

Information-theoretic multiplicities of chemical bond in Shull's model of H₂

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Abstract Alternative information-theoretic (IT) measures of the chemical bond multiplicity and its covalent/ionic composition in the orbital communication theory (OCT) are examined using Shull's natural orbital (NO) model of the homopolar bond in H₂. In OCT a molecule is treated as an information (probability-scattering) system, generated by the network of conditional probabilities (from the quantum mechanical superposition principle) linking elementary events of the adopted perspective. For the first time this atomic orbital (AO) invariant, *two*-NO description of Shull allows one to examine in several alternative representations the behavior of the previously adopted IT indices, of the channel average *communication noise* (OCT-covalency) and *information flow* (OCT-ionicity), with changing internuclear distance R , from the united atom ($R = 0$) to the separated atoms limit (SAL) ($R \rightarrow \infty$). The adopted references include the *two*-electron *atomic* and *ionic* functions of the model, as well as the alternative *one*-electron functions, of the AO and NO sets, respectively. The numerical results for the Wang function description of H₂ are reported and a general agreement with the accepted chemical intuition is tested. Joint probabilities of Shull's reference states are linked to the energy partitioning. The incorrect SAL behavior of the OCT-ionicity index, giving rise to the constant (interaction independent) overall multiplicity measure, emphasizes a need for a revision of these IT bond descriptors. The modified set of indices is proposed, reflecting the complementary *localization* (determinicity) and *delocalization* (indeterminicity) aspects of the communication system in question.

Here A , \mathbf{A} , and \mathbf{A} respectively denote the scalar quantity, row vector and a square/rectangular matrix. The logarithm of the information measure is taken to an arbitrary but fixed base: $\log = \log_2$ corresponds to information measured in *bits* (*binary digits*), while $\log = \ln$ expresses the amount of information in *nats* (*natural units*): 1 nat = 1.44 bits.

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The novel IT-ionicity now reflects the *diagonal* (*intra*-orbital, additive) information propagation in the molecular channel, while the modified IT-covalency accordingly measures the effect of its *off-diagonal* (*inter*-orbital, nonadditive) probability scatterings. These components are shown to give rise to the interaction strength dependent overall IT bond-order, which adequately reflects the chemical intuition.

Keywords Bond ionic/covalent components · Bond multiplicity/order · Chemical bond descriptors · Energy partitioning · Information theory · Molecular communication systems · Natural orbitals · Orbital communication theory · Shull model of H₂

1 Introduction

For a chemical understanding of the bonding patterns in molecules such intuitive chemical concepts as *atoms-in-molecules* (AIM) or multiplicities (orders) of the chemical bonds and their atomic/covalent and ionic components are paramount, e.g. [1–4]. In general, the semantics of these traditional chemical descriptors is not sharply defined in modern quantum mechanics so that they can be ultimately classified as Kantian noumenons of chemistry, e.g., [5]. It has been demonstrated elsewhere that the *Information Theory* (IT) [6–13] can be successfully used to elucidate their more precise meaning in terms of the entropy/information quantities [1–4, 14–23]. In this IT perspective on the molecular electronic structure the molecular states, their associated electron distributions and probability currents carry the complete information about the system bonding patterns. Indeed, some of these chemical characteristics are “entropic” in character, being primarily designed to reflect the spin “pairing” patterns between electrons, rather than the molecular energetics itself.

For example, the displacements in the molecular information distribution, relative to the *promolecular* reference consisting of the nonbonded constituent atoms in the molecular positions, have been investigated and the least-biased partition of the molecular electron distributions into subsystem contributions, e.g., densities of AIM have been investigated. This IT approach to the AIM partition of the molecular electron density has been shown to lead to the “stockholder” fragments of Hirshfeld [24]. Information theory also facilitates a deeper insight into the nature of bonded atoms [1–3, 14–23], the electron fluctuations between AIM [25], and a thermodynamic-like description of molecules [25–27]. It also increases our understanding of the elementary reaction mechanisms [28]. Moreover, by using the complementary Shannon and Fisher measures of the information content of the electronic distribution, in both the position and momentum spaces, it has been demonstrated that these IT probes allow one to precisely locate the substrate bond-breaking and the product bond-forming stages along the reaction coordinate, which are not seen on the reaction energy profile alone [29, 30].

