J Math Chem (2009) 45:1041–1054
DOI 10.1007/s10910-008-9391-6

ORIGINAL PAPER

Entropic descriptors of the chemical bond in H_2: local resolution of stockholder atoms

Roman F. Nalewajski

Received: 17 December 2007 / Accepted: 22 February 2008 / Published online: 13 June 2008

Abstract The information systems of the local spatial "events" of two-electrons in the stockholder atoms-in-molecules (AIM) are established for the three-representative states of the hydrogen molecule in the minimum basis set description: the ground (*bonding*, singlet) state, the singly-excited (*non-bonding*, triplet) state describing the free atoms of the system "promolecule", and the doubly-excited (*anti-bonding*, singlet) state. The Hirshfeld atoms reflect the molecular electron densities thus reflecting the bonding and anti-bonding polarizations of AIM in the corresponding molecular states. Their integral entropy-covalency and information-ionicity descriptors are expressed in terms of the relevant Shannon entropies of the molecular/promolecular and atomic probability distributions of electrons, the numerical values of which have been previously reported. The resulting estimates of the information-theoretic bond indices provide the entropic "fingerprints" of the bonding conditions in these three prototype electron configurations, which reflect upon the associated displacements in the information contained in the molecular electronic distribution relative to the initial, promolecular reference. A brief discussion of such changes due to the AIM contraction and/or promotion in the molecule and their mutual polarizations implied by the bonding/antibonding character of the molecular state is presented. This analysis uncovers the information origins of the covalent bond in this prototype molecular system.

Keywords Bond indices · Chemical-bond theory · Communication theory · Covalent/ionic bond composition · Hydrogen molecule · Information theory · Local information channels · Stockholder atoms

R. F. Nalewajski (✉)
Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland
e-mail: nalewajs@chemia.uj.edu.pl

1 Introduction

The Information Theory (IT) [1–4] has been recently applied to several issues in the theory of molecular structure and reactivity [5–28]. In particular, general, thermodynamic-like information principles determining the system electronic structure have been examined [5–9] and the information-theoretic approach to Atoms-in-Molecules (AIM) has been proposed [5,6,10–12], which rationalizes and extends the "stockholder" rule of Hirshfeld [13] for an exhaustive division of the molecular electron density into AIM components. The Communication Theory of the chemical bond has been formulated [5,14–26] at global and local levels of resolving the electron probabilities of the whole molecular systems, their constituent fragments, and orbital components. The IT concepts have also been used in quantifying the reactivity concepts [5,27] and providing the information perspective on several classical problems in quantum chemistry, e.g., molecular similarity [2,24], the Valence-Bond theory [25], the electron localization [5,28], orbital hybridization [29], and the role of the Pauli exclusion principle [26].

In this communication approach the molecule is interpreted as the information channel at the adopted resolution and representation of the electronic probabilities, which together specify the associated "input" and "output" "events" in propagating ("scattering") the molecular or "promolecular" input probabilities via the network of the chemical bonds connecting the system constituent atoms. The average *conditional-entropy* (entropy-covalency) descriptor in such a probability network measures its average communication "noise", which reflects the extra "disorder" (indeterminacy) generated in the electron probabilities due to their delocalization in the molecule via the system chemical bonds. The wider is such a probability scattering from the given atomic "input" to all atomic "outputs", i.e., the higher the degree of sharing the valence electrons between the system constituent atoms, the larger the amount of the system "noise" in propagating the molecular electron probabilities and hence its bond-covalency. The average *mutual-information* (information-ionicity) index of all chemical bonds in the molecule measures the amount of information flowing through such a molecular information network, from the promolecular input to the molecular output, thus emphasizing the "order" (determinacy) in the probability scattering. The more deterministic (localized) is the information scattering from the given AIM in the molecular communication channel, the more of the initial (input) amount of information reaches the channel output, against the dissipating influence of the information scattering.

Therefore, in this probabilistic approach the covalent component reflects the *delocalization* aspect of the system valence electrons, dispersed via the network of all chemical bonds generated by the system occupied molecular orbitals (MO), while the ionic component describes the complementary *localization* facet of the flow of information in the molecule. This IT description explains the information origins of the chemical bond and it accounts for the intuitively expected competition between the covalent and ionic bond components [5]. The numerical values of the entropy/information indices depend on the adopted representation of the electron probabilities, e.g., MO [20,21], atomic orbitals (AO) [22,29], etc., and their spatial resolution, e.g., coarse-grained description in terms of constituent atoms and their collections [5,14–20] and the fine-grained local description [23,26].

The AIM-resolved communication systems have been shown to generate the bond indices in bits, the units corresponding to the base 2 in the logarithmic, Shannon measure of information, which are close to the chemical bond multiplicities in model systems [5]. However, little is known about the information levels involved in the local description of molecular probabilities, with only preliminary results being reported previously, on the overall information-distances and their densities [30,31], displacements in the Shannon entropy of stockholder AIM [12,32] and the H_2 bond descriptors in communication theory [26].

