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ORIGINAL PAPER

Communication-theory perspective on valence-bond theory

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Abstract The information-theoretic (IT) approach to the electronic structure of molecules, called the Communication Theory of the chemical bond, is used to explore the entropy/information "bond-orders" of the system Valence-Bond (VB) structures, and their covalent/ionic composition. The molecular communication channel in atomic resolution is interpreted as the ensemble-average of the elementary information networks corresponding to the system elementary VB structures, with the probability-weights generated by the coefficients of the familiar VB expansion of the system wave-function. The elementary probability-scattering networks corresponding to a single ionic and covalent bonds of the system constituent diatomic fragments, to be used to construct the communication systems of any VB structure, are identified and their entropy/information descriptors are summarized. The overall bond multiplicities of VB structures are generated using the relevant grouping rules for the entropy/information quantities and the molecular IT bond-order and its covalent/ionic components are obtained as the ensemble averages of the corresponding descriptors of individual VB structures. Illustrative applications to the hydrogen molecule and π-bonds in allyl, butadiene and benzene are reported and discussed. Equating the VB-ensemble average quantities for these π-electron systems with those resulting from the Hückel Molecular Orbital (MO) theory then allows one to extract the VB relative covalency and ionicity measures for all chemical bonds in the molecule. The simple MO and VB descriptions of the hydrogen molecule are compared and the role of a strong overlap between the VB structures is investigated in a more detail. Finally, the entropy/information descriptors of the information distribution in the resultant promolecule $\rightarrow$ Atoms-in-H_2 channel resulting from the sequential information cascade consisting of the promolecular and

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VB probability propagation stages is examined to determine the dependence of the flow of information on the adopted reference system.

Keywords Bond indices · Chemical bonding · Communication theory · Covalent/ionic components · Elementary information systems · Hydrogen molecule · Information theory · Molecular communication systems · Pi-electron systems · Theory of chemical bonds · Valence-bond theory

1 Introduction

The concepts and techniques of Information Theory (IT) [1–4] have recently been applied to diverse problems in the theory of electronic structure [5]. Among other developments, the AIM-resolved Communication Theory of the Chemical Bond (CTCB) has been developed for both the molecular system as a whole and its constituent fragments [5–16]. Its formulations in the orbital and local descriptions have also been proposed [17–21]. In the AIM-resolved formulation the molecule is interpreted as an information channel, in which the molecular or "promolecular" electron 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 probability network measures its average communication "noise", i.e., the extra uncertainty in the distribution of valence electrons in the molecule due to their delocalization via the network of chemical bonds due to the system occupied Molecular Orbitals (MO). It reflects the "disorder" (indeterminacy) in the conditional probability scattering in the molecule. The overall information-ionicity (mutual information) index of all bonds in the system under consideration measures the amount of information flowing through the molecular information network [5], thus emphasizing the "order" (determinacy) in the molecular probability scattering. Therefore, in this probabilistic model the covalent component reflects the *delocalization* aspect of the valence electrons, via the system of chemical bonds generated by the occupied MO, while the ionic component describes the *localization* facet of the molecular electronic structure. This IT description gives a transparent account of the information origins of the chemical bond and it accounts for a competition between the covalent and ionic components of the chemical bond, which also accords with the chemical intuitive expectations and predictions from the MO theory.

In previous developments [5,9,10,17–20] we have explored in some detail the relations between the communication theory perspective and the standard MO and VB [22] theories of the chemical bond. The latter of these two standard quantum-chemical approaches, which has made a strong comeback from 1980s onward [23], connects more directly to the classical chemical concepts. It offers important insights into the elementary chemical processes, generates the key paradigms of chemistry, such as the bonding electron pair and octet rule, successfully tackles many classical issues in the theory of molecular structure and conceptualizes the chemical reactivity. The theory quantitative variants, the ab initio VB methods, e.g., Generalized VB [24] scheme, provide efficient computational tools for determining outcomes of chemical reactions.

The VB ideas have also been proven quite useful in modeling the Born-Oppenheimer potential energy surfaces of elementary chemical reactions, e.g., [25].

It is the main purpose of the present work to explore the VB approach to CTCB, in which the molecular communication channel is effectively generated as the ensemble average of the information channels corresponding to the system admissible VB structures. These probability networks can be generated by combining in the chemical-like fashion the elementary diatomic channels corresponding to the structure constituent covalent and ionic bonds, respectively. Therefore, this IT approach fully preserves, by construction, the global and local covalent/ionic bond compositions of the VB theory. We shall illustrate this ensemble interpretation of CTCB using the textbook applications, e.g., [26–28], involving the homonuclear diatomic fragments: the σ-bond in hydrogen molecule and π-bonds in ethylene, allyl, butadiene and benzene. 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 $\mathbf{X}$ denotes the square or rectangular matrix, the bold-italic $\boldsymbol{X}$ stands for a row vector, while italic X corresponds to the scalar quantity.

2 Elementary building blocks of communication channels of VB structures

In the CTCB formulated in atomic-resolution [5] the bonding patterns of molecules and their fragments are determined by the conditional probabilities of finding one electron on atom j, when the other electron is known to have been located on atom j, $\mathbf{d} = \left\{d(j|i) = P_{i,j}/p_i\right\}$, where the probabilities $\mathbf{P} = \left\{P_{i,j}\right\}$ of the molecular joint *two*-electron atomic events determine to associated *one*-electron probabilities $p_i = \sum_j P_{i,j}, \sum_i p_i = 1$. This gives rise to the channel normalization conditions for each row of $\mathbf{d}$: $\sum_j d(j|i) = 1, i = 1, 2, \ldots$ The conditional probabilities determine the communication network of the molecular information channel (see Fig. 1).