These applications have amply demonstrated that IT concepts and techniques constitute attractive and efficient tools for exploring and understanding the electronic structure of molecules. They facilitate the spatial localization of the

system electrons and chemical bonds, an extraction of the entropic bond-orders and their covalent/ionic composition, and a monitoring of the promotion (polarization/hybridization) and charge-transfer processes, which determine the valence state of bonded atoms. For example, the nonadditive Fisher information in the *Atomic Orbital* (AO) resolution has recently been used as the *Contra-Gradient* (CG) criterion for localizing the bonding regions in molecules [1–3,31–35], while the related information density in the *Molecular Orbital* (MO) resolution has been shown [1–3,36] to determine the vital ingredient of the *Electron-Localization Function* (ELF) [37–40].

The *Communication Theory of the Chemical Bond* (CTCB) has been developed using the basic entropy/information descriptors of the molecular information (communication) channels at various levels of resolving the molecular probability distributions [1–4,41–51]. The entropic probes of the molecular bond structure have provided tools for describing the chemical bond phenomenon in information terms and for an exploration of the information origins of chemical bonds [2]. The *Orbital Communication Theory* (OCT) [2,3,52–58] uses the electronic conditional probabilities in AO resolution, generated using the bond-projected superposition principle of quantum mechanics, to define the molecular information (communication) system. Its average entropy/information measures of the bond covalency/iconicity reflect the average communication “noise” and the flow of information, respectively, in such a molecular network [1–4,52–58].

In OCT the chemical bonding is synonymous with some degree of a communication between AO in the underlying information channel. Since this *one*-electron communication channel depends on the choice of basis set of SCF MO calculations, which determine its elementary events, the minimum basis set of the promolecule-occupied AO or its Maximum-Overlap fit have been recommended for chemical interpretations [57]. On one hand, this probability propagation can be realized *directly*, through the constructive interference of interacting orbitals, i.e., as a “dialogue” between the given pair of orbitals. On the other hand, it can be also effected in an *indirect* manner, through the cascade of other orbitals. The latter mechanism can be compared to the “gossip” spread through the orbital intermediates (AO “bridge”). These two mechanisms generate the associated *through-space* and *through-bridge* contributions to the overall multiplicities (orders) of the system chemical bonds [58–65].

It has been recently suggested [64] that the electron correlation can be included in this OCT approach by using the *Natural Orbital* (NO) framework of the *Configuration Interaction* (CI) theory. This desired extension of the IT treatment would introduce some degree of “universality” (invariance) into the associated patterns of the orbital shapes and occupations (probabilities) for wave functions obtained in a widely different basis sets and CI expansions. The NO description emphasizes the *Hartree–Fock* (HF) like MO (strongly-occupied NO) and it determines the main modes for the Coulomb correlation between electrons (weakly-occupied NO). It also offers a universal framework for understanding the nature of the chemical bond. It is the main purpose of this work to examine diverse entropy/information descriptors of a realistic model of the diatomic (*two*-electron) chemical bond in the *two*-NO description of Shull et al. [66–72]. Atomic units and bits are used throughout.

2 Model summary

The ground state $\Psi(1, 2)$ of two electrons can be resolved into the singlet (antisymmetric) spin factor $\Theta(\sigma_1, \sigma_2) = 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$, where α (spin-up) and β (spin-down) functions stand for two admissible spin states of an electron, and the spatial (symmetric) function $\Phi(\mathbf{r}_1, \mathbf{r}_2) : \Psi(1, 2) = \Phi(\mathbf{r}_1, \mathbf{r}_2)\Theta(\sigma_1, \sigma_2)$. The Shull model uses the *two-term* (orthonormal) NO expansion of the spatial factor,

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = C_1\psi_1(\mathbf{r}_1)\psi_1(\mathbf{r}_2) + C_2\psi_2(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \equiv \Phi(1, 2), \quad (1)$$

with the expansion coefficients $\{C_k\}$ related to the corresponding NO probabilities (occupation numbers) $\{n_k = C_k^2 \text{ or } C_k = \pm n_k^{1/2}\}$ satisfying the relevant normalization requirement: $n_1 + n_2 = 1$. It was shown to contain essentially all of the information associated with a diatomic chemical bond that can be applied without reference to any particular basis set, including the rigorous concepts of the fractional *atomic* and *ionic* character, which complement the “covalent” and “ionic” components introduced by Pauling [73] on intuitive grounds.

