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ORIGINAL PAPER

Entropic bond-descriptors of molecular information systems in local resolution

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Abstract The communication theory of the chemical bond is extended to the local description of electron distributions in molecules. The key concepts of the molecular information channel in local resolution as well as its average-"noise" (conditional-entropy) and information-flow (mutual-information) descriptors are introduced. For a given electron density the information propagation in molecular communication system is compared for the Hartree system of non-interacting spin-less particles, the Kohn–Sham system of non-interacting fermions, and the real molecular system of interacting electrons, in order to separate the effects due to the exchange and Coulomb correlation. The stockholder partition of the molecular electron density into pieces attributed to atoms-in-molecules (AIM) is used to explore the effects due to the inter- and intra-atomic scattering of the electron probability in the local description. In this atomic resolution of a diatomic molecule several illustrative molecular information systems are investigated, which differ in the admissible level of the information scattering between infinitesimal local volume elements. First, the parallel arrangement of the AIM sub-channels, which allows only for the intra-atomic non-local probability scattering, is examined and the relevant grouping-rules are established for combining the atomic entropy/information data into the bond indices of the molecule as a whole. Next, the vertical Hirshfeld channel, admitting only the inter-atomic, local scattering of the electron probability, is used to probe the entropy non-additivity in both the molecular and promolecular systems. Finally, the truly non-local channel of independent

Throughout the paper P denotes a *scalar* quantity, $\boldsymbol{P}$ stands for the *row-vector*, and $\mathbf{P}$ represents the square/rectangular *matrix*.

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atoms in the Hartree limit is discussed, to extract differences in the entropy/information bond descriptors due to the inter-atomic probability scattering.

Keywords Atoms-in-molecules · Chemical-bond components · Electron correlation · Electronic structure theory · Entropy covalency · Information ionicity · Information theory · Molecular communication systems · Probability scattering in molecules · Stockholder atoms-in-molecules

1 Introduction

The concepts and methods of the Information theory (IT) [1–4] have recently been applied to diverse problems in the theory of electronic structure, e.g., [5,6]. The "stockholder" principle of Hirshfeld [7] for the local partition of the molecular electron density into pieces attributed to bonded atoms (Atoms-in-molecules, AIM) has been justified and extended [5,6,8–12] using the information principle of the minimum of the promolecule-referenced entropy-deficiency [3] subject to the local constraint of the exhaustive division. The entropy-displacement and information-distance densities have been explored in a search for novel diagnostic tools of the chemical bond formation and the electron localization in molecular systems [5,6,13–15] and the integral information-distance measures have been applied to quantify the Hammond postulate of the theory of chemical reactivity [16]. The local IT-thermodynamical description of the electron equilibria in molecules has also been proposed [17], in the spirit of the ordinary irreversible thermodynamics.

The AIM-resolved communication theory of the chemical bond has been developed for both the molecular system as a whole and its constituent fragments [5,18–26]. Its formulation in the orbital description has also been proposed [27–30]. It covers the excited-state configurations [29] and bond-indices for separate orbital-transformations involved in the resultant bond-formation processes [30]. This communication-system approach probes the bond covalency and ionicity through the probability (information) scattering in the molecular information channel reflecting the promotion of the constituent free-atoms to their respective valence-states due to the presence of the remaining AIM. The covalent component in this treatment measures the average "noise" in the communication channel, which lowers the information content of the final (output, molecular) probabilities, compared to that contained in the initial (input, promolecular) probabilities. The amount of information reaching the output of the molecular channel, which has survived the dissipation due to the system noise, then reflects the bond-ionicity present in the molecular system under consideration. These IT bond indices complement the bond-order measures, which have previously been designed within the Molecular Orbital (MO) theory, e.g., [31–39].

This probability scattering has been examined in the past at various levels of resolution of the molecular electron distributions, e.g., atomic [5,18–26] or orbital [27–30]. The entropy/information descriptors of the local Hirshfeld channel have also been examined [5,14,19,22]. The orbital approach requires the indirect information scattering, via the probability "chain-rule" involving the effective AO-promotion channel build as a sequence of the elementary channels representing both the intermediate [27,30] or resultant [28,29] orbital transformations and the MO-occupations in the electron configuration in question. In the excited electronic states the probability-conditioning between several electron configurations is required to account for a reduction of the IT bond-multiplicity due to excitations of electrons from the bonding to anti-bonding MO [29]. A similar IT perspective on the valence-state promotion of AIM due to the orbital hybridization has also been investigated [27].

In the Density-Fuctional Theory (DFT) [40–42] the ground-state distribution of electrons represents the basic, local state-"variable" of the molecular system. In this approach a given position of an electron constitutes a separate electron-localization "event", determined by the continuous electron coordinates in the physical space. The electron probability distribution is then defined by the shape-factor $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$ of the electron density $\rho(\boldsymbol{r})$ of the N-electron system. Therefore, in this local-resolution the summations over the discrete AIM or orbital events of the previous atomic and orbital developments have to be replaced by the corresponding integrations over the physical space. The scattering of the electron probabilities also assumes a more direct description: from one local volume element at $\boldsymbol{r}$ to that around another location $\boldsymbol{r}'$, with the probabilities of such an elementary two-point scattering events being measured by the familiar conditional probability $p(\boldsymbol{r}'|\boldsymbol{r}) = p_2(\boldsymbol{r}, \boldsymbol{r}')/p(\boldsymbol{r})$, where $p_2(\boldsymbol{r}, \boldsymbol{r}')$ denotes the joint probability of finding two electrons at the indicated positions. The AIM-resolution of $p(\boldsymbol{r})$ or $\rho(\boldsymbol{r})$ can be subsequently effected using the "stockholder" principle of Hirshfeld [7], which has also been shown to have a solid basis in IT [5,6,8–12].

It is the main purpose of the present work to qualitatively examine illustrative molecular information channels in local resolution and compare their entropy/information descriptors of the system "bond" covalency and ionicity, which reflect the average communication "noise" and the amount of the information flow, respectively. First, in the spirit of the Kohn–Sham DFT [41], the three systems will be compared for the given ground-state density of electrons, which define the Fermi (exchange) and Coulomb electron-correlation effects in molecular systems: the uncorrelated Hartree system, of independent (spinless) particles, the hypothetical KS system of non-interacting fermions, and the real system of interacting electrons. The leading terms of slight differences in their entropy-covalency and information-ionicity descriptors will be identified. They should provide novel IT-descriptors of these two types of electron correlation in molecular systems.

A subsequent stockholder partition of the molecular probability distribution into the associated AIM densities allows one to examine an extra noise and a diminished information flow due to this division. It enlarges the sets of "events" and spreads out the electron probability distributions, thus increasing the electron uncertainty compared to the global description of the molecular system as a whole. In the local description the probability-scattering analysis of the chemical bonds between the stockholder subsystems, which were previously shown to provide attractive concepts for a *chemical* description of molecular systems, allows one to separate the intra- and inter-atomic effects. Several diatomic information systems will be qualitatively examined. First, the parallel arrangement of atomic sub-channels, with only the intra-atomic non-local information scattering being allowed, will be investigated and the relevant grouping-rules will be derived for combining the AIM entropies into those for the molecule as a whole. The vertical Hirshfeld channel, in which the information scattering between stockholder AIM takes place only within each local volume element, will then be used to extract the entropy non-additivities of both bonded atoms in a molecule and the free-atoms in the promolecular reference system. Finally, the truly non-local channel of the independent atoms in the Hartree limit will be used to extract the molecular bonding patterns reflecting the non-local character of both the intra- and inter-atom probability scattering, within the local description of the system distribution of electrons.

We start this analysis with a short reminder of key probability concepts in the molecular electronic structure, including those of exchange (Fermi) and correlation (Coulomb) holes and the hypothetical and real systems, which allow their separation.

2 Probability distributions and correlation holes

Let $\rho_2(\boldsymbol{r}, \boldsymbol{r}')$ denotes the *two*-electron density,

$$\begin{aligned}\rho_2(\boldsymbol{r}, \boldsymbol{r}') &= N(N-1)\int \cdots \int \left|\Psi^*(\boldsymbol{r}, \sigma_1, \boldsymbol{r}', \sigma_2, 3, \ldots, N)\right|^2 d\sigma_1 d\sigma_2 d\boldsymbol{q}_3 \ldots d\boldsymbol{q}_N \\ &\equiv N(N-1) p_2(\boldsymbol{r}, \boldsymbol{r}'), \\ &\quad \textstyle\int\int \rho_2(\boldsymbol{r}, \boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' = N(N-1), \quad \int\int p_2(\boldsymbol{r}, \boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' = 1, \end{aligned} \tag{1}$$

and $p_2(\boldsymbol{r}, \boldsymbol{r}')$ its unity-normalized shape-factor. Here $\boldsymbol{q}_i = (\boldsymbol{r}_i, \sigma_i) \equiv i$ groups the position ($\boldsymbol{r}_i$) and spin (σ_i) coordinates of ith electron, and $\Psi^*(1, 2, \ldots, N)$ denotes the wave-function of an N-electron system in the position representation. The partial normalization of the joint-probability distribution $p_2(\boldsymbol{r}, \boldsymbol{r}')$ of two electrons gives rise to the corresponding one-electron probability density $p(\boldsymbol{r})$, the shape-factor of the electron density $\rho(\boldsymbol{r})$:

$$\textstyle\int p_2(\boldsymbol{r}, \boldsymbol{r}') d\boldsymbol{r}' = p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N, \quad \int p(\boldsymbol{r}) d\boldsymbol{r} = 1. \tag{2}$$

The two-particle densities of Eq. 1 can be expressed in terms of the associated conditional distributions for the fixed position of the reference electron at $\boldsymbol{r}$, any of N, of finding the dependent electron, any of the remaining $(N-1)$, at the monitored position $\boldsymbol{r}'$:

$$\begin{aligned}\rho_2(\boldsymbol{r}, \boldsymbol{r}') \equiv \rho(\boldsymbol{r})\rho(\boldsymbol{r}'|\boldsymbol{r}), \quad &\textstyle\int \rho(\boldsymbol{r}'|\boldsymbol{r}) d\boldsymbol{r}' = N-1, \quad \rho(\boldsymbol{r}'|\boldsymbol{r}) \equiv (N-1) p(\boldsymbol{r}'|\boldsymbol{r}), \\ &p_2(\boldsymbol{r}, \boldsymbol{r}') \equiv p(\boldsymbol{r}'|\boldsymbol{r}) p(\boldsymbol{r}), \quad \textstyle\int p(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1.\end{aligned} \tag{3}$$

We have stressed in the preceding equations that the conditional electron density integrates to $(N-1)$ dependent electrons, while its shape factor, representing the associated probability distribution, is unity normalized.

These conditional distributions of the dependent electron are customarily expressed as the sum of the corresponding independent (spinless) particle contribution of the familiar Hartree limit and the relevant exchange-correlation (xc) hole:

$$\begin{aligned}\rho(\boldsymbol{r}'|\boldsymbol{r}) &= \rho(\boldsymbol{r}') + h_{xc}(\boldsymbol{r}'|\boldsymbol{r}); \quad \textstyle\int h_{xc}(\boldsymbol{r}'|\boldsymbol{r}) d\boldsymbol{r}' = -1, \\ p(\boldsymbol{r}'|\boldsymbol{r}) &= p(\boldsymbol{r}') + f_{xc}(\boldsymbol{r}'|\boldsymbol{r}); \quad \textstyle\int f_{xc}(\boldsymbol{r}'|\boldsymbol{r}) d\boldsymbol{r}' = 0.\end{aligned} \tag{4}$$

As we have indicated in the preceding sum-rules the *density*-hole $h_{xc}(\boldsymbol{r}'|\boldsymbol{r})$ excludes altogether a single electron from around the reference electron (the Pauli principle), while the *probability*-hole $f_{xc}(\boldsymbol{r}'|\boldsymbol{r})$ integrates to zero over the positions of the dependent electrons (see Eqs. 2, 3). It also follows from Eqs. 1–5 that these correlation holes are related through the following relation:

$$h_{xc}(\boldsymbol{r}'|\boldsymbol{r}) = (N-1) f_{xc}(\boldsymbol{r}'|\boldsymbol{r}) - p(\boldsymbol{r}'). \tag{5}$$

