used the AO orthonormality: $\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \mathbf{I}$. We further assume that both atoms of the system "promolecule", consisting of the molecularly placed *free* atoms,
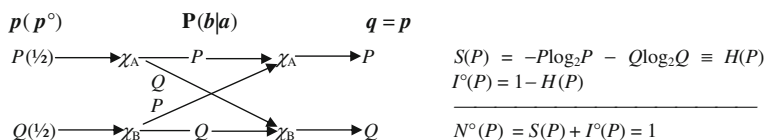
Fig. 3 Communication channel of the 2-AO model of the chemical bond and its entropy/information descriptors (in bits)

contribute a single electron each to the molecular bond system of $N = 2$ electrons: $\boldsymbol{p}_0 = (1/2, 1/2)$.

Let us first examine the *single*-configuration description of this model chemical bond, e.g., in the HF/KS ground-state, when both (spin-paired) electrons occupy the bonding MO ϕ_b. The relevant CBO matrix $\boldsymbol{\gamma}$ reads:

$$\boldsymbol{\gamma} = 2\boldsymbol{C}_b\boldsymbol{C}_b^\dagger = 2\begin{bmatrix} P & \sqrt{PQ} \\ \sqrt{QP} & Q \end{bmatrix}. \tag{73}$$

It generates the following conditional probabilities of AO communications,

$$\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \{P(j|i) = \begin{bmatrix} P & Q \\ P & Q \end{bmatrix}, \tag{74}$$

which determine the classical (probability) channel for AO communications $\boldsymbol{\chi} \to \boldsymbol{\chi}'$ (Fig. 3).

In this *non*-symmetrical binary channel one adopts the molecular input signal, $\boldsymbol{p} = (P, Q)$, to extract the bond IT-covalency measuring the channel average communication noise [9–11]. Adopting the promolecular input signal $\boldsymbol{p}_0 = (1/2, 1/2)$, reflecting that each of the two basis functions has contributed a single electron each to form the chemical bond, allows one to determine the associated index of IT-ionicity relative to this initial, reference signal, which then measures the *information capacity* of this model AO channel.

The bond IT-covalency (conditional entropy $S(\boldsymbol{b}|\boldsymbol{a}) = S(P)$ is thus determined by Binary Entropy Function (BEF) of the two complementary conditional probabilities of AO in MO [Eq. (71)], $H(P) = -P\log_2 P - (1 - P)\log_2(1 - P)$ (see Fig. 4),

$$S(P) = H(P) = -P\log_2 P - Q\log_2 Q. \tag{75}$$

It exhibits the maximum value $H(1/2) = 1$ bit for the symmetric bond $P = Q = 1/2$, e.g., the two prototype covalent bonds in chemistry: the σ bond in H_2 or the π-bond in ethylene. It vanishes for the *lone*-pair configurations, when $P = (0 \text{ or } 1)$, $H(0) = H(1) = 0$, marking the alternative *ion*-pair configurations A^+B^- and A^-B^+, respectively, relative to the initial AO occupations $\boldsymbol{n}_0 = (1, 1)$ in the assumed *covalent* promolecular reference, in which both atoms contribute a single electron each to form the chemical bond A–B.

The complementary mutual-information descriptor of the bond IT-ionicity (information flow) [Eq. (9)], $I_0(P) = 1 - H(P)$, which determines the channel mutual
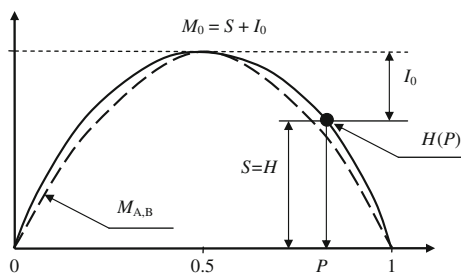
Fig. 4 Conservation of the overall entropic bond multiplicity $M_0(P) = 1$ bit in the 2-AO model of the chemical bond, combining the conditional-entropy (average noise, bond IT covalency) $S(P) = H(P)$ and the mutual-information (information capacity, bond IT ionicity) $I_0(P) = 1 - H(P)$. In MO theory the direct bond-order of Wiberg [87] is represented by the (*broken-line*) parabola $M_{A,B}(P) = 4P(1 - P) \equiv 4PQ$

information relative to the promolecular input, is thus correctly diagnosed to reach the highest value for the two electron-transfer pairs: $I_0(0) = I_0(1) = 1$ bit, and predicted to identically vanish for the purely-covalent, symmetric bond, $I_0(1/2) = 0$. As explicitly shown in Fig. 4, these two components of the chemical bond multiplicity compete with one another, yielding the conserved overall IT bond index [Eq. (11)]: $M_0(P) = S(P) + I_0(P) = 1$ bit, which in OCT marks the full single bond, in the whole range of the admissible bond polarizations $P \in [0, 1]$.