For interpretative purposes the Shull model introduces several reference states of two electrons, expressed in terms of *arbitrary*, normalized space orbitals u and v contributed by the two atoms. The model introduces the “atomic” function, $\Phi_A(1, 2) = N_+\{u(1)v(2) + v(1)u(2)\}$, and two “ionic” states: $\Phi_1^+(1, 2) = N_+\{u(1)u(2) + v(1)v(2)\}$ and $\Phi_1^-(1, 2) = N_+\{u(1)u(2) - v(1)v(2)\}$, with their normalization constants expressed in terms of the overlap integral $S_{u,v} = \langle u|v \rangle$: $N_{\pm} = [2(1 \pm S_{u,v})]^{-1/2}$. Indeed, in accordance with the familiar nomenclature of the *Valence Bond* (VB) theory [74], Φ_A describes the *atomic* distribution of the two electrons, among two different atoms in the system promolecule, while Φ_1^{\pm} mark the associated *ionic* distributions, with the two electrons being assigned to the same atom.

One further observes that the two independent basis functions can be uniquely expressed in terms of the two (basis-set invariant) NO:

$$u = \psi_1\cos\phi + \psi_2\sin\phi \quad \text{and} \quad v = \psi_1\sin\delta - \psi_2\cos\delta, \quad (2)$$

and hence $S_{u,v} = \sin(\delta - \phi)$. For $\phi = \delta = \pi/4$ these relations define the orthogonal transformations:

$$\begin{aligned} u &= 2^{-1/2}(\psi_1 + \psi_2) \quad \text{and} \quad v = 2^{-1/2}(\psi_1 - \psi_2), \quad \text{or} \\ \psi_1 &= 2^{-1/2}(u + v) \quad \text{and} \quad \psi_2 = 2^{-1/2}(u - v). \end{aligned} \quad (3)$$

Therefore the reference states can be explicitly expressed in terms of NO:

$$\begin{aligned} \Phi_A(1, 2) &= 2^{-1/2}\{\psi_1(1)\psi_1(2) - \psi_2(1)\psi_2(2)\}, \quad \text{symmetric;} \\ \Phi_1^+(1, 2) &= 2^{-1/2}\{\psi_1(1)\psi_1(2) + \psi_2(1)\psi_2(2)\}, \quad \text{symmetric;} \\ \Phi_1^-(1, 2) &= 2^{-1/2}\{\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)\}, \quad \text{antisymmetric.} \end{aligned} \quad (4)$$

The symmetry descriptions above refer to the homopolar inversion operation, resulting in the $u \leftrightarrow v$ interchange. These components are mutually orthogonal, thus assuring independence of concepts derived in this framework.

To summarize, a general state of two electrons, covering both the homopolar and heteropolar bonds, can be expressed as a combination of these chemically meaningful references,

$$\Phi(1, 2) = \lambda_A \Phi_A(1, 2) + \lambda_I^+ \Phi_I^+(1, 2) + \lambda_I^- \Phi_I^-(1, 2) \equiv \sum_k \lambda_k \Phi_k(1, 2), \quad (5)$$

where for the (homopolar) H_2 case, which we shall consider in this work, $\lambda_I^- = 0$: $\Phi(H_2) = \lambda_A \Phi_A + \lambda_I^+ \Phi_I^+$. Hence, by the normalization of conditional probabilities $\{P(\vartheta|\Phi)\}$ of observing the reference states $\vartheta = (A, I^+)$ in the molecular state Φ , generated using the superposition principle of quantum mechanics [75],

$$P(A|\Phi) + P(I^+|\Phi) = (\lambda_A)^2 + (\lambda_I^+)^2 = 1. \quad (6)$$

This allows the interpretation $P(A|\Phi)$ and $P(I^+|\Phi)$ as the bond fractional *atomic* and *ionic* characters, respectively [66–72]. We emphasize, that these concepts have been developed without a reference to any particular basis set, with the orthogonal reference functions being closely identified with the accepted chemical intuition.

Consider the specific molecular state of H_2 described by the Wang function,

$$\Phi^W(1, 2) = N [1s_a(1) 1s_b(2) + 1s_b(1) 1s_a(2)] \equiv \Phi_{\text{cov}}^{\text{VB}}(1, 2), \quad (7)$$

representing the symmetrized VB product of two $1s$ AO contributed by atoms a and b , with the molecularly optimized exponents. A gradual decrease of the bond ionicity and the corresponding increase in its atomic character is observed as the interatomic distance R increases [72] (see also Table 1). For the equilibrium internuclear distance $R = 1.40$ this framework implies a substantial bond ionicity $P(I^+|\Phi)$:

$$P(A|\Phi) = 0.68 \quad \text{and} \quad P(I^+|\Phi) = 0.32. \quad (8)$$

Hence, the Shull model predicts 68% atomic character and 32% ionic character of this equilibrium homopolar bond.