The average-noise (IT-covalency) present in the molecular channel is then measured by the conditional entropy [4] of the molecular probabilities for the *molecular*

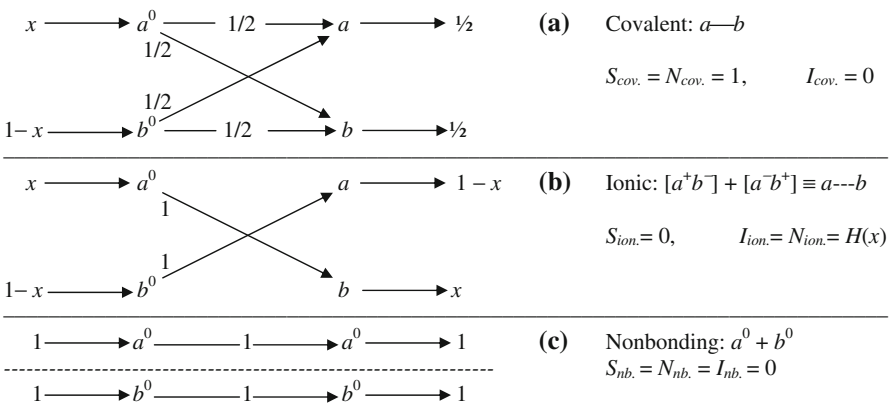


Fig. 1 The elementary communication channels for the homonuclear-diatomic A_1–$A_2 \equiv a - b$ and their IT bond indices

"output" events, $\boldsymbol{B} = \{p_j\}$, given the probabilities of the *molecular* "input" events, $\boldsymbol{A} = \{p_i\}$, both determined by the system ground-state *one*-electron probabilities $\boldsymbol{p} = \boldsymbol{A} = \boldsymbol{B}$:

$$S(\boldsymbol{B}|\boldsymbol{A}) = -\sum_i \sum_j P_{i,j} \log d(j|i) \equiv S. \tag{1}$$

The complementary index is given by the mutual information (IT-ionicity) in the *promolecular* input probabilities $\boldsymbol{A}^0 = \boldsymbol{p}^0 = \{p_i^0\}$, for the valence electrons of the disconnected (separate, non-bonded) free-atomic fragments, and the *molecular* output distribution $\boldsymbol{B} = \boldsymbol{p}$:

$$I(\boldsymbol{A}^0 : \boldsymbol{B}) = \sum_i \sum_j P_{i,j} \log[P_{i,j}/(p_i^0 p_j)] = H(\boldsymbol{p}^0) - S(\boldsymbol{A}|\boldsymbol{B}) \equiv I, \tag{2}$$

where the Shannon entropy of the promolecular input $\boldsymbol{A}^0$

$$H(\boldsymbol{p}^0) = -\sum_i p_i^0 \log p_i^0. \tag{3}$$

Together these two overall bond components give rise to the total IT-index for all bonds in the system under consideration:

$$N(\boldsymbol{A}^0; \boldsymbol{B}) = I(\boldsymbol{A}^0 : \boldsymbol{B}) + S(\boldsymbol{A}|\boldsymbol{B}) = H(\boldsymbol{p}^0) \equiv N. \tag{4}$$

In Fig. 1 these entropy/information indices are reported for the illustrative elementary communication systems of a homonuclear diatomic system A_1—$A_2 \equiv a$—b. These probability propagation networks involve the perfectly-scattering (electron-sharing) *covalent* channel of Panel *a*, giving rise to the purely covalent single (1 bit) bond between the two atoms, and the two noiseless (deterministic) channels of the remaining panels. The ion-pair (electron-transfer) *ionic* channel of Panel *b* generates the IT-ionicity to the amount of the input entropy of Eq. 3 given by the binary entropy function,

$$H(x) = -x \log x - (1 - x) \log(1 - x), \tag{5}$$

which reaches the maximum value for equal input probabilities $x = 1 - x = \frac{1}{2}$: $H(\frac{1}{2}) = 1$.

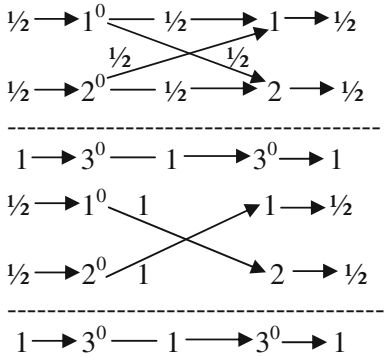
The bonded systems of Fig. 1a, b involve the mutually open Atoms-in-the-Molecule (AIM) $M = (a \,\vdots\, b)$, as reflected by the broken vertical line in the symbol of the molecule M, sharing or transferring the valence electrons in the covalent and ionic channels, respectively. The non-bonding channel of Fig. 1c consists of the separate noiseless channels for each constituent atom [5–12], separated by the horizontal broken line, thus giving rise to the vanishing IT indices of the system chemical bonds. Indeed, it represents the free-atoms of the reference system $M^0 = (a^0 | b^0)$, consisting of the "frozen" non-bonded, mutually-closed atoms shifted to their molecular positions, as reflected by the vertical solid line separating atoms in the *promolecule* M^0. The conditional probability matrices of the three channels of Fig. 1 are:

$$\mathbf{d}_{cov.} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix}, \quad \mathbf{d}_{ion.} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \mathbf{d}_{nb.} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{6}$$