This simple model thus properly accounts for the competition between the bond covalency and ionicity, while preserving the single bond-order measure reflected by the conserved single IT multiplicity of the chemical bond. Similar effects transpire from the quadratic bond indices formulated in the MO theory [87–97]. For example, the plot of Wiberg bond-order [87] for this model (see Fig. 4) is given by the parabola $M_{A,B}(P) = [\gamma_{A,B}(P)]^2 = 4PQ = 4P(1 - P)$, which closely resembles the IT-covalent plot $S(P) = H(P)$ in the same figure. It should be stressed, however, that this "complementary" indexing scheme in OCT has been designed primarily to describe the bonding patterns of the *equilibrium* molecular geometries. It fails to account for a decay in the overall bond multiplicity accompanying bond elongation. For the improved CI-type descriptors, which remedy this shortcoming, see Ref. [45].

In this (minimum basis) 2-AO description there are three *singlet* configurations (of the spin-paired electrons), $\boldsymbol{\Psi} = (\Psi_b, \Psi_n, \Psi_a)$, including the HF/KS *ground*-state (bonding) configuration

$$\Psi_b = |\phi_b \alpha, \phi_b \beta|, \tag{76}$$

the *singly*-excited (S) *non*-bonding configuration

$$\Psi_n^{(1)} = 2^{-1/2}\{|\phi_b \alpha, \phi_a^{(1)} \beta| + |\phi_b \beta, \phi_a^{(1)} \alpha|\}, \tag{77}$$

and the *doubly*-excited (D) *anti*-bonding configuration

$$\Psi_a^{(1)} = |\phi_a^{(1)} \alpha, \phi_a^{(1)} \beta|, \tag{78}$$

into which the CI ground state is expanded in the familiar CI-[*Singles* and *Doubles*] (CISD) approximation:

$$\Psi^{CI}(2) \cong c_b \Psi_b(2) + c_n \Psi_n(2) + c_a \Psi_a(2) \equiv \Psi^{CISD}(2). \tag{79}$$

The *classical* channel, from the *probability* averaging treatment, is now characterized by the ensemble average of communications $\{\chi_i \rightarrow \chi_j\}$ resulting from the internal communications $\{P_{i \rightarrow j}(\alpha)\}$ between the specified pair of AO in each configuration:

$$[\chi_i - p_b P_{i \rightarrow j}(b) \rightarrow \chi_j] + [\chi_i - p_n P_{i \rightarrow j}(n) \rightarrow \chi_j] + [\chi_i - p_a P_{i \rightarrow j}(a) \rightarrow \chi_j]$$
$$\equiv \chi_i - \langle P_{i \rightarrow j} \rangle_{ens.} \rightarrow \chi_j, \tag{80}$$

where the brackets [ ] enclose the separate *internal* AO propagation in each configuration Ψ_α, with the weight being determined by the associated configuration probability p_α.

The corresponding *quantum* channel, from the *amplitude* averaging scheme, combines the following elementary amplitudes,

$$[|\chi_i\rangle - \{p_b A_{i \rightarrow j}(b)\} \rightarrow |\chi_j\rangle] + [|\chi_i\rangle - \{p_n A_{i \rightarrow j}(n)\} \rightarrow |\chi_j\rangle]$$
$$+[|\chi_i\rangle - \{p_a A_{i \rightarrow j}(a)\} \rightarrow |\chi_j\rangle] \equiv |\chi_i\rangle - \langle A_{i \rightarrow j} \rangle_{av.} \rightarrow |\chi_j\rangle. \tag{81}$$

They generate nine modes $\{P_{i \rightarrow j}(\alpha, \beta)\}$ of the probability scattering: three diagonal (*intra*-configuration) modes $\{P_{i \rightarrow j}(\alpha, \alpha) \equiv P_{i \rightarrow j}(\alpha)\}$ and six *off*-diagonal (*inter*-configuration) ones $\{P_{i \rightarrow j}(\alpha, \beta), \alpha \neq \beta\}$.

Therefore, instead of three elementary probability propagations $\{P_{i \rightarrow j}(\alpha)\}$ in the classical CI channel, one identifies nine probability modes $\{P_{i \rightarrow j}(\alpha, \beta)\}$ in the quantum CI system. While the classical communications between AO are purely *intra*-configuration in character, the *non*-classical (quantum) network exibits both the *intra*- and *inter*-configuration communications, with the latter being responsible for the quantum-mechanical interference of configuration communications.

We therefore conclude that more complex, quantum communications in molecules are predicted to be capable of a more efficient dissipation of the input AO information into the electron delocalization ("noise", orbital IT covalency), compared to the simpler classical network. One observes, however, that the *interference* effects, characterizing only the *non*-classical (amplitude) channels, can in some cases help to preserve the communication localization ("order", orbital IT ionicity), i.e., "determinicity" in molecular communications, by increasing or decreasing the AO communication probabilities relative to the associated classical network.

