

On phases and interference of local communications in molecules

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Abstract The role of phases in *local* Communication Theory of the Chemical Bond is investigated. Probability amplitudes of such molecular (*fine-grained*) information systems originate from the superposition principle of quantum mechanics involving the projection onto the bond system defined by the subspace of the state occupied Molecular Orbitals. They are explicitly *phase*-dependent, thus being capable of interference effects. The phase factors of the local *direct* and *indirect* (bridge, cascade) channels are examined and the associated amplitude/probability *sum rules* are established. The entropic descriptors of the local channels, providing the system “covalent” (communication-*noise*) and “ionic” (information-*flow*) components, are investigated using prototype *one*-electron systems. The competition between these information-theoretic measures of the chemical bond covalency (electron delocalization) and ionicity (electron localization) is illustrated in H_2^+ and H_2 .

Keywords Amplitude phases · Chemical bonds · Covalent/ionic components · Entropic multiplicities · Information theory · Interference of communications · Local propagations · Molecular communications

1 Introduction

The *information theory* (IT) [1–8] has been successfully applied to explore the electron probabilities and patterns of chemical bonds in molecules, e.g., [9–20]. Both the electron *probability* distribution, determined by the wave-function *modulus*, and the system *current* density, related to the gradient of the wave-function *phase*, ultimately

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contribute to the *resultant* (quantum) information content of molecular states. The former reveals the *classical* information content, while the latter determines its *non-classical* (quantum) complement in the overall information measure [9, 10, 20–22].

It has been argued elsewhere that many classical problems of theoretical chemistry can be approached afresh using this novel IT perspective, e.g., [9–20]. The displacements of the classical information distribution in a molecule, relative to the *promolecular* reference consisting of its constituent *non-bonded* atoms, have been investigated [11–15, 17–20, 23–25] and the least biased partition of the molecular electron distribution into subsystem contributions, e.g., densities of bonded atoms, has been examined [11–13, 26–33]. This IT approach has been shown to lead to the “stockholder” *atoms-in-molecules* (AIM) of Hirshfeld [34].

The spatial localization of specific chemical bonds and electron localization in atoms and molecules has also been tackled. The *non-additive* Fisher information in the *atomic orbital* (AO) resolution has been used as the *contra-gradient* (CG) criterion for localizing the bonding regions in molecules [11–20, 35–37], while the related information density in the *molecular orbital* (MO) resolution has been shown [11, 38] to determine the vital ingredient of the *electron-localization function* (ELF) [39–41].

The *communication theory of the chemical bond* (CTCB), which uses the entropic descriptors of the molecular information (communication) channels in the AIM, orbital or local resolutions of the electron probability distribution, has also been developed [11–13, 42–59]. The same bond descriptors have been used to provide the information-scattering perspective on the intermediate stages in the electron redistribution processes [60], including the atom “promotion” *via* the orbital hybridization [61], and the communication theory for the excited electron configurations has been developed [62]. The phenomenological description of equilibria in molecular subsystems has been also proposed [11, 63–65], which formally resembles that developed in ordinary thermodynamics [66].

The IT approach introduces into the theory of electronic structure of molecular systems the novel *entropy-representation* [10–22], which complements the familiar *energy-representation* of the molecular quantum mechanics. Such a dual perspective parallels that known from the ordinary thermodynamics. It establishes the equivalent energy and entropy/information principles governing the molecular equilibria, provides a new unifying perspective on the 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 also 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.

Entropic probes of molecular electronic structure have provided attractive tools for describing the chemical bond phenomenon in information terms. For an exploration of the chemical bond multiplicities in the *orbital communication theory* (OCT) [13, 57–59, 67–70] it is vital to examine how the input information is propagated between AO, the typical basis functions used to describe the *bonding* (occupied) MO subspace of SCF LCAO MO calculations. The molecular system can indeed 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], which introduce a new class of descriptors of molecular "connectivities" between AIM. The molecular 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 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 the familiar competition between these two bond components.

The new (through-*bridge*) mechanism of the intermediate orbital communications (entropic interactions) in molecules has also been identified [71–76], which complements the direct, through-*space* bond contributions. The IT approach also covers changes in the bond pattern effected by chemical reactions [77,78]. The equivalence of the *vertical* (*density*-constrained) energy and entropy/information rules in quantum mechanics [21,22,79,80] parallels that of the complementary energy and entropy principles of thermodynamics [66].

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 [76,79–81], calls for the information system of the probability-*amplitude* propagation, with the scattering amplitudes then explicitly depending on phases of the (complex) emitting and monitoring *event*-states. Examining the role of MO phases in local probability propagations in molecules is the main purpose of the present work.

Throughout the article the following tensor notation is used: A denotes a scalar quantity, \mathbf{A} stands for the *row*- or *column*-vector, and \mathbf{A} represents a square or rectangular matrix. The logarithm of the Shannon 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 Orbital and local communications in molecules

An exploration of the chemical bond system in molecular electronic states calls for the AO resolution determined by the basis functions $\chi = (\chi_1, \chi_2, \dots, \chi_m)$ of typical SCF LCAO MO calculations. Within the familiar Hartree–Fock (HF) theory the molecular ground-state of N electrons is defined by the occupied (*bonding*) subspace $\varphi = \chi \mathbf{C} \{ \varphi_s = \phi_s \xi_s, s = 1, 2, \dots, N \}$ of the *singly*-occupied *spin*-MO (SMO), representing N -lowest *one*-particle states, which give rise to the associated Slater determinant:

$$\Psi(N) = \det[\boldsymbol{\varphi}] \equiv |\varphi_1, \varphi_2, \dots, \varphi_N|. \quad (1)$$

Here, $\varphi_s(\mathbf{r}, \sigma) = \phi_s(\mathbf{r}) \xi_s(\sigma)$, ϕ_s denotes the *spatial* MO, and ξ_s stands for one of the two admissible spin states of an electron: $\xi_s \in \{\alpha \text{ (spin-up)}, \beta \text{ (spin-down)}\}$. In the analogous Kohn–Sham (KS) description such determinant of N -lowest KS orbitals, which usually provides quite an adequate description of the system chemical bonds (see e.g., [11–13]), defines the *hypothetical* state of *non-interacting* electrons, which generates the same electron density as does the (correlated) ground state of the *real* (interacting) system.

In OCT the *orbital* channels [3,4,7,8,11–13] propagate probabilities of the electron assignments to basis functions $\boldsymbol{\chi}$ of the SCF LCAO MO calculations, *via* the network of the occupied SMO $\boldsymbol{\varphi}$. The underlying conditional probabilities of the “output” orbital events $\boldsymbol{\chi}'$, given the “input” orbital events $\boldsymbol{\chi}$,

$$\begin{aligned} \mathbf{P}(\boldsymbol{\chi}'|\boldsymbol{\chi}) &= \{P(\chi_j|\chi_i) \equiv P(j|i) \equiv P_{i \rightarrow j} = |A(j|i)|^2 = |A_{i \rightarrow j}|^2\}, \\ P(j|i) &= P(i, j)/p_i \equiv P_{i, j}/p_i, \end{aligned} \quad (2)$$

result from the (bond-projected) *superposition principle* of quantum mechanics [82]. Here $P(i, j) \equiv P_{i, j}$ denotes the probability of the *joint*-event of simultaneously observing $|\chi_i\rangle$ and $|\chi_j\rangle$ in the molecular bond system, while $p_i = \sum_j P(i, j) = n_i/N$ represents the associated probability of $|\chi_i\rangle$ alone, with n_i standing for the average AO occupation number. As also indicated above, these communications are generated by the magnitude (modulus) of the associated quantum (complex) amplitudes $\mathbf{A}(\boldsymbol{\chi}'|\boldsymbol{\chi}) = \{A(j|i) = A_{i \rightarrow j}\}$, of the emitting (*input*) states $\mathbf{a} = |\boldsymbol{\chi}\rangle = \{|\chi_i\rangle\}$ among the monitoring/receiving (*output*) states $\mathbf{b} = |\boldsymbol{\chi}'\rangle = \{|\chi_j\rangle\}$.

A deeper understanding of the molecular electronic structure ultimately calls for the continuous, *local* (“*fine-grained*”) description [81,83], to complement the discrete, *orbital* (“*coarse-grained*”) resolution adopted in OCT. The original *orbital*-communication development can be indeed naturally generalized into this extreme level of resolving electron distributions in molecules, when one examines the information propagations between infinitesimal volume elements around $\mathbf{r} \in \mathfrak{R}$ in the channel input and $\mathbf{r}' \in \mathfrak{R}'$ in its output, respectively, with \mathfrak{R} or \mathfrak{R}' containing the whole physical space of all admissible electron localizations.