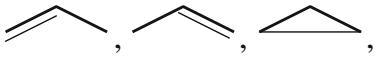
Since each VB structure of the illustrative systems of the present work, the σ-bond in H_2 and π-bonds in ethylene, allyl, butadiene and benzene, involves the pairs of the localized covalent (a—b) and/or ionic (a---b) bonds and possibly some non-bonded atoms $\{a^0\}$, the elementary channels of Fig. 1 and the associated conditional probability matrices of Eq. 6 can serve as the building blocks for construction of communication systems for any admissible structure. This is illustrated in Table 1 for the simplest triatomic composite system, where the conditional probability matrices and the IT bond indices are reported for representative valence bond structures of π-bonds in allyl, for the consecutive numbering of carbon atoms in the π-system chain. The separate information channels corresponding to the mutually-closed diatomic or atomic subsystems of the VB structure then contribute additively to its overall bond indices [5–12]. The corresponding conditional probability matrices of these localized bonds in allyl read:

$$\mathbf{d}[1\text{—}2|3] = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{d}[1\text{---}2|3] = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{7}$$

Table 1 Conditional probabilities for the representative VB structures of π-bonds in allyl, involving a single covalent and ionic bonds, respectively, between atoms 1 and 2 and the non-bonded atom 3 in the carbon chain, and their resultant bond indices relative to the covalent (electron-sharing) "promolecule" $M^0 = \left(\dot{a}^0 \middle| \dot{b}^0 \middle| \dot{c}^0\right)$, when each free atom contributes a single valence electron. Hence, within each bonded subsystem [1—2] or [1---2] equal input probabilities $x = 1 - x = \frac{1}{2}$ are used in the corresponding channels

VB-Structure	Symbol	Information channel	Bond indices
	[1—2/3]		$S = N = 1$, $I = 0$
	[1---2/3]		$S = 0$, $I = N = 1$

It should be observed, that in π-electron systems such as allyl, butadiene and benzene all VB structures exhibiting the same numbers of the covalent and ionic π-bonds, and hence also the same number of the non-bonded carbons, have the same sets of the IT bond indices. This greatly simplifies a calculation of their VB-ensemble average values. Hence, all the covalent VB structures of π-bonds in allyl,



(8)

exhibit 1 bit of the entropy covalency and the vanishing information ionicity, while the corresponding ionic structures,

(9)

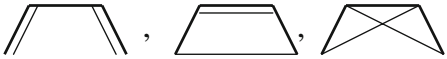
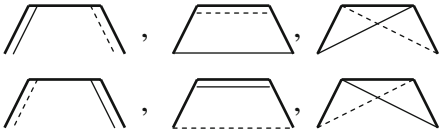
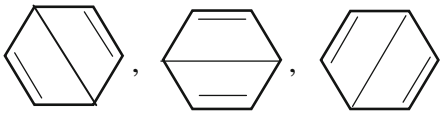
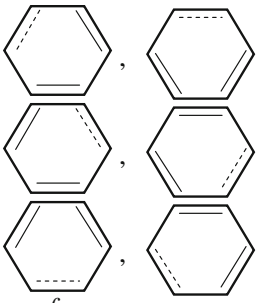
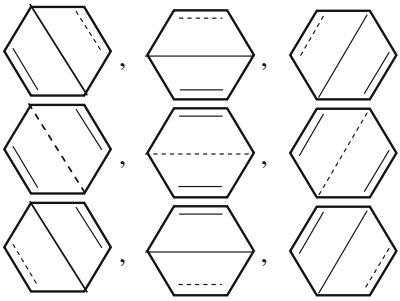
exhibit 1 bit of the information ionicity and the vanishing entropy covalency. There actual participation in the VB-ensemble average indices will be determined by the variationally optimum participations of the VB structures in the system wave-function.

In Table 2 we have summarized the IT bond indices of representative covalent structures in the butadiene $(a-c)$ and benzene $(a-e)\pi$-electron systems, which represent two and three covalent bonds, respectively. We have also included in the table the corresponding ionic structures, involving a single ionic bond, which are next in importance in the VB expansion of the system wave-function [26–28]. By the Rumer [29] rule only the first two butadiene structures shown in the table are linearly independent, while the benzene structures include only the independent Kékulé (a, b) and Dewar $(c-e)$ structures and their singly-ionic derivatives $(f-j)$. The corresponding communication systems have been generated from the elementary diatomic channels of Fig. 1a, b. For example, the conditional probability matrices of the two independent covalent structures of butadiene (consecutive numbering of carbon atoms in the chain) read:

$$\mathbf{d}[1\text{—}2|3\text{—}4] = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} \end{bmatrix},$$

$$\mathbf{d}[1\text{—}4|2\text{—}3] = \begin{bmatrix} \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \end{bmatrix}, \tag{10}$$

Table 2 The most important valence structures of butadiene and benzene and their IT bond indices

VB structures	Bond indices
 *a* , *b* , *c*	$S = N = 2, I = 0$
 *d* , *e* , *f*	$S = 1, I = 1, N = 2$
a , *b*	$S = N = 3, I = 0$
 *c* , *d* , *e*	
 *f* , *g*	$S = 2, I = 1, N = 3$
 *h* , *i* , *j*	

while in their first ionic derivatives [1—2|3---4] and [1—4|2---3], respectively, the information is propagated in accordance with the conditional probabilities:

$$\mathbf{d}[1\text{—}2|3\text{---}4] = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \quad \mathbf{d}[1\text{—}4|2\text{---}3] = \begin{bmatrix} \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \end{bmatrix}. \tag{11}$$

Clearly, as in the information channels of Table 1, equal input probabilities $p_i^0 = p_j^0 = \frac{1}{2}$, corresponding to the electron-sharing promolecular reference, have been assumed to calculate the entropy/information multiplicities of each covalent $(i\text{—}j)$ or ionic $(i\text{---}j)$ bonds in the VB structure under consideration.