8 Orbital coupling and bond multiplicities in prototype VB states

In the 2-AO model the set of four elementary AO products, two *ionic*, $[A^-B^+] = \chi_A(1)\chi_A(2)$ and $[A^+B^-] = \chi_B(1)\chi_B(2)$, and two *covalent*, $[A–B] = \chi_A(1)\chi_B(2)$ and

[B–A] = $\chi_B(1)\chi_A(2)$, span the complete *two*-electron Hilbert space of the familiar VB approach [98]. Through the two spatial configurations of the CID expansion,

$$\Psi_b(2) = P\left[A^-B^+\right] + Q\left[A^+B^-\right] + \sqrt{2PQ}\Psi^{cov.}(2),$$
$$\Psi_a(2) = Q\left[A^-B^+\right] + P\left[A^+B^-\right] - \sqrt{2PQ}\Psi^{cov.}(2), \tag{82}$$

where the *covalent* (atomic) structure of Heitler and London represents the normalized *difference* of both configurations, yielding the symmetrized combination of two covalent products,

$$\Psi^{cov.}(2) \equiv 2^{-1/2}[\Psi_b(2) - \Psi_a(2)] = 2^{-1/2}\{[A - B] + [B - A]\}, \tag{83}$$

it is capable of representing both electronic (singlet) states of this *two*-electron system, e.g., the ground state,

$$\Psi^{CID}(2) \equiv \Psi_+(2) = c_b\Psi_b(2) + c_a\Psi_a(2), \quad |c_b|^2 + |c_a|^2 = 1, \tag{84}$$

and the excited, *anti*-bonding combination,

$$\Psi^{exc.}(2) \equiv \Psi_-(2) = -c_a\Psi_b(2) + c_b\Psi_a(2). \tag{85}$$

They express all prototype *chemical* states of this *two*-electron system in VB theory. For example, for the homomonuclear (symmetric) bond, $P = Q = 1/2$, one defines the *covalent* structure $\Psi^{cov.}(2)$ given by the difference of MO configurations [Eq. (83)] and the *ionic* structure $\Psi^{ion.}(2)$ representing the normalized *sum* of these electron configurations giving the symmetrized combination of two ionic products:

$$\Psi^{ion.}(2) \equiv 2^{-1/2}[\Psi_b(2) + \Psi_a(2)] = 2^{-1/2}\{[A^-B^+] + [A^+B^-]\}, \tag{86}$$

These two reference chemical states correspond to equal configuration probabilities:

$$p^{ion.} = p^{cov.} = (1/2, 1/2) \equiv (1/2)\boldsymbol{I}, \tag{87}$$

thus giving rise to identical CID probability and amplitude MO-ensembles.

Therefore, both the classical (probability) and quantum (amplitude) averaging schemes do not reveal the basic chemical difference between these two prototype VB states, which is embodied in the phases of MO configurations in these two combinations. In particular, the classical averaging of the configuration conditional probabilities gives:

$$\langle\mathbf{P}(\chi'|\chi)\rangle_{ens.} = \mathbf{P}^{cov.}(\chi'|\chi) = \mathbf{P}^{ion.}(\chi'|\chi) = 1/2[\mathbf{P}^b(\chi'|\chi) + \mathbf{P}^a(\chi'|\chi)] = (1/2)\mathbf{1}. \tag{88}$$

Definitions of Eqs. (83) and (86) also imply identical ensemble-average bond-orders between AO in both structures,

$$\langle \boldsymbol{\gamma} \rangle_{ens.} = \sum_{\alpha=b,a} p_\alpha \boldsymbol{\gamma}^\alpha = 1/2(\boldsymbol{\gamma}^b + \boldsymbol{\gamma}^a) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \equiv \mathbf{I}, \tag{89}$$

and hence the diagonal average amplitudes of AO communications,

$$\langle \mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \mathbf{A}^{cov.}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \mathbf{A}^{ion.}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = 2^{-1/2}[\mathbf{A}^b(\boldsymbol{\chi}'|\boldsymbol{\chi}) + \mathbf{A}^a(\boldsymbol{\chi}'|\boldsymbol{\chi})] = \mathbf{I}. \tag{90}$$

They generate the *deterministic* (diagonal) average CID channel:

$$\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \langle \mathbf{P}^{cov.}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \langle \mathbf{P}^{ion.}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \{[\langle A(\chi_j|\chi_i) \rangle_{av.}]^2\} = \mathbf{I}. \tag{91}$$

