J Math Chem (2009) 45:776–789
DOI 10.1007/s10910-008-9380-9

ORIGINAL PAPER

# Manifestations of Pauli exclusion principle in communication-theory of the chemical bond

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Received: 25 January 2008 / Accepted: 26 February 2008 / Published online: 14 June 2008


**Abstract** The implications of the Pauli exclusion principle for the entropy/information indices of the chemical bond formulated within the communication theory approach are explored. The spatial information channels in the local, *two*-electron resolution are derived for the singlet and triplet states of two electrons, modeling the chemical bonding and non-bonding states in a molecule, respectively. Their average conditional-entropy (covalency) and mutual-information (ionicity) descriptors are compared against those characterizing the separate atoms and an upper-bound to the information-theoretic bond-order for the molecular orbital "events" is determined. An illustrative application to AO channels in $H_2$ generates numerical values of the information-theoretic indices for this prototype covalent bond. The molecular information systems are interpreted as the ensemble averages of the elementary deterministic (zero-covalency) information networks. Examples of such a channel synthesis include model binary channels and that representing the elementary valence-bond (*VB*) covalent structure in $H_2$. The ensemble representation of the spin channel for the triplet state of two electrons, averaged over the three spin-projection components, offers an entropic perspective on the spin-pairing in the bond-formation process. The spin-paired (singlet) communication system is obtained by maximizing in the ensemble-average communication system of the triplet state the information-flow (ionicity) to its capacity level.

**Keywords** Bond indices · Chemical bonding · Communication theory · Covalent/ionic components · Elementary deterministic channels · Ensemble of communication channels · Hydrogen molecule · Information theory · Molecular communication systems · Pauli exclusion principle · Singlet channels · Theory of chemical bonds · Triplet channels

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## 1 Introduction

The information theory (IT) [1–4] has been recently applied to several issues in the theory of electronic structure [5]. In particular, the communication theory of the chemical bond has been developed in atomic resolution, for both the molecular system as a whole and its constituent fragments [5–16]. In this approach the molecule is interpreted as an information channel in which the molecular or "promolecular" input atomic probabilities are propagated ("scattered") via the network of chemical bonds connecting the system constituent atoms. The bond entropy-covalency (conditional entropy) descriptor of such a molecular probability network measures its average communication "noise", which reflects the extra "disorder" (indeterminacy) generated in the electron probabilities due to a delocalization in the molecule. The stronger is the probability scattering from a given atomic "input" among all atomic "outputs", i.e., the higher the degree of the electron sharing between the system constituent atoms, the stronger the system "noise" level and its bond covalency. The overall information-ionicity (mutual-information) index of all bonds in the molecule then measures the amount of information flowing through such a molecular information network [5], from the *promolecular* input to the *molecular* output, thus emphasizing the "order" (determinacy) in the molecular probability scattering.

Therefore, in this probabilistic model the covalent component reflects the *delocalization* aspect of the system valence electrons, via the network of all chemical bonds generated by the occupied molecular orbitals (MO), while the ionic component describes the complementary *localization* facet of the molecular electronic structure. This IT description explains the information origins of the chemical bond and it accounts in a dichotomous way for the intuitively expected competition between the covalent and ionic components of the chemical bond. The theory extensions into the orbital and local descriptions have also been proposed [17–21].

The spatial probability distributions of electrons reflect the intervention of the Pauli exclusion principle, which gives rise to the exchange correlation between spin-like electrons. In the present work we shall examine some of its manifestations by exploring the local information channels of two electrons in the model molecular singlet and triplet states, respectively, and by comparing the resulting estimates of the average (global) entropy/information indices against those describing the reference state of two non-bonded (separate) atoms.

The ensemble-average representation of the covalent communication systems, recently introduced within the communication theory perspective on the valence-bond (VB) theory [22], will be used to synthesize the molecular channels from the elementary channels, for which the conditional-entropy index identically vanishes, thus resolving the noisy (covalent) channels in terms of the elementary deterministic (ionic) information networks. The illustrative examples of such a synthesis/resolution will be given, related to the binary channels, spatial covalent VB structure, and the average spin-channel of two electrons in the triplet sate [5]. The latter application admits an ensemble interpretation of the spin-pairing in the covalent chemical bond.

In what follows the entropic quantities are measured in bits, which correspond to the base 2 of the logarithmic measure of information [2]. The bold symbol **X** denotes the square or rectangular matrix, the bold-italic $\boldsymbol{X}$ stands for a row vector, while italic $X$ corresponds to a scalar quantity.