It has been demonstrated that the global bonding patterns emerging from the communication-theory for all illustrative molecular systems are generally in accord with the chemical intuition. For example, it has been shown that in the benzene carbon ring the total bond index is lower than 3 bits value expected for the *triple* conjugated π-bond, which characterizes (see the next chapter) the mutually closed diatomic fragments of cyclohexatriene. In other words, the aromaticity of π electrons manifests itself in *lowering* the molecular entropy/information index relative to the reference of 3 bits level predicted for the three separate π bonds. Therefore, the natural tendency of the delocalized π electrons in benzene is to destabilize the regular hexagonal structure towards the distorted, alternated system of hexatriene. This is in accord with the modern outlook on the influence of σ and π electrons on aromaticity [23,30]. These modern MO and VB approaches indeed predict the π bonds to favor the distorted (cyclohexatriene-like) structure, while the dominating σ-bond stabilization is responsible for the regular hexagon structure of the benzene ring.

3 Bond indices of VB structures and relative bond composition

The entropy/information descriptors of the separate communication systems of the preceding section, which represent the mutually closed diatomic or atomic subsystems, have to be combined into the corresponding bond indices of the VB structure as a whole. The relevant grouping rules have been already developed elsewhere [12]. For the set of elementary bonding or non-bonding channels $\{\alpha\}$ of Fig. 1 in the sth VB structure, which give rise to the IT indices $\{S_\alpha = N_\alpha = 1, I_\alpha = 0\}$ for the covalent diatomic fragment and $\{S_\alpha = 0 I_\alpha = N_\alpha = 1\}$ for the ionic diatomic subsystem, one first establishes the group probabilities in the structure under consideration, $\boldsymbol{P}_s = \{P_\alpha^s\}$. The corresponding bond indices (Eqs. 1–4) for this structure are then determined using the following grouping axioms [5–12]:

$$S_s = H(\boldsymbol{P}_s) + \sum\nolimits_\alpha P_\alpha^s S_\alpha \equiv H(\boldsymbol{P}_s) + \bar{S}_s, \quad I_s = \sum\nolimits_\alpha P_\alpha^s I_\alpha, \quad N_s = S_s + I_s. \tag{12}$$

These quantities have to be subsequently VB-ensemble averaged using the probabilities $\{\pi_s\}$ of the (orthogonalized) VB structures in the expansion of the system wave-function:

$$\langle S\rangle_{VB} = \sum\nolimits_s \pi_s S_s, \quad \langle I\rangle_{VB} = \sum\nolimits_s \pi_s I_s, \quad \langle N\rangle_{VB} = \sum\nolimits_s \pi_s N_s. \tag{13}$$

In the illustrative π-electron systems of the preceding section the group probabilities are proportional to the number of carbon atoms in the constituent subsystems of the VB structure in question. Consider first the allyl structures of Table 1 and Eqs. 8 and 9. In the representative covalent structure $s = [a—b|c]$ of the allyl π-system, consisting of a diatomic fragment $a—b$ and non-bonded atom c, $\boldsymbol{P}_s = \left(\frac{2}{3}, \frac{1}{3}\right)$, thus giving rise to $H(\boldsymbol{P}_s) = \log_2 3 - \frac{2}{3}$, $\bar{S}_s = \frac{1}{3} \times 0 + \frac{2}{3} \times 1 = \frac{2}{3}$, and hence the structure resultant entropy-covalency $S_s = \log_2 3 = 1.585$. This result applies to all covalent structures of Eq. 8, for which $I_s = 0$, i.e., $N_s = S_s = 1.585$. Thus, ensemble averaging of Eq. 13 over the covalent structures only gives the purely covalent bond of the same average multiplicity:

$$\langle S\rangle_{VB}^{cov.} = \langle N\rangle_{VB}^{cov.} = 1.585, \quad \langle I\rangle_{VB}^{cov.} = 0 \tag{14}$$

equal to that predicted in the Hückel MO approximation [5] for this molecular system,

$$S^{MO} = 1.524, \quad I^{MO} = 0.061, \quad N^{MO} = 1.585. \tag{15}$$

This marginal ionicity can be generated in the VB theory by including the ionic structures of Eq. 9. Since each of them exhibits $S_\alpha = 0$ and $I_\alpha = 1$, $S_s = 0$ and $I_s = \frac{2}{3}$ and hence by including only ionic structures in the VB expansion of the allyl wave-function Ψ_{VB} one obtains:

$$\langle S\rangle_{VB}^{ion.} = 0.918, \quad \langle I\rangle_{VB}^{ion.} = 0.667, \quad \langle N\rangle_{VB}^{ion.} = 1.585. \tag{16}$$