One recalls that the two prototype VB states, $\Psi^{cov.}(2)$ and $\Psi^{ion.}(2)$, also represent the reference *atomic* and *ionic* dissociation limits, respectively, with the former attributing single electrons to different atoms and the latter locating both electrons on a single AO. The ionic structure indeed represents the equal participation of two admissible *ion*-pairs, relative to the assumed (atomic) promolecular reference. The fully coupled, classical communication system $\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{ens.} = (1/2)\mathbf{1}$ represents in OCT the purely covalent communication system, $\langle S(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{ens.} = 1$ bit and $\langle I_0(\boldsymbol{\chi} : \boldsymbol{\chi}') \rangle_{ens.} = 0$, of the complete dissipation of the initial (input) information into the communication "noise" [11–13]. It thus reflects the maximum IT-covalency and hence the minimum IT-ionicity in this model chemical bond (see Fig. 4). It should be also observed that for the strictly deterministic average amplitude channel, $\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \mathbf{I}$, the IT-covalent bond component indeed vanishes, $\langle S(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = 0$, with the complementary IT-ionic index of the channel information capacity relative to the assumed atomic promolecule, $\langle I_0(\boldsymbol{\chi} : \boldsymbol{\chi}') \rangle_{av.} = 1$ bit, indeed marking a single purely ionic chemical bond [11–13].

One could intuitively expect from the definition of Eq. (86) that the *ionic* VB-structure represents only the *intra*-atomic orbital communications (*inter*-atomically decoupled), in which the amplitude scatterings between different atoms, $|\chi_A\rangle \to |\chi_B\rangle$ and $|\chi_B\rangle \to |\chi_A\rangle$, identically vanish with only the *intra*-AO, fully deterministic communications $|\chi_A\rangle \to |\chi_A\rangle$ and $|\chi_B\rangle \to |\chi_B\rangle$ remaining. This conjecture is seen to be supported by the average bond-orders in this ionic state, which also reflect its average communication amplitudes of Eq. (90). The equal mixture of the CBO matrices for two configurations involved in $\Psi^{ion.}(2)$ thus gives the expected average amplitudes, which correctly describe the average AO populations $\{\langle n_i \rangle_{ens.} = 1\}$ of electrons in this orbitally decoupled state, equal to those in the assumed atomic *promolecule*. They generate the purely deterministic average communications in this ionic reference state:

$$\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{av.} = \mathbf{I} \equiv \mathbf{P}^{ion.}(\boldsymbol{\chi}'|\boldsymbol{\chi}). \tag{92}$$

Fig. 5 The diagonal (*upper channel*) and *off*-diagonal (*lower channel*) communications in two prototype VB structures
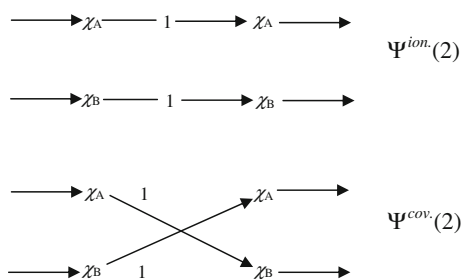
This intuitively correct prediction from the quantum (*amplitude*) CID MO-ensemble is in contrast to that resulting from the classical (*probability*) averaging scheme, which implies the full spectrum of orbital communications expected in the fully delocalized state $\Psi^{cov.}(2)$,

$$\langle \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) \rangle_{ens.} = (1/2)\mathbf{1} \equiv \mathbf{P}^{cov.}(\boldsymbol{\chi}'|\boldsymbol{\chi}), \tag{93}$$

containing the equal mixture of both the *intra-* and *inter*-AO communications in Fig. 3.

One would also expect that the prototype covalent structure of Eq. (83) should indeed equally explore both the *off*-diagonal (delocalized) communications $|\chi_A\rangle \to |\chi_B\rangle$ and $|\chi_B\rangle \to |\chi_A\rangle$ and the localized $|\chi_A\rangle \to |\chi_A\rangle$ and $|\chi_B\rangle \to |\chi_B\rangle$ propagations of $\Psi^{ion.}(2)$, since then the IT-*covalency*, reflected by the molecular conditional entropy $S(\boldsymbol{\chi}'|\boldsymbol{\chi})$, reaches its maximum value of 1 bit of information, while the channel IT-*ionicity*, measured by the mutual information relative to the promolecular reference, $I^0(\boldsymbol{\chi} : \boldsymbol{\chi}')$, identically vanishes. This expectation is indeed realized only in the *classical* probability averaging of Eq. (88).

Therefore, neither of the two averaging schemes in the CID MO-ensemble gives the intuitively expected predictions for *both* these complementary apects of the chemical bond in the 2-AO model. This analysis seems to confirm the "classical" character of the bond-*ionic* IT multiplicity, being correctly represented by the *probability*-averaging over configurations. The complementary bond-*covalency* appears to constitute the "quantum" aspect of the bonding pattern in a molecule, the overall IT multiplicity of which requires the *amplitude*-averaging over configurations.