Alternatively, the pair-distribution functions can be used to describe the electron correlation effects in a more symmetrical manner:

$$\begin{aligned} n(\boldsymbol{r}, \boldsymbol{r}') &\equiv \rho_2(\boldsymbol{r}, \boldsymbol{r}')/[\rho(\boldsymbol{r})\rho(\boldsymbol{r}')] = \rho(\boldsymbol{r}'|\boldsymbol{r})/\rho(\boldsymbol{r}') \\ &= \frac{N-1}{N} p_2(\boldsymbol{r}, \boldsymbol{r}')/[p(\boldsymbol{r})p(\boldsymbol{r}')] = \frac{N-1}{N} p(\boldsymbol{r}'|\boldsymbol{r})/p(\boldsymbol{r}') \equiv \frac{N-1}{N} g(\boldsymbol{r}, \boldsymbol{r}'), \end{aligned} \tag{6}$$

where $n(\boldsymbol{r}, \boldsymbol{r}')$ and $g(\boldsymbol{r}, \boldsymbol{r}')$ stand for the density- and probability(shape)-pair distributions, respectively. They are related to the corresponding holes of Eq. 4:

$$h_{xc}(\boldsymbol{r}'|\boldsymbol{r}) = \rho(\boldsymbol{r}')[n(\boldsymbol{r}, \boldsymbol{r}') - 1], \quad f_{xc}(\boldsymbol{r}'|\boldsymbol{r}) = p(\boldsymbol{r}')[g(\boldsymbol{r}, \boldsymbol{r}') - 1]. \tag{7}$$

In the Kohn–Sham (KS) formulation of DFT one examines the so called adiabatic, ground-state connection between the real (interacting) molecular system and the hypothetical KS system of non-interacting electrons moving in the appropriately defined, effective *one*-body potential, for the conserved density $\rho(\boldsymbol{r})$ of the interacting system. This is effected by an appropriate scaling the electron-repulsion energy with the coupling constant λ, i.e., of the electronic charge with $\lambda^{1/2}$, which gives rise to KS system for $\lambda = 0$, and the real system for $\lambda = 1$. The electrons (fermions) exhibit only the exchange (x), spin-dependent correlation in the KS limit, involving only the spin-like electrons,

$$h_{xc}^{\lambda=0}(\boldsymbol{r}'|\boldsymbol{r}) = h_x(\boldsymbol{r}'|\boldsymbol{r}) \equiv h_{xc}^{KS}(\boldsymbol{r}'|\boldsymbol{r}), \quad f_{xc}^{\lambda=0}(\boldsymbol{r}'|\boldsymbol{r}) = f_x(\boldsymbol{r}'|\boldsymbol{r}) \equiv f_{xc}^{KS}(\boldsymbol{r}'|\boldsymbol{r}), \tag{8}$$

while the full correlation effects, including those due to the Coulomb, charge-dependent contribution, is recovered in the real system:

$$h_{xc}^{\lambda=1}(\boldsymbol{r}'|\boldsymbol{r}) = h_{xc}(\boldsymbol{r}'|\boldsymbol{r}), \quad f_{xc}^{\lambda=1}(\boldsymbol{r}'|\boldsymbol{r}) = f_{xc}(\boldsymbol{r}'|\boldsymbol{r}). \tag{9}$$

This allows one to separate the correlation (c) holes:

$$h_c(\boldsymbol{r}'|\boldsymbol{r}) = h_{xc}(\boldsymbol{r}'|\boldsymbol{r}) - h_x(\boldsymbol{r}'|\boldsymbol{r}), \quad f_c(\boldsymbol{r}'|\boldsymbol{r}) = f_{xc}(\boldsymbol{r}'|\boldsymbol{r}) - f_x(\boldsymbol{r}'|\boldsymbol{r}). \tag{10}$$

Yet another reference system of the non-interacting *spinless* (distinguishable) particles of the same ground-state density $\rho(\boldsymbol{r})$ is important in defining the exchange

$$\textit{Input}: \mathbf{A} \qquad \mathbf{P}(\mathbf{B}|\mathbf{A}) = \{p(\boldsymbol{r}'|\boldsymbol{r})\} \qquad \textit{Output}: \mathbf{B}$$

$$p^0(\boldsymbol{r}) \longrightarrow \boldsymbol{r} —— p(\boldsymbol{r}'|\boldsymbol{r}) \longrightarrow \boldsymbol{r}' \longrightarrow \int p^0(\boldsymbol{r})\, p(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r} = p^*(\boldsymbol{r}')$$

Scheme 1 The molecular information (communication) system in local resolution

correlation. This Hartree reference is devoid of any electron correlation with

$$\begin{aligned}
&\rho_2^{\text{Hartree}}(\boldsymbol{r},\boldsymbol{r}') = \rho(\boldsymbol{r})\rho(\boldsymbol{r}'), \quad \rho^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}) = \rho(\boldsymbol{r}'), \quad h_{xc}^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}) = 0,\\
&\quad \int \rho_2^{\text{Hartree}}(\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' = N^2,\\
&p_2^{\text{Hartree}}(\boldsymbol{r},\boldsymbol{r}') = p(\boldsymbol{r})p(\boldsymbol{r}'), \quad p^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}) = p(\boldsymbol{r}'), \quad f_{xc}^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}) = 0,\\
&\quad \int p_2^{\text{Hartree}}(\boldsymbol{r},\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' = 1. \qquad (11)
\end{aligned}$$

This allows one to formally define the exchange holes as differences between conditional distributions in the KS and Hartree limits:

$$h_x(\boldsymbol{r}'|\boldsymbol{r}) = \rho^{\lambda=0}(\boldsymbol{r}'|\boldsymbol{r}) - \rho^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}), \; f_x(\boldsymbol{r}'|\boldsymbol{r}) = p^{\lambda=0}(\boldsymbol{r}'|\boldsymbol{r}) - p^{\text{Hartree}}(\boldsymbol{r}'|\boldsymbol{r}). \quad (12)$$

3 Information propagation in the local resolution of electron probabilities

The three levels of treating the electron correlation in molecules, which mark the Hartree, KS, and real systems of the preceding section, provide natural stages in examining the information propagation in local-resolution of the *two*-electron distributions (see Scheme 1). By convention the electron-localization "events" in the channel input (**A**) are identified by $\boldsymbol{r}$, while those in the channel output (**B**) are denoted by $\boldsymbol{r}'$. The conditional probability density $\mathbf{P}(\mathbf{B}|\mathbf{A}) \equiv \{p(\boldsymbol{r}'|\boldsymbol{r})\}$, for all input and output locations then determines the system (continuous) propagation "matrix", which determines the "communication" connections between electron positions in the input and output of the molecular information system. The initial probability distribution $p^0(\boldsymbol{r})$ shapes the channel input signal, while the promoted distribution combining the scattered contributions from all inputs,

$$p^*(\boldsymbol{r}') = \int p^0(\boldsymbol{r})p(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}, \qquad (13)$$

represents the system output signal. In the stationary, ground-state communication system the promoted probabilities represent the molecular probabilities: $p^*(\boldsymbol{r}) = p(\boldsymbol{r})$.

Let us first examine the information channels of the separate reference systems (Scheme 2), and their complementary entropy/information descriptors: the molecular conditional-entropy index, for the molecular input distribution $p^0(\boldsymbol{r}) = p(\boldsymbol{r})$, which measures the average "noise" in the molecular stationary channel giving rise to

$p^*(\boldsymbol{r}') = p(\boldsymbol{r}')$,

$$\begin{aligned} S(\mathbf{B}|\mathbf{A}) &\equiv S(p^*|p) = -\int\int p_2(\boldsymbol{r}, \boldsymbol{r}') \log p(\boldsymbol{r}'|\boldsymbol{r}) d\boldsymbol{r} d\boldsymbol{r}' = S(\mathbf{A}, \mathbf{B}) - S(\mathbf{A}) \\ &\equiv S(\mathbf{A}|\mathbf{B}) \equiv S(p|p^*) \\ &\equiv -\int\int p_2(\boldsymbol{r}', \boldsymbol{r}) \log p(\boldsymbol{r}|\boldsymbol{r}') d\boldsymbol{r} d\boldsymbol{r}' = S(\mathbf{A}, \mathbf{B}) - S(\mathbf{B}) \equiv S(\mathbf{B}|\mathbf{A}) \\ &= S[p_2] - S[p], \end{aligned} \tag{14}$$

and the mutual information reflecting the amount of information flowing through the channel:

$$\begin{aligned} I(\mathbf{A}^0 : \mathbf{B}) \equiv I(p^0 : p) &= \int\int p_2(\boldsymbol{r}', \boldsymbol{r}) \log[p(\boldsymbol{r}|\boldsymbol{r}')/p^0(\boldsymbol{r})]\, d\boldsymbol{r} d\boldsymbol{r}' \\ &= S(\mathbf{A}^0) - S(\mathbf{A}|\mathbf{B}) = S[p^0] + S[p] - S[p_2]. \end{aligned} \tag{15}$$

Here, the one- and two-electron Shannon entropies read:

$$\begin{aligned} S(\mathbf{A}^0) \equiv S[p^0] = -\int p^0(\boldsymbol{r}) \log p^0(\boldsymbol{r}) d\boldsymbol{r}, \quad S(\mathbf{A}) = S(\mathbf{B}) = S[p], \\ S(\mathbf{A}, \mathbf{B}) \equiv S[p_2] = -\int\int p_2(\boldsymbol{r}', \boldsymbol{r}) \log p_2(\boldsymbol{r}', \boldsymbol{r})\, d\boldsymbol{r} d\boldsymbol{r}'. \end{aligned} \tag{16}$$

It should be emphasized, that one applies the molecular input distribution $p(\boldsymbol{r})$ to generate the IT-covalency index, as a purely molecular phenomenon, and one uses the promolecular input signal $p^0(\boldsymbol{r})$, to estimate the system IT-ionicity, as a difference (displacement) phenomenon in the bond-formation process [5,18–26].

The promolecular entropy $S[p^0]$ marks the initial amount of information contained in the input probability density $p^0(\boldsymbol{r})$ of the free constituent atoms. Due to the probability scattering this information is partly dissipated as the communication noise, which reflects the system IT-covalent bond component $S(\mathbf{A}|\mathbf{B})$, and partly preserved as the IT-ionic component $I(\mathbf{A}^0 : \mathbf{B})$, thus conserving the overall information index with reference to $\mathbf{A}^0$:

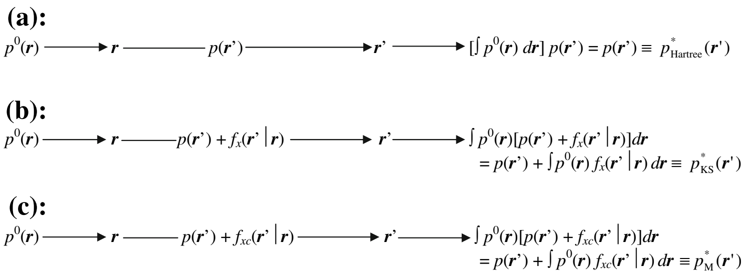
$$N(\mathbf{A}^0; \mathbf{B}) \equiv N(p^0; p) = S(\mathbf{A}|\mathbf{B}) + I(\mathbf{A}^0 : \mathbf{B}) = S(\mathbf{A}^0). \tag{17}$$

When the logarithm base 2 is applied the entropic quantities are measured in bits.

Consider first the Hartree communication system in local resolution, for the molecule as a whole (Scheme 2a), in which the output events are independent of the input events, due to the absence of any electron-correlation effects. The conditional and output probability distributions are thus given by the molecular shape-factor $p(\boldsymbol{r}')$, thus giving rise to the following entropy/information descriptors of Eqs. 14–17:

$$\begin{aligned} S^{\text{Hartree}}(p|p) = S[p], \quad I^{\text{Hartree}}(p^0 : p) = S[p^0] - S[p], \\ N^{\text{Hartree}}(p^0; p) = S[p^0]. \end{aligned} \tag{18}$$

Therefore, the IT-covalency index measuring the average-noise of the Hartree system, of independent spin-less particles distributed in accordance with the molecular electron probability $p(\boldsymbol{r}')$, is given by the Shannon entropy of this distribution. The IT-ionicity



Scheme 2 The locally-resolved information channels of the reference systems: Hartree (Panel a), Kohn–Sham (Panel b), and molecular (Panel c)

of this system, with respect to the reference electron probabilities $p^0(\boldsymbol{r})$ of the system atomic "promolecule", is seen to reflect the difference in the information content of the two compared probability distributions, while the overall index reflects the original information content measured by the Shannon entropy of the initial probability density.

As indicated in Scheme 2b, the Fermi hole introduces a mutual dependence between the elementary output and input events in the Kohn–Sham information channel in local resolution. It should be observed, that for the given molecular input, when $p^0(\boldsymbol{r}) = p(\boldsymbol{r})$, the deviation of the promoted probability density $p^*_{\mathrm{KS}}(\boldsymbol{r}')$ from the molecular shape factor $p(\boldsymbol{r}')$ vanishes exactly for each output location, $p(\boldsymbol{r}')+\int p(\boldsymbol{r}) f_x(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = p(\boldsymbol{r}')$, since such an input signal generates the same, stationary molecular distribution in the output of the ground-state channel. Therefore, at each point $\boldsymbol{r}'$ the deviation $\delta p^*_x(\boldsymbol{r}') \equiv p^*_{\mathrm{KS}}(\boldsymbol{r}') - p(\boldsymbol{r}')$ must identically vanish for any output location $\boldsymbol{r}'$ of an electron:

$$\delta p^*_x(\boldsymbol{r}') = \int p(\boldsymbol{r}) f_x(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = 0. \tag{19a}$$

This equation constitutes an additional integral constraint, the stationary sum-rule, for the Fermi probability-hole.