Clearly, a realistic VB representation of this electronic state must include the combination of the dominant covalent structures, giving rise to the covalent component $\Phi^{cov.}$, and the marginal contribution from the ionic structures. generating the independent ionic component $\Phi^{ion.}$, which is (Schmidt) orthogonalized relative to $\Phi^{cov.}$, so that $\langle\Phi^{cov.}|\Phi^{ion.}\rangle = 0$:

$$\Psi_{VB}^{cov.+ion.} = \mu\Phi^{cov.} + \nu\Phi^{ion.}. \tag{17}$$

The squares of moduli of the above expansion coefficient then reflect the relative overall covalency $|\mu|^2$ and ionicity $|\nu|^2$ of all bonds in the system. Therefore, by interpreting the bond ionicity index of Eq. 15 as approximating the corresponding VB-ensemble average value,

$$I^{MO} = 0.061 \cong \langle I\rangle_{VB}^{cov.+ion.} = \frac{2}{3}|\nu|^2, \tag{18}$$

gives roughly $|\nu|^2 = 0.091$ estimate of the relative VB-ionicity in allyl. Alternatively, one could use the relation

$$S^{MO} = 1.524 \cong \langle S\rangle_{VB}^{cov.+ion.} = 1.585|\mu|^2 + 0.918|\nu|^2, \tag{19}$$

to estimate $|\mu|^2 \approx 0.909$. This rough Hückel theory estimate thus indicates that π-bonds in allyl are about 91% VB-covalent and 9% VB-ionic.

Turning now to the butadiene data of Table 2, when for each VB structure $\boldsymbol{P}_s = \left(\frac{1}{2}, \frac{1}{2}\right)$ and $H(\boldsymbol{P}_s) = 1$, one finds $\left\{S_s = N_s = 1 + 2 \times \frac{1}{2} \times 1 = 2, I_s = 0\right\}$ for each covalent structure and $\{I_s = N_s = 1, S_s = 0\}$ for each ionic structure. This further implies

$$\langle S\rangle_{VB}^{cov.} = \langle N\rangle_{VB}^{cov.} = 2, \langle I\rangle_{VB}^{cov.} = 0; \quad \langle S\rangle_{VB}^{ion.} = 1, \langle I\rangle_{VB}^{ion.} = 1, \langle N\rangle_{VB}^{ion.} = 2. \tag{20}$$

Using again the Hückel theory predictions [5] $\left\{S^{MO} = 1.944, I^{MO} = 0.056, N^{MO}{=}2\right\}$ as representative of the VB-ensemble including both covalent and ionic structures,

$$2|\mu|^2 + |\nu|^2 = 1.944, \quad |\nu|^2 = 0.056, \tag{21}$$

then gives the following relative covalency and ionicity estimates: $|\mu|^2 \approx 94\%$ and $|\nu|^2 \approx 6\%$.

In benzene the three diatomic subsystems exhibiting the covalent or ionic bonds give rise to $\boldsymbol{P}_s = \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)$ and $H(\boldsymbol{P}_s) = \log_2 3 = 1.585$. This implies for each covalent structure exhibiting three covalent bonds $\left\{S_s = N_s = 1.585 + (3 \times \frac{1}{3} \times 1) = 2.585, I_s = 0\right\}$ and hence $\langle S\rangle_{VB}^{cov.} = \langle N\rangle_{VB}^{cov.} = 2.585$ and $\langle I\rangle_{VB}^{cov.} = 0$. For the remaining VB structures exhibiting a single ionic bond and two covalent bonds one similarly finds $\left\{S_s = 1.585 + (2 \times \frac{1}{3} \times 1) = 2.252, I_s = \frac{1}{3} \times 1 = \frac{1}{3}, N_s = 2.585\right\}$, and hence also $\left\{\langle S\rangle_{VB}^{ion.} = 2.252, \langle I\rangle_{VB}^{ion.} = \frac{1}{3}, \langle N\rangle_{VB}^{ion.} = 2.585\right\}$. The previously reported IT results from the Hückel theory, $\left\{S^{MO} = 2.551, I^{MO} = 0.034, N^{MO} = 2.585\right\}$, when interpreted as approximating $\left\{\langle S\rangle_{VB}^{cov.+ion.}, \langle I\rangle_{VB}^{cov.+ion.}, \langle N\rangle_{VB}^{cov.+ion.}\right\}$, respectively,

$$|\mu|^2 2.585 + |\nu|^2 2.252 = 2.551, \quad \frac{1}{3}|\nu|^2 = 0.034, \tag{22}$$

give rise to the relative bond composition of $|\mu|^2 \approx 90\%$ VB-covalent and $|\nu|^2 \approx 10\%$ VB-ionic character.

Therefore, the overall IT bond index for benzene $N = 2.585$ is lower than 3 bits value expected for the *triple* conjugated π-bond, which characterizes the Kékulé structures of the mutually closed diatomic fragments in cyclohexatriene. In other words, the aromaticity of π electrons manifests itself in *lowering* the molecular entropy/information index relative to the reference of 3 bits level predicted for the three separate π bonds. Therefore, the natural tendency of the delocalized π electrons in benzene is to destabilize the regular hexagonal structure towards the distorted, alternated system

of hexatriene. This is in accord with the modern outlook on the influence of the σ and π electrons on aromaticity [23,30]. These modern VB and MO approaches indeed predict the π bonds to favour the distorted (cyclohexatriene-like) structure, while the dominating σ-bond stabilization is responsible for the regular hexagon geometry of the benzene ring. As we have emphasized above, this delocalized character of π-bonds in benzene is also marked by a slightly higher bond ionicity, compared to that observed in butadiene, where a degree of bond alternation is observed, approximately at the level observed in allyl where the bond alternation is precluded by symmetry.