In the present work we shall examine the integral information-theoretic descriptors of the simplest local communication systems of stockholder atoms in the bonding, non-bonding and anti-bonding states of H_2. In these three representative electron configurations the Hirshfeld atoms reflect the molecular electron densities, so that they give rise to entropy/information descriptors manifesting the presence of the single covalent bond in the (singlet) ground-state of the molecule, the promolecular collection of free atoms in the singly excited (triplet) configuration, and the anti-bonded atoms in the doubly excited (singlet) state of the hydrogen molecule. It is the main purpose of this work to establish the relevant information channels for these illustrative molecular states and to estimate the overall bond indices and their average IT-covalent and IT-ionic components, which will be expressed in terms of the Shannon entropies of the molecular/promolecular probability densities and their AIM pieces.

2 Local promolecular and molecular information systems in atomic representation

Consider the simplest two-orbital model of the chemical bond [5] in a diatomic molecule $M = A\text{–}B \equiv (A\!\mid\!B)$, containing the mutually-opened bonded atoms A and B, as symbolized by the broken vertical line separating them. They contribute the (real) orthogonalized atomic orbitals (OAO) $a(\boldsymbol{r})$ and $b(\boldsymbol{r})$, respectively, and a single valence electron each, to form the system chemical bond. In order to extract displacements in the associated entropy-covalency and information-ionicity descriptors we shall also examine the system atomic promolecule $M^0 = (A^0|B^0)$, which marks the initial stage of the bond-formation process; it consists of the free atoms A^0 and B^0 in their molecular positions, which are mutually-closed as symbolized by the *solid* line separating atomic symbols.

This reference state can be regarded as the limiting (no-bond) form of the system two molecular orbitals (MO), bonding, $\bar{\varphi} = \sqrt{P}a + \sqrt{Q}b$, and anti-bonding, $\tilde{\varphi} = -\sqrt{Q}a + \sqrt{P}b$, where the controlling OAO probability parameters P and Q satisfy the normalization relation of the two MO: $P + Q = 1$. Indeed, $\bar{\varphi} \to a$ and $\tilde{\varphi} \to b$ in the limit $P \to 1$, for the vanishing "mixing" probability $Q \to 0$, which characterizes the non-bonded atoms of the promolecule. The maximum chemical bond is predicted for the equal participation of the two OAO in MO, when $P = Q = 1/2$, e.g., for the σ-bond in H_2 or the π-bond in ethylene. In what follows we shall examine such a maximum-delocalization chemical bonding of $M = A_1\text{–}A_2$. The reported numerical values of the entropic bond-indices for H_2 will be measured in bits. This corresponds to the base 2 of the logarithmic (Shannon) measure of information.

In this analysis we shall compare the two-electron communication systems in the local resolution of the Hirshfeld atoms, which can be derived from the electronic densities of the three electron configurations of H_2, identified by the corresponding spatial parts of the system wave-function:

the *bonding* ground (singlet) state $\bar{\Phi}(1,2) = \bar{\varphi}(1)\bar{\varphi}(2)$,
the *non-bonding* singly-excited (triplet) state, equivalent to the promolecular Slater determinant, $\Phi(1,2) = 2^{-1/2}[\bar{\varphi}(1)\tilde{\varphi}(2) - \bar{\varphi}(2)\tilde{\varphi}(1)] = |ab| \equiv \Phi^0(1,2)$, and
the *anti-bonding* doubly-excited (singlet) state $\tilde{\Phi}(1,2) = \tilde{\varphi}(1)\tilde{\varphi}(2)$.

In what follows all quantities related to the bonding and anti-bonding states will be marked by the “bar” and “tilde” symbols, respectively, while the superscript “0” will identify the corresponding promolecule-reference analogs, in accordance with the above convention adopted for MO and the system wave-functions.

2.1 Non-bonded atoms

The common electron density $\rho^0(\boldsymbol{r})$ of the promolecular and non-bonding states, twice the associated one-electron probability distribution (shape-factor) $p^0(\boldsymbol{r})$ of this two-electron system, is the sum of the normalized probability densities $\{p_X^0(r)\}$ of the free atoms:

$$\begin{aligned} \rho^0(\boldsymbol{r}) &\equiv 2p^0(\boldsymbol{r}) = a^2(\boldsymbol{r}) + b^2(\boldsymbol{r}) = p_A^0(\boldsymbol{r}) + p_B^0(\boldsymbol{r}), \\ \int p^0(\boldsymbol{r})d\boldsymbol{r} &= \int p_X^0(\boldsymbol{r})d\boldsymbol{r} = 1, \end{aligned} \tag{1}$$

which determine the local promolecular communication channel shown in Fig. 1. By convention, in this diagram the local atomic events of electron “1” define the information “input”, while those relating to electron “2” determine the information output. It should be observed that in absence of any quantum-mechanical interaction between the two OAO the joint two-electron probability density,

$$\begin{aligned} P^0(1,2) = \left|\Phi^0(1,2)\right|^2 &= 1/2[p_A^0(1)p_B^0(2) + p_B^0(1)p_A^0(2)] \\ &\equiv P[A^0(1), B^0(2)] + P[B^0(1), A^0(2)], \end{aligned} \tag{2}$$

integrates to the one-electron distribution of Eq. 1:

$$\int P^0(1,2)d\boldsymbol{r}_2 = p^0(1) = 1/2[p_A^0(1) + p_B^0(1)] \equiv P_A^0(1) + P_B^0(1). \tag{3}$$