This local description [81,83], which we shall further develop in the present analysis, uses the basis functions $\{|\mathbf{r}\rangle\}$ of the familiar *position representation* of quantum mechanics, identified by the continuous labels of the spatial coordinates of an electron. They determine both the input $\mathbf{a} = \{|\mathbf{r}\rangle\}$ and output $\mathbf{b} = \{|\mathbf{r}'\rangle\}$ of the *local* molecular channel determined by the relevant conditional probabilities,

$$\left\{ P(\mathbf{r}'|\mathbf{r}) = P_{\mathbf{r} \rightarrow \mathbf{r}'} = |A(\mathbf{r}'|\mathbf{r})|^2 = |A_{\mathbf{r} \rightarrow \mathbf{r}'}|^2 \right\}, \quad P(\mathbf{r}'|\mathbf{r}) = \pi(\mathbf{r}, \mathbf{r}')/p(\mathbf{r}), \quad (3)$$

where $\pi(\mathbf{r}, \mathbf{r}') = P_{\mathbf{r}, \mathbf{r}'} = |A_{\mathbf{r}, \mathbf{r}'}|^2$ again denotes the joint probability of simultaneously observing the two locations in the bond system of a molecule, and the associated probability of a single location,

$$p(\mathbf{r}) = \rho(\mathbf{r})/N = \int \pi(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \quad (4)$$

represents the *shape*-factor of the molecular electron density $\rho(\mathbf{r})$.

In the simplest (*one*-determinantal) orbital approximation one takes into account only a single orbital configuration, e.g., the ground-state $\Psi(N)$ [Eq. (1)], the occupied SMO of which give rise to all physical properties of the system under consideration. This configuration is uniquely identified by its *singly*-occupied (physical) SMO subspace $\varphi = (\varphi_1, \varphi_2, \dots, \varphi_N)$, or by the associated *spatial* MO functions, $\phi = (\phi_1, \phi_2, \dots, \phi_N) = \chi \mathbf{C}$. They define the corresponding (idempotent) SMO and MO projectors onto this bond subspace,

$$\hat{P}_\varphi \equiv \sum_{s=1}^N |\phi_s\rangle \langle \phi_s| = |\varphi\rangle \langle \varphi|, \quad (\hat{P}_\varphi)^2 = \hat{P}_\varphi \quad \text{or} \quad \hat{P}_\phi \equiv |\phi\rangle \langle \phi|, \quad (\hat{P}_\phi)^2 = \hat{P}_\phi, \quad (5)$$

which generate the system *charge-and-bond-order* (CBO) matrix, i.e., the (idempotent) *one*-electron *density matrix* in the AO representation,

$$\begin{aligned} \boldsymbol{\gamma} &= \langle \chi | \varphi \rangle \langle \varphi | \chi \rangle \equiv \langle \chi | \hat{P}_\varphi | \chi \rangle = \langle \chi | \phi \rangle \langle \phi | \chi \rangle = \mathbf{C} \mathbf{C}^\dagger = \{\gamma_{i,j} = \mathbf{c}_i \mathbf{c}_j^\dagger\} \\ \text{tr } \boldsymbol{\gamma} &\equiv \sum_i \gamma_{i,i} = N \sum_i p_i \equiv \sum_i n_i = N; \end{aligned} \quad (6)$$

here the rectangular matrix of the LCAO MO expansion coefficients, $\mathbf{C} = \langle \chi | \varphi \rangle = \langle \chi | \phi \rangle = \{\mathbf{C}_s\} = \{\mathbf{c}_i\}$ groups the *column*-vectors $\mathbf{C}_s = \{C_{i,s}, i = 1, 2, \dots, m\}$ defining $\phi_s = \chi \mathbf{C}_s$, i.e., the *s*th column of \mathbf{C} , and *row*-vectors $\mathbf{c}_i = \{C_{i,s}, s = 1, 2, \dots, N\}$, multiplying χ_i in all occupied MO combinations, i.e., the *i*th row of \mathbf{C} . The density matrix idempotency,

$$\begin{aligned} \boldsymbol{\gamma}^2 &= \langle \chi | \hat{P}_\varphi | \chi \rangle \langle \chi | \hat{P}_\varphi | \chi \rangle = \langle \chi | \hat{P}_\varphi \hat{P}_\varphi | \chi \rangle \\ &= \mathbf{C}(\mathbf{C}^\dagger \mathbf{C})\mathbf{C}^\dagger = \mathbf{C} \mathbf{C}^\dagger = \boldsymbol{\gamma}, \end{aligned} \quad (7)$$

follows from the assumed AO and MO orthonormalities,

$$\langle \chi | \chi \rangle = \mathbf{I}_m \quad \text{and} \quad \langle \varphi | \varphi \rangle = \langle \phi | \phi \rangle = \langle \varphi | \chi \rangle \langle \chi | \chi \rangle \langle \chi | \varphi \rangle = \mathbf{C}^\dagger \mathbf{I}_m \mathbf{C} = \mathbf{C}^\dagger \mathbf{C} = \mathbf{I}_N, \quad (8)$$

which further imply [see Eq. (7)]:

$$\hat{P}_\varphi \hat{P}_\chi \hat{P}_\varphi = |\varphi\rangle (\mathbf{C}^\dagger \mathbf{C}) \langle \varphi| = \hat{P}_\varphi. \quad (9)$$

Indeed, for the occupied MO φ expressed in the given basis χ , the action of the AO projector onto the occupied-MO projector amounts to identity operation, $\hat{P}_\chi = |\chi\rangle \langle \chi| = 1$, and hence

$$\hat{P}_\varphi \hat{P}_\chi \hat{P}_\varphi = (\hat{P}_\varphi)^2 = \hat{P}_\varphi. \quad (10)$$

$$\text{(a)} \quad \gamma_{ij} = \langle \chi_i | \hat{\rho} \rangle \langle \hat{\rho} | \chi_j \rangle = \sum_s C_{i,s} C_{j,s}^* \equiv \mathbf{c}_i \mathbf{c}_j^\dagger \equiv \Gamma_{i,j}$$

input | bond system | output

$$\text{(b)} \quad \gamma(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{\rho} \rangle \langle \hat{\rho} | \mathbf{r}' \rangle = \sum_s \varphi_s(\mathbf{r}) \varphi_s^*(\mathbf{r}') = \varphi(\mathbf{r}) \varphi^\dagger(\mathbf{r}') \equiv \Gamma_{\mathbf{r},\mathbf{r}'}$$

input | bond system | output

Fig. 1 Elementary amplitudes $\Gamma_{i,j} = \gamma_{i,j}$ (Panel a) and $\Gamma_{\mathbf{r},\mathbf{r}'} = \gamma(\mathbf{r}, \mathbf{r}')$ (Panel b), of the joint *two*-AO density $\Omega(i, j) = |\Gamma_{i,j}|^2$ and the joint *two*-point density $\Omega(\mathbf{r}, \mathbf{r}') = |\Gamma_{\mathbf{r},\mathbf{r}'}|^2$, measuring the AO and local representations of the SMO (bond) projection operator $\hat{P}_\varphi : \gamma_{i,j} = \langle \chi_i | \hat{P}_\varphi | \chi_j \rangle$ and $\gamma(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{P}_\varphi | \mathbf{r}' \rangle$. Here, the *row*-vectors $\{c_i\}$ combine the LCAO MO coefficients multiplying χ_i in N occupied MO, collected as the i -th row of \mathbf{C}

The representative element $\gamma_{i,j}$ of the CBO matrix thus offers a transparent interpretation of amplitudes of the scattering density, which is shown in Fig. 1a. In this elementary *two*-orbital amplitude the *ground*-state SMO projector \hat{P}_φ represents the molecular bond system, which defines a network of molecular connections (“circuitry”, “wiring” system), $|\chi_i\rangle$ specifies the *input* AO event of the signal origin, while the other orbital $|\chi_j\rangle$ states the *output* AO event of the signal monitoring/receiving.

In the *one*-electron Hilbert space the CBO matrix element has a simple “geometric” interpretation as the scalar product (“overlap”) between the bond projected (*non*-orthogonal) AO, $|\chi^b\rangle = \hat{P}_\varphi |\chi\rangle = \{|\chi_i^b\rangle = \hat{P}_\varphi |\chi_i\rangle = \sum_s |\phi_s\rangle \langle \phi_s | \chi_i\rangle \equiv \sum_s |\phi_s\rangle \phi_{s,i}^* = \sum_s |\phi_s\rangle C_{i,s}^*\}$:

$$\gamma_{i,j} = \langle \chi_i | \hat{P}_\varphi | \chi_j \rangle = \left(\langle \chi_i | \hat{P}_\varphi \right) \left(\hat{P}_\varphi | \chi_j \rangle \right) \equiv \langle \chi_i^b | \chi_j^b \rangle \equiv S_{i,j}^b. \tag{11}$$

Indeed the *bond*-subspace $|\varphi\rangle$ has a lower dimensionality compared to that of the AO space, so that the *non*-orthogonal AO projections $|\chi^b\rangle$ effectively span only the N -dimensional (bond) subspace itself. Hence, a generally *non*-vanishing *bond*-overlap $S_{i,j}^b = \gamma_{i,j}$ in fact measures the (complex) projection of $|\chi_j^b\rangle$ onto $|\chi_i^b\rangle$.