A similar conclusion follows from Scheme 2c corresponding to the real (interacting) molecular system M, in which the resultant probability-hole $f_{xc}(\boldsymbol{r}'|\boldsymbol{r})$ determines modifications of the promoted (output) probability density relative to the molecular shape factor determining the input distribution. Again, for the molecular input signal $p^0(\boldsymbol{r}) = p(\boldsymbol{r})$, which marks the stationary channel,

$$\delta p^*_{xc}(\boldsymbol{r}') = \int p(\boldsymbol{r}) f_{xc}(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = 0. \tag{19b}$$

The hole resolution of Eq. 10 then implies the associated stationary sum-rule for the Coulomb probability-hole:

$$\delta p^*_c(\boldsymbol{r}') = \int p(\boldsymbol{r}) f_c(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = 0. \tag{19c}$$

These sum-rules for the stationary probability distribution, of the vanishing *input*-integrated first-moments of the probability-holes in the system ground-state, constitute additional constraints on their shape, with respect to the *reference*-electron position. They complement the familiar sum-rules of Eq. 4, involving integration over the *dependent*-electron position.

Consider as an illustration the exact exchange in the Hartree–Fock theory, in which the density-hole expressed in terms of the singly-occupied spin-MO $\boldsymbol{\varphi}^{\sigma} = \{\varphi_{j\sigma}\}$ reads:

$$h_x(\boldsymbol{r}'|\boldsymbol{r}) = \frac{-1}{\rho(\boldsymbol{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} \Omega^{\sigma}_{j,k}(\boldsymbol{r})\Omega^{\sigma}_{k,j}(\boldsymbol{r}'), \quad \Omega^{\sigma}_{j,k}(\boldsymbol{r}) = \varphi^{*}_{j\sigma}(\boldsymbol{r})\varphi_{k\sigma}(\boldsymbol{r}). \tag{20}$$

It can be straightforwardly verified that it satisfies the correct output-normalization of Eq. 4:

$$\begin{aligned} \int h_x(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}' &= \frac{-1}{\rho(\boldsymbol{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} \Omega^{\sigma}_{j,k}(\boldsymbol{r}) \int \Omega^{\sigma}_{k,j}(\boldsymbol{r}')d\boldsymbol{r}' \\ &= \frac{-1}{\rho(\boldsymbol{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j}^{N_\sigma} \Omega^{\sigma}_{j,j}(\boldsymbol{r}) = -1, \end{aligned} \tag{21}$$

and generates the familiar expression for the exchange energy in terms of the exchange integrals:

$$\begin{aligned} E_x[\rho] &= 1/2 \int\int \rho(\boldsymbol{r})h_x(\boldsymbol{r}'|\boldsymbol{r})|\boldsymbol{r}'-\boldsymbol{r}|^{-1}d\boldsymbol{r}\, d\boldsymbol{r}' \\ &= -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} \int\int \Omega^{\sigma}_{j,k}(\boldsymbol{r})\Omega^{\sigma}_{k,j}(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}' = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} K^{\sigma}_{j,k}. \end{aligned} \tag{22}$$

The associated probability-hole, from Eq. 5, reads:

$$f_x(\boldsymbol{r}'|\boldsymbol{r}) = [h_x(\boldsymbol{r}'|\boldsymbol{r}) + p(\boldsymbol{r}')]/(N-1), \quad \int f_x(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}' = 0. \tag{23}$$

When substituted into Eq. 19a it gives:

$$\begin{aligned} (N-1)\int p(\boldsymbol{r})f_x(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} &= (N-1)\left\{-\frac{1}{N} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k}^{N_\sigma} \int \Omega^{\sigma}_{j,k}(\boldsymbol{r})d\boldsymbol{r}\Omega^{\sigma}_{k,j}(\boldsymbol{r}') + p(\boldsymbol{r}')\right\} \\ &= (N-1)\left\{\frac{-\rho(\boldsymbol{r}')}{N} + p(\boldsymbol{r}')\right\} = 0, \end{aligned} \tag{24}$$

thus indeed satisfying the stationary sum-rule for the KS system, which involves the integration over the input-event locations of an electron in the molecular information system.

Next, let us examine the entropy/information descriptors of the correlated information systems of Scheme 2b and c. In the stationary KS system the conditional probabilities

$$p^{KS}(\boldsymbol{r}'|\boldsymbol{r}) = p(\boldsymbol{r}') + f_x(\boldsymbol{r}'|\boldsymbol{r}) \equiv g_x(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}'), \quad \int p^{KS}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1,$$
$$g_x(\boldsymbol{r},\boldsymbol{r}') = 1 + f_x(\boldsymbol{r}'|\boldsymbol{r})/p(\boldsymbol{r}') \equiv 1 + y_x(\boldsymbol{r},\boldsymbol{r}'), \quad |y_x(\boldsymbol{r},\boldsymbol{r}')| << 1, \tag{25}$$

define the joint *input–output* probabilities

$$p_2^{KS}(\boldsymbol{r},\boldsymbol{r}') = p(\boldsymbol{r})p^{KS}(\boldsymbol{r}'|\boldsymbol{r}), \quad \int p_2^{KS}(\boldsymbol{r},\boldsymbol{r}')d\boldsymbol{r}' = p(\boldsymbol{r}). \tag{26}$$

They give rise to the (stationary) conditional-entropy index (see Eq. 25):

$$\begin{aligned} S^{KS}(p^*_{KS}|p) = S^{KS}(p|p) &= -\int\int p_2^{KS}(\boldsymbol{r},\boldsymbol{r}')\log p^{KS}(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}\, d\boldsymbol{r}' \\ &= -\int\int p_2^{KS}(\boldsymbol{r},\boldsymbol{r}')\log[g_x(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')] \\ &= S[p] - \int\int p(\boldsymbol{r})y_x(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' \\ &\quad -\frac{1}{2}\int\int p(\boldsymbol{r})y_x^2(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' + O(y_x^3) \\ &\cong S[p] - \frac{1}{2}\int\int p(\boldsymbol{r})y_x^2(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}'. \end{aligned} \tag{27a}$$

In this short derivation we have used the quadratic Taylor expansion of $\log(1+y_x) = y_x(1-1/2y_x)$ and observed that the linear term in y_x vanishes by the stationary sum-rule (19a). Therefore, to the quadratic term in y_x (Eq. 25) $S^{KS}(p^*_{KS}|p) \approx S[p] = S^{Hartree}(p|p)$ (see Eq. 18).

Consider now the mutual-information quantity of the communication system 2b. Using Eq. 15 gives

$$\begin{aligned} I^{KS}(p^0 : p) &= \int\int p^0(\boldsymbol{r})p^{KS}(\boldsymbol{r}'|\boldsymbol{r})\log[p^{KS}(\boldsymbol{r}|\boldsymbol{r}')/p^0(\boldsymbol{r})]\, d\boldsymbol{r}\, d\boldsymbol{r}' = S[p^0] - S^{KS}(p|p) \\ &\cong S[p^0] - S[p] + \frac{1}{2}\int\int p(\boldsymbol{r})y_x^2(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' \approx S[p^0] - S[p] \\ &= I^{Hartree}(p^0 : p). \end{aligned} \tag{27b}$$

Again, to the quadratic term in y_x, the mutual information index of the local KS information system equals that in the Hartree limit (Eq. 18). One also observes that the entropy/information indices of Eq. 27a and b conserve the overall IT index of the KS system at the promolecular information level:

$$N^{KS}(p^0; p) = S^{KS}(p|p) + I^{KS}(p^0 : p) = S[p^0] = N^{Hartree}(p^0; p). \tag{27c}$$

The corresponding entropic quantities for the local communication system of the real (interacting) molecular system M (Scheme 2c) are obtained by replacing in Eqs. 27a–c the exchange conditional probabilities and Fermi holes with the full (resultant) exchange-correlation quantities:

$$p(\boldsymbol{r}'|\boldsymbol{r}) = p(\boldsymbol{r}') + f_{xc}(\boldsymbol{r}'|\boldsymbol{r}) \equiv g_{xc}(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}'), \qquad \int p(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}' = 1,$$
$$g_{xc}(\boldsymbol{r},\boldsymbol{r}') = 1 + f_{xc}(\boldsymbol{r}'|\boldsymbol{r})/p(\boldsymbol{r}') \equiv 1 + y_{xc}(\boldsymbol{r},\boldsymbol{r}'), \quad |y_{xc}(\boldsymbol{r},\boldsymbol{r}')| << 1. \tag{28}$$

Therefore, to the second-order of the Taylor expansion of the entropy/information quantities in powers of y_{xc}:

$$\begin{aligned}
S^M(p|p) &= \int\int p(\boldsymbol{r})p(\boldsymbol{r}'|\boldsymbol{r})\log[p(\boldsymbol{r}|\boldsymbol{r}')]\,d\boldsymbol{r}\,d\boldsymbol{r}' \cong S[p] \\
&\quad -\frac{1}{2}\int\int p(\boldsymbol{r})y_{xc}^2(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')\,d\boldsymbol{r}\,d\boldsymbol{r}' \\
&\approx S[p] = S^{\text{Hartree}}(p|p), \\
I^M(p^0:p) &= S[p^0] - S(p|p) \cong S[p^0] - S[p] + \frac{1}{2}\int\int p(\boldsymbol{r})y_{xc}^2(\boldsymbol{r},\boldsymbol{r}')p(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}' \\
&\approx S[p^0] - S[p] = I^{\text{Hartree}}(p^0:p), \qquad (29) \\
N^M(p^0;p) &= S(p|p) + I(p^0:p) = S[p^0] = N^{\text{Hartree}}(p^0;p).
\end{aligned}$$

To summarize, for the given molecular probability density $p(\boldsymbol{r})$ the overall IT bond indices of the Hartree, Kohn–Sham and the real molecular systems with respect to the free-atom reference distribution $p^0(\boldsymbol{r})$ conserve the initial information content measured by the Shannon entropy of the promolecular probability density. In the correlated systems the leading terms describing a deviation from the Hartree values of the entropy/information descriptors are quadratic in the relative hole $y_\alpha(\boldsymbol{r},\boldsymbol{r}') = f_\alpha(\boldsymbol{r}'|\boldsymbol{r})/p(\boldsymbol{r}')$, $\alpha = x, xc$. They represent an extra noise in the correlated communication system, which effectively diminishes the amount of its information flow.

4 Probability densities in the stockholder partition of molecular electron densities into AIM distributions

As another illustrative example let us consider the Hirshfeld (H) [7] partition of the electron density

$$\begin{aligned}
\rho(\boldsymbol{r}) &= N\int\cdots\int\left|\Psi^*(r,\sigma_1,2,3,\ldots,N)\right|^2 d\sigma_1 d\boldsymbol{q}_2\ldots d\boldsymbol{q}_N \equiv Np(\boldsymbol{r}), \\
&\int\rho(\boldsymbol{r})d\boldsymbol{r} = N, \quad \int p(\boldsymbol{r})\,d\boldsymbol{r} = 1, \qquad (30)
\end{aligned}$$

of a molecular system M into densities $\boldsymbol{\rho}^H(\boldsymbol{r}) = \{\rho_Z^H(\boldsymbol{r})\}$ of its constituent bonded-atoms $\{Z^H = A^H, B^H, \ldots\}$: $\rho(\boldsymbol{r}) = \sum_Z \rho_Z^H(\boldsymbol{r})$. This exhaustive division is defined by the following "stockholder" principle:

$$\begin{aligned}
\rho_X^H(\boldsymbol{r}) &= \rho_X^0(\boldsymbol{r})[\rho(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho_X^0(\boldsymbol{r})w(\boldsymbol{r}) \\
&= \rho(\boldsymbol{r})[\rho_X^0(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho(\boldsymbol{r})d_X^H(\boldsymbol{r}), \quad \sum_X d_X^H(\boldsymbol{r}) = 1. \qquad (31)
\end{aligned}$$

The row vector $\boldsymbol{\rho}^0(\boldsymbol{r}) = \{\rho_Z^0(\boldsymbol{r})\}$ groups the densities of the free-atoms, giving rise to the reference electron density $\rho^0(\boldsymbol{r}) = \sum_Z \rho_Z^0(\boldsymbol{r})$ of the (iso-electronic) promolecule M^0 consisting of the non-bonded atoms $\{Z^0 = A^0, B^0, \ldots\}$ shifted to their actual positions in M:

$$N^0 = \int \rho^0(\boldsymbol{r})\, d\boldsymbol{r} = \sum\nolimits_Z \int \rho_Z^0(\boldsymbol{r})\, d\boldsymbol{r} = \sum\nolimits_Z N_Z^0 = N$$
$$= \sum\nolimits_Z \int \rho_Z^H(\boldsymbol{r})\, d\boldsymbol{r} = \sum\nolimits_Z N_Z^H. \quad (32)$$

The effective electron populations $\boldsymbol{N}^H = \{N_Z^H\}$ and $\boldsymbol{N}^0 = \{N_Z^0\}$ group the numbers of electrons of the bonded and free atoms, respectively.