Its two contributions determine the promolecular input probabilities of both non-bonded atoms in Fig. 1. The corresponding conditional probability densities,

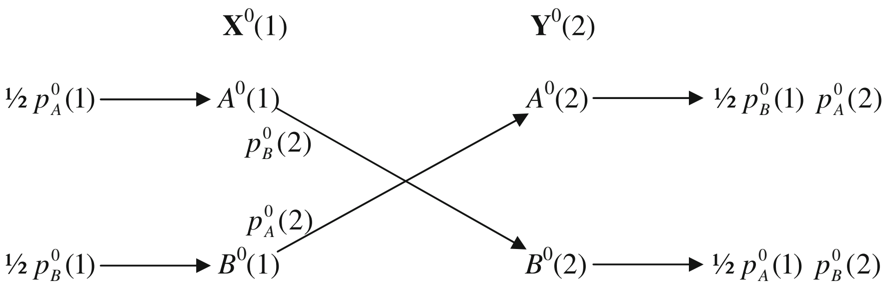

Fig. 1 The two-electron information channel for the promolecular reference $M^0 = (A^0|B^0)$ of a diatomic molecule $M = A–B = (A \mathrel{\vdots} B)$. In H_2 this channel is also representative of the singly-excited (non-bonding) triplet state of two electrons in the molecule. Here, $\mathbf{X}^0(1)$ and $\mathbf{Y}^0(2)$ respectively represent the local "input" events of electron "1" and the local "output" events of electron "2", for the non-bonded (free) atoms of the promolecule

which determine the non-vanishing (inter-atomic) communications in this information systems, read:

$$\begin{aligned} P[B^0(1)|A^0(2)] &= P[B^0(1), A^0(2)]/P_A^0(1) = p_B^0(2), \\ P[A^0(1)|B^0(2)] &= P[A^0(1), B^0(2)]/P_B^0(1) = p_A^0(2). \end{aligned} \tag{4}$$

Thus, the sum of input probability densities of the local atomic events in Fig. 1 reconstructs the one-electron distribution of Eq. 3, while the output probabilities sum up to the two-electron density of Eq. 2.

The conditional-entropy density of the channel output given input for the information system of Fig. 1,

$$\begin{aligned} S^0[\mathbf{Y}^0(2)|\mathbf{X}^0(1)] \equiv S^0(1,2) = -\frac{1}{2}[&p_A^0(1)p_B^0(2)\log_2 p_B^0(2) \\ &+ p_B^0(1)p_A^0(2)\log_2 p_A^0(2)], \end{aligned} \tag{5}$$

integrates to the average entropy-covalency of this promolecular channel:

$$S^0 = \iint S^0(1,2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{1}{2}(H[p_A^0] + H[p_B^0]) = H[p_H^0], \tag{6}$$

where the Shannon entropy of the electron distribution $p(\boldsymbol{r})$

$$H[p] = -\int p(\boldsymbol{r})\log_2 p(\boldsymbol{r})d\boldsymbol{r}. \tag{7}$$

Its numerical value for the free hydrogen atom has been reported elsewhere [5,12]: $H[p_H^0] = 4.18$ bits.

The corresponding expression for the mutual-information density contained in the channel inputs and outputs,

$$I^0[\mathbf{X}^0(1):\mathbf{Y}^0(2)] \equiv I^0(1,2) = \frac{1}{2}\left[p_A^0(1)p_B^0(2)\log_2\frac{2}{p_A^0(1)} + p_B^0(1)p_A^0(2)\log_2\frac{2}{p_B^0(1)}\right], \quad (8)$$

generates the average information-ionicity of this promolecular information system:

$$I^0 = \iint I^0(1,2)d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = 1 + \frac{1}{2}(H[p_A^0] + H[p_B^0]) = 1 + H[p_H^0] = 5.18\,\text{bits}. \quad (9)$$

Hence, these two average components give rise to the total bond index of the local channel of the two non-bonded hydrogen atoms in $H_2{}^0 = (H^0|H^0)$:

$$N^0 = S^0 + I^0 = 9.36\,\text{bits}. \quad (10)$$

This level of the overall information index thus provides the reference for estimating the bonding and anti-bonding effects in the two remaining (molecular) states of interest.

2.2 Bonded stockholder atoms

The promolecular probability density $p^0(\boldsymbol{r})$ and its free-atomic components $\{p_X^0(\boldsymbol{r})\}$ determine the local ("stockholder") shares $\{d_X^H(\boldsymbol{r})\}$ of the probability distribution $p_X^H(\boldsymbol{r})$ of the bonded Hirshfeld atom X^H in the given molecular one-electron probability density $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/2$:

$$\left\{d_X^0(\boldsymbol{r}) = \frac{p_X^0(\boldsymbol{r})}{p^0(\boldsymbol{r})} = p(X^0|\boldsymbol{r}) = d_X^H(\boldsymbol{r}) = \frac{\bar{p}_X^H(\boldsymbol{r})}{\bar{p}(\boldsymbol{r})} = \bar{p}(X^H|\boldsymbol{r}) = \frac{\tilde{p}_X^H(\boldsymbol{r})}{\tilde{p}(\boldsymbol{r})} = \tilde{p}(X^H|\boldsymbol{r})\right\}. \quad (11)$$

As indicated above these promolecular ratios determine the local conditional probabilities $\{p(X^0|\boldsymbol{r}) = \bar{p}(X^H|\boldsymbol{r}) = \tilde{p}(X^H|\boldsymbol{r})\}$ that electron found at the specified location $\boldsymbol{r}$ is attributed to the given atom X^H, thus satisfying the relevant normalization condition $\sum_X d_X^H(\boldsymbol{r}) = 1$ for any chosen position of an electron.