## 2 Spatial singlet and triplet MO-channels and their entropy/information descriptors

Let us examine the two-electron information systems in local resolution implied by the general spatial parts $\Phi_S(1,2) = 2^{-1/2}[\varphi(1)\psi(2) + \varphi(2)\psi(1)]$ and $\Phi_T(1,2) = 2^{-1/2}[\varphi(1)\psi(2) - \varphi(2)\psi(1)]$ of the molecular singlet $\Psi_S(1,2) = \Phi_S(1,2)\Sigma_0^S(1,2)$ and triplet $\Psi_T(1,2;M) = \Phi_T(1,2)\Sigma_M^T(1,2)$ states of two electrons occupying the specified pair of the (real) orthonormal MO, $\varphi$ and $\psi$. They generate the associated probability distributions $p_\varphi(\boldsymbol{r}) = \varphi^2(\boldsymbol{r})$ and $p_\psi(\boldsymbol{r}) = \psi^2(\boldsymbol{r})$, as well as their overlap distribution $g(\boldsymbol{r}) = \varphi(\boldsymbol{r})\psi(\boldsymbol{r})$. In accordance with Pauli's requirement of the overall anti-symmetric character of the *two*-fermion wave-function the corresponding spin functions of two electrons, $\Sigma_0^S(1,2)$ and $\{\Sigma_M^T(1,2), M = -1, 0, 1\}$, for the overall spin projection $M\hbar$, are anti-symmetric and symmetric with respect to exchanging the identity of two electrons, respectively.

The singlet two-electron distribution,

$$\begin{aligned} P^S(1,2) &= |\Phi_S(1,2)|^2 \\ &= \frac{1}{2}\left\{p_\varphi(1)p_\psi(2) + p_\varphi(2)p_\psi(1) + 2g(1)g(2)\right\}, \\ \int\int P^S(1,2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 &= 1, \end{aligned} \tag{1}$$

partly integrates to the molecular one-electron input $[P^S(1)]$ and output$[P^S(2)]$ densities, respectively,

$$\begin{aligned} \int P^S(1,2)d\boldsymbol{r}_2 \equiv P^S(1) = \frac{1}{2}\left[p_\varphi(1) + p_\psi(1)\right] \text{ and} \\ \int P^S(1,2)d\boldsymbol{r}_1 = P^S(2) = \frac{1}{2}\left[p_\psi(2) + p_\varphi(2)\right]. \end{aligned} \tag{2}$$

In the last equation we have observed that the orthogonality of two MO, $\langle\varphi|\psi\rangle = 0$, implies that $\int g(\boldsymbol{r})d\boldsymbol{r} = 0$.

By convention [21], the local MO-events of electron 1, $\boldsymbol{A}(1) = \{\varphi(1), \psi(1)\}$, determine the input in the molecular information system, with the molecular input probabilities $P^S[\varphi(1)] = \frac{1}{2}p_\varphi(1)$ and $P^S[\psi(1)] = \frac{1}{2}p_\psi(1)$, respectively (see Fig. 1). Similarly, the local MO-events of electron 2, $\boldsymbol{B}(2) = \{\varphi(2), \psi(2)\}$, define the output in the molecular information channel, as also indicated in the schematic diagram of Fig. 1.

The two admissible variants of the molecular singlet channel shown in this figure correspond to alternative limiting interpretations of the MO overlap density term in $P^S(1,2)$. More specifically, in the *maximum-covalency* interpretation of panel *a* it is equally attributed to the two diagonal probability propagations $\varphi(1) \to \varphi(2)$ and

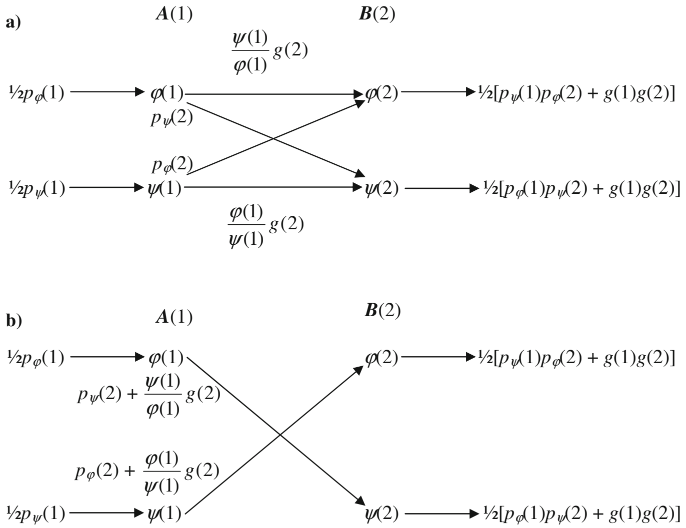


**Fig. 1** The maximum covalency (panel *a*) and ionicity (panel *b*) local information channels of two electrons in the spatial singlet state

$\psi(1) \to \psi(2)$, and in the *maximum-ionicity* interpretation of panel *b* it is equally ascribed as the correction to the two cross (off-diagonal) scatterings $\varphi(1) \to \psi(2)$ and $\psi(1) \to \varphi(2)$. The former case gives rise to a more "noisy" (IT-covalent) information channel, while the latter represents a more deterministic (IT-ionic) probability propagation in the molecule. Their associated conditional entropy and mutual-information descriptors, mark the upper bounds of the delocalization-covalency and localization-ionicity, respectively, available in this local singlet channel.

The triplet spatial function $\Phi_T(1, 2)$ expressed in terms of MO generates the two-electron distribution of the simultaneous local input-output events,

$$\begin{aligned} P^T(1, 2) &= |\Phi_T(1, 2)|^2 \\ &= \frac{1}{2}\left\{p_\varphi(1)p_\psi(2) + p_\varphi(2)p_\psi(1) - 2g(1)g(2)\right\}, \\ \int\int P^T(1, 2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 &= 1, \end{aligned} \tag{3}$$

which admits only the probability scattering in the "deterministic" channel of Fig. 2, due to the negative character of the overlap probability correction.