The conditional probabilities of AO communications *via* its occupied SMO subspace [Eq. (2)] in this *ground*-state configuration,

$$\mathbf{P}(\chi' | \chi) = \{P(j|i) = \gamma_{i,j} \gamma_{j,i} / \gamma_{i,i} = |\Gamma_{i,j}|^2 / n_i \equiv \Omega(i, j) / n_i\}, \tag{12}$$

also identify the associated *joint*-probabilities of AO pairs:

$$\mathbf{P}(\chi', \chi) = \{P(i, j) = P_{i,j} = \Omega(i, j) / N = p_i P(j|i) = \gamma_{i,j} \gamma_{j,i} / N\}, \tag{13}$$

where the normalized AO probabilities $\mathbf{p} = \{p_i = \gamma_{i,i} / N \equiv n_i / N\}$ [see Eq. (6)]. It can be straightforwardly verified that these *two*-AO distributions also satisfy the expected normalizations:

$$\begin{aligned}\sum_j P(i, j) &= (1/N) \sum_j \gamma_{i,j} \gamma_{j,i} = n_i/N = p_i, \\ \sum_j P(j|i) &= (1/n_i) \sum_j \gamma_{i,j} \gamma_{j,i} = n_i/n_i = 1.\end{aligned}\quad (14)$$

To summarize, the CBO matrix elements $\{\gamma_{i,j}\}$ directly measure the *amplitudes* $\{\Gamma_{i,j}\}$ of the AO-pair densities $\{\Omega(i, j) = |\Gamma_{i,j}|^2\}$ and the associated probabilities $\{P(i, j) = \Omega(i, j)/N\}$. The communication amplitudes are proportional to the corresponding (*input*-renormalized) CBO matrix elements:

$$\mathbf{A}(\chi'|\chi) = \{A(j|i) = A_{i \rightarrow j} = \gamma_{i,j}/(\gamma_{i,i})^{1/2} = \Gamma_{i,j}/(n_i)^{1/2}\}. \quad (15)$$

The amplitudes $\{\Gamma_{i,j}\}$ and $\{A_{i \rightarrow j}\}$ of the signal propagation in molecular bond-system reflect both moduli and phases of $\{\gamma_{i,j}\}$, thus being capable of the communication “interference” [76, 79, 80].

The *fine*-grained approach adopts the local basis set of the precise localization states $\{|r\rangle\}$ of an electron, in which the occupied SMO projector gives rise to the ordinary (idempotent) *one*-electron density matrix. For example, for the *single*, ground-state Slater determinant of Eq. (1) in HF or KS theories one finds:

$$\begin{aligned}\gamma(\mathbf{r}, \mathbf{r}') &= \langle \mathbf{r}|\varphi\rangle\langle\varphi|\mathbf{r}'\rangle = \langle \mathbf{r}|\hat{\mathbf{P}}_\varphi|\mathbf{r}'\rangle = \sum_s \phi_s(\mathbf{r})\phi_s(\mathbf{r}')^* \equiv \Gamma_{\mathbf{r},\mathbf{r}'} \\ &= (\langle \mathbf{r}|\hat{\mathbf{P}}_\varphi\rangle\langle\hat{\mathbf{P}}_\varphi|\mathbf{r}'\rangle) \equiv (\langle \mathbf{r}^b|\mathbf{r}'^b\rangle) \equiv S_{\mathbf{r},\mathbf{r}'}^b, \\ \text{tr } \gamma(\mathbf{r}, \mathbf{r}') &\equiv \int \gamma(\mathbf{r}, \mathbf{r})d\mathbf{r} = \int \rho(\mathbf{r})d\mathbf{r} = N,\end{aligned}\quad (16)$$

$$\begin{aligned}\int \gamma(\mathbf{r}, \mathbf{r}')\gamma(\mathbf{r}', \mathbf{r}'')d\mathbf{r}' &= \langle \mathbf{r}|\phi\rangle \int \langle\phi|\mathbf{r}'\rangle\langle\mathbf{r}'|\phi\rangle d\mathbf{r}' \langle\phi|\mathbf{r}''\rangle \\ &= \langle \mathbf{r}|\phi\rangle\langle\phi|\phi\rangle\langle\phi|\mathbf{r}''\rangle = \langle \mathbf{r}|\phi\rangle\langle\phi|\mathbf{r}''\rangle = \gamma(\mathbf{r}, \mathbf{r}'').\end{aligned}\quad (17)$$

Above, we have used the MO orthonormality of Eq. (8), $\rho(\mathbf{r}) = Np(\mathbf{r})$ stands for the electron density, while $p(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})/N$ denotes its “shape” (probability) factor [see Eq. (4)]. The elementary amplitude $\Gamma_{\mathbf{r},\mathbf{r}'}$ of the joint *two*-point density $\Omega(\mathbf{r}, \mathbf{r}') = |\Gamma_{\mathbf{r},\mathbf{r}'}|^2$ is thus directly determined by $\gamma(\mathbf{r}, \mathbf{r}')$ (see Fig. 1b), while the associated *two*-point probability distribution $\pi(\mathbf{r}, \mathbf{r}') = \Omega(\mathbf{r}, \mathbf{r}')/N$. The relevant normalization conditions are summarized in two preceding equations. We have also given in Eq. (16) the geometric interpretation of the $\gamma(\mathbf{r}, \mathbf{r}')$ kernel in molecular Hilbert space, as the *bond*-overlap $S_{\mathbf{r},\mathbf{r}'}^b = \langle \mathbf{r}^b|\mathbf{r}'^b\rangle$ measuring the scalar product between the (*non*-orthogonal) bond-projected local basis vectors $\{|\mathbf{r}^b\rangle = \hat{\mathbf{P}}_\varphi|\mathbf{r}\rangle\}$.

The local information system involves these strict localization events in both its input $\mathbf{a} = \{|\mathbf{r}\rangle\}$ and output $\mathbf{b} = \{|\mathbf{r}'\rangle\}$. The elementary communication *amplitude* is then determined by the locally renormalized kernel of Eq. (16) and Fig. 1b,

$$A(\mathbf{r}'|\mathbf{r}) = A_{\mathbf{r} \rightarrow \mathbf{r}'} = \gamma(\mathbf{r}, \mathbf{r}')/[\gamma(\mathbf{r}, \mathbf{r})]^{1/2} = \Gamma_{\mathbf{r},\mathbf{r}'}/[\rho(\mathbf{r})]^{1/2}, \quad (18)$$

which ultimately determines the associated conditional *probability* between the two electron-localization states,

$$\begin{aligned} P(\mathbf{r}'|\mathbf{r}) &= P_{\mathbf{r}\rightarrow\mathbf{r}'} = |\Gamma_{\mathbf{r},\mathbf{r}'}|^2/\rho(\mathbf{r}) = |A_{\mathbf{r}\rightarrow\mathbf{r}'}|^2 = \gamma(\mathbf{r},\mathbf{r}')\gamma(\mathbf{r}',\mathbf{r})/\gamma(\mathbf{r},\mathbf{r}) \\ &= \Omega(\mathbf{r},\mathbf{r}')/\rho(\mathbf{r}), \end{aligned} \quad (19)$$

and the joint *two*-point probability distribution:

$$\pi(\mathbf{r},\mathbf{r}') = p(\mathbf{r})P(\mathbf{r}'|\mathbf{r}) = \Omega(\mathbf{r},\mathbf{r}')/N. \quad (20)$$

One directly verifies the required normalizations of these *two*-point probability distributions using the idempotency property of the density matrix [Eq. (17)]:

$$\begin{aligned} \int \pi(\mathbf{r}',\mathbf{r}')d\mathbf{r}' &= (1/N) \int \Omega(\mathbf{r},\mathbf{r}')d\mathbf{r}' = \gamma(\mathbf{r},\mathbf{r})/N = p(\mathbf{r}), \\ \int P(\mathbf{r}'|\mathbf{r})d\mathbf{r}' &= [\rho(\mathbf{r})]^{-1} \int \Omega(\mathbf{r},\mathbf{r}')d\mathbf{r}' = \gamma(\mathbf{r},\mathbf{r})/\rho(\mathbf{r}) = 1. \end{aligned} \quad (21)$$