The molecular electron density in the bonding (ground) state $\bar{\Phi}$, when two spin-paired electrons occupy the bonding MO,

$$\bar{\varphi} = \frac{1}{\sqrt{2}}(a+b), \quad (12)$$

$$\bar{\rho}(\boldsymbol{r}) = 2\bar{\varphi}^2(\boldsymbol{r}) \equiv 2\bar{p}(\boldsymbol{r}), \tag{13}$$

can be then exhaustively decomposed into the corresponding contributions of stockholder atoms:

$$\bar{\rho}(\boldsymbol{r}) = a^2(\boldsymbol{r}) + b^2(\boldsymbol{r}) + 2a(\boldsymbol{r})b(\boldsymbol{r}) = \sum_X \bar{\rho}(\boldsymbol{r})d_X^H(\boldsymbol{r}) \equiv \sum_X \bar{\rho}_X^H(\boldsymbol{r}). \tag{14}$$

Expressing these electron/probability densities in terms of OAO gives:

$$\begin{aligned} \bar{\rho}_A^H(\boldsymbol{r}) &= \bar{p}_A^H(\boldsymbol{r}) = p_A^0(\boldsymbol{r}) + 2a(\boldsymbol{r})b(\boldsymbol{r})\left[1 + \frac{p_A^0(\boldsymbol{r})}{p_B^0(\boldsymbol{r})}\right]^{-1} \\ \bar{\rho}_B^H(\boldsymbol{r}) &= \bar{p}_B^H(\boldsymbol{r}) = p_B^0(\boldsymbol{r}) + 2a(\boldsymbol{r})b(\boldsymbol{r})\left[1 + \frac{p_B^0(\boldsymbol{r})}{p_A^0(\boldsymbol{r})}\right]^{-1}. \end{aligned} \tag{15}$$

The corresponding expressions for the anti-bonding state $\tilde{\Phi}$, with two spin-paired electrons occupying the anti-bonding MO

$$\tilde{\varphi} = \frac{1}{\sqrt{2}}(-a + b), \tag{16}$$

then read:

$$\begin{aligned} \tilde{\rho}(r) &= 2\tilde{\varphi}^2(\boldsymbol{r}) \equiv 2\tilde{p}(\boldsymbol{r}) = a^2(\boldsymbol{r}) + b^2(\boldsymbol{r}) - 2a(\boldsymbol{r})b(\boldsymbol{r}) \\ &= \sum_X \tilde{\rho}(\boldsymbol{r})d_X^H(\boldsymbol{r}) \equiv \sum_X \tilde{\rho}_X^H(\boldsymbol{r}), \end{aligned} \tag{17}$$

where,

$$\begin{aligned} \tilde{\rho}_A^H(\boldsymbol{r}) &= \tilde{p}_A^H(\boldsymbol{r}) = p_A^0(\boldsymbol{r}) - 2a(\boldsymbol{r})b(\boldsymbol{r})\left[1 + \frac{p_A^0(\boldsymbol{r})}{p_B^0(\boldsymbol{r})}\right]^{-1}, \\ \tilde{\rho}_B^H(\boldsymbol{r}) &= \tilde{p}_B^H(\boldsymbol{r}) = p_B^0(\boldsymbol{r}) - 2a(\boldsymbol{r})b(\boldsymbol{r})\left[1 + \frac{p_B^0(\boldsymbol{r})}{p_A^0(\boldsymbol{r})}\right]^{-1}. \end{aligned} \tag{18}$$

Using Eq. 14 one can thus naturally decompose the joint two-electron probability densities in the bonding and anti-bonding molecular states into the four atom-pair contributions, which define the local information systems of Fig. 2:

$$\begin{aligned} \bar{P}(1,2) &= \left|\bar{\Phi}(1,2)\right|^2 = \bar{\varphi}^2(1)\bar{\varphi}^2(2) = \bar{p}(1)\bar{p}(2) \\ &= \frac{1}{4}\sum_X\sum_Y \bar{p}_X^H(1)\bar{p}_Y^H(2) \equiv \sum_X\sum_Y \bar{P}[X^H(1), Y^H(2)], \end{aligned}$$