This (orthogonal) NO perspective differs substantially from the familiar (nonorthogonal) VB approach of Heitler and London [74]. The latter uses the separated atom $1s$ exponent in a combination of the covalent VB structure of Eq. (7) and the ionic VB function $\Phi_I^+(1, 2) \equiv \Phi_{\text{ion}}^{\text{VB}}(1, 2)$ of Eq. (5), for which Pauling [73] predicts 5% bond ionicity. These VB structures are known to be strongly nonorthogonal, $\langle \Phi_{\text{ion}}^{\text{VB}} | \Phi_{\text{cov}}^{\text{VB}} \rangle = 0.96$, so that the truly independent ionic correction to $\Phi_{\text{cov}}^{\text{VB}}$ is determined by the Schmidt-orthogonalized component of $\Phi_{\text{ion}}^{\text{VB}}$, $\Psi_{\text{ion}} = 3.362\Phi_{\text{ion}}^{\text{VB}} - 3.428\Phi_{\text{cov}}^{\text{VB}}$ [76]. In the optimum ground-state wave function for the equilibrium separation between nuclei, $\Phi = 0.998\Phi_{\text{cov}}^{\text{VB}} + 0.058\Psi_{\text{ion}}$, one thus predicts from the quantum superposition principle

Table 1 Fractional atomic and ionic characters (conditional probabilities of reference states) of the Wang function for H₂ in the Shull 2-NO description [64] (columns 2, 3), the joint probability of two reference states (column 4) and the overall (column 5) and resonance (column 6) conditional entropies of the the communication system of Fig. 1. In columns 7 and 8 the diagonal probability X of the corresponding AO channel (Fig. 3a) and the associated entropy covalency $H(X)$ are reported. The last two columns report modified additive (column 9) and nonadditive (column 10) contributions to the overall bond index of column 8

R	$P(A \Phi)$	$P(I^+ \Phi)$	$P(A \wedge I^+ \Phi)$	$S(\mathbf{B} \mathbf{A})_\Phi$	$S(A, I^+)_\Phi$	X	$H(X)$	$M_{ion}(X)$	$M_{cov}(X)$
1	2	3	4	5	6	7	8	9	10
0.000	0.536	0.464	0.249	0.996	0.499	0.501	1.000	0.499	0.501
0.734	0.576	0.424	0.244	0.983	0.497	0.506	1.000	0.497	0.503
1.404 ^a	0.679	0.321	0.218	0.905	0.479	0.534	0.997	0.483	0.514
1.798	0.744	0.256	0.190	0.821	0.455	0.568	0.987	0.464	0.523
2.992	0.892	0.108	0.097	0.494	0.326	0.721	0.854	0.340	0.514
4.027	0.965	0.035	0.033	0.219	0.162	0.882	0.523	0.160	0.363
5.050	0.991	0.009	0.009	0.074	0.002	0.965	0.220	0.050	0.170
10.02	1.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000

^aEquilibrium distance

$$P(\Phi_{cov}^{VB}|\Phi) = 0.997 \quad \text{and} \quad P(\Psi_{ion}|\Phi) = 0.003, \quad (9)$$

and hence roughly purely-covalent character of the chemical bond in H₂.

Additional insight into the model predictions comes from energetic considerations [72], by examining the expectation value of the system electronic Hamiltonian $H(1, 2)$ in the ground state $\Phi(H_2)$:

$$\begin{aligned} \langle E \rangle_\Phi &= \langle \Phi | H | \Phi \rangle = (\lambda_A)^2 \langle \Phi_A | H | \Phi_A \rangle + (\lambda_I^+)^2 \langle \Phi_I^+ | H | \Phi_I^+ \rangle + 2\lambda_A \lambda_I^+ \langle \Phi_A | H | \Phi_I^+ \rangle \\ &\equiv P(A|\Phi)H_{A,A} + P(I^+|\Phi)H_{I,I} + 2\lambda_A \lambda_I^+ H_{A,I}. \end{aligned} \quad (10)$$

These three energy terms give the following contributions to the system total energy $\langle E \rangle_\Phi = -1.139$; $P(A|\Phi)H_{A,A} = -0.380$, $P(I^+|\Phi)H_{A,I} = -0.071$, and cross term $2\lambda_A \lambda_I^+ H_{A,I} = -0.687$. Both diagonal matrix elements $H_{A,A}$ and $H_{I,I}$ indicate that the reference states Φ_A and Φ_I^+ are neither strongly bonding nor strongly antibonding. It is the cross-term, which is seen to represent the largest (60%) contribution to the system electronic energy.