The two-electron conditional-entropy density resulting from the singlet channel of Fig. 1a reads:

$$\begin{aligned} S^S(1, 2)_{max.} &= S^S[\boldsymbol{B}(2)|\boldsymbol{A}(1)]_{max.} \\ &= -\frac{1}{2}\Big[p_\psi(1)p_\varphi(2)\log_2 p_\varphi(2) \\ &\quad + p_\varphi(1)p_\psi(2)\log_2 p_\psi(2) + g(1)g(2)\log_2 g^2(2)\Big]. \end{aligned} \tag{4}$$

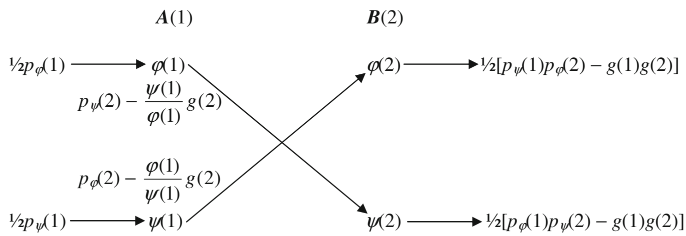


**Fig. 2** The local information channel of two electrons in the spatial triplet state

It gives the following upper-bound to the average communication noise (IT-covalency) in the MO-singlet communication network:

$$\langle S^S \rangle_{max.} = S^S(\boldsymbol{B}|\boldsymbol{A})_{max.} = \iint S^S(1,2)_{max.} \quad d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{1}{2}\left\{H[p_\psi] + H[p_\varphi]\right\}, \tag{5}$$

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

$$H[p] = -\int p(\boldsymbol{r}) \log_2 p(\boldsymbol{r}) d\boldsymbol{r}. \tag{6}$$

Therefore, the maximum value of the communication noise in this model singlet channel amounts to the arithmetic average of the Shannon entropies of the two MO probability distributions.

The upper-bound of the singlet IT-ionicity is determined by a more "deterministic" channel of Fig. 1b. Let us denote the two cross-over conditional probabilities of this information system by

$$\bar{p}_\psi(2) = p_\psi(2) + \frac{\psi(1)}{\varphi(1)} g(2) \quad \text{and} \quad \bar{p}_\varphi(2) = p_\varphi(2) + \frac{\varphi(1)}{\psi(1)} g(2). \tag{7}$$

In terms of these modified MO probabilities the maximum of the two-electron mutual-information density in this model singlet state of two electrons becomes:

$$\begin{aligned} I^S(1,2)_{max.} &= I^S[\boldsymbol{A}(1) : \boldsymbol{B}(2)]_{max.} \\ &= P^S(1,2) - 1/2\,\bar{p}_\psi(2) p_\varphi(1) \log_2 p_\varphi(1) \\ &\quad -\frac{1}{2}\bar{p}_\varphi(2) p_\psi(1) \log_2 p_\psi(1). \end{aligned} \tag{8}$$

Taking into account the MO orthogonality, which implies

$$\int \bar{p}_\varphi(2) d\boldsymbol{r}_2 = \int p_\varphi(2) d\boldsymbol{r}_2 = \int \bar{p}_\psi(2) d\boldsymbol{r}_2 = \int p_\psi(2) d\boldsymbol{r}_2 = 1, \tag{9}$$

one thus obtains the maximum average IT-ionicity in the model singlet channel:

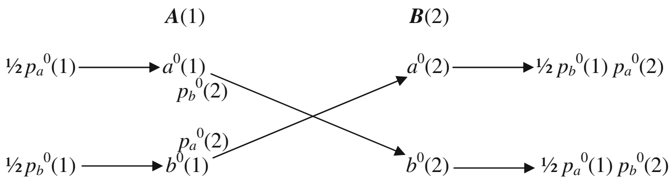


**Fig. 3** The spatial two-electron (triplet) channel in the separate-atom (dissociation) limit $A^0 + B^0$

$$\begin{aligned}\langle I^S\rangle_{max.} &= I^S(\boldsymbol{A}:\boldsymbol{B})_{max.}\\ &= \int\int I^S(1,2)_{max.}\, d\boldsymbol{r}_1 d\boldsymbol{r}_2\\ &= 1+\frac{1}{2}\left\{H[p_\psi]+H[p_\varphi]\right\} = 1+\langle S^S\rangle_{max.}\end{aligned} \tag{10}$$

Hence, Eqs. 5 and 10 give the corresponding maximum estimate of the total bond index of the MO-channel:

$$\langle N^S\rangle_{max.} = N^S(\boldsymbol{A};\boldsymbol{B})_{max.} = \langle S^S\rangle_{max} + \langle I^S\rangle_{max.} = 1 + H[p_\psi] + H[p_\varphi]. \tag{11}$$