4 Chemical bond in hydrogen molecule

We conclude with a short comment on the non-orthogonality of VB structures of $H_2 = H_a$—H_b and its role in shaping the effective covalent–ionic bond composition. At the equilibrium bond length $R = R_e = 1.415$ a.u. the overlap integral between the two $1s$ orbitals of the two hydrogen atoms, $\langle 1s_a|1s_b\rangle = \mathcal{S}(R) = \exp(-R)\left(1 + R + \frac{R^2}{3}\right)$ gives $\mathcal{S}(R_e) = 0.749$. Hence, the normalized spatial parts of the covalent and ionic VB structures,

$$\begin{aligned}\Phi^{cov.}(1,2) &= \mathcal{N}[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)],\\ \Phi^{ion.} &= \mathcal{N}[1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)],\\ \mathcal{N} &= [2(1+\mathcal{S}^2)]^{-1/2} = 0.566.\end{aligned} \tag{23}$$

give rise to their high degree of non-orthogonality $\Sigma = \langle\Phi^{cov.}|\Phi^{ion.}\rangle = 4\mathcal{S} = 0.960$. Therefore, in order to establish the independent ionic contribution to the wave function of Eq. 17 one has to Schmidt-orthogonalize $\Phi^{ion.}$ relative to $\Phi^{cov.}$,

$$\tilde{\Phi}^{ion.} = (1-\Sigma^2)^{-1/2}(\Phi^{ion.} - \Sigma\Phi^{cov.}) = 3.362\Phi^{ion.} - 3.418\Phi^{cov.}, \tag{24}$$

while the inverse transformation reads:

$$\Phi^{ion.} = 0.960\Phi^{cov.} + 0.281\tilde{\Phi}^{ion.}. \tag{25}$$

Let us now compare the degrees of the *independent* VB-ionicity implied by the familiar simple MO description in this minimum basis set, giving rise to equal participation of the covalent and ionic structures,

$$\Psi_{MO} = n(\Phi^{cov.} + \Phi^{ion}), \quad n = [2(1+\Sigma)]^{-1/2} = 0.505, \tag{26}$$

and the optimum VB description at the equilibrium bond length [31]:

$$\Psi_{VB}^{cov.+ion.} = 0.454(\Phi^{cov.} + 0.256\Phi^{ion.}). \tag{27}$$

When expressed in terms of the independent ionic component of Eq. 24 the MO wave-function reads:

$$\Psi_{MO} = 0.990\Phi^{cov.} + 0.141\tilde{\Phi}^{ion.}, \tag{28}$$

thus predicting 98% of the VB-covalency and 2% of the independent VB-ionicity. The VB wave-function of Eq. 27 similarly gives:

$$\Psi_{VB}^{cov.+ion.} = 0.998\Phi^{cov.} + 0.058\tilde{\Phi}^{ion.}, \tag{29}$$

and hence 99.7% of the VB-covalency and 0.3% of the independent VB-ionicity. Therefore, both these descriptions predict a practically vanishing ionicity of the H—H bond, in accordance with an intuitive chemical expectation.

The chemical bond is a "difference" phenomenon, depending on the applied initial promolecular state [5,32–36]. In the hydrogen molecule it may involve the following three references: the symmetrical (covalent) promolecule $(\mathrm{H}_a + \mathrm{H}_b) \equiv \alpha$, in which each neutral atom contributes a single electron to form the chemical bond, or one of the broken-symmetry, ion-pair (coordination) promolecules, $(\mathrm{H}_a^+ + \mathrm{H}_b^-) \equiv \beta$ or $(\mathrm{H}_a^- + \mathrm{H}_b^+) \equiv \gamma$. In what follows we shall examine this influence of the promolecule selection on the flow of information in the resultant sequential information-cascades III [4,16,20], which consists of the promolecular communication stage I and the VB-structure stage II, with the outputs of channel I constituting the inputs of channel II:

$$\boldsymbol{A} \rightarrow \mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A}) \rightarrow \boldsymbol{B} \rightarrow \mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) \rightarrow \boldsymbol{C}. \tag{30}$$

The role of the preceding step in this series is thus limited to shaping the input probabilities of the next step. Above $\boldsymbol{A}$ stands for the input probabilities of the three admissible promolecular references, $\boldsymbol{A} = \boldsymbol{P}^I = (P_\alpha, P_\beta, P_\gamma)$, $P_\alpha + P_\beta + P_\gamma = 1$, with the covalent promolecule α corresponding to $P_\alpha = 1$ and $P_\beta = P_\gamma = 0$, and the coordination reference β, with the electron pair on the atomic anion H_B^-, identified by $P_\beta = 1$ and $P_\alpha = P_\gamma = 0$, while the symmetrized ionic reference ensemble will be identified by $P_\alpha = 0$ and $P_\beta = P_\gamma = \frac{1}{2}$.

The output probabilities of stage I, $\boldsymbol{B} = \boldsymbol{A}\mathbf{P}_I(\boldsymbol{B}|\boldsymbol{A})$, now represent the input probabilities of the free atoms-in-promolecule (AIP) at stage II, the output of which,

$$\boldsymbol{C} = \boldsymbol{B}\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B}) = \boldsymbol{A}[\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B})] \equiv \boldsymbol{A}\mathbf{P}_{\mathrm{III}}(\boldsymbol{C}|\boldsymbol{A}), \tag{31}$$

is seen to be determined by the resultant conditional probabilities $\mathbf{P}_{\mathrm{III}}(\boldsymbol{C}|\boldsymbol{A})$ given by the product of the conditional probabilities $\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}|\boldsymbol{A})$ and $\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}|\boldsymbol{B})$ of the two stages in the sequential cascade.

The very nature of the three promolecular states determine the first factor in this product of the probability scattering sequence. It is summarized in Fig. 2 showing a diagrammatic representation of the first communication system in the sequence of Eq. 30.