3 Two-electron communication system

Each selection of the (orthogonal) molecular reference states $\{\Psi_k\}$, in terms of which the system wave function Ψ is expanded,

$$\Psi = \sum_k C_k \Psi_k, \quad \langle \Psi_k | \Psi_l \rangle = \delta_{k,l}, \quad C_k = \langle \Psi_k | \Psi \rangle, \quad \sum_k |C_k|^2 \equiv \sum_k P(\Psi_k | \Psi) = 1, \quad (11)$$

determines the associated set of the conditional probabilities $\{P(l|k)_\Psi = P(\Psi_k \rightarrow \Psi_l)_\Psi\} = \mathbf{P}(\mathbf{B}|\mathbf{A})$, of detecting in the molecular ground state Ψ the

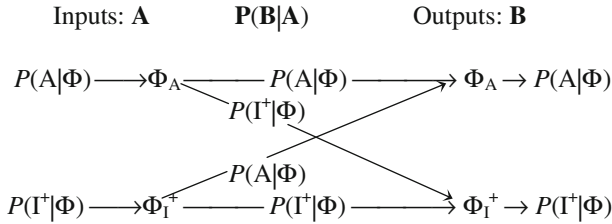


Fig. 1 The ground-state channel for H₂ in the Shull model

reference state Ψ_l , when the system was known to be initially in state Ψ_k . Such molecular “events” define the input (source) ($\mathbf{A} = \{\Psi_k\} \equiv \{k\}$) and output (receiver) ($\mathbf{B} = \{\Psi_l\} \equiv \{l\}$) of the relevant two-electron communication channel.

We have identified above the reference-state probability in the molecular ground state, $P(\Psi_k|\Psi) \equiv P(k|\Psi)$, as the square of the modulus of the corresponding expansion coefficient, $P(k|\Psi) = |C_k|^2$, in accordance with the superposition principle of quantum mechanics [75].

The probability propagation in this information network are also generated using the ground-state-projected superposition principle [52, 75]. It defines the associated joint probabilities of the two reference events in the specified molecular state:

$$P(\mathbf{A} \wedge \mathbf{B}|\Psi) = \{P(k \wedge l|\Psi) = P(l \wedge k|\Psi) = |\langle \Psi_k|\Psi \rangle \langle \Psi|\Psi_l \rangle|^2 = P(k|\Psi)P(l|\Psi)\}. \tag{12}$$

These product joint probabilities indicate that the channel input events are independent of its output events. They are seen to conform to the required normalizations:

$$\sum_k P(l \wedge k|\Psi) = P(l|\Psi), \quad \sum_l P(l \wedge k|\Psi) = P(k|\Psi), \quad \sum_k \sum_l P(l \wedge k|\Psi) = 1. \tag{13}$$

Hence, the representative conditional probability in state Ψ , of observing Ψ_l given the state Ψ_k , reads:

$$P(l|k)_\Psi = P(\Psi_k \rightarrow \Psi_l)_\Psi = P(l \wedge k|\Psi)/P(k|\Psi) = P(l|\Psi), \quad \sum_l P(l|k)_\Psi = 1. \tag{14}$$

For example, in the homopolar case of H₂ the two reference states (Φ_A, Φ_I^+) used to express the wave function Φ define the (2 × 2) molecular information system of Fig. 1, defined by the conditional probabilities of Eq. (6):

$$P(A|A)_\Phi = P(A|I^+)_\Phi = P(A|\Phi) = (\lambda_A)^2, \tag{15}$$

$$P(I^+|A)_\Phi = P(I^+|I^+)_\Phi = P(I^+|\Phi) = (\lambda_I^+)^2.$$

probabilities [Eq. (12)]. Hence the resultant IT bond index is entirely reflected by the Shannon entropy of the input/output probability distribution of Eq. (17):

$$N(\mathbf{A}^0; \mathbf{B})_\Phi = S(\mathbf{B}|\mathbf{A})_\Phi + I(\mathbf{A}^0 : \mathbf{B})_\Phi = S(\mathbf{B}|\mathbf{A})_\Phi = H(\mathbf{A}) = H(\mathbf{B}). \quad (20)$$

We thus conclude that, relative to SAL, this communication description of the model chemical bond in H_2 predicts its purely covalent character. After all, this is indeed what chemists intuitively associate with this prototype homopolar chemical bond.