Now, let us briefly examine the reference dissociation channel, in which the two (spin-like, indistinguishable) electrons occupy singly the two Atomic Orbitals (AO) $a^0$ and $b^0$ originating from the separate (free) atoms $A^0$ and $B^0$, respectively, which generate the probability distributions $p_a^0(\boldsymbol{r}) = [a^0(\boldsymbol{r})]^2$ and $p_b^0(\boldsymbol{r}) = [b^0(\boldsymbol{r})]^2$. This separate-atom channel is shown in Fig. 3. It results from the corresponding (anti-symmetric) wave-function,

$$\Phi_T^0(1,2) = |a^0 b^0| = 2^{-1/2}[a^0(1)b^0(2) - a^0(2)b^0(1)], \tag{12}$$

and the associated two-electron distribution for these non-overlapping atoms:

$$\begin{aligned}P_T^0(1,2) &= |\Phi_T^0(1,2)|^2\\ &= \frac{1}{2}\left[p_a^0(1)p_b^0(2) + p_a^0(2)p_b^0(1)\right],\\ \int\int P_T^0(1,2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 &= 1.\end{aligned} \tag{13}$$

The following average bond indices describe this truly non-bonding limit:

$$\begin{aligned}\langle S_T^0\rangle &= S^T(\boldsymbol{B}^0|\boldsymbol{A}^0) = \frac{1}{2}\left\{H[p_a^0]+H[p_b^0]\right\},\\ \langle I_T^0\rangle &= I^T(\boldsymbol{A}^0:\boldsymbol{B}^0) = 1+\frac{1}{2}\left\{H[p_a^0]+H[p_b^0]\right\},\\ \langle N_T^0\rangle &= N^T(\boldsymbol{A}^0;\boldsymbol{B}^0) = 1 + H[p_a^0] + H[p_b^0].\end{aligned} \tag{14}$$

## 3 Bond indices of illustrative AO-channels in $H_2$

In this section we examine the two-electron information systems in local resolution of the AO events, which are implied by the bonding (singlet), ground-state and the non-bonding (triplet), singly-excited) state of two electrons in the simplest, two-orbital model of the covalent chemical bond in $H_2 \equiv$ A–B. We shall also estimate their associated integral entropy/information descriptors. In this minimum basis set description the two hydrogen atoms contribute a single electron each, initially occupying the two (mutually orthogonalized) $1s$ atomic orbitals (OAO) centered on two nuclei, $\boldsymbol{\chi}(\boldsymbol{r}) = \{a(\boldsymbol{r}) \in \mathrm{A}, b(\boldsymbol{r}) \in \mathrm{B}\}$, which generate the respective atomic probability distributions: $\{p_a(\boldsymbol{r}) = a^2(\boldsymbol{r}), p_b(\boldsymbol{r}) = b^2(\boldsymbol{r})\}$. These basis functions give rise to the bonding and antibonding MO: $\varphi^+ = 2^{-1/2}(a+b)$ and $\varphi^- = 2^{-1/2}(a-b)$, respectively, in terms of which

$$\begin{aligned}
\Phi_S(1,2) &= \varphi^+(1)\varphi^+(2) = 2^{-1/2}[\Phi_{cov.}(1,2) + \Phi_{ion}(1,2)],\\
\Phi_{cov.}(1,2) &= 2^{-1/2}[a(1)b(2) + b(1)a(2)],\\
\Phi_{ion}(1,2) &= 2^{-1/2}[b(1)b(2) + a(1)a(2)];\\
\Phi_T(1,2) &= 2^{-1/2}[\varphi^+(1)\varphi^-(2) - \varphi^+(2)\varphi^-(1)] \equiv |\varphi^+\varphi^-| = |ab|; \qquad (15)
\end{aligned}$$

here the two-electron basis functions $\Phi_{cov.}(1,2)$ and $\Phi_{ion}(1,2)$ denote the familiar covalent and ionic VB-structures. The final equality between the two spatial Slater determinants determining $\Phi_T(1,2)$ follows from the fact that the singly-occupied MO are physically *equivalent* to the singly occupied OAO, thus generating the same wave-function.

The singlet spatial function determines the associated two-electron distribution:

$$\begin{aligned}
P_S(1,2) &= |\Phi_S(1,2)|^2 = \frac{1}{4}[\bar{p}_a(1) + \bar{p}_b(1)][\bar{p}_a(2) + \bar{p}_b(2)]\\
&= \frac{1}{4}[\bar{p}_a(1)\bar{p}_a(2) + \bar{p}_a(1)\bar{p}_b(2) + \bar{p}_b(1)\bar{p}_a(2) + \bar{p}_b(1)\bar{p}_b(2)]\\
&\equiv \{P[a(1),a(2)] + P[a(1),b(2)] + P[b(1),a(2)]\\
&\quad + P[b(1),b(2)]\}, \qquad (16)
\end{aligned}$$

where the molecularly modified probability distributions of bonded atoms

$$\bar{p}_x(\boldsymbol{r}) = p_x(\boldsymbol{r}) + a(\boldsymbol{r})b(\boldsymbol{r}) \equiv p_x(\boldsymbol{r}) + c(\boldsymbol{r}), \quad x = a, b. \qquad (17)$$

In the last line of Eq. 16 we have interpreted the four contributions as corresponding probabilities of the simultaneous OAO events of two electrons. Their partial integrations over coordinates of the single electron give rise to the molecular probabilities $\boldsymbol{P}(1) = \{P[a(1)], P[b(1)]\}$ of the "input" events $\boldsymbol{A}(1) = \{a(1), b(1)\}$ and the molecular probabilities $\boldsymbol{P}(2) = \{P[a(2)], P[b(2)]\}$ of the output events $\boldsymbol{B}(2) = \{a(2), b(2)\}$, respectively:

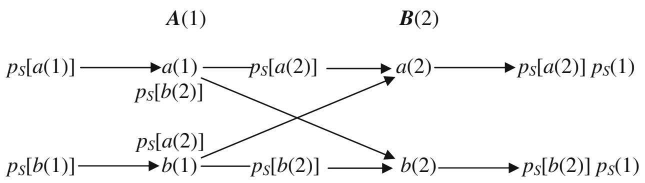


**Fig. 4** The spatial two-electron singlet channel in $H_2$

$$\int P_S(1,2)d\boldsymbol{r}_2 = \frac{1}{2}[\bar{p}_a(1) + \bar{p}_b(1)] = p_S[a(1)] + p_S[b(1)] = p_S(1),$$
$$\int P_S(1,2)d\boldsymbol{r}_1 = \frac{1}{2}[\bar{p}_a(2) + \bar{p}_b(2)] = p_S[a(2)] + p_S[b(2)] = p_S(2). \quad (18)$$

Hence the molecular conditional probabilities of the molecular output, given the molecular input:

$$\begin{aligned}\mathbf{P}[\boldsymbol{B}(2)|\boldsymbol{A}(1)] &= \Big\{P[y(2)|x(1)] \\ &= P[x(1), y(2)]/p[x(1)] = p[y(2)] \\ &= \frac{1}{2}\bar{p}_y(2), x, y = a, b\Big\}.\end{aligned} \quad (19)$$

These probabilities define the two-electron communication system of the local AO-events shown in Fig. 4. Its conditional-entropy density reads:

$$\begin{aligned}S_S[\boldsymbol{B}(2)|\boldsymbol{A}(1)] = S_S(1,2) &= -\sum_x \sum_y p_S[x(1)]p_S[y(2)]\log_2 p_S[y(2)] \\ &= -p_S(1)\sum_y p_S[y(2)]\log_2 p_S[y(2)] \equiv p_S(1)\sum_y h[y(2)] \\ &= p_S(1)\{p_S(2) - \frac{1}{2}\sum_y \bar{p}_y(2)\log_2 \bar{p}_y(2)\} \equiv p_S(1)\{p_S(2) \\ &\quad -\frac{1}{2}\sum_y h[\bar{y}(2)]\}.\end{aligned} \quad (20)$$

Integrating over positions of two electrons then gives the corresponding average conditional-entropy in the system ground-state:

$$\begin{aligned}S_S &= \int\int S_S(1,2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &= 1 + \frac{1}{2}\sum_y H[\bar{p}_y],\end{aligned} \quad (21)$$

where the Shannon entropy

$$\begin{aligned}H[\bar{p}_y] &= \int h[\bar{y}(\boldsymbol{r})]d\boldsymbol{r} \\ &= -\int \bar{p}_y(\boldsymbol{r})\log_2 \bar{p}_y(\boldsymbol{r})d\boldsymbol{r}.\end{aligned} \quad (22)$$

The probability distribution of the bonded-atom (Eq. 3) should strongly resemble that of the Hirshfeld [5,23–25] ("stockholder") *Atoms-in-Molecules* (AIM), $\bar{p}_y \cong p_y^H$, for which $H[p_y^H] = 3.8$ [5,25], and hence $S_S \cong 4.8$.

Let us now examine the two-electron mutual-information density of the communication channel of Fig. 4,

$$\begin{aligned} I_S[\boldsymbol{A}(1):\boldsymbol{B}(2)] &= I_S(1,2) \\ &= \sum_x \sum_y p_S[x(1)]p_S[y(2)]\log_2\{p_S[y(2)]/(p_S[y(2)]p_S(1))\} \\ &= -p_S(2)p_S(1)\log_2 p_S(1), \end{aligned} \tag{23}$$

which gives rise to the average IT-ionicity index

$$I_S = \int\int I_S(1,2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 = H[p_S]. \tag{24}$$

This index can be also estimated using the previously reported molecular one-electron entropy $H[\rho] = 6.6$ [5,25], where $\rho = 2p_S$ stands for the molecular ground-state density: $H[p_S] = \frac{1}{2}H[\rho] + 1 = 4.3$ bits. These local-resolution estimates for the Hirshfeld AIM thus predict the overall bond index in $H_2 : N_S = S_S + I_S = 9.1$.