Therefore, the density-matrix kernel $\gamma(\mathbf{r},\mathbf{r}')$ fully determines all local communications between the system infinitesimal volume-elements *via* the subspace of the configuration occupied SMO:

$$\{\pi(\mathbf{r},\mathbf{r}') = P_{\mathbf{r},\mathbf{r}'}[\gamma]\}, \{P(\mathbf{r}'|\mathbf{r}) = P_{\mathbf{r}\rightarrow\mathbf{r}'}[\gamma]\} \quad \text{and} \quad \{A(\mathbf{r}'|\mathbf{r}) = A_{\mathbf{r}\rightarrow\mathbf{r}'}[\gamma]\}. \quad (22)$$

While the local conditional probability $P(\mathbf{r}'|\mathbf{r})$ is independent of the spatial phase of the “*off*-diagonal” part of $\gamma(\mathbf{r},\mathbf{r}')$, for $\mathbf{r}' \neq \mathbf{r}$, which determines the *non*-local communications $\{|\mathbf{r}\rangle \rightarrow |\mathbf{r}'\rangle\}$, its amplitude $A(\mathbf{r}'|\mathbf{r})$ is seen to be explicitly dependent upon the relative phase of MO in the two locations involved, which also determines the resultant phase of $\gamma(\mathbf{r},\mathbf{r}')$. Clearly, this dependence vanishes for the “*diagonal*” part of $\gamma(\mathbf{r},\mathbf{r}')$, i.e., the local communications $\{|\mathbf{r}\rangle \rightarrow |\mathbf{r}\rangle\}$, when

$$\{\pi(\mathbf{r},\mathbf{r}) = \rho(\mathbf{r})^2/N, \quad P(\mathbf{r}|\mathbf{r}) = \rho(\mathbf{r}), \quad A(\mathbf{r}|\mathbf{r}) = \rho(\mathbf{r})^{1/2}\}. \quad (23)$$

One also observes, that both locations of an electron enter symmetrically into the joint probabilities $\pi(\mathbf{r},\mathbf{r}')$ and the associated density distribution $\Omega(\mathbf{r},\mathbf{r}')$, while in the *directed* conditional probabilities $P_{\mathbf{r}\rightarrow\mathbf{r}'}$ and $P_{\mathbf{r}'\rightarrow\mathbf{r}}$ or in the associated amplitudes $A_{\mathbf{r}\rightarrow\mathbf{r}'}$ and $A_{\mathbf{r}'\rightarrow\mathbf{r}}$ the two position labels are *non*-symmetrical with respect to their exchange (“*transposition*”), as explicitly indicated by the arrow specifying the direction of the underlying communication: $\mathbf{r} \rightarrow \mathbf{r}'$ or $\mathbf{r}' \rightarrow \mathbf{r}$. However, one could also define the *average* communications *between* the two locations, $\mathbf{r} \leftrightarrow \mathbf{r}'$, without any specific reference to their directions, by combining the “*forward*” ($\mathbf{r} \rightarrow \mathbf{r}'$) and “*reverse*” ($\mathbf{r}' \rightarrow \mathbf{r}$) communications for the two specified locations of an electron. This defines the *symmetric* communication links and the associated amplitudes:

$$\{P(\mathbf{r} \leftrightarrow \mathbf{r}') = P_{\mathbf{r}\leftrightarrow\mathbf{r}'} = [P(\mathbf{r}'|\mathbf{r}) + P(\mathbf{r}|\mathbf{r}')]/2 = \pi(\mathbf{r},\mathbf{r}')/[2\rho_h(\mathbf{r},\mathbf{r}')] \equiv (A_{\mathbf{r}\leftrightarrow\mathbf{r}'})^2\}. \quad (24)$$

Above, the *harmonic* average $\rho_h(\mathbf{r}, \mathbf{r}')$ of densities in the two specified electron positions is defined by the relation:

$$\rho_h(\mathbf{r}, \mathbf{r}')^{-1} \equiv \rho(\mathbf{r})^{-1} + \rho(\mathbf{r}')^{-1} \text{ or } \rho_h(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') / [\rho(\mathbf{r}) + \rho(\mathbf{r}')]. \quad (25)$$

It reflects the ratio between the square of the associated *geometric* average, $\rho_g(\mathbf{r}, \mathbf{r}') \equiv [\rho(\mathbf{r})\rho(\mathbf{r}')]^{1/2}$, and the *arithmetic* average $\rho_a(\mathbf{r}, \mathbf{r}') \equiv [\rho(\mathbf{r}) + \rho(\mathbf{r}')]/2 = N p_a(\mathbf{r}, \mathbf{r}')$ of the two densities:

$$2\rho_h(\mathbf{r}, \mathbf{r}') = 2\rho(\mathbf{r})\rho(\mathbf{r}') / [\rho(\mathbf{r}) + \rho(\mathbf{r}')] = \rho_g(\mathbf{r}, \mathbf{r}')^2 / \rho_a(\mathbf{r}, \mathbf{r}') \geq 0. \quad (26)$$

Hence, the *symmetric* (*non-directional*, positive) amplitude of such mutual communications between the two specified locations reads:

$$\begin{aligned} A_{\mathbf{r} \leftrightarrow \mathbf{r}'} &= [\gamma_g(\mathbf{r}, \mathbf{r}') / \rho_g(\mathbf{r}, \mathbf{r}')] p_a(\mathbf{r}, \mathbf{r}')^{1/2}, \\ \gamma_g(\mathbf{r}, \mathbf{r}') &= \Omega(\mathbf{r}, \mathbf{r}')^{1/2} = |\gamma(\mathbf{r}, \mathbf{r}')|, \\ p_a(\mathbf{r}, \mathbf{r}') &= \rho_a(\mathbf{r}, \mathbf{r}') / N. \end{aligned} \quad (27)$$

3 Phases in local *direct* and *cascade* communications

Consider first the *direct* communication $\mathbf{r} \rightarrow \mathbf{r}'$ between the two locations in a molecule, defined by the amplitude of Eq. (18), the phase of which is determined by that of the amplitude $\Gamma_{\mathbf{r}, \mathbf{r}'} = \gamma(\mathbf{r}, \mathbf{r}')$ of the joint *two-point* distribution [Eq. (16)]. Assuming generally complex MO,

$$\phi_s(\mathbf{r}) = R_s(\mathbf{r}) \exp[i\Phi_s(\mathbf{r})], \quad s = 1, 2, \dots, N, \quad (28)$$

one obtains the following expression for the density-matrix kernel:

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \sum_s \phi_s(\mathbf{r})\phi_s(\mathbf{r}')^* = \sum_s R_s(\mathbf{r})R_s(\mathbf{r}') \exp\{i[\Phi_s(\mathbf{r}) - \Phi_s(\mathbf{r}')]\} \\ &\equiv \sum_s m_s(\mathbf{r}, \mathbf{r}') \exp\{i f_s(\mathbf{r}, \mathbf{r}')\} \equiv M(\mathbf{r}, \mathbf{r}') \exp\{iF(\mathbf{r}, \mathbf{r}')\}, \end{aligned} \quad (29)$$

where the resultant *modulus* $M(\mathbf{r}, \mathbf{r}')$ and *phase* $F(\mathbf{r}, \mathbf{r}')$ parts of $\gamma(\mathbf{r}, \mathbf{r}')$, representing the bond system as a whole, depend upon the constituent MO distributions: $\{m_s(\mathbf{r}, \mathbf{r}')\}$ and $\{f_s(\mathbf{r}, \mathbf{r}')\}$. The latter represent *relative* MO phases in two locations, $\{f_s(\mathbf{r}, \mathbf{r}') = \Phi_s(\mathbf{r}) - \Phi_s(\mathbf{r}')\}$, which identically vanish for the diagonal scattering $\mathbf{r} \rightarrow \mathbf{r}$, when $\gamma(\mathbf{r}, \mathbf{r}) = \sum_s [R_s(\mathbf{r})]^2 = M(\mathbf{r}, \mathbf{r}) = \rho(\mathbf{r})$.