It should be also observed that the energy contributions of Eq. (10) reflect specific channel communications. In particular, the diagonal energy terms, $P(\mathbf{A}|\Phi)H_{\mathbf{A},\mathbf{A}} = P(\mathbf{A}|\mathbf{A})_\Phi H_{\mathbf{A},\mathbf{A}}$ and $P(\mathbf{I}^+|\Phi)H_{\mathbf{I},\mathbf{I}} = P(\mathbf{I}^+|\mathbf{I}^+)_\Phi H_{\mathbf{I},\mathbf{I}}$, can be associated with the probability amplitudes of the corresponding joint probabilities,

$$[P(\mathbf{A} \wedge \mathbf{A})_\Phi]^{1/2} = P(\mathbf{A}|\Phi) \quad \text{and} \quad [P(\mathbf{I}^+ \wedge \mathbf{I}^+)_\Phi]^{1/2} = P(\mathbf{I}^+|\Phi), \quad (21)$$

behind the $\Phi_{\mathbf{A}} \rightarrow \Phi_{\mathbf{A}}$ and $\Phi_{\mathbf{I}^+} \rightarrow \Phi_{\mathbf{I}^+}$ information propagations, respectively. The cross-energy term,

$$[P(\mathbf{A}|\Phi)P(\mathbf{I}^+|\Phi)]^{1/2} (H_{\mathbf{A},\mathbf{I}} + H_{\mathbf{I},\mathbf{A}}), \quad (22)$$

can be similarly related to the cross scatterings $\Phi_{\mathbf{A}} \rightarrow \Phi_{\mathbf{I}^+}$ and $\Phi_{\mathbf{I}^+} \rightarrow \Phi_{\mathbf{A}}$. Indeed, one observes that its probability factor

$$[P(\mathbf{A}|\Phi)P(\mathbf{I}^+|\Phi)]^{1/2} = [P(\mathbf{A} \wedge \mathbf{I}^+)_\Phi]^{1/2} = [P(\mathbf{I}^+ \wedge \mathbf{A})_\Phi]^{1/2}, \quad (23)$$

also reflects the off-diagonal probability amplitudes in the molecular ground state Φ , of the corresponding simultaneous events involving two different reference states. To summarize, the joint probabilities of the reference states supplemented with the relevant matrix elements of the system Hamiltonian provide a transparent energy-partitioning perspective associated with specific communications in the molecular information system.

Of interest also is the *inter*-state conditional entropy measuring contributions due to the *cross*-state probability propagations, between different reference states,

$$\begin{aligned} S(\mathbf{A}, \mathbf{I}^+)_\Phi &\equiv -P(\mathbf{A} \wedge \mathbf{I}^+|\Phi)[\log P(\mathbf{A}|\Phi) + \log P(\mathbf{I}^+|\Phi)] \\ &= -P(\mathbf{A} \wedge \mathbf{I}^+|\Phi)\log P(\mathbf{A} \wedge \mathbf{I}^+|\Phi) \\ &= -P(\mathbf{A}|\Phi)P(\mathbf{I}^+|\Phi)\log[P(\mathbf{A}|\Phi)P(\mathbf{I}^+|\Phi)]. \end{aligned} \quad (24)$$

This noise index reflects the *resonance* between atomic and ionic states, which lies behind the fluctuational (Charge-Shift) mechanism [77] of chemical interactions.

Table 1 summarizes variations of the state probabilities (columns 2–4) and entropies (columns 5 and 6) in H_2 with increasing internuclear distance R (column 1). These IT covalency descriptors have been obtained using the probability data [72] for the Wang function [Eq. (7)]. Both the overall conditional entropy $S(\mathbf{B}|\mathbf{A})_\Phi$ and its *cross*-state (resonance) contribution $S(\mathbf{A}, \mathbf{I}^+)_\Phi$ are seen to gradually decrease as R increases. In