It is of interest to compare these bonding-state predictions with the corresponding descriptors of the molecular non-bonding (triplet) state of Eq. 15 and the promolecular reference state $\Phi_T^0(1,2) = |a^0 b^0|$ of two indistinguishable electrons occupying the non-overlapping, separated-atom orbitals $\boldsymbol{\chi}^0(\boldsymbol{r}) = \{a^0(\boldsymbol{r}), \mathrm{b}^0(\boldsymbol{r})\}$, giving rise to the atomic probability densities $\{p_a^0(\boldsymbol{r}), p_b^0(\boldsymbol{r})\}$, at large internuclear distances of the *Separated-Atom-Limit* (SAL), when the differential overlap vanishes: $c^0(\boldsymbol{r}) = a^0(\boldsymbol{r})b^0(\boldsymbol{r}) = 0$. This wave-function determines the two-electron information channel shown in Fig. 3. Its average conditional-entropy (IT-covalency) index $S_T^0 \equiv \langle S_T^0\rangle = H^0 = \frac{1}{2}\sum_x H[p_x^0] = 4.2$ and the complementary mutual-information (IT-ionicity) index $I_T^0 \equiv \langle I_T^0\rangle = 1 + H^0 = 5.2$ [5,25] thus generate the overall index $N_T^0 \equiv \langle N_T^0\rangle = S_T^0 + I_T^0 = 9.4$. Therefore, in the local AO-resolution the bonding (singlet) state generates an increased value of the average two-electron covalency (electron delocalization) and decreased level of the average two-electron ionicity (electron localization), relative to the reference, non-bonding state of the two separated atoms. The molecular channel thus becomes somewhat more "noisy" (less deterministic) compared to the dissociation limit as a result of forming the chemical bond.

The molecular Slater determinant $\Phi_\mathrm{T}(1,2) = |ab|$ involves the non-vanishing differential overlap $c(\boldsymbol{r}) \neq 0$, which determines the effective exchange "holes" $h_x^a(2\,|1)$ and $h_x^b(2\,|1)$ around the reference electron 1 in the two-electron probability density for the triplet state:

$$\begin{aligned} P_T(1,2) = |\Phi_T(1,2)|^2 &= \frac{1}{2}\,[p_a(1)p_b(2) + p_b(1)p_a(2) - 2c(1)c(2)] \\ &= \frac{1}{2}\,\{[p_a(1)p_b(2) - c(1)c(2)] + [p_b(1)p_a(2) - c(1)c(2)]\} \end{aligned}$$

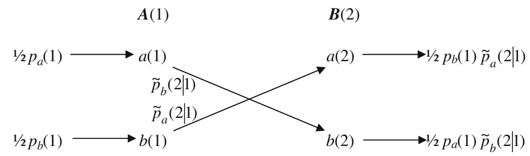


**Fig. 5** The spatial two-electron triplet channel in $H_2$

$$\equiv \frac{1}{2}\left\{p_a(1)[p_b(2) + h_x^b(2\,|1)] + p_b(1)[p_a(2) + h_x^a(2\,|1)]\right\}$$
$$\equiv \frac{1}{2}\{p_a(1)\tilde{p}_b(2\,|1) + p_b(1)\tilde{p}_a(2\,|1)\}. \quad (25)$$

We further observe that, due to the orthonormality of OAO,

$$\int \tilde{p}_b(2\,|1)d\boldsymbol{r}_2 = \int p_b(2)d\boldsymbol{r}_2 = \int \tilde{p}_a(2\,|1)d\boldsymbol{r}_2 = \int p_a(2)d\boldsymbol{r}_2 = 1. \quad (26)$$

The distribution of Eq. 25 determines the communication system of Fig. 5. It generates the associated IT-ionicity density $I_T(1,2) = P_T(1,2) - \frac{1}{2}\sum_x p_x^0(1)\log_2 p_x^0(1)$ and hence the average mutual-information index $I_T = 1 + \frac{1}{2}\sum_x H[p_x^0] = 5.2$ bits. The atomic electron distributions in the molecular triplet state are those characterizing the OAO of the free atoms at molecular positions, which determine the system *promolecule* [23]. Therefore, the probability densities $(p_a, p_b)$ are already partly delocalized compared to $(p_a^0, p_b^0)$, thus being close to the Hirshfeld AIM distributions $(p_a^H, p_b^H)$. Therefore, interpreting the triplet channel as the promolecular channel consisting of two mutually-closed Hirshfeld atoms gives $S_T \cong \frac{1}{2}\sum_x H[p_x^H] = 3.8$ [5,25]. Such an assumption correctly recovers the mutual-information (IT-ionicity) index $I_T = I_T^0 = 1 + H^0 = 5.2$ thus generating the overall index $N_T = S_T + I_T \cong 9$.

To summarize, although both molecular states slightly diminish the initial, "promolecular" bond index $N^0 = 9.4$, $N^S = 9.1 \cong N^T = 9$, a manifestation of an effective contraction of the AIM distributions, they are seen to roughly conserve it at about 9 bits value. The bonding (singlet) channel exhibits an increased level of the average communication noise and a diminished flow of information, relative to SAL-estimates, while the opposite trends are detected in the non-bonding (triplet) channel, which in fact describes the promolecular reference state.

It should be stressed, that these AO-channels differ from the MO-channels discussed in Sect. 2, since the two approaches differ in their choices of the input/output "events". Since in the singlet (bonding) state the two electrons occupy the bonding MO $\varphi = \psi = \varphi^+$, its probability distribution is given by the "shape" factor of the molecular electron density: $p = (\varphi^+)^2 = \frac{\rho}{2}$. One can therefore use the previously reported [5,25] value of $H[\rho] = 6.6$ to estimate

$$H[p] = \frac{1}{2}H[\rho] + 1 = 4.3, \quad (27)$$

and hence also the bounds of Eqs. 5, 10, and 11,

$$\langle S^S \rangle_{max} = 4.3,\ \langle I^S \rangle_{max} = 5.3,\ \langle N^S \rangle_{max.} = 9.6, \tag{28}$$

which correspond to the two-electron MO-channels. A comparison of the total index with those estimated from the local AO-channels shows that both approaches predict roughly 9 bits of the total bond index, with the AO events generating a slightly higher value of the entropy covalency.