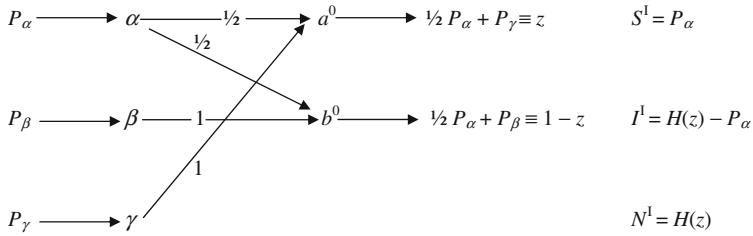


Fig. 2 The promolecular stage I of the sequential cascade (or the non-bonding cascade) of Eq. 30, with the promolecular input and AIP (AIM) output, and its entropy/information indices

The associated conditional probability matrix,

$$\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}\big|\boldsymbol{A}) = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ 0 & 1 \\ 1 & 0 \end{bmatrix} = \mathbf{P}_{\mathrm{I}}(\boldsymbol{B}\big|\boldsymbol{A})\mathbf{d}_{nb.} = \mathbf{P}_{\mathrm{III}}^{nb.\cdot}(\mathbf{C}\,|\mathbf{A}), \tag{32}$$

also represents the product channel for the non-bonding structure, since then the second stage probabilities $\mathbf{d}_{nb.}$ represent the identity transformation. Therefore, the entropy/information indices in Fig. 2 have a double interpretation:

$$\begin{aligned} S^{\mathrm{I}} &= S(\boldsymbol{B}\big|\boldsymbol{A}) = S_{\mathrm{III}}^{nb.\cdot}(\mathbf{C}\,|\mathbf{A}), \quad I^{\mathrm{I}} = I(\boldsymbol{A}:\boldsymbol{B}) = I_{\mathrm{III}}^{nb.\cdot}(\boldsymbol{A}:\boldsymbol{C}), \\ N^{I} &= N(\boldsymbol{A};\boldsymbol{B}) = N_{\mathrm{III}}^{nb.\cdot}(\boldsymbol{A};\boldsymbol{C}). \end{aligned} \tag{33}$$

The elementary covalent and ionic channels of Fig. 1 provide the conditional probabilities $\mathbf{P}_{\mathrm{II}}(\boldsymbol{C}\big|\boldsymbol{B})$ of Eq. 6 for the remaining VB structures in hydrogen molecule giving rise to the product probabilities

$$\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}\big|\boldsymbol{A})\mathbf{d}_{cov.} = \mathbf{P}_{\text{¼III}}^{cov.\cdot}(\boldsymbol{C}\big|\boldsymbol{A}) = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix},$$

$$\mathbf{P}_{\mathrm{I}}(\boldsymbol{B}\big|\boldsymbol{A})\mathbf{d}_{nb.} = \mathbf{P}_{\mathrm{III}}^{ion.\cdot}(\boldsymbol{C}\,|\boldsymbol{A}) = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{34}$$

These covalent and ionic sequential cascades are summarized in Fig. 3, while the resultant non-bonding cascade is represented by the diagram of Fig. 2 with the AIP (a^0, b^0) being replaced by AIM (a, b).

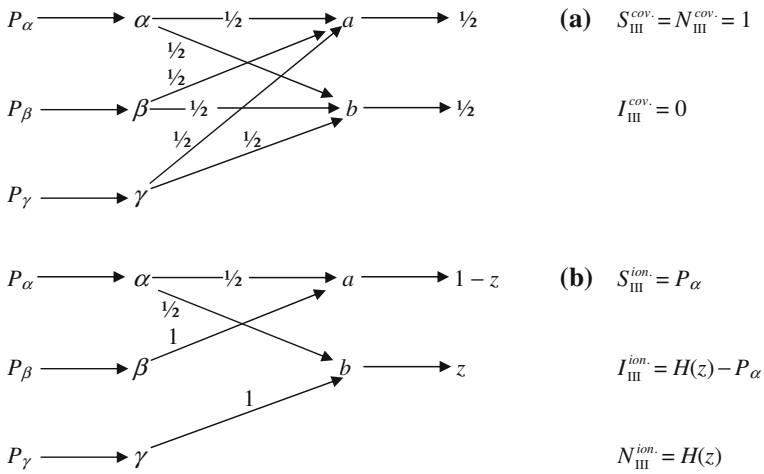


Fig. 3 Sequential cascades with the promolecular input and molecular (AIM) output for the covalent (Panel **a**) and ionic (Panel **b**) VB structures and their entropy/information indices

It should be emphasized, that the entropy/information quantities of Eq. 33 and those reported in Fig. 3,

$$S_{\mathrm{III}}^{cov.} = S_{\mathrm{III}}^{cov.}(\boldsymbol{C}|\boldsymbol{A}), \quad I_{\mathrm{III}}^{cov.} = I_{\mathrm{III}}^{cov.}(\boldsymbol{A}:\boldsymbol{C}), \quad N_{\mathrm{III}}^{cov.} = N_{\mathrm{III}}^{cov.}(\boldsymbol{A};\boldsymbol{C}), \quad \text{and}$$
$$S_{\mathrm{III}}^{ion.} = S_{\mathrm{III}}^{ion.}(\boldsymbol{C}|\boldsymbol{A}), \quad I_{\mathrm{III}}^{ion.} = I_{\mathrm{III}}^{ion.}(\boldsymbol{A}:\boldsymbol{C}), \quad N_{\mathrm{III}}^{ion.} = N_{\mathrm{III}}^{ion.}(\boldsymbol{A};\boldsymbol{C}), \tag{35}$$

reflect the information dissipated and preserved in the cascade in question, rather then directly describing the chemical bond multiplicities. The latter can be generated only from the molecular channels consisting of the atomic (AIP) input and (AIM) output, which reflect the molecular promotion of the initially non-bonded atoms of the promolecule [5].