Next we examine the *indirect*, *multi-stage* (bridge, cascade) communications in molecular bond systems. The simplest, *single-cascade* scattering (Fig. 2a), between the terminal points \mathbf{r} (input) and \mathbf{r}' (output) involve a single intermediate location $\mathbf{r}'' = \mathbf{r}^{(1)}$. The relevant joint distribution amplitude $\Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}'')$ for such a *three-point*

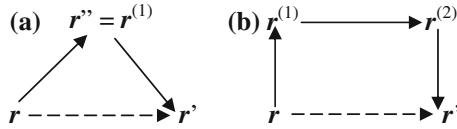


Fig. 2 Direct (broken arrows) and indirect (solid arrows) scattering between terminal locations r (input) and r' (output), in the single- (Panel a) and double- (Panel b) cascades, involving the single $\{r^{(1)}\}$ and double $\{r^{(1)}, r^{(2)}\}$ intermediate points (bridges), respectively

cascade propagation $r \rightarrow r^{(1)} \rightarrow r'$ is given by the product of the two amplitudes for each direct scattering stage:

$$\begin{aligned} \Gamma(r, r'; r'') &= \Gamma_{r, r''} \Gamma_{r'', r'} = \gamma(r, r'') \gamma(r'', r') \\ &= M(r, r'') M(r'', r') \exp\{i [F(r, r'') + F(r'', r')]\} \\ &\equiv M(r, r'; r'') \exp[iF(r, r'; r'')]. \end{aligned} \tag{30}$$

Integrating this indirect amplitude contribution over all admissible intermediate positions [see Eq. (17)] recovers the direct amplitude:

$$\int \Gamma(r, r'; r'') dr'' = \int \gamma(r, r'') \gamma(r'', r') dr'' = \gamma(r, r'). \tag{31}$$

The resultant modulus in Eq. (30) is given by the product of moduli for each direct scattering in the bridge propagation,

$$M(r, r'; r'') = M(r, r'') M(r'', r'), \tag{32}$$

while the resultant phase is determined by the sum or relative phases of the two direct stages involved:

$$F(r, r'; r'') = F(r, r'') + F(r'', r'). \tag{33}$$

The product of two communication amplitudes at each stage of the through-bridge signal propagation then determines the resultant indirect amplitude,

$$\begin{aligned} A(r \rightarrow r'; r'') &= A_{r \rightarrow r''} A_{r'' \rightarrow r'} = \Gamma_{r, r''} \Gamma_{r'', r'} / [\rho(r) \rho(r'')]^{1/2} = \Gamma(r, r'; r'') / \rho_g(r, r'') \\ &= [M(r, r'; r'') / \rho_g(r, r'')] \exp[iF(r, r'; r'')], \end{aligned} \tag{34}$$

the square of which gives rise to the associated resultant conditional probability of the local single-cascade channel:

$$P(r \rightarrow r'; r'') = |A(r, r'; r'')|^2 = P_{r \rightarrow r''} P_{r'' \rightarrow r'}. \tag{35}$$

Its bridge-normalization reads [73]:

$$\int dr'' [\int dr' P(r \rightarrow r'; r'')] = \int dr'' P(r''|r) = 1. \tag{36}$$

It should be observed that the phase factor of $A(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}'')$, determined by that of $\Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}'')$ [Eq. (30)], disappears in $P(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}'')$. This is not the case in the parallel cascades generated by the *multi*-determinantal wave functions of the *configuration–interaction* (CI) theory [44, 80, 81].

These *single*-cascade results can be straightforwardly generalized into any *bridge*-order. Consider, e.g., the *double*-cascade of Fig. 2b, in which the indirect signal propagation involves two intermediate points $\mathbf{r}^{(1)}$ and $\mathbf{r}^{(2)}$. Its joint distribution amplitude $\Omega(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)})$ for the *double*-cascade propagation $\mathbf{r} \rightarrow [\mathbf{r}^{(1)} \rightarrow \mathbf{r}^{(2)}] \rightarrow \mathbf{r}'$ is now given by the product of three direct amplitudes:

$$\begin{aligned} \Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) &= \gamma(\mathbf{r}, \mathbf{r}^{(1)}) \gamma(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}) \gamma(\mathbf{r}^{(2)}, \mathbf{r}') \\ &= M(\mathbf{r}, \mathbf{r}^{(1)}) M(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}) M(\mathbf{r}^{(2)}, \mathbf{r}') \exp \left\{ i \left[F(\mathbf{r}, \mathbf{r}^{(1)}) \right. \right. \\ &\quad \left. \left. + F(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}) + F(\mathbf{r}^{(2)}, \mathbf{r}') \right] \right\} \\ &\equiv M(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) \exp \left[i F(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) \right]. \end{aligned} \quad (37)$$

Again, the integration over the two intermediate outputs $\mathbf{r}^{(1)}$ and $\mathbf{r}^{(2)}$ recovers the direct amplitude:

$$\int d\mathbf{r}^{(1)} \int d\mathbf{r}^{(2)} \Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) = \int d\mathbf{r}^{(1)} \gamma(\mathbf{r}, \mathbf{r}^{(1)}) \gamma(\mathbf{r}^{(1)}, \mathbf{r}') = \gamma(\mathbf{r}, \mathbf{r}'). \quad (38)$$

The associated communications are now determined by the *double*-bridge amplitude:

$$\begin{aligned} A(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) &= A(\mathbf{r}^{(1)}|\mathbf{r}) A(\mathbf{r}^{(2)}|\mathbf{r}^{(1)}) A(\mathbf{r}'|\mathbf{r}^{(2)}) = \Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) / [\rho(\mathbf{r}) \rho(\mathbf{r}^{(1)}) \rho(\mathbf{r}^{(2)})]^{1/2}, \\ &= \{M(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) / [\rho(\mathbf{r}) \rho(\mathbf{r}^{(1)}) \rho(\mathbf{r}^{(2)})]^{1/2}\} \exp[iF(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)})]. \end{aligned} \quad (39)$$

It generates the associated conditional probabilities,

$$P(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)}) = |A(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)})|^2 = [M(\mathbf{r}, \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)})]^2 / [\rho(\mathbf{r}) \rho(\mathbf{r}^{(1)}) \rho(\mathbf{r}^{(2)})], \quad (40)$$

which satisfy the relevant consecutive bridge normalizations:

$$\begin{aligned} \int d\mathbf{r}^{(1)} \int d\mathbf{r}^{(2)} [\int d\mathbf{r}' P(\mathbf{r} \rightarrow \mathbf{r}'; \mathbf{r}^{(1)}, \mathbf{r}^{(2)})] &= \int d\mathbf{r}^{(1)} [\int d\mathbf{r}^{(2)} \int d\mathbf{r}' P(\mathbf{r} \rightarrow \mathbf{r}^{(2)}; \mathbf{r}^{(1)})] \\ &= \int d\mathbf{r}^{(1)} P(\mathbf{r}^{(1)}|\mathbf{r}) = 1. \end{aligned} \quad (41)$$

It thus follows from Eqs. [(30), (34)] and [(37), (39)] that the resultant phase exhibited by the amplitude of the signal *bridge*-propagation is given by the sum of the relative phases (*phase*-shifts) in each of its consecutive direct stages [see Eq. (29)].

Consider a single particle ($N = 1$) occupying the (bonding) MO $\phi_b(\mathbf{r}, \sigma) = \phi_b(\mathbf{r})\xi(\sigma)$. This illustrative example gives:

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \Gamma_{\mathbf{r}, \mathbf{r}'} = \phi_b(\mathbf{r}) \phi_b^*(\mathbf{r}'), \quad \rho(\mathbf{r}) = p(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}) = |\phi_b(\mathbf{r})|^2, \\ A(\mathbf{r}'|\mathbf{r}) &= \phi_b(\mathbf{r}) \phi_b^*(\mathbf{r}') / p(\mathbf{r})^{1/2}, \quad \pi(\mathbf{r}, \mathbf{r}') = \Omega(\mathbf{r}, \mathbf{r}') = p(\mathbf{r}) p(\mathbf{r}'), \quad P(\mathbf{r}'|\mathbf{r}) = p(\mathbf{r}'). \end{aligned} \quad (42)$$

In this simplest case the two locations are independent of each other, thus giving rise to the *factorized* joint probability of the two position arguments in $\pi(\mathbf{r}, \mathbf{r}')$. It should be emphasized that all these distributions are *single*-electron in character, with both locations referring to the admissible positions of an electron in the molecular bond system.

4 Entropic descriptors of local communications

Consider now the overall entropy/information descriptors [3,4,7,8,11–13] of a transmission of the electron-assignment “signals” in the local *information* channel of a molecule, originating from its bond system determined by the occupied SMO subspace φ . In this “device” the signal emitted from the continuous “inputs” $\mathbf{r} \in \mathfrak{R}$ of the channel “source” is propagated *via* the SMO into the continuous “outputs” $\mathbf{r}' \in \mathfrak{R}'$ of the channel “receiver”. The network of communications in the *classical* (probability) channel,

$$\{p(\mathbf{r}) \rightarrow \mathbf{r} \rightarrow P(\mathbf{r}'|\mathbf{r}) \rightarrow \mathbf{r}' \rightarrow p'(\mathbf{r}')\}, \quad (43)$$

is determined by the conditional probabilities $\{P(\mathbf{r}'|\mathbf{r})\}$, while the amplitudes $A(\mathbf{r}'|\mathbf{r})$ determine the associated *quantum* (amplitude) scattering system:

$$\{A(\mathbf{r}) \equiv [\rho(\mathbf{r})]^{1/2} \rightarrow |\mathbf{r}\rangle \rightarrow A(\mathbf{r}'|\mathbf{r}) \rightarrow |\mathbf{r}'\rangle \rightarrow \int d\mathbf{r} \gamma(\mathbf{r}, \mathbf{r}') \equiv A(\mathbf{r}')\}. \quad (44)$$

We again emphasize that the interference of this amplitude system gives rise to the resultant phases of the admissible cascade channels, which conserve the stationary molecular communications in the *multi*-stage scatterings involving intermediate particle locations.