In the alternative CID perspective [45] on the information origins of the two bond components and on the overall entropic measure of the chemical bond-order one separates the deterministic ("additive", localized) diagonal communications $|\chi_A\rangle \to |\chi_A\rangle$ and $|\chi_B\rangle \to |\chi_B\rangle$, from the cross ("*non*-additive", delocalized) probability propagations $|\chi_A\rangle \to |\chi_B\rangle$ and $|\chi_B\rangle \to |\chi_A\rangle$ between AO (Fig. 5). The former are then linked to the bond ionicity effects, while the latter are ascribed to the chemical bond covalency. In this approach the overall conditional entropy generates the interaction-dependent IT index of the chemical bond *overall* multiplicity, which correctly vanishes in the SAL and was shown to compare favourably with the Wiberg index of quantum chemistry (Fig. 4).

As we have already observed above, the predictions of AO communications in both VB structures are the same in the given averaging scheme of the CID MO-ensemble, thus failing to distinguish the fundamental chemical difference in these two proto-type bonding situations. In order to remedy this shortcoming one has to recognize the configuration *phases* in Eqs. (83) and (86). For the ionic structure this proposition again leads to the average amplitudes generated by the *diagonal* bond orders of Eq. (89),

$$\langle \boldsymbol{\gamma}^{ion.} \rangle_{ens.} = 1/2(\boldsymbol{\gamma}^b + \boldsymbol{\gamma}^a) = \mathbf{I}, \tag{94}$$

while for the covalent structure one then obtains the average CBO-difference matrix:

$$\langle \boldsymbol{\gamma}^{cov.} \rangle_{ens.} = 1/2(\boldsymbol{\gamma}^b - \boldsymbol{\gamma}^a) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \equiv \mathbf{1} - \mathbf{I}. \tag{95}$$

These average matrix elements (communication amplitudes) thus correctly ascribe the deterministic diagonal (*intra*-AO) communications $|\chi_A\rangle \to |\chi_A\rangle$ and $|\chi_B\rangle \to |\chi_B\rangle$ to $\Psi^{ion.}(2)$, while the *off*-diagonal (*inter*-AO) probability propagations $|\chi_A\rangle \to |\chi_B\rangle$ and $|\chi_B\rangle \to |\chi_A\rangle$ are identified as originating from $\Psi^{cov.}(2)$. This is schematically illustrated in Fig. 5. A similar partitioning of these elementary AO communications in the H_2 information system has been also conjectured elsewhere [99].

In this novel perspective the AO communications are thus classified as the *intra*-AO (ionic) or *inter*-AO (covalent). This conforms to the accepted chemical intuition, in which the localized AO propagations of $\Psi^{ion.}(2)$ are exclusively associated with the bond ionicity, and the delocalized AO scatterings are solely responsible for the electron sharing (covalent) effects of the chemical bond. The same classification then applies to the conditional entropy contributions to the IT bond order: the AO diagonal terms $H(diag.) \equiv V_{ion.}$ are then ionic in character, the *off*-diagonal contribution $H(ndiag.) \equiv V_{cov.}$ generates a modified measure of the bond covalency, and their sum, $V = V_{cov.} + V_{ion.} = S$, i.e., the overall *conditional entropy* of the average AO channel in the CI MO-ensemble [Eq. (93)], now stands for the *overall* entropic measure of the bond multiplicity.

For example, in the HF/KS 2-AO communication system (Fig. 3) probed by the molecular input probabilities $\boldsymbol{p} = (P, Q)$ one then predicts:

$$V_{ion.}(P) = -P^2 \log P - Q^2 \log Q, \quad V_{cov.}(P) = -PQ \left[\log P + \log Q \right]. \tag{96}$$

These two entropic components give the associated global measure of the modified bond multiplicity index, equal to BEF $H(P)$,

$$V(P) = V_{cov.}(P) + V_{ion.}(P) = (P + Q) \left[-P \log P - Q \log Q \right] = H(P). \tag{97}$$

This new index compares favourably with the Wiberg bond order in Fig. 4 and is interaction-dependent. It vanishes in the heteronuclear (*ionic*) dissociation limit, $\Psi^{CID}(2) = \Psi^{ion.}(2)$, at large separation between atoms, $R_{AB} \to \infty$, when ($P = 1$ and $Q = 0$) or ($P = 0$ and $Q = 1$). This result $V_{ion.}(\infty) = 0$ represents the vanishing

noise descriptor of the first deterministic channel in Fig. 5. It should be also observed that in the symmetric case of H_2 at the equilibrium separation between nuclei, when $P = Q = 1/2$,

$$V_{ion.}(1/2) = V_{cov.}(1/2) = 1/2 \quad \text{and} \quad V(1/2) = 1. \tag{98}$$

For the spin-*unrestricted* (UHF/UKS) orbitals in this homonuclear (*atomic*) dissociation limit $R_{AB} \to \infty$, both MO represent the corresponding AO, i.e., again ($P = 1$ and $Q = 0$) or ($P = 0$ and $Q = 1$) and $\Psi^{CID}(2) = \Psi^{cov.}(2)$. Therefore, one again predicts $V_{cov.}(\infty) = 0$, the vanishing overall noise descriptor of the second deterministic channel in Fig. 5.