A reference to Eq. 31 shows that these AIM densities satisfy the local principle of the "stockholder" rule, which can be stated as the following equality between the local molecular and promolecular conditional probabilities of bonded and free atoms, respectively, which by analogy with the stockmarket reflect the atomic shares in the molecular "profit" $\rho(\boldsymbol{r})$ or promolecular "investment" $\rho^0(\boldsymbol{r})$:

$$d_Z^H(\boldsymbol{r}) = \rho_Z^H(\boldsymbol{r})/\rho(\boldsymbol{r}) \equiv d^H(Z|\boldsymbol{r}) = d_Z^0(\boldsymbol{r}) = \rho_Z^0(\boldsymbol{r})/\rho^0(\boldsymbol{r}) \equiv d^0(Z|\boldsymbol{r}),$$
$$\sum\nolimits_Z d^H(Z|\boldsymbol{r}) = \sum\nolimits_Z d^0(Z|\boldsymbol{r}) = 1. \quad (33)$$

Alternatively, these stockholder atomic densities can be viewed as the locally modified densities of free atoms, which are obtained using the universal (unbiased) enhancement factor $w(\boldsymbol{r}) = \rho(\boldsymbol{r})/\rho^0(\boldsymbol{r})$.

One could extract the overall number of electrons N from both the molecular and subsystem densities, in order to establish the associated AIM partition $p(\boldsymbol{r}) = \sum_Z \pi_Z^H(\boldsymbol{r})$ of the molecular shape-factor $p(\boldsymbol{r})$ (Eq. 30) into the corresponding pieces attributed to the stockholder atoms,

$$\boldsymbol{\pi}^H(\boldsymbol{r}) = \{\pi_Z^H(\boldsymbol{r}) = \rho_Z^H(\boldsymbol{r})/N \equiv \pi^H(Z, \boldsymbol{r})\},$$
$$\rho(\boldsymbol{r}) = Np(\boldsymbol{r}) = N \sum\nolimits_Z [\rho_Z^H(\boldsymbol{r})/N] \equiv N[\sum\nolimits_Z \pi_Z^H(\boldsymbol{r})], \quad (34)$$
$$\sum\nolimits_Z \int \pi_Z^H(\boldsymbol{r}) d\boldsymbol{r} = \sum\nolimits_Z (N_Z^H/N) \equiv \sum\nolimits_Z P_Z^H = 1,$$

where $p(\boldsymbol{r})$ and $\boldsymbol{\pi}^H(\boldsymbol{r})$ stand for the *molecularly*-normalized shape-factors of the system as a whole and of its Hirshfeld AIM, respectively, while the vector $\boldsymbol{P}^H = \{P_Z^H\}$ groups the condensed probabilities of finding an electron of M on the specified AIM.

The normalization of Eq. 34 reflects the important fact that bonded atoms are constituent parts of the molecule, so that the full normalization condition has to involve the summation/integration over the complete set of one-electron events, consisting of all possible "values" of the discrete argument Z (atomic label) and all spatial locations of an electron, identified by continuous coordinates $\boldsymbol{r}$ in the subsystem probability distributions $\boldsymbol{\pi}^H(\boldsymbol{r}) = \{\pi^H(Z, \boldsymbol{r})\}$.

The same type of normalization has to be adopted for the free-atom pieces of the promolecular probability distribution and those of its free-atom components, respectively:

$$p^0(\boldsymbol{r}) = \rho^0(\boldsymbol{r})/N^0 = \sum\nolimits_Z \pi_Z^0(\boldsymbol{r}),$$
$$\boldsymbol{\pi}^0(\boldsymbol{r}) = \boldsymbol{\rho}^0(\boldsymbol{r})/N = \{\pi_Z^0(\boldsymbol{r}) = \rho_Z^0(\boldsymbol{r})/N^0 \equiv \pi^0(Z, \boldsymbol{r})\}, \quad (35)$$
$$\sum\nolimits_Z \int \pi_Z^0(\boldsymbol{r}) d\boldsymbol{r} = \sum\nolimits_Z (N_Z^0/N) \equiv \sum\nolimits_Z P_Z^0 = 1;$$

here $\boldsymbol{P}^0 = \{P_Z^0\}$ collects the condensed probabilities of observing an electron of M^0 on the specified free atom. The full normalization of the shape (probability) factors $\boldsymbol{\pi}^0(\boldsymbol{r}) = \{\pi^0(Z, \boldsymbol{r})\}$ of the non-bonded atoms in the promolecular reference-system again involves the summation over the discrete atomic "variable" Z and the integration over all positions $\boldsymbol{r}$ of an electron, the latter representing the continuous arguments identifying the localization "event" of the electron distribution measurement of an atomic fragments in M^0.

In fact, the unity(atom)-normalized densities of the separate fragments,

$$\begin{aligned} \boldsymbol{p}^H(\boldsymbol{r}) &= \{p_Z^H(\boldsymbol{r}) \equiv \pi^H(Z, \boldsymbol{r})/P_Z^H \equiv p^H(\boldsymbol{r}|Z)\}, \\ \boldsymbol{p}^0(\boldsymbol{r}) &= \{p_Z^0(\boldsymbol{r}) \equiv \pi^0(Z, \boldsymbol{r})/P_Z^0 \equiv p^0(\boldsymbol{r}|Z)\}, \\ \int p^H(\boldsymbol{r}|Z)d\boldsymbol{r} &= \int p^0(\boldsymbol{r}|Z)d\boldsymbol{r} = 1, \end{aligned} \tag{36}$$

represent the complementary set of conditional probabilities of finding an electron at $\boldsymbol{r}$ in the separate Z^H or Z^0, in which the atomic label is not a variable but the parameter. Indeed, the normalization of such conditional distributions involves the integration over the position variable only. It should be stressed, that the probabilities $\boldsymbol{\pi}^H(\boldsymbol{r})$ [or $\boldsymbol{\pi}^0(\boldsymbol{r})$] describe the atomic fragments of a larger molecular/promolecular system, while $\boldsymbol{p}^H(\boldsymbol{r})$ [or $\boldsymbol{p}^0(\boldsymbol{r})$] represent a single (separated) atomic system.

The share factors $\boldsymbol{d}^H(\boldsymbol{r}) = \{d^H(Z|\boldsymbol{r})\} = \boldsymbol{d}^0(\boldsymbol{r})$ (see Eq. 33) represent yet another set of the conditional probabilities for the atomic stockholder subsystems in the molecule, with the reversed roles of parameters and variables, compared to $\boldsymbol{p}^H(\boldsymbol{r}) = \{p^H(\boldsymbol{r}|Z)\}$. Indeed, in $d^H(Z|\boldsymbol{r})$ or $d^0(Z|\boldsymbol{r})$ the atomic label Z represents the discrete "variable", while the electron position $\boldsymbol{r}$ denotes the continuous "parameter".

As we have already remarked above, in the stockholder division each free subsystem density (or its shape factor) is locally modified in accordance with the molecular (atom-independent) density-enhancement factor $w(\boldsymbol{r})$:

$$w_Z^H(\boldsymbol{r}) \equiv \rho_Z^H(\boldsymbol{r})/\rho_Z^0(\boldsymbol{r}) = \rho(\boldsymbol{r})/\rho^0(\boldsymbol{r}) = \pi_Z^H(\boldsymbol{r})/\pi_Z^0(\boldsymbol{r}) = p(\boldsymbol{r})/p^0(\boldsymbol{r}) \equiv w(\boldsymbol{r}). \tag{37}$$

Therefore, this division is devoid of any atomic bias and as such appears to be fully objective. Indeed, this partition result from the minimum principle of the entropy-deficiency (missing-information) [3] in the AIM distributions relative to their free-atom analogs, subject to the constraint of the exhaustive division [5,6,8–11]. It also naturally follows from the related local information principle formulated in terms of the information-distance density [5,6]. These information principles have recently been extended to cover the stockholder division of many-electron densities [5,12].

The bonded atoms of the molecule can be involved in both the intra- and inter-atomic probability scattering, between local volume elements attributed to the same or different AIM, respectively. An example of the intra-atomic information channel is provided by the parallel arrangement of the elementary sub-channels describing the separate AIM, while the so called *vertical* Hirshfeld channel [5,14,19,22] admits only the local inter-atomic probability scattering, in the spirit of the stockholder division principle. Finally, the Hartree-channel of independent atoms combines both types of the information dissipation. In the following sections we shall examine how these

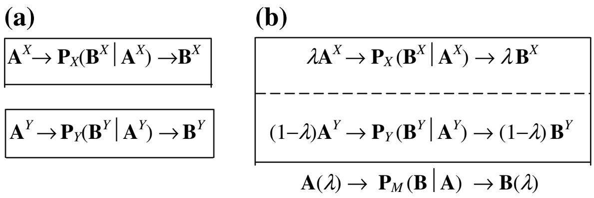


Fig. 1 The local communication systems of the separate stockholder AIM (Panel a), defined by the intra-atom conditional probabilities $\mathbf{P}_Z(\mathbf{B}^Z|\mathbf{A}^Z) \equiv P_Z(\boldsymbol{r}'|\boldsymbol{r})$, $Z = X, Y$, and their parallel arrangement (Panel b) into the combined information system of a diatomic molecule $M = X\text{–}Y$, characterized by the molecular conditional probabilities $\mathbf{P}_M(\mathbf{B}|\mathbf{A}) = \mathbf{P}_M(\boldsymbol{r}'|\boldsymbol{r}) = \{P(\boldsymbol{r}'; Z'|\boldsymbol{r}; Z) = P_Z(\boldsymbol{r}'|\boldsymbol{r})\delta_{Z,Z'}\}$. The inputs(outputs) of each separate AIM and the molecule cover the whole physical space: $\mathbf{A}^X = \mathbf{A}^Y = \mathbf{A} = \{\boldsymbol{r}\}$ and $\mathbf{B}^X = \mathbf{B}^Y = \mathbf{B} = \{\boldsymbol{r}'\}$. It should be observed that the normalized input probabilities $\{\boldsymbol{P}(\mathbf{A}^Z) = p_Z(\boldsymbol{r})\}$ of the separate sub-channels represent the conditional (*intra*-group) probabilities in the combined system: $\{p_Z(\boldsymbol{r}) = \rho_Z(\boldsymbol{r})/N_Z \equiv p(\boldsymbol{r}|Z)\}$, $N_Z = \int \rho_Z(\boldsymbol{r})\, d\boldsymbol{r}$, which exhibit the relevant normalizations: $\int p_Z(\boldsymbol{r})\, d\boldsymbol{r} = \int p(\boldsymbol{r}|Z) d\boldsymbol{r} = 1$, $Z = X, Y$. The corresponding output probabilities of the separate atoms $\{\boldsymbol{P}(\mathbf{B}^Z) = q_Z(\boldsymbol{r}')\}$ are also conditional in character: $\{q_{Z'}(\boldsymbol{r}') \equiv q(\boldsymbol{r}'|Z')\}$, $\int q_{Z'}(\boldsymbol{r}')\, d\boldsymbol{r}' = \int q(\boldsymbol{r}'|Z')\, d\boldsymbol{r}' = 1$, $Z' = X, Y$. They are related to the AIM input probabilities by the integral transformation: $q_Z(\boldsymbol{r}') = \int p_Z(\boldsymbol{r})\ \mathbf{P}_Z(\boldsymbol{r}'|\boldsymbol{r})\ d\boldsymbol{r}$. In the molecular (combined) communication system the molecular values of these probabilities are obtained by multiplying the separate-atom (conditional) probability distribution by the atom condensed probability, $\pi^H(Z, \boldsymbol{r}) = P_Z^H p_Z(\boldsymbol{r})$, where $\boldsymbol{P}^H = \{P_Z^H = N_Z^H/N\} \equiv (\lambda = N_X^H/N,\ 1-\lambda = N_Y^H/N)$, or by multiplying the molecular probability $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$ by the atom share-factor in the system as a whole: $d_Z^H(\boldsymbol{r}) \equiv d(Z|\boldsymbol{r}) = \rho_Z^H(\boldsymbol{r})/\rho(\boldsymbol{r}) = p_Z^H(\boldsymbol{r})/p(\boldsymbol{r})$. Thus, in the stockholder partitioning $\boldsymbol{P}(\mathbf{A}(\lambda)) = \boldsymbol{P}(\boldsymbol{r}';\ M) = \{\pi^H(Z,\ \boldsymbol{r})\}$ and $\boldsymbol{P}(\mathbf{B}(\lambda)) = \boldsymbol{Q}(\boldsymbol{r}';\ M) = \{\pi^H(Z',\ \boldsymbol{r}')\}$. These probabilities are related by the molecular conditional probabilities $\mathbf{P}_M(\boldsymbol{r}'|\boldsymbol{r})$: $\boldsymbol{P}_M(\mathbf{B}(\lambda)) = [\lambda\boldsymbol{P}(\mathbf{B}^X), (1-\lambda)\boldsymbol{P}(\mathbf{B}^Y)] \equiv \boldsymbol{P}_M(\mathbf{A}(\lambda))\mathbf{P}_M(\mathbf{B}|\mathbf{A}) = [\lambda\boldsymbol{P}(\mathbf{A}^X), (1-\lambda)\boldsymbol{P}(\mathbf{A}^Y)] \begin{bmatrix} \mathbf{P}_X(\mathbf{B}^X|\mathbf{A}^X) & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_Y(\mathbf{B}^Y|\mathbf{A}^Y) \end{bmatrix} = \boldsymbol{Q}(\boldsymbol{r}'; M) = \int \boldsymbol{P}(\boldsymbol{r}; M)\mathbf{P}_M(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = [\int \pi_X^H(\boldsymbol{r}) P_X(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}, \int \pi_Y^H(\boldsymbol{r}) P_Y(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}]$