In Eq. (44) the molecular amplitude $A(\mathbf{r}) \equiv [\rho(\mathbf{r})]^{1/2}$ shapes the *input*-signal of the quantum channel [see also Eq. (18)], which characterizes how this communication system is used in the ground-state of the molecule. The resultant *output*-amplitude $A(\mathbf{r}')$ has the following geometrical interpretation [see Eq. (16)]: this continuous “summation” (“contraction”) of $\gamma(\mathbf{r}, \mathbf{r}')$ over the input events $|\mathfrak{R}\rangle = \{|\mathbf{r}\rangle\}$ in the molecular (*one*-electron) Hilbert space,

$$A(\mathbf{r}') = \int d\mathbf{r} \gamma(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r} (\langle \mathbf{r} | \hat{P}_\varphi) (\hat{P}_\varphi | \mathbf{r}') \equiv \langle \mathfrak{R}^b | \mathbf{r}'^b \rangle, \quad (45)$$

represents the scalar product between the (N -dimensional) *bond*-subspace projection of the *infinitely*-dimensional (continuous) vector space spanned by the position basis-set vectors, $|\mathfrak{R}^b\rangle = \{|\mathbf{r}^b\rangle = \hat{P}_\varphi |\mathbf{r}\rangle = \sum_s |\phi_s\rangle \phi_s^*(\mathbf{r})\} \equiv \hat{P}_\varphi |\mathfrak{R}\rangle$, and the corresponding projection of the specified output state-vector, $|\mathbf{r}'^b\rangle = \hat{P}_\varphi |\mathbf{r}'\rangle$. In other words, this resultant output amplitude amounts to the N -dimensional projection of $|\mathbf{r}'^b\rangle$ onto $|\mathfrak{R}^b\rangle$.

Therefore, in determining the purely molecular descriptors of the local channels the input signal in the classical and quantum local channels is characterized by the *molecular* probability distribution $p(\mathbf{r})$ and the associated amplitude $A(\mathbf{r})$, respectively.

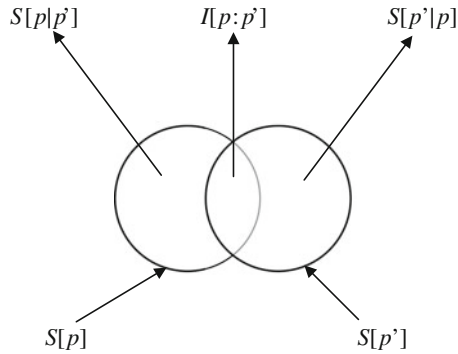


Fig. 3 Qualitative diagram of the *conditional-entropy* and *mutual-information* quantities for two spatial probability distributions $p(\mathbf{r})$ and $p'(\mathbf{r}')$ of Eq. 43. Two circles enclose areas representing the entropies $S[p]$ and $S[p']$ of the molecular input and output probability densities, respectively, while their common (overlap) area corresponds to the mutual information $I[p : p']$ in these two distributions. The remaining part of each circle represents the corresponding conditional entropy, $S[p|p']$ or $S[p'|p]$, measuring the residual uncertainty about events in one set of local events, when one has the full knowledge of the occurrence of events in the other set of local outcomes. The area enclosed by the envelope of two circles then represents the entropy of the “product” (joint) distribution: $S[\pi] = S[p] + S[p'] - I[p : p'] = S[p] + S[p'|p] = S[p'] + S[p|p']$

The transmission of signals in the communication channel is randomly disturbed thus exhibiting a communication *noise*. The classical signal propagation is described by the conditional-probability kernel $P(\mathbf{r}'|\mathbf{r})$ of the *local*-outputs given *local*-inputs, while the associated amplitude kernel $A(\mathbf{r}'|\mathbf{r})$ determines the amplitude propagation. The output signal $p'(\mathbf{r}')$ then conserves the input distribution [see Eq. (21)]:

$$p'(\mathbf{r}') = \int p(\mathbf{r})P(\mathbf{r}'|\mathbf{r})d\mathbf{r} = \int p(\mathbf{r})[\pi(\mathbf{r}, \mathbf{r}')/p(\mathbf{r})]d\mathbf{r} = \int \pi(\mathbf{r}, \mathbf{r}')d\mathbf{r} = p(\mathbf{r}'). \quad (46)$$

The Shannon entropy of the joint (“product”) distribution $\pi(\mathbf{r}, \mathbf{r}')$ can be expressed as the sum of the average entropy in the “marginal” (input) probability distribution $p(\mathbf{r})$,

$$S[p] = - \int p(\mathbf{r}) \log p(\mathbf{r}) d\mathbf{r} \quad (47)$$

and the average *conditional entropy* in the *local*-outputs given *local*-inputs (see Fig. 3),

$$S[p'|p] = - \int \int \pi(\mathbf{r}, \mathbf{r}') \log P(\mathbf{r}'|\mathbf{r}) d\mathbf{r} d\mathbf{r}' = - \int p(\mathbf{r}) [\int P(\mathbf{r}'|\mathbf{r}) \log P(\mathbf{r}'|\mathbf{r}) d\mathbf{r}'] d\mathbf{r}, \quad (48)$$

$$\begin{aligned} S[\pi] &= - \int \int \pi(\mathbf{r}, \mathbf{r}') \log \pi(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' = - \int \int p(\mathbf{r})P(\mathbf{r}'|\mathbf{r}) [\log p(\mathbf{r}) + \log P(\mathbf{r}'|\mathbf{r})] d\mathbf{r} d\mathbf{r}' \\ &= - \int p(\mathbf{r}) \log p(\mathbf{r}) d\mathbf{r} [\int P(\mathbf{r}'|\mathbf{r}) d\mathbf{r}'] - \int p(\mathbf{r}) [\int P(\mathbf{r}'|\mathbf{r}) \log P(\mathbf{r}'|\mathbf{r}) d\mathbf{r}'] d\mathbf{r} \\ &\equiv S[p] + S[p'|p], \end{aligned} \quad (49)$$

The conditional entropy $S[p'|p]$ represents the extra amount of the information about the occurrence of the output local events, given that the local input events are known to have already occurred. In other words: the amount of entropy/information $S[\pi]$ in the joint probability density of *simultaneously* observing the *input–output* localization

events $\{(\mathbf{r}, \mathbf{r}') \equiv (\mathbf{r} \wedge \mathbf{r}')\}$, the arguments of the two continuous molecular probability distributions p and p' , respectively, i.e., of the emitted and received signals in the molecular ground-state channel, equals to the amount of information $S[p]$ received by observing the *input* events $\{\mathbf{r}\}$, supplemented by the extra information $S[p'|p]$ provided by the occurrence of the output events $\{\mathbf{r}'\}$, when $\{\mathbf{r}\}$ are known to have occurred already.

The common amount of the information in two dependent local events \mathbf{r} and \mathbf{r}' , $I(\mathbf{r} : \mathbf{r}')$, measuring the information about \mathbf{r} provided by the occurrence of \mathbf{r}' , determines the *mutual information* in these two local events:

$$\begin{aligned} I(\mathbf{r} : \mathbf{r}') &= \log[\pi(\mathbf{r}, \mathbf{r}')/p(\mathbf{r})p'(\mathbf{r}')] = \log[P(\mathbf{r}|\mathbf{r}')/p(\mathbf{r})] \\ &\equiv \log[P(\mathbf{r}'|\mathbf{r})/p'(\mathbf{r}')] = I(\mathbf{r}' : \mathbf{r}). \end{aligned} \tag{50}$$

It vanishes, when both events are independent, $\pi(\mathbf{r}, \mathbf{r}') = \pi^{ind.}(\mathbf{r}, \mathbf{r}') \equiv p(\mathbf{r})p'(\mathbf{r}')$, 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

$$I(\mathbf{r} : \mathbf{r}') = I(\mathbf{r}) - I(\mathbf{r}|\mathbf{r}') = I(\mathbf{r}') - I(\mathbf{r}'|\mathbf{r}) = I(\mathbf{r}) + I(\mathbf{r}') - I(\mathbf{r}, \mathbf{r}'), \tag{51a}$$

where the *self*-information of the joint *two*-point event $I(\mathbf{r}, \mathbf{r}') = -\log\pi(\mathbf{r}, \mathbf{r}')$, $I(\mathbf{r}) = -\log p(\mathbf{r})$, $I(\mathbf{r}|\mathbf{r}') = -\log P(\mathbf{r}|\mathbf{r}')$, etc.