## 4 Ensemble-average channels of deterministic components

A straightforward superposition of probabilities implies that any non-deterministic (covalent) communication channel, exhibiting a finite conditional entropy (noise, covalency) component, can be expressed as the ensemble average of the relevant deterministic channels, in which only the mutual-information (information-flow, ionic) descriptor does not vanish. Consider as an illustration of this classical rule the binary channels (*BC*) of Fig. 6, either symmetric (*SBC*, panel *a*), defined by a single crossover conditional probability $\omega$, or non-symmetric (*NBC*, panel *b*), in which two such parameters are required to fully determine the communication network between the system input $\boldsymbol{A} = (a_1, a_2)$ and output $\boldsymbol{B} = (b_1, b_2)$ events, described by the conditional probabilities of the output given input, $\mathbf{P}(\boldsymbol{B}|\boldsymbol{A}) = \{P(b_j|a_i) \equiv P(j|i)\}$. For any given input they satisfy the usual normalization: $\sum_j P(j|i) = 1$. In the proper communication system, as opposed to its deterministic components, the input and output

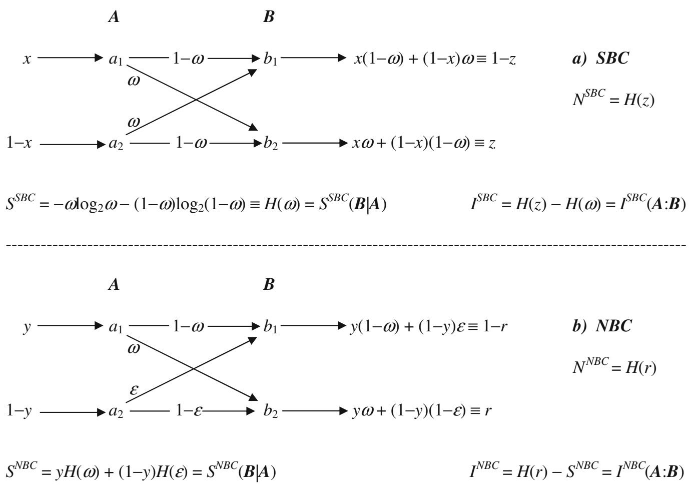


**Fig. 6** Examples of binary information systems consisting of two inputs and outputs: the symmetric binary channel (*SBC*) defined by a single independent conditional cross-over probability $P(b_2|a_1) = P(b_1|a_2) = \omega$ (panel *a*) and a general non-symmetric binary channel (*NBC*) exhibiting different cross-over probabilities $P(b_2|a_1) = \omega$ and $P(b_1|a_2) = \varepsilon$. Relevant expressions for the entropy/information bond descriptors (in bits), including the conditional-entropy *S*(IT-covalency), mutual-information *I* (IT-ionicity), and total bond index $N = S + I$, are also reported

probabilities, $\boldsymbol{P}(\boldsymbol{A}) = \{P(a_i) \equiv P(i)\}$ and $\boldsymbol{P}(\boldsymbol{B}) = \{P(b_j) \equiv P(j)\}$, respectively, are also assumed to be normalized: $\sum_i P(i) = \sum_j P(j) = 1$.

The elementary deterministic channels for representing the *SBC* are shown in Fig. 7a, while Fig. 7b presents a related resolution of the *NBC* of Fig. 6. In Figs 8 and 9 two particular applications of such an ensemble partition are presented. In Fig. 8 the elementary deterministic channels of panels *a* and *b*, representing the ionic and

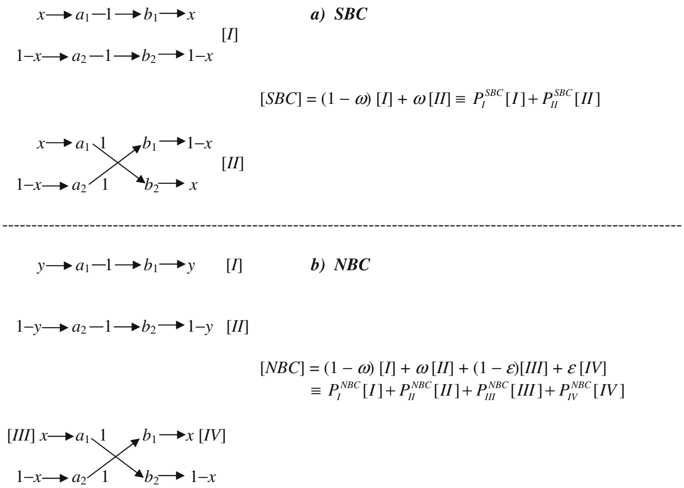


**Fig. 7** Ensemble-average resolutions of the binary channels of Fig. 6 into the relevant elementary deterministic channels $\{[\alpha]\}$, with the appropriate probability weights $\{P_\alpha^{BC}\} : [BC] = \sum_\alpha P_\alpha^{BC}[\alpha]$