different types of the electron probability scattering affect the system entropy/information descriptors. To simplify this qualitative discussion the diatomic molecule $M = X - Y$ and the related atomic promolecule $M^0 = (X^0|Y^0)$ have been examined. We shall also address the grouping problem of combining the separate-atom indices into those characterizing the whole information system of the parallely-arranged atomic sub-channels (see also [30]).

5 Parallely-arranged information systems of separate AIM in diatomics

Let us examine the molecular communication system resulting from the parallel arrangement of Fig. 1, of the two sub-channels of the separate atoms in the diatomic molecule M. The separate (disconnected) sub-channels of atoms X and Y are generated by their internal conditional probabilities $\mathbf{P}_X(\mathbf{B}^X|\mathbf{A}^X) = \mathbf{P}_X(\boldsymbol{r}'|\boldsymbol{r})$ and $\mathbf{P}_Y(\mathbf{B}^Y|\mathbf{A}^Y) = \mathbf{P}_Y(\boldsymbol{r}'|\boldsymbol{r})$, respectively. In the molecular system they are combined in a parallel manner into a single channel of Panel b, defined by the molecular conditional probabilities $\mathbf{P}_M(\mathbf{B}|\mathbf{A}) = \mathbf{P}_M(\boldsymbol{r}'|\boldsymbol{r}) = \{P(\boldsymbol{r}'; Z'|\boldsymbol{r}; Z) = P_Z(\boldsymbol{r}'|\boldsymbol{r})\delta_{Z,Z'}\}$, which admit only the intra-atomic probability scattering.

In the "stockholder" partitioning of $\rho(\boldsymbol{r}) = \sum_Z \rho_Z^H(\boldsymbol{r}) = N \sum_Z p_Z^H(\boldsymbol{r})$ of the molecular electron density $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$ into the AIM pieces $\{\rho_Z^H(\boldsymbol{r}) = \rho(\boldsymbol{r})[\rho_Z^0(\boldsymbol{r})/\rho^0(\boldsymbol{r})] \equiv \rho(\boldsymbol{r})d_Z^H(\boldsymbol{r}) = N\pi_Z^H(\boldsymbol{r})\}$, the local probability weight of atom Z in M as a whole is determined by the atomic share-factor $d_Z^H(\boldsymbol{r}) = \rho_Z^H(\boldsymbol{r})/\rho(\boldsymbol{r}) = \pi_Z^H(\boldsymbol{r})/p(\boldsymbol{r})$; here the probability distribution of atom Z in M, $\pi_Z^H(\boldsymbol{r}) = \rho_Z^H(\boldsymbol{r})/N$, represents the joint probability $\pi_Z^H(\boldsymbol{r}) = \pi^H(Z, \boldsymbol{r})$, which satisfies the molecular normalization

$$\sum_Z \int \pi^H(Z, \boldsymbol{r}) d\boldsymbol{r} = \sum_Z N_Z^H/N = \sum_Z P_Z^H = 1. \tag{38}$$

Above, the (condensed) probabilities of the two AIM in M, $\boldsymbol{P}^H = \{P_Z^H = N_Z^H/N\} \equiv (\lambda = N_X^H/N,\ 1-\lambda = N_Y^H/N)$. The promolecular share-factor $d_Z^0(\boldsymbol{r}) = d_Z^H(\boldsymbol{r})$ is similarly given by the ratio of the free-atom density $\rho_Z^0(\boldsymbol{r})$ shifted to the atomic position in a molecule, to the overall density $\rho^0(\boldsymbol{r}) = \sum_Z \rho_Z^0(\boldsymbol{r}) = N^0 p^0(\boldsymbol{r})$ of the atomic promolecule $M^0 = (X^0|Y^0)$, defined by the sum of non-bonded (mutually-closed) atomic contributions: $d_Z^0(\boldsymbol{r}) = \rho_Z^0(\boldsymbol{r})/\rho^0(\boldsymbol{r}) = \pi_Z^0(\boldsymbol{r})/p^0(\boldsymbol{r})$. The atomic probability in the promolecule, $\pi_Z^0(\boldsymbol{r}) = \rho_Z^0(\boldsymbol{r})/N^0$, again represents the joint probability $\pi_Z^0(\boldsymbol{r}) = \pi^0(Z, \boldsymbol{r})$, which satisfies the promolecular normalization

$$\sum_Z \int \pi^0(Z, \boldsymbol{r}) d\boldsymbol{r} = \sum_Z N_Z^0/N = \sum_Z P_Z^0 = 1. \tag{39}$$

Therefore, the atomic share-factor represents both the molecular and the promolecular conditional probabilities, of attributing the local density at $\boldsymbol{r}$ to atom Z, $d_Z^H(\boldsymbol{r}) \equiv d^H(Z|\boldsymbol{r}) \equiv d^0(Z|\boldsymbol{r})$, satisfying the proper normalization: $\sum_Z d^H(Z|\boldsymbol{r}) = \sum_Z d^0(Z|\boldsymbol{r}) = 1$. It should be stressed, that in this internal scattering of electron probabilities the continuous sets of the electron-localization events of each (open) stockholder atom and that of the system as a whole are identical, covering the whole physical space: $\mathbf{A}^X = \mathbf{A}^Y = \mathbf{A} = \{\boldsymbol{r}\}$ and $\mathbf{B}^X = \mathbf{B}^Y = \mathbf{B} = \{\boldsymbol{r}'\}$.

The local, unity-normalized molecular or promolecular probabilities of an electron in each *separate* atom,

$$\{\boldsymbol{P}(\mathbf{A}^Z) = \rho_Z^H(\boldsymbol{r})/N_Z^H = p_Z^H(\boldsymbol{r})\} \quad \text{or} \quad \{\boldsymbol{P}^0(\mathbf{A}^Z) = \rho_Z^0(\boldsymbol{r})/N_Z^0 = p_Z^0(\boldsymbol{r})\}, \tag{40}$$

also represent the conditional (*intra*-group) probabilities in the combined system,

$$\begin{aligned}
&\{p_Z^H(\boldsymbol{r}) = [\rho_Z^H(\boldsymbol{r})/N]/(N_Z^H/N) \equiv \pi^H(Z, \boldsymbol{r})/P_Z^H = p^H(\boldsymbol{r}|Z)\},\\
&\{p_Z^0(\boldsymbol{r}) = [\rho_Z^0(\boldsymbol{r})/N^0]/(N_Z^0/N^0) \equiv \pi^0(Z, \boldsymbol{r})/P_Z^0 = p^0(\boldsymbol{r}|Z)\},
\end{aligned} \tag{41}$$

as indeed reflected by their normalizations: $\int p^H(\boldsymbol{r}|Z)d\boldsymbol{r} = \int p^0(\boldsymbol{r}|Z)d\boldsymbol{r} = 1$. Above, the (condensed) probabilities of AIM in M, $\boldsymbol{P}^H = \{P_Z^H = N_Z^H/N\} \equiv (\lambda, 1-\lambda)$, or of free-atoms in M^0, $\boldsymbol{P}^0 = \{P_Z^0 = N_Z^0/N^0\}$, and the joint probabilities of an electron attributed to atom Z to be located at $\boldsymbol{r}$:

$$\pi^H(Z, \boldsymbol{r}) = P_Z^H p^H(\boldsymbol{r}|Z) \quad \text{and} \quad \pi^0(Z, \boldsymbol{r}) = P_Z^0 p^0(\boldsymbol{r}|Z). \tag{42}$$

These joint probabilities can also be expressed in terms of the alternative set of atomic conditional probabilities represented by the atomic shares in the local molecular or promolecular densities $\{d^H(Z|\boldsymbol{r}) \equiv d^0(Z|\boldsymbol{r})\}$:

$$\pi^H(Z,\boldsymbol{r}) = p(\boldsymbol{r})d^H(Z|\boldsymbol{r}) \quad \text{and} \quad \pi^0(Z,\boldsymbol{r}) = p^0(\boldsymbol{r})d^0(Z|\boldsymbol{r}). \tag{43}$$

To summarize, in the parallely-combined molecular communication system the joint-probability distribution $\pi^H(Z,\boldsymbol{r})$ is thus obtained by either multiplying the (conditional) probability function $p^H(\boldsymbol{r}|Z)$ of the separate atom by the condensed AIM probability P_Z^H, or by multiplying the molecular probability function $p(\boldsymbol{r})$ by the local share-factor $d_Z^H(\boldsymbol{r}) \equiv d^H(Z|\boldsymbol{r})$ of the Hirshfeld AIM in the system as a whole. Therefore, in the stockholder partitioning the input probability vector of the combined system reads:

$$\begin{aligned} &\boldsymbol{P}(\mathbf{A}) \equiv \boldsymbol{P}(\boldsymbol{r}, M) = \{\pi^H(Z,\boldsymbol{r}) = p(\boldsymbol{r})d^H(Z|\boldsymbol{r}) = P_Z^H p^H(\boldsymbol{r}|Z)\},\\ &\sum\nolimits_Z d^H(Z|\boldsymbol{r}) = \int d\boldsymbol{r} p^H(\boldsymbol{r}|Z) = 1. \end{aligned} \tag{44}$$

This is also symbolically depicted in Fig. 1b.

Therefore, the normalized input and output probabilities of the parallel molecular channel read:

$$\begin{aligned} \boldsymbol{P}(\mathbf{A}(\lambda)) &= [\lambda \boldsymbol{P}(\mathbf{A}^X), (1-\lambda)\boldsymbol{P}(\mathbf{A}^Y)] = [\pi_X^H(\boldsymbol{r}), \pi_Y^H(\boldsymbol{r})],\\ \boldsymbol{P}(\mathbf{B}(\lambda)) &= [\lambda \boldsymbol{P}(\mathbf{A}^X)\mathbf{P}_X(\mathbf{B}^X|\mathbf{A}^X), (1-\lambda)\boldsymbol{P}(\mathbf{A}^Y)\mathbf{P}_Y(\mathbf{B}^Y|\mathbf{A}^Y)]\\ &= [\lambda \boldsymbol{P}(\mathbf{B}^X), (1-\lambda)\boldsymbol{P}(\mathbf{B}^Y)]. \end{aligned} \tag{45}$$

Hence, the conditional probabilities $\mathbf{P}_M(\mathbf{B}|\mathbf{A})$ transforming the input probabilities into the output probabilities in the combined, molecular channel,

$$\begin{aligned} \boldsymbol{P}(\mathbf{A}(\lambda))\mathbf{P}_M(\mathbf{B}|\mathbf{A}) &= \boldsymbol{P}(\mathbf{B}(\lambda))\\ &\equiv [\lambda \boldsymbol{P}(\mathbf{A}^X), (1-\lambda)\boldsymbol{P}(\mathbf{A}^Y)] \begin{bmatrix} \mathbf{P}_X(\mathbf{B}^X \left| \mathbf{A}^X \right.) & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_Y(\mathbf{B}^Y \left| \mathbf{A}^Y \right.) \end{bmatrix} = \boldsymbol{Q}(\boldsymbol{r}'; M)\\ &= \int \boldsymbol{P}(\boldsymbol{r}; M)\mathbf{P}_M(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = [\int \pi_X^H(\boldsymbol{r})P_X(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}, \int \pi_Y^H(\boldsymbol{r})P_Y(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r}], \end{aligned} \tag{46}$$

assume the block-diagonal form:

$$\mathbf{P}_M(\mathbf{B}\,|\mathbf{A}) = \begin{bmatrix} \mathbf{P}_X(\mathbf{B}^X \left| \mathbf{A}^X \right.) & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_Y(\mathbf{B}^Y \left| \mathbf{A}^Y \right.) \end{bmatrix} \equiv \begin{bmatrix} P_X(\boldsymbol{r}'\,|\boldsymbol{r}) & \mathbf{0} \\ \mathbf{0} & P_Y(\boldsymbol{r}'\,|\boldsymbol{r}) \end{bmatrix}. \tag{47}$$

6 Combination rules for entropic descriptors of the parallel stockholder AIM

Let us now examine the grouping of the entropy/information descriptors of separate atoms into those for the molecular communication system as a whole. We shall illustrate these combination rules for the diatomic case of the preceding section.