In a general case of the constituent atoms contributing several AO to the molecular bond system one adopts the usual atomic resolution [91], in which the sum of the *intra*-atomic diagonal-scattering contributions again reflects the atomic ionicity, the atom *off*-diagonal conditional probabilities between different AO generate the *atomic* IT covalency index, reflecting the AIM promotion in the presence of the remaining atoms, and the *inter*-atomic information propagation terms reflect the true chemical bonding between different atoms.

9 Conclusion

It has been amply demonstrated elsewhere that IT provides an attractive, novel perspective on the molecular equilibria, multiplicity, composition and localization of chemical bonds in molecular systems, and their information origins. We have presented in this analysis some new developments in CTCB covering the *local* information systems and the CI MO-ensemble generalization of the *single*-configuration OCT.

All these approaches introduce the communication perspective on several classical issues in the theory of bond multiplicities and their covalent/ionic composition. The *inter*-atomic conditional probabilities in HF or KS theories, generated from the bond-projected superposition principle of quantum mechanics, are proportional to the quadratic (Wiberg-type) bond indices formulated in the SCF MO description. Therefore, the strong *inter*-orbital communications correspond to strong Wiberg bond-order contributions. The OCT treatment of the localized (diatomic) chemical interactions in polyatomics has also been developed [11–13,69]. This approach reproduces the Wiberg bond multiplicity in diatomic molecules and allows one to resolve the overall IT bond-order of the localized bond into the associated IT covalent/ionic components. In typical polyatomic molecules these localized-bond multiplicities were also shown to closely approximate the quadratic Wiberg index of quantum chemistry, at the same time providing its IT-covalent/ionic resolution [69].

In this work OCT has been extended to cover the *multi*-determinantal CI-type wave functions. The effective MO-ensemble approach, which recognizes the phases of the CI configurations, has been advocated for extracting chemical interpretation from the molecular AO information channels. In the CID treatment of the 2-AO model the "diagonal" (*intra*-orbital) communications have been associated with the IT bond

ionicity, while the complementary covalent component has been attributed to the "*off-diagonal*" (*inter*-orbital) probability scatterings.

It should be emphasized that the two CI MO-ensemble approaches, the *classical* (probability) and *quantum* (amplitude) averaging schemes, can be also applied to weight the local channels in each configuration used in the underlying CI expansion of the system ground state. The classical local probabilities are then calculated as the ensemble average probabilities in each configuration [see Eq. (22)]:

$$\langle P_{\boldsymbol{r} \to \boldsymbol{r'}} \rangle_{ens.} = \sum_{\alpha} p_{\alpha} P_{\boldsymbol{r} \to \boldsymbol{r'}}(\alpha), \tag{99}$$

while the associated quantum probabilities $\langle P_{r \to r'} \rangle_{av.} = [\langle A_{r \to r'} \rangle_{av.}]^2$ are generated by the squares of the resultant average amplitudes [see Eq. (23)]:

$$\langle A_{\boldsymbol{r} \to \boldsymbol{r'}} \rangle_{av.} = \sum_{\alpha} p_{\alpha} A_{\boldsymbol{r} \to \boldsymbol{r'}}(\alpha), \tag{100a}$$

preferably recognizing the configuration phases in the ground state:

$$\langle A_{\boldsymbol{r} \to \boldsymbol{r'}} \rangle_{av.} = \sum_{\alpha} \text{sign}(c_{\alpha}) \, p_{\alpha} A_{\boldsymbol{r} \to \boldsymbol{r'}}(\alpha). \tag{100b}$$

References

1. R.A. Fisher, Proc. Camb. Phil. Soc. **22**, 700 (1925)
2. B.R. Frieden, *Physics from the Fisher Information: A Unification*, 2nd edn. (Cambridge University Press, Cambridge, 2004)
3. C.E. Shannon, Bell Syst. Tech. J. **27**, 379, 623 (1948)
4. C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication* (University of Illinois, Urbana, 1949)
5. S. Kullback, R.A. Leibler, Ann. Math. Stat. **22**, 79 (1951)
6. S. Kullback, *Information Theory and Statistics* (Wiley, New York, 1959)
7. N. Abramson, *Information Theory and Coding* (McGraw-Hill, New York, 1963)
8. P.E. Pfeifer, *Concepts of Probability Theory*, 2nd edn. (Dover, New York, 1978)
9. R.F. Nalewajski, J. Math. Chem. **51**, 297 (2013)
10. R.F. Nalewajski, Entropic Concepts in Electronic Structure Theory. Found. Chem. (in press). doi:10.1007/s10698-012-9168-7
11. R.F. Nalewajski, *Information Theory of Molecular Systems* (Elsevier, Amsterdam, 2006)
12. R.F. Nalewajski, *Information Origins of the Chemical Bond* (Nova, New York, 2010)
13. R.F. Nalewajski, *Perspectives in Electronic Structure Theory* (Springer, Heidelberg, 2012)
14. R.F. Nalewajski, in Mathematical Chemistry, ed. by W.I. Hong (Nova Science Publishers, New York, 2011), pp. 247–325
15. R.F. Nalewajski, in *Chemical Information and Computation Challenges in 21st Century*, ed. by M.V. Putz (Nova Science Publishers, New York, 2012), pp. 61–100
16. R.F. Nalewajski, P. de Silva, J. Mrozek, in *Theoretical and Computational Developments in Modern Density Functional Theory*, ed. by A.K. Roy (Nova, New York, 2012), pp. 561–588