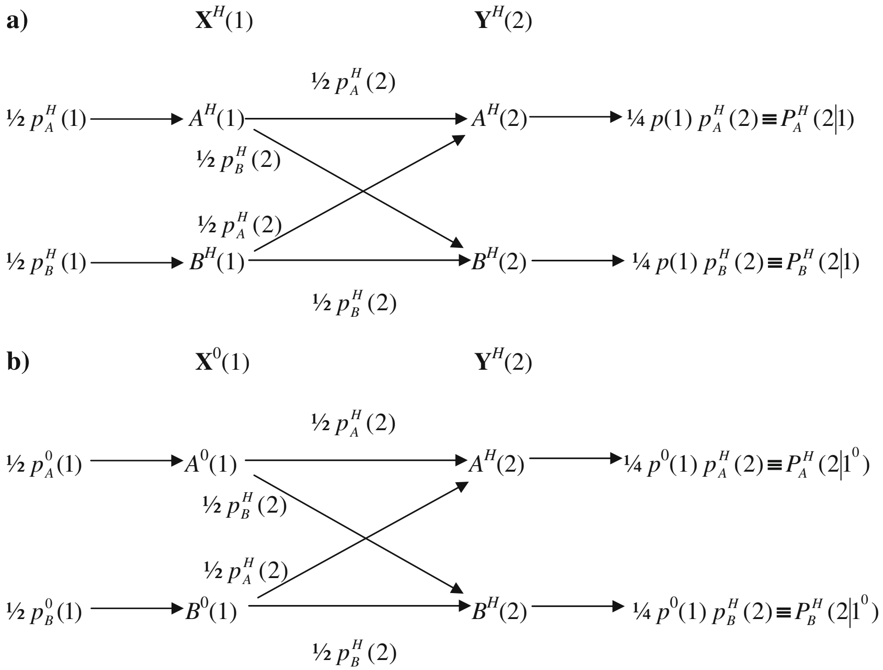

Fig. 2 The two-electron information channels for diatomic $M = A\text{–}B = (A^H \mid B^H)$ in the Hirshfeld (H) bonded-atom representation for estimating the entropy-covalency (Panel **a**) and information-ionicity (Panel **b**) of the chemical bond. Here, $\mathbf{X}^H(1)$ and $\mathbf{Y}^H(2)$ respectively represent the local "input" events of electron "1" and the local "output" events of electron "2", for the bonded or anti-bonded stockholder atoms in the molecule. The relevant channels for the bonding and anti-bonding states of H_2 are obtained by putting $\{p_Y^H = \bar{p}_Y^H\}$ or $\{p_Y^H = \tilde{p}_Y^H\}$, respectively

$$\tilde{P}(1,2) = \left|\tilde{\Phi}(1,2)\right|^2 = \tilde{\varphi}^2(1)\tilde{\varphi}^2(2) = \tilde{p}(1)\tilde{p}(2)$$
$$= \frac{1}{4}\sum_X \sum_Y \tilde{p}_X^H(1)\tilde{p}_Y^H(2) \equiv \sum_X \sum_Y \tilde{P}[X^H(1), Y^H(2)]. \qquad (19)$$

These pair-distributions partially integrate to the associated one-electron probability densities:

$$\int \bar{P}(1,2)d\boldsymbol{r}_2 = \bar{p}(1) = \frac{1}{2}\sum_X \bar{p}_X^H(1) \equiv \sum_X \bar{P}_X^H(1),$$
$$\int \tilde{P}(1,2)d\boldsymbol{r}_2 = \tilde{p}(1) = \frac{1}{2}\sum_X \tilde{p}_X^H(1) \equiv \sum_X \tilde{P}_X^H(1). \qquad (20)$$

The resolutions of Eqs. 19 and 20 generate the associated conditional probabilities of the molecular communication links in these networks:

$$\bar{P}[Y^H(2)|X^H(1)] = \bar{P}[X^H(1), Y^H(2)]/\bar{P}_X^H(1) = \frac{1}{2}\bar{p}_Y^H(2),$$
$$\tilde{P}[Y^H(2)|X^H(1)] = \tilde{P}[X^H(1), Y^H(2)]/\tilde{P}_X^H(1) = \frac{1}{2}\tilde{p}_Y^H(2). \tag{21}$$

In determining the entropy/information indices of these channels let us first consider the ground-state channel. The conditional-entropy density of the information system shown in Fig. 2a reads:

$$\bar{S}[\mathbf{Y}^H(2)|\mathbf{X}^H(1)] \equiv \bar{S}(1,2) = -\sum_X\sum_Y \bar{P}[X^H(1), Y^H(2)]\log_2 \bar{P}[Y^H(2)|X^H(1)]$$
$$= \bar{P}(1,2) - \frac{1}{2}\bar{p}(1)\sum_Y \bar{p}_Y^H(2)\log_2 \bar{p}_Y^H(2). \tag{22}$$

Hence, after integrating over positions of the two electrons one determines the average entropy covalency in the bonding state of H_2,

$$\bar{S} = \iint \bar{S}(1,2)d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = 1 + \frac{1}{2}(H[\bar{p}_A^H] + H[\bar{p}_B^H])$$
$$= 1 + H[\bar{p}_H^H] = 4.77\,\text{bits}, \tag{23}$$

where we have used the previously reported value of $H[\bar{p}_H^H] = 3.77$ bits [5,12].

It should be observed that the numerical values of Shannon entropies used in this analysis have been obtained from the large basis-set DFT calculations [12], which contain both the OAO contraction/promotion in the molecule and approximately take into account the electron correlation. Therefore, these numerical data go beyond the simple two-orbital model which has been used to construct the MO and the associated information systems of the present analysis.