It follows from Eq. 43 that the AIM probability distributions $\boldsymbol{\pi}^H(\boldsymbol{r}) = \{\pi^H(Z, \boldsymbol{r}) \equiv \pi_Z^H(\boldsymbol{r})\}$ and $\boldsymbol{\pi}^0(\boldsymbol{r}) = \{\pi^0(Z, \boldsymbol{r}) \equiv \pi_Z^0(\boldsymbol{r})\}$ add up to the molecular and promolecular shape-factors:

$$\sum_Z \pi^H(Z, \boldsymbol{r}) = p(\boldsymbol{r}) \sum_Z d^H(Z|\boldsymbol{r}) = p(\boldsymbol{r}),$$
$$\sum_Z \pi^0(Z, \boldsymbol{r}) = p^0(\boldsymbol{r}) \sum_Z d^0(Z|\boldsymbol{r}) = p^0(\boldsymbol{r}), \tag{48}$$

where we have used the normalization of share factors as conditional probabilities [see Eq. (44)]. Therefore the Shannon entropy contained in the molecular probability density can be expressed in terms of the AIM distributions $\boldsymbol{\pi}^H(\boldsymbol{r})$ and their local shares $\boldsymbol{d}^H(\boldsymbol{r}) = \{d^H(Z|\boldsymbol{r}) \equiv d_Z^H(\boldsymbol{r})\}$:

$$\begin{aligned} S[p] &= -\int p(\boldsymbol{r}) \log p(\boldsymbol{r})\, d\boldsymbol{r} \equiv S^{total}[\boldsymbol{\pi}^H] \\ &= -\sum_Z \int \pi^H(Z, \boldsymbol{r}) \log[\pi^H(Z, \boldsymbol{r})/d^H(Z|\boldsymbol{r})]\, d\boldsymbol{r} \\ &= -\sum_Z \int \pi^H(Z, \boldsymbol{r}) \log \pi^H(Z, \boldsymbol{r}) d\boldsymbol{r} - \int p(\boldsymbol{r})[-\sum_Z d^H(Z|\boldsymbol{r}) \log d^H(Z|\boldsymbol{r})] d\boldsymbol{r} \\ &= \sum_Z S[\pi_Z^H] - \int p(\boldsymbol{r}) s[\boldsymbol{d}^H(\boldsymbol{r})]\, d\boldsymbol{r} \equiv S^{add}[\boldsymbol{\pi}^H] + S^{nadd}[\boldsymbol{\pi}^H]. \end{aligned} \tag{49}$$

The first, additive term in the stockholder AIM resolution, $S^{add}[\boldsymbol{\pi}^H] = \sum_Z S[\pi_Z^H]$, carries the sum of entropies of atomic distributions in the molecule, while the second, non-additive term, $S^{nadd}[\boldsymbol{\pi}^H] = S^{total}[\boldsymbol{\pi}^H] - S^{add}[\boldsymbol{\pi}^H] = -\int p(\boldsymbol{r}) s[\boldsymbol{d}^H(\boldsymbol{r})] d\boldsymbol{r}$, represents the negative (molecularly-weighted) mean-value of the conditional-entropy density generated by the AIM share-factors.

The additive term in Eq. 49 can be further expressed using Eq. 42 in terms of the condensed AIM probabilities $\boldsymbol{P}^H = (\lambda, 1 - \lambda)$ and the probability distributions $\boldsymbol{p}^H(\boldsymbol{r}) = \{p_Z^H(\boldsymbol{r})\}$ of the separate AIM. Let us first examine the entropies of electron probabilities in the separate non-bonded or bonded atoms, the building units of the promolecular and molecular systems, respectively. The Shannon average entropies of the separate free-atoms $\{Z^0\}$ characterized by the probability distributions of Eq. 41 are given by the integrals

$$S[p_Z^0] = -\int p^0(\boldsymbol{r}|Z) \log p^0(\boldsymbol{r}|Z) d\boldsymbol{r}, \quad Z = X^0, Y^0, \tag{50}$$

while the entropies of the separate AIM read:

$$S[p_Z^H] = -\int p^H(\boldsymbol{r}|Z) \log p^H(\boldsymbol{r}|Z) d\boldsymbol{r}, \quad Z = X^H, Y^H. \tag{51}$$

The additive entropy $S^{add}[\boldsymbol{\pi}^H]$ of the molecular input probabilities of AIM, $\boldsymbol{P}(\mathbf{A}(\lambda)) = [\lambda \boldsymbol{P}(\mathbf{A}^X), (1 - \lambda)\boldsymbol{P}(\mathbf{A}^Y)]$ can now be expressed using the following grouping rule:

$$\begin{aligned} S^{add}[\boldsymbol{\pi}^H] &= S(\mathbf{A}(\lambda)) = -\sum_{Z=X,Y} \int \pi^H(Z,\boldsymbol{r}) \log \pi^H(Z,\boldsymbol{r}) d\boldsymbol{r} \\ &= -\sum_{Z=X,Y} \int P_Z^H p^H(\boldsymbol{r}|Z) \log[P_Z^H p^H(\boldsymbol{r}|Z)] d\boldsymbol{r} \\ &= -\sum_{Z=X,Y} P_Z^H \log P_Z^H - \sum_{Z=X,Y} P_Z^H \int p^H(\boldsymbol{r}|Z) \log p^H(\boldsymbol{r}|Z) d\boldsymbol{r} \\ &\equiv H(\lambda) + \{\lambda S[p_X^H] + (1-\lambda) S[p_Y^H]\}, \\ H(\lambda) &= -\lambda \log \lambda - (1-\lambda)\log(1-\lambda). \end{aligned} \tag{52}$$

The condensed AIM entropy term $S(\boldsymbol{P}^H)$, which gives rise to the binary entropy $H(\lambda)$, represents the group-uncertainty, while the rest measures the mean value of the intra-atomic (conditional) uncertainties for each stockholder subsystem, weighted using the AIM condensed probabilities $\boldsymbol{P}^H$. These contributions describe the "experiment" of removing the molecular uncertainty, or equivalently of acquiring the information about the diatomic system. The first term identifies the atom the electron-location outcome is in, which removes the $S(\boldsymbol{P}^H)$ part of the overall uncertainty. The second term is similarly associated with the uncertainties $\{S[p_Z^H]\}$ of local outcomes within each atom, which have to weighted in accordance to with their corresponding condensed probabilities $\boldsymbol{P}^H$ in the molecule.

The non-additive entropy in Eq. 49,

$$\begin{aligned} S^{nadd}[\boldsymbol{\pi}^H] &= \sum\nolimits_Z \int p(\boldsymbol{r}) d^H(Z|\boldsymbol{r}) \log d^H(Z|\boldsymbol{r})\, d\boldsymbol{r} \\ &= \sum\nolimits_Z \int \pi^H(Z,\boldsymbol{r}) \log d^H(Z|\boldsymbol{r})\, d\boldsymbol{r}, \end{aligned} \tag{53}$$

can be alternatively expressed as the $\boldsymbol{P}^H$-weighed average of the AIM entropy-deficiencies (missing informations) of Kullback and Leibler [3]. We first express in the preceding expression the molecular distributions $\boldsymbol{\pi}^H(\boldsymbol{r})$ of AIM in terms of the separate AIM distributions $\boldsymbol{p}^H(\boldsymbol{r})$ (Eq. 42):

$$S^{nadd}[\boldsymbol{\pi}^H] = \sum\nolimits_Z P_Z^H \int p^H(Z,\boldsymbol{r}) \log d^H(Z|\boldsymbol{r})\, d\boldsymbol{r}. \tag{54}$$

Using Eq. 49 one then expresses the share-factor $d^H(Z|\boldsymbol{r})$ in terms of P_Z^H and $p^H(Z,\boldsymbol{r})$:

$$\begin{aligned} S^{nadd}[\boldsymbol{\pi}^H] &= \sum\nolimits_Z P_Z^H \int p^H(Z,\boldsymbol{r}) \log[P_Z^H p^H(Z,\boldsymbol{r})/p(\boldsymbol{r})] d\boldsymbol{r} \\ &= \sum\nolimits_Z P_Z^H \log P_Z^H + \sum\nolimits_Z P_Z^H \int p^H(Z,\boldsymbol{r}) \log[p^H(Z,\boldsymbol{r})/p(\boldsymbol{r})] d\boldsymbol{r} \\ &\equiv H(\lambda) + \sum\nolimits_Z P_Z^H \Delta S[p_Z^H|p], \end{aligned} \tag{55}$$

where $\Delta S[p_Z^H|p]$ measures the cross-entropy (entropy deficiency, missing information) [3] in the separated AIM distribution $p^H(Z, \boldsymbol{r})$ in reference to the molecular distribution $p(\boldsymbol{r})$. This final expression shows, that the non-additive entropy in AIM resolution is given by the sum of entropies generated by the atomic condensed probabilities and the $\boldsymbol{P}^H$-weighed average value of the entropy deficiencies of bonded atoms relative to the molecular probability distribution.

One could also derive a similar AIM-resolved expression for the molecular entropy deficiency relative to the promolecular probability density:

$$\begin{aligned}\Delta S[p|p^0] &= \int p(\boldsymbol{r}) \log[p(\boldsymbol{r})/p^0(\boldsymbol{r})]d\boldsymbol{r} \equiv \Delta S^{total}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0] \\ &= \sum_{Z=X,Y} \int \pi^H(Z,\boldsymbol{r}) \log \frac{\pi^H(Z,\boldsymbol{r})}{\pi^0(Z,\boldsymbol{r})} d\boldsymbol{r} \\ &= \sum\nolimits_Z \Delta S[\pi_Z^H|\pi_Z^0] \equiv \Delta S^{add}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0]. \end{aligned} \tag{56}$$

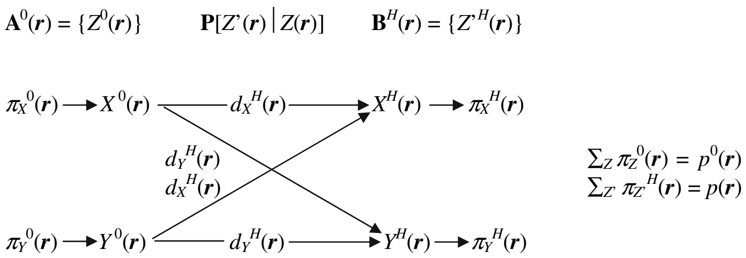
It follows from the above equality $\Delta S^{total}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0] = \Delta S^{add}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0]$ that the non-additive entropy deficiency of the stockholder AIM exactly vanishes [5,8,14]:

$$\Delta S^{nadd}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0] = \Delta S^{total}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0] - \Delta S^{add}[\boldsymbol{\pi}^H|\boldsymbol{\pi}^0] = 0. \tag{57}$$

Finally, let us summarize the combination formulas for the conditional entropy (IT-covalency) and mutual-information (IT-ionicity) descriptors of the molecular communication system of Fig. 1b, in terms of the entropy/information bond-indices for the communication systems of the separate AIM fragments of Fig. 1a [5,30]:

$$\begin{aligned} S(\mathbf{B}^Z|\mathbf{A}^Z) &= -\int\int p^H(\boldsymbol{r}|Z) P_Z(\boldsymbol{r}'|\boldsymbol{r}) \log P_Z(\boldsymbol{r}'|\boldsymbol{r})\, d\boldsymbol{r}\, d\boldsymbol{r}', \\ I(\mathbf{A}^{0,Z} : \mathbf{B}^Z) &= \int\int p^0(\boldsymbol{r}|Z) P_Z(\boldsymbol{r}'|\boldsymbol{r}) \log[P_Z(\boldsymbol{r}'|\boldsymbol{r})/p^0(\boldsymbol{r}|Z)]\, d\boldsymbol{r}\, d\boldsymbol{r}' \\ &= S[p_Z^0] - S(\mathbf{B}^Z|\mathbf{A}^Z), \\ N(\mathbf{A}^{0,Z}; \mathbf{B}^Z) &= S(\mathbf{B}^Z|\mathbf{A}^Z) + I(\mathbf{A}^{0,Z} : \mathbf{B}^Z) = S[p_Z^0], \quad Z = X, Y. \end{aligned} \tag{58}$$