Thus, the information in the joint occurrence of two local input and output events \mathbf{r} and \mathbf{r}' , respectively, is the information in the occurrence of \mathbf{r} plus that in the occurrence of \mathbf{r}' minus the mutual information. Clearly, for independent events, when $\pi(\mathbf{r}, \mathbf{r}') = \pi^{ind.}(\mathbf{r}, \mathbf{r}')$ and hence $I(\mathbf{r} : \mathbf{r}') = 0$, $I^{ind.}(\mathbf{r}, \mathbf{r}') = I(\mathbf{r}) + I(\mathbf{r}')$.

The mutual information of the local event with itself defines its *self*-information:

$$I(\mathbf{r} : \mathbf{r}) \equiv I(\mathbf{r}) = \log[P(\mathbf{r}|\mathbf{r})/p(\mathbf{r})] = -\log p(\mathbf{r}), \tag{51b}$$

since $P(\mathbf{r}|\mathbf{r}) = 1$. It vanishes, when $p(\mathbf{r}) = 1$, i.e., when there is no uncertainty about the occurrence of \mathbf{r} , 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. (47) can be thus interpreted as the mean value of *self*-information densities in individual events, $\{I(\mathbf{r}) = -\log p(\mathbf{r})\}$, $S[p] = \int p(\mathbf{r})I(\mathbf{r})d\mathbf{r}$. One similarly defines the average *mutual information* in two probability distributions (see Fig. 3) as the mean value of the mutual information quantities for individual joint-localization events:

$$\begin{aligned} I[p : p'] &= \iint \pi(\mathbf{r}, \mathbf{r}')I(\mathbf{r} : \mathbf{r}')d\mathbf{r}d\mathbf{r}' = \iint \pi(\mathbf{r}, \mathbf{r}') \log[\pi(\mathbf{r}, \mathbf{r}')/\pi^{ind.}(\mathbf{r}, \mathbf{r}')]d\mathbf{r}d\mathbf{r}' \\ &= S[p] + S[p'] - S[\pi] = S[p] - S[p|p'] = S[p'] - S[p'|p] \geq 0, \end{aligned} \tag{52}$$

where the equality holds only for the independent input and output distributions. Indeed, the amount of uncertainty in p' can only decrease, when p has been known

beforehand, $S[p'] \geq S[p'|p] = S[p'] - I[p : p']$, with equality being observed only when the two sets of events are independent, thus giving *non*-overlapping entropy circles in Fig. 3.

The average mutual information is an example of the *entropy deficiency* (cross entropy, missing information, information distance, directed divergence) of Kullback and Leibler [5,6]. Indeed, for the continuous *joint*-probability scheme identified by the dependent events $\{(\mathbf{r}, \mathbf{r}')\}$ and their probabilities $\pi(\mathbf{r}, \mathbf{r}')$, this discrimination information in π with respect to the reference distribution of independent joint events $\pi^{ind.}(\mathbf{r}, \mathbf{r}')$ is defined by the functional of Eq. (52): $\Delta S[\pi|\pi^{ind.}] = I[p : p'] \geq 0$. This quantity provides a measure of the information-distance between the two distributions compared, and hence also the criterion of their information resemblance. The more the two joint distributions differ from one another, the larger the information distance. Notice that $\Delta S[\pi|\pi^{ind.}] = 0$ marks the vanishing surprisals in all joint events, i.e., when the two probability distributions are identical. The average mutual information thus reflects a degree of a dependence between events defining the dependent and independent probability densities. A similar information-distance interpretation can be attributed to the average conditional entropy of Eq. (48): $S[p'|p] = S[p'] - \Delta S[\pi|\pi^{ind.}]$.

The average conditional entropy descriptor of the local probability channel is thus given by the following functional of $\gamma(\mathbf{r}, \mathbf{r}')$ for the molecular ground-state configuration:

$$\begin{aligned} S[p'|p] &= -\iint P(\mathbf{r}, \mathbf{r}') \log P(\mathbf{r}'|\mathbf{r}) d\mathbf{r} d\mathbf{r}' = -\iint P_{\mathbf{r},\mathbf{r}'}[\gamma] \log P_{\mathbf{r} \rightarrow \mathbf{r}'}[\gamma] d\mathbf{r} d\mathbf{r}' \equiv S_{\mathfrak{N} \rightarrow \mathfrak{N}'}[\gamma] \\ &= -N^{-1} \iint \gamma(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{r}', \mathbf{r}) \{\log[\gamma(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{r}', \mathbf{r})] - \log \gamma(\mathbf{r}, \mathbf{r})\} d\mathbf{r}' d\mathbf{r} \\ &\equiv -N^{-1} \iint \Omega(\mathbf{r}, \mathbf{r}') \log \Omega(\mathbf{r}, \mathbf{r}') d\mathbf{r}' d\mathbf{r} + N^{-1} \iint \Omega(\mathbf{r}, \mathbf{r}') d\mathbf{r}' d\mathbf{r} \log \rho(\mathbf{r}) d\mathbf{r} \\ &= N^{-1} (S[\Omega] - S[\rho]). \end{aligned} \quad (53)$$

It thus reflects the difference between the Shannon-entropy

$$S[\Omega] = -\iint \Omega(\mathbf{r}, \mathbf{r}') \log \Omega(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (54)$$

of the *two*-point distribution $\Omega(\mathbf{r}, \mathbf{r}') = |\Gamma_{\mathbf{r},\mathbf{r}'}|^2$,

$$\Omega(\mathbf{r}, \mathbf{r}') = \Omega_{\mathbf{r},\mathbf{r}'}[\gamma] = \gamma(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{r}', \mathbf{r}) = NP(\mathbf{r}, \mathbf{r}'), \quad (55)$$

and the entropy of the electron density $\rho(\mathbf{r}) = Np(\mathbf{r})$,

$$S[\rho] = -\int \rho(\mathbf{r}) \log \rho(\mathbf{r}) d\mathbf{r} = -N \int p(\mathbf{r}) [\log N + \log p(\mathbf{r})] d\mathbf{r} = -N \log N + NS[p]. \quad (56)$$

The electron distribution of the system *promolecule* [11,34] is described by the the sum of the molecularly placed electron densities $\{\rho_X^0(\mathbf{r})\}$ of the free constituent atoms,

$$\rho^0(\mathbf{r}) = Np^0(\mathbf{r}) = \sum_X \rho_X^0(\mathbf{r}), \quad (57)$$

determining the diagonal part $\rho^0(\mathbf{r}) = \gamma^0(\mathbf{r}, \mathbf{r})$ of the promolecular density matrix

$$\gamma^0(\mathbf{r}, \mathbf{r}') = \sum_X \chi_X^0(\mathbf{r}, \mathbf{r}'). \quad (58)$$

The shape factor $p^0(\mathbf{r})$ provides the reference input signal for establishing the corresponding “difference” descriptor of the information-flow in the local channel, given by the mutual information:

$$\begin{aligned} I[p^0 : p] &= \int [f P(\mathbf{r}, \mathbf{r}')] \log [P(\mathbf{r}'|\mathbf{r})/p^0(\mathbf{r})] d\mathbf{r}' d\mathbf{r} \equiv I_{\mathfrak{R} \rightarrow \mathfrak{R}'}[\gamma, \gamma^0] \\ &= -S_{\mathfrak{R} \rightarrow \mathfrak{R}'}[\gamma] - N^{-1} \int [f \Omega(\mathbf{r}, \mathbf{r}') d\mathbf{r}'] \log p^0(\mathbf{r}) d\mathbf{r} \\ &\equiv -S_{\mathfrak{R} \rightarrow \mathfrak{R}'}[\gamma] + S[p] + \Delta S[p|p^0], \end{aligned} \quad (59)$$

where the entropy deficiency in the molecular (ground-state) probability p , relative to the promolecular distribution p^0 ,

$$\Delta S[p|p^0] = \int p(\mathbf{r}) \log [p(\mathbf{r})/p^0(\mathbf{r})] d\mathbf{r} \equiv \int p(\mathbf{r}) I(\mathbf{r}) d\mathbf{r}, \quad (60)$$

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

$$I[p : p'] = -S_{\mathfrak{R} \rightarrow \mathfrak{R}'}[\gamma] + S[p|\gamma] \equiv I_{\mathfrak{R} \rightarrow \mathfrak{R}'}[\gamma]. \quad (61)$$

The corresponding overall bond multiplicity indices [11–13], combining the relevant conditional entropy and mutual information descriptors, thus read:

$$\begin{aligned} M[p^0; p] &= S[p'|p] + I[p^0 : p] = S[p] + \Delta S[p|p^0], \\ M[p; p'] &= S[p'|p] + I[p : p'] = S[p]. \end{aligned} \quad (62)$$

Therefore, the purely molecular overall IT bond multiplicity, of the molecular probability channel probed by the molecular input signal, recovers the Shannon entropy of the ground-state probability of electrons. The difference index

$$\Delta M \equiv M[p^0; p] - M[p; p'] = \Delta S[p|p^0], \quad (63)$$

reflects the overall similarity between the molecular probability distribution p and the promolecular reference p^0 . It disappears in the *separated atoms limit* (SAL), where the two distributions become identical.