For the mutual-information density in the information system of Fig. 2b for the bonding molecular state one similarly finds:

$$\bar{I}[\mathbf{X}^0(1):\mathbf{Y}^H(2)] \equiv \bar{I}(1,2) = \sum_X\sum_Y \bar{P}[X^0(1), Y^H(2)]\log_2 \frac{\bar{P}[Y^H(2)\,|X^H(1)]}{\bar{P}_Y^H(2\,|1^0)}$$
$$= \bar{p}(2)p^0(1)[1 - \log_2 p^0(1)]. \tag{24}$$

where $\bar{P}[X^0(1), Y^H(2)] = P_X^0(1)\bar{P}[Y^H(2)\,|X^H(1)]$. It gives rise to the average information-ionicity of the bonded hydrogen atoms in H_2:

$$\bar{I} = \iint \bar{I}(1,2)d\boldsymbol{r}_1\, d\boldsymbol{r}_2 = 1 + H[p^0] = 5.72\,\text{bits}. \tag{25}$$

In this estimate we have used the promolecular Shannon entropy $H[p^0] = 4.72$ bits, which can be derived from the previously reported quantity $H[\rho^0] = 2(H[p^0] - 1) = 7.45$ bits [5,12].

Finally, the two average bond components of Eqs. 23 and 25 give rise to the overall ground-state index $\bar{N} = \bar{S} + \bar{I} = 10.49$ bits.

Thus, one detects an increased level of the average noise and the amount of information flowing in the local channel of the bonded hydrogen atoms, compared to the non-bonding/promolecular state. They give rise to an increase of the overall index by about one bit, which identifies a presence of the single chemical bond. However, contrary to the previous analysis using the global approach in atomic resolution [5,14–20], which predicts only a marginal level of the information-ionicity and the entropy-covalency of roughly 1 bit value, the present local estimates exhibit increases of approximately half a bit in both bond components.

It should be observed at this point, that the local information channels in atomic representation exhibit the net result of competing influences from a contraction of the bonded atoms due to the presence of the other atom, which effectively increases a degree of the electron localization, and from the electron delocalization via the chemical bond (see Fig. 3). The atomic contraction is indeed reflected by the Shannon entropies of the free and bonded hydrogen atoms (in bits), $H[\bar{p}_H^H] = 3.8 < H[p_H^0] = 4.2$, which measure the uncertainty level in these two electron distributions. In the communication theory approach the "localization" aspect is reflected by the magnitude of the information-flow (mutual-information) index, which emphasizes the "deterministic" aspect of the probability propagation in the molecule. It also reflects the mutual dependence (correlation) of the two electrons in the contracted, molecular distribution. The delocalization part of these two opposing effects increases the communication noise in the molecular channel, measured by the conditional-entropy index.

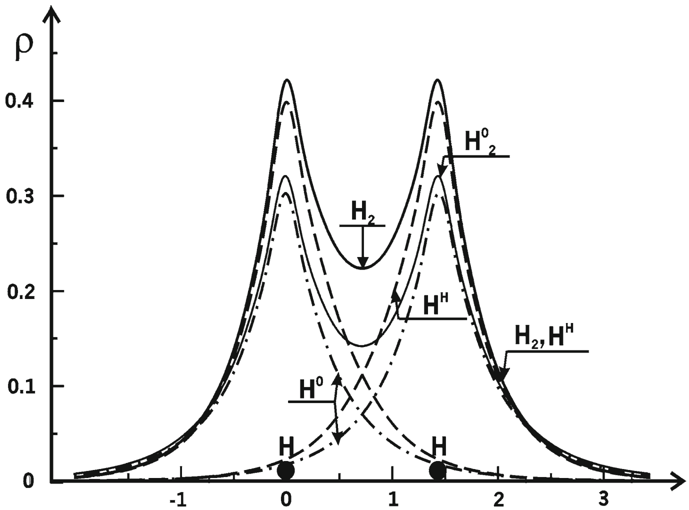

Fig. 3 The Hirshfeld electron densities (H^H) of bonded hydrogen atoms obtained from the ground-state molecular density $\rho = \bar{\rho}$ of H_2. The free-hydrogen densities (H^0) and the resulting electron density of the promolecule $H_2^0 \equiv (H^0|H^0)$ are also shown for comparison. The density 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

In other words, the contraction of AIM lowers the delocalization ("disorder") facet of the spatial distribution of electrons, thus raising a degree of their localization ("order") by increasing the average amount of information flowing through the local channel. This phenomenon escapes the shape-insensitive, global resolution of atomic probabilities. Accordingly, the OAO-mixing into the bonding MO increases the uncertainty in the information scattering, thus giving rise to more communication noise in the molecule, compared to the promolecular reference. The local predictions of Eqs. 23 and 25 reflect both these molecular "displacements", which accompany the formation of the covalent chemical bond in the hydrogen molecule.