The molecular conditional-entropy, mutual-information and overall bond indices of the molecular information channel of Fig. 1b, consisting of the molecular output probabilities $\boldsymbol{P}(\mathbf{B}(\lambda)) = [\lambda\boldsymbol{P}(\mathbf{B}^X), (1-\lambda)\boldsymbol{P}(\mathbf{B}^Y)]$ and the molecular, $\boldsymbol{P}(\mathbf{A}(\lambda)) = [\lambda\boldsymbol{P}(\mathbf{A}^X), (1-\lambda)\boldsymbol{P}(\mathbf{A}^Y)]$, or promolecular, $\boldsymbol{P}(\mathbf{A}^0(\lambda)) = [\lambda\boldsymbol{P}(\mathbf{A}^{0,X}), (1-\lambda)\boldsymbol{P}(\mathbf{A}^{0,Y})]$, input probabilities, are given by the following combinations of the corresponding



Scheme 3 The vertical Hirshfeld channel for a diatomic molecule X–Y

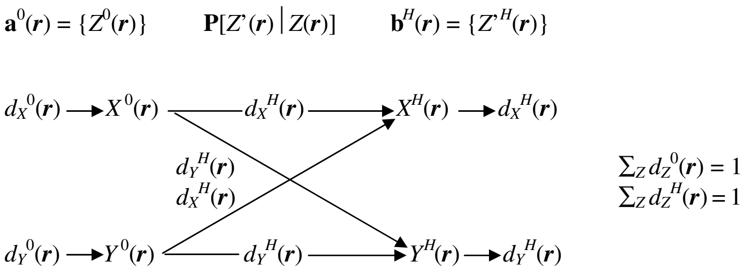
separate-AIM quantities defined in the preceding equation:

$$
\begin{aligned}
S(\mathbf{B}(\lambda)|\mathbf{A}(\lambda)) &= \sum_{Z=X,Y} P_Z^H S(\mathbf{B}^Z \,|\, \mathbf{A}^Z),\\
I(\mathbf{A}(\lambda):\mathbf{B}(\lambda)) &= H(\lambda) + \sum_{Z=X,Y} P_Z^H I(\mathbf{A}^{0,Z}:\mathbf{B}^Z),\\
N(\mathbf{A}^0(\lambda);\mathbf{B}(\lambda)) &= S(\mathbf{B}(\lambda)|\mathbf{A}(\lambda)) + I(\mathbf{A}^0(\lambda):\mathbf{B}(\lambda))\\
&= H(\lambda) + \sum_{Z=X,Y} P_Z^H [S(\mathbf{B}^Z \,|\, \mathbf{A}^Z) + I(\mathbf{A}^{0,Z}:\mathbf{B}^Z)]\\
&= H(\lambda) + \sum_{Z=X,Y} P_Z^H N(\mathbf{A}^{0,Z};\mathbf{B}^Z)\\
&= H(\lambda) + \sum_{Z=X,Y} P_Z^H S[p_Z^0]. \qquad (59)
\end{aligned}
$$

7 Vertical Hirshfeld channel

The main purpose of this section is to summarize the fully-local treatment of the entropy/information descriptors of the bonded stockholder AIM, relative to the free-atom, promolecular reference, using the so called *vertical* Hirshfeld channel [5,14,19,22] shown in Scheme 3. In this approach the molecular system is viewed as a collection of infinitesimal volume elements, inside which the local probability scattering between AIM, $Z^0(\boldsymbol{r}) \to Z'^H(\boldsymbol{r})$, takes place. Due to the local character of this one-electron information-propagation scheme, in the spirit of the stockholder division of the molecular electron density, it requires only the integration over one-point coordinates in calculating the average entropic descriptors of molecules and their atomic fragments.

These "vertical" flows of information in molecules conserve the fixed molecular electron density $\rho(\boldsymbol{r})$ or its shape factor $p(\boldsymbol{r})$. The local information channel of Scheme 3 involves a given infinitesimal volume element at the specified position in space of an electron, which determines both the input and output event of its spatial localization. The promolecular-input probability densities are determined by the free-atom distributions $\boldsymbol{\pi}^0(\boldsymbol{r})$ of Eq. 36, while the molecular-output probability densities $\boldsymbol{\pi}^H(\boldsymbol{r})$ of Eq. 35 describe the stockholder AIM. The local matrix-kernel determining



Scheme 4 The locally-normalized stockholder-channel for a diatomic molecule X–Y

the probability-propagation in the vertical channel,

$$\mathbf{P}^H(\boldsymbol{r}'|\boldsymbol{r}) = \partial\boldsymbol{\pi}^H(\boldsymbol{r}')/\partial\boldsymbol{\pi}^0(\boldsymbol{r}) = \{P[Z'(\boldsymbol{r}')|Z(\boldsymbol{r})]$$
$$= \{\partial\pi^H_{Z'}(\boldsymbol{r}')/\partial\pi^H_Z(\boldsymbol{r}) = d^H_{Z'}(\boldsymbol{r}')\delta(\boldsymbol{r}'-\boldsymbol{r})\}, \tag{60}$$

in which each row is identical, is generated by the local share-factors of AIM. This choice of the scattering kernel is in the spirit of the stockholder division defining the atomic fragments and satisfies the required normalization of each row in $\mathbf{P}^H(\boldsymbol{r}'|\boldsymbol{r})$:

$$\sum_{Z'} \int P[Z'(\boldsymbol{r}')|Z(\boldsymbol{r})]d\boldsymbol{r}' = 1. \tag{61}$$

It should be observed, however, that the input probabilities in Scheme 3 are not unity-normalized (see Eq. 33). One could alternatively examine the locally-normalized channel shown in Scheme 4 [5,14,19,22], which generates the entropy/information descriptors per unit probability density at $\boldsymbol{r}$, obtained by dividing the input probabilities in Scheme 3 by the promolecular shape factor $p^0(\boldsymbol{r})$. Therefore, the locally-normalized stockholder channel involves the promolecular shares $\boldsymbol{d}^0(\boldsymbol{r})$ in its input, equal to the molecular shares in the Hirshfeld scheme, $\boldsymbol{d}^0(\boldsymbol{r}) = \boldsymbol{d}^H(\boldsymbol{r})$, which also determine both the probability scattering and the output probabilities in the vertical channel.

In the local-scattering matrix of Eq. 60 the probability of scattering to the specified output AIM is independent of the input free-atom. It is seen to be governed by the same local conditional probability $d^H(Z'|\boldsymbol{r}) = d^0(Z'|\boldsymbol{r})$, which characterizes the atomic division of both the molecular and promolecular shape-factors of the corresponding electron densities. Therefore, the local communication channels of Schemes 3 and 4 extend the stockholder rule to the realm of the probability/information scattering in molecules.

One should observe the basic difference between the information system of Fig. 1b and that depicted in Schemes 3 and 4. In the former case the molecularly-weighted information scattering takes place only between different localities inside each atom (*non*-local, *intra*-atomic covalency), with all *inter*-atomic communication links identically vanishing (see Eq. 46). In the latter case, the vertical information scattering inside each local subsystem from each input atom to all constituent AIM of the system under consideration provides a basis for estimating the local, *inter*-atomic measure of the system IT-covalency.

The atomic shares $\boldsymbol{d}^H(\boldsymbol{r}) = \boldsymbol{d}^0(\boldsymbol{r})$, which define the locally-normalized Hirshfeld channel of Scheme 4, generate the identical input and output entropy densities, identified by the lower-case symbols (Compare Eq. 49)

$$s(\mathbf{a}^0(\boldsymbol{r})) = s(\mathbf{b}^H(\boldsymbol{r})) = -\sum\nolimits_Z d_Z^H(\boldsymbol{r}) \log d_Z^H(\boldsymbol{r}) \equiv s(\boldsymbol{d}^H(\boldsymbol{r})). \tag{62}$$

The local conditional-entropy contribution also gives

$$\begin{aligned} s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})) &= -\sum\nolimits_Z \sum\nolimits_{Z'} d_Z^0(\boldsymbol{r}) d_{Z'}^H(\boldsymbol{r}) \log d_{Z'}^H(\boldsymbol{r}) \\ &= -\sum\nolimits_{Z'} d_{Z'}^H(\boldsymbol{r}) \log d_{Z'}^H(\boldsymbol{r}) = s(\boldsymbol{d}^H(\boldsymbol{r})). \end{aligned} \tag{63}$$

Hence the corresponding mutual-information density identically vanishes in the vertical channel:

$$\begin{aligned} i(\mathbf{a}^0(\boldsymbol{r}) : \mathbf{b}^H(\boldsymbol{r})) &= -s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})) - \sum\nolimits_Z \sum\nolimits_{Z'} d_Z^0(\boldsymbol{r}) d_{Z'}^H(\boldsymbol{r}) \log d_Z^0(\boldsymbol{r}) \\ &= s(\boldsymbol{d}^0(\boldsymbol{r})) - s(\boldsymbol{d}^H(\boldsymbol{r})) = 0. \end{aligned} \tag{64}$$

This zero information-flow density, measuring the information-ionicity density in the Hirshfeld channel, reflects the independence of the channel output probabilities on its input. These two local entropy/information descriptors per unit input probability density thus generate the purely IT-covalent overall information density:

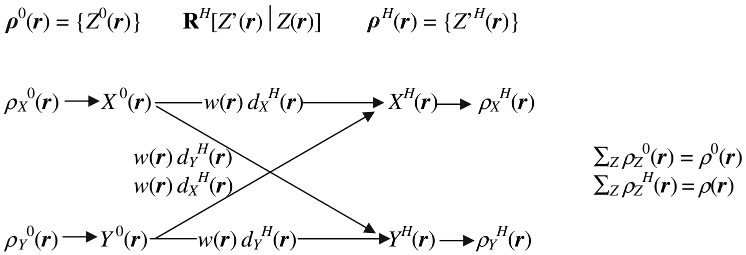
$$n(\mathbf{a}^0(\boldsymbol{r}); \mathbf{b}^H(\boldsymbol{r})) = s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})) + i(\mathbf{a}^0(\boldsymbol{r}) : \mathbf{b}^H(\boldsymbol{r})) = s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})). \tag{65}$$

The local entropies of the vertical Hirshfeld channel can be subsequently *shape*-averaged over the whole space, using either the molecular $[p(\boldsymbol{r})]$ or promolecular $[p^0(\boldsymbol{r})]$ probability distributions as local ensemble "weights". For example, the corresponding average conditional entropies read:

$$\begin{aligned} \langle s(\mathbf{b}^H|\mathbf{a}^0)\rangle &= \int p(\boldsymbol{r}) s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})) d\boldsymbol{r} = \int p(\boldsymbol{r}) s(\boldsymbol{d}^H(\boldsymbol{r})) d\boldsymbol{r} = S[\boldsymbol{\pi}^H] - S[p], \\ \langle s(\mathbf{b}^H|\mathbf{a}^0)\rangle_0 &= \int p^0(\boldsymbol{r}) s(\mathbf{b}^H(\boldsymbol{r})|\mathbf{a}^0(\boldsymbol{r})) d\boldsymbol{r} = \int p^0(\boldsymbol{r}) s(\boldsymbol{d}^0(\boldsymbol{r})) d\boldsymbol{r} = S[\boldsymbol{\pi}^0] - S[p^0]. \end{aligned} \tag{66}$$

These two measures of the average communication noise in the local channel of Scheme 3 can be regarded as alternative descriptors of the IT-covalency in the vertical Hirshfeld channel. Therefore, by regarding $S[p] = S^{total}[\boldsymbol{\pi}^H]$ (or $S[p^0] = S^{total}[\boldsymbol{\pi}^0]$) as *total* entropy in atomic resolution and $S[\boldsymbol{\pi}^H] = S^{add}[\boldsymbol{\pi}^H]$ (or $S[\boldsymbol{\pi}^0] = S^{add}[\boldsymbol{\pi}^0]$) as the corresponding *additive* contribution, the negative average entropies of Eq. 66 can be interpreted as measuring the corresponding *non-additive* entropies:

$$\begin{aligned} S^{nadd}[\boldsymbol{\pi}^H] &= S^{total}[\boldsymbol{\pi}^H] - S^{add}[\boldsymbol{\pi}^H] \equiv -\langle s(\mathbf{b}^H|\mathbf{a}^0)\rangle, \\ S^{nadd}[\boldsymbol{\pi}^0] &= S^{total}[\boldsymbol{\pi}^0] - S^{add}[\boldsymbol{\pi}^0] \equiv -\langle s(\mathbf{b}^H|\mathbf{a}^0)\rangle_0. \end{aligned} \tag{67}$$