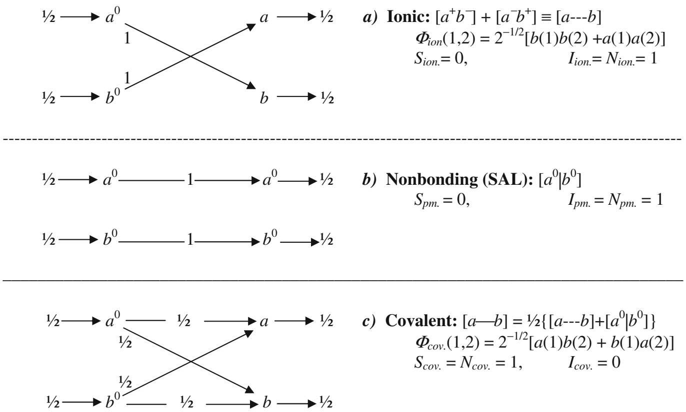


**Fig. 8** The independent (deterministic) communication channels for the elementary ionic and non-bonding (SAL) structures in the homonuclear-diatomic $A_1 - A_2 \equiv a - b$, and the dependent (scattering) channel [*a*–*b*] for the covalent structure expressed as the ensemble average of the ionic and non bonding channels with equal probability-weights: $[a—b] = \frac{1}{2}\left\{[a{-}{-}{-}b] + [a^0|b^0]\right\}$. The conditional-entropy *S* (IT-covalency), mutual-information *I* (IT-ionicity), and total $N = S + I$ bond indices (in bits) for each channel are also reported for equal input probabilities $P(a^0) = P(b^0) = \frac{1}{2}$ giving rise to equal output probabilities $P(a) = P(b) = \frac{1}{2}$

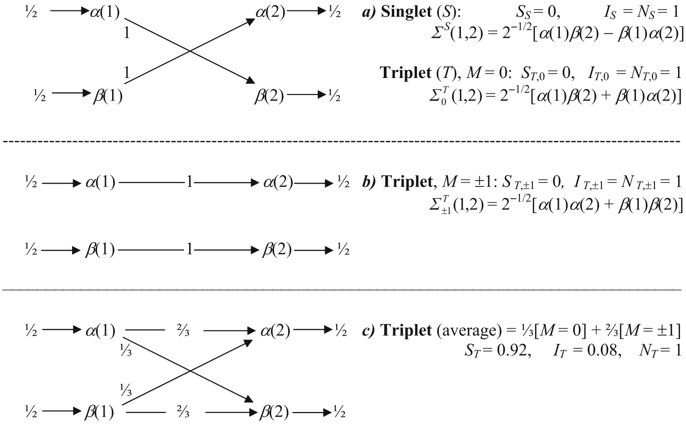


**Fig. 9** The deterministic spin channels of two electrons (panels *a* and *b*) for their singlet and triplet states and the ensemble average triplet communication channel (panel *c*) : $\frac{1}{3}[M = 0] + \frac{2}{3}[M = \pm 1]$. The corresponding bond indices for each channel are also reported for the equal input probabilities $P[\alpha(1)] = P[\beta(1)] = \frac{1}{2}$ giving rise to equal output probabilities $P[\alpha(2)] = P[\beta(2)] = \frac{1}{2}$

non-bonding (SAL) valence bond (*VB*) structures of a homonuclear diatomic, are used to construct the associated information system corresponding to the covalent structure of panel *c*. Recently, such elementary diatomic channels have been used to generate the communication systems of the *VB* structures in the polyatomic $\pi$-electron systems [26]. Figure 9 reports how the average spin channel for the triplet state of two electrons (panel *c*) can be decomposed in terms of the elementary deterministic triplet channels [$M$] for the overall spin projection measured by the resultant quantum number $M = 0, \pm 1$, respectively. As a result of the ensemble mixing of the purely IT-ionic elementary channels [see the associated mutual-information (information-flow) indices $I \equiv I(\boldsymbol{A} : \boldsymbol{B})$] the IT-covalency is generated in the average channels, as explicitly reflected by the reported conditional-entropy (communication noise) indices $S \equiv S(\boldsymbol{B}|\boldsymbol{A})$.

It follows from Fig. 9 that the spin-pairing, e.g., that accompanying a formation of the covalent chemical bond A–B, when the spatial factor $\Phi_{cov.}(1, 2)$ is accompanied by the singlet spin function $\Sigma^S(1, 2)$ giving rise to the information channel of Fig. 9a, involves a complete transformation of the average spin-covalency $S_T = 0.92$ present in the average triplet spin channel 9*c* into the same amount of spin-ionicity, so that in the purely ionic, deterministic singlet channel of Fig. 9a, only 1 bit of the spin-ionicity remains. This signifies that no information is dissipated in the form of the communication noise in this channel.

This offers the IT perspective on the spin-pairing in the bond-formation process, which amounts to a removal of the contribution from the $[M = \pm 1]$ channel in the ensemble average triplet channel. Clearly, by the Hund's rule, the triplet spin state is favored energetically, so that spin pairing in the covalent *VB* structure 8*c* can have only an *entropic* origin. As we have already argued above, the singlet communication system is obtained by maximizing the information-flow in the ensemble average triplet channel to the channel capacity level of $I = 1$.

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