It follows from Fig. 3a that the output AIM probabilities of the resultant promolecule→AIM communications in the covalent cascade are independent of the input signal, thus predicting the vanishing flow of information in such a sequential channel (see also Fig. 4a): $I(\boldsymbol{A}:\boldsymbol{C}) = 0$. For the specific case of $P_\alpha = 1$, when $H(\boldsymbol{A})$ vanishes, the whole output entropy $S(\boldsymbol{C}|\boldsymbol{A}) = \boldsymbol{H}(\boldsymbol{C}) = 1$ thus represents the extra uncertainty in the AIM probabilities due to the probability scattering in the channel.

The identical set of the entropy/information descriptors of the remaining two cascades predicts the flow of information to the amount $I(\boldsymbol{A}:\boldsymbol{C}) = H(z) - P_\alpha$, which is represented by the overlap area in the diagram of Fig. 4b, and the complementary part $S(\boldsymbol{C}|\boldsymbol{A}) = P_\alpha$ of the output entropy $\boldsymbol{H}(\boldsymbol{C}) = H(z)$ representing the extra communication noise generated in the system. Let us now briefly examine several limiting choices of the promolecular input signal:

(i) The covalent promolecule, when $P_\alpha = 1 \Rightarrow H(\boldsymbol{A}) = 0$ and $z = 1 - z = \frac{1}{2} \Rightarrow H(\boldsymbol{C}) = 1$, gives the same predictions as those resulting from the covalent cascade: $S(\boldsymbol{C}|\boldsymbol{A}) = 1$ and $I(\boldsymbol{A}:\boldsymbol{C}) = 0$;

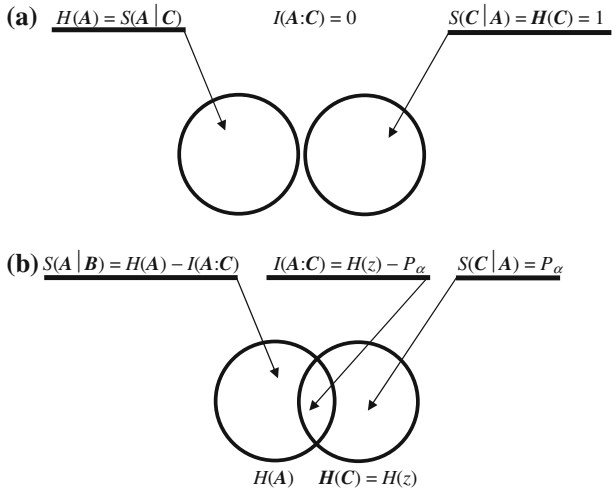


Fig. 4 The information diagrams for the resultant promolecule→AIM communication systems of the covalent (Panel **a**) and ionic/nonbonded (Panel **b**) VB structures. The non-overlapping entropy circles of the promolecular input and AIM output in Panel **a** signify the vanishing amount of information flowing through the covalent cascade

(ii) The broken symmetry ionic promolecule, e.g., $P_\beta = 1 \Rightarrow H(\boldsymbol{A}) = 0$, when $z = 0$ and $1 - z = 1 \Rightarrow H(\boldsymbol{A}) = 0$, gives $S(\boldsymbol{C}|\boldsymbol{A}) = H(\boldsymbol{C}) = I(\boldsymbol{A}:\boldsymbol{C}) = 0$, i.e., the zero noise and information flow in the communication system;

(iii) In the symmetrized ionic reference case, for $P_\beta = P_\gamma = \frac{1}{2} \Rightarrow H(\boldsymbol{A}) = 1$, when again $z = 1 - z = \frac{1}{2} \Rightarrow H(\boldsymbol{C}) = 1$, the whole input information content flows through the system $I(\boldsymbol{A}:\boldsymbol{C}) = 1$, with no extra noise being created, $S(\boldsymbol{C}|\boldsymbol{A}) = 0$, due to the deterministic character of the cascade;

(iv) For the equal mixture of the covalent and the symmetrized ionic references, $P_\alpha = \frac{1}{2}$ and $P_\beta = P_\gamma = \frac{1}{4} \Rightarrow H(\boldsymbol{A}) = \frac{3}{2}$, when $z = 1 - z = \frac{1}{2} \Rightarrow H(\boldsymbol{C}) = 1$, the input information is partly dissipated as communication noise, $S(\boldsymbol{C}|\boldsymbol{A}) = \frac{1}{2}$, and partly flows through the system, $I(\boldsymbol{A}:\boldsymbol{C}) = \frac{1}{2}$.

To summarize, the highest level of the average communication noise generated by the promolecule→AIM cascades involving the deterministic VB structures (ionic and non-bonded) of H_2 is predicted for the covalent promolecular reference, while the highest amount of information flowing through such sequential channels is predicted for the symmetrized ionic reference state. The broken symmetry references give rise to noiseless, zero information-flow channel, in which there is no uncertainty involved either in the promolecular input or the AIM output. The promolecular reference involving a mixture of the covalent and ionic promolecules generates partly covalent (noisy) and partly ionic (deterministic) transformation of the cascade input information.

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