17. R.F. Nalewajski, in *Frontiers in Modern Theoretical Chemistry: Concepts and Methods* (Dedicated to B. M. Deb), eds. by P.K. Chattaraj, S.K. Ghosh (Taylor & Francis/CRC, London, 2013), pp. 143–180
18. R.F. Nalewajski, Struct. Bond. **149**, 51 (2012)
19. R.F. Nalewajski, Sci. Tech. **1**, 105 (2012)
20. R.F. Nalewajski, in *Advances in Quantum Systems Research*, ed. by Z. Ezziane (Nova, New York, 2012), in press
21. R.F. Nalewajski, in *Quantum Matter Chemistry*, ed. by A. Herman (American Scientific Publishers), in press
22. R.F. Nalewajski, J. Math. Chem. **51**, 369 (2013)
23. R.F. Nalewajski, Ann. Phys. (Leipzig) **525**, 256 (2013)
24. R.F. Nalewajski, E. Świtka, A. Michalak, Int. J. Quantum Chem. **87**, 198 (2002)
25. R.F. Nalewajski, E. Świtka, Phys. Chem. Chem. Phys. **4**, 4952 (2002)
26. R.F. Nalewajski, E. Broniatowska, J. Phys. Chem. A. **107**, 6270 (2003)
27. R.F. Nalewajski, R.G. Parr, Proc. Natl. Acad. Sci. USA **97**, 8879 (2000)
28. R.F. Nalewajski, R.G. Parr, J. Phys. Chem. A **105**, 7391 (2001)
29. R.F. Nalewajski, R. Loska, Theor. Chem. Acc. **105**, 374 (2001)
30. R.F. Nalewajski, Chem. Phys. Lett. **372**, 28 (2003)
31. R.G. Parr, P.W. Ayers, R.F. Nalewajski, J. Phys. Chem. A **109**, 3957 (2005)
32. R.F. Nalewajski, Phys. Chem. Chem. Phys. **4**, 1710 (2002)
33. R.F. Nalewajski, Adv. Quantum Chem. **43**, 119 (2003)
34. R.F. Nalewajski, E. Broniatowska, Theor. Chem. Acc. **117**, 7 (2007)
35. F.L. Hirshfeld, Theor. Chim. Acta (Berl.) **44**, 129 (1977)
36. R.F. Nalewajski, Int. J. Quantum Chem. **108**, 2230 (2008)
37. R.F. Nalewajski, J. Math. Chem. **47**, 667 (2010)
38. R.F. Nalewajski, P. de Silva, J. Mrozek, J. Mol. Struct: THEOCHEM **954**, 57 (2010)
39. R.F. Nalewajski, A.M. Köster, S. Escalante, J. Phys. Chem. A **109**, 10038 (2005)
40. A.D. Becke, K.E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990)
41. B. Silvi, A. Savin, Nature **371**, 683 (1994)
42. A. Savin, R. Nesper, S. Wengert, T.F. Fässler, Angew. Chem. Int. Ed. Engl. **36**, 1808 (1997)
43. R.F. Nalewajski, J. Phys. Chem. A **104**, 11940 (2000)
44. R.F. Nalewajski, J. Math. Chem. **49**, 2308 (2011)
45. R.F. Nalewajski, J. Math. Chem. **51**, 7 (2013)
46. R.F. Nalewajski, K. Jug, in *Reviews of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*, vol. I, ed. by K.D. Sen (World Scientific, Singapore, 2002), p. 148
47. R.F. Nalewajski, Struct. Chem. **15**, 391 (2004)
48. R.F. Nalewajski, Mol. Phys. **102**, 531, 547 (2004)
49. R.F. Nalewajski, Mol. Phys. **103**, 451 (2005)
50. R.F. Nalewajski, Mol. Phys. **104**, 1977, 2533 (2006)
51. R.F. Nalewajski, Theor. Chem. Acc. **114**, 4 (2005)
52. R.F. Nalewajski, J. Math. Chem. **38**, 43 (2005)
53. R.F. Nalewajski, J. Math. Chem. **43**, 265 (2008)
54. R.F. Nalewajski, J. Math. Chem. **45**, 607 (2009)
55. R.F. Nalewajski, J. Math. Chem. **45**, 709 (2009)
56. R.F. Nalewajski, J. Math. Chem. **45**, 776 (2009)
57. R.F. Nalewajski, J. Math. Chem. **45**, 1041 (2009)
58. R.F. Nalewajski, Int. J. Quantum Chem. **109**, 425, 2495 (2009)
59. R.F. Nalewajski, J. Math. Chem. **47**, 709 (2010)
60. R.F. Nalewajski, J. Math. Chem. **49**, 592 (2011)
61. R.F. Nalewajski, J. Math. Chem. **43**, 780 (2008)
62. R.F. Nalewajski, J. Phys. Chem. A **111**, 4855 (2007)
63. R.F. Nalewajski, Mol. Phys. **104**, 3339 (2006)
64. R.F. Nalewajski, J. Phys. Chem A **107**, 3792 (2003)
65. R.F. Nalewajski, Mol. Phys. **104**, 255 (2006)
66. R.F. Nalewajski, Ann. Phys. (Leipzig) **13**, 201 (2004)
67. H.B. Callen, *Thermodynamics: An Introduction to the Physical Theories of the Equilibrium Thermostatics and Irreversible Thermodynamics* (Wiley, New York, 1960)
68. R.F. Nalewajski, Adv. Quantum Chem. **56**, 217 (2009)