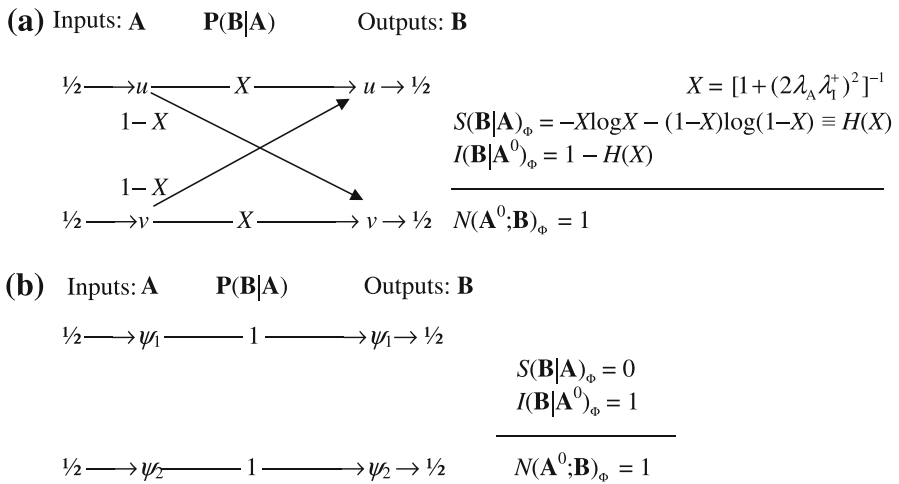


Fig. 3 The ground-state orbital channels, AO (a) and NO (b) in the Shull model for H_2 (Wang function) and their OCT bond indices

the range $R \in [0, 1.8]$ the overall bond order stays above 0.8 bits, marking a strong single covalent bond, and it fast decays for larger distances. At the equilibrium distance the overall entropic bond multiplicity of 0.90 bits is seen to combine the resonance entropy of 0.48 bits and the remaining diagonal contributions due to the *intra*-state probability scatterings.

4 Orbital channels

Let us now consider the communication systems determined by the two sets of *one*-electron functions: NO, $\psi = (\psi_1, \psi_2) \equiv \{\psi_k\}$, and (orthogonal) AO, $\chi = (u, v) \equiv \{\chi_i\}$, for $\phi = \delta = \pi/4$. The 2-NO expansion of Eqs. (1) and (5) generates the following *Charge and Bond Order* (CBO), 1-density matrix in these two orbital representations:

$$\begin{aligned} \gamma^{\text{NO}} &= \{N \langle \psi_k | \Psi \rangle \langle \Psi | \psi_l \rangle = \langle \psi_k | \{n_1 | \psi_1 \rangle \langle \psi_1 | + n_2 | \psi_2 \rangle \langle \psi_2 | \} | \psi_l \rangle\} = \{n_k \delta_{k,l}\}, \\ & \quad n_1 = (\lambda_A + \lambda_1^+)^2, n_2 = (\lambda_A - \lambda_1^+)^2, \\ \gamma^{\text{AO}} &= \{N \langle \chi_i | \Psi \rangle \langle \Psi | \chi_j \rangle = \langle \chi_i | \{n_1 | \psi_1 \rangle \langle \psi_1 | + n_2 | \psi_2 \rangle \langle \psi_2 | \} | \chi_j \rangle\} = \{\gamma_{i,j}\} \quad (25) \\ &= \begin{bmatrix} 1 & 2\lambda_A \lambda_1^+ \\ 2\lambda_A \lambda_1^+ & 1 \end{bmatrix}. \end{aligned}$$

They determine the corresponding orbital communication channels, shown in Fig. 3, determined by the AO/NO conditional probabilities $\{P(\chi_j | \chi_i)_\phi \equiv P(j|i)_\phi = P(i \wedge j | \Phi) / P(i | \Phi)\}$ and $\{P(\psi_l | \psi_k)_\phi \equiv P(l|k)_\phi = P(k \wedge l | \Phi) / P(k | \Phi)\}$, respectively.

Let us first examine the entropic bond covalency of the AO channel, listed in column 8 of Table 1. As expected, for the equilibrium bond length it recovers the bond composition predicted in Eq. (9). These equilibrium bond indices agree qualitatively

with bond components of the *two*-electron channel of Fig. 1, but the AO channel additionally uncovers the competition between these OCT measures of the bond covalency and ionicity, for the conserved overall bond index $N(\mathbf{A}^0; \mathbf{B})_\Phi = 1$.

For the first time, however, these numerical results allow one to examine the behavior of such IT multiplicities with internuclear distance, from the united (He) atom at $R = 0$ to the SAL at $R \rightarrow \infty$. One observes that at shorter distances, including the equilibrium bond length, the two AO strongly mix to form NO, $X(R) \approx 1/2$, and hence practically all input information is dissipated as noise at the channel output. At large distances this constructive AO interference in the bonding NO gradually disappears, $X(\infty) = 1$, so that AO communications become perfectly deterministic (localized) in character thus preserving in the system output the whole input information.

Therefore, this IT interpretation correctly reflects the average noise and information flow components of the AO information systems. The intraatomic character of AO communications in SAL is thus synonymous with the purely atomic character of the molecular state in this limit, in perfect agreement with Shull's definition of this dissociation state. However, in OCT $H[X(\infty)] = H(1) = 0$ and hence $I[X(\infty)] = 1$, contrary to prevailing chemical intuition, which was well reflected by Shull's NO indexing: $[\lambda_1^+(\infty)]^2 = 0$. This difficulty has been resolved previously by regarding the SAL as a collection of the separate atomic channels, each with the vanishing (intraatomic) ionicity [1].