Scheme 5 The flow diagram for the electron density in the vertical Hirshfeld channel of Scheme 3

It is also of interest to explore the *displacement* in the entropy non-additivity due to the electron delocalization accompanying the bond formation. It is measured by the difference between the two non-additive entropies of the preceding equation:

$$\begin{aligned}\Delta S^{nadd} &= S^{nadd}[\boldsymbol{\pi}^H] - S^{nadd}[\boldsymbol{\pi}^0] = (S[\boldsymbol{\pi}^0] - S[\boldsymbol{\pi}^H]) + (S[p^0] - S[p]) \\ &\equiv \Delta S[\boldsymbol{\pi}] - \Delta S[p]. \end{aligned} \tag{68}$$

The integral conditional-entropy and mutual-information descriptors of the vertical channel of Scheme 3 are:

$$\begin{aligned} S(\mathbf{B}^H|\mathbf{A}^0) &= -\sum\nolimits_Z \sum\nolimits_{Z'} \int \pi_Z^0(\boldsymbol{r}) d_{Z'}^H(\boldsymbol{r}) \log d_{Z'}^H(\boldsymbol{r}) d\boldsymbol{r} \\ &= -\sum\nolimits_{Z'} \int p^0(\boldsymbol{r}) d_{Z'}^H(\boldsymbol{r}) \log d_{Z'}^H(\boldsymbol{r}) d\boldsymbol{r} \\ &= \langle s(\mathbf{b}^H|\mathbf{a}^0)\rangle_0 = S[\boldsymbol{\pi}^0] - S[p^0], \\ I(\mathbf{A}^0 : \mathbf{B}^H) &= -S(\mathbf{B}^H|\mathbf{A}^0) + S[\boldsymbol{\pi}^0] = S[p^0], \\ N(\mathbf{A}^0; \mathbf{B}^H) &= S(\mathbf{B}^H|\mathbf{A}^0) + I(\mathbf{A}^0 : \mathbf{B}^H) = S[\boldsymbol{\pi}^0]. \end{aligned} \tag{69}$$

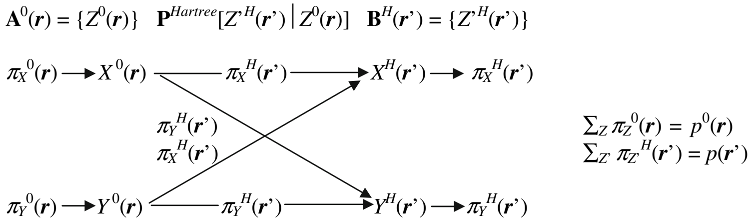
It again predicts the overall IT bond-order to the amount of the (additive) Shannon entropy $S[\boldsymbol{\pi}^0] = S^{add}[\boldsymbol{\pi}^0]$ contained in the input probabilities of the free atoms building the promolecule. Part of this entropy measure is seen to be carried by a non-vanishing information-flow (IT-ionicity), measured by the promolecular Shannon entropy $S[p^0]$. It also predicts the complementary amount $S[\boldsymbol{\pi}^0] - S[p^0]$ to be dissipated as the communication noise (IT-covalency) in the vertical Hirshfeld channel.

Finally, it follows from Eqs. 31 and 35 that by multiplying the input and conditional (scattering) probabilities in Scheme 3 by the local molecular enhancement factor $w(\boldsymbol{r})$ one obtains the associated flow diagram for the electron density in the vertical Hirshfeld channel (Scheme 5). Indeed, it can be straightforwardly verified that the density-flow "communication" connections defining this network,

$$\mathbf{R}^H(\boldsymbol{r}'|\boldsymbol{r}) = w(\boldsymbol{r})\mathbf{P}^H(\boldsymbol{r}'|\boldsymbol{r}), \tag{70}$$

give rise to the Hirshfeld output densities:

$$\int \boldsymbol{\rho}^0(\boldsymbol{r})\mathbf{R}^H(\boldsymbol{r}'|\boldsymbol{r})d\boldsymbol{r} = \boldsymbol{\rho}^H(\boldsymbol{r}). \tag{71}$$



Scheme 6 The diatomic (non-local) communication channel for the independent Hirshfeld atoms in the Hartree-limit

8 Independent atoms in the Hartree limit

Consider next the Hartree-limit in atomic resolution, when the input $\{Z^0(\boldsymbol{r})\}$ and output $\{Z'^H(\boldsymbol{r}')\}$ "events" of localizing the charge-free, spinless particles, in either the free-atoms of the promolecular distribution or the bonded-atoms of the molecular distribution, are statistically independent. This gives rise to the non-local channel shown in Scheme 6. Indeed, the joint probabilities $P[Z^0(\boldsymbol{r}), Z'^H(\boldsymbol{r}')] = \pi_Z^0(\boldsymbol{r})\, \pi_{Z'}^H(\boldsymbol{r}')$ give rise to conditional probabilities of the output given input:

$$\mathbf{P}^{Hartree}(\boldsymbol{r}'|\boldsymbol{r}) = \{P[Z'^H(\boldsymbol{r}')|Z^0(\boldsymbol{r})] = P[Z^0(\boldsymbol{r}), Z'^H(\boldsymbol{r}')]/\pi_Z^0(\boldsymbol{r}) = \pi_{Z'}^H(\boldsymbol{r}')\}. \quad (72)$$

One should observe that this channel admits for the electron probability (information) scattering between different volume elements of the same and different atoms, thus generating both the intra- and inter-atom contributions to the system communication noise, which diminishes the initial amount of information $S[\boldsymbol{\pi}^0]$, which also characterizes the vertical information system of Scheme 3.

Its integral entropy/information bond-descriptors read:

$$\begin{aligned} S^{\mathrm{Hartree}}(\mathbf{B}^H|\mathbf{A}^0) &= -\sum_Z \sum_{Z'} \int\int \pi_Z^0(\boldsymbol{r})\pi_{Z'}^H(\boldsymbol{r}') \log \pi_{Z'}^H(\boldsymbol{r}') d\boldsymbol{r} d\boldsymbol{r}' \\ &= -\sum_{Z'} \int \pi_{Z'}^H(\boldsymbol{r}') \log \pi_{Z'}^H(\boldsymbol{r}') d\boldsymbol{r}' = S[\boldsymbol{\pi}^H], \\ I^{\mathrm{Hartree}}(\mathbf{A}^0 : \mathbf{B}^H) &= -S^{\mathrm{Hartree}}(\mathbf{B}^H|\mathbf{A}^0) - \sum_Z \int \pi_Z^0(\boldsymbol{r}) \log \pi_Z^0(\boldsymbol{r}) d\boldsymbol{r} = S[\boldsymbol{\pi}^0] - S[\boldsymbol{\pi}^H], \\ N^{\mathrm{Hartree}}(\mathbf{A}^0; \mathbf{B}^H) &= S^{\mathrm{Hartree}}(\mathbf{B}^H|\mathbf{A}^0) + I^{\mathrm{Hartree}}(\mathbf{A}^0 : \mathbf{B}^H) = S[\boldsymbol{\pi}^0]. \end{aligned} \quad (73)$$

A comparison between these IT indices and their analogs (Eq. 70) describing the vertical channel of Scheme 3 reveals a different partition of the same overall index $N^{\mathrm{Hartree}}(\mathbf{A}^0; \mathbf{B}^H) = N(\mathbf{A}^0; \mathbf{B}^H) = S[\boldsymbol{\pi}^0]$ into the ionic and covalent parts. In the non-local channel of Scheme 6 there is a more substantial noise-dissipation (IT-covalency) part of the original information content [see Eqs. (66) and (67)],

$$S^{\mathrm{Hartree}}(\mathbf{B}^H|\mathbf{A}^0) = S[\boldsymbol{\pi}^H] > S(\mathbf{B}^H|\mathbf{A}^0) = S[\boldsymbol{\pi}^0] - S[p^0] = S^{nadd}[\boldsymbol{\pi}^0], \quad (74)$$

thus giving rise to a lower amount of the information-flow (IT-ionicity) part of $S[\boldsymbol{\pi}^0]$:

$$I^{\text{Hartree}}(\mathbf{A}^0 : \mathbf{B}^H) = S[\boldsymbol{\pi}^0] - S[\boldsymbol{\pi}^H] = \Delta S[\boldsymbol{\pi}] < I(\mathbf{A}^0 : \mathbf{B}^H) = S[p^0]. \quad (75)$$

9 Conclusion

The Information Theory offers a novel perspective on the origins of the chemical bond, its covalent/ionic composition, and the bond-multiplicity measures. This communication-theory approach explores the effective delocalization of electrons via the system chemical bonds, which manifests itself through the scattering of electron probabilities in the appropriately defined molecular information channel. The bond-covalency effects are then reflected by the average communication “noise” created by this information scattering, as measured by the conditional-entropy quantity of IT, which effectively diminishes the amount of information in the channel output probabilities, compared to the initial information content of the “input” probabilities of the system promolecule composed of the free-atom densities shifted to their AIM positions. This diminished level of the information-flow in the molecular information system is measured by the complementary, mutual-information descriptor, which reflects the bond IT-ionicity. These two IT-components conserve the initial, promolecular level of the information content, which reflects the overall bond-index in the communication theory approach. In this way one obtains a transparent description of the competition between the covalent and ionic components of the system chemical bonds for the valence electrons of the constituent free-atoms.

In the past the entropy/information descriptors of molecular communication systems have been explored in the condensed (reduced) atomic or orbital resolutions, in a search for adequate bond-order probes which give predictions in a general accord with the accepted chemical (intuitive) bonding patterns in molecules. The coarse-grained AIM description treats the atomic building-blocks as whole units, while the orbital approach adopts the AO-promotion perspective in extracting the entropy/information indices in both the ground- and excited electron configurations. In the present work we have extended this analysis to the fine-grained, local description of electron distributions in the molecule, its promolecular prototype, and their atomic fragments.

First, we have qualitatively examined within the Kohn–Sham DFT perspective, how different levels of the electron correlation in molecules affect the IT bond indices. This comparison has been carried out for the fixed electron density in the non-correlated Hartree system of spin-less, non-interacting particles, the hypothetical Kohn–Sham system of non-interacting fermions, and the real system of interacting electrons. These limiting molecular systems respectively correspond to the conditional probability of two electrons being reflected by the vanishing correlation hole, the exchange (Fermi) hole, and the full exchange-correlation hole, including the Coulomb contribution. The stationary sum-rules of the probability scattering in the local resolution have been established and illustrated using the Hartree–Fock theory. The leading terms in the extra communication-noise, compared to that in the Hartree system, due to the increasing level of the included electron correlation have also been identified.

An extra “spread” of the electron probabilities in a larger set of the electron localization “events” of the system constituent atoms increases the overall uncertainty in electron distribution, in the same way as does the AO resolution compared to the condensed (reduced) description of the system atomic fragments. This effect has been examined using the stockholder partition of the molecular probability distribution into densities of bonded atoms. In order to separate the effects due to the different categories of the probability-scattering between AIM, we have examined three reference channels involving the locally-resolved (unreduced) channels of constituent atoms. First, the molecular channel generated by the parallel arrangement of the (internal) non-local atomic sub-channels has been discussed and the relevant grouping principles for its entropy-information descriptors have been derived. Its resultant IT indices have been shown to reflect the molecularly-weighted mean values of the internal bond-indices, which separately reflect the promoted (valence) states of AIM. The second illustrative information system, the so called vertical Hirshfeld channel, admits only the local inter-atom probability scattering. The ensemble of such local information networks, with the molecular or promolecular electron shape-factors providing the relevant probability-weights for the current electron location in space, were shown to reflect the non-additivities in the entropy-covalency descriptor. Finally, the non-local molecular channel in the Hartree limit of independent stockholder atoms, has been examined and its additional contributions due to the switching-on the inter-atomic information propagation have been discussed. We have qualitative demonstrated that, as intuitively expected, this extra scattering effect generates higher entropy-covalency and hence lower information-ionicity, compared to IT quantities characterizing the vertical Hirshfeld channel.

The present qualitative study opens a way to future numerical calculations of the probability/information concepts designed in this analysis. It should be observed, however, that within the KS DFT one then has to extract the anisotropic correlation holes explicitly. It remains to be seen how their known deficiencies in the KS DFT, compared to much more realistic spherically-averaged correlation holes, which fully determine the system electronic energy, affect the predicted IT bond descriptors.

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