69. R.F. Nalewajski, D. Szczepanik, J. Mrozek, Adv. Quantum Chem. **61**, 1 (2011)
70. R.F. Nalewajski, D. Szczepanik, J. Mrozek, J. Math. Chem. **50**, 1437 (2012)
71. R.F. Nalewajski, J. Math. Chem. **47**, 692, 808 (2010)
72. R.F. Nalewajski, J. Math. Chem. **49**, 806 (2011)
73. R.F. Nalewajski, J. Math. Chem. **49**, 371, 546 (2011)
74. R.F. Nalewajski, P. Gurdek, J. Math. Chem. **49**, 1226 (2011)
75. R.F. Nalewajski, Int. J. Quantum Chem. **112**, 2355 (2012)
76. R.F. Nalewajski, P. Gurdek, Struct. Chem. **23**, 1383 (2012)
77. R.F. Nalewajski, Int. J. Quantum Chem. **113**, 766 (2013)
78. S. López-Rosa, *Information-Theoretic Measures of Atomic and Molecular Systems*, PhD Thesis, University of Granada 2010
79. S. López-Rosa, R.O. Esquivel, J.C. Angulo, J. Antolín, J.S. Dehesa, N. Flores- Gallegos, J. Chem. Theory Comput. **6**, 145 (2010)
80. H. Shull, J. Am. Chem. Soc. **82**, 1287 (1960)
81. H. Shull, J. Am. Chem. Soc. **86**, 1469 (1964)
82. H. Shull, J. Phys. Chem. **66**, 2320 (1962)
83. S. Hagstrom, H. Shull, Rev. Mod. Phys. **35**, 624 (1963)
84. P.A.M. Dirac, *The Principles of Quantum Mechanics*, 4th edn. (Clarendon, Oxford, 1958)
85. R.F. Nalewajski, On Phases and Interference of Local Communications in Molecules, J. Math. Chem. (in press)
86. R.F. Nalewajski, J. Math. Chem. **44**, 414 (2008)
87. K.A. Wiberg, Tetrahedron **24**, 1083 (1968)
88. M.S. Gopinathan, K. Jug, Theor. Chim. Acta (Berl.) **63**, 497, 511 (1983)
89. K. Jug, M.S. Gopinathan, in *Theoretical Models of Chemical Bonding*, Vol. II, ed. by Z.B. Maksić, (Springer, Heidelberg, 1990), p. 77.
90. I. Mayer, Chem. Phys. Lett. **97**, 270 (1983)
91. R.F. Nalewajski, A.M. Köster, K. Jug, Theor. Chim. Acta (Berl.) **85**, 463 (1993)
92. R.F. Nalewajski, J. Mrozek, Int. J. Quantum Chem. **51**, 187 (1994)
93. R.F. Nalewajski, S.J. Formosinho, A.J.C. Varandas, J. Mrozek, Int. J. Quantum Chem. **52**, 1153 (1994)
94. R.F. Nalewajski, J. Mrozek, G. Mazur, Can. J. Chem. **100**, 1121 (1996)
95. R.F. Nalewajski, J. Mrozek, A. Michalak, Int. J. Quantum Chem. **61**, 589 (1997)
96. J. Mrozek, R.F. Nalewajski, A. Michalak, Polish J. Chem. **72**, 1779 (1998)
97. R.F. Nalewajski, Chem. Phys. Lett. **386**, 265 (2004)
98. W. Heitler, F. London, Z. Physik **44**, 455 (1927)
99. R.F. Nalewajski, Mol. Phys. **104**, 365 (2006)