2.3 Anti-bonded stockholder atoms

It directly follows from Fig. 2 that the corresponding average bond components in the anti-bonding molecular state $\tilde{\Phi}(1, 2)$ are given by the following expressions (see Eqs. 23 and 25):

$$\begin{aligned}\tilde{S} &= 1 + \frac{1}{2}(H[\tilde{p}_A^H] + H[\tilde{p}_B^H]) = 1 + H[\tilde{p}_H^H],\\ \tilde{I} &= 1 + H[p^0] = 5.7\,\text{bits}.\end{aligned} \tag{26}$$

In order to estimate the average conditional-entropy index $\tilde{S}$ one requires the Shannon entropy $H[\tilde{p}_H^H]$, of the electron probability distribution of the anti-bonding stockholder hydrogen in the doubly excited singlet state of H_2, $\tilde{p}_H^H \equiv p_H^0 - \Delta p$, where $\Delta p(\boldsymbol{r}) = 2a(\boldsymbol{r})b(\boldsymbol{r})\left[1 + \frac{p_A^0(\boldsymbol{r})}{p_B^0(\boldsymbol{r})}\right]^{-1}$ (Eq. 18). One also observes, that the normalizations of the probability distributions of the free- and stockholder atoms further imply the closure relation

$$\int \Delta p(\boldsymbol{r})\, d\boldsymbol{r} = 0. \tag{27}$$

The $H[\tilde{p}_H^H]$ term can be realistically estimated from the previously reported [5,12] values of $H[p_H^0] = 4.18$ bits and (see Eq. 15) $H[\bar{p}_H^H] = H[p_H^0 + \Delta p] = 3.77$ bits, using the first-order expansion of the Shannon functional (in natural units, for log = ln):

$$\begin{aligned}\Delta H[\Delta p] &= H[p^0 + \Delta p] - H[p^0] \cong \int \left(\frac{\delta H}{\delta p(\boldsymbol{r})}\right)_{p^0} \Delta p(\boldsymbol{r})d\boldsymbol{r}\\ &= -\int \Delta p(\boldsymbol{r})[1 + \ln p^0(\boldsymbol{r})]d\boldsymbol{r} = -\int \Delta p(\boldsymbol{r}) \ln p^0(\boldsymbol{r})d\boldsymbol{r},\end{aligned} \tag{28}$$

where we have used Eq. 27. Therefore $\Delta H[\Delta p] \cong -\Delta H[-\Delta p]$ which implies

$$H[\tilde{p}_H^H] \cong H[p_H^0] - (H[\bar{p}_H^H] - H[p_H^0]) = 4.6\,\text{bits} \tag{29}$$

and hence (in bits): $\tilde{S} \cong 5.6$, $\tilde{N} = \tilde{S} + \tilde{I} \cong 11.3$.

Therefore, this nonbonding state of H_2 is characterized in the local resolution of atomic representation by the overall information-theoretic index higher than that describing the bonding (ground) state of H_2. This extra increase is solely due to the average entropy-covalency component, with the information-ionicity level of the bonding-state being conserved in the anti-bonding electron configuration of the molecule. This extra increase in the communication noise level reflects the polarization of the electron densities of the anti-bonded hydrogen atoms away from the bonding region between the two nuclei, into the non-bonding regions of space exhibiting very low probability values.

It should be also stressed, that the entropy/information descriptors of molecular communication channels in the local resolution reflect both the *intra*- and *inter*-atomic "promotions" in the molecule. The former characterizes what chemists call the "valence"-state of each AIM, while only the latter refers to the mutual "bonding" between two atoms. The extra "spreading" of the anti-bonding hydrogen atoms into the nonbonding regions of space, compared to the free-atom distribution, opposite to that observed in the bonding AIM of Fig. 3, contributes mainly to the internal promotion of each atom. Therefore, the extra-increase in their entropy-covalency of anti-bonding hydrogen atoms, compared to that describing their bonding analogs, should be more appropriately attributed to their internal "valency" in this molecular state. The conserved level of the information-flow index testifies to the same average degree of determinism (correlation, localization) in the probability scattering in the two molecular states.

3 Conclusion

The promolecular level of the bond-information in the local resolution of atomic probabilities, $N^0 \cong 9.4$ bits, which represents the initial-state reference for determining the bonding/anti-bonding displacements in the molecule, is much higher than the 1 bit value characterizing the related information channel of a single chemical bond in the integral (global) resolution of electronic events [5]. It should be observed, however, that the displacement $\Delta N = \bar{N} - N^0 \cong 1$ bit gives a connection to this previously reported estimate of the IT bond-order in H_2 from the integral probabilities in atomic representation. In the local AIM channels the bonding and anti-bonding molecular states generate an increase in the overall bond index to $\bar{N} \cong 10.5$ and $\tilde{N} \cong 11.3$ bits, respectively. As we have argued above this reflects both the AIM promotion and electron-sharing due to the mixing of AO into MO, which accompany a presence of the covalent bond or its opposite.

In the ground-state of H_2 both electrons occupy the bonding MO, relatively contracted (less diffused) compared to both the free-atom distribution and an even more spread anti-bonding MO defining the doubly-excited configuration of the molecule. Therefore, the increase in the noise-level observed in the bonding molecular state should be attributed solely to the electron delocalization towards the bond-partner. This increase is seen to be much higher in the anti-bonding state, due to a diffuse character of the MO involved. This difference reflects mainly the extra promotion (spread) of the anti-bonded AIM, away from the bonding region between the two nuclei.