For the fixed internuclear distance R of the heteronuclear system the binary entropy $H(X)$ can be alternatively regarded as function of the complementary atomic probabilities, $P \equiv P(u|\psi_1) = |\langle u|\psi_1\rangle|^2$ or $Q \equiv P(v|\psi_1) = 1 - P = |\langle v|\psi_1\rangle|^2$: e.g., $H[X(P)] \equiv H(P)$. These probability variables reflect relevant conditional probabilities of AO in the bonding NO ψ_1 , and reflect the bond polarization. It has been demonstrated elsewhere that the entropy function $H(P)$ is well represented by the corresponding Wiberg [78] bond-order of the 2-AO model, $M_{u,v} = (\gamma_{u,v})^2$, given by the parabola $M_{u,v}(P) = 4PQ$. The corresponding OCT covalency/ionicity indices of the 2-AO model then correctly describe the P -variations in the bond composition, including the partially polarized bonds and the limiting *ion*-pair electron configurations, when both electrons are located on a single AO, e.g., [1–4, 56].

Therefore, in an attempt to bring the limiting (SAL) value of the communication bond indices to a qualitative agreement with intuitive expectations, one could alternatively regard the overall AO noise index $S(\mathbf{B}|\mathbf{A})_\Phi = H(X)$ as a measure of the *total* entropic bond order:

$$M_{u,v} = S_{intra} + S_{inter} \equiv S(\mathbf{B}|\mathbf{A})_\Phi. \quad (26)$$

This overall measure is explicitly interaction-sensitive, thus correctly reflecting its R -dependence and the vanishing value in the SAL. It can be subsequently partitioned into contributions due to the diagonal (*intra*-orbital) and *off*-diagonal (*inter*-atomic) communications between AO. The former focuses on the information transferred inside both AO, reflecting the channel deterministic (electron localization) component, which in OCT is linked to the bond *ionicity* feature. The latter characterizes the AO “resonance”, i.e., the *inter*-atomic probability scatterings, due to electron delocalization,

which is regarded by chemist as the essence of the bond covalency, i.e., the electron sharing between the two atoms.

To summarize, this modified IT indexing system in OCT uses the “additive” (AO localization) noise component,

$$\begin{aligned} M_{ion}(X) &\equiv S_{intra}(X) = -\sum_i P(i \wedge i | \Phi) \log P(i|i)_\Phi \\ &= -P(u \wedge u | \Phi) \log P(u|u)_\Phi - P(v \wedge v | \Phi) \log P(v|v)_\Phi = -X \log X, \end{aligned} \quad (27)$$

as a measure of the *ionic* bond order, and the cross-state, “nonadditive” (AO scattering) noise term,

$$\begin{aligned} M_{cov}(X) &\equiv S_{inter}(X) = -\sum_{i \neq j} P(i \wedge j | \Phi) \log P(j|i)_\Phi \\ &= -P(u \wedge v | \Phi) [\log P(u|v)_\Phi + \log P(v|u)_\Phi] = -(1 - X) \log(1 - X) \\ &= H(X) - M_{ion}(X), \end{aligned} \quad (28)$$

as a descriptor of the bond *covalency*.

The numerical values of these modified bond components in OCT are listed in the last two columns of the table. In many respects these new descriptors adequately reflect the accepted chemical intuition, in accord with the (basis set invariant) Shull’s description. The main virtue of this novel indexing of IT bond orders is that for the current distance R between both atoms the new overall measure $S(\mathbf{B}|\mathbf{A})_\Phi = H[X(R)]$ now reflects the strength of the AO coupling $X(R)$ in NO, thus correctly vanishing in the SAL; this is contrary to the constant overall IT bond order $N(\mathbf{A}^0; \mathbf{B})_\Phi = 1$ bit in Fig. 3, intended for the fixed (equilibrium) geometry indexing, irrespective of the actual internuclear distance R . The new measure of the bond ionic character now monotonically decays with increasing R , although more slowly than that observed in the partial ionic character of the Shull model. For $R < 1.8$ a.u. these new bond components roughly predict $M_{ion}(X) \approx M_{cov}(X) \approx 1/2$, when orbitals strongly interact chemically, and then they gradually diminish to zero as the bond elongation continues.

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