As an illustration, let us again consider the simplest case invoked at the end of Sect. 3, of a single electron ($N = 1$) occupying the lowest SMO, $\varphi(\mathbf{r}, \sigma) = \phi(\mathbf{r})\xi(\sigma)$. The relevant electron distributions [see Eq. (42)] then read:

$$\begin{aligned}\gamma(\mathbf{r}, \mathbf{r}') &= \Gamma_{\mathbf{r}, \mathbf{r}'} = \phi(\mathbf{r})\phi^*(\mathbf{r}'), \quad p(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}) = |\phi(\mathbf{r})|^2, \quad A(\mathbf{r}'|\mathbf{r}) = \phi(\mathbf{r})\phi^*(\mathbf{r}') / [p(\mathbf{r})]^{1/2}, \\ \pi(\mathbf{r}, \mathbf{r}') &= \Omega(\mathbf{r}, \mathbf{r}') = p(\mathbf{r})p(\mathbf{r}'), \quad P(\mathbf{r}'|\mathbf{r}) = p(\mathbf{r}').\end{aligned}\quad (64)$$

The two locations are independent of each other, thus giving rise to the *factorized* form of $\pi(\mathbf{r}, \mathbf{r}')$ and, hence, to the vanishing mutual information $I[p : p'] = 0$.

In what follows we examine the two model systems: the hydrogen-like atom $H(Z)$, $\phi(\mathbf{r}) = 1s(\mathbf{r}) = (Z^3/\pi)^{1/2}\exp(-Zr)$, and the model “half”-bond in H_2^+ , calculated for the equilibrium bond length in H_2 , $R_e[H_2] = 1.4$ a.u., when

$$\phi(\mathbf{r}) = \phi_b(\mathbf{r}) = N_b[1s_A(\mathbf{r}) + 1s_B(\mathbf{r})].\quad (65)$$

Here, the normalization constant for this internuclear distance $N_b = 0.534$.

In the simplest atomic system $H(Z)$ the relevant average noise (conditional entropy) can be calculated analytically. The relevant distributions of Eq. (64),

$$\begin{aligned}\gamma(\mathbf{r}, \mathbf{r}') &= (Z^3/\pi)\exp[-Z(\mathbf{r} + \mathbf{r}')], \quad p(\mathbf{r}) = (Z^3/\pi)\exp(-2Zr), \\ \pi(\mathbf{r}, \mathbf{r}') &= \Omega(\mathbf{r}, \mathbf{r}') = p(\mathbf{r})p(\mathbf{r}'), \quad P(\mathbf{r}'|\mathbf{r}) = p(\mathbf{r}'),\end{aligned}\quad (66)$$

give for the molecular input and output distributions, $p' = p$,

$$\begin{aligned}S[p' | p] &= -\int \int p(\mathbf{r})p(\mathbf{r}')\log p(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = [\int p(\mathbf{r})d\mathbf{r}][-\int p(\mathbf{r}')\log p(\mathbf{r}')d\mathbf{r}'] \\ &= S[p] = 3 - \ln(Z^3/\pi) \text{ [nats]}.\end{aligned}\quad (67)$$

For the hydrogen atom ($Z = 1$) it predicts

$$S[p] = 3 + \ln\pi = 6.1 \text{ nats} = 8.8 \text{ bits}.\quad (68)$$

The entropy of Eq. (67) correctly predicts a decreasing noise content in local communications with increasing nuclear charge of the hydrogen-like atom, which exactly vanishes for the critical value

$$Z^* = \exp[(3 + \ln\pi)/3] = 7.75 \text{ a.u.}\quad (69)$$

In examining $H_2^+[R_{AB} = 1.4 \text{ a.u.}]$ one uses the numerically estimated [11, 25] value of the Shannon entropy for $H_2[R_{AB} = 1.4 \text{ a.u.}]$, $S[\rho] = 6.6$ bits. This gives the associated entropy $S[p]$ of the probability (shape factor) [see Eq. (56)],

$$S[p] = 1/2\{S[\rho] + 2\log_2 2\} = 4.3 \text{ bits},\quad (70)$$

which also marks the conditional entropy in $H_2^+[R_{AB} = 1.4 \text{ a.u.}]$. Since the entropy of Eq. (68) also determines the noise level of the corresponding promolecule, one

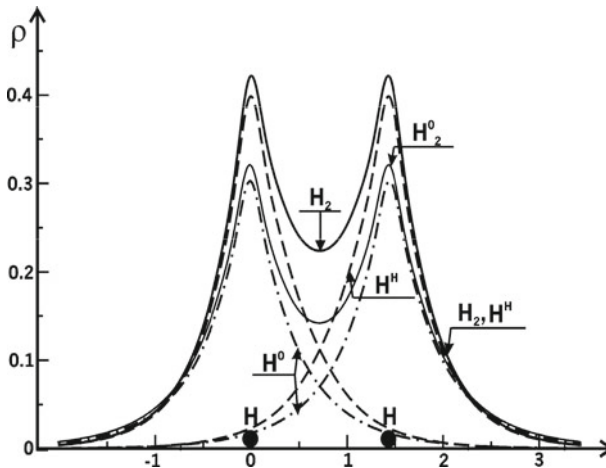


Fig. 4 The Hirshfeld electron densities of bonded hydrogen atoms (H^H) obtained from the molecular density (H_2). The free-hydrogen densities (H^0) and the resulting electron density of the promolecule (H_2^0) are also shown for comparison. The density and inter-nuclear distance are in a.u. The zero cusps at nuclear positions are the artifacts of the Gaussian basis set used in DFT calculations [11,25]

thus concludes that this prototype (covalent) *half*-bond marks a decisive lowering of the communication noise, by about 4.5 bits, compared to the free-hydrogen entropy in this artificially shortened bond of H_2^+ . It is expected to be much lower at the equilibrium distance $R_e[H_2^+] = 2.0$ a.u., since then the perturbing influence of the bond partner should be less felt by both AIM.

Indeed, the increased “order”, *localization* influence in the molecule is due to an effective contraction of the AIM distributions (see Fig. 4), relative to the *free*-atom density, due to the presence of the unshielded nucleus of the other atom. A similar effect has been observed in H_2 [11,25], where $S[\rho^0] = 7.4$ bits or $S[p^0] = 4.7$ bits, thus again predicting a slight lowering, by about 0.4 bits, of the average conditional entropy in the molecule $S[p] = 1/2\{S[\rho] + 2\log_2 2\} = 4.3$ bits, $S[p] = 4.3$ bits, relative to its promolecular reference $S[p^0] = 4.7$ bits, despite the opposite effect of the electron *delocalization* via the covalent chemical bond.

5 Conclusion

Information Theory provides an attractive perspective on the molecular equilibria, multiplicity, composition/localization of chemical bonds and their information origins. We have presented in this analysis some new developments in the *local* information systems within the *single*-configuration CTCB, derived using the (bond-projected) superposition principle of quantum mechanics. The probability amplitude of the joint, *two*-point events in the molecular bond system, defined by the configuration occupied SMO, is then given by the *one*-electron density matrix. These *joint*-probabilities define the associated *conditional*-probabilities, which determine the system classical communication links. The interference and phase relations in the sequential cas-

caedes of the molecular amplitudes have been examined. The conditional-entropy and mutual-information descriptors of such local networks, measuring the channel average communication “noise” and information flow, respectively, have been linked to the chemical covalency and ionicity characteristics.

This *local communication theory* (LCT) introduces the classical (probability) and quantum (amplitude) channels of the *direct* and *indirect* communications between infinitesimal volume elements in molecules, and links their entropic descriptors to generalized IT bond multiplicities and their covalent/ionic components. This development can be straightforwardly generalized into the *multi-determinantal* (CI) description using either the CI ensembles of the occupied SMO [80,81] or the *natural orbital* (NO) framework [44].

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