It should be finally emphasized, that in the *local* probabilistic models one preserves the information about the relative phases of AO in MO. It is embodied in the corresponding MO distributions of Eqs. 14 and 17. This knowledge disappears in the global probabilities of AIM, generated by the quantum-mechanical superposition principle [5,33]. This shortcoming of the integral probabilistic models creates the necessity for using the conditional-probability projection techniques to establish the information channels reflecting the diminished multiplicity of chemical bonds in excited states [20]. As we have demonstrated in the present analysis the locally-resolved communication channels in the Hirshfeld-AIM representation are capable of distinguishing the bonding and anti-bonding electron configurations, as does the non-additive component of the molecular Fisher information in atomic resolution [9].

References

1. (a) R.A. Fisher, Proc. Cambridge Phil. Soc. **22**, 700 (1925); (b) See also B.R. Frieden, *Physics from the Fisher Information – A Unification* (Cambridge University Press, Cambridge 2000)
2. (a) C.E. Shannon, Bell System Tech. J. **27**, 379, 623 (1948); (b) See also C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication* (University of Illinois, Urbana, IL, 1949)
3. (a) S. Kullback, R.A. Leibler, Ann. Math. Stat. **22**, 79 (1951); (b) See also S. Kullback, *Information Theory and Statistics* (Wiley, New York, 1959)
4. N. Abramson, *Information Theory and Coding* (McGraw-Hill, New York, 1963)
5. R.F. Nalewajski, *Information Theory of Molecular Systems* (Elsevier, Amsterdam, 2006) and refs. therein.
6. (a) R.F. Nalewajski, Adv. Quant. Chem. **43**, 119 (2003); (b) Ibid. Int. J. Mol. Sci. **3**, 237 (2002)
7. R.F. Nalewajski, Chem. Phys. Lett. **372**, 28 (2003); **375**, 196 (2003)
8. R.F. Nalewajski, Mol. Phys. **104**, 255 (2006)
9. R.F. Nalewajski, Int. J. Quantum Chem. (K. Jankowski issue) (in press)
10. (a) R.F. Nalewajski, R.G. Parr, Proc. Natl. Acad. Sci. USA **97**, 8879 (2000); (b) R.F. Nalewajski, R.G. Parr, J. Phys. Chem. A **105**, 7391 (2001); (c) R.F. Nalewajski, R. Loska, Theoret. Chem. Acc. **105**, 374 (2001); (d) R.F. Nalewajski, Phys. Chem. Chem. Phys. **4**, 1710 (2002); (e) R.F. Nalewajski, J. Phys. Chem. A **107**, 3792 (2003); Ann. Phys. (Leipzig) **13**, 201 (2004); (f) R.G. Parr, P.W. Ayers, R.F. Nalewajski, J. Phys. Chem. A **109**, 3957 (2005)
11. R.F. Nalewajski, E. Broniatowska, Theor. Chem. Acc. **117**, 7 (2007)
12. R.F. Nalewajski, E. Broniatowska, J. Phys. Chem. A **107**, 6270 (2003)
13. F.L. Hirshfeld, Theoret. Chim. Acta **44**, 129 (1977)
14. (a) R.F. Nalewajski, J. Phys. Chem. A **104**, 11940 (2000); (b) Ibid. Mol. Phys. **102**, 531, 547 (2004); **103**, 451 (2005)
15. (a) R.F. Nalewajski, K. Jug, in *Reviews of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*, Vol. I, ed. by K.D. Sen (World Scientific, Singapore, 2002), p. 148; (b) R.F. Nalewajski, Struct. Chem. **15**, 391 (2004)
16. R.F. Nalewajski, Mol. Phys. **104**, 365, 493, 1977, 2533 (2006)
17. R.F. Nalewajski, J. Math. Chem. **38**, 43 (2005)
18. R.F. Nalewajski, Theoret. Chem. Acc. **114**, 4 (2005)
19. R.F. Nalewajski, Chem. Phys. Lett. **386**, 265 (2004)
20. R.F. Nalewajski, Mol. Phys. **104**, 2533, 3339 (2006)
21. R.F. Nalewajski, J. Math. Chem. **43**, 265 (2008)
22. R.F. Nalewajski, J. Math. Chem. **43**, 780 (2008)
23. R.F. Nalewajski, J. Math. Chem. (in press) doi:10.1007/s10910-007-9318-7
24. R.F. Nalewajski, J. Math. Chem. (in press) doi:10.1007/s10910-007-9345-4
25. R.F. Nalewajski, J. Math. Chem. (in press) doi:10.1007/s10910-008-9385-4
26. R.F. Nalewajski, J. Math. Chem. (in press) doi:10.1007/s10910-008-9380-9
27. R.F. Nalewajski, E. Broniatowska, Chem. Phys. Lett. **376**, 33 (2003)
28. R.F. Nalewajski, A.M. Köster, S. Escalante, J. Phys. Chem. A **109**, 10038 (2005)

29. R.F. Nalewajski, J. Phys. Chem. A **111**, 4855 (2007)
30. R.F. Nalewajski, E. Świtka, A. Michalak, Int. J. Quantum Chem. **87**, 198 (2002)
31. R.F. Nalewajski, E. Świtka, Phys. Chem. Chem. Phys. **4**, 4952 (2002)
32. R.F. Nalewajski, E. Broniatowska, Int. J. Quant. Chem. **101**, 349 (2005)
33. R.F. Nalewajski, Mol. Phys. **104**, 1977 (2006)